Assessing the main opportunities of integrated biorefining from agro-bioenergy co/by-products and agroindustrial residues into high-value added products associated to some emerging markets: A review

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From agricultural residual biomass and waste into marketable high-value added co/by-products and recovery of energy: an overview on the main opportunities of integrated biorefining

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A B S T R A C T

Market implementation of integrated biorefinery requires reliable and advanced processing units combined with eco-friendly and economically profitable production chains. Future developments of the biorefinery systems should include either crop cultivation with selected genotypes that maximize full chain performance either the use of marketable agricultural residual biomass and agro-waste. The aim of the present work was to review the main biorefining opportunities of disposable agricultural residues, agricultural co/by-products and agro-wastes into a broad range of green chemicals and high-value added co/by-products valuable in some emerging technological sectors. The current status and future perspectives of conversion starting from agricultural residual biomasses and agro-wastes into high-value co/by-products, green chemicals and energy recovery by an approach of integrated biorefinery has been considered. After a recognition on nature, origin and European classification of the main categories of organic residuals from crops, forestry, agro-industrial food processing, aquaculture, fisheries and agro-wastes, this paper has focused its challenge on the main biofuel co/by-products associated to the thermochemical and biological conversion processes. The high-value added co/by-products from the biofuel chains related to some chemical basic-platforms (e.g., succinic acid, cellulose, lignin, glycerin, etc.) have been presented and discussed. Then, a special attention towards potential applications of the high-value added co/by-products and green chemicals in three emerging fields (renewable and sustainable farming systems, bioplastic industry and cell and tissue engineering in biomedical applications) for actual and future players has been given and discuss. Finally, this paper has addressed own concern on the actual and potential biorefining opportunities in the EU and in Italy.

Keywords:

Biofuel chain; Bioplastic; Cell and tissue engineering; Green chemical; Lignin; Organic farming system; Recycling.

Contents

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1. Introduction

The international petrochemical production of chemicals and polymers are actually estimated at about 330 Mtons worldwide. The primary production is determined by a small number of basic elements as methanol, ethylene, propylene, butadiene, benzene, toluene and xylene. These elements are mainly converted into polymers, plastics and various fine chemicals with specific functions and features. All the industrial materials made from fossil sources can be technically replaced by biomass resources albeit in many cases the production costs of bio-based materials from biomass exceeds the cost of petrochemicals. However, an efficient conversion depends on the gradual reconversion of the production chains from fossil sources into biomass-based raw materials.

Plants and marine algae (microalge and macroalgae or seaweeds) are considered as true 'living biorefinery' (Clark, 2007) because they are the main renewable energy resources that provide liquid, gaseous and solid biofuels capable to convert carbon dioxide (CO_2) and water into primary and secondary metabolites through a photosynthesis process. Primary metabolites are represented by carbohydrates (fermentable sugars, cellulose, hemicellulose, starch) and lignin, also called lignocellulosic matter or lignocellulose, presents in high amount in such biomass. Secondary metabolites are instead high-value added green chemicals (gums, resins, rubber, terpenes, terpenoids, flavonoids, phenolic substances, steroids, triglycerides, tannins, fatty acids, esters, alkaloids, furan molecules, glucosinolates, brassinosteroids) presents in lower amount in plants and algae. The secondary metabolites can be utilized for producing high-value added products and chemicals (food flavors, functional food, feedstuff, pharmaceuticals, cosmetics, nutraceutical, phytosanitary drugs, bioplastics, lubricants and other biomaterials) in integrated biorefineries.

The Directive 2009/28/EC on the promotion of the use of energy from renewable sources defines the term 'biomass' as "*The biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related* *industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste*". This mean that biomass belongs to a wide range of organic feedstocks which can be used in the supply chain of biorefineries (Osamu and Carl, 1989). The total biomass production worldwide is approximately 100 billion tons organic dry matter per year from land sources and 50 billion tons per year from aquatic sources. The major part of it is used as food, feedstuff, energy and industrial raw material, where food use is only 1.25 % of total biomass. The remaining amount of biomass sources as wood, agro-waste, manure, household waste, wastewater sludge, industrial waste, etc. are underutilized or recycled into the earth ecosystem. The main challenge is to transform complex and heterogeneous residual materials into valuable industrial raw materials from residual biomass in place of fossil sources. Biomass contributes to supply energy approximately for 12 % of the global status on renewable energy, while its contribution ranges from 40 % to 50 % in many developing countries (Garg and Datta 1998). The importance of plant biomass as a natural feedstock for the biofuel industrial chains can increase in the future and plant biomass can be a promising source of raw material suitable for biorefining into high-value added products, green chemicals and energy recovery. The feedstock that currently is considered in biorefinery consists of plant biomass either derived from dedicated energy crops either from agricultural organic residual resources defined as 'underutilized resource' (Fig. 1). These includes raw feedstocks that are finely converted into many biorefining outputs including energy recovery (power, electricity, heat), biofuels and overall a wide range of green chemicals and bio-based products (lubricants, adhesives, paints, detergents, pharmaceutical and healthcare products, cotton, and linen). Enhancement of biomass utilization requires effort to develop new technological systems in which conversion process, energy recovery and production of bio-based co-products are efficiently linked within an eco-friendly and efficient biorefining systems (Osamu and Carl, 1989).

Energy recovery and biofuel production are performed from two main sources, agricultural crops and agricultural residues. Energy production from agricultural crops can be divided into two main groups: liquid and solid biofuels. Liquid biofuel (ethanol and biodiesel) covers energy sources burned in engines derived from annually harvested agricultural crops as sugarcane, sugar beet, sunflower, wheat, maize and rape. Solid biofuel (coal) covers energy sources for power generation through electricity and heat output from short rotation forestry or SRF (poplar and willow), residues from harvesting (straws, wood chips, wood shavings, aspen chips, olive brash residues, branches, foliage, roots, tubers) and grass production. Agricultural residues include corn stalks, rice husks, corn stover, wheat straw, cropping residues, unmarketable products, vegetable processing leftovers, spent coffee-ground, defatted olive marc, sugar beet bagasse, tomato-waste, cardoon-waste, vegetable-waste, which are converted to produce heat and electrical power. Also, gaseous biofuel, as methane (CH_4) and hydrogen (H_2) covers energy sources to produce power from dedicated energy crops (triticale, corn, sugar beet) associated with bio-wastes (manure, slurry, sludge, municipal solid waste or MSW) by anaerobic digestion and fermentation.

Green chemicals and bio-based outputs are also derived from agricultural crops and agricultural residues. Many review papers are available in literature for biofuel production from energy crops, or green chemicals from specific feedstock, or next-generation biofuels, or related chemicals from no-food crops. An exhaustive, excellent and comprehensive review on the production of first- and second-generation biofuels is given by Naik et al. (2010). Most of them have critically examined the current status and future technologies used to convert corn or lignocellulose into fuel ethanol; or integration of lignocellulose with forest biomass; or conversion of hemicellulose from corn germ, fiber, gluten from corn-ethanol plant into value added chemicals; or detoxification of hydrolysates from fermentation processes by bacteria; or ethanol product separation and dehydration. For example, Clark et al. (2006) reported the use of green chemical technologies to transform low value waste biomass into green chemicals like; Chew and Bhatia (2008) reported on the different types of catalysts and their role in the catalytic processes for production of biofuels in a typical palm oil and oil palm based refinery in Malaysia; Rowlands et al.

(2008) reported the challenges, opportunities in the context of Australian perspective; Mabee et al. (2005) assessed the emerging transformation sector in Canada; and Gomez et al. (2008) reported on the under pinning research necessary to enable the cost effective production of sustainable liquid biofuels from biomass with a particular focus on the aspect related to plant cell walls and their bioconversion. On the other hand, fewer referred papers on the biorefining opportunities of agricultural residues, agricultural co/by-products and agro-wastes into high-value added co/by-products and fine green chemicals through an approach of integrated biorefinery have been found in literature especially in relation to some selected application sectors.

The main challenge of the present paper was to review the biorefining opportunities of disposable agro-wastes into a broad variety of valuable and marketable green chemicals and high-value added co/by-products giving a particular attention to some new emerging markets.

2. Categories of agricultural residual biomasses and wastes: definitions and European classification

The sustainable use of residual biomasses and wastes is expected to play a substantial role in the future energy systems because the potential bioenergy provided by dedicated energy crops is yet limited worldwide; all the lands are multi-functional; lands are also needed for food, feed, timber, fiber production; nature conservation and climate protection according to ‘greening policies’ in the European Union (EU) are needed. Large-scale cultivation of dedicated biomass affect bioenergy potential, global food prices and water availability. Furthermore, bioenergy potential for climate change mitigation remains unclear due to large uncertainties about future agricultural yield improvements and land availability for energy crop plantations. Therefore an integrated policy for energy use, land use, sustainable food systems development, greenhouse gas (GHG)-emissions reduction, soil preservation and water management must be encouraged and managed (Popp et al., 2014).

In contrast to fossil resources, assessing the lignocellulosic biomass resources potential in developing countries (Ullah et al. 2015), bulk agricultural raw materials such as wheat, rice or corn have till a few years ago been continuously low (and even declining) in price because of increasing agricultural yields, a tendency that has recently drastically changed with the competition between biomass for food use versus biomass for chemicals or biofuels use. There are some biomass feedstocks that avoid the competition for land such as the residual biomasses and wastes. For example, the biodiesel share from wastes as animal fats and cooking oils increase to 15 % in total biodiesel output; Brazilian ethanol derives from wastes and by-products by the milling process in place of sugar crops able to generate heat and electricity permitting the industry to operate without significant fossil fuel inputs and achieving GHG saving of about 80–90 % in comparison to fossil fuel. Second-generation biofuels from residual biomass are needed for diversification of market and de-carbonization of production chains in the longer term. For example, no-edible oilseeds of jatropha, high-content erucic acid seeds of Indian mustard and green seeds of canola can be used as biofuels sources, including green diesel from aquatic biomass and microalgae, for producing first and second generation biofuels.

The use of residual biomass and waste suitable for producing either second-generation biofuels either high-added value co-products from biorefineries which do not require any new agricultural land and present limited or zero environmental risks, needs to be globally encouraged (Ullah et al. 2015). At the same time, crop residues, especially straws, have alternative uses in animal feeding and bedding and when returned to the soil meet important ecosystem services essential to maintenance and restoration of fertility and erosion protection. Nevertheless, such biomass might contribute modestly to replace uses of fossil fuels in the longer time. The use of agro-waste, bio-waste, MSW, and surplus forest growth, establishing energy crop plantations on currently unused land, may be more expensive than creating large-scale energy plantations on arable land. Moreover, the processing of residual biomass feedstocks into second-generation biofuels have either more energy requirement because it can need high energy inputs for pre-treatment of lignocellulosic matter as a steam explosion, either more environmental impacts resulting from the processing of biomass through technologies that can require higher water consumption in lignocellulose processing.

2.1. Organic residuals from agricultural activities

Neither the EU Renewable Energy Directive (RED) nor the EU Fuel Quality Directive (FQD) here named as RED-FQD contains institutional definitions for wastes, residues, or co-products both according to the Directives 2009/30/EC (amending both the Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and the Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels, and repealing the Directive 93/12/EC) and 2009/28/EC (amending both the Directives 2001/77/EC and 2003/30/EC). Yet the RED-FQD provides disparate treatment for the raw material depending on the classification of waste, or residue, or co-product. This treatment has implications for the amount of energy counted toward the target, applicability of sustainability criteria and GHG accounting. Although the European Commission (EC, 2010) sets out some additional considerations in determining whether a raw material result be a waste, or a residue, or a co-product, there is nevertheless still much uncertainty. This paper briefly examines the classification of raw materials, residues, co-products and wastes within RED-FQD definitions and the issues-associated with their conversion into green chemicals and high-value added co/by-products.

RED-FQD considers some raw materials and residues not related to the biofuel production chains suitable to be defined as co-products according to the following treatment: 1) co-products must meet all the sustainability criteria; 2) for purposes of the GHG-savings criterion, co-products are apportioned emissions based on the energy-allocation method which divides emissions among co-products according to their energy content. The EC (2010) proposal does not define a co-products, whether a residue is considered one implication for how GHG emissions are accounted for that residue. In general, to prevent loopholes, co-products should be considered all the raw materials that are typically co-products of marketable value in alternative uses, such as agricultural and forestry residues or materials, that can constitute a considerable outcome of a process in terms of economic added-value. In all the instances where the main process has been deliberately modified to produce a larger quantity or another quality of the material at the same costs of the main product, then it is defined a co-product. This approach ensure that emissions are adequately apportioned to residues that are actually co-products based on the energy-allocation method (or energy content-based), and this could include emissions from cultivable land and/or land-use change (LUC).

