

From biomass to advanced biofuel: the greendiesel case

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World, European and Italian biofuel scenario

Different biochemical platforms for biodiesel

Lipids (from oleaginous crops, animal fat and microalgae)

Sugars: fermentation to lipids or chemical conversion to HC

Bio-oils

Summary and Conclusions



- Consumption of biofuels increases from 1.3 mboe/d (66 Mton/y) in 2011 to 4.1 mboe/d (208 Mton/y) in 2035, to meet 8% of road-transport fuel demand (3% in 2011). The European Union will reach 15% of fuel demand in 2035. Advanced biofuels, helping to address sustainability concerns about conventional biofuels, gain market share after 2020, reaching 20% of biofuels supply in 2035. This is mainly due to the stringent regulations introduced in many countries. (World Energy Outlook 2013, International Energy Agency)
- ✓ EU Renewable Energy Directive (RED) requires biofuels to reach 10% of total automotive fuels by the year 2020. Advanced biofuels from non-food, waste biomass will be counted 2x (double counting).



Italian biofuel scenario

Italian Government adopted a new DM (10 Oct. 2014) for the compliance of EU RED:

Planning a progressive diffusion of biofuel to reach 10% by 2020



- Defining the raw materials considered for advanced biofuel production: e.g. Algae; Biomass fraction of mixed municipal waste; Straw; Animal manure and sewage sludge; Palm oil mill effluent and empty palm fruit bunches; Tall oil pitch; Crude glycerine; Bagasse; Grape marcs and wine lees; Nut shells; Husks; Cobs cleaned of kernels of corn; Biomass fraction of wastes and residues from forestry and forest-based industries, i.e. needles, tree tops, saw dust, cutter shavings, black liquor, brown liquor, fibre sludge, lignin and tall oil; Other non-food cellulosic material.
- Defining the raw materials that are not considered for advanced biofuel production: e.g. recycled cooking oils; animal fats of I and II categories.







EU needs more diesel than gasoline

Since several years EU gasoline market demand is continuosly decreasing, while diesel is increasing. In Italy both demands are decreasing, gasoline more than diesel. This results in an increase of diesel/gas.



Different bio-chemical platforms for biodiesel





Lipids from oleaginous crops

Vegetable oils are triglyceride esters of fatty acids.

Since 2000, they are the feedstock for the production of biodiesel and, more recently, of Green Diesel.





The World production of FAME in 2013: **24.7** Mtons. The major feedstocks were soybean, rapeseed and palm oil.

Conventional Biodiesel (FAME) process





The homogeneous technology has two main shortcomings:

→ a restricted range of feedstocks: the presence of free fatty acids (FAA) and moisture in the feedstock causes the catalyst deactivation and the formation of soap as a by-product (i.e. FFA<0,5% and moisture <0,2%);

→ the alkaline catalyst must be neutralised, and the resulting salt is difficult and costly to remove from the glycerol to reach a saleable grade.

Different heterogenous catalysts have been considered to overcome the above drawbacks, including (see e.g. A.F. Lee, K. Wilson, Recent developments in heterogeneous catalysis for the sustainable production of biodiesel, Catal. Today (2014)):

- basic: zeolites (X, ETS-10); Oxides (ZnO, CaO, MgO);
- acidic: zeolites, Amberlyst 15, Sulphated Al₂O₃-ZrO₂.

TIM



FAME process: heterogeneous catalysis









Conventional FAME biodiesel drawbacks

- Poor oxidative stability due to the olefinic double bonds
- Affected by cold weather (can gel)
- Solvent properties promote degradation of rubber and elastomers
- Is biodegradable (i.e. can cause biofouling)
- More NOx formation than conventional diesel
- Formation of deposits at injector tips

Deposits at injector tips on a HPCR fuel system, leading to poor starting and running behavior (power loss, instability, smoke). Engine operated on RME B100 in a tractor in the field .

[Biodiesel, ULSD and Engine Performance, V. Stiffler-Claus (Jonh-Deere) 19 March 2009]











- No low value glycerol by-production : propane is the main byproduct
- Can process high free fatty acids low value oils and fats

► The conventional biodiesel blending-wall, currently limits biodiesel blending at 7% max, but this constraint is relevant only for FAME and can be overcome by use of HVO/ Renewable Diesel to meet EU's RED.

Several companies (Neste Oil, BP, PetroBras, Syntroleum/Tyson Foods, ConocoPhilipps, Haldor Topsoe, Nippon Oil, Axens and eni/UOP) have developed proprietary technologies for HVO to green diesel and green jet. Neste Oil is the leading renewable diesel producer in the world, with four facilities producing high-quality renewable diesel with a total production capacity of 2 million tons annually.



Rotterdam Next BTL plant started up Sept. 2011.





