# Chapter 6 Municipal Waste Treatment, Technological Scale up and Commercial Exploitation: The Case of Bio-waste Lignin to Soluble Lignin-like Polymers

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Abstract The present chapter addresses municipal bio-waste, as worldwide easily available concentrated source of organic matter to convert to and recycle as valuable products for further use. Municipal bio-waste contains polysaccharides and lignin as major components. On the other hand, these are major components of biomass, generally. This implies that technology used for treating municipal bio-waste is likely applicable to other bio wastes, as well. Current biomass treatment technology addresses mainly the production of biofuel by fermentation of the polysaccharide fraction. Lignin is an insoluble recalcitrant material withstanding biochemical and chemical treatment. It inhibits fermentation microorganisms. Thus, the separation of lignin from the fermentable organic fractions is necessary. In addition, the separated lignin is regarded as secondary process waste, which needs disposal. A number of technologies are currently available for this purpose. These include lignin combustion, pyrolysis, hydrocracking, or aerobic fermentation. Yet, the bio-waste lignin fraction has further potential that can be exploited by low energy consumption chemical technology. The valorisation of lignin in this fashion would contribute important economic and environmental improvements to current waste treatment practices. Taking an Italian municipal bio-waste treatment plant as empirical case study, the present chapter reviews work performed in the last decade for the valorisation of lignin originating from the organic humid fraction and gardening residues obtained from the separate source collection of municipal bio-wastes. The work covers also agriculture residues, although in a relatively very limited extent. The chapter reports processes and applications related to new speciality chemicals stemming for research developed at EU technology readiness level 5. The results prospect sustainable processes and products, and the possibility to realize a business model with reduced entrepreneurial risk for the conversion of a municipal bio-waste treatment plant to biorefinery producing fuel and bio-based chemicals. However, the chapter does not provide the reader with a strong methodology for evaluating the potential sustainability. In addition, the proposed

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business model with reduced entrepreneurial risk is at a very early stage. It relies mostly on assumptions that need validation. The results related to agriculture residues demonstrate that, although mainly focused on municipal bio-waste, the developed technology is applicable as well to other bio-waste types.

**Keywords** Muncipal bio-waste • Bio-waste valorisation • Bio-based specility chemicals • Biosurfactants • Biopolymers • Biostimulants

### 6.1 Introduction

Solid bio-waste originates from industrial, agriculture and urban activities. Industrial bio-waste includes wastes from the food processing and pharmaceutical industry. Bio-wastes from agriculture activities are post-harvest plants and residual fruit left in the field. Municipal solid wastes contains from 18 to 60% bio-waste (Twardowska et al. 2010). It comprises food wastes and green wastes from private gardening and public park trimming activities in approximate 1.6 ratio, respectively (David et al. 2010; Ricci-Jürgensen 2012). Food waste is a major contributor to total waste production. Food wastes are often not properly treated and recycled, unlike recyclable materials such as papers. Hence, food waste often ends up in landfill along with regular waste. This creates alarming impact on environment and health hazard as methane and bacteria build up from food waste in landfill.

In the last decade, public opinion sensitivity to food waste issues has grown. This involves both fabrication and product distribution (Segre et al. 2009; Segre and Gaiani 2011). Food waste has two opposite faces. On one hand, it represents an economic and environmental burden. On the other hand, it contains valuable chemical exploitable energy. Food waste come from households, restaurants, food manufacturers, and farms (David et al. 2010) at the stages of food production, processing, retailing and consumption. As of 2013, half of all food is wasted worldwide (Huffington Post 2013; FAO 2011). Loss and wastage occurs at all stages of the food supply chain or value chain. In low-income countries, most loss (81–97% of total food waste) occurs during production, while in developed countries much food waste occurs at the consumption stage (about 100 kg per person per day, amounting to 32–60% of total food waste). In Europe, the total 89 million t food loss and waste per year arises 47% from household, 16% from catering, 6% from retail and wholesale and 44% from manufacturing activities (Barilla Center for Nutrition 2012).

The above data points out that, for abundance and easy availability, the organic humid fraction of urban wastes is potentially the most convenient exploitable source of recyclable renewable organic matter. According to various statistics, American families throw out between 14 and 25% of the food and beverages they buy. This can cost the average family \$1365–\$2275 annually (Plumer 2012). The majority of waste from households consists of food wastes, close to 60% (David et al. 2010). Their environmental impact has grown dramatically, due to the

increase of population urbanization and consumption habits. This has generated higher costs for society due to the need to dispose higher amounts of wastes. On the other hand, the population urbanization has resulted in the creation of a low entropy source of chemical energy by concentrating the bio-wastes in confined spaces. As taxpayers have already paid collection costs, municipal bio-wastes are a negative cost source of chemical energy (Sheldon-Coulson 2011).

Several technologies are in principle available to recycle and exploit the potential chemical energy of bio-waste for the production of thermal and electrical energy, and of value added chemicals. However, the removal (Canilha et al. 2012; Parsell et al. 2015; Liew 2011; Arato et al. 2005) and conversion of lignin to benefit products (Clark 2007; Ma et al. 2014) is a critical point and a major issue for the valorisation of dedicated or residual biomass as source of renewable fuels and chemicals. This is because lignin inhibits fermentation microorganisms, and is an insoluble recalcitrant material withstanding biochemical and chemical treatment. Lignin is the second most abundant organic component next to cellulose in the vegetable world. The emerging biomass refinery industry will inevitably generate an enormous amount of lignin. Development of selective biorefinery lignin-to-bioproducts conversion processes will play a pivotal role in significantly improving the economic feasibility and sustainability of biofuel production from renewable biomass.

Current biomass treatment technology (Canilha et al. 2012; van Ree and van Zeeland 2014) mainly focused to the production of biofuel by fermentation, such as biogas and bioethanol, adopts several biomass pretreatment methods to remove lignin from the fermentable fraction and/or processes the residual lignin fraction by combustion, pyrolysis, hydrocracking, or aerobic fermentation. These processes, respectively, convert the chemical energy to thermal and electric energy, produce hydrocarbons and other platform chemicals, and compost for landscaping and/or soil fertilization use (Luque and Clark 2013). Yet, the bio-waste lignin fraction has further potential (Ragauskas et al. 2014) that can be exploited by low energy consumption chemical technology. The valorisation of lignin in this fashion would contribute important economic and environmental improvements to current waste treatment practices.

The present chapter reviews work performed for urban and agriculture bio-waste lignin valorisation (LV) to bio-based chemicals, in connection with the state of art of bio-waste management technology and related economic and environmental aspects. It shows potential process and products sustainability stemming from research developed at technology readiness level 5 (Nasa 2015; European Commission 2014). It points out how integrated biochemical and low energy consumption green chemical processes may contribute to the realization of a sustainable biorefinery producing fuel and chemicals from bio-waste. Hereinafter, the chapter comprises different Sects. (6.2–6.5). Section 6.2 reviews the state of art of bio-waste management technology. It describes also a typical waste treatment plan located in Italy, the Acea Plant. This plant treats municipal bio-waste through the most advanced integrated anaerobic and aerobic fermentation technology. For this reason, in the performed research work, the Acea plant represents a highly relevant empirical case study. Section 6.3 describes low temperature hydrolysis and

oxidation processes developed, starting from different streams of the Acea plant, and the chemical nature of the related products. Section 6.4 describes the applications of the products obtained through the above processes. Section 6.5 addresses the problems and perspectives for scaling the developed processes and products to commercial production level. It proposes also a possible stepwise business development strategy with reduced entrepreneurial risk, which may effectively turn a conventional bio-waste management plant into a biorefinery through a virtuous bio-waste cycle. However, the business model is conceived at a very early stage. In addition, the reduced entrepreneurial risk relies mostly on author's assumptions, after considering research results and referenced real cost data.

# 6.2 State of the Art of Bio-waste Management Technology: Environmental and Economic Aspects

### 6.2.1 Environmental Problems

In addition to prevention at source, bio-waste management options include collection (separately or with mixed waste), anaerobic digestion and composting, incineration, and landfilling. The environmental and economic impacts of different treatment methods depend significantly on local conditions such as population density, infrastructure and climate as well as on markets for associated products (energy and composts).

Landfilling is still the most used municipal bio-waste disposal method in the EU. The majority of countries still landfilled more than half of their municipal waste in 2010 (European Environmental Agency 2013). Biodegradable waste decomposes in landfills to produce landfill gas and leachate. The landfill gas, if not captured, contributes considerably to the greenhouse effect as it consists mainly of methane, which is 23 times more powerful than carbon dioxide in terms of climate change effects (European Commission 2015). The leachate, if not collected in accordance with the *Landfill Directive* 1999/31/EC, can contaminate groundwater and soil. Landfills may also be a source of nuisance for neighbouring areas as they generate bio-aerosols, odours, and visual disturbance. An additional negative impact of landfilling is the area of land used, which is bigger than for other waste treatment technological methods. Landfills must be constructed and managed in line with the EU *Landfill Directive* (impermeable barriers, methane capturing equipment) to avoid environmental damage from the generation of methane and effluent.

The first step of modern waste treatment practices is separation into recyclables (glass, metals) and inert materials (stones etc.), paper, plastics, textiles, and biodegradable humid matter. Options are separate source collection of municipal solid wastes and/or mechanical separation of unsorted wastes. Wastes' separation is achieved by various mechanical-physical means (CP Manufacturing 2012). There are many types of machinery for municipal solid waste processing from size

reduction to separation of different fraction, and many companies offering suitable equipment. Choice of a machinery/technology for waste sorting depends upon various factors including waste characteristics/composition, purpose for separation (e.g. material and energy recovery etc.) and following processing steps.

Incineration can be viewed as energy recovery or as a disposal. Incineration requires previous separation of materials. These are humid degradable bio-waste (Department for environmental food and rural affairs 2013) and inorganic materials, which lower the efficiency of incineration by their water content or are incombustible and do not contribute to the energy content of the waste. Others may be paper, plastics and textiles, if they can be reprocessed and recycled to further use. The mixture of the separated combustible materials is named refuse-derived fuel. Its energy content may run up to over 50% more than that of the pristine raw municipal solid waste. Incineration of bio-waste as a part of mixed municipal waste may be used to recover energy from a carbon-neutral source, providing an alternative to e.g. fossil fuels and contributing to climate change. The environmental impact of incinerating municipal bio-waste arises mainly from greenhouse gas emission, heavy metals, dioxin, loss of organic matter and other resources contained in biomass, and disposal of ashes and slags.

Bio-waste composting and anaerobic digestion may be classified as recycling, when compost (or digestate) is used on land or for the production of growing media. If no such use is envisaged, it should be classified as pre-treatment before landfilling or incineration. In addition, anaerobic digestion (producing biogas for energy purposes) should be seen as energy recovery. Composting is the most common biological treatment option (some 95% of current biological treatment operations). Anaerobic digestion is especially suitable for treating wet bio-waste, including fat (e.g. kitchen waste). It produces a gas mixture (mainly methane-50 to 75%-and carbon dioxide) in controlled reactors. Biogas can reduce greenhouse gas emissions most significantly, if it is used as a biofuel for transport or directly injected into the gas distribution grid. Its use as biofuel could result in significant reductions of greenhouse gas emissions, showing a net advantage with respect to other transport fuels. The residue from the process, the digestate, can be composted and used for similar purpose as compost, thus improving overall resource recovery from waste. The use of compost and digestate as soil improvers and fertilizers offers agronomic benefits such as improvement of soil structure, moisture infiltration, water-holding capacity, soil microorganisms and supply with nutrients.

