Developing technologies for biofuels

Francesco Palombo
Biofuels Technology Program
R&D Center

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AGENDA

- The Brazilian energy matrix
- Experience in biofuels for transportation
- Petrobras developments in 2nd generation biofuels
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THE BRAZILIAN ENERGY MIX

Domestic Energy Supply

TOTAL 2012: 257,299 MM toe

Renewables

Petroleum Products
Natural Gas
Coal/Coke
Uranium
Hydraulic
Firewood/Charcoal
Sugarcane Products
Other

38,5%
11,0%
31,9%
15,5%
6,1%
14,2%
16,4%
6,0%
4,8%
14,2%
8,2%
21,2%
12,6%
6,0%
4,3%
5,2%

Source: Ministerio Minas e Energia/BEN (2012)
Energy Consumption by Sector

Brazil 2012

- Transportation: 31.3%
- Industry: 35.1%
- Energy sector: 9.0%
- Housing: 9.4%
- Non-energetic use: 6.6%
- Services: 4.5%
- Farming: 4.1%

Source: MME

2011: 245.8 Mtep
2012: 253.4 MM toe

Increase: 3.1%
Brazilian Energy Use for Transportation

<table>
<thead>
<tr>
<th>Total</th>
<th>M toe</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>79,308</td>
</tr>
<tr>
<td>2011</td>
<td>73,989</td>
</tr>
</tbody>
</table>

**Total increase:** 7.2%

**Transportation Fuels 2012 Consumption**

- Gasoline, +17.3% (shortage of hydrated ethanol)
- Diesel, +6.2%
- Hydrated ethanol, -7.5%
- Anhydrous ethanol, +9.7%

Source: MME
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Ethanol in Brazil: 40 years of Experience

The ethanol fuel program

Ethanol Program Implemented (BLENDS)
Gasohol and Ethanol Cars (2nd oil shock)
LDV and HDV Emissions Control Program (PROCONVE)
Gasohol and Flex fuel Cars
Future Mobility Technology
Ethanol 2G ??

Program for oil imports reduction
Environmental Benefits (Legislated Emissions)
GHG emissions

70’s 80’s 90’s 00’s Future
Biodiesel Market Evolution

Law 11097/2005 - established mandatory content of biodiesel in diesel. The addition of biodiesel to diesel has been negotiated by stakeholders considering technical limitations.

Higher percentages may be used, once authorized by the National Petroleum and Biofuels Agency-ANP for testing or use in:
- Proprietary or specific vehicle fleets;
- Sea, river or railroad transport;
- Electric power generation;
- Specific industrial process.
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# Biomass Processing Routes - 1\textsuperscript{ST} Gen

<table>
<thead>
<tr>
<th>Biofuels type</th>
<th>Biomass feedstock</th>
<th>Production process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioethanol *</td>
<td>Sugar beets, \textit{sugar cane}, grains</td>
<td>Hydrolysis &amp; fermentation</td>
</tr>
<tr>
<td>Pure vegetable oil</td>
<td>Oil crops (rape seed, soy bean)</td>
<td>Cold pressing / extraction</td>
</tr>
<tr>
<td>Biodiesel *</td>
<td>Oil crops (rape seed, \textit{soy bean})</td>
<td>Cold pressing / extraction &amp; transesterification</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>Waste / cooking / frying oil</td>
<td>Transesterification</td>
</tr>
<tr>
<td>Biogas</td>
<td>(Wet) biomass</td>
<td>Digestion</td>
</tr>
<tr>
<td>Bio - ETBE</td>
<td>Bioethanol</td>
<td>Chemical synthesis</td>
</tr>
</tbody>
</table>
# The Lignocellulose Biomass

## Composition

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Hemicellulose</th>
<th>Cellulose</th>
<th>Lignin</th>
<th>Ashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat (straw)</td>
<td>28.9</td>
<td>30.5</td>
<td>16.4</td>
<td>11.2</td>
</tr>
<tr>
<td>Sugar Cane (bagasse)</td>
<td>22.6</td>
<td>41.3</td>
<td>18.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Sugar Cane (straw)</td>
<td>32.7</td>
<td>41.4</td>
<td>22.8</td>
<td>11.7</td>
</tr>
<tr>
<td>Rice (straw)</td>
<td>22.7</td>
<td>37.0</td>
<td>13.6</td>
<td>19.8</td>
</tr>
<tr>
<td>Wood</td>
<td>24.0</td>
<td>39.8</td>
<td>24.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Lignocellulosic wastes contain high OXYGEN level !!!

Sugar Cane (straw) composition

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.306</td>
</tr>
<tr>
<td>Carbon (%wt.)</td>
<td>41.6</td>
</tr>
<tr>
<td>Hydrogen (%wt.)</td>
<td>5.8</td>
</tr>
<tr>
<td>Nitrogen (%wt.)</td>
<td>0.45</td>
</tr>
<tr>
<td>Sulfur (%wt.)</td>
<td>0.08</td>
</tr>
<tr>
<td>Oxygen (%wt.)</td>
<td>40.4</td>
</tr>
<tr>
<td>Ashes (%wt.)</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Biomass Conversion Routes

Lignocellulosic Biomass
- Hydrolysis/Fermentation → Ethanol
- Pyrolysis → Bio-Oil
  - Refining
  - Gasification → Syngas
    - Fischer Tropsch
    - Fischer Tropsch Modified
- Chemical → Isosorbide

Sugars Starch
- Hydrolysis/Fermentation → Alcohols, Hydrocarbons

Vegetable Oils Fats
- Transesterification → Biodiesel
- Estherification
- Hydrolysis/Fermentation
- Hydrotreatment
  - HVO, H-Bio (Green Diesel)
Biofuels Technological Strategy

