Venice’s Green Refinery:  
process and products innovation  
Giacomo Rispoli
Highlights

• Scenario
• Eni vision
• Eni/Honeywell UOP Ecofining™ technology
• Eni Green Refinery in Venice
• Looking to the future
• Conclusion
Scenario

• The European refining industry is living a major economic crisis, characterized by very low operating margins, bear fuels market and consequent refining overcapacity installed.

• This crisis was cracking down on the Venice Refinery in a particular way, due to its simple process scheme made by hydroskimming plus visbreaker/thermal cracker, without any catalytic conversion units.
Europe and biofuels

• **EU's Climate Change Package** with EU targets by 2020:
  - 20% reduction in greenhouse gas emissions,
  - 20% improvement in energy efficiency,
  - 20% share for renewable in the EU energy mix.

• **EU Directives on biofuels**:
  - **Renewable Energy Directive**
    RED 2009/28/CE
  - **Fuel Quality Directive**
    FQD 2009/30/CE

  10% of renewable energy in the transportation sector.
  Second generation biofuels counted twice.
Biofuels demand

Biofuel consumption by area: 2011 and 2020

UE27: consumption and target

The blending-wall limits biodiesel FAME blending at 7% max. This constraint can be overcome by using new generation renewable Hydrotreated Vegetable Oil (HVO).

Source: Parpinelli
Eni vision

- Refining industry crisis
- EU biofuels scenario
- ECOFINING™ Technology

Reducing refining overcapacity?

Biorefinery

Reinventing petroleum refinery!
Eni approach

- Eni was able to turn a critical situation into a great opportunity by investing in the innovative Green Refinery project for the conversion of the Venice petroleum refinery into a “Biorefinery”.

- The Green Refinery idea is focused on the application of Eni/Honeywell UOP Ecofining™ technology and results from the long term “Eni Green Strategy”.

- That’s the “make option”: eni entered the biofuels market, producing a new generation of very high quality biofuels starting from renewable feedstocks.
Eni Green Strategy results

Eni/Honeywell UOP Ecofining™ patent 2007

2012

“Refinery conversion to a biorefinery” Eni patent

2013

Green Refinery Project

May 2014

Green fuels production starts from Venice Green Refinery

2016

Green fuels production increase in Venice

Green Refinery Project

Eni Green Refinery Project

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Eni Green Refinery Project
EU and U.S. promote the transition to 2nd generation fuels and feedstocks.

**FEEDSTOCKS**

1st gen. **Agrifood Feedstocks**

2nd gen. **Agricultural non-food, Agro/Urban waste Feedstocks**

3rd gen. **Non-agricultural High Innovation Feedstocks**

**OPPORTUNITIES**

- large & liquid markets
- support from the EU and U.S. regulatory targets
- environmental impact favorable
- valorization waste materials
- Not in competition for use of the land resource
- high technological added value
- potentially large yields

**RISKS**

- strong social and environmental impacts (Food vs fuel)
- climate risk
- possible phase-out legislation
- high production costs and complex logistics
- climate risk for some productions
- immature technologies
- strong investment in R & D required
- high production costs

**FEEDSTOCKS**

- Diesel
- Biodiesel FAME
- Ethanol
- Gasoline
eni/Honeywell UOP goal on biofuels

- Produce real “drop-in” biofuels, totally hydrocarbon, instead of fuel bio-additives.
- Focus on path toward new generation feedstocks.

Conventional Oxygenated Biofuels
- Ethanol
- Biodiesel

First Generation
- Natural oils (vegetables, greases)

"Other" Oils: Camelina, Jatropha

Advanced Generation
- Lignocellulosic biomass, algae oils

Hydrocarbon Biofuels
- Diesel
- Jet
- Gasoline
Biofuels process: conventional vs new generation

**Biofuels process:**

**Conventional vs New Generation**

**Biodiesel Conventional Process:**
- **Feed**
  - Methanol
  - Biological feedstocks
- **Process**
  - Transesterification
- **Product**
  - Biodiesel FAME (Fatty Acid Methyl Esters)
  - Glycerine

**Biofuels New Generation Process:**
- **Feed**
  - Biological feedstocks
- **Process**
  - HYDROTREATMENT
- **Product**
  - Green Diesel (HVO)
  - Green Jet (HEFA-SPK)
  - Green Naphtha
  - Green GPL
  - CO₂/H₂O

**Eni Green Diesel**: high quality product obtained by means of hydrotreating (HVO) with paraffinic composition (oxygen free).
ECOFINING™ technology

Jointly developed by Eni and Honeywell’s UOP to produce excellent biofuels, with high quality independent from the renewable feedstocks used, that can be of:

- 1st generation: edible vegetable oils;
- 2nd generation: tallow, used cooking oils;
- 3rd generation: oils from algae and waste.
ECOFINING™ technology

Hydrogen

RENEWABLE FEEDS
Vegetable oils
Tallow
Used cooking oils
Oils from algae, waste

1st reaction stage

2nd reaction stage

Products separation

Light fuels
(Green LPG, Green Naphtha)
GREEN JET
GREEN DIESEL

Free Fatty Acid

Triglyceride

Green Diesel

& Green Naphtha

Propane

Straight Chain Paraffins
# ECOFINING™: typical yields

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>%wt</th>
</tr>
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<tbody>
<tr>
<td>Renewable oils</td>
<td>100</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1,5 – 3,8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product</th>
<th>%wt</th>
<th>%v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>4-5</td>
<td>7-9</td>
</tr>
<tr>
<td>Naphtha</td>
<td>1 - 8</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Diesel</td>
<td>75 - 85</td>
<td>88 - 98</td>
</tr>
</tbody>
</table>