The environmental impact of composting is mainly limited to some greenhouse gas emissions and volatile organic compounds. The impact on climate change due carbon sequestration is limited and mostly temporary. The agricultural benefits of compost use are evident (European Commission 2015; CalRecycle 2016) but there is debate about their proper quantification (e.g. by comparison to other sources of soil improvers), while the main risk is soil pollution from bad quality compost. As bio-waste is easily contaminated during mixed waste collection, its use on soil can lead to accumulation of hazardous substances in soil and plants. Typical contaminants of compost include heavy metals and impurities (e.g. broken glass). There is also a potential risk of contamination by persistent organic substances such as

polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls or polycyclic aromatic hydrocarbons (Fiedler 1998; Lerda 2011; Lingle 2008). The use of anaerobic digestate has an additional limitation, which arises from the amount of ammonia produced during anaerobic digestion because of organic N mineralization. The application of high doses of bio-waste sourced fertilizers to soil enhances environmental problems. For example, maintaining agronomic benefits in soil requires compost application rates of 10 t per ha and year (Sortino et al. 2014). Other negative implications arise from significant long-distance product transport.

#### 6.2.2 Economic Aspects

The currently practiced technologies to treat bio-wastes suffer process costs not compensated by the value of the obtained products (Montoneri et al. 2011; Tang 2012). Nevertheless, bio-waste treatment is necessary to reduce mass, volume and chemical reactivity of the large amount of waste components produced by the modern society. As this implies a cost for citizens, at the current technology state of art the issue is assessing, for each case, which technology may have the lowest impact on the overall economics of waste management.

A recent work (Tang 2012) for instance, has compared two scenarios for managing wastes in Guanghan. Scenario I assumes a waste management system with source separation and separate collection of all types of recyclable materials and that the rest waste flows directly to the landfill. Scenario II differs from Scenario I in that metals are not separated at source, but flows with the rest waste to an incinerator before landfilling, where advanced technologies are applied to control air quality and to recovery energy, ferrous metal and non-ferrous metals. The result is that the benefit outweighs the cost by two million euro when comparing Scenario II to Scenario I, indicating a higher efficiency in resource allocation.

However, the result is highly sensitive to variations in the borrowing cost and the investment cost of equipment and technology. For the specific Guanghan case study, the following conclusions are drawn. The result of the cost benefit analysis indicates potential economic savings for the waste management system in Guanghan as a whole. It is therefore worthwhile for the policy makers to consider adding waste incineration to their agenda of improving the city's waste management system for environmental protection and for economic efficiency.

For the fermentation technologies, a cost benefits analysis has been published for the Acea waste treatment plant, taken as case study (Montoneri et al. 2011). The plant operates according to the ultimate trend to optimize the economy and to reduce the environmental impact of municipal bio-waste treatment. This consists in integrating anaerobic and aerobic fermentation. The Acea plant (Fig. 6.1) processes municipal bio-waste collected from an area of 2200 km<sup>2</sup> populated by 800,000 inhabitants distributed over 100 municipalities. These bio-wastes amount to about 50,000 t year<sup>-1</sup>. The published (Montoneri et al. 2011) cost revenue analysis indicates a process cost of 156  $\in$  bio-waste t<sup>-1</sup>, which is compensated by the



Fig. 6.1 Aerial view of Acea Pinerolese Industriale municipal waste management plant

revenue of 66 and  $1 \in t^{-1}$  from biogas and compost sales, respectively, and  $90 \in t^{-1}$  from tipping fee and energy recovery incentives. There are a few other similar plants in Italy (Ispra 2012). The composting and anaerobic digestion plants operating in Italy (Centemero 2015) are 240 and 43, respectively. The current trend is to increase the number of anaerobic digestion facilities, in order to integrate compost plants as in the Acea example.

By comparison, 980 and 650 composting and anaerobic digestion plants, respectively, operate in Germany (European Compost Network 2010). Throughout Europe, the potential of organic waste is estimated at 115 Mt year<sup>-1</sup> (Bart 2010a). There are about 2000 composting sites, with processing capacities ranging from 200 to 70,000 t year<sup>-1</sup>.

A recent comprehensive report has been published in 2015 on the distribution of the bio-waste production and treatment facilities throughout Europe (European Environmental Agency 2013). In spite of the claimed benefits for agriculture (European Commission 2015; CalRecycle 2016) the compost marketability is poor. This implies that the product requires alternative uses. The current alternative is the use for land restoration or landfill cover. The market value of compost for use in agriculture, based on its content and market value of the key N, P and K nutrients, is calculated  $4-6 \in t^{-1}$  (WRAP 2016). Real EU market prices in 2005/2006 are reported in the 0–30  $\in t^{-1}$  range (Barth 2010b).

Most demand for compost is in advanced countries with mature markets. There is no real demand in starting countries, probably because compost products and

their benefits are not well known, yet. Bulk retail prices in USA are reported in the range of  $2-50 t^{-1}$ , depending on the type of sourcing material, location, and use (McEntee 2011, cited in US Environmental Protection Agency 2013). These prices do not include municipal operations that give compost away free of charge.

The Italian case study Acea plant adopts the most advanced bio-waste treatment technology, which is based on the integration of anaerobic and aerobic fermentation (Montoneri et al. 2011). The Acea plant (Fig. 6.1) contains four sections; two for the treatment of solid wastes by anaerobic and aerobic digestion, the third one for treating wastewaters and the last one being a landfill area equipped for biogas collection. The four plant sections are interconnected to maximize biogas and compost yields from bio-waste, thus minimizing bio-refuse disposal to landfill.

The plant allows large operational flexibility to produce different types of compost depending on the nature and relative ratios of the bio-residues constituting the aerobic phase feed. In the plant material balance, most of the plant biogas comes from equal amounts of biogas produced in the bioreactors processing the bioorganic (humid) fraction feed and biogas collected from the landfill area, while the sewage sludge section contributes for only a small part. The total amount of the plant biogas is more than enough for covering the plant energy consumption. Exceeding electrical and thermal energy produced by biogas is sold to the electrical network and to the nearby Pinerolo town residential and commercial districts. In spite of these desirable features, the process economy of the Acea plant, as well as that of all other waste management plants spread in the world, is not profitable due to operational costs exceeding the market value of the energy and/or materials produced (Montoneri et al. 2011).

### 6.3 Bio-waste Lignin Valorisation (LV) by Low Temperature Green Chemical Processes

The consideration of municipal bio-wastes as source of bio-based chemicals to recycle to the chemical industry is relatively new. Currently practised technology has been developed based mainly on the waste fuel value (see Sect. 6.1). Indeed, incineration producing thermal power is the main option to cope with the large amounts of municipal bio-waste. Anaerobic digestion produces biogas and residual organic matter, which needs disposal. Aerobic digestion although being an exothermal process is not exploited to recover energy, but allows to decrease the waste volume and yields a residual matter which is proposed as soil amending agent.

Current research proceeds along three types of processes, i.e. biochemical, thermal and chemical. Biochemical and thermal processes (pyrolysis and hydroc-racking) disrupt the proximates of natural organic matter to obtain small platform molecules. Biochemical processes must cope with the recalcitrant lignin fraction which resists both chemical and biochemical treatment. Thermal processes disrupt

all organic matter into simple molecules, but consume a relatively high amount of energy. Low temperature chemical processes are options, to use alone or combined with biochemical and/or thermal processes. Chemical processes require green solvents. No solvent is greener and more available than water.

Recent work (Montoneri et al. 2011; Rosso et al. 2015), shows that low temperature hydrolysis allows obtaining useful lignin-like soluble polymeric products from biomass. Contrary to biochemical and thermo-chemical processes, low temperature hydrolysis does not disrupt the natural molecular structures, but converts them in soluble fragments saving the original C types and functional groups as much as possible and, in doing so, requires low energy consumption and/or amount of equipment needed. Oxidation at room temperature of these polymeric products in water is a further option, which may allow widening the range of obtainable value added biopolymers and simple molecules (Montoneri et al. 2016). Table 6.1 summarizes the main features distinguishing the three types of processes.

	Biochemical	Thermal (no	Chemical		
		combustion)	Hydrolysis	Oxidation	
Main products	Small molecules: methane, ethanol, lactic acid, platform molecules in general	Small molecules: hydrocarbons	Soluble biopolymers keeping the pristine original C types and functional groups	Biosurfactants and soluble aliphatic poly hydroxy acids	
Problems	<ul> <li>Inhibition from recalcitrant</li> <li>lignin fraction</li> <li>Product</li> <li>recovery from</li> <li>diluted water</li> <li>solution</li> <li>Residual lignin</li> </ul>	High energy consumption	Recalcitrant residual insoluble lignin needs disposal or upgrading to marketable product	Recalcitrant residual insoluble lignin needs disposal or upgrading to marketable product	
Possible option/integration	Bio-waste feed pretreatment by chemical hydrolysis to separate soluble lignin from insoluble fermentable matter (Fig. 6.2, III)	Apply to residual lignin from biochemical and/or chemical processes (Fig. 6.2)	Treatment of residual insoluble lignin by pyrolysis or hydrocracking, or combustion (Fig. 6.2, III)	Treatment of residual insoluble lignin by pyrolysis or hydrocracking, or combustion (Fig. 6.2)	
	Composting residual lignin, followed by the compost chemical treatment (Fig. 6.2, II)				

Table 6.1 Main features of bio-waste treatment processes, and possible options/integration

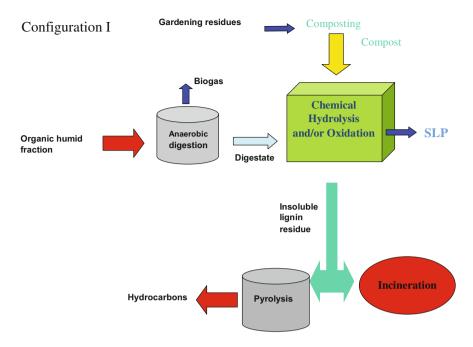
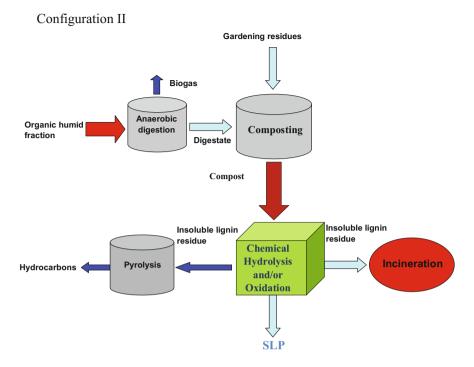


Fig. 6.2 Possible configuration of biochemical, chemical and thermal processes for the treatment of municipal bio-waste, featuring the chemical hydrolysis of the anaerobic fermentation digestate or of composted gardening residue for the production of soluble lignin biopolymers (SLP), followed by pyrolysis or combustion of the insoluble lignin residue

No process alone allows represents the optimum treatment. Figures 6.2, 6.3 and 6.4 show some hypothetical plausible plant configurations, which integrate the biochemical, chemical, thermal processes, and eventually incineration, for the treatment of municipal bio-waste. Obviously, many other configurations are possible. The optimum one should be worked out for each bio-waste type.