The EC proposal contains no additional guideline to determine in which sub-category a residue belongs, and no definitions or indicative lists for residues and co-products despite purporting to establish the regulatory framework that will operate through 2020, e.g. capping food-based crops and promoting so-called second generation biofuels (wastes and residues) through double- and quadruple-counting. It should also be noted that second-generation biofuels compete with renewable heating, cooling and electricity needed to meet the 20 % target in addition the oleochemical industry and animal husbandry which uses agricultural residues and animal fats as feed.

RED-FQD provides differential treatment to sub-categories of residues. Residues are divided into four main sub-categories from crop, forestry, aquaculture-fisheries and agro-industrial processing. Each sub-category falls in determining the sustainability criteria that it must meet and how the GHG savings criterion is calculated, which is further impacted by whether the residue is considered a co-product. For these reasons, determining the sub-category of a residue and whether it is a co-product, that has significant implications. RED-FQD provides a little guideline on how to categorize residues or how to determine their status as a co-product, creating always uncertainty. Drawing from the European proposal, an indicative short list of raw materials and residues includes: crop residues (primary and secondary), forestry residues (primary and secondary), animal fats and animal manure.

2.1.1. Crop residues

RED-FQD accords to term 'crop residues' the following treatment: 1) crop residues must meet all the sustainability criteria; 2) for purposes of the GHG-savings criterion, crop residues are considered to have zero life-cycle GHG emissions up to the process of collection of those materials meaning zero-emissions from cultivable land and LUC. It is unclear what constitutes a crop residue. Residues from agriculture are sometimes considered as crop residues, sometimes as processing residues, sometimes as agro-waste. In general, there are two types of agricultural residues, those from primary agricultural (crop residues) produced when harvesting crops, such as straw and stover (IEA, 2010), and those from secondary agricultural produced during the processing of crops into food or other products, such as nutshells and bagasse (IEA, 2010). Both primary and secondary agricultural residues have alternative uses to biofuel production so there is an opportunity cost to their use. Diverting agricultural residues already used for another purpose, such as animal feed or pellets, results in additional land to replace them. Removing unused primary agricultural residues otherwise left on the land, decreases soil quality and needs in the additional chemical fertilizer use. The EU proposal does not address agricultural residues in any meaningful way. Figure 2 shows the agricultural straw residues per square kilometer potentially available for recovery of energy and/or biorefinery uses in the EU (Monforti et al., 2013).

Factors that determine the amount of residues include: 1) crop type and yields, 2) biomass ratio between crop residues and crop main products, and 3) percentages of residues removed from the field for other potential use. The maximum amount of crop residues that can be removed from the field without significantly affecting soil fertility is most debated. Some authors consider crop residues as currently unused waste material and make a strong case for its use for biofuel production (Sommerville, 2006). Others authors perceive crop residues as a valuable resource that provides irreplaceable environmental services (Smil, 1999) and argue removal of crop residues would exacerbate risks of soil erosion by water and wind, deplete soil organic matter, degrade soil quality, increase non-point source pollution, decrease agronomic productivity, reduce crop yields per unit input of fertilizers and water (Lal, 2007). The importance of retaining residues on fields depends on the specific local conditions (USDA, 2006). Drawing from the European proposal, an indicative short list of primary and secondary agricultural and crop residues include: straws, stover, husks and cobs; press cakes from rape and soybean seeds; olive marc and lees, including grapes, olives and other fruit; bagasse, including sugar beet pulps; palm kernel meals and palm oil mill effluents; and empty fruit bunches and nutshells.

2.1.2. Forestry residues

RED-FQD accords to term ‘forestry residues’ the following treatment (IEA, 2010): 1) forestry residues must meet all the sustainability criteria; 2) for purposes of the GHG savings criterion, there is no unique treatment. It is not always clear what constitutes a forestry residue. Residues from forestry may sometimes be considered as forestry residues, sometimes as processing residues, sometimes as co-products. In general, there are two types of forestry residues, the primary forestry residues produced when harvesting timber, such as treetops, branches and stumps (IEA, 2010); and the secondary forestry residues produced during processing of biomass-based materials or products, such as sawdust, bark and scrap-wood (IEA, 2010). Encouraging use of unused primary forestry residues as an alternative to biofuel production otherwise left on the land causes loss of soil organic matter, soil carbon and habitat for biodiversity.

RED-FQD does not contain a specific sustainability scheme for managing forestry residues. Instead, the sustainability criteria were adopted for agricultural products and residues which were expected to be the predominant raw materials for biofuel production in the future. This is evident in the focus on preventing direct LUC where new agricultural cultivation systems are almost always required for land conversion. Forestry products and residues are typically harvested in the absence of direct LUC. Forests are thinned or residues are salvaged, resulting in degraded forests but not always deforested ones. RED-FQD needs to report on requirements for a sustainability scheme for biomass energy uses, other than biofuels and bio-liquids, and to submit proposals for a sustainability scheme for forest biomass. If the analysis done for that purpose demonstrates that it would be appropriate to introduce amendments in relation to forest biomass in the calculation methodology, or in the sustainability criteria relating to carbon stocks applied to biofuels and bio-liquids, at the same time the EC shall make proposals in this regard. Instead, the EC has published a report (EC, 2010) which has analysed several issues related to a sustainability scheme acknowledging the need for public intervention when the intensified use of forest biomass drivers to environmental risks during production and consumption. Despite the legislative mandates seem be appropriate, the way choice to include indirect land-use change (ILUC) factors in RED-FQD in un-clear. Given that the EC appears incapable of addressing sustainability issues in a fast manner, the responsibility falls upon European Parliament in absence of sustainability scheme for forest biomass. The EC proposal incentivizes the forestry residues use for biofuel production that compete with energy production for scarce forestry resources, and a sustainability scheme for forest biomass should be established. Drawing from the European proposal, an indicative short list of forestry residues includes: treetops, branches, stumps, leaves, sawdust, cutter shavings, scrap wood, wood pulp and wood chip.

2.1.3. Aquaculture and fisheries residues

RED-FQD accords to term 'aquaculture and fisheries residues' the following treatment: 1) aquaculture and fisheries residues must meet all the sustainability criteria; 2) for purposes of the GHG-savings criterion. RED-FQD only considers as primary aquaculture and fisheries residues those directly produced by aquaculture and fisheries activities, but not those related to the processing of aquaculture and fisheries products according to the EC. This distinction however is unclear. At this time, aquaculture and fisheries residues have uncertain market penetration and suffer from a lack of information. Drawing from the European proposal, an indicative short list of aquaculture and fisheries residues includes: brown, red and green marine macroalgae or seaweeds, fish scales, viscera and scraps.

2.1.4. Agro-industrial processing residues

RED-FQD considers as 'agro-industrial processing residues' those concentrated at the processing sites according them the following treatment: 1) processing residues need only meet the GHG savings criterion; 2) for purposes of the GHG-savings criterion, processing residues shall be considered to have zero life-cycle GHG-emissions up to the process of collection of those materials. The EC (2010) defines processing residues as "*A substance that is not the end product(s) that a production process directly seeks to produce… it is not a primary aim of the production process and the process has not been deliberately modified to produce it*". This definition is however vague, because it not always provide an exhaustive distinction among other agricultural residues and agro-industrial processing residues.

The EC proposal fails to address issues associated with processing residues. In large part this is because the definitions and categories are sometime unclear. Assuming the agricultural, forestry, aquaculture and fisheries residues as described above, the processing residues would include those from agricultural, forestry, aquaculture and fisheries residues (primary or secondary) as well as animal waste, MSW and post-consumer biomass products although they are products themselves considered waste. Drawing from the European proposal, an indicative short list of processing residues includes: oil-less seed cakes or meals, crude glycerin, sugary molasses, defatted olive marc, spent coffee-grounds, exhausted beet pulps, tall oil pitch and animal fats.

2.2. Wastes

RED-FQD accords to term 'waste' the following treatment: 1) wastes need only meet the GHG savings criterion; 2) wastes are considered to have zero life-cycle GHG-emissions up to the process of collection of those materials, meaning no land-use emissions including soil carbon. Demonstrating compliance with the 10 % target, "*the contribution made by biofuels produced from wastes… shall be considered to be twice that made by other biofuels*". RED-FQD does not define wastes but the EC states that the concept of waste is in line with the objectives of RED-FQD. As an amendment to RED only, it references the definition in the 'Waste Framework Directive' (WFD) which defines waste as "*any substance or object which the holder discards or intends or is required to discard*" stating in pertinent part 'waste' shall be defined by the Directive 2008/98/EC on waste repealing previous directives. Substances that have been intentionally modified or contaminated to meet this definition are not included in this category. This definition is supplemented by the requirement that substances cannot be "*intentionally modified or contaminated*" to meet the definition, which is intended to prevent the practice of "*adding waste material to a material that was not waste*" in order to make it waste. The definition of waste requires nevertheless further specifications. While the definition is a welcome contribution, it does not prevent the use of substances before the end of their useful lifetime. For example, used cooking oils require no technological developments for exploitation and is subject to ever-increasing imports from abroad. Markets have increased the used cooking oils being diverted toward second-generation biofuel production before it reaches the end of its lifetime especially since their consumption has implemented double-counting for these biofuels. In the UK, for example, used cooking oils represent 50 % of biodiesel consumption (https://www.gov.uk/government). Any increase in demand for cooking oils increase demand for oleaginous crops to produce more cooking oils with associated land-use implications. The solution to the unused-cooking-oil problem can be addressed. For example, ensuring wastes conform to the waste hierarchy would require prevention, preparation for reuse and recycling of it before energy recovery. Wastes are already subject to extensive treatment and in national waste management plans in the EU.

'Recovery' term refers to operations where the wastes replaces materials that would otherwise have been used to fulfill a particular function in the plant or in the wider economy, such as fuel oil in transportation. Annex II of WFD sets out a non-exhaustive list of recovery operations from waste and specifically includes "*use principally as a fuel or other means to generate energy*". The EU may only depart from the waste hierarchy for specific waste streams whenever justified by lifecycle thinking on impacts of the generation and management of such waste. Waste recycling corresponds with the objectives and complements existing in the EU policies on waste prevention and management. The definition of waste should be modified applying this requirement for wastes originating abroad or otherwise include language in the definition that achieves the same result since the waste hierarchy is only applicable in the EU. In both instances, whether the wastes originate abroad or within the EU, adequate assurances should be required to prevent circumvention. Drawing from the European proposal, an indicative short list of wastes for use as raw materials in biorefinery includes: cooking oils, biomass fraction of mixed MSW, biomass fraction of industrial waste and sewage sludge.

3. The biorefinery

3.1. Concept and definitions

According to International Energy Agency (IEA), Bioenergy Task 42 (http://www.ieabioenergy.task42-biorefineries.com), a 'biorefinery' is defined as "*The sustainable processing of biomass into a spectrum of marketable products (food, feed, materials and chemicals) and energy (fuels, power, heat)*". The goal idea of a biorefinery is to transform biomass into useful bio-based products using a wide range of feedstocks and integrated technologies. A biorefinery can be seen as an integrated system that converts biomass into purified materials and molecules that are usable as bio-based products that are usually produced from fossil sources. A biorefinery can also be considered as a facility, a process, a plant, or a clusters of facilities, that integrate biomass conversion processes by various technologies among them to contemporaneously produce biofuels, power (heat and electricity), high-value products and fine green chemicals in alternative to petrolchemicals refineries. The biorefinery system is based on a conversion of various feedstock including biomass production, transformation, processing and end-use. Many research papers on the biorefinery are available in literature. An overview of the different biorefinery systems and the current status of biorefineries, weaknesses, opportunities and threats analysis is given by Kamm et al. (2006), Fernando et al. (2006) and de Jong and Jungmeier (2015). Biorefinery which uses specific feedstocks as straw, corn and forest-based residues are available in literature (USDE, 2004;

Jungmeier et al., 2013). There are many research papers which gives information on biorefinery concept using multiple and varied feedstocks (Koutinas et al., 2007; Naik et al., 2010).

