ENEA technological platform for biofuels and green chemistry

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Roadmap of biofuels as part of sustainable fuels

On December 2023, COP28 recognized the crucial needs to accelerate the reduction of emissions from road transport on a through development of infrastructure and rapid deployment of zero and low-emission vehicles by utilizing zero- and low-carbon fuels.
According to the IEA scenario for net zero, biofuels will play a major role to decarbonize the road transport to 2030. Thereafter, electrification will be the prominent lever while biofuels and hydrogen-based fuels will be mainly used for shifting to aviation and shipping.
Sustainable fuels provide more than 75% of energy for aviation and shipping, and more than 25% of industry supply by 2050.
IEA data indicated that the share of biofuels in G7 road fuel consumption has remained around 5% over the last decade and has contributed to reducing road emissions by over 150 Mt CO2 in 2022, relative to 2000.
On the whole the IEA report issued on January 2024 indicated that biofuels demand is set to expand 38 billion liters over 2023-2028 corresponding to near 30% increase compared to the last five-years period. In fact, the total biofuel demand will rise by 23% by 2028 with respect to 2022 corresponding to 200 billion liters with an internal distribution of 26,4 bl renewable diesel, 117,5 bl ethanol, 52,9 bl biodiesel, 5,2 bl liters and biojet fuels.
Most of the new biofuel demand comes from emerging economies, such as Brazil, Indonesia and India and will be mainly satisfied by bioethanol and biodiesel. Advanced economies, including European Union, United States, Canada and Japan are also implementing some biofuels supporting policies even if the growth in these countries is constrained by the recent rising of electric vehicle adoption. Renewable diesel and biojet fuels will be the primary growth

[1] ENEA is the National Agency for New Technologies, Energy and Sustainable Economic Development, a public research body hosting 2300 researchers, technologists and administrative staff, aimed at research, technological innovation and the provision of advanced services to enterprises, public administration and citizens in the sectors of energy, the environment and sustainable economic development (article 4, Law no. 22 of 28 December 2015). ENEA has highly qualified personnel, advanced laboratories, experimental facilities for the realization of projects, studies, tests, assessments, analyses and training services, with particular reference to product and process innovation and the valorization of results to contribute to the development and competitiveness of the national economic system. Since its foundation in the 1960s, its strengths have been applied research, technology transfer and technical-scientific support to companies, associations, territories, central and local administrations: for this reason - unlike other research institutions - the Agency depends on the Ministry of the Environment and Energy Security.
Its focus sectors are energy technologies (renewable sources, energy storage, smart grids), for which the Agency is also the coordinator of the Energy National Technology Cluster, nuclear fusion and nuclear safety (the Agency is the reference national research coordinator), energy efficiency (with the National Agency for Energy Efficiency), technologies for renewables, energy storage, cultural heritage, seismic protection, food safety, pollution, life sciences, strategic raw materials, climate change.
Among the emerging issues, ENEA supports the productive system as well as public authorities (Ministry of the Environment and Energy Security and Ministry of Enterprises and Made in Italy in particular) in the transition towards the circular economy and the resource efficiency.

segments in these countries, where a consumption of 18 billion liters is foreseen over the period 2023-2028, with the United States and Europe accounting for near 80% of this increase.
The next decade will be essential to commercialize the technologies necessary for future success.

Introduction

Motorized transport on land, sea and air is still strongly dependent on oil, and more generally, on combustion engines that run on liquids or natural gas. Transport accounts for more than a third of CO2 emissions from end - use sectors.
According to the last Renewable Energy Directive 2023/2413 each Member State shall set an obligation on fuel suppliers ensuring a share of renewable energy in the final energy consumption for transport of at least 29 % by 2030 or greenhouse gas intensity reduction of at least 14,5 % by 2030. The share of advanced biofuels/biogas and renewable fuels of non biological origin-RFNBO- is at least 1% in 2025 and 5.5 % in 2030, of which a share of at least 1% is foreseen from RFNBO in 2030.
Member States, with maritime ports, shall endeavor to ensure that as of 2030 the share of RFNBO in the total amount of energy supplied to the maritime transport sector is at least 1.2 %. As effect of this supporting policies the share of biofuels consumed has increased.