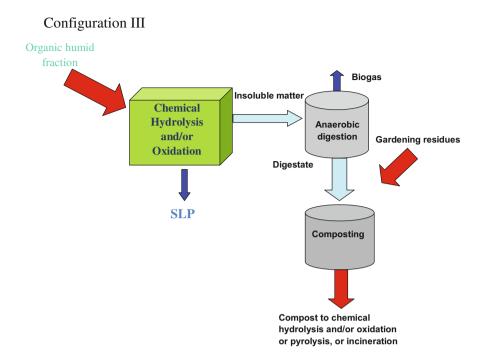
The plant configurations in Figs. 6.2, 6.3 and 6.4 are hypothetical, since the bio-waste chemical hydrolysis and/or oxidation process are not operating in real environment, yet. However, at laboratory and 500 L capacity pilot plant scale, several soluble bio-based polymeric substances with molecular weight ranging from 14 to several hundred kDa have been obtained by acid and/or alkaline hydrolysis at 60–100 °C of different urban (Rosso et al. 2015; Franzoso et al. 2015a, b, c; Nisticò et al. 2016) and agriculture (Franzoso et al. 2015b, c, 2016; Baglieri et al. 2014) residues, as collected and after anaerobic and/or aerobic biodegradation. The acid hydrolysates have at least one order of magnitude lower molecular weight than the alkaline hydrolysates. All products contain aliphatic and aromatic C types, and several acid and basic functional groups. The acid hydrolysates contain mainly polysaccharide moieties. The alkali hydrolysates contain mainly lignin-like aromatic moieties. Hereinafter, these polymers will be referred to according to their



**Fig. 6.3** Possible configuration of biochemical, chemical and thermal processes for the treatment of municipal bio-waste: composting of the anaerobic digestate mixed with gardening residues (as the Acea process in Fig. 6.1), which is followed by the chemical hydrolysis of the compost for the production of soluble lignin biopolymers (SLP), and ultimately by pyrolysis or combustion of the insoluble lignin residue

solubility properties and main constituents, i.e. soluble saccharide polymers (SSP) and soluble lignin-like polymers (SLP). The above chemical features are reported to be associated to surface-active properties. The higher molecular weight SLP exhibit similar behaviour as small molecule surfactants at concentration lower than 2 g  $L^{-1}$  in water, whereas they behave more likely polyelectrolytes at higher concentration (Montoneri et al. 2010). Composted urban bio-wastes contain more lignin-like matter than the as collected wastes. This is the likely reflection of microbial biodegradation converting the pristine polysaccharide matter to carbon dioxide and water, but not capable to metabolize lignin as well.

For the production of the SLP, a completely green process has been developed at pilot scale (Sortino et al. 2014). In the process, the reaction of the bio-waste feed and water at alkaline pH is performed at relatively mild temperature. The liquid hydrolysate is separated from the insoluble solid. The former is fed to a 5 kDa cut off ultrafiltration membrane. The membrane retentate is dried to yield the SLP. The permeate is recycled to the hydrolysis reactor for further use. Both the SLP and the insoluble product have been proven useful in multiple applications in the chemical industry and/or agriculture (see next subsection). Thus, in the above process,



**Fig. 6.4** Possible configuration of biochemical, chemical and thermal processes for the treatment of municipal bio-waste, featuring the chemical treatment of the as collected organic humid fraction of municipal bio-waste to produce the soluble lignin biopolymers (SLP), and thus to reduce the lignin content of the feed to the anaerobic digestion reactor. The successive steps are similar to those in Fig. 6.2

solvent and reagent are completely recycled, and no waste is produced, which requires a secondary treatment. Furthermore, most recent work (Rosso et al. 2015) has investigated an alternative hydrolysis process carried out by microwave heating, compared to conventional heating. Non-conventional energy sources such as microwave, compared to conventional heating, can dramatically enhance reaction rates in organic synthesis (Tabasso et al. 2014) and thus allow reducing reagents contact time (Hu and Wen 2008) and reactor volume. This, in principle, is an important step toward the construction of plants that are more compact, cost-effective and safer (Sanders et al. 2012). Therefore, the hydrolysis of a composted municipal bio-waste, taken as case study, has been investigated (Rosso et al. 2015) as a function of solid-liquid contact time, temperature, liquid/solid ratio, and pH. It has been found that similar product yield and type are obtained by conventional and microwave heating. However, by microwave heating, the required solid/liquid contact time is over two order of magnitude shorter than by conventional heating. These findings offer worthwhile scope for further work aimed to compare microwave and conventional heating options for operational and capital costs.

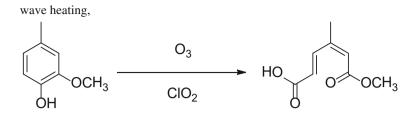


Fig. 6.5 Oxidation of lignin

Room temperature oxidation of SLP has been reported very recently (Montoneri et al. 2016). According to literature (Brunow et al. 1998; Niemel et al. 1985), ozonisation of native lignin destroys double bonds and aromatic rings, leaving the side chains intact in the form of carboxylic acids (Fig. 6.5). In this fashion, the reaction in Fig. 6.5 can ultimately lead to the formation of four C atoms dicarboxylic moieties, –(HOOC)CH–CH(COOH). Application of this reaction to SLP has allowed converting the pristine lignin aromatic ring to aliphatic carboxylic moieties. Thus, new oxidized, and/or more hydrophilic biopolymers have been obtained. These are high molecular weight biosurfactants, with improved colour and surface activity properties, and lower molecular weight aliphatic polycarboxylic acids are higher oxidation products. These have no surface activity. However, they are potentially valuable for the manufacture of biodegradable polymers (Chiellini and Solaro 2003) and/or value added small platform molecules (Quesada et al. 1999; Clark et al. 2014) to recycle to the chemical industry.

The SSP production process (Franzoso et al. 2015a, b) was not investigated as well as the SLP process (Rosso et al. 2015). The SSP were mainly products of the acid hydrolysis of the bio-waste polysaccharide fraction, and therefore were out of the scope focused on the valorisation of lignin. In the treatment of bio-waste, polysaccharides constitute the fermentable organic fractions. Thus, the SSP are mainly regarded as intermediates for the production of small molecules, such as methane or bioethanol, by fermentation. In the context of the work focused on the valorisation of lignin, the SSP products were obtained to assess, by comparison with SLP, their performance for the manufacture of composite biodegradable polymers. The results, described hereinafter, did not warrant further development work dedicated to SSP.

# 6.4 Bio-waste Lignin Valorisation (LV): Applications of Products Derived from Urban Food and Agriculture Wastes

Several papers have reported the performance of the above SLP, and/or SSP, in diversified fields; e.g. in the formulation of detergents, textile dyeing baths, flocculants, dispersants and binding agents for ceramics manufacture



Fig. 6.6 Schematic representation of the sourcing urban bio-wastes, materials obtained by anaerobic and aerobic digestions, and virtual molecular fragment and application fields of soluble bio-based substances obtained by chemical processing of digestate and compost materials by hydrolysis

(Montoneri et al. 2011), emulsifiers (Vargas et al. 2014), auxiliaries for soil/water remediation (Montoneri et al. 2014; Avetta et al. 2013; Gomis et al. 2014; Mostofa et al. 2013), and enhanced oil recovery (Baxter et al. 2014), nanostructured materials for chemical (Boffa et al. 2014; Deganello et al. 2015; Testa et al. 2015) and biochemical catalysis (Magnacca et al. 2012), plastic materials (Franzoso et al. 2015a, b, c, 2016; Nisticò et al. 2016), soil fertilizers and plant biostimulants for agriculture (Sortino et al. 2014; Baglieri et al. 2014; Sortino et al. 2013; Fascella et al. 2015; Rovero et al. 2015; Mozzetti Monterumici et al. 2015; Massa et al. 2016), animal feed supplements (Dinuccio et al. 2013; Biagini et al. 2016; Montoneri et al. 2013), and auxiliaries for eco-friendly anaerobic fermentation of urban bio-wastes (Francavilla et al. 2016a, b) and manure (Riggio et al. 2016).

The wide range of applications arises from the fact that these bio-based soluble products are constituted by a mix of polymeric molecules containing organic C and N distributed over a variety of aliphatic and aromatic C moieties substituted by acid and basic functional groups which are bonded to several mineral elements such as Na, K, Ca, Mg, Al and Fe. Figure 6.6 shows a virtual molecular fragment representing the SLP organic chemical features. The C moieties in this fragment are the memories of the protein, fats, polysaccharide and lignin proximate constituting the pristine bio-waste.

They are associated to the products properties as surfactants, agents for sequestering or carrying small molecules and mineral ions in solution, photosensitizers and reactive biopolymers.

One main drawback of the bio-based listed in Fig. 6.6 is the black colour. This is a critical feature in surfactant assisted fabric detergency and textile dyeing. Fabric yellowing has been found to be the critical deficiency in SLP assisted washing (Savarino et al. 2010) or dyeing (Savarino et al. 2009). The results of previous work on the ozonisation of native lignin (Brunow et al. 1998; Niemel et al. 1985) allowed expecting that ozonisation of SLP would destruct the lignin-like aromatic chromophores' moieties and thus yield lighter coloured products. Montoneri et al. (2016) have reported that this is true. The high molecular weight oxidized biosurfactants are light coloured and have improved surface activity properties, compared to the pristine SLP. Thus, wider marketability opportunities are expected for the oxidized SLP biosurfactants.

Based on product performance and/or potential marketability for the tested applications, at the current state of product development, the short term most feasible and appealing uses of SSP and SLP seem to be in agriculture, plastics manufacture, and in anaerobic digestion processes. In a few cases, the performance of SLP in agriculture was studied in comparison with the insoluble hydrolysate product recovered together with SLP. Similarly, to SLP, the insoluble product was proven a valid fertilizer for the cultivation of several food (Sortino et al. 2014; Rovero et al. 2015) and hornamental (Massa et al. 2016) plants.

### 6.4.1 Performance and Perspectives for SLP Used in Agriculture

Several universities (Sortino et al. 2014; Baglieri et al. 2014; Jindřichová et al. 2016), the Italian center of agriculture research (Fascella et al. 2015; Massa et al. 2016) and Isagro SpA (2014), a company operating on a global level, in about 70 countries, in the market of agropharmaceuticals, have studied effects of SLP as auxiliaries for agriculture. The addition of SLP to soil at 145 kg  $ha^{-1}$  dose has been found to increase significantly tomato and red pepper plant photosynthetic activity, growth and productivity, and/or product quality, by 10-20% relatively to farm routine practice with no SLP soil treatment (Sortino et al. 2014). Compared with most biofertilizers used at 20-30 t ha<sup>-1</sup> dose, the effect/dose ratio exhibited by SLP appears guite remarkable. It prospects several economic and environmental benefits for farmers and soil, respectively. Isagro (2014) has proven the beneficial effects of SLP on tomato, as well as on wheat and tobacco. Other workers have demonstrated that the hydrolysates of urban bio-wastes and post-harvest agriculture residues are capable to enhance growth, productivity, and/or plant photosynthetic activity and protein production, for a variety of other plants such as maize (Fascella et al. 2015), beans (Franzoso et al. 2016), radish (Monzetti Monterumeci et al. 2015),

**Table 6.2** Increments (w/w%) of crop production (unless otherwise specified) for different plants cultivated in the presence of SLP from different urban and agriculture source,<sup>a</sup> relative to control plants with no added SLP

Plant	CVDF	CVD	CV	D	TP
Tomato Lycopersicon <sup>b</sup>	20	20	20		
Tomato Micro Tom <sup>c</sup>	46		1	16	
Pepper <sup>d</sup>		66			
Maize <sup>e</sup>	120				
Bean <sup>f</sup>					77–278 <sup>j</sup>
Radish <sup>g</sup>					0
Wheat <sup>c</sup>	10		9	9	
Tobacco <sup>c</sup>	6		0	0	
Euphorbia <sup>h</sup>	233			117	
Hibiscus <sup>i</sup>			15 <sup>k</sup>	25 <sup>k</sup>	

<sup>a</sup>Digestate (D) from anaerobic fermentation of urban organic humid waste; compost made from gardening residues (CV), and from their mixes with D (CVD) and with D and sewage sludge (CVDF); post-harvest tomato plant (TP)

<sup>b</sup>Sortino et al. (2014) <sup>c</sup>Isagro (2014) <sup>d</sup>Sortino et al. (2013) <sup>e</sup>Rovero et al. (2015) <sup>f</sup>Baglieri et al. (2014) <sup>g</sup>Mozzetti et al. (2015) <sup>h</sup>Fascella et al. 2015 <sup>i</sup>Massa et al. (2016) <sup>j</sup>Biomass protein production <sup>k</sup>Total biomass weight

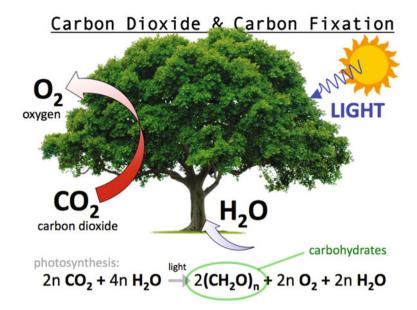


Fig. 6.7 Photosynthesis reaction promoting plant growth

euphorbia x lomi (Fascella et al. 2015), and hibiscus (Massa et al. 2016). The SLP have also been proven efficient plant disease suppressants (Jindřichová et al. 2016).