3.2. Biorefining systems

Biorefineries were classified basing on a variety of many features: 1) technological processes (conventional and advanced biorefineries or most correctly first-, second-, and third-generation biorefineries), 2) type of raw materials (whole crop biorefineries, oleochemical biorefineries, lignocellulosic feedstock biorefineries, green biorefineries, forestry biorefineries and marine biorefineries), 3) main type of intermediates produced (syngas platform biorefineries, sugar platform biorefineries, oil platform biorefineries), 4) main type of conversion process (thermochemical biorefineries, biochemical biorefineries). IEA Bioenergy Task 42 give a more appropriate classification system (Cherubini et al., 2009; Jungmeier et al., 2009). This approach is based on a schematic representation from raw biomass chains to end-products platforms which consist of four main features able to identify, classify and describe the different biorefinery systems. Figure 3 shows an example of flow chart on the physical, chemical, biological and thermal conversion processes, or combination among them, for producing multiple bio-based products.

The main raw materials are constituted by perennial grasses, starchy crops (e.g. wheat and maize), sugar crops, lignocellulosic primary biomass and residues, oil, algae and waste. These materials can be processed into biorefineries able to give primary platforms of single molecules carbon-based as starch, sucrose, cellulose, hemicellulose, lignin and oils; organic herbal solutions and oil of pyrolysis from lignocellulosic feedstock. These primary platforms can be converted into a wide range of secondary platforms that provide marketable products using combinations of thermal, chemical and biological processes. Biomass can be submitted to four different types of conversion processes: 1) physical (mechanical pressing), 2) biological (fermentation and anaerobic digestion),

3) thermochemical (incineration, gasification and pyrolysis), chemical and biochemical (extraction and chemical synthesis). Basing on a valorization of residual biomasses and wastes, in this paper we will focused on two conversion types: biological and thermochemical. Both processes produce solid residues with a high content of marketable protein as livestock feed that can be sold as animal feed or burnt for power generation. In particular, the fermentation processes are currently used in the first-generation biorefineries for the production of fuel ethanol from sugars and starches. The fermentation can be adopted in integrated platforms for the production of multiple or simple molecules that can serve as elements for synthesizing a wide variety of chemical compounds. Evolution of second-generation fermentation processes can produce a similar range of platform chemicals through the transformation of sugars, cellulose and lignin. These technologies are still in a development phase which needs additional stages to first break-down the plant's structural materials into fermentable sugars using microorganisms or chemical treatment by whole plants. These processes improve the range of usable raw materials and increase the proportion of raw material actually converted into useful products. Second-generation biorefineries can offer higher yields per hectare of raw material compared to first generation biorefineries.

3.3. Biorefining drivers

The development of biorefineries is necessary to produce a broad variety of bio-based products into an efficient construction set system (Kamm and Kamm, 2004). Each biorefinery refines and converts its corresponding raw material into a multitude of valuable bio-products. The products from biorefinery also includes specific products that usually are not produced in petroleum refineries (Kamm et al., 2006). Therefore it is necessary to develop new technologies as: 1) biorefinery lignocellulosic-based including effective pretreatment and separation in lignin, cellulose and hemicellulose; 2) further development of thermal, chemical and mechanical processes; 3) development of biological processes; 4) combination of biotechnological and chemical processes.

The traditional drivers for establishment of biorafineries are: 1) sustainability aspects, 2) processing and kinds of biomass, 3) spectrum of marketable products, biofuels and energy, and 4) market competitiveness. The transition toward a bio-based economy needs instead of multiple drivers: 1) an over dependency of many countries on fossil fuel imports; 2) the anticipation that oil, gas, coal and phosphorus will reach peak production in the next future; 3) the need for countries to diversify their energy sources; 4) the global issue of climate change and the need to reduce GHG emissions; 5) the need to stimulate regional and rural development with appropriate policies. The recent rise in oil prices and in consumer demand for eco-friendly products, population growth and limited supplies of non-renewable resources, have opened new opportunities for bio-based chemicals. Emerging markets require increasing amounts of oil and other products derived from fossil fuels, and this is leading towards a more market competitiveness. In addition, security of supply chain for biorefinery is an important driver for bio-based products and bio-energy. Any economic process that produces material commodities diminishes the availability of energy in the future, and therefore the perspective of producing other goods and material things. In addition, soil organic matter is degraded following to economic process, so less reliance can be put in future economic activity. Raw materials concentrated in underground deposits, once released in the environment can be collected and reused in the economic cycle only in a much smaller quantity and with higher energy consumption. Matter and energy enter together into the economic process.

The use of chemicals from renewable sources shows GHG-saving throughout their life cycle when compared to the equivalent conventional petrochemical sources. Emissions of CO_2 during the production and consumption of bio-based products are offset by the CO_2 captured during the growth of biomass used to produce them. The potential in reducing GHG emissions from the set-up of second-generation biorefineries varies between 30 % and 85 % if compared to petrochemical sources. In the EU, for example, the adoption of biorefinery system is seen as a key-technology able to put into effect the effort to mitigate climate change and such ensure security of supply against fluctuations in crude oil prices. Biorefining gives support for agricultural development providing additional market opportunities for farmers and growers, moreover, the decentralized production systems can provide new sources of income and employment opportunities in rural areas. Much of the agro-industrial waste is still a relevant cost to the industry, due to the higher cost of disposal. In parallel to this situation that we can consider inefficient, the market for bioplastics and tools in renewable and sustainable farming systems is experienced by exceptional population growth in Europe. These high value-added materials have considerable importance from the industrial and economic point of view and their exploitation is a key-step in the development of an new economy based on recycling of renewable resources, named as 'bio-based economy', or 'circular economy', or more briefly 'bio-economy'. For example, business opportunities for a circular economy based on biofuel co-products is shown in Figure 4.

Once defined the global context, it should be noted that, particularly in Italy, operate important biorefining players connected to a significant production of agro-industrial waste type, as well as several developers of technologies for the exploitation of alternative biomass. Due to the fact that these secondary raw materials are produced on large areas, bio-based production favors a decentralized structure. Equipment for biomass processing at regional level can bring benefits to local economy as well as a simplification of logistic platforms and contractual situations, and lower capital requirements as opposed to a large central biorefinery.

Another main driver for the development and implementation of biorefinery processes is the transportation sector (Elvers, 2006). Significant amounts of renewable fuels are necessary in the short and middle term to meet policy regulations both inside and outside in the EU. Biofuels have to fill in a large fraction of this demand, specifically for heavy duty road transport and in the aviation sector (Huber et al., 2006). Both conventional biofuels (ethanol, biodiesel) and advanced biofuels (lignocellulosic methanol, butanol, Fischer-Tropsch-diesel/kerosene) generally cannot be produced in a profitable way at current crude oil prices (Ocic, 2005). This implicates that they can enter into market only if they are forced by proper governmental regulation, or if significant financial support are provided. This artificial market will not be lasting because a significant reduction in biofuel production costs is required to create a sustainable market. A very promising approach to reduce biofuel production costs is to use biofuel-driven biorefineries for the co-production of value-added products with biofuels from biomass resources by a very efficient integrated approach. To be a viable option, the production of bio-based energy, materials, chemicals and biofuels, should be able to improve the global economy and it also could be an additional source of income. In this perspective, the main driver for the creation of biorefineries is the answer to sustainability demand. The development of biorefineries must be designed in an adequate way that is sustainable from the environmental, social and economic point of view. This new industrial development, if properly applied, will encourage direct and indirect employment, creation of new professional figures and a better quality of life. Biorefineries will still have to be combined with existing infrastructures, and many considerations must be made as regards to the source of biomass in terms of competition for food, impact on consumption and quality of water, LUC, carbon stocks in the long term, net balance of GHG-emissions and impact on the biodiversity. Furthermore, the amount and type of energy used to operate inputs-outputs into biorefinery chains and related transportation costs should be carefully considered in the near future. Biorefining requires further innovation offering opportunities to all economic sectors. Building a bio-based economy can help to overcome difficulties laying the foundation of an eco-friendly industry.

The recent adoption of the biorefinery complexity index (BCI) in biorefinery models might add relevant information on the assessment and comparison of different biorefinery systems. The BCI is a relevant indicator for industry, decision makers as well as investors. These additional information are generated to assist the biorefinery players in their strategies to implement the most promising systems such minimizing technical and economic risks. The conflicts between energy and food production can be avoided or reduced developing technologies based on agricultural residual biomass and waste.

3.4. The economic concept of value-added product

Economic value of fossil feedstock suitable to be substituted by biomass shows large differences. The lowest values are attributed to heat production, whereas the highest values are associated with replacement of fossil-derived bulk chemicals or with recovery of energy from organic residuals and agro-waste. The economic value of biomass is determined by the revenue derived from the various valuable co/by-products on the market and production costs. In most of the cases, products with a relative high market value are associated with high production costs and vice versa. In addition, also the size of the market is relevant for the economic feasibility of biorefining. In most of the cases, products with a high market value have a relative small market as liquid industrial biorefineries and transportation fuels.

When co-products are used by industries, ‘green credits’ can be attributed to the biofuel production chains. Green credits include GHG savings associated to avoiding land use, or energy, or irrigation water, or both. The challenge is to decide how to distribute quantities of potential credits between the fuel and the by-products. For the evaluation of GHG-emission savings, the following two methods have been developed. Firstly, in the ‘substitution approach’, it is determined by what by-products are used and what by-products would otherwise have been used to perform the function. Secondly, in the ‘allocation approach’, total emissions are divided between the fuel of interest and the related by-products in proportion to some attribute that they share. Common methods can include three allocation types: 1) allocation by mass, 2) allocation by value market, 3) allocation by energy content. It is not possible to know for certain what is really the substituted product for a fuel supplier, and thus GHG emissions of these substituted products are always uncertain. For example, by-products used as animal feed can replace many different animal feed products which have different GHG-emission performances. For reasons of feasibility, the Directive 2009/28/EC recommends to apply the allocation method by energy content for to determine GHG savings if compared to fossil fuels: *"Co-products from the production and use of fuels should be taken into account in the calculation of greenhouse gas emissions. The substitution method is appropriate for the purposes of policy analysis, but not for the regulation of individual economic operators and individual consignments of transport fuels. In those cases the energy allocation method is the most appropriate method, as it is easy to apply, is predictable over time, minimizes counter-productive incentives and produces results that are generally comparable with those produced by the substitution method. For the purposes of policy analysis the Commission should also, in its reporting, present results using the substitution method."*.

4. High-value added co/by-products from the biofuel chains associated to chemical basic-platforms

Biofuel industry has evolved rapidly over the last three decades with developments in processing techniques and expansion of biofuel crops and other agricultural commodities being considered as a strategic feedstock (Table 1). The installed power values show that the global biofuel production capacity is increased from 1.58 billion liters in 2010 to 4.21 billion liters in 2013 (WBA, 2014). Global expansion of biofuel production is projected to continue during the next decade although at a slower pace than over the last half decade. Currently, around 74 % of the global production of liquid biofuels is in the form of ethanol and the remaining part in the form of biodiesel and bio-oil. In 2012–2014 global fuel ethanol production reached 108 billion liters and those of biodiesel amounted to 28 billion liters. The two world's top fuel ethanol producers, the USA and Brazil, accounted for around 75 % of total production, but biodiesel output is less concentrated than ethanol. The EU remains the core business of global biodiesel production with 12 billion liters representing about 77,6 % of total share (Biofuels Barometer, 2012). Indonesia will surpass the USA and Brazil in the latter years of the outlook period to become the second largest biodiesel producer behind the EU. Fuel ethanol production in the USA is projected to be relatively flat over the next decade due to the ethanol blend wall and a general declining gasoline use (USDA, 2015). Global fuel ethanol and biodiesel production are both expected to expand reaching almost 135 and 39 billion liters by 2024 respectively (FAO, 2015). In 2040 the share of biofuels in road transport fuels would range from 5 % to 18 % globally, from 11 % to 31 % in the EU, and from 11 % to 29 % in the USA (IEA, 2015). Further expansion of biofuel production is expected in the Brazil and Argentina. A strong expansion in biofuel production was observed in the USA, EU and China changing biofuel policies. These increasing were not sufficient to fully satisfy biofuel policy objectives in the USA and EU.

The increased biofuel production has led to criticism and concerns about food availability while it is feared that rising demand for agricultural land-use change will lead to deforestation, grassland conversion and increasing of GHG-emissions (Elobeid et al., 2012; Khanna and Zilberman, 2012). Central to the debate is how the increased biomass requirements for sustainable biofuel production could fit with area expansion, or yield improvement, or increased cropping intensity. Increasing of demographic growth, rising economic aspirations of developing countries, requirements for geopolitical energy security, deteriorated economics of fossil-based products and increasing of public pressure for environmental sustainability, have all put the biorefineries concept on the top of strategic agenda of the biorefining players. At the same time, production of biofuels from alternative biomass sources and especially valorization of agro-waste and other organic residuals which do not compete with food, land and water, is believed to be the main challenge for building a sustainable biofuel industry. Moreover, there are many opportunities and demand growing for the conversion of residual biomass and waste into energy (biofuels, heat, electricity, power) and bio-based green products considering population growth, changing consumption patterns, dietary preferences and fruit/vegetable postharvest losses. In addition to that, the innovation potential of bio-based technologies will allow the production of new molecules for fuel, chemical and material applications which are not usually available from the fossil resources.

