



## Green Refinery: reinventing petroleum refineries



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# Venice Biorefinery

## introduction

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.

In this critical situation **eni** took the opportunity to invest in the innovative Green Refinery project which leads at the conversion of the existing Venice Refinery into a "Biorefinery", able to produce a new generation of very high quality biofuels, mainly Green Diesel but also Green Jet, Green Naphtha and Green LPG, each one exploitable as biocomponents for transportation fuels, starting from biological feedstocks, using proper know how generated in **eni** research & development center.

The Green Refinery project is the most evident result of long term "**eni Green strategy**", with a background of several years of investment in the Research aimed at developing new technologies on renewable fuels. This strategy is encouraged by the European biofuels scenario, strongly related the EU environmental policy aimed at reducing the CO<sub>2</sub> emissions.

The Green fuels produced by the Green Refinery have several different applications, overcoming the conventional automotive market:

- the Green Diesel has already been successfully tested by the **Italian Navy**, for developing a green fleet
- the Green Jet has already been successfully tested by air company on commercial flight.

In the Venice site, the **eni** long term Green Strategy allowed to turn a critical situation into the opportunity of entering the new business of renewable fuels in a leadership position.

## european biofuels regulation

Since 2008, the first European regulations regarding biofuels is defined in the EU's Climate Change Package, which aims to achieve the EU climate targets by 2020 (Renewable Energy Directive 2009/28/CE):

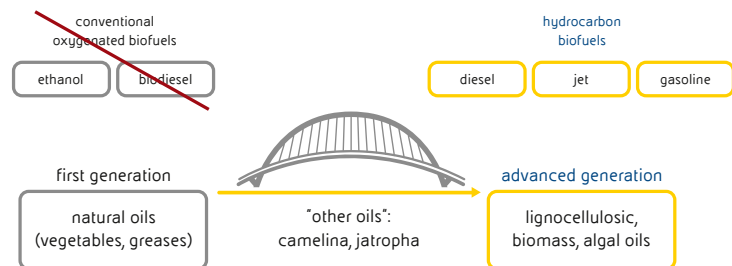
- 20% reduction in greenhouse gas emissions
- 20% improvement in energy efficiency
- 20% share for renewable in the EU energy mix.

The RED 20-20-20 is supported by the Fuel Quality Directive (FQD 2009/30/CE) on the promotion of the use of energy from renewable sources and GHG saving.

## eni vision on biofuels

**eni** and Honeywell UOP shared their efforts since 2006 to produce real "drop-in" biofuels instead of fuel additives, able to be easily integrated in existing refining and transportation infrastructure in order to reduce capital costs, minimizing value chain disruptions, and reducing investment risk.

**eni/UOP** jointly research and development activities aimed at patent on 2007 a new hydrotreatment process, called Ecofining™, for the production of a new type of biofuels, totally hydrocarbon, predominately Green Diesel, but also Green Jet, Green LPG and Green Naphtha, of excellent quality independent by the renewable feedstocks used: from 1<sup>st</sup> gen. (edible vegetable oils), to 2<sup>nd</sup> gen. (tallow, used cooking oils) and 3<sup>rd</sup> gen. (oils from algae and waste).



The Ecofining™ is a bridge technology | oriented to the advanced biomass feedstock

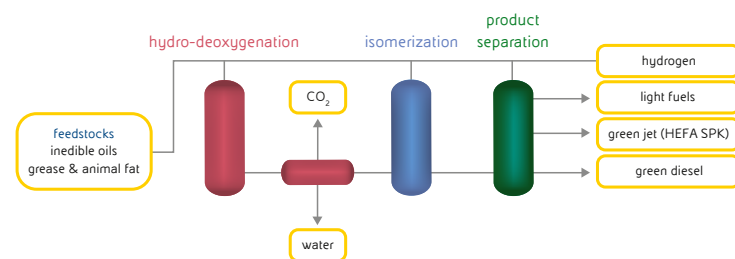
- **eni Green Strategy:** innovation in developing distinctive technologies environmental friendly.
- Development of process for producing renewable biofuels in compliance with European Directives.