CO$_2$ and H$_2$O are also produced by the deoxygenation reaction.
# Green Diesel quality

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fossil Diesel ULSD</th>
<th>Conventional Biodiesel (FAME)</th>
<th>ECOFINING™ Green Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIO content</td>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Oxygen, %</td>
<td>0</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.840</td>
<td>0.880</td>
<td>0.780</td>
</tr>
<tr>
<td>Sulphur, ppm</td>
<td>&lt;10</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Heating Value, MJ/kg</td>
<td>43</td>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>Cloud Point, °C</td>
<td>-5</td>
<td>From -5 to +15</td>
<td>Up to -20</td>
</tr>
<tr>
<td>Distillation range, °C</td>
<td>200 - 350</td>
<td>340 - 355</td>
<td>200 - 320</td>
</tr>
<tr>
<td>Polyaromatics, %w</td>
<td>11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nox emissions</td>
<td>Standard</td>
<td>+ 10%</td>
<td>-10%</td>
</tr>
<tr>
<td>Cetane</td>
<td>51</td>
<td>50-65</td>
<td>70-90</td>
</tr>
<tr>
<td>Oxydation stability</td>
<td>Standard</td>
<td>Pour</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
Other uses for Green Diesel: the Green Fleet project

eni and the Italian Navy defined an agreement, within the frame of the Navy Green Fleet Project, to formulate and produce a new military ship bio-fuel by means of the Ecofining™ Technology.

The new bio-fuel (containing more than 50% of Green Diesel) has been successfully tested for the very first time in Europe on the Italian Military Ship Foscari on last January.
Eni Green Refinery

- The **Green Refinery** is the result of the **first conversion of a petroleum refinery into a biorefinery** by mean of the application of Ecofining™ technology.

- This innovative idea has been patent filed by Eni on September 2012 (n° MI2012A001465).

- Revamping the existing units in Venice significantly reduces the required **investment cost, estimated in 1/4 to 1/5** of a new Ecofining™ grass root unit of the same capacity and intensively sped up project timing.
Green Refinery Project: two steps

• Today, STEP 1: the Ecofining™ is operating in balance with the hydrogen from the refinery hydroskimming section.

• Tomorrow, STEP 2, on 2016: H₂ production from a new steam reformer will allow to maximize the Ecofining™ capacity.
More than 300,000 t/a of Green Diesel production and additional conventional products such as EURO 5 gasoline and LPG, integrated with bio-quote of Green Naphtha and Green LPG from the Ecofining™ unit.
A technology challenge

- **New feedstock material**: different handling due to the poor cold flow properties and organic acidity.

- **Conversion of two existing diesel HDS units into the two reaction stages of the Ecofining™ process.**

- Integrating the Ecofining™ unit into the previous refinery scheme (utilities, ancillaries, etc.).

- Separating for the 1st step of operation, the derived biological material from the fossil material still running in part of the hydroskimming section of the former petroleum refinery (different blow down, sewers, slop tanks, etc).
A technology challenge

- **Corrosion prevention** for equipment:
  - Upstream systems: Fatty acids ➔ impact on the tracing system selection;
  - Downstream systems: Acidic gases & liquids ➔ impact on the metallurgy of the circuit.

- **“New acid gas”** management:
  - CO$_2$ rich gas, with small amount of H$_2$S coming from sulfur injection to Deoxy section;
  - H$_2$S recovery from acid gas by amine separation from CO$_2$ and H$_2$S reuse as sulfiding agent in deoxy reactors.
The start up: a successful experience

• The Eni Green Refinery start up in the new configuration was very smooth without any issues;
• The ECOFINING™ unit **successfully started up in May 2014**, producing high quality Green Diesel.
• The unit performance, its operation stability and its response to changes are overcoming expectations.
• The integration with the hydroskimming section and with the utilities, facilities and offsite of the previous refinery is successful.
The update: after 4 months of operation

- An **unplanned shut down** of the unit was required after 3 months of operation for **high delta P** on the reactor guard bed catalyst;
- A quick turnaround allowed to replace the filtering material inside the first bed of the deoxy reactors;
- Delta P increase was related to the entrainment of dusty material from existing piping and tanks reused for the revamping;
- Filtration has been therefore improved.
Next improvement...

- Eni is looking for feeding the Green Refinery with additional **advanced biofuel feedstocks**:  
  - Tallow;  
  - Used cooking oils.


- **Focus on short supply chain**: advanced feedstock from the region surroundings for improving the local economy.
Looking to the future (eni R&D)...

- **New biofuels**: a new innovative process is under development for producing new 2nd generation biofuels.

- **Bio-oils from microalgae**: eni has a pilot plant operating since 2010 in the Gela refinery, Sicily, constituted by algae farm and oil recovery plant.
Conclusions

The Venice Green Refinery is the result of the long term eni “Green Strategy”, made by investment on R&D activities aimed at developing innovative biofuel technology and renewable sources. The Green Refinery shows dual innovation:

**ON PROCESS**

1st conversion in the world of a conventional petroleum refinery into a Biorefinery, by means of the Ecofining™ proprietary technology, which allowed to renew the obsolete Venice Refinery into a high innovative industrial process scheme.

**ON PRODUCT**

Launch on the market of new high quality biofuels: Green Diesel, Green jet, Green LPG and Green Naphtha.

Green diesel, in particular, will be distinctive of eni Diesel fuel, assuring premium quality for stronger competition.
Thank you