Biofuel chains produce both fuels and many co/by-products, and the type and quantity of them strongly depends on the production chain type (Fig. 5). Co/by-products output is relatively high in the USA, EU and China due to the large share of grains used in ethanol production with high feed yields, but it is relatively low in Brazil where ethanol production is dominated by sugar cane which usually generate less feed co-products. Co-product generation is generally lower for rape and soybean used in biodiesel industry. Significant developments are under way to commercialize next-generation biofuels albeit these are unlikely to be produced in large amount in the short term, furthermore the co-products from these feedstock are unlikely to have applications in the animal feed market (FAO, 2012). Estimates on impact of biofuel production often use models for LUC impacts with limited ability to incorporate economic and environmental implications ignoring generation of co/by-products (Golub and Hertel, 2012). Ignoring co-product outputs in the biofuel sustainability scheme, is such ignored leading towards an overestimation of land requirements and GHG-emissions.

The following points of the paper summarize the strategic consequences for the two main biofuel production chains that are traditionally associated to chemical basic-platforms used in the sectors of transportation, automotive, aviation, chemical and industrial energy.

4.1. Fuel ethanol chain

First-generation fuel ethanol is mostly done from maize (or corn) and wheat in the USA. Sugarcane is the predominant feedstock for ethanol production in Brazil and South Africa. Sweet sorghum, cassava and other non-grain crops are the main feedstock for China. However, an increase in the off-take of wheat can also be observed in China, Canada and the EU. The USA is the global leader in grain ethanol production accounting for roughly 90 % of total grain use followed by the EU, China and Canada. Maize accounted for the majority of grain use for ethanol in the USA and China. European and Canadian producers principally use wheat and maize for producing fuel ethanol. Feedstock for fuel ethanol chain vary significantly depending on the country and an estimated 143 million tons of grain is globally used. The fuel ethanol share demand of corn, wheat and other coarse grains is about 6 % of global total grains production. Fuel ethanol sector accounts for 13 % of global maize consumption and 20 % of global sugarcane production. In 2014, most fuel ethanol was produced from sugar crops (61 %) with the remainder from grains (39 %). The production of first-generation fuel ethanol from starchy crops is among the earliest processing of value-added products (Naik et al., 2010). Sugar can be obtained either directly from sugarcane, sugar beet, or sweet sorghum, or derived from the conversion of starch contained in cereal grains (e.g. wheat, maize and barley), millets, root crops and tuber crops (e.g. potato and cassava). While the basic processes for production of fuel ethanol from sugary and starchy crops are similar, there are clear advantages in producing ethanol directly from sugary crops rather than from starchy crops because additional processes require conversion of starch into sugar before fermentation. The conversion of complex polysaccharides in the biomass feedstock (starch) into simple sugars (glucose) is an high-temperature processing carried out with acids and enzymes as catalyst. Because of this additional step, energy requirements and GHG balances are more favourable for producing fuel ethanol directly from sugar crops when compared to starchy crops. For example, the energy requirement for converting sugar into fuel ethanol directly from sugar cane or maize is about half of the energy input needed using starchy crops (Prieler and Fischer, 2009). Sugarcane and sugar beet bagasse are also two important sources of fuel ethanol and related co-products. Due to co-generation of heat and electricity, Brazilian sugarcane ethanol industry operates every day without significant fossil fuel inputs achieving a high overall GHG saving (80–90 %) in comparison to fossil fuel. Sugar beet bagasse is instead very expensive to transport because it must be processed quickly before the sucrose deterioration. Therefore all the sugar beet processing plants are located near the production areas. This limited storage time is a major drawback of sugar beet use for ethanol production. Despite the simple processing technique, the cost of ethanol production from sugar beet is approximately twice that those of sugarcane-based ethanol in Brazil, or maize-based ethanol in the USA (USDA, 2006) because this is primarily due to differences in feedstock costs.

Starchy-based fuel ethanol chain produces different co/by-products depending on the feedstock and production process. Sugar beet by-products from industry include either the beet-top which can be used as green fodder, either the beet-pulp and filter cake can be used as cattle feed. About one-third of the volume of grain processed for fuel ethanol is used to produce animal feed as co-products, thus the equivalent of two-thirds of the grain are used to produce only ethanol. Two processes are widely employed for ethanol production, the wet milling and dry milling. The main difference among them is the treatment type of the cereal grain before fermentation and differences among them in resulting by-products are evident. Wet-mill process generates as co-products vegetable oil, corn gluten meal (CGM) and fibre. Dry-mill process generates as co-products wet distillers grains with soluble (WDGS) that can be sold to nearby markets. The dried form, also named dried distillers grains with soluble (DDGS), can be transported over long distances and is available for domestic markets and for exports. DDGS is a high quality feedstuff ration for dairy cattle, beef cattle, swine, poultry and in aquaculture. The feed is partially replaced by corn, soybean meal and di-calcium phosphate in livestock and poultry feeds. However, nutrient composition and quality of WDGS and DDGS can widely vary depending on the feedstock use, geographical location and time of harvesting of the ethanol crops. Very many papers are found in literature about WDGS, DDGS and CGM. Especially, the opportunities and challenges of biofuel co-products as livestock feed are reviewed by FAO (2012); the estimated displaced products and ratios of distillers co-products from corn ethanol plants and the implications of lifecycle analysis are critically studied by Arora et al. (2010); and the global economic and environmental implications of biofuel co-products employed as livestock feeds are analyzed by Popp et al. (2016).

Second-generation fuel ethanol is mainly done from a wide range of lignocellulosic sources (dedicated energy crops as giant reed, or mischantus, or SRF, etc.; agricultural residues as straw, or wood, or plant-waste, etc.) which require some additional pre-treatment steps (thermochemical or biochemical) able to separate cellulose, hemicellulose and lignin among them before successive processes of hydrolysis, fermentation, etc. At the end of processing are generated a multitude of co/by-products depending on the feedstock used and process employed. Table 2 summarizes the main high-value added co/by-products derived from the fuel ethanol production chain which use residual lignocellulosic matter.

The thermochemical processes use heat to convert lignocellulosic-based feedstock into biofuels, and are used to break-down biomass chemical bonds (Naik et al., 2010). The products of thermochemical conversion differs among them depending on the type of process implemented (gasification or pyrolysis). Gasification uses partial oxidation of biomass at higher temperatures to create synthesis gas, primarily carbon monoxide (CO) and H_2, which is then converted into fuel ethanol and other alcohols by fermentation or in a catalytic reactor. Gasification, which operates at temperatures between 700 °C and 1,000 °C in shortage of oxygen, converts biomass into a gaseous mixture, known as ‘syngas’, containing H_2, CO, CO_2, CH_4 and synthetic fuels. The syngas can be burned directly in engines, or used to produce methanol and hydrogen, or converted by the Fischer-Tropsch process into synthetic fuel (gasoline diesel, kerosene, butanol and dimethyl ether) used as propellant in diesel engines. Pyrolysis (or 'thermal cracking'), unlike gasification, operates at lower temperatures (300-700 °C) in total absence of oxygen and it is particularly suitable for raw feedstock with higher content in lignin, such as wood-based sources (forestry residues and SRF). Such conditions of temperature and strong anaerobiosis cause the break-down of chemical bonds giving rise to gaseous products (syngas), liquid (bio-oil) and solid (biochar) in various proportions that depend on the applied method of pyrolysis (fast, slow or conventional) and processing parameters (temperature, pressure and residence time). The main high-value compounds are phenols, organic acids, furfural and levoglucosans. Partial combustion at low temperatures in absence of oxygen produces pyrolysis oil that is then refined to liquid biofuels (USDE, 2008). Biochar is the solid residue from the process of pyrolysis carried out at low temperature, low heating rates and with very short residence time. Other co-products of pyrolysis or gasification include olefins (alkenes being used in the production of polyethylene and other materials) and various higher alcohols. Hydrogen resulting from the gasification of biomass or lignin may be an important fuel source used in fuel cells. The major advantage of a pyrolysis biorefinery is the possibility of decentralized production of bio-oil in regions where abundant residual biomass is readily available, making it possible to keep the minerals within the country of origin and creating the premise of cost-effective transport of resulting liquids. The basis for creating high-value compounds is the cost-effective fractionation of the pyrolysis oil. Fractionation will result in various qualities of oil which can be transformed though further upgrading into fine chemicals, petrochemicals, automotive fuels and energy.

The lignocellulosic-based feedstock is treated to separate the hemicelluloses from the cellulose and lignin using biochemical processes (Naik et al., 2010). The cellulose is treated by enzymatic or acid hydrolysis to break-down the long-chain glucose units before ethanol production. Ethanol is then produced by the fermentation of these simple sugars with specific microbes (generally yeasts) into specific feedstock (Greer, 2005; NREL, 2007). Many co-products released during the production of ethanol such as cellulose, hemicellulose, lignin, furfural, amino-acid, peptide and protein, as well as gases released during fermentation, can be used to make a variety of marketable co/by-products. In fact, fermentation process of pre-treated feedstocks have the potential to produce a wide range of different green chemicals together to ethanol (xylose, succinic acid, lactic acid, citric acid, 1,3-propanediol, lysine and glutamic acid) that are already being produced through fermentation processes on a commercial scale within established markets (nutraceuticals, personal care cosmetic ingredients, elastomers, polymers, adhesives and surfactants). The production of cellulose nanofibers in conjunction with ethanol may also be a profitable way using wheat straw feedstock as reported by Leistritz et al. (2006a). Wheat straw appears to be the most promising feedstock for this material due to its high cellulose content when compared to other grasses (Leistritz et al., 2006b). Nanofibers are made from non-hydrolyzed cellulose and are combined with resins to produce moldable and reinforced composites for the automotive, aerospace and other industries. The production of xylose from giant reed (Shatalov and Pereira, 2012), a major component of hemicellulose, can be fermented by specific microbes (especially bacteria) for producing ethanol, but also may be processed to produce furfural, a chemical used as feedstock for producing resins or xylitol used as a sweetener (Ebert, 2008). Moreover, pentose sugars from hemicellulose down-stream can be also valuable as feedstuff in animal feed. The production of furan molecules (2-furaldehyde or furfural, 5-hdroxymethylfurfural or 5-HMF, and 5-hydroxymethyl-2-furancarboxaldehyde) derived from dehydration of xylose and arabinose can be used as flavourings in foods, as well as in pharmaceutical products, cosmetics and fragrances without toxic effects on human health and food safety (Rigal and Gaset 1983; Morales 2008). The short-chain glucose not used to make ethanol may be instead used to produce a range of organic acids, superior alcohols and polymers. Some of these compounds are food additives and others can be used in industry to produce a wide variety of products including solvents, detergents, textiles and plastics, including biodegradable plastics (Snell et al., 2009). As case-study particularly interesting is those of succinic acid, one co-product derived from sugar-based feedstock (mainly hydrolysates of potato pulp and sweet corn or pressed banana pulp juice) by fermentation with selected bacteria strains (e.g. *Escherichia coli*) and/or yeast strains (e.g. *Saccharomyces cerevisiae*). Succinic acid appears to be very promising serving as the main replacement for petroleum-derived maleic anhydride. Succinic acid is a molecule-key in multiple practical applications (Fig. 6) for producing pyrrolidones, polyurethanes, polybutylene succinate, food, surfactants, solvents, detergents, plasticizers in engineered plastics, fibers, coatings, pigments, freezing point depression agents and pharmaceuticals (Ebert, 2007). It is predicted that the market for succinic acid would grow substantially if the current high price to decrease (Wyman, 2003). The production of high-value added proteins in livestock feed may be carried out before biomass pre-treatment as proposed by 'Abengoa Bioenergy' commercial site located at Hugoton, Kansas (USA) (Feinman, 2007). 'Michigan State University' has developed a method using an alkaline treatment followed by membrane filtration for to remove from 60 % to 80 % of proteins from leaves of late-season switchgrass and agricultural residues containing about 3–6 % protein (Robinson, 2008). The conversion lands from soybean and corn to switchgrass may be more acceptable if animal protein for livestock is also produced (Greene, 2004).

