ENEA activities on Biofuels and Biorefineries for Renewable Energy

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Bioenergy, Biorefinery and Green Chemistry Division

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Bioenergy in Italy

- Domestic and district heating (wood and wood residues)
- Process heat and/or CHP at agro-industrial factories (wood industries, distilleries etc.)
- Electricity production and/or CHP at power plants (lignocellulosic biomass, vegetable oils, biogas)
- Liquid biofuels for transport (biodiesel, bioethanol, ETBE)

CAVIRO distillery CHP and biogas plant (Faenza, Italy)
Contribution to gross energy consumption from renewable energy sources in Italy in 2014

<table>
<thead>
<tr>
<th>Source: GSE, 2015</th>
<th>Bioenergy</th>
<th>Hydropower</th>
<th>Heat pumps</th>
<th>Solar</th>
<th>Wind</th>
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<tr>
<td>Mtoe</td>
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<td>2.1</td>
<td>1.3</td>
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</table>
ENEA activities and research groups on bioenergy and green chemistry

Biomass to energy pathways
Biomass combustion

Saluggia

Microalgae for biogas and biofuels
Energy crops
Biomethane / Biohydrogen

Casaccia

WEB GIS of biomass availability
Energy crops
Thermochemical processes
2nd generation biofuels

Trisaia
Bioenergy, Biorefinery and Green Chemistry Division  
(G. Braccio)

Laboratories:

- **Biomass and Biotechnology for Energy**  
  *(V. Pignatelli)*

- **Technologies and Processes for Biorefineries and Green Chemistry**  
  *(I. De Bari)*

- **Thermochemical Processes for Biomass and Waste Valorization**  
  *(G. Cornacchia)*
Biofuels are today the only direct substitute for oil in transport that is available on a significant scale.

The proposed target concerning with 10% renewable energy included in the total fossil fuels consumed within EU by 2020 could be fulfilled only if a significant amount of “second generation” biofuels will be produced and sell on the market, in order to avoiding possible competition with food crops.

2nd generation biofuels can be produced without environmentally harmful impacts because of:

- use of no-food feedstock, as cellulose (forestry / agriculture residues, grasses) and other non-conventional raw material (glycerol, organic wastes, algae etc.)
- higher potential to reduce GHG
- New processes and technological approaches, including biotechnological ones.
BIOLOGICAL PROCESSES FOR ENERGY, BIOFUEL AND OTHER VALUABLE PRODUCTS FROM BIOMASS

- Advanced processes for biogas clean-up and upgrading to produce biomethane suitable both for injection into the natural gas delivering grid as well as for transport biofuel.

- Production of hydrogen-rich biogas (hydromethane) by advanced anaerobic fermentation processes of waste biomass.

- Ethanol and hydrogen production from raw glycerol arising from biodiesel industry by anaerobic fermentation with mixed bacteria cultures.

- Ethanol from lignocellulosic biomass by cellulose enzymatic hydrolysis and fermentation, suitable as renewable transportation fuels directly by mixing with gasoline or via conversion to ETBE, TAEE etc.

- Production of biofuels (biogas and/or bio-oil) from CO₂ & sunlight through micro-organism based production (algae, bacteria etc.) and further upgrading into transportation fuels and valuable bio-products.

Current ENEA RTD activities on new technologies for bioenergy and/or “2nd generation” biofuels production.
Research activities on biogas production

- Pilot anaerobic digester (6 m³) for testing innovative biogas production processes at ENEA Casaccia Research Centre

- Experimental cultivation of Jerusalem Artichoke for biogas production at ENEA Casaccia Research Centre

- Experimental cultivation of microalgae for biogas or liquid biofuels production at ENEA Casaccia Research Centre
Biofuel consumption (%) in the EU 27 in 2014

- Bioethanol: 19.10%
- Biodiesel: 79.72%
- Vegetable oil: 0.23%
- Biomethane: 0.95%

Total biofuel consumption in the EU (2014): 13 Mtoe (4.9% of total energy consumption in the EU transport sector)

Elaboration on data from EurObserv’ER - Biofuels Barometer 2015
Experimental photo-bioreactor for \( \text{H}_2\text{S} \) removal from biogas by means of a biological clean-up process based on the anoxygenic photosynthesis reaction at ENEA Casaccia Research Centre

