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**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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(Article begins on next page)

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

4  
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12  
13 A B S T R A C T

14  
15 Market implementation of integrated biorefinery requires reliable and advanced processing units combined with eco-  
16 friendly and economically profitable production chains. Future developments of the biorefinery systems should include  
17 either crop cultivation with selected genotypes that maximize full chain performance either the use of marketable  
18 agricultural residual biomass and agro-waste. The aim of the present work was to review the main biorefining  
19 opportunities of disposable agricultural residues, agricultural co/by-products and agro-wastes into a broad range of  
20 green chemicals and high-value added co/by-products valuable in some emerging technological sectors. The current  
21 status and future perspectives of conversion starting from agricultural residual biomasses and agro-wastes into high-  
22 value co/by-products, green chemicals and energy recovery by an approach of integrated biorefinery has been  
23 considered. After a recognition on nature, origin and European classification of the main categories of organic residuals  
24 from crops, forestry, agro-industrial food processing, aquaculture, fisheries and agro-wastes, this paper has focused its  
25 challenge on the main biofuel co/by-products associated to the thermochemical and biological conversion processes.  
26 The high-value added co/by-products from the biofuel chains related to some chemical basic-platforms (e.g., succinic  
27 acid, cellulose, lignin, glycerin, etc.) have been presented and discussed. Then, a special attention towards potential

28 applications of the high-value added co/by-products and green chemicals in three emerging fields (renewable and  
29 sustainable farming systems, bioplastic industry and cell and tissue engineering in biomedical applications) for actual  
30 and future players has been given and discuss. Finally, this paper has addressed own concern on the actual and potential  
31 biorefining opportunities in the EU and in Italy.

32

33 *Keywords:*

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

35

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## 69 1. Introduction

70

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

79 Plants and marine algae (microalga and macroalga or seaweeds) are considered as true  
80 'living biorefinery' (Clark, 2007) because they are the main renewable energy resources that  
81 provide liquid, gaseous and solid biofuels capable to convert carbon dioxide (CO<sub>2</sub>) and water into  
82 primary and secondary metabolites through a photosynthesis process. Primary metabolites are  
83 represented by carbohydrates (fermentable sugars, cellulose, hemicellulose, starch) and lignin, also  
84 called lignocellulosic matter or lignocellulose, presents in high amount in such biomass. Secondary  
85 metabolites are instead high-value added green chemicals (gums, resins, rubber, terpenes,  
86 terpenoids, flavonoids, phenolic substances, steroids, triglycerides, tannins, fatty acids, esters,  
87 alkaloids, furan molecules, glucosinolates, brassinosteroids) presents in lower amount in plants and  
88 algae. The secondary metabolites can be utilized for producing high-value added products and  
89 chemicals (food flavors, functional food, feedstuff, pharmaceuticals, cosmetics, nutraceutical,  
90 phytosanitary drugs, bioplastics, lubricants and other biomaterials) in integrated biorefineries.

91 The Directive 2009/28/EC on the promotion of the use of energy from renewable sources  
92 defines the term 'biomass' as "*The biodegradable fraction of products, waste and residues from*  
93 *biological origin from agriculture (including vegetal and animal substances), forestry and related*

94 *industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial*  
95 *and municipal waste*". This mean that biomass belongs to a wide range of organic feedstocks which  
96 can be used in the supply chain of biorefineries (Osamu and Carl, 1989). The total biomass  
97 production worldwide is approximately 100 billion tons organic dry matter per year from land  
98 sources and 50 billion tons per year from aquatic sources. The major part of it is used as food,  
99 feedstuff, energy and industrial raw material, where food use is only 1.25 % of total biomass. The  
100 remaining amount of biomass sources as wood, agro-waste, manure, household waste, wastewater  
101 sludge, industrial waste, etc. are underutilized or recycled into the earth ecosystem. The main  
102 challenge is to transform complex and heterogeneous residual materials into valuable industrial raw  
103 materials from residual biomass in place of fossil sources. Biomass contributes to supply energy  
104 approximately for 12 % of the global status on renewable energy, while its contribution ranges from  
105 40 % to 50 % in many developing countries (Garg and Datta 1998). The importance of plant  
106 biomass as a natural feedstock for the biofuel industrial chains can increase in the future and plant  
107 biomass can be a promising source of raw material suitable for biorefining into high-value added  
108 products, green chemicals and energy recovery. The feedstock that currently is considered in  
109 biorefinery consists of plant biomass either derived from dedicated energy crops either from  
110 agricultural organic residual resources defined as 'underutilized resource' (Fig. 1). These includes  
111 raw feedstocks that are finely converted into many biorefining outputs including energy recovery  
112 (power, electricity, heat), biofuels and overall a wide range of green chemicals and bio-based  
113 products (lubricants, adhesives, paints, detergents, pharmaceutical and healthcare products, cotton,  
114 and linen). Enhancement of biomass utilization requires effort to develop new technological  
115 systems in which conversion process, energy recovery and production of bio-based co-products are  
116 efficiently linked within an eco-friendly and efficient biorefining systems (Osamu and Carl, 1989).

117 Energy recovery and biofuel production are performed from two main sources, agricultural  
118 crops and agricultural residues. Energy production from agricultural crops can be divided into two

119 main groups: liquid and solid biofuels. Liquid biofuel (ethanol and biodiesel) covers energy sources  
120 burned in engines derived from annually harvested agricultural crops as sugarcane, sugar beet,  
121 sunflower, wheat, maize and rape. Solid biofuel (coal) covers energy sources for power generation  
122 through electricity and heat output from short rotation forestry or SRF (poplar and willow), residues  
123 from harvesting (straws, wood chips, wood shavings, aspen chips, olive brash residues, branches,  
124 foliage, roots, tubers) and grass production. Agricultural residues include corn stalks, rice husks,  
125 corn stover, wheat straw, cropping residues, unmarketable products, vegetable processing leftovers,  
126 spent coffee-ground, defatted olive marc, sugar beet bagasse, tomato-waste, cardoon-waste,  
127 vegetable-waste, which are converted to produce heat and electrical power. Also, gaseous biofuel,  
128 as methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) covers energy sources to produce power from dedicated  
129 energy crops (triticale, corn, sugar beet) associated with bio-wastes (manure, slurry, sludge,  
130 municipal solid waste or MSW) by anaerobic digestion and fermentation.

131 Green chemicals and bio-based outputs are also derived from agricultural crops and  
132 agricultural residues. Many review papers are available in literature for biofuel production from  
133 energy crops, or green chemicals from specific feedstock, or next-generation biofuels, or related  
134 chemicals from no-food crops. An exhaustive, excellent and comprehensive review on the  
135 production of first- and second-generation biofuels is given by [Naik et al. \(2010\)](#). Most of them  
136 have critically examined the current status and future technologies used to convert corn or  
137 lignocellulose into fuel ethanol; or integration of lignocellulose with forest biomass; or conversion  
138 of hemicellulose from corn germ, fiber, gluten from corn-ethanol plant into value added chemicals;  
139 or detoxification of hydrolysates from fermentation processes by bacteria; or ethanol product  
140 separation and dehydration. For example, [Clark et al. \(2006\)](#) reported the use of green chemical  
141 technologies to transform low value waste biomass into green chemicals like; [Chew and Bhatia](#)  
142 [\(2008\)](#) reported on the different types of catalysts and their role in the catalytic processes for  
143 production of biofuels in a typical palm oil and oil palm based refinery in Malaysia; [Rowlands et al.](#)

144 (2008) reported the challenges, opportunities in the context of Australian perspective; Mabee et al.  
145 (2005) assessed the emerging transformation sector in Canada; and Gomez et al. (2008) reported on  
146 the under pinning research necessary to enable the cost effective production of sustainable liquid  
147 biofuels from biomass with a particular focus on the aspect related to plant cell walls and their  
148 bioconversion. On the other hand, fewer referred papers on the biorefining opportunities of  
149 agricultural residues, agricultural co/by-products and agro-wastes into high-value added co/by-  
150 products and fine green chemicals through an approach of integrated biorefinery have been found in  
151 literature especially in relation to some selected application sectors.

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

155

156

## 157 **2. Categories of agricultural residual biomasses and wastes: definitions and European** 158 **classification**

159

160 The sustainable use of residual biomasses and wastes is expected to play a substantial role in  
161 the future energy systems because the potential bioenergy provided by dedicated energy crops is yet  
162 limited worldwide; all the lands are multi-functional; lands are also needed for food, feed, timber,  
163 fiber production; nature conservation and climate protection according to 'greening policies' in the  
164 European Union (EU) are needed. Large-scale cultivation of dedicated biomass affect bioenergy  
165 potential, global food prices and water availability. Furthermore, bioenergy potential for climate  
166 change mitigation remains unclear due to large uncertainties about future agricultural yield  
167 improvements and land availability for energy crop plantations. Therefore an integrated policy for  
168 energy use, land use, sustainable food systems development, greenhouse gas (GHG)-emissions

169 reduction, soil preservation and water management must be encouraged and managed (Popp et al.,  
170 2014).

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

186 The use of residual biomass and waste suitable for producing either second-generation  
187 biofuels either high-added value co-products from biorefineries which do not require any new  
188 agricultural land and present limited or zero environmental risks, needs to be globally encouraged  
189 (Ullah et al. 2015). At the same time, crop residues, especially straws, have alternative uses in  
190 animal feeding and bedding and when returned to the soil meet important ecosystem services  
191 essential to maintenance and restoration of fertility and erosion protection. Nevertheless, such  
192 biomass might contribute modestly to replace uses of fossil fuels in the longer time. The use of  
193 agro-waste, bio-waste, MSW, and surplus forest growth, establishing energy crop plantations on

194 currently unused land, may be more expensive than creating large-scale energy plantations on  
195 arable land. Moreover, the processing of residual biomass feedstocks into second-generation  
196 biofuels have either more energy requirement because it can need high energy inputs for pre-  
197 treatment of lignocellulosic matter as a steam explosion, either more environmental impacts  
198 resulting from the processing of biomass through technologies that can require higher water  
199 consumption in lignocellulose processing.

200

### 201 *2.1. Organic residuals from agricultural activities*

202

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

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

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

241 RED-FQD provides differential treatment to sub-categories of residues. Residues are  
242 divided into four main sub-categories from crop, forestry, aquaculture-fisheries and agro-industrial

243 processing. Each sub-category falls in determining the sustainability criteria that it must meet and  
244 how the GHG savings criterion is calculated, which is further impacted by whether the residue is  
245 considered a co-product. For these reasons, determining the sub-category of a residue and whether it  
246 is a co-product, that has significant implications. RED-FQD provides a little guideline on how to  
247 categorize residues or how to determine their status as a co-product, creating always uncertainty.  
248 Drawing from the European proposal, an indicative short list of raw materials and residues includes:  
249 crop residues (primary and secondary), forestry residues (primary and secondary), animal fats and  
250 animal manure.

251

### 252 *2.1.1. Crop residues*

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

267 agricultural straw residues per square kilometer potentially available for recovery of energy and/or  
268 biorefinery uses in the EU (Monforti et al., 2013).