Processing Lipids with the UOP/eni Ecofining[™] Process



- Two catalytic stage process (DeCO₂ HDO and hydroisomerization) to achieve high yield green diesel, allowing control of cloud point;
- Product is an high cetane diesel blending component
- ► Co-production of green LPG, naphtha, and jet fuel possible
- Very feed flexible: rapeseed, soybean, carinata, palm, pennycress, jatropha, camelina, tallow, lard, used cooking oils and algal oil.













- Using proven Ecofining technology.
- 500 kt/y of animal fat and used cooking oil
 to 400 kt/y of green diesel and 65 kt/y LPG and Naphta.
- Co-location at existing refinery.
- In operation since June 2013.









The Green refinery in Venice

- In 2013 eni started up the Green Refinery project based on the conversion of the two existing hydrodesulfurization (HDS) units to the new hydrorefining process.
- The new processing scheme converts biological feedstocks (vegetable oils, animal fats, and used cooking oils) into high-quality renewable/biofuels (diesel, naphtha, LPG and, potentially, jet fuel).
- This facility is on stream since April 2014 and yields approximately 300,000 tpy of renewable, green diesel.
- The final configuration should be completed in 2015 with an overall production of 500 Ktpy.





G. Rispoli et al. Hydrocarbon Processing, 2013, 92, p. 95

http://www.eni.com/en_IT/sustainability/pages/green-refinery-project-porto-marghera.shtml



The Gela refinery conversion

Rome, 6 November 2014 – An agreement was signed between the Ministry for Economic Development, in the presence of the Minister Federica Guidi, the deputy minister Claudio De Vincenti and Eni chief executive Claudio Descalzi. The new phase of industrialisation foresees the development of upstream activities, the construction of a green refinery that will lead to the conversion of the Gela refinery to a bio refinery, a logistics hub for local crudes and green products, the environmental remediation and the establishment of centres of competence focused on safety to support Eni's productive units.

Green Refinery

The construction of a Green Refinery that will lead to the conversion of the Gela refinery in a bio refinery. The new Green refinery will have a production capacity for vegetable oil of some 750k tonnes/year. The conversion will make use of the proprietary ecofining technology, developed and patented by Eni, that will enable the production of green diesel, highly environmentally sustainable biofuel, and will also be able to process second generation raw materials.

Guayule project

Through its Versalis subsidiary, Eni is committed to conducting a feasibility study for a project for the production of latex based on natural products and the relative agricultural supply chain. In particular, an evaluation will be made, together with the Sicilian Regional government, of the creation of a guayulebased agricultural supply chain and the construction of a latex production plant with a capacity of around 5 k tonnes/year within the Gela refining facility.



http://www.eni.com/en_IT/media/focus-on/focus-on-gela.html



Ecofining[™] Reactions: hydrotreating



The hydroprocessing stage is carried out at moderate temperature using a bimetallic hydrotreating catalyst specifically tailored for the selected feedstock.

- 310 °C

- Ni-Mo or Co-Mo catalyst

All olefinic bonds are saturated, resulting in a product consisting of only linear-paraffins. But linear paraffins have high melting point \rightarrow poor cold properties!!

This requires a hydroisomerization stage, catalyzed by a bifunctional catalyst (i.e. metal loaded acidic zeolites, sulphonated oxides, SAPOs, mesoporous silica-aluminas)



Green Diesel Fuel Properties



	Petroleum ULSD	Biodiesel (FAME)	Green Diesel
Oxygen Content, %	0	11	0
Energy Density, MJ/kg	43	38	44
Cloud Point, °C	-5	-5 to +15	-20 to +10
Cetane	40 - 52	50-65	70-90
Sulphur, ppm	<10	<2	<2
Specific Gravity	0.84	0.88	0.78
Energy Content, BTU/gal	129 K	118 K	123 K
Poly-Aromatics, vol-%	4 - 12	0	0
Colour	Clear	Light to Dark Yellow	Clear
Oxidative Stability	Baseline	Poor	Baseline



High quality product, with properties meeting or exceeding Petroleum fuels



G. Rispoli et al. ERTC 17th Annual Meeting 13 November, 2012 Vienna, Austria



Renewable diesel from tall oil: the UPM technology

12 January 2015:

"The world's first wood-based renewable diesel biorefinery has started commercial production in UPM Lappeenranta Biorefinery Finland".