## the Ecofining™ technology

The Ecofining™ process consists of two stages of reactions: a first one where the triglycerides contained in the biological feedstock are completely deoxygenated under hydrogen partial pressure, in a sour environment, on a proprietary metallic catalyst, producing a mix of linear paraffins, CO<sub>2</sub> and water.

The product of the first stage is then processed in a second stage of reaction where this mix of linear paraffins is isomerized, always under hydrogen partial pressure, on proprietary catalyst, in order to branch the linear chains for improving the cold flow properties of the final products.

The Ecofining™ process maximizes the Green Diesel production, producing also Green Naphtha and Green LPG and optionally Green Jet, each one valued as biocomponents for transportation fuels.



Simplified Ecofining™ process flow scheme |

The overall biofuels yields from the Ecofining™ unit overcome are between 85 to 95%wt. One of the main advantages of the Ecofining™ process is the possibility to precisely control the cold flow properties of the main product, the Green Diesel, due to the second stage of the reaction, which allows to easily reach also Alpine quality (Cloud point -20°C). The product properties can be controlled independent of the type of bio-feedstock used.

## Green Diesel: a high quality product

The Green Diesel, due to its chemical composition, made by pure paraffins, linear and branched in different proportions related to the degree of isomerization required, is an optimum biocomponent for blending in diesel fuel Euro 5 (EN:590) without any limitation. The high quality of the Green Diesel is highlighted by:

- higher heating value and energy density than that FAME, meaning that less Green Diesel is required for satisfy the same biomandate
- very high cetane number
- optimum cold flow properties reachable thanks to the isomerization stage of the Ecofining™ process
- low density, which makes it a very good blending component for refiners which are usually limited in accepting heavy gasoil basis in the diesel blend
- low aromatics content.

Another advantage in comparison to the FAME is that the Green Diesel has exactly the same behavior as the fossil diesel for storage,





logistic, loading facilities, without any problems related to stability, water separation, microbiological fouling, precipitation above cloud point and filter plugging which characterizes the FAME.

	Ultra Low Sulphur Diesel	Biodiesel FAME	Green Diesel Ecofining™
Bio content	0	100	100
Oxygen Content, %	0	11	0
Specific Gravity	0.840	0.880	0.780
Sulfur content, ppm	<10	<1	<1
Heating Value MJ/kg	43	38	44
Cloud Point, C	-5	-5 to +15	up to -20
CFPP additive sens.	Baseline	Baseline	Excellent
Distillation, C	200 to 350	340 to 355	200 to 320
Polyaromatics, %w	11	0	<2
NOx Emission	Baseline	+10%	-10%
Cetane	51	50-65	70-90
Oxidation Stability	Baseline	Poor	Excellent

The Green Diesel properties in comparison to the petroleum Ultra Low Sulphur Diesel and the conventional biodiesel FAME