In this contest, ENEA has a number of R&D activities and a strategic projects portfolio in cooperation with national and international stakeholders on the optimization of different biomass-based value chains. The main challenges regard the development and demonstration of qualified innovative processes, technologies and components for the production of sustainable liquid and gaseous biofuels. The final scope is to provide suitable and scalable technological solutions.
ENEA R&D on second-generation biofuels is focused on both thermochemical and biotechnological conversion processes of different biomass resources. More precisely, biotechnological processes mainly consist in fermentation of biomass derived carbohydrates into alcohol fuels and microbial oils, syngas fermentation, anaerobic digestion of humid biomass to biogas/biohydrogen.

Production of advanced bioethanol to be used in the transport sector has been demonstrated over a number of feedstocks, namely agroforestry biomass, poliannual and grass biomass crops. The process steps consist in the biomass pre-treatment, enzymatic hydrolysis, fermentation, and alcohol separation. Biomass pre-treatment is carried out with saturated steam at moderate temperatures (200 °C approximately) enabling a deep biomass destructuration which facilitates the following separation of its main components (cellulose, hemicellulose, lignin).
Thermochemical processes mainly rely on biomass gasification to carbon monoxide and hydrogen which represent a versatile platform for the production of energy and liquid and gaseous biofuels.
R&D activities on microalgae and other photosynthetic microorganisms to exploit energy and non-energy products, include the study, design, implementation and testing in open ponds systems. Besides the engineering skills, the Division laboratories include genomics and proteomics platforms supporting the discovery of novel genes involved in the biosynthesis and in the biomass biological degradation.

Production of biofuels through the sugars platform

Since the 1990s, ENEA's activities were focused on the evaluation of sustainable crops for industrial applications and tests fields planted with poliannual species in ENEA Research Centre Trisaia and the productivities were monitored over years. In more recent time, ENEA was partner of some industrial players, namely Biochemetex and Novamont, who made relevant investment in the construction of innovative biorefineries fed with poliannual crops. In particular, Giant Reed (Arundo donax) was selected as raw material for the BioChemtex Demo Plant in Crescentino (Vercelli, Italy) and tailor made processes were developed in the PRIT and BIOLYFE projects for the production of second generation bioethanol. Common Cardoon (Cynara cardunculus) was selected by Novamont® as raw material for The Matrica Biorefinery in Porto Torres (Sardinia) and the development of a cardoon based bio-refinery was part of strategic projects in the Italian Cluster of the Green Chemistry (BIT3G, REBIOCHEM).
The reliability of a local biomass supply is a key element for the biorefinery development. ENEA has created a GIS based national database, the National Atlas of Biomass, enabling a detailed assessment of the distribution and type of biomass at provinces level. ENEA carries out analysis on local biomass availability by an integrated evaluation of the agro-climatic vocation for instance in abandoned lands.