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

284

### 285 2.1.2. *Forestry residues*

286 RED-FQD accords to term 'forestry residues' the following treatment (IEA, 2010): 1)  
287 forestry residues must meet all the sustainability criteria; 2) for purposes of the GHG savings  
288 criterion, there is no unique treatment. It is not always clear what constitutes a forestry residue.  
289 Residues from forestry may sometimes be considered as forestry residues, sometimes as processing  
290 residues, sometimes as co-products. In general, there are two types of forestry residues, the primary  
291 forestry residues produced when harvesting timber, such as treetops, branches and stumps (IEA,

292 [2010](#)); and the secondary forestry residues produced during processing of biomass-based materials  
293 or products, such as sawdust, bark and scrap-wood ([IEA, 2010](#)). Encouraging use of unused primary  
294 forestry residues as an alternative to biofuel production otherwise left on the land causes loss of soil  
295 organic matter, soil carbon and habitat for biodiversity.

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

317 residues includes: treetops, branches, stumps, leaves, sawdust, cutter shavings, scrap wood, wood  
318 pulp and wood chip.

319

### 320 2.1.3. *Aquaculture and fisheries residues*

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

330

### 331 2.1.4. *Agro-industrial processing residues*

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

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

349

## 350 2.2. Wastes

351

352 RED-FQD accords to term ‘waste’ the following treatment: 1) wastes need only meet the  
353 GHG savings criterion; 2) wastes are considered to have zero life-cycle GHG-emissions up to the  
354 process of collection of those materials, meaning no land-use emissions including soil carbon.  
355 Demonstrating compliance with the 10 % target, *“the contribution made by biofuels produced from  
356 wastes... shall be considered to be twice that made by other biofuels”*. RED-FQD does not define  
357 wastes but the EC states that the concept of waste is in line with the objectives of RED-FQD. As an  
358 amendment to RED only, it references the definition in the ‘Waste Framework Directive’ (WFD)  
359 which defines waste as *“any substance or object which the holder discards or intends or is required  
360 to discard”* stating in pertinent part ‘waste’ shall be defined by the Directive 2008/98/EC on waste  
361 repealing previous directives. Substances that have been intentionally modified or contaminated to  
362 meet this definition are not included in this category. This definition is supplemented by the  
363 requirement that substances cannot be *“intentionally modified or contaminated”* to meet the  
364 definition, which is intended to prevent the practice of *“adding waste material to a material that  
365 was not waste”* in order to make it waste. The definition of waste requires nevertheless further

366 specifications. While the definition is a welcome contribution, it does not prevent the use of  
367 substances before the end of their useful lifetime. For example, used cooking oils require no  
368 technological developments for exploitation and is subject to ever-increasing imports from abroad.  
369 Markets have increased the used cooking oils being diverted toward second-generation biofuel  
370 production before it reaches the end of its lifetime especially since their consumption has  
371 implemented double-counting for these biofuels. In the UK, for example, used cooking oils  
372 represent 50 % of biodiesel consumption (<https://www.gov.uk/government>). Any increase in  
373 demand for cooking oils increase demand for oleaginous crops to produce more cooking oils with  
374 associated land-use implications. The solution to the unused-cooking-oil problem can be addressed.  
375 For example, ensuring wastes conform to the waste hierarchy would require prevention, preparation  
376 for reuse and recycling of it before energy recovery. Wastes are already subject to extensive  
377 treatment and in national waste management plans in the EU.

378 ‘Recovery’ term refers to operations where the wastes replaces materials that would  
379 otherwise have been used to fulfill a particular function in the plant or in the wider economy, such  
380 as fuel oil in transportation. Annex II of WFD sets out a non-exhaustive list of recovery operations  
381 from waste and specifically includes “*use principally as a fuel or other means to generate energy*”.  
382 The EU may only depart from the waste hierarchy for specific waste streams whenever justified by  
383 lifecycle thinking on impacts of the generation and management of such waste. Waste recycling  
384 corresponds with the objectives and complements existing in the EU policies on waste prevention  
385 and management. The definition of waste should be modified applying this requirement for wastes  
386 originating abroad or otherwise include language in the definition that achieves the same result  
387 since the waste hierarchy is only applicable in the EU. In both instances, whether the wastes  
388 originate abroad or within the EU, adequate assurances should be required to prevent  
389 circumvention. Drawing from the European proposal, an indicative short list of wastes for use as

390 raw materials in biorefinery includes: cooking oils, biomass fraction of mixed MSW, biomass  
391 fraction of industrial waste and sewage sludge.

392

393

### 394 **3. The biorefinery**

395

#### 396 *3.1. Concept and definitions*

397

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

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

416

### 417 3.2. *Biorefining systems*

418

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

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

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

454

### 455 3.3. *Biorefining drivers*

456

457 The development of biorefineries is necessary to produce a broad variety of bio-based  
458 products into an efficient construction set system (Kamm and Kamm, 2004). Each biorefinery  
459 refines and converts its corresponding raw material into a multitude of valuable bio-products. The  
460 products from biorefinery also includes specific products that usually are not produced in petroleum  
461 refineries (Kamm et al., 2006). Therefore it is necessary to develop new technologies as: 1)  
462 biorefinery lignocellulosic-based including effective pretreatment and separation in lignin, cellulose

463 and hemicellulose; 2) further development of thermal, chemical and mechanical processes; 3)  
464 development of biological processes; 4) combination of biotechnological and chemical processes.

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

483 The use of chemicals from renewable sources shows GHG-saving throughout their life cycle  
484 when compared to the equivalent conventional petrochemical sources. Emissions of CO<sub>2</sub> during the  
485 production and consumption of bio-based products are offset by the CO<sub>2</sub> captured during the growth  
486 of biomass used to produce them. The potential in reducing GHG emissions from the set-up of  
487 second-generation biorefineries varies between 30 % and 85 % if compared to petrochemical

488 sources. In the EU, for example, the adoption of biorefinery system is seen as a key-technology able  
489 to put into effect the effort to mitigate climate change and such ensure security of supply against  
490 fluctuations in crude oil prices. Biorefining gives support for agricultural development providing  
491 additional market opportunities for farmers and growers, moreover, the decentralized production  
492 systems can provide new sources of income and employment opportunities in rural areas. Much of  
493 the agro-industrial waste is still a relevant cost to the industry, due to the higher cost of disposal. In  
494 parallel to this situation that we can consider inefficient, the market for bioplastics and tools in  
495 renewable and sustainable farming systems is experienced by exceptional population growth in  
496 Europe. These high value-added materials have considerable importance from the industrial and  
497 economic point of view and their exploitation is a key-step in the development of a new economy  
498 based on recycling of renewable resources, named as 'bio-based economy', or 'circular economy',  
499 or more briefly 'bio-economy'. For example, business opportunities for a circular economy based  
500 on biofuel co-products is shown in [Figure 4](#).

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

508         Another main driver for the development and implementation of biorefinery processes is the  
509 transportation sector ([Elvers, 2006](#)). Significant amounts of renewable fuels are necessary in the  
510 short and middle term to meet policy regulations both inside and outside in the EU. Biofuels have to  
511 fill in a large fraction of this demand, specifically for heavy duty road transport and in the aviation  
512 sector ([Huber et al., 2006](#)). Both conventional biofuels (ethanol, biodiesel) and advanced biofuels

513 (lignocellulosic methanol, butanol, Fischer-Tropsch-diesel/kerosene) generally cannot be produced  
514 in a profitable way at current crude oil prices (Ocic, 2005). This implicates that they can enter into  
515 market only if they are forced by proper governmental regulation, or if significant financial support  
516 are provided. This artificial market will not be lasting because a significant reduction in biofuel  
517 production costs is required to create a sustainable market. A very promising approach to reduce  
518 biofuel production costs is to use biofuel-driven biorefineries for the co-production of value-added  
519 products with biofuels from biomass resources by a very efficient integrated approach. To be a  
520 viable option, the production of bio-based energy, materials, chemicals and biofuels, should be able  
521 to improve the global economy and it also could be an additional source of income. In this  
522 perspective, the main driver for the creation of biorefineries is the answer to sustainability demand.  
523 The development of biorefineries must be designed in an adequate way that is sustainable from the  
524 environmental, social and economic point of view. This new industrial development, if properly  
525 applied, will encourage direct and indirect employment, creation of new professional figures and a  
526 better quality of life. Biorefineries will still have to be combined with existing infrastructures, and  
527 many considerations must be made as regards to the source of biomass in terms of competition for  
528 food, impact on consumption and quality of water, LUC, carbon stocks in the long term, net balance  
529 of GHG-emissions and impact on the biodiversity. Furthermore, the amount and type of energy  
530 used to operate inputs-outputs into biorefinery chains and related transportation costs should be  
531 carefully considered in the near future. Biorefining requires further innovation offering  
532 opportunities to all economic sectors. Building a bio-based economy can help to overcome  
533 difficulties laying the foundation of an eco-friendly industry.

534         The recent adoption of the biorefinery complexity index (BCI) in biorefinery models might  
535 add relevant information on the assessment and comparison of different biorefinery systems. The  
536 BCI is a relevant indicator for industry, decision makers as well as investors. These additional  
537 information are generated to assist the biorefinery players in their strategies to implement the most

538 promising systems such minimizing technical and economic risks. The conflicts between energy  
539 and food production can be avoided or reduced developing technologies based on agricultural  
540 residual biomass and waste.

541

#### 542 3.4. *The economic concept of value-added product*

543

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

553 When co-products are used by industries, ‘green credits’ can be attributed to the biofuel  
554 production chains. Green credits include GHG savings associated to avoiding land use, or energy,  
555 or irrigation water, or both. The challenge is to decide how to distribute quantities of potential  
556 credits between the fuel and the by-products. For the evaluation of GHG-emission savings, the  
557 following two methods have been developed. Firstly, in the ‘substitution approach’, it is determined  
558 by what by-products are used and what by-products would otherwise have been used to perform the  
559 function. Secondly, in the ‘allocation approach’, total emissions are divided between the fuel of  
560 interest and the related by-products in proportion to some attribute that they share. Common  
561 methods can include three allocation types: 1) allocation by mass, 2) allocation by value market, 3)  
562 allocation by energy content. It is not possible to know for certain what is really the substituted

563 product for a fuel supplier, and thus GHG emissions of these substituted products are always  
564 uncertain. For example, by-products used as animal feed can replace many different animal feed  
565 products which have different GHG-emission performances. For reasons of feasibility, the Directive  
566 2009/28/EC recommends to apply the allocation method by energy content for to determine GHG  
567 savings if compared to fossil fuels: *“Co-products from the production and use of fuels should be  
568 taken into account in the calculation of greenhouse gas emissions. The substitution method is  
569 appropriate for the purposes of policy analysis, but not for the regulation of individual economic  
570 operators and individual consignments of transport fuels. In those cases the energy allocation  
571 method is the most appropriate method, as it is easy to apply, is predictable over time, minimizes  
572 counter-productive incentives and produces results that are generally comparable with those  
573 produced by the substitution method. For the purposes of policy analysis the Commission should  
574 also, in its reporting, present results using the substitution method.”*.