Membrane separation pilot plant for biomethane production, able to treat up to 350 m\(^3\) biogas / h, at ENEA Trisaia Research Centre
Bioconversion of lignocellulosic biomass to fuels and chemicals

• Development of microbial processes for hydrolysis of lignocellulosic materials by Anaerobic Ruminal Fungi

• Isolation and characterization of hydrolytic and hydrogen-producing bacterial strains

• Bacterial hydrolysis and saccharification of cellulose and hemicelluloses to fermentable monosaccharides
Processes optimization: fermentation and anaerobic digestion

- Statistical optimization of substrate composition
- Scaling up activities: Two Stage AD plant
  ENEA-CRA Patent number PCT/IB2014/059942

- Enrichment of suitable inocula for methane production by bioaugmentation of hydrogen producer communities
Characterization of microbial communities by molecular techniques

- Selection of suitable inocula for the hydrogen production stage, exploring the microbial diversity in natural ecosystems
- Investigating and monitoring the structure and functionality of the microbial communities during fermentation, AD and clean up processes

- Construction of 16S rDNA libraries
- Denaturing gradient gel electrophoresis (DGGE)
- Amplified ribosomal DNA restriction analysis (ARDRA)
- Fluorescence In Situ Hybridization (FISH)
Bioconversion of crude glycerol into ethanol, hydrogen and biochemical compounds

- The aim of the activities is to increase the glycerol consumption, maximizing production of hydrogen and ethanol.

- Lab scale fed-batch experiments in non-sterile conditions by using increasing glycerol concentration to enhance substrate degradation ability.
Microbial production of lipids

- Depending on the microorganism, the lipid yield could reach ~70% of the microorganism biomass.
- Co-utilizzazione of C& and C5 is possible.
- **Fermentation strategies ensuring an optimized C/N ratio can improve the process yields**.
Biorefinery and Green Chemistry: conversion of biomass into liquid fuels and chemicals

- Steam explosion
- Thermal process
- Bio-chemical process

- Hydolysis
- Fermentation

- Gassification
- Pyrolysis

- Pressing
- Transesterification

- Bioethanol
- Biodiesel
- Sundiesel
- Bio oil
- F. Tropsch

- Cereals: grain, sugar
- Straw
- Oleaginous plant
- Vegetable oil
ENEA involvement in the "Cluster" projects (sustainable biochemicals and bioproducts)

**Project ALBE**
Project leader: VERSALIS
Sustainable technologies for the production of new **elastomers** and **lubricant oils**

**Project BIT3G**
Project leader: NOVAMONT
Third generation biorefineries (oils to **bioplastics**, **biolubricants**, **bioherbicides** etc.)

**Project REBIOCHEM**
Project leader: MATER-BIOTECH
Chemicals from biomass (i.e. **BDO**, **5HMF** etc.)
Dedicated crops for biofuels and biobased products

**BIOFUELS DRIVEN BIOREFINERIES**

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<tr>
<td>Glucan</td>
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<td>Mannan</td>
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<tr>
<td>Lignin</td>
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</table>

**SECOND BIOETHANOL process:** demonstration scale for the step of lignocellulosic hydrolysis and fermentation

**BIOCHEMICALS DRIVEN BIOREFINERIES**

- **SEEDS**
- **VEGETABLE OILS**
- **AZELAIC ACID**
- **PELARGONIC ACID**

**Residue from Cardoon**

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<tbody>
<tr>
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<td>Galactan</td>
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<tr>
<td>Lignin</td>
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**POLYESTERS**

**Bioplastics, Biolubricants.....**
Production of 2G bioethanol from crops suitable for phytoremediation of contaminated soils

Acorus calamus  Arundo donax  Canna indica  Carex pseudoc.  Carex elata  Cladium mariscus  Cyperus longus  

Glyceria maxima  Iris pseudacorus  Helianthus tuberosus  Juncus effusus  Lythrum salicaria  Miscanthus x g.  Phalaris arundinacea  Sorghum bicolor  

Pirragmites australis  Scirpus sylvaticus  Symphytum officinalis  Typha domingensis  Typha latifolia  Carex riparia  Vetiveria zyanoides  