All performance tests have compared the alkaline soluble hydrolysate product and/or the insoluble hydrolysate product with known commercial products for their effects on several plant response indicators. Some tests have compared the SLP with their pristine sourcing materials, and/or with the insoluble hydrolysate product. In all cases, the SLP effects have been found equal or better than the products investigated for comparison. Table 6.2 summarizes the effects of the SLP obtained from different urban and agriculture wastes on the productivity of investigated plants. The effects clearly depend on the type of SLP and the tested plant. This fact implies that a waste treatment plant may produce a wide variety of SLP tailored for the cultivation of specific plants, depending on the variety of bio-waste sources, treatments types and processes configuration (Figs. 6.2, 6.3 and 6.4).

In this context, particularly interesting is the work by Sortino et al. (2013, 2014) pointing out a possible role of SLP as interphase between agriculture and human activities. These authors discuss the effects of SLP on plant photosynthetic activity in relation to other work (Gomis et al. 2014) that reports SLP as photosensitizer promoting C mineralization of organic pollutants. They propose that, depending upon the experimental conditions, SLP could promote C fixation or mineralization. Both processes occur in nature (Mostofa et al. 2013). The first promotes plant growth through photosynthesis (Fig. 6.7), starting from carbon dioxide and water. The second is the opposite process. It occurs in soil and water, and converts natural organic matter into carbon dioxide and water.

natural organic matter displays physical properties such as the absorption of energy form ultraviolet and photosynthetically available radiation. By their chemical nature (Montoneri et al. 2011) and properties (Sortino et al. 2014; Montoneri et al. 2010) the SLP have been shown to resemble natural organic matter. The idea that SLP may promote either C fixation or mineralization is rather intriguing. It proposes a virtuous role of SLP entering the C cycle to generate benefits for agriculture and the environment.

### 6.4.2 Performance and Perspectives for SSP and SLP Used for Plastics Manufacture

Both the soluble saccharide (SSP) and lignin-like (SLP) bio-polymers, isolated from municipal bio-waste and/or agriculture residues, have been tested as components of blended films with synthetic polyethylene copolymers (Franzoso et al. 2015a, b, c, 2016; Nisticò et al. 2016), i.e. polyvinyl alcohol-co-ethylene (EVOH) and polyethylene-co-acrylic acid (PEEA). These commercial polymers derived from fossil sources are used for the manufacture of a great variety of articles of every-day life. Research for substituting synthetic polymers with bio-waste derived polymers is justified by a number of presumed economic and environmental benefits for the chemical industry and the management of wastes. They include lower consumption of fossil sources, availability of articles that are more compatible with the environment, and the valorisation of the bio-waste sourced products as speciality chemicals.

The realization of these perspectives implies the indispensable and essential conditions that the performance was not lower, and the cost of the biobased article was not higher, compared to the current commercial articles. For the SSP and SLP blends, the reported results (Franzoso et al. 2015a, b, c, 2016) have demonstrated that the above performance condition is satisfied by the blends containing not more than 10% SSP or SLP. Blends with higher biopolymers content have poor unacceptable mechanical properties.

Table 6.3 summarizes the mechanical properties of the best performing SSP and SLP blends. An important property of polymers, which conditions their end-uses, is the response to the application of a force, as indicated by two main types of behaviour: elastic and plastic. Elastic materials will return to their original shape once the force is removed. Plastic materials will not regain their shape. Most materials demonstrate a combination of elastic and plastic behaviour, showing plastic behaviour after the elastic limit has been exceeded. For plastic films, the most common indicators of mechanical properties are the Young's modulus and the strain at break (The engineering toolbox 2013). The Young's Modulus or Modulus of Elasticity is a measure of stiffness of an elastic material. It is used to describe the elastic properties of the material when it is stretched. It can be used to predict the

Sample	Young's modulus (MPa)	Stress at yield point or maximum stress (MPa)	Strain at break (%)	Stress at break (MPa)
EVOH	352	33	86	26
EVOH-SSP <sub>T</sub> 0.1	747	43	$35 \pm 2$	32
EVOH-SLP <sub>T</sub> 0.1	389	44	$14 \pm 3$	41
EVOH-SSP <sub>IR</sub> 0.1	1043	39	$70 \pm 10$	32
EVOH-SLP <sub>M</sub> 0.06	352	53	40	0
EVOH-SLP <sub>D</sub> 0.06	1082	62	42.3	44
PEAA	30.4	4.7	>300	10.6
PEAA-SLP <sub>M</sub> 0.1	76.1	9.3	280	13.5
PEAA-SLP <sub>M</sub> 0.2	135.6	13.7	257	19.3
PEAA-SLP <sub>M</sub> 0.3	172.2	17.1	55	16.1
PEAA-SSP <sub>IR</sub> 0.1	23.9	4.4	>300	9.9
PEAA- SSP <sub>IR</sub> 0.2	43.4	6.7	>300	15.1
PEAA- SSP <sub>IR</sub> 0.3	23.8	4.6	>300	9.1
	Extruded rods			
	Bending modulus (MPa)	Flexural strength (MPa)		
EVOH	3900	118		
EVOH-SLP <sub>D</sub> 0.05	3100	102		
EVOH-SLP <sub>D</sub> 0.1	3000	108		
EVOH-SLP <sub>V</sub> 0.05	3300	113		
EVOH-SLP <sub>V</sub> 0.1	3000	101		

Table 6.3 Mechanical data for different SSL and SLP blend films with synthetic polymers

Mechanical data for different SSL and SLP blend films with synthetic polymers obtained by solvent casting (unless otherwise indicated): *EVOH* neat polyvinyl alcohol-co-ethylene; *PEAA* neat polyethylene-co-acrylic acid; A–B  $\rho$  blends: A EVOH or PEAA; B soluble saccharide polymer by acid hydrolysis of tomato plant powder (SSP<sub>T</sub>) or of the insoluble residue after alkaline hydrolysis (SSP<sub>IR</sub>), or B soluble lignin polymer by alkaline hydrolysis of urban bio-waste digestate (SLP<sub>D</sub>), of compost of urban vegetable gardening residues (SLP<sub>V</sub>), and of compost of mixed urban vegetable gardening residues, digestate and sewage sludge (SLP<sub>M</sub>);  $\rho = B/A$  w/w ratio in the blend. Data selected from published work for best performing SLP<sub>M</sub> and SLP<sub>D</sub> blends (Franzoso et al. 2015a), PEAA blends (Franzoso et al. 2015c) and extruded blends

elongation of the object as long as the stress is less than the yield strength of the material. The stress at yield point is the applied force above which the material acquires a permanent deformation. Above this point, further applied stress causes elongation of the material until fracture (Key to Metals AG 2014). The strain at break is the % elongation of the material until it breaks. The stress at break is the tensile stress when the test specimen tears (Ensinger Gmbh n.d.).

For rigid objects, indicators of their end-use performance are the bending modulus and the flexural strength. The bending modulus indicates the tendency for a material to bend (wiseGEEK n.d.). It is a measure of how a certain material will strain when weight or force is applied to bend it, before a permanent deformation occurs. The flexural stress is the maximum amount of bending stress that can be applied before rupture or failure of the material occurs. The data reported in Table 6.3 show in most cases that the poly vinyl alcohol-co-ethylene blends, which contain 6% SLP obtained from the Acea urban food wastes anaerobic digestate (EVOH-SLP<sub>D</sub>0.06) and 10% SSP obtained from post-harvest tomato plant (EVOH-SSP<sub>IR</sub>0.1) exhibit up to three times higher stiffness, but lower strain at break than the neat synthetic polymer (Franzoso et al. 2015a). The EVOH blends containing the soluble lignin-like polymers SLP biopolymers obtained from the bio-waste digestate (EVOH-SLP<sub>D</sub>0.06) and from the compost (EVOH-SLP<sub>M</sub>0.06) exhibit higher maximum stress than the EVOH blends containing the soluble saccharide or lignin-like polymers obtained from post-harvest tomato plants. This means that the blends containing the soluble lignin-like polymers obtained from urban bio-wastes, compared to the neat synthetic polymer and to the blends containing the tomato plant sourced biopolymers, can bear higher load before undergoing permanent deformation. However, their elongation before breaking is significantly reduced, compared to the neat synthetic polymer. Similar trends are shown by the polyethylene-co-acrylic acids blends, although it is much less evident the relative decrease of the strain at break for the blends, compared to the neat synthetic polymer. Also in the case of the polyethylene-co-acrylic acid blends, the films containing the soluble lignin-like polymers (PEAA-SLP) compared to the neat synthetic polymer and to the films containing the soluble saccharide biopolymers, exhibit higher Young's modulus and stress at yield point, but lower strain at break. This behaviour is the likely reflection of the different chemical nature of the two biopolymers. The soluble lignin-like polymers save the memory of the parent lignin, a though not ductile material, compared to polysaccharides. The melt extruded poly vinyl alcohol-co-ethylene blends could be obtained with SLP, but not with SSP. The latter did not withstand the 200 °C processing temperature of the melt extrusion. The extruded EVOH blends containing the SLP exhibited lower bending and flexural strength, compared to the neat synthetic polymer. The results indicate that it is possible to enhance the mechanical strength of the tested synthetic polymers. However, this occurs with some loss of the elongation capacity. The blend properties appear to depend strongly, not only on the type of and content of biopolymers (i.e. soluble lignin-like versus soluble saccharide biopolymers), but also on the processing technology.

The SLP blends mechanical data, coupled to the effects of the SLP in agriculture, prospect a virtuous scenario where mulch film fabricated with the above reinforced blends, at end of their service life, might contribute their beneficial properties to plants. From the economic point of view, substitution of 5-10% of synthetic polymers with SLP is expected to be cost effective (see Sect. 6.5.2).

# 6.4.3 Performance and Perspectives for SLP Used in Anaerobic Digestion Processes

The improvement of current municipal bio-waste anaerobic fermentation processes is pending upon the achievement of two main objectives (Al Seadi et al. 2008; Sereno 2010): i.e. enhancing the biogas  $CH_4/CO_2$  ratio and reducing the mineralization of organic N. The former is directly related to the biogas heat value. The other has relevance for the environmental impact of the process digestate. In both cases, ammonia has an important role. Ammonia inhibits methanogenic bacteria, which are especially sensitive to this compound. Ammonia is collected with the digestate. This is normally recycled to farmland. Ammonia emission and/or nitrate leaching can occur due to inappropriate handling, storage and application of digestate as fertiliser (Martins 1992).

