Venice’s Biorefinery and Green Diesel: process and product innovation

Giacomo Rispoli, Executive Vice President, Eni Refining & Marketing

25-27 May, 2017 - Gela, Italy
Topics

- Eni Case Study: how converting existing fossil Refinery into a BioRefinery, for production of a new generation very high quality biodiesel.....

- ..... and at the same time counteracting the structural fossil Refinery overcapacity, and saving employment

- Description of Eni-Uop Ecofining™ Technology;

- Thanks to this new Biodiesel component availability, the launch on fuel market a new premium diesel, with very good characteristics both on engine performance and mainly on environmental impact.
The history of the Venice Refinery

**The Start**
1926

**The War**
1944

**Rebuilt**
1948

**Today**
2015
Venice Refinery geographic position
Refining crisis

- High energy cost
- Environmental constraints
- Decrease of demand
- Old refining system

Low operating margins

Refining overcapacity
Eni vision

EU Refinery Industry Crisis

Refinery Capacity Reduction?

Bio Quality Improvement

Biorefinery

ECOFINING™ Technology

EU biofuels Scenario


Re-Design a traditional Refinery!
The EU legislation on biofuels

  Incentives and regulates the renewable energy production and forces Members States to have a minimum 10% renewable in energy content in selling transport fuels @ 2020.

- **Fuel Quality Directive (2009/30/EC):**
  Gives the guidelines on fuels quality and controls GHG emissions due to transportation fuels (sustainability criteria for biofuels).

* Only for Plant in operation after 1° Jan. 2017
The EU legislation on biofuels

On September 2015 a Revision of the Fuel Quality Directive (FQD) and Renewable Energy Directive (RED) has been released by the EU:

THE SO-CALLED ILUC DIRECTIVE (1513/2015)

The Key elements of this Directive are:

The contribution of biofuels produced from 'food' crops is capped at 7% (vs. the 10 % renewables in transport target)

The other 3% will come from a variety of several NON EDIBLE alternatives:
• Biofuels from Used Cooking Oil and Animal Fats (double counted)
• Renewable electricity in rail (counted 2.5 times)
• Renewable electricity in electric vehicles (counted 5 times)
• Advanced biofuels (double counted and with a sub target of 0.5%, possible increased in the future)

Under discussion the RED II for the next decades, more stringent criteria on:
• Minimum REN % on Energy Total
• Minimim CHG Reduction
• No more double counting
• Increase Advanced Mandatory
• Minimum for UCO or Animal Fat
The EU legislation on biofuels

Advanced Biomasses/Biofuels

a) Algae if cultivated on land in ponds or photobioreactors.
b) Biomass fraction of mixed municipal waste, of private households and of industrial waste not fit for use in the food or feed chain
c) Straw.
d) Animal manure and sewage sludge.
e) Palm oil mill effluent and empty palm fruit bunches.
f) Tall oil pitch.
g) Crude glycerine.
h) Bagasse.
i) Grape marcs and wine lees.
j) Nut shells.
k) Husks.
l) Cobs cleaned of kernels of corn.
m) Biomass fraction of wastes and residues from forestry and forest-based industries.
The Refinery conversion

Traditional Refinery

Conventional products

Crude oil

Green Refinery

Green LPG
Green Naphtha
Green Diesel

Conventional products

Palm oil
Virgin Naphtha

blending

Logistics

LPG
Gasoline
Jet + Diesel
Fuel oil + Bitumen
Eni vision on biofuels

- Produce real “drop-in” fuels instead of fuel additives.
- Leverage existing refining/transportation infrastructure:
  - Lowers capital costs, minimizes value chain disruptions, and reduces investment risk.
- Focus on path toward advanced generation feedstocks.

**Oxygenated Biofuels**
- Ethanol
- Biodiesel

**Hydrocarbon Biofuels**
- Diesel
- Jet
- Gasoline

“Other” Oils: Camelina, Jatropha

First Generation
- Natural oils (vegetables, greases)

Advanced Generation
- Lignocellulosic biomass, algal oils
Standard options for bio-fuels

**Gasoline**
- **bio-ethanol**: according to EN228, the maximum O₂ content allowed is 3.7 %w, or 10 % v CH₃CH₂OH (E10) which correspond to ~ 6.7 % on energy basis.
- **ETBE**

**Diesel**: FAME- according to EN590, the maximum FAME content allowed is 7 %v which corresponds to ~ 6.4 % on energy basis

Possible Engines Damages (not covered by producers)

**BIODIESEL CONVENTIONAL PROCESS:**
- **Feed**: Methanol, Biofeedstock
- **Process**: Transesterification
- **Products**: Biodiesel FAME (Fatty Acid Methyl Esters), Glycerine