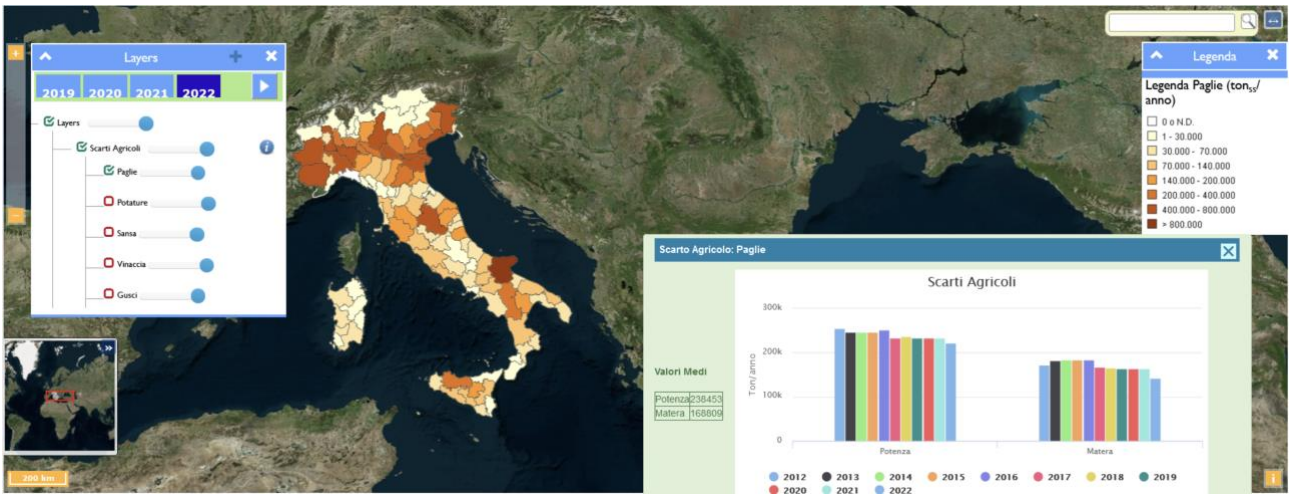

Figure 1 - ENEA National Atlas of Biomass: a view

Various initiatives are on-going in Europe to promote the development of a bio-based economy. Increasing the share of advanced biofuels in the transport sector and finding new bio-based products derived from renewable natural resources are only some of them.

A number of platform chemicals and advanced biofuels can be produced from sugars derived from lignocellulosic biomass using a **biorefinery approach**. Such approach consists in the maximum exploitation of the biomass barrel aimed at increasing the conversion efficiency.

ENEA activities support the development of new integrated biorefinery models through the implementation of cutting-edge processes and technologies for the production and conversion of some platform molecules from the biomass conversion, namely **sugars, lignin, and oils.**

Among the various biorefineries scheme, the sugars platform involves the breakdown of the raw materials into sugars which can be fermented, dehydrated or hydrogenated to produce a spectrum of chemicals. The three main steps of the biomass conversion and include: i) the biomass pre-treatment/fractionation to facilitate the enzymatic digestion, ii) the hydrolysis at high solids content (the so-called high gravity hydrolysis) and iii) the sugars upgrade and conversion to a number of bio-based products mainly through fermentation (e.g. bioethanol, microbial lipids, lactic acid) (Figure 2).

Figure 2 - Biomass derived sugars through pre-treatment (P) and enzymatic Hydrolysis (EH)

Pretreatment and fractionation through Steam Explosion (Figure 3) can be considered a flexible processes scheme since it uses saturated steam to produce high degrees of biomass destructuration. The use of small amounts of additives could catalyze the process at mild conditions. The type of additive could determine a different fractionation scheme. At the ENEA Trisaia Research Centre, the pilot station for biomass fractionation consists of three units of compatible size (Figure 4). The digester is able to process 300 kg/h biomass in the continuous mode. This technology is suitable to treat different biomass. The cellulose reach stream could reach purity of 80% and a lignin stream containing less than 2% sugars can be separated.