575

576

#### 577 **4. High-value added co/by-products from the biofuel chains associated to chemical basic-** 578 **platforms**

579

580 Biofuel industry has evolved rapidly over the last three decades with developments in  
581 processing techniques and expansion of biofuel crops and other agricultural commodities being  
582 considered as a strategic feedstock (Table 1). The installed power values show that the global  
583 biofuel production capacity is increased from 1.58 billion liters in 2010 to 4.21 billion liters in 2013  
584 (WBA, 2014). Global expansion of biofuel production is projected to continue during the next  
585 decade although at a slower pace than over the last half decade. Currently, around 74 % of the  
586 global production of liquid biofuels is in the form of ethanol and the remaining part in the form of  
587 biodiesel and bio-oil. In 2012–2014 global fuel ethanol production reached 108 billion liters and

588 those of biodiesel amounted to 28 billion liters. The two world's top fuel ethanol producers, the  
589 USA and Brazil, accounted for around 75 % of total production, but biodiesel output is less  
590 concentrated than ethanol. The EU remains the core business of global biodiesel production with 12  
591 billion liters representing about 77,6 % of total share ([Biofuels Barometer, 2012](#)). Indonesia will  
592 surpass the USA and Brazil in the latter years of the outlook period to become the second largest  
593 biodiesel producer behind the EU. Fuel ethanol production in the USA is projected to be relatively  
594 flat over the next decade due to the ethanol blend wall and a general declining gasoline use ([USDA,](#)  
595 [2015](#)). Global fuel ethanol and biodiesel production are both expected to expand reaching almost  
596 135 and 39 billion liters by 2024 respectively ([FAO, 2015](#)). In 2040 the share of biofuels in road  
597 transport fuels would range from 5 % to 18 % globally, from 11 % to 31 % in the EU, and from 11  
598 % to 29 % in the USA ([IEA, 2015](#)). Further expansion of biofuel production is expected in the  
599 Brazil and Argentina. A strong expansion in biofuel production was observed in the USA, EU and  
600 China changing biofuel policies. These increasing were not sufficient to fully satisfy biofuel policy  
601 objectives in the USA and EU.

602         The increased biofuel production has led to criticism and concerns about food availability  
603 while it is feared that rising demand for agricultural land-use change will lead to deforestation,  
604 grassland conversion and increasing of GHG-emissions ([Elobeid et al., 2012](#); [Khanna and](#)  
605 [Zilberman, 2012](#)). Central to the debate is how the increased biomass requirements for sustainable  
606 biofuel production could fit with area expansion, or yield improvement, or increased cropping  
607 intensity. Increasing of demographic growth, rising economic aspirations of developing countries,  
608 requirements for geopolitical energy security, deteriorated economics of fossil-based products and  
609 increasing of public pressure for environmental sustainability, have all put the biorefineries concept  
610 on the top of strategic agenda of the biorefining players. At the same time, production of biofuels  
611 from alternative biomass sources and especially valorization of agro-waste and other organic  
612 residuals which do not compete with food, land and water, is believed to be the main challenge for

613 building a sustainable biofuel industry. Moreover, there are many opportunities and demand  
614 growing for the conversion of residual biomass and waste into energy (biofuels, heat, electricity,  
615 power) and bio-based green products considering population growth, changing consumption  
616 patterns, dietary preferences and fruit/vegetable postharvest losses. In addition to that, the  
617 innovation potential of bio-based technologies will allow the production of new molecules for fuel,  
618 chemical and material applications which are not usually available from the fossil resources.

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

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

635

636

637

#### 638 4.1. *Fuel ethanol chain*

639

640 First-generation fuel ethanol is mostly done from maize (or corn) and wheat in the USA.  
641 Sugarcane is the predominant feedstock for ethanol production in Brazil and South Africa. Sweet  
642 sorghum, cassava and other non-grain crops are the main feedstock for China. However, an increase  
643 in the off-take of wheat can also be observed in China, Canada and the EU. The USA is the global  
644 leader in grain ethanol production accounting for roughly 90 % of total grain use followed by the  
645 EU, China and Canada. Maize accounted for the majority of grain use for ethanol in the USA and  
646 China. European and Canadian producers principally use wheat and maize for producing fuel  
647 ethanol. Feedstock for fuel ethanol chain vary significantly depending on the country and an  
648 estimated 143 million tons of grain is globally used. The fuel ethanol share demand of corn, wheat  
649 and other coarse grains is about 6 % of global total grains production. Fuel ethanol sector accounts  
650 for 13 % of global maize consumption and 20 % of global sugarcane production. In 2014, most fuel  
651 ethanol was produced from sugar crops (61 %) with the remainder from grains (39 %). The  
652 production of first-generation fuel ethanol from starchy crops is among the earliest processing of  
653 value-added products (Naik et al., 2010). Sugar can be obtained either directly from sugarcane,  
654 sugar beet, or sweet sorghum, or derived from the conversion of starch contained in cereal grains  
655 (e.g. wheat, maize and barley), millets, root crops and tuber crops (e.g. potato and cassava). While  
656 the basic processes for production of fuel ethanol from sugary and starchy crops are similar, there  
657 are clear advantages in producing ethanol directly from sugary crops rather than from starchy crops  
658 because additional processes require conversion of starch into sugar before fermentation. The  
659 conversion of complex polysaccharides in the biomass feedstock (starch) into simple sugars  
660 (glucose) is an high-temperature processing carried out with acids and enzymes as catalyst. Because  
661 of this additional step, energy requirements and GHG balances are more favourable for producing  
662 fuel ethanol directly from sugar crops when compared to starchy crops. For example, the energy

663 requirement for converting sugar into fuel ethanol directly from sugar cane or maize is about half of  
664 the energy input needed using starchy crops (Prieler and Fischer, 2009). Sugarcane and sugar beet  
665 bagasse are also two important sources of fuel ethanol and related co-products. Due to co-  
666 generation of heat and electricity, Brazilian sugarcane ethanol industry operates every day without  
667 significant fossil fuel inputs achieving a high overall GHG saving (80–90 %) in comparison to  
668 fossil fuel. Sugar beet bagasse is instead very expensive to transport because it must be processed  
669 quickly before the sucrose deterioration. Therefore all the sugar beet processing plants are located  
670 near the production areas. This limited storage time is a major drawback of sugar beet use for  
671 ethanol production. Despite the simple processing technique, the cost of ethanol production from  
672 sugar beet is approximately twice that those of sugarcane-based ethanol in Brazil, or maize-based  
673 ethanol in the USA (USDA, 2006) because this is primarily due to differences in feedstock costs.

674 Starchy-based fuel ethanol chain produces different co/by-products depending on the  
675 feedstock and production process. Sugar beet by-products from industry include either the beet-top  
676 which can be used as green fodder, either the beet-pulp and filter cake can be used as cattle feed.  
677 About one-third of the volume of grain processed for fuel ethanol is used to produce animal feed as  
678 co-products, thus the equivalent of two-thirds of the grain are used to produce only ethanol. Two  
679 processes are widely employed for ethanol production, the wet milling and dry milling. The main  
680 difference among them is the treatment type of the cereal grain before fermentation and differences  
681 among them in resulting by-products are evident. Wet-mill process generates as co-products  
682 vegetable oil, corn gluten meal (CGM) and fibre. Dry-mill process generates as co-products wet  
683 distillers grains with soluble (WDGS) that can be sold to nearby markets. The dried form, also  
684 named dried distillers grains with soluble (DDGS), can be transported over long distances and is  
685 available for domestic markets and for exports. DDGS is a high quality feedstuff ration for dairy  
686 cattle, beef cattle, swine, poultry and in aquaculture. The feed is partially replaced by corn, soybean  
687 meal and di-calcium phosphate in livestock and poultry feeds. However, nutrient composition and

688 quality of WDGS and DDGS can widely vary depending on the feedstock use, geographical  
689 location and time of harvesting of the ethanol crops. Very many papers are found in literature about  
690 WDGS, DDGS and CGM. Especially, the opportunities and challenges of biofuel co-products as  
691 livestock feed are reviewed by [FAO \(2012\)](#); the estimated displaced products and ratios of distillers  
692 co-products from corn ethanol plants and the implications of lifecycle analysis are critically studied  
693 by [Arora et al. \(2010\)](#); and the global economic and environmental implications of biofuel co-  
694 products employed as livestock feeds are analyzed by [Popp et al. \(2016\)](#).

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

703         The thermochemical processes use heat to convert lignocellulosic-based feedstock into  
704 biofuels, and are used to break-down biomass chemical bonds ([Naik et al., 2010](#)). The products of  
705 thermochemical conversion differs among them depending on the type of process implemented  
706 (gasification or pyrolysis). Gasification uses partial oxidation of biomass at higher temperatures to  
707 create synthesis gas, primarily carbon monoxide (CO) and H<sub>2</sub>, which is then converted into fuel  
708 ethanol and other alcohols by fermentation or in a catalytic reactor. Gasification, which operates at  
709 temperatures between 700 °C and 1,000 °C in shortage of oxygen, converts biomass into a gaseous  
710 mixture, known as ‘syngas’, containing H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and synthetic fuels. The syngas can be  
711 burned directly in engines, or used to produce methanol and hydrogen, or converted by the Fischer-  
712 Tropsch process into synthetic fuel (gasoline diesel, kerosene, butanol and dimethyl ether) used as

713 propellant in diesel engines. Pyrolysis (or ‘thermal cracking’), unlike gasification, operates at lower  
714 temperatures (300-700 °C) in total absence of oxygen and it is particularly suitable for raw  
715 feedstock with higher content in lignin, such as wood-based sources (forestry residues and SRF).  
716 Such conditions of temperature and strong anaerobiosis cause the break-down of chemical bonds  
717 giving rise to gaseous products (syngas), liquid (bio-oil) and solid (biochar) in various proportions  
718 that depend on the applied method of pyrolysis (fast, slow or conventional) and processing  
719 parameters (temperature, pressure and residence time). The main high-value compounds are  
720 phenols, organic acids, furfural and levoglucosans. Partial combustion at low temperatures in  
721 absence of oxygen produces pyrolysis oil that is then refined to liquid biofuels (USDE, 2008).  
722 Biochar is the solid residue from the process of pyrolysis carried out at low temperature, low  
723 heating rates and with very short residence time. Other co-products of pyrolysis or gasification  
724 include olefins (alkenes being used in the production of polyethylene and other materials) and  
725 various higher alcohols. Hydrogen resulting from the gasification of biomass or lignin may be an  
726 important fuel source used in fuel cells. The major advantage of a pyrolysis biorefinery is the  
727 possibility of decentralized production of bio-oil in regions where abundant residual biomass is  
728 readily available, making it possible to keep the minerals within the country of origin and creating  
729 the premise of cost-effective transport of resulting liquids. The basis for creating high-value  
730 compounds is the cost-effective fractionation of the pyrolysis oil. Fractionation will result in various  
731 qualities of oil which can be transformed through further upgrading into fine chemicals,  
732 petrochemicals, automotive fuels and energy.

