Bioenergy, biorefineries and green chemistry: ENEA projects to advance a more sustainable economy

With the widespread use of biomass for energy purposes, Italy is one of the leading countries engaged to exploit this potential renewable source for the production of bio-based products including chemicals, polymers, materials, feed and bioenergy, pursuing a cascading approach (biorefinery). It is true that substantial breakthrough have been achieved but the fact remains that R&D efforts are still necessary to address both technological and non-technological barriers. Development and demonstration of qualified innovative processes, technologies and components for the generation of both electric and thermal power in small-sized plants and the production of second-generation biofuels and sustainable biobased products, are the main challenges that needs to be addressed. In the above context, ENEA, in cooperation with both national and international stakeholders, has a number of R&D activities and a strategic projects portfolio. The focal point of ENEA's activities as well as brief description of some prototype technologies, are described in the present communication

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Biogas production from waste materials is one of the main research topics. Initiatives underway are aimed at the production and upgrade of biogas for electric power generation or for the grid. Innovative technologies are tested for the energetic valorisation of the digestate.

R&TD on second-generation biofuels is focused on both thermochemical and biochemical conversion processes of lignocellulosic materials. More precisely, fermentation of carbohydrates into bioethanol, production of hydrogen through fermentation of humid biomass and biofuels from microalgae cultures are some of the main activities. An important research infrastructure is available at ENEA Trisaia Research Centre for the biomass gasification to carbon monoxide and hydrogen, which represents a versatile platform for the production of energy and liquid biofuels, for instance, through the Fischer-Tropsch process.

Production of second-generation bioethanol to be used in the transport sector using a number of feedstocks, namely agroforestry biomass, poliannual and grass biomass crops, has been the focus in a number of R&D programmes. The process comprises the biomass pretreatment, the enzymatic hydrolysis, and fermentation, and finally the 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 separation of its main components (cellulose, hemicellulose, lignin).

R&TD activities on microalgae and other photosynthetic micro-organisms for the production of energy and non-energy products through bench scale optimization and final testing of pilot plants.

Also, the ENEA laboratories include a Genomics and Proteomics platform supporting the discovery of novel genes involved in the biological biomass degradation and in the biosynthesis of value-added molecules.

Technologies and Processes for Biorefinery and Green Chemistry

A number of initiatives are underway 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.

As an example, a number of 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. Already in the early 1990s, ENEA was pioneer in the evaluation of sustainable crops for industrial applications and test fields were planted with poliannual species at ENEA Trisaia Research Centre. The biomass productivities were monitored continuously over the years.

More recently, ENEA has strengthened some alliances with industrial stakeholders, including Biochemetex and Novamont, with significant investments 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 under 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 biorefinery was part of strategic projects in the Italian Cluster of the Green Chemistry (BIT3G, REBIOCHEM).

Amongst various biorefineries scheme, sugars platform involves the breakdown of raw materials into sugars, which can be fermented, dehydrated or hydrogenated to produce a spectrum of chemicals. R&TD activities in cooperation with industries and research organizations are underway on the three main steps of the biomass conversion and include: i) biomass pre-treatment/fractionation to facilitate the enzymatic digestion; ii) hydrolysis at high solids content (the so-called high gravity hydrolysis); and iii) sugars upgrade and conversion to a number of bio-based products, mainly through fermentation (e.g. bioethanol, microbial lipids, lactic acid).

Pretreatment and fractionation through *Steam Explosion* can be considered as a flexible process 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. 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.

The reliability of a local biomass supply is a key element for biorefineries development. It is worth to note that a national GIS-based database and National Atlas of Biomass was created by ENEA enabling a detailed assessment of the distribution and type of biomass at province level (http://www.atlantebiomasse.enea.it/). In addition, ENEA carries out analysis on the local biomass potential for instance in abandoned lands by applying an integrated evaluation of the agro-climatic vocation. The full development of biorefineries in the future will imply both technological and non-technological challenges. One main objective of the future research in the conversion of lignocellulosic materials will regard the exploitation of lignin, currently considered as a side stream and used for the production of heat and electricity to make biorefinery self-sufficient. The question is: how does the biorefinery energy balance look if part of the lignin is used to produce bioaromatics/biochemicals?

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 and, thus, support the National and European industrial system to scout and focus on advanced new technologies. In relation to the exploitation of biomass, activities are mainly focused on the development of gasification processes for the production of gaseous energy carriers of higher value, available for direct application in CHP production or, after 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.

R&D activities are mainly focused on the development of small to medium size technologies for power production using low value feedstocks. Five 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 kW_{th} to 1000 kWth, are available at the ENEA Trisaia Research Centre.

Recently, an updraft fixed bed gasification plant, based on 150 kWth reactor with steam/air gasifying agent, operates with feedstock of high biogenic fraction and a generating producer gas of LHV 5-6 MJ/Nm^3dry is implemented. The plant is equipped with a wet purification system operated with biodiesel. The produced gas was considered to generate a gaseous stream with a high H_2/CO ratio (> 2), to be used in the synthesis of biofuels (e.g. methanol) [10], or to produce hydrogen of fuel cell grade. To this aim, after the biodiesel scrubbing, the gas stream is addressed to a section for gas upgrading and CO_2 removal.