4.2. Biodiesel chain

First- and second-generation biodiesel is currently manufactured from vegetable oils extracted by organic solvents from edible-seeds of dedicated oleaginous crops (e.g., rape, sunflower, soybean and palm oil), no-edible oilseeds of energy crops (jatropha, mustard, carinata and canola), as well as from food waste (cooking oils and fats). Biodiesel is produced by trans-esterification process of lipids catalyzed with alkali, acid or enzyme (Naik et al., 2010). Oilseeds represent the most source of oil for biodiesel output. Global biodiesel production is based largely on vegetable oil, mostly from rape seed in the EU and soybean seed in the USA, Brazil and Argentina. Soybean and rape oilseed has a 70 % share of the total feedstock used in biodiesel production worldwide. An estimated 6 million tons of rapeseed oil and 7 million tons of soybean oil are used globally in the production of biodiesel representing about 70 % of the total feedstock used in global production (Licht 2013). The biodiesel share demand of rape, soybean and oil palm seeds is around 11 % of global vegetable oil production. The highest biodiesel yields were observed for oil palm (Indonesia and Malaysia). There are other feedstock of minor importance for producing biodiesel, such as castor bean in Brazil, sunflower in the EU, jatropha and coconut in Mozambique. Biodiesel production also includes waste feedstock as exhausted cooking oils (the main feedstock in China) and animal fats. The share of animal fats and exhausted cooking oils increased to 15 % in total biodiesel output. In Europe, the relative share of cooking oils and fats (mainly tallow) in biodiesel production is increased as the EU policy have allowed to these wastes to be double-counted in transportation targets. The continuously growth demand for protein meal has been the main driver in the recent years, behind the expansion of oilseed production. This has increased the share of protein meal in the value-added of oilseeds favoring soybean over other oilseed crops. Compared with coarse grains and other feed ingredients, protein meal prices have stayed for long time. In the 2014-2015, global oilseeds production reached 530 million tons (soybean 320 million tons and rape 70 million tons). At the same time, soybean production increased faster than production of rape and sunflower in the same years. Vegetable oil production increased to 180 million tons (out of this 60 million tons palm oil) in the same period. Vegetable oil in biofuel production account for about 20 million tons per year. Demand growth has slowed in recent times due to stagnating biodiesel production from vegetable oils in more developed countries. Production of rapeseed in Canada and in the EU is expected to grow much slower than in the previous decade as high oil-containing oilseeds, like rapeseed are more affected by the slower growth in vegetable oil prices.

The processing of vegetable oils provide either oil-less seed cakes or meals as main co-products of extraction, either glycerin (or glycerol) as principal by-product of trans-esterification. Table 3 summarizes the main high-value added co/by-products from the biodiesel production chain. The main co/by-products that are released by extracting oil from oleaginous energy crop seeds and then refining it for to remove free fatty acids and other impurities are known as oil-seed cakes or meals, an important protein source which has an high-value added in livestock feed. In the case of soybean, the feed demand for soymeal has driven and drives soybean production growth. Growth of soymeal feed production is accelerated in the early 1990s, rapidly propelled growing demand for animal feed in developing countries (FAO, 2006). In oil extraction, soybean yield range from 18 % to 19 % oil and from 73 % to 74 % meal (Schnittker, 1997) while a remaining biomass is considered as a waste. Soymeal is used primarily in the diet of monogastric species, particularly chickens and to a lesser extent pigs. About 0.4 tons of vegetable oil and 0.6 tons of rapeseed cake are produced per ton of rapeseed which is excellent for livestock feed. The feed demand for soymeal has skyrocketed over the past four decades reaching 130 million tons in 2002 worldwide. This far outstrips the second largest oilcake made of rape and mustard seed with 20.4 million tons of production in 2002. Different sources of protein for animal feed differ among them in protein content. The highest protein content occurs in fish meal (60 %), meat and bone meal (55 %) and soy meal (48–50 %). The medium protein content animal feed includes skim milk powder (35 %), rapeseed meal (32 %), sunflower seed meal (28 %), peas and beans (23 %) and corn gluten feed (22 %). In the EU, the use of meat and bone meals in livestock feed was prohibited in 2000 in a fight against mad cow disease (or BSE). As a result, more than 400,000 tons of high-quality protein feedstuff from animal sources had to be replaced by protein from vegetable sources with subsequent rising imports of soy cake. Oil production from oil palm can provide several animal feed. By chopping, drying, cubing and pelletizing, oil palm fronds can be transformed into an attractive source for ruminant feed, while oil palm trunks are a readily available source of fiber in animal feeding. Oil palm fronds, used either alone either combined with other ingredients as palm kernel cake and palm oil mill effluent, have been successfully transformed into feed in pellet or cube form for ruminant species. Palm oil by-products include palm soap stock, palm acid oil and palm fatty acid distillates. They have a wide range of quality and composition and also consist of many impurities and minor components. Oleo-chemical biorefineries based on the fatty acids platform derived from palm oil have found applications in food, paper, plastics, rubber, lubricants, soap, cosmetics, toiletries, surfactants, pharmaceuticals, fertilizers and textiles.

The principal by-product of transesterification of mono- di- and triglycerides for biodiesel production is a glycerin (Srivastava and Prasad, 2000; Meher et al., 2006). As biodiesel production soars, so does crude natural glycerin. Trans-esterification of vegetable oils yields produce about 100 kg of glycerin for every ton of biodiesel produced. The bio-glycerin can substitute conventional fossil glycerin serving as manifold use in food and beverages industry, medical and pharmaceutical applications, plastic industries and to produce nitroglycerine. The surplus of glycerin endangers the economic viability of an expanding biodiesel production because biorefiners operate on narrow profit margins and often sell glycerin to subsidize biorefinery production. Currently, surplus glycerin is disposed by incineration. The challenge is to find some high-value added alternatives to glycerol incineration and thereby improve environmental benefits and economic viability of the biodiesel supply chain. There is a limited demand for glycerin suitable for producing food, beverage, personal care and oral products, as well as pharmaceutical and industrial uses. However, crude glycerin can also be utilized as an excellent feed ingredient in livestock rations to replace fossil-based glycerin. For example, crude glycerin contains similar energy to that provided from maize for pig livestock rations. Crude glycerin has also huge opportunities in biomaterial applications including chemicals, monomers, plasticizers, hydrogen generation and polyesters production.

5. High-value added co/by-products associated to some emerging fields

There are nowadays many new business opportunities and some emerging industrial sectors that may be better positioned than others starting from the biofuel chains. Offering new business opportunities is not the only way in which the production of bio-based products will affect different industries. In addition, a number of underlying trends have put high-value bio-based products on the top of strategic agenda of the main players in many biorefineries. In this section we have highlighted on three new application sectors considered most interesting for the big players: 1) renewable and sustainable farming systems, 2) bioplastic industry and 3) cell and tissue engineering in biomedical applications.

5.1. End-use of organic residuals: from waste to sustainable tools in renewable farming systems

The growing global demand for lignocellulosic biomass resources potential will lead to an increasing focus on agricultural productivity in developing countries (Ullah et al. 2015). New crops and novel traits will make it a real potentiality to use of less fertile land, less irrigation water and in reducing GHG-emissions. This may open new market opportunities overall for developing countries to participate into a new management of the limited agricultural resources worldwide. This greater focus on agricultural productivity will also lead to a substantial increase in soil amendment and fertilizer use, especially in countries where the best agricultural practices are not spread into renewable and sustainable farming systems. For example, nitrogen and phosphorus from digestate can easily be manufactured from anaerobic process of agricultural residual biomass or waste, and thus mineral fertilizers can be quickly replaced from it by organic farmers. However, it is worth noting that the carbon footprint of fertilizers is high and can have detrimental effects on water supply.

The increasing demand of regulatory mandates for biomass will increase substantially the market size for agricultural and forestry high-value added co/by-products, and may shift the relative economies of food/feed production toward other land uses, as cellulosic energy crops, such opening up new opportunities for farmers and growers in developing countries. Agricultural commodities prices may also be influenced by the increased production of bio-based materials in biorefineries. However, the impact on food prices strongly depends on the kind of feedstock used in the production process. Second-generation feedstock (such as lignocellulose residues or jatropha) tends for example to have very little influence on food prices. On the other hand, first-generation feedstock (particularly corn, wheat, palm oil and rapeseed) could contribute to increasing food prices if used excessively without providing additional capacity for the production of these inputs. For a more sustainability of the agricultural commodity production chains, growers and farmers employ more renewable sources to supply food chain according to EU policies.

5.1.1. Soil amendments and soil fertilizers

Although large amounts of residual biomasses easily on-farm available to farmers and growers can find new applications in advanced cropping systems by conversion into compost, biochar and exhausted seed pellets/meals, very little amount of them are nevertheless really used in agriculture because the mechanisms by which they improves soil fertility and increases plant yield are yet poorly known in terms of agronomic value, crop response and soil health benefits. A potential emerging market for biofuel co/by-products that producers may consider marketable beyond the soil organic amendments is represented by those of soil biofertilizers for plant growth in the cropping systems under greenhouse condition. De Corato et al. (2015) have given a review on the phytosanitary application flows of co/by-products originated from the biofuel production chains focusing their challenge on the ecological and physiological effects of them with: 1) the beneficial soil microbiota, 2) the direct interaction between glucosinolates and furfural bioactivity with soil-borne plant pathogens and 3) the indirect interaction among plant pathogens and biochar. In this paper biofuel co/by-products were classified on a basis of their target (soil or plant) or their action modality on the soil, crop or microbiota as follows: 1) soil amendments (compost, biochar and oil-less seed cakes); 2) soil fertilizers (digestate, DDGS and oil-less seed cakes); 3) phytosanitary drugs (biofumigants, fungicides and herbicides); 4) plant biostimulants (compost teas, seaweed extracts and brassino-steroids).

Compost is a stabilized organic matter deriving from the bio-oxidation process of un-decomposed feedstock based on the MSW, crop biomass residues and plant-waste (Fig. 7). Composting is an efficient, cost-effective and environmentally safe oxidative biological process for recycling many residual agricultural biomass types into new cropping production cycles (Maniadakis et al. 2004). It is a very simple technology consisting of user-friendly small composting plants equipped with tools already available on a farm where un-degraded organic biomasses are transformed and stabilized into mature composts through an aerobic bio-oxidation process (Christian et al. 2009). Composting contributes to solve the problem of disposing agricultural biomasses and vegetable feedstock providing to farmers a self-supply of quality compost for the improvement of agricultural productivity (Scotti et al. 2016). In some developed horticultural areas of Italy, significant amounts of MSW, agricultural wastes and residues, such as vegetable and fruit by-products, cropping residues, garden wastes, unmarketable products, vegetable processing leftovers, food waste, etc. are daily produced. They represent an important source of organic matter suitable to be composted and returned to soil for to improve fertility (Pane et al. 2015). Composting is a sustainable oxidative biological conversion in which biodegradable organic compounds are transformed into stable humified organic matter under controlled and accelerated conditions (at least three months) without recovery of energy giving only stabilization of organic waste and nutrients re-cycling. It is generally performed through a process diagram consisting of four mains steps (Fig. 8): 1) mixing of raw materials containing un-stabilized organic compounds (sugars, lipids and proteins), mineral nutrients, water and microbiota; 2) building of compost piles less than 5 m^3 in volume for achieve an adequate aeration of them; 3) bio-oxidation of the un-stabilized organic compounds for producing water, CO_2 and heat (more than 65 °C) to achieve sanitization against harmful and pathogen microbiota without energy recovery; and 4) final curing where finished (or cured) compost contains stabilized organic matter (mainly humic substances), carbon, nitrogen, phosphorus, micronutrient, heavy metals, water and a broad range of a beneficial microbiota. Compost utilization, in combination with soil substrates as peat, perlite and vermiculite, may give several benefits for plant growing as fertilizer, stimulant, improver of soil structure and fertility, including suppression of soil-borne plant diseases in horticultural soil-less systems if used a the proper rates (between 10 % and 30 % by volume). However, not all the composts are suppressive and its level vary, as well as the range of the suppressed target-pathogens. A recent study given by De Corato et al. (2016) has tested three next-generation suppressive green composts provided from a varied feedstock of agro-energy co-products and agricultural wastes such as processing residues (spent coffee-ground, defatted olive marc and wood chip), plant-wastes (artichoke, fennel and tomato) and steam explosion liquid-wastes derived from the steam explosion (SE) pre-treatment of wheat straw, miscanthus and giant reed in suppressing soil-borne plant diseases in horticultural soil-less systems under greenhouse condition. The capability to suppress plant pathogen depends on the direct antifungal actions of biostimulants and/or humic fractions, by activities of antagonistic microbes causing microbiostasis, fungistasis and hyperparasitism, by release of antimicrobial compounds (antibiotic-like) causing antibiosis, and by activation of systemic disease-resistance in host plants (Avilés et al., 2011).