The European Nitrate Directive (91/676/EEC) restricts the input of mineral nitrogen on farmland, aiming to protect the ground and surface water from pollution. Downstream technology is available for separating CH<sub>4</sub> from CO<sub>2</sub> and for removing excess inorganic N from the digestate (Zhao et al. 2010; Mirbagheri et al. 2010; Provolo and Riva 2009). This however requires additional process costs, which affect negatively the waste treatment economy and in turn on taxpayers. The separation of CH<sub>4</sub> from CO<sub>2</sub> in the biogas and the abatement of ammonia from the digestate can run 0.13–0.44  $\in$  N m<sup>-3</sup> biogas (Zhao et al. 2010) and 1.6 \$ kg<sup>-1</sup> N (Burke 2013), respectively. The problem of organic N mineralization is well known also in animal husbandry, which in turn affects agriculture. These two activities are strongly interrelated in as much as agriculture provides feed for animals and these provide manure to recycle to soil as fertilizer for agriculture. Proteins are the main source of ammonia during animal feed digestion, due to proteolytic bacteria activity. Indeed, deficient intestinal fermentation results in increased proteolysis and release of toxic substances, such as ammonia and amines. In this fashion, manure may have negative environmental impact, because of greenhouse gases emission and leaching of mineral nitrogen through soil and ground water. For example, the typical levels of aerial ammonia in a pig farm facility vary from 5 to 35 ppm (Ji et al. 2006), while suggested threshold limit values of ammonia concentration are at 25 ppm level. Greater aerial ammonia level not only reduces the pig growth, but also is harmful to human health.

Recently, various SLP have been tested (Montoneri et al. 2013) as diet supplements to modulate pigs ileal fermentation of a protein feed. These were isolated from the soluble hydrolysates of different streams from the Acea waste treatment plant: i.e. the digestate, and several composts made from the digestate, gardening wastes, and sewage sludge, alone or mixed in different relative weight ratios. The study was carried out in vitro, using the cecal content collected from slaughtered pigs as incubation liquor. The reported results clearly point out reduced proteolysis and N mineralization by 7–17% caused by the compost derived SLP added to the fermentation liquor at 0.1-0.2% concentration. The digestate derived SLP has opposite effect. Consistently with these findings, in vivo animal study were

performed (Dinuccio et al. 2013; Biagini et al. 2016), by feeding rabbits with diet supplemented containing 0.05 and 0.25% of SLP isolated from the composted gardening wastes. The reported results demonstrate 25% reduction of ammonia emission from freshly produced manure of rabbits fed with diet containing 0.25% SLP (Dinuccio et al. 2013; Montoneri et al. 2013) and no toxicity for animals by SLP (Biagini et al. 2016). Following these findings, four materials were sampled from the case study Acea plant (Fig. 6.1). These were the as collected bio-waste organic humid fraction, the digestate sampled from the anaerobic fermentation reactor, the compost made from a digestate-gardening waste mix (Francavilla et al. 2016b) and the compost made from gardening waste only (Francavilla et al. 2016a). The SLP were then obtained from the two compost and added in separate lab experiments to 6 L bioreactors containing a mix of the as collected organic humid fraction and digestate, similar to that contained in the plant bioreactors in routine operation. The intent was to assess whether the same ammonia reduction effects by SLP, which had been found in the above animal studies (Mozzetti Monterumeci et al. 2015; Montoneri et al. 2013) occurred in the anaerobic digestion of the organic humid fraction of urban waste, which was normally processed in the Acea plant. In the lab experiments (Francavilla et al. 2016a, b), the SLP obtained from the two different composts were added at 0.05 and 0.20% concentration to the fermentation liquor sampled from the Acea anaerobic digestion reactor. The anaerobic digestion of the control (no added SLP) and the treated (added SLP) fermentation liquor was carried out in parallel reactors operated at 55 °C for 12 days, until the biogas production became negligible. During this time, the control and treated fermentation liquor produced the same amount of biogas. However, the ammonia content of the control fermentation increased by 24%. On the contrary, the fermentation liquors, containing 0.05 and/or 0.20% added SLP, produced no ammonia. In addition, the methane/carbon dioxide mol/mol ratio in the biogas produced by the fermentation liquor containing 0.20% SLP was apparently about 9% higher than that of the control liquor. The results obtained with the two different SLP indicated that the above effects were different upon changing the bio-waste feed and the type of added SLP. This finding offers worthwhile scope for further research scope in order to optimize the type and amount of SLP as a function of the bio-waste feed. Aside from this, for a municipal waste treatment plant as the case study Acea plant (Fig. 6.1), the lab scale results obtained in the SLP assisted anaerobic digestion of the urban organic humid fraction (Francavilla et al. 2016a, b) prospect the realization of a virtuous in-house material cycle with attracting potential economic and environmental benefits. In essence, the plant biogas digestate would be exploited as source of SLP to be added to the biogas reactor, in order to produce digestate with reduced ammonia content and biogas with enhanced methane content. This scenario offers the highest potential economic benefits to the case study Acea plant (see Sect. 6.5.1), as well as to any other similar plant that integrated its anaerobic and aerobic fermentation processes with the compost chemical hydrolysis facility producing the SLP. The plant, in fact, could take advantage from the lower in-house SLP production cost in place of the ammonia abatement costs with the current technology (Table 6.3; Sect. 6.5.1).

The above results obtained for the anaerobic digestion of urban bio-waste are highly relevant also in other contexts. A very important one is animal manure, which is a strong source of ammonia emission (Ji et al. 2006). The entire manure production in the EU is estimated 1.4 billion t  $yr^{-1}$  (Foged et al. 2012). This production results from a myriad of farms spread over large areas (Eurostat 2016). Thousands of anaerobic digestion installations throughout EU member states are currently processing only about 8% of the manure production, equal to 108 million t  $yr^{-1}$ , containing 556,000 t nitrogen. These range from small on-farm to large centralized facilities. The available technology for the secondary treatment of the manure digestate (Burke 2013; Zarebska 2015) requires high capital cost investments, which cannot be borne by small farms. It is obvious that these circumstances require a simple economically sustainable solution to the problem of ammonia production in the anaerobic fermentation of manure. This solution should be applied locally, in on-farm installations of any size, thus avoiding collection and transportation costs of the digestate to larger centralized plants for secondary treatment. The results obtained in the SLP assisted anaerobic digestion of urban bio-wastes (Francavilla et al. 2016a, b) prospect that anaerobic digestion in the presence of SLP does not require secondary treatment of the digestate for reducing the ammonia content, and that therefore no capital cost for digestate processing facilities is necessary. Based on these perspectives, Riggio et al. (2016) have investigated the anaerobic digestion of cow manure in the presence of 0.2% SLP. They found that the addition of SLP to the fermentation slurry inhibited the production of ammonia during the manure fermentation. These findings offer further environmental and economic argument for scaling the SLP production to commercial level.

# 6.5 Scaling Promising Technology to Commercial Production Level

Assessing the feasibility of transferring new technology to the market place must take in consideration its promising aspects as well as the impeding factors. For the above-described LV technology, promising features are the following ones. Firstly, urban bio-wastes are negative cost sources (Sheldon-Coulson 2011). Secondly, the hydrolysis process has been tested at prototype level by conventional heating, and a preliminary operational cost evaluation has been obtained (Montoneri et al. 2011). Thirdly, products have been tested for their performance as speciality chemicals at laboratory level and in representative environment (Rosso et al. 2015). Fourthly, the above described research has involved cooperation of the author at the University of Torino and several other public research institutions (see references in Sect. 6.4), and potential end-users of the collected research results, such as Acea (Montoneri et al. 2011; Francavilla et al. 2016a, b) and Isagro (2014). By these features, according to the Nasa (2015) and the European Commission technology readiness level (TRL) definitions (European Commission 2014), the LV technology TRL may be estimated 4-5. The assignment of TRL numbers to processes and products allows a common understanding of technology status, helping decisions that concern the

development and transitioning of technology, and evaluating the connected risk (United States Department of Defense 2011). Guidelines for converting research into commercial success have been published (European Commission 2013, 2016). There are some conditions for a successful scale up of process/product from research (TRL 5) to industrial/commercial (TRL 6-9) level:

- The production process must be economically and environmentally viable
- A sizable market exists
- The product is accepted by the consumer
- All players, with the proper knowledge on resource acquisition, production technology and product marketability, are actively involved.

In the specific case of the LV technology, the SLP products have been obtained by assessed biochemical processes (i.e. anaerobic digesting and composting) coupled to pilot chemical hydrolysis. The chemical process is a green process. It involves the hydrolysis of the bio-waste in water at relatively low temperature ( $60 \,^{\circ}$ C), low energy consumption, complete recycle of solvent and reagents, no formation of unusable product to dispose, and no need of secondary process effluent treatment. The above biochemical and chemical processes have been shown to convert natural cellulose, lignin, protein and fat matter present in urban food and/or gardening wastes, and/or in post-harvest plants, to several SSP and SLP products. As cellulose, lignin, proteins and fats are the major organic constituents of living matter, the above biochemical and chemical processes can be applied to most dedicated crops and bio-organic residues. Thus, an even wider range of products can be obtained, depending on the starting bio-organic material. These features are basic requirements for a successful market-oriented exploitation of the developed bio-waste processes and products (European Commission 2013).

Fulfilling all conditions for successful scale up of the LV technology to commercial production level requires the active participation of different operators, which have proven know how in diversified fields, such as waste collection and management, process engineering, and product technological development and marketing. A recent study (Morone et al. 2015), taking the Italian bioplastics market as case study, has performed a social network analysis to assess the potential of bio-waste for bioplastics production. It shows that the Italian bioplastics producers' network offers great opportunities for the development of a technological niche based on bio-waste valorisation. However, the system is weak especially as far as expectations are concerned, as these are generally low and, more critically, are low for those actors occupying central positions in the network. This shortcoming could jeopardize the niche development process, if no appropriate policy actions are undertaken. More specifically, this study could support decision makers in developing specific strategies to unlock the enormous potential of bio-waste as well of the bioplastics sector by empowering knowledge creation and its diffusion, and by supporting strategic collaboration schemes. For instance, policy measures could be introduced to stimulate social learning as a driver of expectations.

Another study (Sheldon-Coulson 2011) has evaluated the commercial viability of cellulosic bio-refineries in the urban corridor linking New York and Philadelphia. A mature technology such as the non-commercialized Biofine process was taken as case study. This process has been realized at demo scale to obtain the well-known multipurpose platform chemical levulinic acid from carbohydrate feedstock. The results of the study indicate extremely healthy economic returns by scaling up the demo plant to commercial production. However, these returns are not high enough to convince private entrepreneurship to undertake the technology and integration risk of an early stage-venture, without public participation to share the relevant risks.

While the above levulinic acid is a well-known product, risks are even higher, and particularly critical, in the case of new products for several reasons:

- Product not known in the market.
- Difficulty to identify the right market type, and assess the product market desirability, sale value and saleable amount.
- Allocation of the product in government approved marketed product categories and/or development, implementation, assessment, monitoring and evaluation of environmental policy and legislation dedicated to a new product category.

Products such as thermal and/or electrical energy, and fuel, hydrocarbons or platform chemicals with well-defined chemical structure and composition, obtained by bio-waste combustion and pyrolysis, respectively, have a well-assessed market. The SLP do not fall into such categories. They are new products, need market assessment, and therefore imply higher risks for private entrepreneurship. On the other hand, their social impact is much lower than that of energy and fuel. Thus, for politicians, chemical products are less relevant, due to their lower social impact compared to fuel, and thermal and electrical energy. This fact, for the specific case of the LV technology, implies unlikely assumptions of new venture risks by public bodies.