As shown in Figure 1, a 500 kW_{th} staged pilot plant is based on a three stages gasification process carried out in different units.

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 the possibility of using a wide range of biomass feedstocks (including low value residues, e.g. AD sludge) as solid fuels.

Innovative thermal processes for treatment of residues and wastes were developed in order to recover carbon fibres and energy from end-of-life composites, produce activated carbon and energy from scrap tires and waste biomass, produce high added value technical ceramics and energy from scrap tires and waste glass, convert chemical energy of non-recyclable waste (refuse derived fuel, automotive shredder residues, manure, sewage sludge, waste plastics) in more flexible energetic vectors such as char, bio-oil, and syngas. Preliminary tests conducted on bench scale continuous rotary kiln with mass rate of about 1 kg/h provided useful information for the scale-up of pyrolysis/gasification process of tires, sewage sludge, ASR, and digestate.

A pilot scale rotary kiln system to process automotive shredder residues and waste biomass at a maximum mass rate of 10 kg/h and equipped with a gravity settler to collect char has been built. The raw gas is purified by the gas treatment system composed of an spray tower, panel filter and a scrubber working with alkaline solution. Also, a rotary kiln plant, with treatment capacity of 30 kg/h, was built up with an indus-

Fig. 1 Three stages gasification pilot plant

trial partner SICAV Srl. It is a 4 meters long rotating drum reactor with internal diameter of 0.4 m. The main purpose of this plant was to develop and optimize a thermochemical process to convert waste/biomass to solid products with high added value "Activated carbon" and synthesis gas.
A "batch" fixed bed pyrolysis plant with reactor capacity of 5 m^3 has also been realized to recover carbon fibres from scraps and composite waste materials (Figure 2). The ENEA-patented process allows the recovery of the carbon fibres that still retain 90% of the mechanical properties of virgin fibres. Moreover, the recovery cost is about 20% lower than the commercial cost. The patented process was validated in the continuous rotary kiln (Figure 2). Moreover it was sold to a SME that is building up an industrial plant for the recovery of carbon fibres by ENEA patent.
A fluidized bed gasifier was built to treat refuse derived fuel with a mass rate of 10 kg/h. It has a raw gas cleaning section and catalytic modules of steam reforming and water gas shift for hydrogen enrichment. A technological integrated platform was realized to dispose waste tires, to produce high added value material, such as nanometric silicon carbide, to recovery power.

Biomass and Biotechnology for Energy

Development of efficient biomass conversion processes and innovative technologies for the conversion of different biomass (including no-food crops and microalgae) into biofuels and chemicals by means of biological processes are the main goals of R&D activities on Biomass and Biotechnology for Energy. Activities are mainly focused on the selection and use of microbial pools for the production of second-generation biofuels, applying the biorefinery concept and microbial ecology approach for sustainable energy production.
Research activities are mainly focused on the enhancement of biogas production from lignocellulosic wastes by a biological co-treatment and its scale-up, development of two-stage anaerobic digestion processes for hydrogen and methane production from organic wastes, ethanol and hydrogen production from raw glycerol arising from biodiesel industry by anaerobic fermentation with mixed bacteria cultures and experimental cultivation of microalgae to produce biofuels and/or high-value products for chemicals. Such goals are pursued through selection of functional consortia by means of bio-augmentation, acclimatization and enrichment and the statistical optimization, in order to increase their productivity and stability for a further scale-up and industrial exploitation.
Lignocellulosic substrates represent the main potential energetic stock among organic wastes. When lignocellulosic wastes are used as sole substrate, the hydrolysis step represents the bottleneck of the whole process; if they are used in co-digestion with other substrates, they become the limiting factor of the process efficiency. Recently, biological treatments of lignocellulosic wastes are gaining more attention thanks to the low energy requests, mild operational conditions, and low production of toxic and unwanted by-products.
An innovative approach (based on

Fig. 2 Pyrolysis fixed bed plant

the development of microbial processes for hydrolysis of lignocellulosic materials by Anaerobic Ruminal Fungi - ARF) through Anaerobic Digestion (AD) of lignocellulosic biomass was tested at ENEA in two different series of experiments, where the second experiment was a scale-up (10x) of the best results obtained in the first one. A mathematical model to predict methane production was calibrated on the first experiment while data from the scale-up experiment were used to validate it.

The bio-augmentation approach is innovative because the breakdown of lignocellulosic biomass promoted by ARF is not performed upstream, as imposed by typical pre-treatments, but it is totally integrated and concurrent within the AD process. The obtained results enlighten interesting perspectives for the application of bio-augmentation in the AD process, providing a co-treatment of lignocellulosic wastes. Moreover, the microbial bio-augmentation leads to even better results in a greater process scale. This aspect is under investigation with increasing process scale.