Biochar is the solid co-product from pyrolysis process obtained using lignocellulosic biomass (Fig. 9). Biochar, that is used in sustainable and renewable agriculture as improver of soil structure (Table 2), can be burned like coal or used as a soil additive to improve soil fertility in preventing nutrients and water losses. Biochar can also be used to sequester carbon from environment and may remain in the soil for hundreds of years. Crop productivity under extensive and/or intensive agriculture conditions can be related to direct or indirect effect of biochar suppling plant nutrients, increasing soil water retention and soil cationic exchange capacity, correcting soil pH and improving physical-chemical properties, transforming phosphorus and sulfur into peptides, neutralizing phytotoxic compounds in the soil, promoting beneficial mycorrhizal fungi, modifying relations between soil microbiota and related ecological functions, and increasing plant resistance to biotic stresses (Elad et al., 2011). Also, biochar has recently been proposed to synergize with suppressive composts sourced from poultry manure in suppressing soil-borne plant disease by beneficial soil applications (Jindo et al., 2012). Similarly to compost, also biochar is able to suppress soil-borne plant pathogens with different action mechanisms providing nutrients and improving their availability and water uptake; stimulating a beneficial microbiota that provide direct protection against pathogens via antibiosis, competition and parasitism; and altering microbial population in the soil which cause a shift toward beneficial microorganisms populations promoting plant growth and activating resistance mechanisms against disease development (Buonanomi et al., 2015).

Oil extraction, which can be carried out with chemical solvents, cold pressing or a combination of both methods, provides oil-less seed cakes as one of the main co-products from biodiesel production chain (Fig. 7). These co-products, after grinding or pelleting, can be incorporated directly into the soil as meals or pellets (Table 3) playing a crucial role in suppressing soil-borne fungal diseases (Buonanomi et al., 2007). In contrast to matured compost, oil-less seed pellets/meals from Indian mustard and flax are un-decomposed organic materials very rich in carbon and nitrogen easily available to soil microbial dynamics that provide nutrients for the native microbial populations involved in nutrient-recycling of carbon, nitrogen, phosphorus, potassium, and in plant disease suppression (Wang et al., 2012). Adding seed pellets/meals into the soil at the proper proportions, the bacterial community structure is such regulated because seed meal/pellet may contribute to plant health inducing a fungistatic action via competition for nutrients among beneficial soil microbiota and soil-borne pathogens (Zaccardelli et al., 2013). Recently, the residual oil-less seed cake rich in protein derived from oil extraction of cardoon seeds for producing bioplastics should be employed in organic farming systems in suppressing soil-borne plant pathogens (Pugliese et al., 2017). Also, efficacy of *Brassica carinata* pellets able to inhibit mycelial growth and chlamydospores germination of *Phytophthora nicotianae* at different temperature regimes was reported by Serrano-Pérez et al. (2017). Nevertheless, soil amendments with seed cake may sometime induce the growing of harmful microbes (saprophytes, pathogens, etc.) because this is not organic matter adequately stabilized and such could induce a detrimental disease-conductive effect by increasing the soil population level of soil-borne plant pathogen (Chung et al., 1988).

Amongst treatment technologies for organic waste, landfill is a very ancient technique in which all MSW and refuses accumulate in large ditches, or valleys, or specially excavated holes in the land, are decomposed by bacteria sourced from waste to produce gaseous biofuel, especially methane. Landfill methane is used not only for power generation but also for firing brick kilns and for producing steam in industry. Nevertheless landfill is a process unsustainable, it is discouraged in many countries (landfill ban/taxes), it no allow recuperation of nutrients and sometimes allow recuperation of energy (landfill gas) but with lower efficiency and poor emissions of CH_4. The same purpose is nowadays achieved accordingly with the latest technologies able to produce concomitantly biogas and digestate (as main co-product) through anaerobic digestion of MSW and plant biomass (Fig. 10) in suitable bioreactors. The anaerobic digestion is one of the most mature technologies for producing biogas from biomass, overall methane, that allow stabilization of organic waste as digestates, recuperation of nutrients from the digestates (soil fertilizer/soil improver) and overall recovery of energy (biogas) from a broad variety of feedstock as: 1) MSW, 2) dedicated crops (wheat, triticale, maize, sugar beet), 3) animal waste (slurry, sludge, manure), 4) residual biomasses and agro-wastes (corn stalks, rice husks, corn stover, wheat straw, cropping residues, unmarketable products, vegetable processing leftovers, spent coffee-ground, defatted olive marc, sugar beet bagasse, tomato-waste, cardoon-waste, vegetable-waste). However, biogas production relies greatly on the co-digestion of mixtures by animal slurries and/or manure with annual energy crops, particularly triticale and maize, that provide an equilibrate carbon/nitrogen ratio to the end-product. The biogas produced is then tapped and used either in houses or in power stations. The most important co-product from the biogas chain is commonly known as digestate. The digestates, containing relevant amount of nitrogen, phosphorus and many micronutrients, are suitable for producing organic fertilizers after an adequate time of aerobic stabilization if used as organic input in agriculture accordingly with the Italian legal limits. Digestates have a variable degree of carbon/nitrogen rates due to their variable origin and composition of the feedstocks, which means that they can be rapidly decomposed (digestates with lower carbon/nitrogen rates) or slowly decomposed (digestates with higher carbon/nitrogen rates) into the soil releasing nutrients available to plant growth in a timely manner. More recently, composting and anaerobic digestion can be integrated among them into a more complex flow chart as, for example, in a comprehensive managing of poultry manure (Fig. 11) able to minimize negative impacts caused by soil-borne pathogens and reduced soil quality (Darby et al., 2006). Other interesting flow chart of sorting digestion and separation of MSW is shown in Figure 12 where biogas, digestate and composted sludge cake are simultaneously co-produced starting from the same waste.

Dried distillers grain and oilseed cakes/meals from brassicaceae should be re-considered in this review also as effective fertilizer sources for promoting plant growth (Table 3). In addition to content of macro- and micronutrients needed to support plant growth, these co-products have both a lower carbon/nitrogen ratio which means that they are rapidly decomposable into the soil releasing nitrogen quickly available to plant growth (Snyder et al. 2010). This property is of particular interest to organic agriculture markets, where nutrient sources and fertilizers containing available readily inorganic nitrogen to positive impact corn yield are scarce (Nelson et al. 2009). Competition with animal feed markets has prevented widespread adoption of biofuel co-products as biofertilizers. DDGS and oilseed pellets/meals particularly hold more value-added as animal feed than as fertilizer source. Therefore, animal producers are willing to pay for feed materials based on their feed value instead for lower-value fertilizers. However, fertilizers market may become more appealing to biofuel producers due to DDGS feed quality issues, over-production of DDGS, high costs of oilseed meals/pellets, and increased interest of organic farmers toward alternative nutrient-rich fertilizers applicable into sustainable farming systems (Abe et al. 2010).

5.1.2. Phytosanitary drugs

Oil-less seed cakes derived from some *Brassicaceae* species (e.g. *B. carinata*, *B. napus, B. juncea*, *Sinapis alba*, etc.) for producing biodiesel show a particular ability for their uses in plant disease management in biofumigation applications (Fig. 7) that goes well beyond the soil amendment effect (Table 3). Due to their biofumigation properties against plant pathogens and microbial contaminants of seeds, oil-less seed meals from *Brassicaceae* are applicable in the biological disinfection of soils, plant growing substrates, seeds, vegetable and fruit under postharvest condition (Pane et al., 2013). Biofumigation effect depend on the glucosinolates content into seed meal. Glucosinolates are a wide class of secondary metabolites present in most *Brassicaceae* species which are quickly converted into a wide spectrum of volatile antimicrobial substances (thiocyanates, isothiocyanates, nitriles, etc.) bioactive against plant pathogens by the myrosinase-mediated hydrolysis enzymatic-complex when dry seed meal is wetted by soil water or by water nebulization. *B. carinata* is the most studied energy crop that provide ideal formulations for several biofumigation applications that could be a promising and eco-friendly safe method for the control of soil-borne plant pathogens and microbial contaminants when thiocyanates, isothiocyanates and nitriles are instantaneously released by soil treatment with dry seed meal of *B. carinata*.

Crude glycerine has received a special attention in phytosanitary applications (Fig. 7) as carbon-source into media for bacterial growth (Table 3). In fact it has been tested as: 1) an additive in liquid-formulations of biocontrol agents (*Trichoderma*) for extending their shelf-life (Sriram et al., 2011); 2) a conjugate to a biocontrol agent (*Acremonium*) for controlling cucumber powdery mildew (Malathrakis and Klironomou, 1992); 3) for the synthesis of chemical fungicides derivatives of glycerin as a dithiocarbamate (Len et al., 1996); and 4) a carrier of antibiotics able to reduce disease incidence of some plant pathogenic bacteria in navy bean seeds (Liang et al., 1992).

Pelargonic acid (PA) has been isolated for the first time in the form of ester from leaves of the ornamental plant *Pelargonium roseum* as main component of its essential oil. PA is a fatty acid industrially obtained from oxidative break-down of oleic acid contained in un-defatted olive marc, the main processing residue of the olive oil production chain. PA (Table 3) shows no selective effective herbicide action only if applied in the post-emerging phase against a wide spectrum of weeds belonging to various annual and poly-annual mono- and di-cotyledons species. PA is an eco-friendly co-product from the olive oil chain because it directly operates by desiccation of weed leaf surface without release of residual chemicals in the soil and environment.

Furfural and other volatile microbial inhibitors (organic acids at low molecular weight) were nowadays co-produced with ethanol during the processing of lignocellulosic matter, for example from wheat straw, using an innovative pilot-scaled paddle dryer for the production of ethanol which include at the same time both inhibitors removal and high-solids enzymatic hydrolysis (Viola et al., 2016). Among the two units of biomass pre-treatment and bioconversion ethanol, there is an innovative intermediate step that operate a simultaneous detoxification and liquefaction of pre-treated biomass by SE generating a condensation liquid waste (SELW) which contains a mix of furfural and organic acids at low molecular weight as the formic and acetic acids (Fig. 13). The SELWs that have been obtained from pre-treatment of wheat straw, giant reed and miscanthus have been directly tested for their antimicrobial properties (Table 2) as fungicide against plant pathogenic fungi (De Corato et al., 2014), as nematocide against plant parasitic nematodes (Crow and Luc, 2014) and as bactericide towards mushroom pathogenic bacteria (Bruno et al., 2015). As afore-mentioned, SELWs have also been used in increasing suppressive properties of three green composts sourced from a feedstock of agro-energy co-products and agricultural wastes (De Corato et al., 2016).

Moreover, certain plant extracts containing secondary metabolites as terpenes, terpenoids, flavonoids, isoflavones and phenolic substances that are extracted from biofuel plant-waste such as jatropha seed cake, sunflower residues and soybean tissues (Table 3), have also been investigated for their potential antifungal activity (Gatto et al., 2011) although the studies in this field are still in a preliminary phase.

5.1.3. Plant biostimulants

Many researches have focused on the plant biostimulants due to increasing attention about the use of natural substances able to potentiate crop growth and improve quality of the crop yields (Storer et al., 2016). The development of new products derived from compost, such as ‘compost teas’ (Fig. 7), is increased in the recent years due to their positive effects on the main quality parameters of horticultural crops as mini watermelons (Liguori et al., 2015). Compost teas are defined as organic products obtained through a liquid-phase compost extraction, variable from few hours to two weeks, with or without active aeration, and with addition of nutrients derived from residual biomass that provides sugar (molasses, etc.) and protein (casein, etc.). In particular, compost teas can show this particular bioactivity on plants due to their content in aromatic substances, hormone-like organic molecules and useful microorganisms. Compost tea-based treatments can exert protective effects against plant diseases occurrence and/or stimulate an enhanced plant physiological status with improvements in quantity and quality of crop production. The most widely described uses of compost tea are related, almost exclusively, to its ability in suppressing plant pathogens similarly to suppressive composts. Compost teas are usually applied by foliar spray on crops and by soil drenching.