733 The lignocellulosic-based feedstock is treated to separate the hemicelluloses from the  
734 cellulose and lignin using biochemical processes (Naik et al., 2010). The cellulose is treated by  
735 enzymatic or acid hydrolysis to break-down the long-chain glucose units before ethanol production.  
736 Ethanol is then produced by the fermentation of these simple sugars with specific microbes  
737 (generally yeasts) into specific feedstock (Greer, 2005; NREL, 2007). Many co-products released

738 during the production of ethanol such as cellulose, hemicellulose, lignin, furfural, amino-acid,  
739 peptide and protein, as well as gases released during fermentation, can be used to make a variety of  
740 marketable co/by-products. In fact, fermentation process of pre-treated feedstocks have the potential  
741 to produce a wide range of different green chemicals together to ethanol (xylose, succinic acid,  
742 lactic acid, citric acid, 1,3-propanediol, lysine and glutamic acid) that are already being produced  
743 through fermentation processes on a commercial scale within established markets (nutraceuticals,  
744 personal care cosmetic ingredients, elastomers, polymers, adhesives and surfactants). The  
745 production of cellulose nanofibers in conjunction with ethanol may also be a profitable way using  
746 wheat straw feedstock as reported by [Leistriz et al. \(2006a\)](#). Wheat straw appears to be the most  
747 promising feedstock for this material due to its high cellulose content when compared to other  
748 grasses ([Leistriz et al., 2006b](#)). Nanofibers are made from non-hydrolyzed cellulose and are  
749 combined with resins to produce moldable and reinforced composites for the automotive, aerospace  
750 and other industries. The production of xylose from giant reed ([Shatalov and Pereira, 2012](#)), a major  
751 component of hemicellulose, can be fermented by specific microbes (especially bacteria) for  
752 producing ethanol, but also may be processed to produce furfural, a chemical used as feedstock for  
753 producing resins or xylitol used as a sweetener ([Ebert, 2008](#)). Moreover, pentose sugars from  
754 hemicellulose down-stream can be also valuable as feedstuff in animal feed. The production of  
755 furan molecules (2-furaldehyde or furfural, 5-hydroxymethylfurfural or 5-HMF, and 5-  
756 hydroxymethyl-2-furancarboxaldehyde) derived from dehydration of xylose and arabinose can be  
757 used as flavourings in foods, as well as in pharmaceutical products, cosmetics and fragrances  
758 without toxic effects on human health and food safety ([Rigal and Gaset 1983](#); [Morales 2008](#)). The  
759 short-chain glucose not used to make ethanol may be instead used to produce a range of organic  
760 acids, superior alcohols and polymers. Some of these compounds are food additives and others can  
761 be used in industry to produce a wide variety of products including solvents, detergents, textiles and  
762 plastics, including biodegradable plastics ([Snell et al., 2009](#)). As case-study particularly interesting

763 is those of succinic acid, one co-product derived from sugar-based feedstock (mainly hydrolysates  
764 of potato pulp and sweet corn or pressed banana pulp juice) by fermentation with selected bacteria  
765 strains (e.g. *Escherichia coli*) and/or yeast strains (e.g. *Saccharomyces cerevisiae*). Succinic acid  
766 appears to be very promising serving as the main replacement for petroleum-derived maleic  
767 anhydride. Succinic acid is a molecule-key in multiple practical applications (Fig. 6) for producing  
768 pyrrolidones, polyurethanes, polybutylene succinate, food, surfactants, solvents, detergents,  
769 plasticizers in engineered plastics, fibers, coatings, pigments, freezing point depression agents and  
770 pharmaceuticals (Ebert, 2007). It is predicted that the market for succinic acid would grow  
771 substantially if the current high price to decrease (Wyman, 2003). The production of high-value  
772 added proteins in livestock feed may be carried out before biomass pre-treatment as proposed by  
773 ‘Abengoa Bioenergy’ commercial site located at Hugoton, Kansas (USA) (Feinman, 2007).  
774 ‘Michigan State University’ has developed a method using an alkaline treatment followed by  
775 membrane filtration for to remove from 60 % to 80 % of proteins from leaves of late-season  
776 switchgrass and agricultural residues containing about 3–6 % protein (Robinson, 2008). The  
777 conversion lands from soybean and corn to switchgrass may be more acceptable if animal protein  
778 for livestock is also produced (Greene, 2004).

779

#### 780 4.2. Biodiesel chain

781

782 First- and second-generation biodiesel is currently manufactured from vegetable oils  
783 extracted by organic solvents from edible-seeds of dedicated oleaginous crops (e.g., rape,  
784 sunflower, soybean and palm oil), no-edible oilseeds of energy crops (jatropha, mustard, carinata  
785 and canola), as well as from food waste (cooking oils and fats). Biodiesel is produced by trans-  
786 esterification process of lipids catalyzed with alkali, acid or enzyme (Naik et al., 2010). Oilseeds  
787 represent the most source of oil for biodiesel output. Global biodiesel production is based largely on

788 vegetable oil, mostly from rape seed in the EU and soybean seed in the USA, Brazil and Argentina.  
789 Soybean and rape oilseed has a 70 % share of the total feedstock used in biodiesel production  
790 worldwide. An estimated 6 million tons of rapeseed oil and 7 million tons of soybean oil are used  
791 globally in the production of biodiesel representing about 70 % of the total feedstock used in global  
792 production (Licht 2013). The biodiesel share demand of rape, soybean and oil palm seeds is around  
793 11 % of global vegetable oil production. The highest biodiesel yields were observed for oil palm  
794 (Indonesia and Malaysia). There are other feedstock of minor importance for producing biodiesel,  
795 such as castor bean in Brazil, sunflower in the EU, jatropha and coconut in Mozambique. Biodiesel  
796 production also includes waste feedstock as exhausted cooking oils (the main feedstock in China)  
797 and animal fats. The share of animal fats and exhausted cooking oils increased to 15 % in total  
798 biodiesel output. In Europe, the relative share of cooking oils and fats (mainly tallow) in biodiesel  
799 production is increased as the EU policy have allowed to these wastes to be double-counted in  
800 transportation targets. The continuously growth demand for protein meal has been the main driver  
801 in the recent years, behind the expansion of oilseed production. This has increased the share of  
802 protein meal in the value-added of oilseeds favoring soybean over other oilseed crops. Compared  
803 with coarse grains and other feed ingredients, protein meal prices have stayed for long time. In the  
804 2014-2015, global oilseeds production reached 530 million tons (soybean 320 million tons and rape  
805 70 million tons). At the same time, soybean production increased faster than production of rape and  
806 sunflower in the same years. Vegetable oil production increased to 180 million tons (out of this 60  
807 million tons palm oil) in the same period. Vegetable oil in biofuel production account for about 20  
808 million tons per year. Demand growth has slowed in recent times due to stagnating biodiesel  
809 production from vegetable oils in more developed countries. Production of rapeseed in Canada and  
810 in the EU is expected to grow much slower than in the previous decade as high oil-containing  
811 oilseeds, like rapeseed are more affected by the slower growth in vegetable oil prices.

812           The processing of vegetable oils provide either oil-less seed cakes or meals as main co-  
813 products of extraction, either glycerin (or glycerol) as principal by-product of trans-esterification.  
814 [Table 3](#) summarizes the main high-value added co/by-products from the biodiesel production chain.  
815 The main co/by-products that are released by extracting oil from oleaginous energy crop seeds and  
816 then refining it for to remove free fatty acids and other impurities are known as oil-seed cakes or  
817 meals, an important protein source which has an high-value added in livestock feed. In the case of  
818 soybean, the feed demand for soymeal has driven and drives soybean production growth. Growth of  
819 soymeal feed production is accelerated in the early 1990s, rapidly propelled growing demand for  
820 animal feed in developing countries ([FAO, 2006](#)). In oil extraction, soybean yield range from 18 %  
821 to 19 % oil and from 73 % to 74 % meal ([Schnittker, 1997](#)) while a remaining biomass is  
822 considered as a waste. Soymeal is used primarily in the diet of monogastric species, particularly  
823 chickens and to a lesser extent pigs. About 0.4 tons of vegetable oil and 0.6 tons of rapeseed cake  
824 are produced per ton of rapeseed which is excellent for livestock feed. The feed demand for  
825 soymeal has skyrocketed over the past four decades reaching 130 million tons in 2002 worldwide.  
826 This far outstrips the second largest oilcake made of rape and mustard seed with 20.4 million tons  
827 of production in 2002. Different sources of protein for animal feed differ among them in protein  
828 content. The highest protein content occurs in fish meal (60 %), meat and bone meal (55 %) and soy  
829 meal (48–50 %). The medium protein content animal feed includes skim milk powder (35 %),  
830 rapeseed meal (32 %), sunflower seed meal (28 %), peas and beans (23 %) and corn gluten feed (22  
831 %). In the EU, the use of meat and bone meals in livestock feed was prohibited in 2000 in a fight  
832 against mad cow disease (or BSE). As a result, more than 400,000 tons of high-quality protein  
833 feedstuff from animal sources had to be replaced by protein from vegetable sources with subsequent  
834 rising imports of soy cake. Oil production from oil palm can provide several animal feed. By  
835 chopping, drying, cubing and pelletizing, oil palm fronds can be transformed into an attractive  
836 source for ruminant feed, while oil palm trunks are a readily available source of fiber in animal

837 feeding. Oil palm fronds, used either alone either combined with other ingredients as palm kernel  
838 cake and palm oil mill effluent, have been successfully transformed into feed in pellet or cube form  
839 for ruminant species. Palm oil by-products include palm soap stock, palm acid oil and palm fatty  
840 acid distillates. They have a wide range of quality and composition and also consist of many  
841 impurities and minor components. Oleo-chemical biorefineries based on the fatty acids platform  
842 derived from palm oil have found applications in food, paper, plastics, rubber, lubricants, soap,  
843 cosmetics, toiletries, surfactants, pharmaceuticals, fertilizers and textiles.

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

861

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

863

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

872

### 873 *5.1. End-use of organic residuals: from waste to sustainable tools in renewable farming systems*

874

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

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

899

#### 900 *5.1.1. Soil amendments and soil fertilizers*

901           Although large amounts of residual biomasses easily on-farm available to farmers and  
902 growers can find new applications in advanced cropping systems by conversion into compost,  
903 biochar and exhausted seed pellets/meals, very little amount of them are nevertheless really used in  
904 agriculture because the mechanisms by which they improves soil fertility and increases plant yield  
905 are yet poorly known in terms of agronomic value, crop response and soil health benefits. A  
906 potential emerging market for biofuel co/by-products that producers may consider marketable  
907 beyond the soil organic amendments is represented by those of soil biofertilizers for plant growth in  
908 the cropping systems under greenhouse condition. [De Corato et al. \(2015\)](#) have given a review on  
909 the phytosanitary application flows of co/by-products originated from the biofuel production chains  
910 focusing their challenge on the ecological and physiological effects of them with: 1) the beneficial  
911 soil microbiota, 2) the direct interaction between glucosinolates and furfural bioactivity with soil-

912 borne plant pathogens and 3) the indirect interaction among plant pathogens and biochar. In this  
913 paper biofuel co/by-products were classified on a basis of their target (soil or plant) or their action  
914 modality on the soil, crop or microbiota as follows: 1) soil amendments (compost, biochar and oil-  
915 less seed cakes); 2) soil fertilizers (digestate, DDGS and oil-less seed cakes); 3) phytosanitary drugs  
916 (biofumigants, fungicides and herbicides); 4) plant biostimulants (compost teas, seaweed extracts  
917 and brassino-steroids).