Several research activities have been and are presently carried out on the development of advanced anaerobic digestion processes, aimed at increasing energy production from organic wastes (manure, crude glycerol, cheese whey) through a two-stage fermenter, made of two separate reactors, the first producing hydrogen and the second one methane. Anaerobic digestion of ricotta cheese whey (RCW) has been extensively studied at ENEA. The results of these research show that the two-phase reactor configuration improves the energy efficiency of the process in terms of total energy production and methane quality. The two-stage process has been patented (ENEA-CRA Patent number PCT/IB2014/059942), leading to the construction of a pilot plant with a size of a first stage reactor of 0.3 m^3 volume and a second stage reactor of 3 m^3 at the Monterotondo (Roma) Research Centre of CREA (Figure 3), and some full-scale plants are currently in advanced stages of construction.

Furthermore, ENEA has developed a technology making use of raw glycerol - by-product of the industrial biodiesel production - by way of innovative anaerobic fermentation processes to obtain bioethanol, hydrogen or synthesis intermediates (lactic and succinic acid, 1-3 propanediol) for chemical industry. Enrichment of activated sewage sludge allowed to select a suitable microbial culture able to grow on crude glycerol as the only carbon source, using this simple medium without any extra-nutrient supplements.

The process developed at ENEA laboratories has been patented (Patent No. RM2011A000480). It is to be noted that in the framework of European R/S project "GRAIL", trials on both lab-scale fermenters and pilot plant are in progress. Next step of the research will involve the development of a continuous process, both at lab as well as pilot plant scale. Preliminary tests for the scale-up of the process have been carried out on a pilot bioreactor of 50 L at the ENEA Trisaia Research Centre (Figure 4) and appears to be quite promising for beginning the continuous fermentation.

Cultivation of microalgae to produce biofuels, food products with high nutritional power and/or high-value products for chemical industry are in progress at the ENEA Casaccia Research Centre.

The main target of these research is the realization of innovative, simplified and low-cost systems for microalgal cultures, both at laboratory scale (PET used bottles), as well as outdoors.

A brief of activities, already completed or in progress, is given below:

Fig. 3 Two-stage anaerobic digestion pilot plant at CREA Research Centre in Monterotondo

Fig. 4 Pilot fermenter at ENEA Trisaia Research Centre

- Bioenergy: use of liquid digestate as fertilizer for microalgae crops to be used for biogas production;
- Green chemistry: *Botryococcus braunii* and *Dunaliella salina* production experiments for enhancing their content in oleic acid and dienes;
- Production of nutraceuticals: production of *Artrhrospira platensis* (spirulina) to be used as a food supplement or as a source of natural dyes (phycocyanin) for food, cosmetics and chemical analysis;
- Restoration of cultural heritage: screening and evaluation of micro- and macro-algae for the production of polysaccharides extracts to be applied on paper works (manuscripts, books, drawings) deteriorated or at risk of deterioration.

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REFERENCES

1. H. Stichnothe, H. Storz, D. Meier, I. de Bari and S.R. Thomas (2016) Development of Second-Generation Biorefineries, in *Developing the Global Bioeconomy*. DOI: http://dx.doi.org/10.1016/B978-0-12-805165-8.00002-1

2. Liuzzi, F., De Bari, I., Kaouther, Z., Braccio, G. (2016). Optimization of Catalyzed Pretreatment and Fractionation of Cardoon In Proceedings of the 24th European Biomass Conference & Exhibition 6-9 June– Amsterdam p. 1217 - 1220 (ISBN 978-88-89407-165)

3. M.T. Petrone, G. Stoppiello, I. De Bari, Environmental impact of cardoon-based second-generation sugars production, in Proceedings of Ecomondo 2016

4. D. Barisano, G. Canneto, F. Nanna, G. Braccio. Steam/Oxygen Biomass Gasification in a 1000 kWth ICBFB Pilot Plant. In Proceedings of the 23rd European Biomass Conference and Exhibition, 1-4 June 2015, Vienna (Austria). pp. 550-554

5. K. Gallucci, F Micheli, D. Barisano, A. Villone, P.U. Foscolo, L. Rossi. CO2 Sorption-Enhanced Processes by Hydrotalcite-Like Compounds at Different Temperature Levels. *Int. J. Chem. React. Eng.*, 13, 143-152, 2015

6. Lembo G., Massini G., Mazzurco Miritana V., Fenice M., Felici C., Liberatore R., Signorini A. "Anaerobic digestion of ricotta cheese whey: effect of phase separation on methane production and microbial community structure". In *Proceeding of the 24th European Biomass Conference & Exibition 6-9 June 2016*, Amsterdam p. 599-607 (ISBN 978-88-89407-165)

7. Barbato F., Pignatelli V, Venditti A., Bianco A., Guarcini L., Bottari E., Festa M.R., Cogliani E.,. "Scenedesmus dimorphus (Turpin) Kützing growth with digestate from biogas plant in outdoor bag photobioreactors". *Natural Product Research*, Vol. 30, No. 2 (2016), 185–191. DOI: 10.1080/147864l9.2015.1050392