The brown seaweed *Laminaria digitata* is traditionally used as a fertilizer that spread on the land (Table 3). In the 18th century it was burnt to extract the potash it contained for use in the glass industry. In the 19th century it was used for the extraction of iodine. Both these uses died out when cheaper sources for these products became available. *L. digitata* is still used as an organic fertilizer, but it is also employed for the extraction of alginic acid or alginate, the manufacture of toothpastes and cosmetics, and in food industry for binding, thickening and molding (Table 3). *L. digitata* is used in Asia (mainly Japan and China) for making dashi, a soup stock, and for other culinary purposes in functional food. Many biorefining companies use *L. digitata* in industrial applications including bio-architecture, solar energy, next-generation biofuels, green chemicals and more else (Sikes et al., 2010). Seaweed extracts have good biostimulant properties (Table 3) able to induce plant growth for crop development due to presence of a large number of growth-stimulating compounds (Khan et al., 2009). It is proved that new methods basing on the seaweed extracts as biostimulants are applied for to increase efficiency of plant cultivation thanks to action of phytohormone-like substances able to regulate growth and develop of many crops (Tuhy et al., 2013). Also, a very strong biological effect regarding to antifungal activity of crude extracts from biofuel-used brown and red seaweeds against postharvest diseases on fresh fruit under storage condition has recently been investigated and attributed to higher content of fatty acids, phenolic substances and polysaccharides into crude extracts (Table 3) obtained by a supercritical carbon dioxide technique (De Corato et al., 2017).

Brassinosteroids are a wide range of secondary metabolites extracted from plant-waste, seed and press-cake of *B. carinata* and *B. napus* (Table 3). They have a very strong effect in stimulating plant-growth on the plant cells or tissues of many herbaceous and horticultural crops (wheat, tomato, bean, lettuce, tobacco and beet) both in open field and under greenhouse condition determining: 1) increasing of productivity, 2) improving of quality of the marketable main product, 3) increasing of disease suppression and resistance to abiotic stress, and 4) aestivation and advanced maturation of fruit (Bardi and Rosso, 2013). Trough phytohormone-like mechanisms, brassicasteroid promotes cell division of the meristematic tissues, stem elongation, foliar expansion, seed germination and tolerance to abiotic and biotic stress. Brassica-steroids are usually applied on crops by foliar spray and radical treatments.

5.2. Bioplastic industry

Bioplastics feedstock generally derive from flour or starch of corn, wheat or other grains, but also from a wide variety of residual cellulose feedstock (Table 2). However, recent researches show the huge potential of DDGS and CGM including soybean meal to produce bio-composite material polymeric and thermoplastic (Table 3). More recently, a cellulose acetate biofilm active with essential oil of edible-plant (oregano) and clay (montmorillonite) has been tested for controlling biotic postharvest losses in food packaging and during shelf-life (Pola et al., 2016). Azelaic acid obtained from break-down of oleic acid (together to pelargonic acid) was used for making bioplastics (Table 3). Crude glycerin can also be fermented by selected bacteria via 1,3-propanediol to produce bio-based poly(tri-methylene terephthalate) or fermented to produce poly(hydroxy alkanoates) (Table 3).

The term ‘bioplastic’ encompasses a whole family of materials which differ from the conventional plastics because they are bio-based, or biodegradable, according to definition given by the European Bioplastics (http://en.european-bioplastics.org/bioplastics). Bioplastics already play an important role for food packaging, shelf life, gastronomy, consumer electronics and automotive. In these market segments, bioplastics are used to manufacture products intended for short term use, such as mulch films or catering products, as well as in durable applications, such as mobile phone cover or interior components for car. Biodegradable plastics no compostable are also most used as mulching in protected agriculture for greenhouse, tunnel and soil for controlling diseases of horticultural crops or increasing seedling growth (Fig. 14). The terminology used in the bioplastics sector is sometimes misleading; while most people use the term bioplastic to mean a plastic produced from a biological source, there is no such a general agreement on biodegradability. All plastics (both bio-based and petrochemical-based) are technically biodegradable, meaning they can be degraded by microbes under suitable conditions. However, many degrade at such slow rates that they are to be considered non-biodegradable. Some biodegradable petrochemical-based plastics may be used as additive to improve the performance of commercial bioplastics. In addition, the biodegradability is an high-value added of some types of bioplastics. On the other hand, non-biodegradable bioplastics are referred to as durable. The degree of biodegradation varies with temperature, polymeric stability and available oxygen content. Consequently, most bio-based plastics will only degrade in the tightly controlled conditions of industrial composting units. In addition to being bio-based, some bioplastics are both biodegradable and compostable able to produce compost in so far as they meet the requirements specified by the UNI EN 13432:2002 and by the certification programs released by leading international bodies that define how and what bioplastic must be quickly biodegraded under industrial composting condition for it to be called 'compostable'. The term 'biodegradable plastic' has also been used by producers of specially modified petrochemical-based plastics which appear to biodegradability. This type of plastic may be referred to degradable plastic, or oxy-degradable plastic, or photodegradable plastic, because the process is not initiated by microbial action. While some degradable plastics manufacturers argue that degraded plastic residue will be attacked by microbes, these biodegradable materials do not meet the requirements of the commercial composting standard defined by the UNI EN 13432:2002. There are two main advantages in the use of plastics sources from biomass when compared to their traditional versions: 1) they save non-renewable resources, and 2) they are almost carbon neutral.

The poly(hydroxy alkanoates) or PHAs are a large group of bio-based polyesters from biomass refineries with over 100 different types of monomers with different properties and functionalities with attractive qualities for thermo-processing applications (Snell et al., 2009). PHAs are aliphatic polyesters produced via fermentation of renewable feedstock directly by the microorganisms. PHAs are thermoplastic polyesters synthesized by various types of bacteria such as *Bacillus*, *Pseudomonas*, *Ralstonia* and *Rhodococcus* through the fermentation of sugars or lipids. Under certain culture conditions, these linear macromolecules accumulate into bacterial cell in the form of microscopic granules to reach high concentrations up to 90 % on dry weight basis of the total bacterial mass. The PHAs accumulated in the form of granules serve as an energy reserve. These polyesters concentrates in the bacterial cells has an high refractive index under microscopy observation. The PHAs that granule are then recovered by destroying the cells. The biosynthesis of PHAs is usually obtained by special culture conditions, such as lack of nutrients like phosphorus, nitrogen and trace elements, or lack of oxygen, or/and excess supply of carbon sources. Depending on the microorganism and culture conditions, homo-polyesters or co-polyesters are synthesized with different acid hydroxyl-alcanoates. The alkyl group can have a number of carbon atoms between 1 and 15, can be linear or branched and can contain various types of substituents depending on the bacterial strain. For example, bacteria of the genus *Ralstonia* produce short side chain (1-5 carbon atoms), while *Pseudomonas* produce medium-sized side chain (more than 5 carbon atoms). An interesting conversion way from second-generation sugars into high-value added lipids which could will be bio-converted into PHAs by bacteria is those operated by oleaginous yeasts. The main part of these lipids belong to triglycerides which are deeply studied as a new feedstock able to provide bioplastics. In a recent study (Mastrolitti et al., 2015), the yeast *Cryptococcus curvatus* has been investigated for the conversion of second-generation sugars from hydrolysates of cardoon plant-wastes into triglycerides accumulated into the living cells (Fig. 15). The great variability of the side chains of single monomers give to PHAs extremely variable physical characteristics: for example, melting point varies between 40 °C and 180 °C. These materials are biodegradable and are used in the production of bioplastics. Also mechanical properties and biocompatibility of PHAs can be modified tweaking the surface or by combining it with other polymers, enzymes and inorganic materials. PHAs are thermoplastic polymers, can be processed with conventional equipment, they are ductile and elastic, with variable properties according to their chemical composition (homo- or co-polyesters). PHAs are also stable to UVs, unlike other types of bioplastics as poly(L-lactic acid), and show a low water permeability. PHAs are soluble in halogenated solvents as chloroform or dichloroethane. Their crystallinity can vary from 10 % up to 70 %. Their processing, impact resistance and flexibility improve with a higher percentage of valerate in the material.

The poly(hydroxyl butyrate) or PHB, belonging to the group of PHAs, has similar mechanical properties like poly(propylene) or bio-based poly(ethylene) and has a good moisture resistance. PHB is a biodegradable compostable polymer which is produced by bacteria *Cupriavidus necator* and *Pseudomonas* sp. in response to stress conditions as lack of macronutrients, or lack of oxygen, and/or excess supply of carbon sources. PHB is produced by the action of three enzymes. The first (3-ketothiolase enzyme or PhaA) catalyzes the condensation of two acetyl-CoA molecules, the acetoacetyl-CoA is reduced to 3-hydroxybutyryl-CoA (3HB-CoA) by the catalysis of the second enzyme (NADPH-dependent acetoacetyl-Coa reductase or PhaB). The third (PHA synthase or PhaC) incorporates 3HB-CoA in a PHB growing chain. The poly(hydroxyl butyric) acid, synthesized from pure PHB, is relatively fragile and rigid, whereas copolymers of PHB, which may include other fatty acids such as acid beta-hydroxyvalerate, can have more elastic properties.

The poly(L-lactic acid) or PLA is the polymer of lactic acid. The synthesis is done through several phases: separation of the fibers and gluten, liquefaction and saccharification, fermentation with re-use in the culture medium of the protein separated from starch, purification and concentration of saline solutions of lactic acid, and ending polymerization. The industrial fermentation takes place thanks to a bacterium of the genus *Lactobacillus*; it must be used in high purity to avoiding influence on the optical purity of the acid produced. Sugar, molasses and more else residual sugary biomasses are used as feedstock. *Bacillus coagulans* is alternatively used for PLA synthesis. PLA has properties intermediate to those of polystyrene. As for the biodegradability, hydrolysis occur under conditions of temperature higher than 60 ° C and humidity more than 20 %.

5.3. Cell and tissue engineering

Sodium alginate, the sodium salt of alginic acid, is an anionic polysaccharide comprising of mannuronic acid and guluronic acid residues. It is mainly extracted from cellular walls of brown seaweeds which are actually used for third-generation biofuel production (mainly ethanol) either in synergy either in place of microalgae (Milledge et al., 2014), but it is also produced from bacterial sources being extracted from biofilms (Donati and Paoletti, 2009). Through binding with water, it forms a viscous gum by water absorbing and quickly solidifying. Its colour ranges from white to yellowish-brown, and it is sold in granular or powdered forms. Alginates from different seaweeds often have variations in chemical structure and physical properties: some of them may be yielded as alginate that gives a strong gel, another a weaker gel, some may readily give a cream/white alginate, and another difficultly forming gel. Owing to its gelling, thickening, stabilizing and viscose properties, alginate is traditionally a prominent component for food (Holdt and Kraan, 2011), textile and paper industries (Pallerla and Chambers, 1997). Alginate is a well-known biomaterial that is used in pharmaceutical and biomedical fields (Augst et al., 2006; Gombotz and Wee, 2012), for drug delivery (Tønnesen and Karlsen, 2002) and in tissue engineering (Kuo and Ma, 2001; Machida-Sano et al., 2010) due to its high bio-compatibility, low toxicity, low cost, simply and quickly gelation mechanism (Lee and Mooney, 2001). Just as an example in the botanical field, 3 %

Na-alginate with 0.1 M calcium chloride has been found to be a better mix for producing encapsulated nodal segments for plant regeneration by non-embryogenic synthetic seeds (Verma et al., 2015). A recent research regarding to use of a sodium alginate matrix suitable for immobilized-yeasts having an antagonistic bioactivity against green mould disease on citrus fruit caused by the phytopathogenic fungus *Penicillium digitatum* under postharvest condition has been carried out (De Corato et al., 2017).