Figure 3 - Pretreatment plant at ENEA Trisaia Research Centre

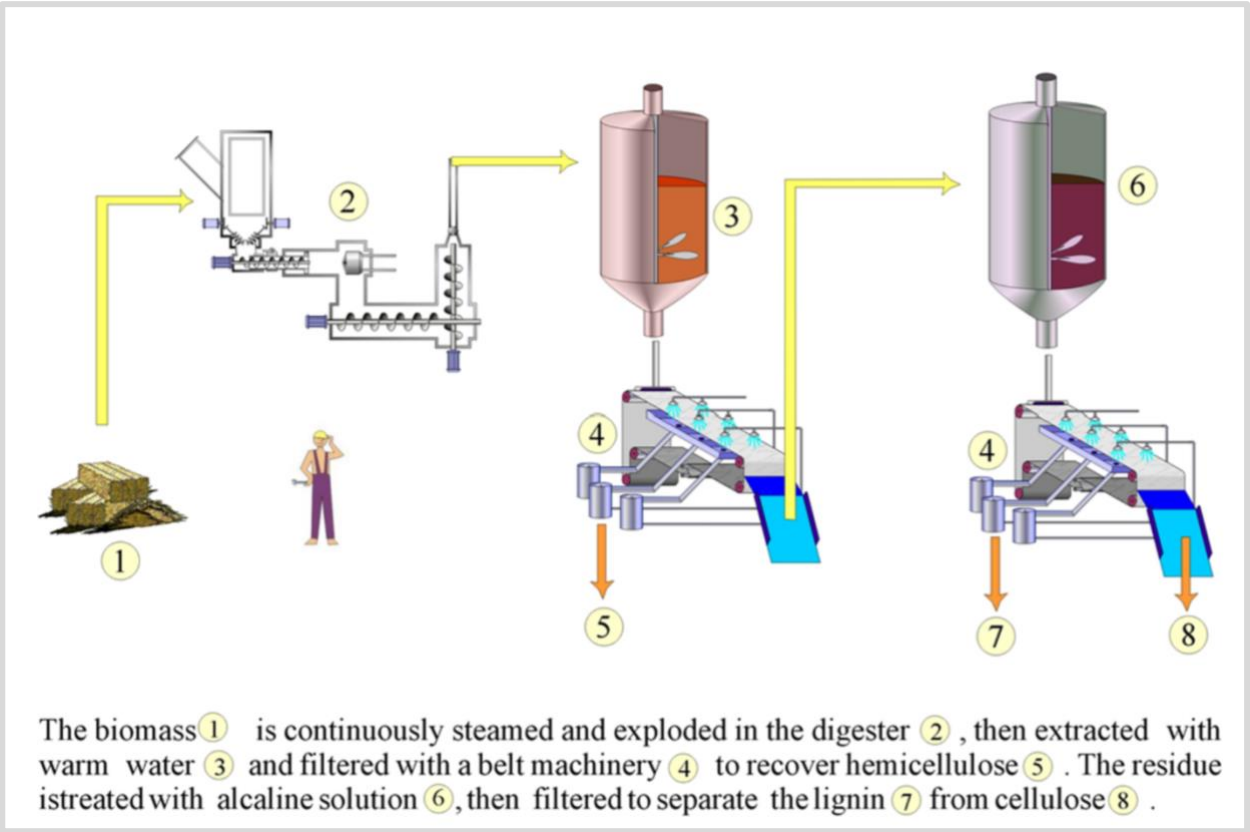

Figure 4 - ENEA Steam Explosion Continuous Plant

Some main technological challenges in the future will regard the exploitation of lignin, currently considered a side stream and used for the production of heat and electricity to make the biorefinery self-sufficient.
Hydrodeoxygenation (HDO) of lignin derived compounds to cycloalkanes is an option to produce aviation fuels. Lignin depolymerisation, with selective bonds cleavage, is the major challenge for converting this macromolecule into biofuels and value added chemicals.

Thermo-chemical Processes for the Exploitation of Biomass, Residues and Wastes

Research and development activities on thermochemical conversion processes are based on gasification and pyrolysis. In relation to the exploitation of biomass, the activities are mainly focused on the development of gasification processes for the production of gaseous energy carriers for direct application in CHP production or, after a proper cleaning and conditioning, as a gas of synthesis to produce derived fuels (e.g. hydrogen, SNG, Fischer-Tropsch liquids, methanol, DME). From the produced gas, chemicals can also be synthesized.

Pilot-scale gasification plants based on different reactor design (fixed bed, fluidized bed and staged gasifiers), effective gas cleaning and conditioning unit and size ranging from 120 kWth to 1,000 kWth, are available in the Research Centre of Trisaia.

Fixed bed (upcraft) - Air/stream 150kWth

Fixed bed (downcraft) - Air/stream 150-450kWth

Dual fluidized bed gasifier - Steam 500kWth

Internally circulating fluidized bed - Air/O2/steam 1MWth

Updraft fixed bed gasification plant (Figure 5) based on 150 kWth reactor with steam/air gasifying agent, operate with many feedstock and generate a gas of LHV 5-6 MJ/Nm3dry. The plant is equipped with a wet purification system consisting of a biodiesel scrubber. The produced gas can be used to generate a gaseous stream with a high H2/CO ratio (> 2) for the synthesis of biofuels (e.g. methanol) or to produce hydrogen of fuel cell grade.