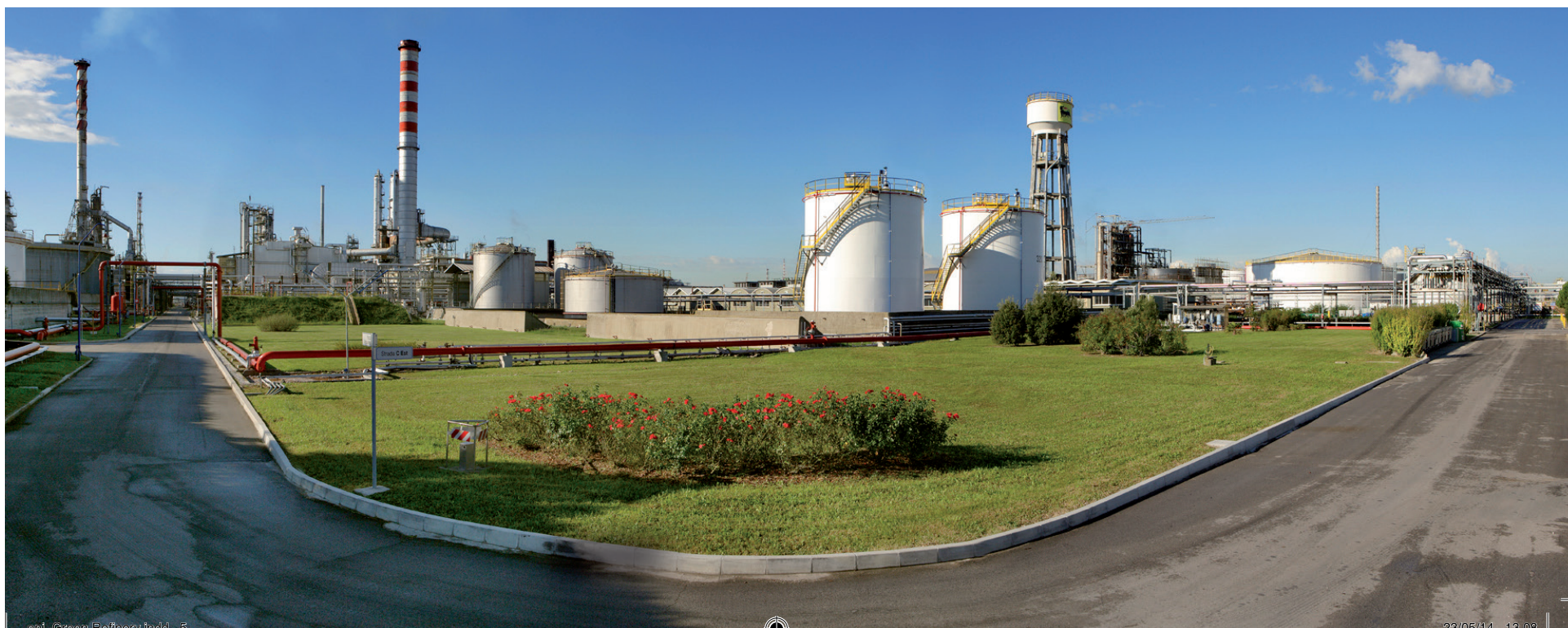
The Green Diesel, replacing in eni's fuel products the conventional biodiesel, will lead up to have a distinctive premium quality Diesel, with final customers benefits.

## the first industrial application for the conversion of a conventional refinery into a biorefinery

The Green Refinery project is the first conversion of a conventional petroleum refinery into a Biorefinery by mean of the Ecofining™ technology.

This innovative idea, patent filed in September 2012, n° MI2012A001465, will contribute to promote the industrial application of the Ecofining™ technology.

The revamp of the existing units in Venice intensely sped up the realization of the project, reducing significantly the required investment cost, estimated in 1/5 of a new Ecofining™ grass root unit of the same capacity.