Finally, concluding this overview, a special attention must be focused on the lignin sector (Table 2). Lignin, second only to cellulose in natural abundance, is an important constituent in biomass. The main use of lignin is as a fuel to fire the boilers used for pulp production. Due to its abundance and low price, lignin is of industrial interest to convert them into high-value added products such as biomaterial, adsorbent and thermal insulator. Lignin is now being isolated from the fuel ethanol production chain, and it being separated from lignocellulosic matter by standard pre-treatment procedures, it is nowadays the main co-product with ethanol. Using mild methods to separate early lignin from the lignocellulosic matter will preserve its structure, such allowing more potential uses (Holladay et al., 2007). The 'Lignol Innovation' Company uses wood and agricultural residues in their pilot plant to produce both ethanol and high purity lignin (Greer, 2009). This form of lignin has large-scale commercial potential as a replacement for petroleum-based products currently used in the manufacturing of industrial coatings, gels and emulsifiers (ILI, 2009). Several attempts have also been reported in literature on lignin as a part of biomaterials composites with hydroxyapatite, or as a carrier in laxative formulations, or as an allergenic reducer for latex rubber. Lignin can also be used to generate more energy for ethanol plant operations, or used as a dispersant and binder in concrete admixtures, or as the principal component in thermoplastic blends, polyurethane foams or surfactants. However, only from 1 % to 2 % is isolated from pulping liquors and used to prepare polymeric materials, as polyurethanes, phenolic and epoxy-resins. Another important use for lignin is in the production of carbon fiber. Spun and woven into a fabric, carbon fiber is combined with resins to form reinforced plastic. This material is similar to fiberglass with high tensile strength and low weight that is used in aircraft, automobiles and sporting goods (Holladay et al., 2007). Pure lignin derived from the pre-treatment of lignocellulosic matter for producing ethanol (Fig. 16) is potentially utilized for innovative and interesting biomedical applications in cell and/or tissue engineering. Composites and blends of lignin are yet known in literature with cellulose alone or cellulose acetate (Sescousse et al., 2010), or xanthan gum (Raschip et al., 2007), or poly(ethylene oxide) (Kadla and Kubo, 2003), or poly(vinyl alcohol) (Kubo and Kadla, 2003), or PLA (Li et al, 2003), or poly(4-vinylpyridine) (Cunxiu et al., 2005). Even though there may be only weak interaction between lignin and principal constituent, nevertheless addition of lignin may offer advantages to basic-material such as more control over water uptake and improved mechanical properties (Raschip et al., 2007). Generally, lignin is not cytotoxic if used up to moderate concentration. Apart from lower hydrophilicity and higher stability, another potential advantage of lignin is its potential antimicrobial activity. Although antimicrobial properties of the phenolic units delivery from purified lignin degradation are well documented (Baurhoo et al., 2008), there are nevertheless some controversy in literature about antimicrobial activity of both pure lignin and lignin-based materials. Importance of conjugating lignin with polysaccharides derived from cellular walls of brown seaweeds for *in vivo* expression of various kinds of immune-potentiating activity is also reported (Sakagami et al., 1991). More recently, lignin was proposed to produce hybrid alginate–lignin aerogels with relevant perspectives in biomedical applications. The relationships between hydrophilicity and hydrophobicity of the lignin surface is an important factor that allow a good cell adhesion. When combined with alginate, lignin is expected to reduce hydrophilicity of alginate and hence provide more suitable environment for cells to adhere, grow and differentiate into a porous matrix. Bearing in mind ultimate stability of lignin, it was also expected that the presence of lignin may abate the scaffold degradation rate and help to match it with the rate of new bone tissue regeneration. These features may also have a beneficial effect with respect to biomedical applications. A study of novel non-cytotoxic alginate-lignin hybrid aerogels combining with the supercritical carbon dioxide technique and employed as scaffolds for tissue engineering purpose has been recently studied (Quraishi et al., 2015). Potential applications of lignin as lignosulphonates in food industry (fishgelatin films) have also been reported by (Núñez-Flores et al., 2012). Many comprehensive reviews on the pure lignin and lignin-based materials are however available in literature (Khitrin et al., 2012; Azadi et al., 2013).

6. Biorefining outlook in the EU and in Italy

Feedstock that can be considered in the EU and in Italy suitable for biorefinining are: 1) MSW; 2) agricultural waste, animal husbandry waste and agro-industrial residues; 3) forest residues after forest cleaning. On the other hand, the chemical basic-platforms currently produced in industrial-scale from this multiple feedstock are represented by the fuel ethanol; biodiesel; methane; acetic acid; lactic acid and the polymer derived from it as polylactic acid; 1,3-propanediol used in poly(trimethylene terephthalate) synthesis; xylose produced from hardwood and used to produce xylitol as sweetener; furfural produced from residual biomass including corncobs, cottonseed hull bran, oat hulls, and used to produce pesticides; sorbitol produced by hydrogenation of dextrose and used as an alternative to xylitol.

6.1. An overview in the EU

The shift towards a bio-economy recently recognized by the EU through the adoption of a dedicated strategy outlining the need to move towards a post-petroleum society in order to respond to the key challenges, is focused in the coming years. The EU has also emphasized the pivotal role of bio-based products and markets development by reviewing the EU industrial policy. In February 2012, the EU adopted the new bioeconomy strategy to shift Europe towards a greater and more sustainable use of renewable resources moving towards a sustainable bioeconomy (Vivekanandhan et al. 2013). While the bio-economy strategy itself is a good start, Europe today still remains a long way from establishing optimal framework conditions for the biorefining industry. In 2010, about 62 % of renewable energy in the EU was generated from biomass and even if this share is expected to decrease to 57 % in 2020. The total bioenergy contribution to the EU mix is expected to increase from 3600 PJ in 2010 to about 5900 PJ in 2020.

In general, the European market for soaps, detergents and other similar products amounted to approximately 30 billion euros; between 30 % and 50 % of these products contain bio-based enzymes, as proteases and lipases, for detergent applications. In Europe, the production of enzymes is strong and it suggests a potential increase of their use in food, paper and textile production. Germany has developed commercial operations using the biomass-to-liquid technology. A demonstration plant was built in Freiburg in collaboration with Shell using wood as raw material. Austria has developed a new technology based on grass and silage since 1999s with the aim of exploiting the fibers, proteins and lactic acid components. The forest resources of Scandinavia are being targeted for the production of cellulosic ethanol. Neste Oil in Finland with Petrobras in Brazil are the big producers of diesel from hydrogenated vegetable oils and animal fats at the Porvoo biorefinery. The biodiesel production has interested Total (France) and OMV (Austria). ENI VERSALIS are building a new biodiesel facility in Italy (Livorno), the plant will process about 6,500 barrels per day of vegetable oil by the Ecofining technology jointly developed by ENI VERSALIS.

The main European projects regarding to biorefining focus are: 1) ‘FERTIPLUS’ (http://www.fertiplus.eu) addressed to reduce mineral fertilizers and agro-chemicals in agriculture recycling treated organic waste into compost and biochar and improving the combined effects of biochar with anaerobic digestion and composting; 2) 'OLIPHA' (http://www.olipha.eu) focused to investigate a novel and efficient method for the production of PHA polymer-based packaging from olive oil waste water and anaerobic digestion of the remaining by-products; 3) 'TRANSBIO' (http://www.transbio.eu) focused to implement an innovative cascading concept for the valorization of co-products and by-products from the fruit and vegetable processing industry using eco-friendly biotechnological solutions, like fermentation and enzyme-conversion strategies, for to obtain valuable bio-products as bioplastics (PHB), succinic acid chemical platforms, and bio-based enzymes (proteases and lipases) for detergent applications. In addition to that, biofuel co/by-products also create opportunity for the fabrication of various nanostructured materials including three biorefinery projects in the USA using predominantly corn stover. Three commercial second-generation biofuel projects have started in Brazil from corn stover and straw to produce bioplastic materials: 1) 'GRANBIO' for commercial cellulosic ethanol plant, 2) Raizen/Iogens plant, and 3) Solazyme-Bunge plant.

6.2. Big players in Italy

Despite the economic crisis affecting Italy since 2009, the economic sector of 'green chemistry' shows remarkable vitality and is nowadays one of the few with positive growth indicators into green economy. Within this sector is possible to provide a set of possible solutions able to generate new jobs, improve the socio-cultural context, and produce environmental benefits. In this scenario, integrated biorefineries represent a valuable development opportunity in Italy, especially for local communities through the efficient use of distributed renewable resources among countries. The Italian regional structures that operates in waste recycling generally separates raw biomass from fibers, animal feed, MSW and high-value organic compounds obtained from niche crops. The sugar components of biomass can then be separated and concentrated to give the central biorefinery, while the protein fraction can be usefully recovered and used as high quality livestock feed. Among key-actors of green economy basing on a biorefinery approach, three companies stand out in Italy: NOVAMONT, ENI VERSALIS and BIOCHEMTEX.

NOVAMONT innovation strategy is based on the third-generation biorefinery concept and on the approach of a strong multi-disciplinary collaboration with agricultural world, research community and local institutions. In particular, Novamont have partnered with ENEA for building two cluster projects on a green chemistry basis using cardoon crops as renewable source for producing biopolymers from oil seed that will be completed by 2018. The local peculiarities are commended by this way and will maximize the use of waste and residues as valuable inputs and secondary raw materials for biorefineries. Novamont produces and sells various types of biopolymers under the brand name Mater-Bi® or, more recently, the azelaic and pelargonic acids obtained from break-down of residual oleic acid in olive marc. ENI VERSALIS is a chemical company with sole shareholder that manages the production and marketing of petrochemical products (basic chemicals, styrene, bio-elastomers, polyethylene) relying on a range of proprietary technologies, advanced facilities, and a local and efficient distribution network. Versalis aims to be the first company to license the process and build commercial plants, thus providing over 20 million dollars in funding to Genomatica to support the end-to-end process. Just like the bio-succinic acid, the ultimate showdown here is who can produce the most economical bio-butadiene. Versalis have partnered with ENEA for building one cluster project focused on biological conversion of second-generation sugars from guayule bagasse, an alternative crop to gumtree, into bio-butadiene, that will be completed by 2018. BIOCHEMTEX, previously known as Chemtex Italia, is a global leader in the development and engineering of bio-chemical technologies and processes based exclusively on the use of non-food biomass, as an alternative to fossil resources. In partnership with 'Beta Renewables', Biochemtex has created technologies and plants for the production of bioethanol and other chemical products. Following an investment of 150 million euros and seven years of study, the company completed the design of Proesa®, an exclusive technological platform now marketed by Beta Renewables. Proesa® makes it possible to obtain biofuels and numerous chemical intermediates, and has been implemented on an industrial scale in the plant located at Crescentino (Vercelli, Turin), the world's first plant for the production of second-generation bioethanol. Biochemtex is also developing the new technology for the conservation of lignin in bio-naphtha and aromatic compounds (MOGHI) which are used in numerous industrial sectors. Biochemtex, part of the well known Mossi Ghisolfi Group, is placed in Tortona (Alessandria) and has two Research Centre located in Rivalta Scrivia (Alessandria) and Modugno (Bari) where the demonstration system for MOGHI technology will be completed by 2017.

7. Conclusions

Market implementation of integrated biorefinery requires reliable and advanced processing units combined with eco-friendly and economically profitable production chains. Future developments of the advanced biorefinery systems should include either crop cultivation with selected genotypes that maximize full chain performance either the use of agricultural residual biomass and waste. The biomass components are varied in nature (cellulose, glycerin, natural fillers and non-genetically modified starch obtained from various crops, etc.) that should be all given from organic residuals neither competing with food crops nor occupying deforested land or fertile arable land. As residual biomass availability is limited, it should be efficiently used for producing new marketable materials and recovering energy in multi-purpose biorefineries. This requires an optimal biomass conversion with the highest efficiency able to minimize requirements of feedstock from dedicated energy crops which compete with food crops for fertile land and irrigation water. Raw materials from agricultural residual biomasses and wastes can be usefully used as a profitable feedstock for the manufacture of chemical substances and products, as fatty acids from the oilseed crops, exhausted cooking oils and animal fats from food industry; starch from the cereals, potatoes and starchy residues; cellulose and lignin from the lignocellulose crops and/or residues. They have recently received a special attention from policy makers in some Member States as the EU because these residual materials can be converted into marketable chemical intermediates, polymers, lubricants, solvents, surfactants and especially green chemicals, such partially replacing fossil fuel sources. Integrated biorefineries can provide a significant contribution to sustainable development of biofuel market co-generating a broad range of high-value added co/by-products useful in some selected application sectors (e.g., renewable and sustainable farming systems, bioplastic industry and cell and tissue engineering in biomedical applications) starting from a broad range of various and heterogeneous residual biomasses and wastes of different origin and location that otherwise should be disposed or however managed.

At the same time, strengthening of economic viability in selected market sectors (e.g., agriculture, forestry, chemical and energy) are needed. One of the key-prerequisites of a successful biorefinery is to invite stakeholders and players to discuss backgrounds (agriculture/forestry, transportation fuels, chemicals, energy, etc.) common processing topics, necessary researches, develop new trajectories, and overall stimulate deployment of advanced technologies in multi-disciplinary partnerships. Optimal economic development and environmental performance can be only guaranteed linking the most promising high-value added materials and functionalized chemical platforms with the recovery of energy from the widest range of residual raw materials.

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