- Deployment of 1st generation technologies
  - HBIO and Biodiesel
- R&D in 2nd generation technologies
- Creation in 2008 of the affiliate company Petrobras Biocombustivel SA
- Partnership to accelerate technology development for cellulosic ethanol from bagasse

- Develop strategic partnerships to accelerate deployment of 2nd generation technologies
Petrobras Biocombustível - Operational Plants
Sep 2013

Biodiesel – deployment in partnership
Biodiesel – ongoing project
Biodiesel – proprietary plant
Biodiesel – plant in partnership
Biodiesel – deployment in partnership
Ethanol - plant in partnership

Ethanol - plant in partnership
Belém Brasil Bioenergia
Projeto Pará
Usina de Quixadá
Usina de Guamaré
Usina de Candeias
Usina de Montes Claros
Nova Fronteira
Bambuí Bioenergia

Biodiesel
Production Capacity
820,000 m³
5 plants

Vegetable Oil Extraction
Bioóleo (Bahia)
Capacity 130M ton grains/yr
(50% share)

ETHANOL
Installed Capacity
1,500,000 m³
10 plants

Petrobras Biocombustível
270,000 ton/y
Green Diesel

Belém Bioenergia
270,000 ton/y

Guarani

Usina de Passo Fundo
160Mm³/y
Usina de Marialva
183Mm³/y
Usina de Montes Claros
152Mm³/y
Usina de Candeias
217Mm³/y
Usina de Quixadá
108Mm³/y
Guaraní
Belém Bioenergia
PETROBRAS R&D on Biodiesel

- Several vegetable oils were tested including castor oil
- Successful pilot-plant tests (2004-2010)
- Technology support for the industrial unit operation
- Demonstration batch plant on stream since 1st Q 2005
  - Initial capacity: 200 t/yr
  - Upgraded to continuous process 6,000 t/yr (2010)
  - Increasing capacity to 20,000 m³/yr (12/2013)
  - Low catalyst consumption

Studies for better economical use of glycerin
- Injection for Enhanced Oil Recovery (EOR)
- Additive for diesel
- Polymers
HBIO - is a process to convert a blend of vegetable oil or animal fat and fossil feedstock using an existing diesel HDT unit

- Technology already tested in six industrial refineries since 2006
- Use of 5 to 10% of soya oil in the HDT blend increase product cetane number
- Development of dedicated catalyst for hydrogenation of pure vegetable oil
- Economic feasibility depending on legislation (mandate) and feedstock prices
Petrobras is developing a conceptual design of an industrial plant

Opportunities for Brazil
- 2nd larger E1G world producer
- Production increased 117% in ten years
- Increased market for flex fuel cars
- Land availability for new sugarcane crops

Threats
- Increasing sugarcane production costs
- Larger technological gains in competing crops (corn, rice, soybean)

Challenges for E2G
- No proven technology by industry yet
- Economic feasibility strongly affected by the cost of bagasse and enzymes
- Major E1G producers also use bagasse for generation of electric power

Some figures
- Yield: 270 liter/BDMT
- Unit capacity: 40 to 100 MM liter/yr
- Capex: around US$ 200 MM
- Enzymes+ Bagasse: around 60% Opex
Petrobras is developing a process, currently at pilot plant stage.

Opportunities for Brazil
- Expressive bagasse and straw production
- Other agricultural residues can be used
- Drop-in fuel
- Flexibility both at feedstock and at product
- Land availability for sugarcane and other crops

Threats
- Higher production costs compared to conventional jet fuel route

Challenges for Biojet
- Economic feasibility strongly affected by cost of feedstock and CAPEX
- Major E1G producers also use bagasse for generation of electric power

- 15 kg/h of biomass
- Pilot plant for pretreatment, gasification, gas cleaning and conditioning studies
- Fischer-Tropsch synthesis pilot plant and proprietary catalysts
Main challenges:

- Transport and storage: bio-oil is unstable, acid, viscous and may separate itself into two phases
- Upgrading: bio-oil cannot be used directly as a transportation fuel and must be processed

PYROLYSIS PRODUCTS

- Flue Gas: CO, CO₂, N₂, H₂O
- Gas: Methane, ethane, light hydrocarbons, CO, CO₂
- Liquid (bio-oil)
  - One phase or
  - Two phases: organic and aqueous
- Char (coke): as product or burnt for energy production

Bio-oil Upgrading:
How to insert it into a petroleum refining scheme???
Bio-oil Upgrading in FCC co-processing

- Demonstration Scale Tests
  
  **Conventional Pyrolysis + FCC co-processing (refinery)**

- Combined Feed: 10-20% Bio-oil + 80-90% Gasoil
- Bio-oil for tests purchased from BTG/NL

- Co-processing Demonstration Scale (Catalytic Cracking)
- Location: São Mateus do Sul (PR)
- Feed Rate: 200 kg/h
- Purchase of 3 tons of bio-oil from BTG/Netherlands
Conclusion

• Despite the majority share of conventional fuels in the transportation sector, the second-generation renewable fuels can make an important contribution to reduce GHG emissions.

• Technological development can meet the challenge of making new technologies become competitive in the medium term.

• Petrobras also seeks to develop new process routes allowing the integration of biomass for production of fuels and petrochemicals.

• It is essential to integrate the development of future systems for urban mobility and the fuels that will be required to have low environmental impact.
THANK YOU

Francesco Palombo
palombo@petrobras.com.br