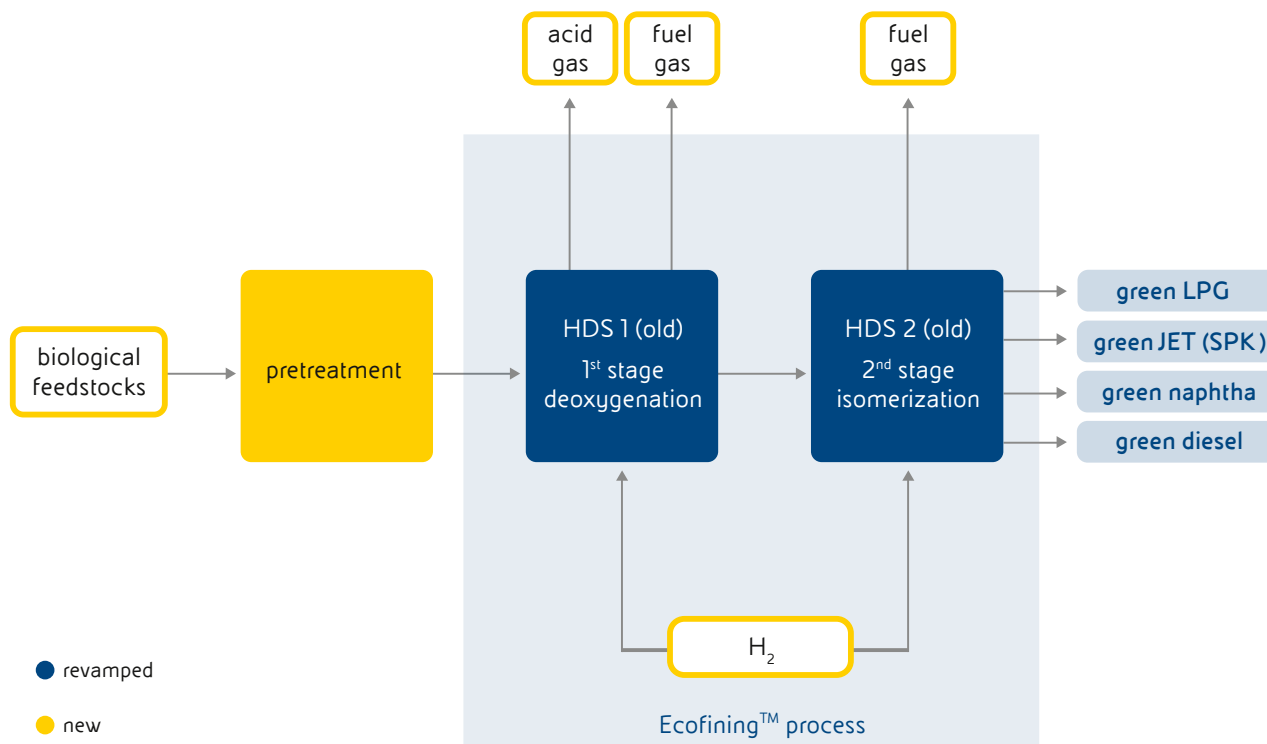
In the first arrangement of the Biorefinery, the Ecofining™ unit will operate in balance with the hydrogen produced by the existing hydroskimming section, fed by imported virgin naphtha. The maximum biofuels production (about 500 kt/y) will be achieved after 2015, when a new hydrogen production unit will be put in operation and to the refinery logistics.

Thanks to the Venice Biorefinery production, **eni** will be able to apply the "make" choice on biofuels, satisfying approximately half of its biofuels needs required for being compliant with the EU environmental normative aimed at reducing the CO<sub>2</sub> emission,

up to now totally provided from external suppliers. The core of the project is the conversion of two existing HDS units into Ecofining™.

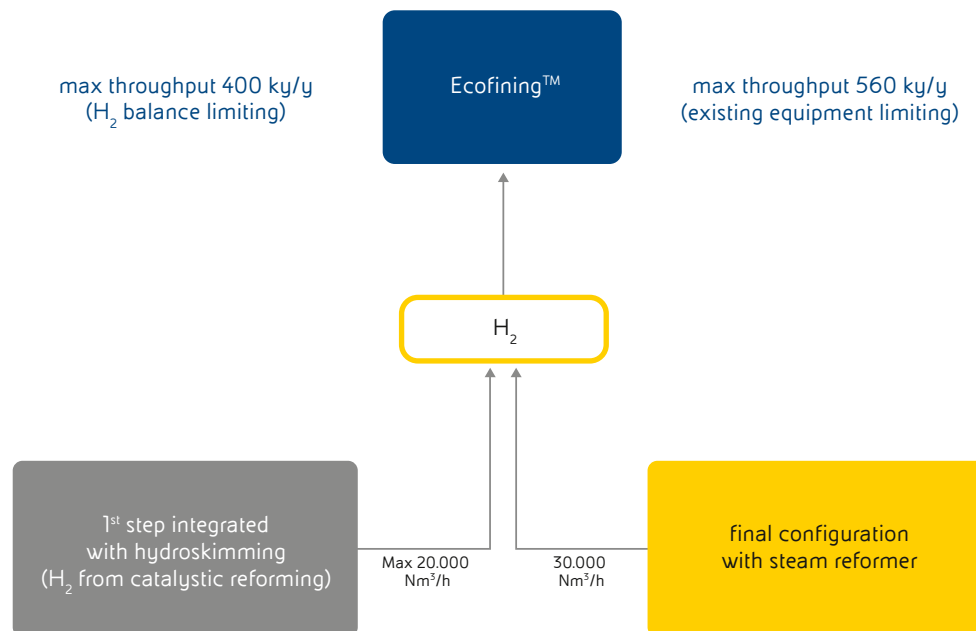
In particular the first one (HDS 1) will be modified in order to operate as hydro-deoxygenation section, mainly replacing the existing desulphurization catalyst with the proprietary deoxy catalyst and with other minor modifications to the existing plant.