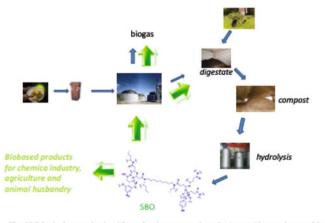
Notwithstanding the above limitations, the finding that SLP may be used as regulator of the bio-waste anaerobic digestion process (Francavilla et al. 2016a, b) offers an attracting opportunity to undertake innovation business with reduced entrepreneurial risk. Indeed, considering the Acea waste management plant (Fig. 6.1) as case study, the integration of the SLP production unit into the existing Acea facility would allow benefiting from the on-site availability of bio-wastes, all necessary utilities and land space, at minimum cost. If SLP was produced only for in-house use (i.e. addition to the biogas production reactors to obtain digestate with reduced ammonia content), no market product allocation would be necessary. Therefore, the above listed risks would not apply. The availability of the SLP production unit for in-house use would allow proceeding cautiously and efficiently to a second scale up stage. Indeed, upon completion of the first stage, enough SLP quantities would be used (see Sect. 6.4.1). Under this condition, further product development and market assessment tests would be carried on in real operational

environment, in order to proceed to full-scale production and product commercialization.

The above strategy would allow optimizing risk management. With reference to the EU proposed types of pathways of market-oriented exploitation (European Commission 2016), the first stage, not necessarily requiring additional research activity, implies a linear and prompt conversion of research outcome into a ready for use technology. The success of this stage does not depend on technology commercialization. Nevertheless, upon completion, it has great potential for optimization and commercialization. The second stage certainly needs additional research activity for product development and market allocation. It sets out as the deferred transformation of research outcome into a product or service available to or ready for the market. Thus, the success of the second stage ends up for depending strongly on product commercialization. The following sustainability evaluation regards the above two acts play, involving one actor in the first act and more actors in the second act. With reference to the range of demonstrated applications (Fig. 6.6), the applications in agriculture and in plastics manufacture seem the most promising ones, based on product maturity and market size. Hereinafter, the estimates of the potential economic impact of adopting this two acts strategy are given for the Acea plant taken as case study.

# 6.5.1 Economic Impact of SLP Production

Figure 6.8 shows a possible virtuous bio-waste material flow through the Acea plant. It involves the existing anaerobic and aerobic digestion sections, integrated with the compost hydrolysis facility to be installed. The key feature is that SLP is



The SBO hydrolysate obtained from food wastes and gardening residues enhances biogas production, lowers ammonia in the digestate, and yields multipurpose biobased products

**Fig. 6.8** Production of SLP (SBO in the figure) from municipal bio-wastes (*blue arrow*), and (*green arrow*) using SLP as additive to the in-house biogas production reactor for ammonia abatement and for the manufacture of multipurpose products for the external market

	Amount (t year <sup>-1</sup> )	$N_{NH3}$ abatement cost ( $\in$ year <sup>-1</sup> )	Facility capital cost (M€)
Organic humid fraction slurry feed to bioreactors	100,000		
N <sub>NH3</sub> amounts in feed	126		
N <sub>NH3</sub> amounts in digestate	156		
N <sub>NH3</sub> production	30		
N <sub>NH3</sub> abatement by 0.05% SLP	25		
Required SLP	50	5,000-25,000	0.2-0.3
Cost of $N_{NH3}$ abatement by conventional technology, $1.4 \in kg^{-1}$		35,000	1–2

Table 6.4 Comparison of ammonia Nitrogen ( $N_{NH3}$ ) abatement costs by conventional and SLP assisted technology for the Acea anaerobic digestion process

produced from the plant compost and used within the same plant to carry on the in-house SLP assisted anaerobic digestion process. The economic impact is expected from the SLP in-house use and from its allocation in the external market of biosurfactants, agriculture auxiliaries and plastics materials. The possibility to allocate the SLP in these markets offers further incentives for implementing SLP production in excess of the amount needed for the plant in-house use.

#### **SLP In-house use**

Table 6.4 reports some pertinent figures based on the virtuous cycle depicted in Fig. 6.8. The figures in the Table are extrapolated according to the following current plant feed and on ammonia abatement rate measured in laboratory studies (Francavilla et al. 2016b). The case study Acea plant processes by anaerobic digestion 100,000 t year<sup>-1</sup> of the municipal bio-waste fermentation slurry. Under normal operational condition, the ammonia nitrogen (N<sub>NH3</sub>) amounts in the bioreactor feed and digestate liquor at fermentation end are 126 and 156 t year<sup>-1</sup>, respectively. The process therefore produces 30  $N_{NH3}$  t year<sup>-1</sup>. The fermentation in the presence of SLP 0.05% will allow abating 25  $N_{NH3}$  t year<sup>-1</sup>, 83% of the yearly N<sub>NH3</sub> production in the absence of added SLP. This will require however production of 50 SLP t year<sup>-1</sup> with a cost of  $5-25 \times 10^3 \text{ }\text{e} \text{ year}^{-1}$ . The cost of abating 25  $N_{NH3}$  t year<sup>-1</sup> by the conventional technology (Burke 2013) would be 35 k  $\notin$  year<sup>-1</sup>. The capital cost of a plant producing 50 SLP t year<sup>-1</sup> is estimated 200– 300 k€. By comparison, the capital cost of the conventional facility for the abatement of the above N<sub>NH3</sub> amounts is about one order magnitude higher. The data shows that operational cost savings of 5–30 k $\in$  year<sup>-1</sup> would be obtained by using SLP addition in place of the conventional technology for abating N<sub>NH3</sub>. However, the capital investment in the SLP option is much lower. To complete this scenario, it should be considered that the SLP production technology is still in the early development stage. Further process development and optimization studies are likely to bring substantial cost reduction for SLP production.

#### SLP allocation in the agriculture market

The agriculture market comprises mostly mineral and organic products, used as fertilizers and/or plant biostimulants. A minor amount of other agriculture auxiliaries, such as plant disease suppressing agents is marketed. However, their price is very high. Benzothiadiazole is one of the most used plant disease suppressants (Burketova et al. 2015). It is sold at about 820 \$ kg<sup>-1</sup> (eBiochem 2016). The major fertilizers market comprises mineral and organic products. The world consumption of mineral fertilizers containing N, P and K was estimated 187 million t in 2014. with demand expected to grow at 1.8% per annum from 2014 to 2018 (FAO 2015). Generally, global consumer price inflation is projected to remain subdued as demand weakens, with falling commodity prices. In advanced economies, risks to activities associated with very low inflation have become important, especially in the Euro area, where large output gaps have contributed to low inflation. The international monetary fund considers that there is the possibility of higher real interest rates, an increase in private and public debt burdens, and weaker demand and output. Major agriculture crops are wheat, coarse grain, rice, and sugar and oil crops. The major mineral fertilizers are urea, diammonium phosphate, phosphate rock, potassium chloride, triple superphosphate with production cost ranging from minimum  $0.11 \in \text{kg}^{-1}$  for phosphate rock to maximum  $0.46 \in \text{kg}^{-1}$  for diammonium phosphate. Over the last two decades, the market outlook for organic fertilizers has not been bright. An article published in the FAO magazine (Fresco 2003) in 2003 had predicted that non-mineral nutrient sources were unlikely to challenge mineral fertilizer in the future. In 2007, other authors (Kelly and Crawford 2007) reported that organic soil management methods contributed to soil fertility improvement, but were inadequate for meeting the rapid and sustainable growth needed in African countries characterized by low food crop production. Consequently, the only means of both maintaining soil fertility and of achieving the required rate of agricultural growth was to increase significantly the quantities of mineral fertilizers. However, the combined use of mineral and organic fertilizers was a possible option to increase crop output and the amount of biomass available for transfer to land on which crops are grown.

There is no question that there has been a spurt in domestic and international demand for greening agriculture across the countries as a result of initiatives of multiple actors such as institutions/organizations, industrial and trading firms, farming communities, civil society and their representatives. A survey (Kolanu and Kumar 2007) reports that, although organic agriculture in India is likely to provide economic opportunities for different stakeholders, thanks to a number of drivers, several factors exist which constrain the development of this practice. A large number of these problems are due to the relatively newness of this sector from the point of view of different players, such as products' producers/distributors/traders, users (farmers), promoters (governments). Most problems arise from missing market regulation, poor selection of good quality products, scares product information, and insufficient government incentives' and farmers education policy. Nevertheless, in the last few years, a new class of organic products named

biostimulants has emerged (du Jardin 2015). A plant biostimulant is any substance or microorganism applied to plants with the aim to enhance nutrition efficiency. abiotic stress tolerance and/or crop quality traits, regardless of its mineral nutrients content. These products modify the physiology of plants, promoting their growth and enhancing their stress response. Compared with biofertilizers, the capacity of biostimulants to promote plant growth under stressful conditions, and at very low doses, is the main distinguishing factor. Biostimulants are generally classified into three major groups based on their source and content. These groups include humic substances, hormone containing products, and amino acid containing products. The humic substances are natural constituents of the soil organic matter, resulting from the decomposition of plant, animal and microbial residues, but also from the metabolic activity of soil microbes using these substrates. Regardless of their source, they include extracts from naturally humified organic matter (e.g. from peat or volcanic soils), from composts and vermicomposts, or from leonardite fossil deposits. The SLP bear similar origin and chemical features as humic substances (Montoneri et al. 2011). Evidence of bio-stimulant properties for SLP has been published (Fascella et al. 2015; Massa et al. 2016). Further work to assess the full potential of SLP biostimulant properties is in progress. Thus, new perspectives are opening for organic substances in general, and for SLP specifically, to replace and/or decrease mineral fertilizers consumption in agriculture. In such scenario, due effective availability of to the worldwide cost municipal bio-wastes (Sheldon-Coulson 2011), as compared to the other humic substances sources, SLP constitute a potentially more viable alternative, which would also contribute reduced depletion of fossil leonardite deposits.

Undoubtedly, now, organic fertilizers belong to a niche market. Some reports estimate the US fertilizer market to be around \$40 billion of which organic fertilizers occupy only about \$60 million. The rest of it is the share of the various artificial fertilizers (Diffen 2016). Organic fertilizers wholesale prices (Alibaba 2016a, b; Ebay 2016) range from 140 \$t^{-1} for solid products containing 10% soluble organics, to 1500 \$t^{-1} for products with >90% soluble organics, and to 3000 \$t^{-1} for products in solution containing 35% organics and other mineral elements. Based on personal interviews by the author of the present chapter with major Italian distributors of peat derived organic fertilizers, the European market wholesale value can be estimated 20–25 million €, mainly in Spain 5–6 million €, Italy 4–5 million € and France 3.5–4.5 million. At a minimum sale price of 1000 €  $t^{-1}$ , this is equivalent to 20–25 thousands t sale.

A most recent paper (Fascella et al. 2015) reports the effects of SLP isolated from municipal bio-waste compost on Euphorbia x Lomi cultivation, in comparison with a commercial product containing humic substances extracted from Leonardite. The SLP are reported more powerful than the commercial Leonardite product in enhancing plant photosynthesis, growth and aesthetic effect, improving flower quality, and optimizing water use efficiency. Enhancement factors of plant performance indicators by SLP range from 1.3 to 8.6 relatively to the control plants, and from 1.2 to 4.5 relatively to plants treated with the commercial Leonardite based product at equal applied dose. The vis-à-vis performance comparison of SLP

with the commercial Leonardite derived product demonstrates that SLP could efficiently replace commercial humic products in the agriculture market. The above commercial Leonardite derived product containing 30% dry matter can be purchased in 1 kg package for  $7 \in \text{kg}^{-1}$  (Fascella et al. 2015). Based on the dry matter content, this price is equivalent to over  $23 \in \text{kg}^{-1}$  dry matter. The SLP production cost has been estimated about 0.1–0.5  $\in \text{kg}^{-1}$  (Montoneri et al. 2011). The figures prospect attracting economic benefits deriving from the allocation of SLP in the organic fertilizer market.