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Figure 5 - The updraft fixed bed gasification plant

The use of conventional gasifiers for the conversion of biomass feedstocks with high moinsture content is not feasible without pretreatment stages such as drying.
A three stage pyrogasifier of 500 kWth is available at ENEA to threat wet biomass (Figure 6).

Figure 6 - Three staged gasification pilot plant

The process starts with the pyrolysis of the supplied biomass. The pyrolysis gas is conveyed to a partial oxidation reactor where tars are mostly cracked and converted into lighter gases. Pyrolysis char is fed to an open core downdraft reactor, with air/steam primary and secondary lines. The char bed also acts as an active carbon filter for raw product gas. Overall, the ultimate results are a producer gas with a very low tar level content and possibility of using a wide range of biomass feedstocks (including low value residues, e.g. AD sludge) as solid fuels.
The syngas produced through thermochemical processes can undergo catalytic upgrading to yield hydrogen or CO/H2 blends, which are well-suited for synthesizing biofuels and e-fuels. Ultra-pure hydrogen for fuel cells can be obtained through separation from syngas using palladium membrane reactors. The integration with catalytic water gas shift reaction further enhances process efficiency and yields.

Figure 7 - Palladium-based membrane reactors for ultrapure H2 production

Research facilities for the production of biofuels through the syngas platform also include SEG - Sorption Enhanced Gasification units enabling the H2 production via gasification intensified with CO2 capture process by CaO and additional sorbents.

Platform For the Production of Advanced Biofuels and Biolubricants (Biolube)

A novel platform was constructed in 2023 and will be available for pilot tests in the next months. Itis a versatile platform projected to produce advanced biolubricants / hydrotreated biofuels for many sectors including the jet fuel sector and in general drop-in blends with conventional fuels.

Figure 8 - Platform For the Production of Advanced Biofuels and Biolubricants (Biolube)

The platform consists of 4 demonstration units and it is currently projected to convert vegetable oils: oligomerization unit; thin film evaporation; hydrogenation; distillation.

The oligomerization unit is aimed at the liquid phase synthesis of macromolecules and consists of a mixed-type reactor with a volume of 300 liters (heated with diathermic oil, Tmax 200 °C) equipped with recirculation on an external exchanger (to control the Process T).

The mixture of oligomers can be fed to the thin film evaporation for the separation of target fractions based on different MW. The unit has been designed to operate at a Tmax of 300 °C and a Pmin of 5 mbar.

The hydrogenation unit consists of a 6" catalytic reactor (Trickle Bed Reactor type) with a length of approx. 6m, designed to operate at Pmax of 80 bar and Tmax of 400 °C.

The platform is completed by a batch distillation unit, with a 30-stage equilibrium column, designed for the separation (at high purity > 95%) of the monomers to be used in the oligomerization process. The unit has been designed to operate at Pmin of 50 mbar and Tmax reboiler of 260 °C.

On the whole ENEA has a number of fully equipped analytical laboratory for the process control and analysis.

ENEA main involvement in international and national organizations

ENEA is one of the founding members of the EERA (European Energy Research Alliance) that is part of the Strategic Energy Technology (SET-Plan) of the EC, is part of ECRA (European Climate Research Alliance), MEDENER (Mediterranean Association of National Agencies for Energy Management), and Enterprise Europe Network (EEN), the largest network of services supporting competitiveness and innovation for SMEs.

ENEA is member of:

- the Biobased Industries Consortium-BIC, a non-profit organisation representing the private sector in a Public-Private Partnership (PPP) with the European Commission, focused on strengthening the bio-based industries sector in Europe;
- SPRING (Italian Circular Bioeconomy Cluster). In particular ENEA participates in the Biofuel, biorefining and carbon markets expert group created by SPRING to address relevant topics in the target sector and elaborate a national position paper for the stakeholders;
- NEST (Network 4 Energy Sustainable Transition), Enlarged Partnership extended to Universities, Research Centres, Enterprises, funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 funded from the European Union - NextGenerationEU. The Spoke 3 "Bio energy and new fuels for a sustainable future" is focused on the development of novel thermochemical, chemical, biochemical and bioelectrical conversion processes and systems to convert bioenergy into useful power, advanced biofuels and value-added products.