- The plant is based on a HT process developed by UPM, and produces approximately 100 kTon/Y of BioVerno diesel.
- The BioVerno diesel is produced out of crude tall oil, a residue of pulp production. A big portion of the raw material come from UPM's own pulp mills in Finland.
- 1 ton of dry pulp mill produces up to 50 kg of crude tall oil (CTO), which contains up to 70% of FFA.
- The world production of CTO is 2 Mton (M. Baumassy, 2014 PCA International Conference September 21-23, Seattle, USA).





separated and directed to waste



http://www.upm.com/EN/MEDIA/All-news/Pages/UPM-Lappeenranta-Biorefinery-is-in-commercialproduction-001-Mon-12-Jan-2015-11-30.aspx

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water treatment



Hydrogen consumption



Depending on oil H_2 consumption ranges between 1.5-3.8%. There are advantages and disadvantages for $DeCO_2$:

- Chemical hydrogen consumption is limited to olefin saturation.
- 🔾 Water is not produced, thereby preserving catalyst performance.
- Rejected CO_2 reduces the overall HC yield (5,5% less).

In practice these reactions occur simultaneously: depending on catalyst and/or conditions (e.g. DeCO₂ is favored with respect to HDO increasing T) it is possible to favor one or the other. (G.W. Huber, P. O'Connor, A. Corma, Applied Catalysis A: General 329 (2007) 120)





Biodisel by decarboxylation of fatty acids









Vegetable oil Methatesis – Elevance process





Versalis and Elevance Partner in Green Innovation for Premium Applications

February 6, 2014 (Milan, Italy/Woodridge, Illinois, USA)

<u>Versalis</u>, the chemical subsidiary of Eni, and <u>Elevance Renewable Sciences. Inc.</u>, a producer of specialty chemicals from natural oils, have signed a Memorandum of Understanding (MoU) to establish a strategic partnership to jointly develop and scale a new metathesis technology to produce bio-chemicals from vegetable oils.

Versalis and Elevance intend to focus on jointly developing and scaling new catalysts, leveraging the significant progress of this technology that has been already accomplished by Elevance. In addition, the partners will assess the design and construction of the first world-scale ethylene metathesis-based production that will utilize renewable oils at the Versalis Porto Marghera site. This will also take advantage of existing infrastructures and production streams.

Elevance and Wilmar International Limited formed a joint venture that now operates the first world-scale biorefinery in Gresik, Indonesia, based on Elevance's proprietary metathesis technology. The commercial-scale manufacturing facility has a capacity of 180,000 Ton with the ability to expand up to 360,000 Ton of products (www.elevance.com).





Oleaginous Algae: third generation lipids





Biodiesel from microalgae project



- > eni has been carrying out a demonstration project within its refinery in Gela (Sicily)
- ponds area of around 1 ha
- algal species capable of growing on flue gases from PO plant and aqueous streams from the wastewater treatment plant of the refinery
- very high lipid yields (15-29 ton/ha/y)
- > downstream recovery of the algal lipids based on a proprietary technology











Sugar Platform from lignocellulosic biomass



The hydrolysis of cellulose and hemicellulose contained in the lignocellulosic biomass to get sugars is a complex step that can be catalyzed by acids or enzymes.



Lipids by sugar fermentation





Oleaginous yeasts can accumulate up to 70% (dry weight) of triglicerides inside their cells.

Lipids yields : up to 20 kg per 100 kg dry biomass

Patent Application WO2010/46051 to eni s.p.a.

UOP/Eni Ecofining™ for green diesel fuels



Microbial oil

yeasts





- Selected yeast strains with high productivity (S. Galafassi et al., Bioresource Technology 111 (2012) 398–403)
- Different feedstocks (e.g. wheat straw, corn stalk, arundo donax)
- Fermentation scaled up to 1.5 m³
- Downstream recovery of microbial oil based on a proprietary technology
- Feasibility studies up to 100 Kton/y





	Oil productivity (t/ha year)
Rapeseed	1.1 - 1.3
Sunflower	1.5 - 1.8
Oil palm	3.8 - 5.4
Arundo donax (40-50 t/ha year) + yeasts fermentation	8
Microalgae	15-29











Algal strains

Chemical conversion of sugars to hydrocarbons





Chemical conversion of sugars to hydrocarbons









- adapted from M. Wright TC Biomass 2013
- http://www.cobalttech.com/news-item/April%2016,%202013.html



Thermochemical process od biomass





Bio-oil: the eni technology







Bio-oil Upgrading – Hydrogenation





Upgrading of bio-oils

FCC upgrading of bio-oil from liquefaction of sorted municipal organic waste

Joint Research Study



Experimental

- Catalytic cracking of bio-oil using an equilibrium FCC catalyst;
- Microactivity Test Unit (MAT) at 530 °C;
- TOS 30 s;
- Catalyst to Oil Ratio = 1-4 g/g
- Elemental analysis of liquefaction Bio-oil: C= 73,2%; H = 9,3 %; N= 4,6 %; S = 0,1 %; O = 12,7%

Reference FCC	equilibrium catalyst propertie
Jnit cell size (Å)	24.30
i/Al (wt/wt)	1.178
urface area (m²/g)	109
/licropores volume (cm³/g)	0.37
Ji (ppm)	1800
/ (ppm)	1800
e (ppm)	5700
la (ppm)	1100



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Upgrading of bio-oils







Biomass Fluid Catalytic Cracking to bio-oil

 ✓ Quite a number of patents and papers report the combination of pyrolysis and catalysis of whole biomass to produce fuels and chemicals.