918 Compost is a stabilized organic matter deriving from the bio-oxidation process of un-  
919 decomposed feedstock based on the MSW, crop biomass residues and plant-waste (Fig. 7).  
920 Composting is an efficient, cost-effective and environmentally safe oxidative biological process for  
921 recycling many residual agricultural biomass types into new cropping production cycles  
922 (Maniadakis et al. 2004). It is a very simple technology consisting of user-friendly small  
923 composting plants equipped with tools already available on a farm where un-degraded organic  
924 biomasses are transformed and stabilized into mature composts through an aerobic bio-oxidation  
925 process (Christian et al. 2009). Composting contributes to solve the problem of disposing  
926 agricultural biomasses and vegetable feedstock providing to farmers a self-supply of quality  
927 compost for the improvement of agricultural productivity (Scotti et al. 2016). In some developed  
928 horticultural areas of Italy, significant amounts of MSW, agricultural wastes and residues, such as  
929 vegetable and fruit by-products, cropping residues, garden wastes, unmarketable products,  
930 vegetable processing leftovers, food waste, etc. are daily produced. They represent an important  
931 source of organic matter suitable to be composted and returned to soil for to improve fertility (Pane  
932 et al. 2015). Composting is a sustainable oxidative biological conversion in which biodegradable  
933 organic compounds are transformed into stable humified organic matter under controlled and  
934 accelerated conditions (at least three months) without recovery of energy giving only stabilization  
935 of organic waste and nutrients re-cycling. It is generally performed through a process diagram  
936 consisting of four mains steps (Fig. 8): 1) mixing of raw materials containing un-stabilized organic

937 compounds (sugars, lipids and proteins), mineral nutrients, water and microbiota; 2) building of  
938 compost piles less than 5 m<sup>3</sup> in volume for achieve an adequate aeration of them; 3) bio-oxidation  
939 of the un-stabilized organic compounds for producing water, CO<sub>2</sub> and heat (more than 65 °C) to  
940 achieve sanitization against harmful and pathogen microbiota without energy recovery; and 4) final  
941 curing where finished (or cured) compost contains stabilized organic matter (mainly humic  
942 substances), carbon, nitrogen, phosphorus, micronutrient, heavy metals, water and a broad range of  
943 a beneficial microbiota. Compost utilization, in combination with soil substrates as peat, perlite and  
944 vermiculite, may give several benefits for plant growing as fertilizer, stimulant, improver of soil  
945 structure and fertility, including suppression of soil-borne plant diseases in horticultural soil-less  
946 systems if used a the proper rates (between 10 % and 30 % by volume). However, not all the  
947 composts are suppressive and its level vary, as well as the range of the suppressed target-pathogens.  
948 A recent study given by [De Corato et al. \(2016\)](#) has tested three next-generation suppressive green  
949 composts provided from a varied feedstock of agro-energy co-products and agricultural wastes such  
950 as processing residues (spent coffee-ground, defatted olive marc and wood chip), plant-wastes  
951 (artichoke, fennel and tomato) and steam explosion liquid-wastes derived from the steam explosion  
952 (SE) pre-treatment of wheat straw, miscanthus and giant reed in suppressing soil-borne plant  
953 diseases in horticultural soil-less systems under greenhouse condition. The capability to suppress  
954 plant pathogen depends on the direct antifungal actions of biostimulants and/or humic fractions, by  
955 activities of antagonistic microbes causing microbiostasis, fungistasis and hyperparasitism, by  
956 release of antimicrobial compounds (antibiotic-like) causing antibiosis, and by activation of  
957 systemic disease-resistance in host plants ([Avilés et al., 2011](#)).

958 Biochar is the solid co-product from pyrolysis process obtained using lignocellulosic  
959 biomass ([Fig. 9](#)). Biochar, that is used in sustainable and renewable agriculture as improver of soil  
960 structure ([Table 2](#)), can be burned like coal or used as a soil additive to improve soil fertility in  
961 preventing nutrients and water losses. Biochar can also be used to sequester carbon from

962 environment and may remain in the soil for hundreds of years. Crop productivity under extensive  
963 and/or intensive agriculture conditions can be related to direct or indirect effect of biochar suppling  
964 plant nutrients, increasing soil water retention and soil cationic exchange capacity, correcting soil  
965 pH and improving physical-chemical properties, transforming phosphorus and sulfur into peptides,  
966 neutralizing phytotoxic compounds in the soil, promoting beneficial mycorrhizal fungi, modifying  
967 relations between soil microbiota and related ecological functions, and increasing plant resistance to  
968 biotic stresses (Elad et al., 2011). Also, biochar has recently been proposed to synergize with  
969 suppressive composts sourced from poultry manure in suppressing soil-borne plant disease by  
970 beneficial soil applications (Jindo et al., 2012). Similarly to compost, also biochar is able to  
971 suppress soil-borne plant pathogens with different action mechanisms providing nutrients and  
972 improving their availability and water uptake; stimulating a beneficial microbiota that provide direct  
973 protection against pathogens via antibiosis, competition and parasitism; and altering microbial  
974 population in the soil which cause a shift toward beneficial microorganisms populations promoting  
975 plant growth and activating resistance mechanisms against disease development (Buonanomi et al.,  
976 2015).

977 Oil extraction, which can be carried out with chemical solvents, cold pressing or a  
978 combination of both methods, provides oil-less seed cakes as one of the main co-products from  
979 biodiesel production chain (Fig. 7). These co-products, after grinding or pelleting, can be  
980 incorporated directly into the soil as meals or pellets (Table 3) playing a crucial role in suppressing  
981 soil-borne fungal diseases (Buonanomi et al., 2007). In contrast to matured compost, oil-less seed  
982 pellets/meals from Indian mustard and flax are un-decomposed organic materials very rich in  
983 carbon and nitrogen easily available to soil microbial dynamics that provide nutrients for the native  
984 microbial populations involved in nutrient-recycling of carbon, nitrogen, phosphorus, potassium,  
985 and in plant disease suppression (Wang et al., 2012). Adding seed pellets/meals into the soil at the  
986 proper proportions, the bacterial community structure is such regulated because seed meal/pellet

987 may contribute to plant health inducing a fungistatic action via competition for nutrients among  
988 beneficial soil microbiota and soil-borne pathogens (Zaccardelli et al., 2013). Recently, the residual  
989 oil-less seed cake rich in protein derived from oil extraction of cardoon seeds for producing  
990 bioplastics should be employed in organic farming systems in suppressing soil-borne plant  
991 pathogens (Pugliese et al., 2017). Also, efficacy of *Brassica carinata* pellets able to inhibit mycelial  
992 growth and chlamydospores germination of *Phytophthora nicotianae* at different temperature  
993 regimes was reported by Serrano-Pérez et al. (2017). Nevertheless, soil amendments with seed cake  
994 may sometime induce the growing of harmful microbes (saprophytes, pathogens, etc.) because this  
995 is not organic matter adequately stabilized and such could induce a detrimental disease-conductive  
996 effect by increasing the soil population level of soil-borne plant pathogen (Chung et al., 1988).

997       Amongst treatment technologies for organic waste, landfill is a very ancient technique in  
998 which all MSW and refuses accumulate in large ditches, or valleys, or specially excavated holes in  
999 the land, are decomposed by bacteria sourced from waste to produce gaseous biofuel, especially  
1000 methane. Landfill methane is used not only for power generation but also for firing brick kilns and  
1001 for producing steam in industry. Nevertheless landfill is a process unsustainable, it is discouraged in  
1002 many countries (landfill ban/taxes), it no allow recuperation of nutrients and sometimes allow  
1003 recuperation of energy (landfill gas) but with lower efficiency and poor emissions of CH<sub>4</sub>. The same  
1004 purpose is nowadays achieved accordingly with the latest technologies able to produce  
1005 concomitantly biogas and digestate (as main co-product) through anaerobic digestion of MSW and  
1006 plant biomass (Fig. 10) in suitable bioreactors. The anaerobic digestion is one of the most mature  
1007 technologies for producing biogas from biomass, overall methane, that allow stabilization of  
1008 organic waste as digestates, recuperation of nutrients from the digestates (soil fertilizer/soil  
1009 improver) and overall recovery of energy (biogas) from a broad variety of feedstock as: 1) MSW,  
1010 2) dedicated crops (wheat, triticale, maize, sugar beet), 3) animal waste (slurry, sludge, manure), 4)  
1011 residual biomasses and agro-wastes (corn stalks, rice husks, corn stover, wheat straw, cropping

1012 residues, unmarketable products, vegetable processing leftovers, spent coffee-ground, defatted olive  
1013 marc, sugar beet bagasse, tomato-waste, cardoon-waste, vegetable-waste). However, biogas  
1014 production relies greatly on the co-digestion of mixtures by animal slurries and/or manure with  
1015 annual energy crops, particularly triticale and maize, that provide an equilibrate carbon/nitrogen  
1016 ratio to the end-product. The biogas produced is then tapped and used either in houses or in power  
1017 stations. The most important co-product from the biogas chain is commonly known as digestate.  
1018 The digestates, containing relevant amount of nitrogen, phosphorus and many micronutrients, are  
1019 suitable for producing organic fertilizers after an adequate time of aerobic stabilization if used as  
1020 organic input in agriculture accordingly with the Italian legal limits. Digestates have a variable  
1021 degree of carbon/nitrogen rates due to their variable origin and composition of the feedstocks,  
1022 which means that they can be rapidly decomposed (digestates with lower carbon/nitrogen rates) or  
1023 slowly decomposed (digestates with higher carbon/nitrogen rates) into the soil releasing nutrients  
1024 available to plant growth in a timely manner. More recently, composting and anaerobic digestion  
1025 can be integrated among them into a more complex flow chart as, for example, in a comprehensive  
1026 managing of poultry manure (Fig. 11) able to minimize negative impacts caused by soil-borne  
1027 pathogens and reduced soil quality (Darby et al., 2006). Other interesting flow chart of sorting  
1028 digestion and separation of MSW is shown in Figure 12 where biogas, digestate and composted  
1029 sludge cake are simultaneously co-produced starting from the same waste.

1030 Dried distillers grain and oilseed cakes/meals from brassicaceae should be re-considered in  
1031 this review also as effective fertilizer sources for promoting plant growth (Table 3). In addition to  
1032 content of macro- and micronutrients needed to support plant growth, these co-products have both a  
1033 lower carbon/nitrogen ratio which means that they are rapidly decomposable into the soil releasing  
1034 nitrogen quickly available to plant growth (Snyder et al. 2010). This property is of particular  
1035 interest to organic agriculture markets, where nutrient sources and fertilizers containing available  
1036 readily inorganic nitrogen to positive impact corn yield are scarce (Nelson et al. 2009). Competition

1037 with animal feed markets has prevented widespread adoption of biofuel co-products as  
1038 biofertilizers. DDGS and oilseed pellets/meals particularly hold more value-added as animal feed  
1039 than as fertilizer source. Therefore, animal producers are willing to pay for feed materials based on  
1040 their feed value instead for lower-value fertilizers. However, fertilizers market may become more  
1041 appealing to biofuel producers due to DDGS feed quality issues, over-production of DDGS, high  
1042 costs of oilseed meals/pellets, and increased interest of organic farmers toward alternative nutrient-  
1043 rich fertilizers applicable into sustainable farming systems (Abe et al. 2010).

1044

#### 1045 5.1.2. Phytosanitary drugs

1046 Oil-less seed cakes derived from some *Brassicaceae* species (e.g. *B. carinata*, *B. napus*, *B.*  
1047 *juncea*, *Sinapis alba*, etc.) for producing biodiesel show a particular ability for their uses in plant  
1048 disease management in biofumigation applications (Fig. 7) that goes well beyond the soil  
1049 amendment effect (Table 3). Due to their biofumigation properties against plant pathogens and  
1050 microbial contaminants of seeds, oil-less seed meals from *Brassicaceae* are applicable in the  
1051 biological disinfection of soils, plant growing substrates, seeds, vegetable and fruit under  
1052 postharvest condition (Pane et al., 2013). Biofumigation effect depend on the glucosinolates content  
1053 into seed meal. Glucosinolates are a wide class of secondary metabolites present in most  
1054 *Brassicaceae* species which are quickly converted into a wide spectrum of volatile antimicrobial  
1055 substances (thiocyanates, isothiocyanates, nitriles, etc.) bioactive against plant pathogens by the  
1056 myrosinase-mediated hydrolysis enzymatic-complex when dry seed meal is wetted by soil water or  
1057 by water nebulization. *B. carinata* is the most studied energy crop that provide ideal formulations  
1058 for several biofumigation applications that could be a promising and eco-friendly safe method for  
1059 the control of soil-borne plant pathogens and microbial contaminants when thiocyanates,  
1060 isothiocyanates and nitriles are instantaneously released by soil treatment with dry seed meal of *B.*  
1061 *carinata*.