Finally ENEA participates since more than ten years in some tasks of the IEA Bioenergy Network and in particular IEA Bioenergy Task42 "Biorefining in the Circular Economy", IEA Bioenergy Task 33: Gasification of Biomass and Wastes.

Advancing Sustainable Biorefineries: Innovations in Bioethanol and Biochemicals

BioLyfe Project

2° Generation Bioethanol: The world's largest demo plant ready to be transferred all over the world. 40.000 tons/y of lignocellulosic (EU Project No. FP7-239204)

Project leader: ENI Versalis

ALBE Project

Environmental sustainability assessment of polymeric materials from renewable sources

Project leader: Biochemtex

BIT3G Project

Development of a biorefinery integrated into the local area to produce high-added value molecules (i.e. oils to convert into bioplastics, biolubricants, bioherbicides)

Project leader: Novamont

Rebiochem Project

Biochemicals from 2nd generation biomass (i.e. bio-butandiol; 5-HMF)

Project leader: Mater-Biotech

COMETA Project

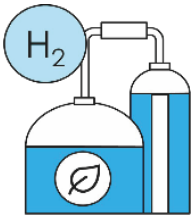
Autoctone Mediterranean crops and their valorisation with advanced green chemistry technologies

Project leader: Novamont

Collaborative research

Three-year collaboration agreement concern research and development activities with Canadian company in the field of biorefineries and 2G sugar production

Coordinator: Comet Biorefining Canada



POR H2

Framework agreement on the research and development of hydrogen a energy carrier for the green revolution and ecological transition

Next generation EU: National Recovery and Resilience Plan

JCA ENI-ENEA

Development of process for the production of microbial oils, biogas/biomethane, intermediates for advanced biofuels and for the production for biochar by valorizing waste and lignocellulosic biomass

Coordinator: ENI Versalis

Ambition Project

Advanced biofuel production with energy system integration.
Horizon 2020

Project Partners: SINTEF; ENEA; LNEG; KIT; DTU; CENER; ASTON University; TNO

BRISK1 and BRISK2 Projects

Biofuels Research Infrastructure for Sharing Knowledge 7FP and Horizon 2020

Project leader: KTH

RISEnergy Project

Research Infrastructure Services for Renewable Energy. Horizon Europe.

Project leader: KIT

INDUSTRIA 2015

PRIT Project

"Pretrattamento italiano"

Large scale project, Industria 2015, Program Efficienza Energetica.

Project Partners: Mossi&Ghisolfi Industries, ENEA, CNR

INDUSTRIA 2015

HYTRACTOR Project

Fuel cell farm tractor powered by hydrogen - New Technologies for Made in Italy, Industria 2015

Project leader: CNH

Valorization of Agricultural and forestry waste

Biochar production and applications: from soil amendment to bioprocess booster

REVINE

Regenerative agricultural approaches to improve ecosystem services in Mediterranean vineyards

Convert biomass of pruning waste in **biochar** in order to improve **carbon storage, vineyard performance and sustainability** in a **circular economy** perspective.

Studying the effect of biochar treatments on vine-associated **microbial communities.**

PNRR - AGRITECH

Study of the effect of **pyrolysis parameters** on the biochar efficacy as soil amendment (study of the effects on **plants and rhizosphere microbial communities**)

Joint Cooperation Agreement ENI SpA - ENEA

Development of thermochemical process to produce **biochar** from **agricultural and forest wastes**.

NEST

Network for Energy Sustainable Technologies
(Green Energies for the Future)

Evaluation of the effects of biochar amendments on **dark fermentation** process performances and microbial community; Biochar boosts *in-situ* **bio-methanation** process for biological biogas upgrading.

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