 ✓ Kior has developed a proprietary technology based on FCC, called BFCC

 ✓ The technology uses traditional FCC catalyst and produces a biocrude than up-graded by HDT

✓ Different catalysts are claimed, including acidic zeolites (ZSM-5, beta, mordenite, ferrierite, Y), solid super acids (sulphonated or fluorinated zirconia, titania, alumina) and solid bases (metal oxides and or hydroxides and or carbonates).

✓The bio-oil can be blended with petroleum derived LCO and processed in a conventional diesel HDT.



Adapted from http://www.kior.com

	Bio-oil	Petroleum-Derived LCO
Mid-boiling point (°C)	220	276
Boiling Point Range (^o C)	70 - 520	114 - 420
Oxygen Content (wt %)	10	<0.5
TAN (mg KOH/g)	7	0.2
Wt% boiling below 215 C	53	13
Wt% boiling above 325 C	24	23

WO Patent 2012/092468 A1 to Kior Inc.





Biomass Fluid Catalytic Cracking to bio-oil

KIUK nails centrosic rules production in QL in optimize production; need for R&D to boost yield and LS January 2014: KiOR halts cellulosic fuels production in Q1 to 9 November 2014: KiOR, Inc. has filed for bankruptcy, although its KIUK, Inc. nas meu ior bankrupicy, aiuiouyn iis Mississippi subsidiary has not, preserving the chance that its Columbus plant could be cold quickly Mississippi subsidiary flas flow, preserving die that its Columbus plant could be sold quickly. cut costs.

✓ KiOR's commercial-scale facility in Columbus (MS): since early 2013 with a capacity of 13 million gallons (around 40 Ktons) of gasoline, diesel, and fuel oil blendstocks annually, enough to fuel 25,000 cars. ✓ Utilizes Southern Yellow Pine whole tree chips as the primary feedstock. \checkmark On a limited campaign base only the plant had produced 894,000 gallons of total fuel in 2013. The ratio between gasoline, diesel and fuel oil is 41% gasoline, 37% diesel, and 22% fuel oil.

KiOR wants to drive yield toward and beyond 80 gallons per ton (\approx 25%), while reducing product cost per gallon.

http://www.greencarcongress.com/2014/01/20140113-kjor.html

Summary: economic comparison

Drop-in biofuel production cost

\$/gallon ■ Feedstock ■ O&M ■ Capital Diamond Sundrop \$5 Kior \$4 \$3 \$2 \$1 \$0 Pioneer Plant Pioneer Plant "nth" plant "nth" plant "nth" plant Pioneer Plant **Pyrolysis** Gasification Green Diesel

Notes: Feedstock costs assumptions are \$0.50/lb for renewable oils and \$50/ton for cellulosic biomass.

Mac Statton, EIA Biofuels Workshop , March 20, 2013 | Washington, DC

Improvements in oleaginous yeasts and microalgae technologies could reduce the incidence of oil costs on green diesel.



Conclusions

- EU Renewable Directive is promoting the diffusion of biofuels, favoring advanced biofuels from non-food, waste biomass with respect to the conventional one's (eg. Bioethanol and FAME).
- ✓ A the moment the only commercial alternative to FAME is represented by HVO, that can also be obtained from "other" oils (non edible oils, waste animal fats, used cooking oils) while waiting for oils from lignocellulosic biomass and algae: i.e. HVO technology is a bridge from first to advanced generation-biofuel.
- ✓ Therefore for advanced biodiesel we do need new, viable technologies to exploit non-food lignocellulosic biomass to oil or to produce algal oil.
- Several different routes have been disclosed to get the goal. Few of them are already at a demonstration scale. For others, significant improvements are still needed in order to make viable large-scale applications.
- ✓ Eventually, the success of one or the other of these technologies will depend on several factors, including the availability and the quality of the feedstocks, the complexity of the process, and the quality of the final biofuel. In most cases, catalysis is playing a very major role.



	Importance	
Low	Medium	High
New transesterfication catalysts A A Th	 One pot hydrolysis and decarboxylation of lipids More robust HVO catalytic system suitable for low lipid qualities Where the better!	 Higher efficient cellulose & hemicellulose hydrolysis to sugars for fermentation or chemical transformations Less steps for sugar to HC High efficient catalysts and catalyst recovery for catalytic pyrolisis of whole biomass Efficient catalytic upgrading of pyrolitic bio-oils



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