1062 Crude glycerine has received a special attention in phytosanitary applications (Fig. 7) as  
1063 carbon-source into media for bacterial growth (Table 3). In fact it has been tested as: 1) an additive  
1064 in liquid-formulations of biocontrol agents (*Trichoderma*) for extending their shelf-life (Sriram et  
1065 al., 2011); 2) a conjugate to a biocontrol agent (*Acremonium*) for controlling cucumber powdery  
1066 mildew (Malathrakis and Klironomou, 1992); 3) for the synthesis of chemical fungicides  
1067 derivatives of glycerin as a dithiocarbamate (Len et al., 1996); and 4) a carrier of antibiotics able to  
1068 reduce disease incidence of some plant pathogenic bacteria in navy bean seeds (Liang et al., 1992).

1069 Pelargonic acid (PA) has been isolated for the first time in the form of ester from leaves of  
1070 the ornamental plant *Pelargonium roseum* as main component of its essential oil. PA is a fatty acid  
1071 industrially obtained from oxidative break-down of oleic acid contained in un-defatted olive marc,  
1072 the main processing residue of the olive oil production chain. PA (Table 3) shows no selective  
1073 effective herbicide action only if applied in the post-emerging phase against a wide spectrum of  
1074 weeds belonging to various annual and poly-annual mono- and di-cotyledons species. PA is an eco-  
1075 friendly co-product from the olive oil chain because it directly operates by desiccation of weed leaf  
1076 surface without release of residual chemicals in the soil and environment.

1077 Furfural and other volatile microbial inhibitors (organic acids at low molecular weight) were  
1078 nowadays co-produced with ethanol during the processing of lignocellulosic matter, for example  
1079 from wheat straw, using an innovative pilot-scaled paddle dryer for the production of ethanol which  
1080 include at the same time both inhibitors removal and high-solids enzymatic hydrolysis (Viola et al.,  
1081 2016). Among the two units of biomass pre-treatment and bioconversion ethanol, there is an  
1082 innovative intermediate step that operate a simultaneous detoxification and liquefaction of pre-  
1083 treated biomass by SE generating a condensation liquid waste (SELW) which contains a mix of  
1084 furfural and organic acids at low molecular weight as the formic and acetic acids (Fig. 13). The  
1085 SELWs that have been obtained from pre-treatment of wheat straw, giant reed and miscanthus have  
1086 been directly tested for their antimicrobial properties (Table 2) as fungicide against plant pathogenic

1087 fungi (De Corato et al., 2014), as nematocide against plant parasitic nematodes (Crow and Luc,  
1088 2014) and as bactericide towards mushroom pathogenic bacteria (Bruno et al., 2015). As afore-  
1089 mentioned, SELWs have also been used in increasing suppressive properties of three green  
1090 composts sourced from a feedstock of agro-energy co-products and agricultural wastes (De Corato  
1091 et al., 2016).

1092 Moreover, certain plant extracts containing secondary metabolites as terpenes, terpenoids,  
1093 flavonoids, isoflavones and phenolic substances that are extracted from biofuel plant-waste such as  
1094 jatropha seed cake, sunflower residues and soybean tissues (Table 3), have also been investigated  
1095 for their potential antifungal activity (Gatto et al., 2011) although the studies in this field are still in  
1096 a preliminary phase.

1097

### 1098 5.1.3. *Plant biostimulants*

1099 Many researches have focused on the plant biostimulants due to increasing attention about  
1100 the use of natural substances able to potentiate crop growth and improve quality of the crop yields  
1101 (Storer et al., 2016). The development of new products derived from compost, such as ‘compost  
1102 teas’ (Fig. 7), is increased in the recent years due to their positive effects on the main quality  
1103 parameters of horticultural crops as mini watermelons (Liguori et al., 2015). Compost teas are  
1104 defined as organic products obtained through a liquid-phase compost extraction, variable from few  
1105 hours to two weeks, with or without active aeration, and with addition of nutrients derived from  
1106 residual biomass that provides sugar (molasses, etc.) and protein (casein, etc.). In particular,  
1107 compost teas can show this particular bioactivity on plants due to their content in aromatic  
1108 substances, hormone-like organic molecules and useful microorganisms. Compost tea-based  
1109 treatments can exert protective effects against plant diseases occurrence and/or stimulate an  
1110 enhanced plant physiological status with improvements in quantity and quality of crop production.  
1111 The most widely described uses of compost tea are related, almost exclusively, to its ability in

1112 suppressing plant pathogens similarly to suppressive composts. Compost teas are usually applied by  
1113 foliar spray on crops and by soil drenching.

1114 The brown seaweed *Laminaria digitata* is traditionally used as a fertilizer that spread on the  
1115 land (Table 3). In the 18<sup>th</sup> century it was burnt to extract the potash it contained for use in the glass  
1116 industry. In the 19<sup>th</sup> century it was used for the extraction of iodine. Both these uses died out when  
1117 cheaper sources for these products became available. *L. digitata* is still used as an organic fertilizer,  
1118 but it is also employed for the extraction of alginic acid or alginate, the manufacture  
1119 of toothpastes and cosmetics, and in food industry for binding, thickening and molding (Table 3). *L.*  
1120 *digitata* is used in Asia (mainly Japan and China) for making dashi, a soup stock, and for other  
1121 culinary purposes in functional food. Many biorefining companies use *L. digitata* in industrial  
1122 applications including bio-architecture, solar energy, next-generation biofuels, green chemicals and  
1123 more else (Sikes et al., 2010). Seaweed extracts have good biostimulant properties (Table 3) able to  
1124 induce plant growth for crop development due to presence of a large number of growth-stimulating  
1125 compounds (Khan et al., 2009). It is proved that new methods basing on the seaweed extracts as  
1126 biostimulants are applied for to increase efficiency of plant cultivation thanks to action of  
1127 phytohormone-like substances able to regulate growth and develop of many crops (Tuhy et al.,  
1128 2013). Also, a very strong biological effect regarding to antifungal activity of crude extracts from  
1129 biofuel-used brown and red seaweeds against postharvest diseases on fresh fruit under storage  
1130 condition has recently been investigated and attributed to higher content of fatty acids, phenolic  
1131 substances and polysaccharides into crude extracts (Table 3) obtained by a supercritical carbon  
1132 dioxide technique (De Corato et al., 2017).

1133 Brassinosteroids are a wide range of secondary metabolites extracted from plant-waste, seed  
1134 and press-cake of *B. carinata* and *B. napus* (Table 3). They have a very strong effect in stimulating  
1135 plant-growth on the plant cells or tissues of many herbaceous and horticultural crops (wheat,  
1136 tomato, bean, lettuce, tobacco and beet) both in open field and under greenhouse condition

1137 determining: 1) increasing of productivity, 2) improving of quality of the marketable main product,  
1138 3) increasing of disease suppression and resistance to abiotic stress, and 4) aestivation and advanced  
1139 maturation of fruit (Bardi and Rosso, 2013). Trough phytohormone-like mechanisms,  
1140 brassicasteroid promotes cell division of the meristematic tissues, stem elongation, foliar expansion,  
1141 seed germination and tolerance to abiotic and biotic stress. Brassica-steroids are usually applied on  
1142 crops by foliar spray and radical treatments.

1143

## 1144 5.2. *Bioplastic industry*

1145

1146 Bioplastics feedstock generally derive from flour or starch of corn, wheat or other grains,  
1147 but also from a wide variety of residual cellulose feedstock (Table 2). However, recent researches  
1148 show the huge potential of DDGS and CGM including soybean meal to produce bio-composite  
1149 material polymeric and thermoplastic (Table 3). More recently, a cellulose acetate biofilm active  
1150 with essential oil of edible-plant (oregano) and clay (montmorillonite) has been tested for  
1151 controlling biotic postharvest losses in food packaging and during shelf-life (Pola et al., 2016).  
1152 Azelaic acid obtained from break-down of oleic acid (together to pelargonic acid) was used for  
1153 making bioplastics (Table 3). Crude glycerin can also be fermented by selected bacteria via 1,3-  
1154 propanediol to produce bio-based poly(tri-methylene terephthalate) or fermented to produce  
1155 poly(hydroxy alkanoates) (Table 3).

1156 The term ‘bioplastic’ encompasses a whole family of materials which differ from the  
1157 conventional plastics because they are bio-based, or biodegradable, according to definition given by  
1158 the European Bioplastics (<http://en.european-bioplastics.org/bioplastics>). Bioplastics already play  
1159 an important role for food packaging, shelf life, gastronomy, consumer electronics and automotive.  
1160 In these market segments, bioplastics are used to manufacture products intended for short term use,  
1161 such as mulch films or catering products, as well as in durable applications, such as mobile phone

1162 cover or interior components for car. Biodegradable plastics no compostable are also most used as  
1163 mulching in protected agriculture for greenhouse, tunnel and soil for controlling diseases of  
1164 horticultural crops or increasing seedling growth (Fig. 14). The terminology used in the bioplastics  
1165 sector is sometimes misleading; while most people use the term bioplastic to mean a plastic  
1166 produced from a biological source, there is no such a general agreement on biodegradability. All  
1167 plastics (both bio-based and petrochemical-based) are technically biodegradable, meaning they can  
1168 be degraded by microbes under suitable conditions. However, many degrade at such slow rates that  
1169 they are to be considered non-biodegradable. Some biodegradable petrochemical-based plastics  
1170 may be used as additive to improve the performance of commercial bioplastics. In addition, the  
1171 biodegradability is an high-value added of some types of bioplastics. On the other hand, non-  
1172 biodegradable bioplastics are referred to as durable. The degree of biodegradation varies with  
1173 temperature, polymeric stability and available oxygen content. Consequently, most bio-based  
1174 plastics will only degrade in the tightly controlled conditions of industrial composting units. In  
1175 addition to being bio-based, some bioplastics are both biodegradable and compostable able to  
1176 produce compost in so far as they meet the requirements specified by the UNI EN 13432:2002 and  
1177 by the certification programs released by leading international bodies that define how and what  
1178 bioplastic must be quickly biodegraded under industrial composting condition for it to be called  
1179 'compostable'. The term 'biodegradable plastic' has also been used by producers of specially  
1180 modified petrochemical-based plastics which appear to biodegradability. This type of plastic may  
1181 be referred to degradable plastic, or oxy-degradable plastic, or photodegradable plastic, because the  
1182 process is not initiated by microbial action. While some degradable plastics manufacturers argue  
1183 that degraded plastic residue will be attacked by microbes, these biodegradable materials do not  
1184 meet the requirements of the commercial composting standard defined by the UNI EN 13432:2002.  
1185 There are two main advantages in the use of plastics sources from biomass when compared to their  
1186 traditional versions: 1) they save non-renewable resources, and 2) they are almost carbon neutral.