The product of this first step of reaction will be sent to the second one existing HDS unit (HDS 2), where linear paraffins are isomerized, thanks to a specific isomerization catalyst.



HDS units rearrangement into the Ecofining™ unit |





- Today, **Step 1**, 2014: Ecofining™ operating in balance with hydrogen from refinery hydroskimming section.
- Tomorrow, **Step 2** within 2015: when the installation of a new steam reforming unit for the hydrogen production will allow to maximize the Ecofining™ capacity.

Green Refinery: steps of the project |

The integration of Ecofining™ unit in the existing process scheme impacts also all the ancillaries units, such as amine units, sour water strippers, acid gas handling, gas concentration, etc, still required for the new process. These units have been easily rearranged for the new operating conditions.

The Green Refinery project has all the advantages coming from a revamping project, in particular the integration with existing facilities provides utilities, ancillaries and all offsite support.

The Green Refinery Project represents a big opportunity for the Venice site of having a new life through innovative and economically sustainable refining operations.

The Biorefinery will assure a new life to the Venice industrial site, by means of economic profitable operations with the additional advantage of consistent reduction of the overall environmental impact.





eni is a major integrated energy company, committed to growth in the activities of finding, producing, transporting, transforming and marketing oil and gas. The company has global operations in 85 countries and employs about 82 thousand people.

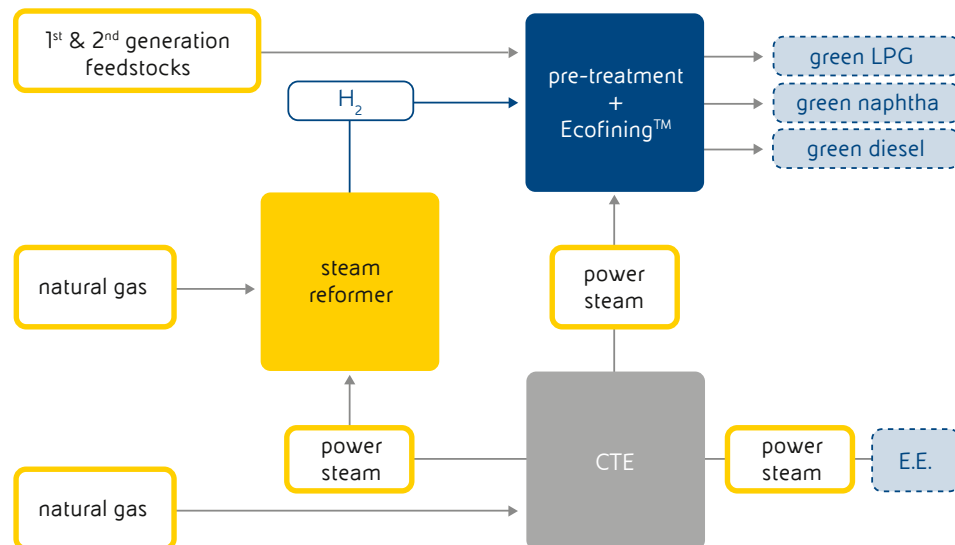
eni's strong presence in the gas market and in the liquefaction of natural gas, consolidated skills in the power generation and refinery activities, strengthened by world class skills in engineering and project management, allow the company to catch opportunities in the market and to realize integrated projects.

eni's business model for the creation of sustainable value is founded on a consolidated operating model in a framework of clear rules of governance using the highest ethical standards and rigorous enterprise risk management.

When implementing its strategy and running its day-to-day operations, eni's efforts are inspired by these key drivers: cooperation, integration, innovation, excellence, inclusion, responsibility. In 2013 eni confirmed its presence in the Dow Jones Sustainability Indices and in the FTSE4Good index.



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Green Refinery final configuration |