LOW CAPEX but LOW QUALITY
Eni’s new approach

Eni’s choice was:
- To minimize Gasoline Biofuels, due to product surplus
- To develop a high quality diesel biofuel, based on proprietary technology

Eni and UOP developed the **ECOFINING™** Process:

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

**1st stage of reaction: Hydrodeoxygenation**

**Reactions:**
- Triglycerides structure cracking;
- Deoxygenation;
- Double bond saturation.

**Products:**
- Mix of linear paraffins (high cetane number, pour cold flow properties: Cloud Point > 20°C).

**By-product:** Green LPG (propane).

**2nd stage of reaction: Hydroisomerization**

**Reactions:**
- Paraffins isomerization;
- Paraffins cracking.

**Products:**
- Green Diesel (excellent cold flow properties).

**By-product:** Green Naphtha.
The quality of GreenDiesel

The Green Diesel, due to its chemical composition made of pure paraffines, is a perfect blending component for diesel fuel Euro 5 (EN:590) up to 30%.

<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>0.820</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>
Green Refinery - Flow Scheme

**FR Naphtha**
- Hydroskimming (FR Naphtha Splitter, Isomerization & Platforming)
- Green Naphtha
  - ECOFINING™
    - HF1
    - HF2
    - Power & steam
  - CTE (COGE)
  - Power & steam
  - Power
  - LPG
  - Gasoline

- Palm oil (400 kt/y)
  - H2

- Natural gas
  - H2

**Green Diesel (75 % vs feed)**
Green Refinery Improved Flow Scheme

Crude vegetable oil (600 kt/y) → Pretreatment + ECOFINING
Animal fats
Used cooking oil

Hydrogen

Steam Reformer

Natural gas → Power & Steam

Power & Steam

Natural gas

CTE

Power

Green LPG
Green Naphtha
Green Jet Fuel
Green Diesel

Crude vegetable oil (600 kt/y)
Eni Green Strategy results

- **2007**: Eni/Honeywell UOP Ecofining™ patent
- **2012**: Permitting completion
- **2013**: First Green Refinery Project starts
- **2014**: May: Green fuels production starts from Venice Biorefinery
- **2017-2019**: Flexibility & capacity Upgrading

**In 2018** Eni will start @ Gela its second Biorefinery, to match the increasing need in biofuels
The success achieved with the Venice bio-refinery, has led Eni to convert Gela refinery into a biorefinery. The project is part of a wider agreement with national and local Institutions to promote a new development for this industrial site and the local economy.

Currently the project is in the phase of completion of the basic engineering design. The first run of production is foreseen in 2018.

The capacity of Gela will be about 710 kton/y. The production of Green Diesel will be about 530 kton/y.
Bio-fuels Sustainability

- Palm oil is supplied to Eni only by suppliers that can guarantee sustainability certification (in particular: ISCC, BSvs, RSB EU RED), in agreement to European Guidelines 28/2009.

- Eni is certified BSvs from January 2014 for biofuels production (certification No. 2BS010167 del 29/01/2014).
Green Diesel Life Cycle Analysis: Fossil Energy Consumption

The ECOFINING™ process for the Green Diesel production allows higher saving in fossil resources than FAME production.
January 2014 - ITS Foscari: 1st European navy ship fed with Green F76
EU and U.S. promote the transition to the second generation

Depending on the feedstock and the time-to-market expected, biofuels can be traced back to different ‘generations’:

- **1st gen.** Agrifood Feedstocks
  - Large & liquid markets
  - Support from the EU and U.S. regulatory targets
  - Strong social and environmental impacts (Food vs fuel)
  - Climate risk
  - Possible phase-out legislation

- **Double counted** Agricultural non-food, Agro/Urban waste Feedstocks
  - Environmental impact favorable
  - Valorization waste materials
  - Strong regulatory support
  - High production costs and complex logistics
  - Climate risk for some productions

- **advanced** Non-agricultural High Innovation Feedstocks
  - Not in competition for use of the land resource
  - High technological added value
  - Potentially large yields
  - Immature technologies
  - Strong investment in R & D required
  - High production costs

**OPPORTUNITIES**
- High technological added value
- Potentially large yields

**RISKS**
The 5 biofuels industry challenges

**FEEDSTOCK AVAILABILITY**

- Greater supply security
  - High productivity feedstocks selection

Rapeseed cultivation in all EU arable land (100 million ha) would satisfy only 40% of the EU consumption of diesel.