1187 The poly(hydroxy alcanoates) or PHAs are a large group of bio-based polyesters from  
1188 biomass refineries with over 100 different types of monomers with different properties and  
1189 functionalities with attractive qualities for thermo-processing applications (Snell et al., 2009). PHAs  
1190 are aliphatic polyesters produced via fermentation of renewable feedstock directly by the  
1191 microorganisms. PHAs are thermoplastic polyesters synthesized by various types of bacteria such  
1192 as *Bacillus*, *Pseudomonas*, *Ralstonia* and *Rhodococcus* through the fermentation of sugars or lipids.  
1193 Under certain culture conditions, these linear macromolecules accumulate into bacterial cell in the  
1194 form of microscopic granules to reach high concentrations up to 90 % on dry weight basis of the  
1195 total bacterial mass. The PHAs accumulated in the form of granules serve as an energy reserve.  
1196 These polyesters concentrates in the bacterial cells has an high refractive index under microscopy  
1197 observation. The PHAs that granule are then recovered by destroying the cells. The biosynthesis of  
1198 PHAs is usually obtained by special culture conditions, such as lack of nutrients like phosphorus,  
1199 nitrogen and trace elements, or lack of oxygen, or/and excess supply of carbon sources. Depending  
1200 on the microorganism and culture conditions, homo-polyesters or co-polyesters are synthesized with  
1201 different acid hydroxyl-alcanoates. The alkyl group can have a number of carbon atoms between 1  
1202 and 15, can be linear or branched and can contain various types of substituents depending on the  
1203 bacterial strain. For example, bacteria of the genus *Ralstonia* produce short side chain (1-5 carbon  
1204 atoms), while *Pseudomonas* produce medium-sized side chain (more than 5 carbon atoms). An  
1205 interesting conversion way from second-generation sugars into high-value added lipids which could  
1206 will be bio-converted into PHAs by bacteria is those operated by oleaginous yeasts. The main part  
1207 of these lipids belong to triglycerides which are deeply studied as a new feedstock able to provide  
1208 bioplastics. In a recent study (Mastrolitti et al., 2015), the yeast *Cryptococcus curvatus* has been  
1209 investigated for the conversion of second-generation sugars from hydrolysates of cardoon plant-  
1210 wastes into triglycerides accumulated into the living cells (Fig. 15). The great variability of the side  
1211 chains of single monomers give to PHAs extremely variable physical characteristics: for example,

1212 melting point varies between 40 °C and 180 °C. These materials are biodegradable and are used in  
1213 the production of bioplastics. Also mechanical properties and biocompatibility of PHAs can be  
1214 modified tweaking the surface or by combining it with other polymers, enzymes and inorganic  
1215 materials. PHAs are thermoplastic polymers, can be processed with conventional equipment, they  
1216 are ductile and elastic, with variable properties according to their chemical composition (homo- or  
1217 co-polyesters). PHAs are also stable to UVs, unlike other types of bioplastics as poly(L-lactic acid),  
1218 and show a low water permeability. PHAs are soluble in halogenated solvents as chloroform or  
1219 dichloroethane. Their crystallinity can vary from 10 % up to 70 %. Their processing, impact  
1220 resistance and flexibility improve with a higher percentage of valerate in the material.

1221 The poly(hydroxyl butyrate) or PHB, belonging to the group of PHAs, has similar  
1222 mechanical properties like poly(propylene) or bio-based poly(ethylene) and has a good moisture  
1223 resistance. PHB is a biodegradable compostable polymer which is produced by bacteria  
1224 *Cupriavidus necator* and *Pseudomonas* sp. in response to stress conditions as lack of  
1225 macronutrients, or lack of oxygen, and/or excess supply of carbon sources. PHB is produced by the  
1226 action of three enzymes. The first (3-ketothiolase enzyme or PhaA) catalyzes the condensation of  
1227 two acetyl-CoA molecules, the acetoacetyl-CoA is reduced to 3-hydroxybutyryl-CoA (3HB-CoA)  
1228 by the catalysis of the second enzyme (NADPH-dependent acetoacetyl-Coa reductase or PhaB).  
1229 The third (PHA synthase or PhaC) incorporates 3HB-CoA in a PHB growing chain. The  
1230 poly(hydroxyl butyric) acid, synthesized from pure PHB, is relatively fragile and rigid, whereas  
1231 copolymers of PHB, which may include other fatty acids such as acid beta-hydroxyvalerate, can  
1232 have more elastic properties.

1233 The poly(L-lactic acid) or PLA is the polymer of lactic acid. The synthesis is done through  
1234 several phases: separation of the fibers and gluten, liquefaction and saccharification, fermentation  
1235 with re-use in the culture medium of the protein separated from starch, purification and  
1236 concentration of saline solutions of lactic acid, and ending polymerization. The industrial

1237 fermentation takes place thanks to a bacterium of the genus *Lactobacillus*; it must be used in high  
1238 purity to avoiding influence on the optical purity of the acid produced. Sugar, molasses and more  
1239 else residual sugary biomasses are used as feedstock. *Bacillus coagulans* is alternatively used for  
1240 PLA synthesis. PLA has properties intermediate to those of polystyrene. As for the  
1241 biodegradability, hydrolysis occur under conditions of temperature higher than 60 ° C and humidity  
1242 more than 20 %.

1243

### 1244 5.3. *Cell and tissue engineering*

1245

1246 Sodium alginate, the sodium salt of alginic acid, is an anionic polysaccharide comprising of  
1247 mannuronic acid and guluronic acid residues. It is mainly extracted from cellular walls of brown  
1248 seaweeds which are actually used for third-generation biofuel production (mainly ethanol) either in  
1249 synergy either in place of microalgae ([Milledge et al., 2014](#)), but it is also produced from bacterial  
1250 sources being extracted from biofilms ([Donati and Paoletti, 2009](#)). Through binding with water, it  
1251 forms a viscous gum by water absorbing and quickly solidifying. Its colour ranges from white to  
1252 yellowish-brown, and it is sold in granular or powdered forms. Alginates from different seaweeds  
1253 often have variations in chemical structure and physical properties: some of them may be yielded as  
1254 alginate that gives a strong gel, another a weaker gel, some may readily give a cream/white alginate,  
1255 and another difficultly forming gel. Owing to its gelling, thickening, stabilizing and viscose  
1256 properties, alginate is traditionally a prominent component for food ([Holdt and Kraan, 2011](#)), textile  
1257 and paper industries ([Pallerla and Chambers, 1997](#)). Alginate is a well-known biomaterial that is  
1258 used in pharmaceutical and biomedical fields ([Augst et al., 2006](#); [Gombotz and Wee, 2012](#)), for  
1259 drug delivery ([Tønnesen and Karlsen, 2002](#)) and in tissue engineering ([Kuo and Ma, 2001](#);  
1260 [Machida-Sano et al., 2010](#)) due to its high bio-compatibility, low toxicity, low cost, simply and  
1261 quickly gelation mechanism ([Lee and Mooney, 2001](#)). Just as an example in the botanical field, 3 %

1262 Na-alginate with 0.1 M calcium chloride has been found to be a better mix for producing  
1263 encapsulated nodal segments for plant regeneration by non-embryogenic synthetic seeds (Verma et  
1264 al., 2015). A recent research regarding to use of a sodium alginate matrix suitable for immobilized-  
1265 yeasts having an antagonistic bioactivity against green mould disease on citrus fruit caused by the  
1266 phytopathogenic fungus *Penicillium digitatum* under postharvest condition has been carried out (De  
1267 Corato et al., 2017).

1268 Finally, concluding this overview, a special attention must be focused on the lignin sector  
1269 (Table 2). Lignin, second only to cellulose in natural abundance, is an important constituent in  
1270 biomass. The main use of lignin is as a fuel to fire the boilers used for pulp production. Due to its  
1271 abundance and low price, lignin is of industrial interest to convert them into high-value added  
1272 products such as biomaterial, adsorbent and thermal insulator. Lignin is now being isolated from the  
1273 fuel ethanol production chain, and it being separated from lignocellulosic matter by standard pre-  
1274 treatment procedures, it is nowadays the main co-product with ethanol. Using mild methods to  
1275 separate early lignin from the lignocellulosic matter will preserve its structure, such allowing more  
1276 potential uses (Holladay et al., 2007). The 'Lignol Innovation' Company uses wood and agricultural  
1277 residues in their pilot plant to produce both ethanol and high purity lignin (Greer, 2009). This form  
1278 of lignin has large-scale commercial potential as a replacement for petroleum-based products  
1279 currently used in the manufacturing of industrial coatings, gels and emulsifiers (ILI, 2009). Several  
1280 attempts have also been reported in literature on lignin as a part of biomaterials composites with  
1281 hydroxyapatite, or as a carrier in laxative formulations, or as an allergenic reducer for latex rubber.  
1282 Lignin can also be used to generate more energy for ethanol plant operations, or used as a dispersant  
1283 and binder in concrete admixtures, or as the principal component in thermoplastic blends,  
1284 polyurethane foams or surfactants. However, only from 1 % to 2 % is isolated from pulping liquors  
1285 and used to prepare polymeric materials, as polyurethanes, phenolic and epoxy-resins. Another  
1286 important use for lignin is in the production of carbon fiber. Spun and woven into a fabric, carbon

1287 fiber is combined with resins to form reinforced plastic. This material is similar to fiberglass with  
1288 high tensile strength and low weight that is used in aircraft, automobiles and sporting goods  
1289 (Holladay et al., 2007). Pure lignin derived from the pre-treatment of lignocellulosic matter for  
1290 producing ethanol (Fig. 16) is potentially utilized for innovative and interesting biomedical  
1291 applications in cell and/or tissue engineering. Composites and blends of lignin are yet known in  
1292 literature with cellulose alone or cellulose acetate (Sescousse et al., 2010), or xanthan gum (Raschip  
1293 et al., 2007), or poly(ethylene oxide) (Kadla and Kubo, 2003), or poly(vinyl alcohol) (Kubo and  
1294 Kadla, 2003), or PLA (Li et al, 2003), or poly(4-vinylpyridine) (Cunxiu et al., 2005). Even though  
1295 there may be only weak interaction between lignin and principal constituent, nevertheless addition  
1296 of lignin may offer advantages to basic-material such as more control over water uptake and  
1297 improved mechanical properties (Raschip et al., 2007). Generally, lignin is not cytotoxic if used up  
1298 to moderate concentration. Apart from lower hydrophilicity and higher stability, another potential  
1299 advantage of lignin is its potential antimicrobial activity. Although antimicrobial properties of the  
1300 phenolic units delivery from purified lignin degradation are well documented (Baurhoo et al.,  
1301 2008), there are nevertheless some controversy in literature about antimicrobial activity of both pure  
1302 lignin and lignin-based materials. Importance of conjugating lignin with polysaccharides derived  
1303 from cellular walls of brown seaweeds for *in vivo* expression of various kinds of immune-  
1304 potentiating activity is also reported (Sakagami et al., 1991). More recently, lignin was proposed to  
1305 produce hybrid alginate–lignin aerogels with relevant perspectives in biomedical applications. The  
1306 relationships between hydrophilicity and hydrophobicity of the lignin surface is an important factor  
1307 that allow a good cell adhesion. When combined with alginate, lignin is expected to reduce  
1308 hydrophilicity of alginate and hence provide more suitable environment for cells to adhere, grow  
1309 and differentiate into a porous matrix. Bearing in mind ultimate stability of lignin, it was also  
1310 expected that the presence of lignin may abate the scaffold degradation rate and help to match it  
1311 with the rate of new bone tissue regeneration. These features may also have a beneficial effect with

1312 respect to biomedical applications. A study of novel non-cytotoxic alginate-lignin hybrid aerogels  
1313 combining with the supercritical carbon dioxide technique and employed as scaffolds for tissue  
1314 engineering purpose has been recently studied (Quraishi et al., 2015). Potential applications of  
1315 lignin as lignosulphonates in food industry (fishgelatin films) have also been reported by (Núñez-  
1316 Flores et al., 2012). Many comprehensive reviews on the pure lignin and lignin-based materials are  
1317 however available in literature (Khitrin et al., 2012; Azadi et al., 2013).