Further commercial opportunity may derive from the growth of the biostimulants market, currently estimated in 200–400 million euros in Europe, probably 800 million worldwide (New Ag International journal 2012; Natale 2012). The latter figure is expected to reach over 2900 million euros in 2019 (Marketsand markets n.d.).

To evaluate the economic perspectives deriving from the allocation of SLP in the above context of products categories, types, and market size and prices, it should be taken in consideration that SLP contain all mineral nutrients needed by plants. These are bonded to the soluble lignocellulosic matter. The research results (see Sect. (6.4.1) point out that the observed effects on plant growth and productivity are because SLP supply the plants the mineral nutrient in readily available soluble form, thus facilitating the nutrients uptake by the plant. Based on their organics and minerals content, the SLP would fall into the high price organic fertilizers' category. It should also be considered that SLP are obtained from composted urban bio-wastes, and that the yearly production of Italian organic humid bio-waste is 4.2 million t (Bastioli 2013), which can potentially yield 300-400 thousand t of SLP. This potential production exceeds the above estimated organic fertilizers market size. It is evident that this market cannot absorb all organic fertilizers that can be obtained from the produced compost. It should also be considered that the SLP have been proven efficient plant disease suppressants (see Sect. 6.4.1). The capacity to induce plant protection against pathogens adds 1-3 order magnitude higher market value (eBiochem 2016) to the product, in comparison with fertilizers for enhancing plant growth (Alibaba 2016a, b; Ebay 2016). Yet, since plant disease suppressants are given at low doses, the market size of these products' category is small. The above literature survey however points out that the organic fertilizers market is in the early stage. Under these perspectives, the SLP might be favoured for their capability to provide an integrated complete plant nourishment, which contains both mineral and organic matter of renewable source. In principle, these products could replace current commercial mineral and organic fertilizers. To appreciate the full potential of SLP uses in agriculture, it should be taken also in consideration the work (Franzoso et al. 2015a, b, c) reporting SLP as potential components of new composite mulch films. Used in agriculture, these films might have multiple function, i.e. protecting plants against negative external influences, creating an ideal microclimate, and slowly releasing the SLP into the soil to stimulate plant and crop growth.

#### SLP allocation in the plastics market

The plastics market is more challenging than the agriculture market. In the recent years, bio-based polymers have raised great interest since sustainable development policies tend to expand with the decreasing reserve of fossil fuel and the growing concern for the environment. These polymers bring a significant contribution to the sustainable development in view of the wider range of disposal options with minor environmental impact. As a result, the market of these environmentally friendly materials is in rapid expansion. However, until now, bio-based polymers have not found extensive applications in industries to replace conventional plastic materials. reasons being their high production costs and sometimes their underperformed properties. Compared to traditional resins costs, which run below  $2 \notin kg^{-1}$  (Kanellos 2009), current biopolymers are from about 2.0 to 7.0 times more expensive (Roland-Holst et al. 2013). The difference depends on the fluctuation of oil prices and on the type of bioplastics, whether they are from dedicated crops, such as starch, or from fermentation, such as polyhydroxylalkanoates. The following cost and production figures for major biopolymers, compared to synthetic polymers, may be found in literature (Roland-Holst et al. 2013). Depending on which bacterial producer is used to generate polyhydroxylalkanoates, the cost of production can range from 4 to 16  $\text{g}^{-1}$ . However, to be commercially viable, these products should be sold 3– 5  $\text{$kg}^{-1}$ . By comparison, polylacticacid is more cost-competitive. This polymer was selling in bulk at approximately  $0.90 \$  lb<sup>-1</sup> in the last quarter of 2011, against polystyrene and polyethylene terephthalate selling at 1.00 and 0.80 lb<sup>-1</sup>, respectively. Packaging is one of the fastest growing sectors for bioplastic consumption. Bioplastic packaging consumption has been estimated to be 125,000 t in 2010 with an estimated market value of 454 million \$ (Roland-Holst et al. 2013). These figures correspond to an average 3.6  $\text{\$ kg}^{-1}$  sale price.

A vast number of biopolymers (e.g. cellulose, chitin, starch, polyhydroxyalkanoates, polylactide, polycaprolactone, collagen and other polypeptides) have been synthesized or are formed in natural environment during the growth cycles of organisms. Most biopolymers are obtained from dedicated crops. The use of land to cultivate plants for energy or chemicals production raises much socio-environmental and moral concern. Negative impacts on land, water and biodiversity, and food production count among the most discussed side effects of this practice (Green Facts 2015; FAO 2008). Using corn as non-food feedstock may cause food price increase and thus can be controversial. Bio-wastes, as sources of biopolymers, have not been much investigated so far. Yet, their valorisation for this scope can potentially overcome the socio-environmental and moral criticalities connected to the exploitation of dedicated crop for producing chemicals.

In this context, the manufacture of the composite plastic films (see Sect. 6.4.1), which contain SLP blended with poly vinyl alcohol-co-ethylene (Franzoso et al. 2015a, c, 2016) and poly ethylene-co-acrylic acid (Franzoso 2015b), is a praise-worthy approach. Poly vinyl alcohol-co-ethylene is a special high cost polymer, with a market price (Alibaba n.d.) of about  $5.5 \in \text{kg}^{-1}$ . The production cost of SLP is estimated 0.1–0.5  $\notin \text{kg}^{-1}$  (Montoneri et al. 2011). This figure is rather attracting,

upon considering that for the production of polylacticacid and other bioplastics, food crops are a major input, and that the incidence of the cost of corn is 0.26 \$ per kg of plastic produced (Roland-Holst et al. 2013). The relatively low SLP production cost prospects that the substitution of a fraction of poly vinyl alcohol-co-ethylene with the cheaper SLP biopolymer should yield a blend with a cost per kg lower or not higher than that for the neat synthetic polymer. Thus, based on the enhanced mechanical strength exhibited by the poly vinyl alcohol-co ethylene-SLP blend, it seems possible to make articles with the bio-waste based blend, which were more eco-friendly, and equally or better performing than those made by the neat synthetic polymer, without increasing the product final market price.

The potential stake of the above perspective can be appreciated considering that bioplastics are currently only in a small portion (under 1%) of global market share of plastics (European Bioplastics 2016; Storz and Vorlop 2013; Plastermat n.d., Nova Institute 2015), which should be around 1–2 million t year<sup>-1</sup>. Worldwide bioplastics demand has grown tremendously over the past several years, albeit still representing a small fraction of global plastics demand. As of 2007, it was estimated that worldwide production of bioplastics amounted to approximately 360,000 metric t (890,000 metric t by 2012). It would reach 1.5–4.4 million metric t by 2020 (Roland-Holst et al. 2013). An average size waste treatment plant (see Sect. 6.5.2) can produce 900 t year<sup>-1</sup> SLP, which in turn would allow obtaining 5000 poly vinyl alcohol-co-ethylene-SLP blend ton year<sup>-1</sup>. Thus, there are interesting revenue and market share expectations for allocating urban refuse sourced biopolymers in the current bioplastic market.

#### SLP allocation in the surfactants market

Further economic and environmental benefits may potentially derive from allocating the SLP in the surfactants' market. In the case of the Acea plant, the production and market allocation of SLP has been calculated yielding six times higher earnings than the current plant selling biogas and compost (Montoneri et al. 2011). The result stems from the likely sale value of SLP in the surfactant market at 1000  $\notin$  per ton against 11  $\notin$  per ton for compost. The global market for surfactants is currently estimated \$32.6 billion per year and is projected to reach a volume of 24 million t and a value of \$42.1 billion by 2020. These figures correspond to an average price of \$1750 per ton (Marketsandmarkets 2015). In principle, this market could absorb the SLP production from 27,000 MBW treatment plants of Acea similar size. Under these circumstances, 75 million t per year of CO<sub>2</sub> emission from fossil C would be saved and all European composting plants could benefit from the added revenue deriving from selling the SLP at about 1750  $\notin$  t<sup>-1</sup> instead of maximum 30 t<sup>-1</sup> from the sale of the pristine compost. The use of SLP, in place of fossil derived chemicals consumed in EU, would allow 15% (55 Mt year<sup>-1</sup>) CO<sub>2</sub> lower emission.

There is a wide range of surfactants, which cover a wide range of applications. Small molecule surfactants, obtained through chemical synthesis from fossil sourced hydrocarbons have an average market price of  $1 \in \text{kg}^{-1}$ . Market prices per

product kg may be even much higher for some high performance biodegradable surfactant molecules, such as rhamnolipids (Montoneri et al. 2016). These products are produced by specialized bacterias. They lower the surface tension of water from 70 down to 28 mN m<sup>-1</sup> at the critical micellar concentration of 0.8–2 g L<sup>-1</sup>. Their market price may run from 30 to 150  $\in$  per kg. The oxidized high molecular weight SLP have shown chemical features similarities with rhamnolipids. However, the former ones do not reach yet the high performance of bacterial surfactants. A real breakthrough would be improving the surface activity properties of the high molecular weight ozonized SLP to match the rhamnolipid biosurfactant properties.

# 6.5.2 Replicability and Transferability of the LV Technology in Real Operational Environment and Expected Benefits

Bio-wastes contain mainly polysaccharides and lignin. Thus, in principle the above-described LV technology is applicable to all kind of bio-wastes. One main consideration related to the scale up of bio-based products to commercial level is the management of the entire supply chains. This is not straightforward, and transitioning from the development stage to commercialization of a material requires an immense amount of coordination. It implies the availability, collection and processing of the sourcing feedstock, and the product distribution. Another challenge facing bio-based producers is securing funding for the difficult transition from research and development to commercialization. In the case of the SLP products, a waste management plant such as the case study Acea plant should be encouraged to invest in the production of SLP, due to presumed benefits (Table 6.4) obtainable from their in-house use. Once available, the SLP production facility would allow producing the product marketability in the agriculture market. This will require establishing joint venture with other companies operating in the production, marketing and distribution of agrochemicals. The successful demonstration of this approach is expected to be a strong drive for the replicability and transferability of the results. Certainly, feedstock for the production of SLP is not a problem worldwide. Moreover, there is large availability of waste management plant, running composting and anaerobic digestion facilities (see Sect. 6.2.1), which would be interested in the economic benefits deriving from integrating the LV technology into the existing fermentation facilities. On the other hand, another important source of bio-waste of the LV technology are farms, which process agriculture residues such as straw and manure by anaerobic digestion. As anticipated in Sect. 6.4.2, these make up another important large market sections, which may benefit from technological transfer of the SLP assisted anaerobic digestion technology. This scenario depicts the following virtuous renewable C cycle. Urban bio-wastes are used to obtain products (SLP) in large urban waste treatment plants. The SLP producer will use the product for its needs, and will sell the produced excess to the farmer customer. In this fashion, producer and customer, regardless of the operational capacity and the required product amount by the latter one, would share the environmental and economic benefits of the SLP.