**PRODUCTION COSTS**

- Costs convergence with petrol/diesel in the long term
  - Exploit opportunities for cogeneration (heat/electricity) if any

**SOCIO ENVIRONMENTAL SUSTAINABILITY**

- Neutrality vs. food commodity prices (food vs. fuel)
  - Ensure reduction CO₂ emissions in the life cycle
    - 2° and 3° generation

**LOGISTICS**

- Optimizing Transportation and Storage To Deal With:
  - Low En. density biomass
  - Perishability of feedstock and products

A small biorefinery 2G 3 mb/d requires 700 kton of cellulose, which are transferred by 50,000 lorries a year, (one every 10 minutes).

**BIO FUELS QUALITY**

- Chemical Characteristics Similar To Petrol/Diesel To Achieve:
  - overconquering blend wall
  - consumer acceptance common network

- Distribution/sales
  - Prospects for long term market car/truck
Next futures developments: alternative feedstocks vs. Palm Oil

- Eni is planning to gradually utilize feedstock non in competition with food production and market

- In February 2015 a first industrial test with second generation feedstock (national UCO) has been concluded.

- Under development and definition collaborations with public operators of wastes to increase the collections of domestic UCO.

- In this way a short and integrate purchasing-line will be created, maximizing locally produced UCO.

- Under evaluation the possible utilizing of Food Palm Oil Refineries byproducts (PFAD) and waste animal fat.
Biofuels longer term perspectives

1 ha pilot plant for algae cultivation in the Gela refinery - Sicily

Lignocellulosic biomass

Saccharification

C6 sugar

C5 sugar

Saccharomyces cerevisiae yeasts

Ecofining

Microbial Lipids

Algal oil

Oleaginous Yeasts

Can accumulate up 70% (dry) of lipids

Project under development by Eni-Donegani Institute in Novara - Piedmont
Eni anticipates the evolution of fuel quality

Thanks to the strong R&D and Industrial structures and facilities

<table>
<thead>
<tr>
<th>Specifics</th>
<th>Eni commitment</th>
<th>Legal validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline 1% vol max Benzene</td>
<td>1997</td>
<td>2000</td>
</tr>
<tr>
<td>Diesel max 10 ppm S</td>
<td>2002</td>
<td>2009</td>
</tr>
<tr>
<td>Gasoline max 10 ppm S</td>
<td>2004</td>
<td>2009</td>
</tr>
<tr>
<td>Diesel max 8% Poliaromatics</td>
<td>Campaing 2010 (*)</td>
<td></td>
</tr>
<tr>
<td>Formula Milano 2% PNA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio content min 10% (Eni Diesel+,15% Green)</td>
<td>2016</td>
<td>2020</td>
</tr>
</tbody>
</table>

(*) Test 4 months in Milan Area, in a period with very high pollution level detected.
New Eni Diesel+

- New Chemical composition (15% Green Diesel)
- Higher Cetane N° and Detergent Additives
- Less Total Aromatics
- Less Poliaromatics
- Less Sulphur
- Better Engine Performances
- Less Consumptions

Less Impact on Environment
Test Activities

- Bench Test @ Istituto Motori di Napoli (CNR) on a Diesel engine 2000 cc allowed to determinate the Eni Diesel+ best formulation.
- Then performances and emissions have been evaluated both on car and heavy duty engines.

- Emission Test on commercial vehicles Euro 5 and 6 @ Eni San Donato Milanese R&D Center.

- Bench Tests for detergent packages performances evaluation.

- CNR Supervision on all in-house activities, for experimentation validation.
New Eni Diesel + benefits

The new Eni Diesel + keep the same features as the Eni Blu Diesel +, and moreover contributes to decrease the environmental impact.

The reduction:
- Of emission depends on the type of vehicles and aftertreatment system;
- Of particulate, before aftertreatment system, is relevant è considerable (up to 20%);
- Of particulate, on traps equipped vehicles, allows to have less regenerations with durability advantages.

Increasing in Cetane n° (>55) concures to combustion efficiency and acoustic comfort (-2db) improvement, with less consumptions.

* depending on fossil matrix, and before smoke aftertreatment system.
The Green Refinery Project and Eni Diesel+ are the results of the LONG TERM ENI R&D GREEN STRATEGY made by continuous investment on R&D activities closely linked to the business aimed at developing innovative biofuel technology in advance of the regulations.

**CONCLUSIONS**

**PRODUCT INNOVATION**

Green diesel, in particular, will be distinctive of Eni Diesel+ fuel, assuring premium quality for stronger competition, and assuring at the same time environment safeguard.

**INDUSTRY KEEPING**

By this strategy we can reduce traditional refining capacity without losing technical and scientific know-how and largely keeping the national refining industry structure.

**PROCESS INNOVATION**

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.
Thank you for your kind attention

giacomo.rispoli@eni.com