1318

1319

## 1320 **6. Biorefining outlook in the EU and in Italy**

1321

1322 Feedstock that can be considered in the EU and in Italy suitable for biorefining are: 1)  
1323 MSW; 2) agricultural waste, animal husbandry waste and agro-industrial residues; 3) forest residues  
1324 after forest cleaning. On the other hand, the chemical basic-platforms currently produced in  
1325 industrial-scale from this multiple feedstock are represented by the fuel ethanol; biodiesel; methane;  
1326 acetic acid; lactic acid and the polymer derived from it as polylactic acid; 1,3-propanediol used in  
1327 poly(trimethylene terephthalate) synthesis; xylose produced from hardwood and used to produce  
1328 xylitol as sweetener; furfural produced from residual biomass including corncobs, cottonseed hull  
1329 bran, oat hulls, and used to produce pesticides; sorbitol produced by hydrogenation of dextrose and  
1330 used as an alternative to xylitol.

1331

### 1332 *6.1. An overview in the EU*

1333

1334 The shift towards a bio-economy recently recognized by the EU through the adoption of a  
1335 dedicated strategy outlining the need to move towards a post-petroleum society in order to respond  
1336 to the key challenges, is focused in the coming years. The EU has also emphasized the pivotal role

1337 of bio-based products and markets development by reviewing the EU industrial policy. In February  
1338 2012, the EU adopted the new bioeconomy strategy to shift Europe towards a greater and more  
1339 sustainable use of renewable resources moving towards a sustainable bioeconomy (Vivekanandhan  
1340 et al. 2013). While the bio-economy strategy itself is a good start, Europe today still remains a long  
1341 way from establishing optimal framework conditions for the biorefining industry. In 2010, about 62  
1342 % of renewable energy in the EU was generated from biomass and even if this share is expected to  
1343 decrease to 57 % in 2020. The total bioenergy contribution to the EU mix is expected to increase  
1344 from 3600 PJ in 2010 to about 5900 PJ in 2020.

1345 In general, the European market for soaps, detergents and other similar products amounted  
1346 to approximately 30 billion euros; between 30 % and 50 % of these products contain bio-based  
1347 enzymes, as proteases and lipases, for detergent applications. In Europe, the production of enzymes  
1348 is strong and it suggests a potential increase of their use in food, paper and textile production.  
1349 Germany has developed commercial operations using the biomass-to-liquid technology. A  
1350 demonstration plant was built in Freiburg in collaboration with Shell using wood as raw material.  
1351 Austria has developed a new technology based on grass and silage since 1999s with the aim of  
1352 exploiting the fibers, proteins and lactic acid components. The forest resources of Scandinavia are  
1353 being targeted for the production of cellulosic ethanol. Neste Oil in Finland with Petrobras in Brazil  
1354 are the big producers of diesel from hydrogenated vegetable oils and animal fats at the Porvoo  
1355 biorefinery. The biodiesel production has interested Total (France) and OMV (Austria). ENI  
1356 VERSALIS are building a new biodiesel facility in Italy (Livorno), the plant will process about  
1357 6,500 barrels per day of vegetable oil by the Ecofining technology jointly developed by ENI  
1358 VERSALIS.

1359 The main European projects regarding to biorefining focus are: 1) 'FERTIPLUS'  
1360 (<http://www.fertiplus.eu>) addressed to reduce mineral fertilizers and agro-chemicals in agriculture  
1361 recycling treated organic waste into compost and biochar and improving the combined effects of

1362 biochar with anaerobic digestion and composting; 2) ‘OLIPHA’ (<http://www.olipha.eu>) focused to  
1363 investigate a novel and efficient method for the production of PHA polymer-based packaging from  
1364 olive oil waste water and anaerobic digestion of the remaining by-products; 3) ‘TRANSBIO’  
1365 (<http://www.transbio.eu>) focused to implement an innovative cascading concept for the valorization  
1366 of co-products and by-products from the fruit and vegetable processing industry using eco-friendly  
1367 biotechnological solutions, like fermentation and enzyme-conversion strategies, for to obtain  
1368 valuable bio-products as bioplastics (PHB), succinic acid chemical platforms, and bio-based  
1369 enzymes (proteases and lipases) for detergent applications. In addition to that, biofuel co/by-  
1370 products also create opportunity for the fabrication of various nanostructured materials including  
1371 three biorefinery projects in the USA using predominantly corn stover. Three commercial second-  
1372 generation biofuel projects have started in Brazil from corn stover and straw to produce bioplastic  
1373 materials: 1) ‘GRANBIO’ for commercial cellulosic ethanol plant, 2) Raizen/Iogens plant, and 3)  
1374 Solazyme-Bunge plant.

1375

## 1376 6.2. *Big players in Italy*

1377

1378 Despite the economic crisis affecting Italy since 2009, the economic sector of ‘green  
1379 chemistry’ shows remarkable vitality and is nowadays one of the few with positive growth  
1380 indicators into green economy. Within this sector is possible to provide a set of possible solutions  
1381 able to generate new jobs, improve the socio-cultural context, and produce environmental benefits.  
1382 In this scenario, integrated biorefineries represent a valuable development opportunity in Italy,  
1383 especially for local communities through the efficient use of distributed renewable resources among  
1384 countries. The Italian regional structures that operates in waste recycling generally separates raw  
1385 biomass from fibers, animal feed, MSW and high-value organic compounds obtained from niche  
1386 crops. The sugar components of biomass can then be separated and concentrated to give the central

1387 biorefinery, while the protein fraction can be usefully recovered and used as high quality livestock  
1388 feed. Among key-actors of green economy basing on a biorefinery approach, three companies stand  
1389 out in Italy: NOVAMONT, ENI VERSALIS and BIOCHEMTEX.

1390 NOVAMONT innovation strategy is based on the third-generation biorefinery concept and  
1391 on the approach of a strong multi-disciplinary collaboration with agricultural world, research  
1392 community and local institutions. In particular, Novamont have partnered with ENEA for building  
1393 two cluster projects on a green chemistry basis using cardoon crops as renewable source for  
1394 producing biopolymers from oil seed that will be completed by 2018. The local peculiarities are  
1395 commended by this way and will maximize the use of waste and residues as valuable inputs and  
1396 secondary raw materials for biorefineries. Novamont produces and sells various types of  
1397 biopolymers under the brand name Mater-Bi® or, more recently, the azelaic and pelargonic acids  
1398 obtained from break-down of residual oleic acid in olive marc. ENI VERSALIS is a chemical  
1399 company with sole shareholder that manages the production and marketing of petrochemical  
1400 products (basic chemicals, styrene, bio-elastomers, polyethylene) relying on a range of proprietary  
1401 technologies, advanced facilities, and a local and efficient distribution network. Versalis aims to be  
1402 the first company to license the process and build commercial plants, thus providing over 20 million  
1403 dollars in funding to Genomatica to support the end-to-end process. Just like the bio-succinic acid,  
1404 the ultimate showdown here is who can produce the most economical bio-butadiene. Versalis have  
1405 partnered with ENEA for building one cluster project focused on biological conversion of second-  
1406 generation sugars from guayule bagasse, an alternative crop to gumtree, into bio-butadiene, that will  
1407 be completed by 2018. BIOCHEMTEX, previously known as Chemtex Italia, is a global leader in  
1408 the development and engineering of bio-chemical technologies and processes based exclusively on  
1409 the use of non-food biomass, as an alternative to fossil resources. In partnership with 'Beta  
1410 Renewables', Biochemtex has created technologies and plants for the production of bioethanol and  
1411 other chemical products. Following an investment of 150 million euros and seven years of study,

1412 the company completed the design of Proesa®, an exclusive technological platform now marketed  
1413 by Beta Renewables. Proesa® makes it possible to obtain biofuels and numerous chemical  
1414 intermediates, and has been implemented on an industrial scale in the plant located at Crescentino  
1415 (Vercelli, Turin), the world's first plant for the production of second-generation bioethanol.  
1416 Biochemtex is also developing the new technology for the conservation of lignin in bio-naphtha and  
1417 aromatic compounds (MOGHI) which are used in numerous industrial sectors. Biochemtex, part of  
1418 the well known Mossi Ghisolfi Group, is placed in Tortona (Alessandria) and has two Research  
1419 Centre located in Rivalta Scrivia (Alessandria) and Modugno (Bari) where the demonstration  
1420 system for MOGHI technology will be completed by 2017.

1421

1422

## 1423 **7. Conclusions**

1424

1425 Market implementation of integrated biorefinery requires reliable and advanced processing  
1426 units combined with eco-friendly and economically profitable production chains. Future  
1427 developments of the advanced biorefinery systems should include either crop cultivation with  
1428 selected genotypes that maximize full chain performance either the use of agricultural residual  
1429 biomass and waste. The biomass components are varied in nature (cellulose, glycerin, natural fillers  
1430 and non-genetically modified starch obtained from various crops, etc.) that should be all given from  
1431 organic residuals neither competing with food crops nor occupying deforested land or fertile arable  
1432 land. As residual biomass availability is limited, it should be efficiently used for producing new  
1433 marketable materials and recovering energy in multi-purpose biorefineries. This requires an optimal  
1434 biomass conversion with the highest efficiency able to minimize requirements of feedstock from  
1435 dedicated energy crops which compete with food crops for fertile land and irrigation water. Raw  
1436 materials from agricultural residual biomasses and wastes can be usefully used as a profitable

1437 feedstock for the manufacture of chemical substances and products, as fatty acids from the oilseed  
1438 crops, exhausted cooking oils and animal fats from food industry; starch from the cereals, potatoes  
1439 and starchy residues; cellulose and lignin from the lignocellulose crops and/or residues. They have  
1440 recently received a special attention from policy makers in some Member States as the EU because  
1441 these residual materials can be converted into marketable chemical intermediates, polymers,  
1442 lubricants, solvents, surfactants and especially green chemicals, such partially replacing fossil fuel  
1443 sources. Integrated biorefineries can provide a significant contribution to sustainable development  
1444 of biofuel market co-generating a broad range of high-value added co/by-products useful in some  
1445 selected application sectors (e.g., renewable and sustainable farming systems, bioplastic industry  
1446 and cell and tissue engineering in biomedical applications) starting from a broad range of various  
1447 and heterogeneous residual biomasses and wastes of different origin and location that otherwise  
1448 should be disposed or however managed.

1449 At the same time, strengthening of economic viability in selected market sectors (e.g.,  
1450 agriculture, forestry, chemical and energy) are needed. One of the key-prerequisites of a successful  
1451 biorefinery is to invite stakeholders and players to discuss backgrounds (agriculture/forestry,  
1452 transportation fuels, chemicals, energy, etc.) common processing topics, necessary researches,  
1453 develop new trajectories, and overall stimulate deployment of advanced technologies in multi-  
1454 disciplinary partnerships. Optimal economic development and environmental performance can be  
1455 only guaranteed linking the most promising high-value added materials and functionalized chemical  
1456 platforms with the recovery of energy from the widest range of residual raw materials.

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## 1459 **References**

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