23 SPECIES
Bench scale tests for the production of EtOH

Data from FITOPROBIO Project (MIPAAF)
2nd generation bioethanol production at industrial scale

Partnership: Mossi & Ghisolfi - ENEA

Pilot Size: 40,000 tonnes/years
Industrial Size: 200,000 t/a

Targets:
- EtOH yield $\geq 0.25 \text{ g/g}_{\text{BIOMASS}}$
- yield per hectare EtOH $\geq 100 \text{ hl/ha}$
- Production Cost $< 0.6-0.7 \text{ €/l}$

CO-Products
- Probiotics & sweeteners
- Fibers
- Biodegradable materials

The biomass is continuously steamed and exploded in the digester, then slurried with warm water and filtered with a belt machinery to recover hemicellulose. The residue is slurried with alkaline solution, then filtered to separate the lignin from cellulose.
Pretreatment and fractionation at pilot scale (300 kg/h)
- Production of second generation sugars
- Process scale-up
- Downstream processing
- Technological platforms for thermal valorization of biomass residues (pyro-gasification)
- Identification of new proteins and key enzymes involved in biomass degradation (proteomics)
- Fully equipped analytical labs for materials characterization and process analysis
<table>
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<th>Equipment</th>
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<tr>
<td>GC-MS &amp; TDS/DIP</td>
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<tr>
<td>Soxhlet System</td>
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<td>Oven</td>
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Current ENEA RTD activities on new technologies for bioenergy and/or “2nd generation” biofuels production

TERMOCHEMICAL PROCESSES FOR ENERGY AND BIOFUEL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

- Liquid biofuels (BTL, biomethanol) and/or hydrocarbons from biomass via gasification, gas cleaning and upgrading and catalytic synthesis (main markets: renewable transportation fuels for jet and diesel engines)

- Substitute natural gas (bio-SNG) and other gaseous fuels (DME) from biomass via gasification

- High-efficiency thermal and power generation via gasification of biomass at a local level (farm, wood processing or agro-industrial factory)

- Bioenergy carriers from biomass (charcoal, bioliquids) via other thermochemical processes like pyrolysis, torrefaction etc.
Pilot plants for biomass gasification at ENEA Trisaia

**Fluidized bed – Internally recirculating**

- **enriched air/steam 1MWth**
- Coupled with ICE for power generation

**Fluidized catalitic bed – Internally recirculating**

- **Air/steam 550kWth**
- Coupled with ICE or FC for power generation, Fisher Tropsch

**UPDRAFT fixed bed**

- **Air/steam 200kWth**
- Coupled with ICE for power generation, Fisher Tropsch

**DOWNDRAFT fixed bed**

- **Air/steam 150-450kWth**
- Coupled with ICE for power generation

**SYNGAS COMPOSITION**

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<td><strong>CH₄</strong></td>
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<tr>
<td><strong>CO₂</strong></td>
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<tr>
<td><strong>H₂O</strong></td>
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<td><strong>H₂O</strong></td>
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<tr>
<td><strong>CO₂</strong></td>
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Steam gasification FICFB plant

- Steam gasifier 500 kWth
- Fast Internally Circulating Fluidized Bed
- “Nitrogen free” Syngas
- Catalytic bed

### Syngas, Vol %

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<thead>
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<tbody>
<tr>
<td>H₂</td>
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<tr>
<td>CO</td>
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<tr>
<td>C₂-C₃</td>
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<tr>
<td>N₂</td>
<td>9 - 13</td>
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- Tar raw gas ~ 9 g/Nm³ secco
- Raw gas yield 1-1.4 Nm³/kg daf
- LHV raw gas 11-13 MJ/Nm³ dry
Combined plant: gasification + Fisher-Tropsch process

Fisher-Tropsch reactor (adiabatic stages)

Products

Methanol and chemicals

“Hydrosin” gasification plant
Integrated cleaning & conditioning of raw gas inside of the reactor
Cost reduction for cleaning is estimated about 20 - 30%. Compact plant with reduced heat loss.

- Ceramic catalytic candles
- High temperature purified syngas
- Advanced application (i.e. HTFC)
- In bed additives for tar conversion
- Gasifier under patent ENEA-UNIVAQ (1MWth ICBFB)
Thanks for your kind attention

Vito Pignatelli

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