The SLP benefits are not limited at the use of the product for reducing the ammonia content in anaerobic digestates. The use of SLP in agriculture would allow reducing the use of commercial fertilizers, and the environmental impact caused by applying high fertilizer doses to soil (see Sect. 6.4.1). The use of SLP to make bio-based plastic blend articles would allow reducing the consumption of synthetic polymers derived from fossil source. The economic and environmental benefits stemming from all these applications may encourage communities worldwide to start or implement further dismissing bio-waste landfilling, and/or to reduce waste incineration practices, in the outlook of more economically rewarding and eco-friendly technology.

Notwithstanding the amount of research carried out, to enter our everyday life the SLP must be assessed for their performance, marketability and sale value in real operational environment, and need life cycle analysis and certification (European Commission 2016). The technological transfer of experimental to industrial and commercial scale may be relatively easy for technologies producing energy or products that are known and assessed in the market. It is more complicated in the case of new technologies, such as the LV technology producing bio-based substances as the SLP, which are not known in the market. These products need not only market assessment, but also legislative acceptance.

According to Italian legislative decree DL 29 April 2010, n. 75, humic extracts, in solid, aqueous suspension or liquid form, obtained from soil, fossil deposits such as peat, and generally from natural humification processes, may be permitted for use as soil improvers or fertilizers for agriculture, if they meet some compositional requirements. The SLP have been demonstrated having chemical composition similar to natural humic substances (Montoneri et al. 2011), and biostimulant performance similar or better than Leonardite sourced humic substances (Fascella et al. 2015). Thus, based on chemical composition and performance, the SLP fall well into the category of fertilizers according to the above Italian legislation.

In addition to these facts, Biagini et al. (2016) have demonstrated that the SLP are not toxic for rabbits. The lack of toxicity has been shown also in pigs fed with a diet containing the same SLP (Montoneri 2012).

A formal request of legislative acceptance for the SLP has not been filed yet with any national authority. Legislative acceptance of new products requires production scale up in order to perform products' on field and laboratory studies, and support by producers' association. For example, recently the Italian Biochar Association (www.ichar.org) has succeeded in getting inclusion of biochar in the list of agriculture soil improvers, which are authorized for use in Italy (see Gazzetta Ufficiale, Serie Generale n° 186 12-8-2015). This result has been accomplished after eight research on biochar, which was started in Italy in 2008. Recently, Mozzetti et al. (2015) have compared the SLP obtained from post-harvest tomato plants and biochar obtained from the pyrolysis of poultry manure and miscanthus. The products were compared for chemical composition and performance in the cultivation of radish. The results show that the SLP and the pristine tomato plants contain lignin, hemicellulose, protein, peptide and/or amino acids moieties, and several mineral elements. The biochar samples contain also similar mineral elements, but the organic fraction is characterized mainly by fused aromatic rings. All materials had positive effects on radish growth.

The comparison of SLP and biochar by Mozzetti et al. (2015), as well as the comparison of SLP and Leonardite sourced humic acids (Fascella et al. 2015), and the lack of toxicity of SLP for plants (Sortino et al. 2014) and for animals (Biagini et al. 2016; Montoneri 2012), offer sound arguments supporting the potential legislative acceptability of SLP for use in agriculture and other sectors.

For the SLP, the task required for the definite market assessment and legislative acceptance may only be accomplished by the construction and operation of a demo plant, which had production capacity adequate for carrying on field tests in near operational environment. This implies risking capital investment. In the case of SLP, this step may be achieved with much reduced entrepreneurial risk by starting with the production of SLP for in-house use. Construction and operation of the SLP production facility, finalized at producing digestate with reduced ammonia content, would also allow producing at very limited risk excess SLP for assessing the perspective to allocate the products in the market for the other uses in the chemical industry and in agriculture (Fig. 6.6). During this time, the capital investment would be paid off by the savings resulting from adopting the SLP technology for abating the ammonia content in the digestate, which is produced routinely in by the plant anaerobic fermentation section. In this fashion, a municipal waste treatment plant, as the Acea plant (Fig. 6.1), might be turned out into a biorefinery with different product lines (Fig. 6.6), where the production output of the different product lines was modulated according to the specific markets' demands. The availability of multipurpose products, such as SLP, is a further benefit, in as much as it allows reducing the risk of saturating a specific market sector. This is a very attracting perspective. Taking the Acea plant as example, the following is a possible stepwise business development strategy in order to maximize the possibility of success and minimize the risk:

- Plan facility for the production of SLP to be integrated into the current waste treatment plant in order to produce SLP in excess of the amount needed for the in-house anaerobic digestion process
- Run performance and marketability tests in real operational environment for SLP use in other market sectors. Produce product formulations for specific uses
- Assess the legislative acceptance of the SLP
- · Scale up SLP production facility according to market assessment results
- Invest in new process/products research and development.

Starting with the SLP production for in-house use seems a viable sustainable route toward the construction of a biorefinery fed with municipal bio-wastes. In the long term, this business strategy will allow collecting data in real operational environment, which will be useful for planning a reliable technology transfer to other waste management plant throughout the world. Such scenario implies positive impact in many sectors. First, under this perspective, waste management facilities would become also producers of value added chemicals. Second, the economic benefits of the integrated plant selling biogas and SLP should in principle results in lower taxes for citizens. Third, the chemical market would consume less non-renewable sources for the manufacture of chemicals and benefit processes cost reduction. Fourth, the distributed nature of the wastes source might align geographically with areas of the region where development of new business opportunities and jobs is of vital interest.

Multiple environmental benefits are expected for agriculture, the use of compost, the anaerobic digestion processes, and the chemical sector. These concern main important issues, such as the reduction of fossil sources consumption and of GHG emission, deriving from substituting synthetic chemicals with bio-waste based products. Multiple diversified investors are likely to act. This scenario will contribute to assess two new technological and socio-economic concepts:

- a municipal bio-waste treatment plant may be turned into a biorefinery for the production of fuel and valuable bio-waste based products with friendly environmental impact;
- municipal bio-wastes may be a source revenue, and not merely a burden for society.

Undoubtedly, the appealing economic benefits of the integrated municipal bio-waste plant producing biogas and SLP might be an important socio economic driver for diverting waste from landfill or from incinerating valuable organic matter. In densely populated areas, the value of land is generally high, which makes it critically costly to use areas for landfill. On the other hand, incinerators need densely populated areas to be operated with enough feed to be operated at optimum efficient capacity. For the same reason, in densely populated areas, an integrated municipal bio-waste plant producing biogas and SLP could be operated at optimum cost-effective size. Thus, in densely populated areas, the integrated municipal bio-waste plant producing biogas and SLP might may become a real viable option to reduce landfills and incineration. Perhaps, the best socio-economic message of such scenario is 'before burning everything up, consider saving what is valuable. Municipal bio-waste contains valuable organic matter and the real waste is dismissing to landfills or burning it'. The present chapter shows that the realization of this scenario may start from a typical waste management plant, as the Acea plant, which started producing SLP for internal use. This would allow developing new business innovation models for municipal bio-waste plants, as well as the definition of guidelines and recommendations for a European Common Policy to support the adoption of business innovation models in the new European bio-based chemical industry.

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### References

- Al Seadi T, Rutz D, Prassl H, Köttner M, Finsterwalder T, Volk S, Janssen R (2008) Biogas handbook. University of Southern Denmark Esbjerg (Niels Bohrs Vej 9-10, DK-6700 Esbjerg, Denmark, R). http://www.lemvigbiogas.com/BiogasHandbook.pdf. Accessed 7 Mar 2016
- Alibaba (2016a) Leonardite humic acid fulvic acid fertilizer. http://www.alibaba.com/trade/search? fsb=y&IndexArea=product\_en&CatId=&SearchText=leonardite+humic+acid+fulvic+acid +fertilizer. Accessed 7 Mar 2016
- Alibaba (2016b) Organic fertilizer market. http://www.alibaba.com/showroom/organic-fertilizermarket.html. Accessed 7 Mar 2016
- Alibaba (n.d.) EVOH—SOARNOL SG-654-NG. http://www.alibaba.com/product-detail/EVOH-SOARNOL-SG-654-NG\_169861914.html. Accessed 6 Mar 2016
- Arato C, Kendal Pye E, Gjennestad G (2005) Appl Biochem Biotechnol 871:121-124
- Avetta P, Bella F, Bianco Prevot A, Laurenti E, Montoneri E, Arques A, Carlos L (2013) ACS Sustain Chem Eng 1:1545–1550
- Baglieria A, Cadilia V, Mozzetti Monterumici C, Gennari M, Tabasso S, Montoneri E, Nardi S, Negre M (2014) Sci Horticulturae 176:194–199
- Barilla Center for Food Nutrition (2012) Food wastes: causes, im-pacts and proposals, https:// www.barillacfn.com/media/publications/food-waste-causes-impact-proposals.pdf. Accessed 7 Mar 2016
- Barth J (2010a) Bio-waste in the context of EU legislation. http://www.google.it/url?sa=t&rct= j&q=&esrc=s&source=web&cd=8&ved=0CF4QFjAHahUKEwjRgsvkx7XIAhWCPxQKHSCv Cqg&url=http%3A%2F%2Fwww.act-clean.eu%2Fdownloads%2F3\_uba\_ifat\_bio-waste\_barth\_final. ppt&usg=AFQjCNELaOtN7OulrqHkwfNxFGoQ9Q0ZGA&sig2=gw-HGCgRZMdR-1Fg6rUrgg. Accessed 7 Mar 2016
- Barth J (2010b) Markets for compost and digestate in Europe. http://compost.it/biblio/2010\_ beacon\_conference\_perugia/2nd\_day/5.c%20-%20Barth.pdf. Accessed 7 Mar 2016
- Bastioli C (2013) Bioplastics: an Italian case study of bioeconomy in Italy. http://www.kyotoclub. org/docs/Bruxelles\_060313\_Bioplastics\_Bastioli.pdf. Accessed 7 Mar 2016
- Baxter MD, Acosta E, Montoneri E, Tabasso S (2014) Ind Eng Chem Res 53:3612-3621
- Biagini D, Gasco L, Rosato R, Peiretti PG, Gai F, Lazzaronia C, Montoneri C, Ginepro C (2016) Anim Feed Sci Technol. doi:10.1016/j.anifeedsci.2016.02.005
- Boffa V, Perrone DG, Magnacca G, Montoneri E (2014) Ceram Int 40:12161-12169
- Brunow G, Lundquist K, Gellerstedt G (1998) In: Sjostro E, Alen R (eds) Analytical methods in wood chemistry, pulping and papermaking. Springer Science and Business Media, Berlin. https://books.google.it/books?id=U-0k4NCbbNQC&pg=PR6&lpg=PR6&dq=Eero+Sj%C3% B6str%C3%B6m,+Raimo+Alen,+1998&source=bl&ots=38EM\_u6Nd\_&sig=i74LLwJL2FK KarHUP-5FLQ\_JHng&hl=it&sa=X&ei=sV-YVNjNOYbkUuiZgPAO&ved=0CCMQ6AEwAA. Accessed 7 Mar 2016
- Burke DA (2013) Economical recovery of ammonia from anaerobic digestate. In: Waste to worth, spreading science and solutions. Denver, CO. http://www.extension.org/pages/67578/ economical-recovery-of-ammonia-from-anaerobic-digestate#.VEYae51H5b0. Accessed 7 Mar 2016)
- Burketova L, Trda L, Ott PG, Valentova O (2015) Biotechnol Adv 33:994-1004
- CalRecycle (2016) Organic materials management, compost use in agriculture, Jan 15. http:// www.calrecycle.ca.gov/organics/farming/; http://ec.europa.eu/environment/waste/compost/.../ econanalysis\_finalreport.pdf; http://ec.europa.eu/.../waste/.../econanalysis\_execsum.pdf. Accessed 3 Mar 2016
- Canilha L, Chandel AK, dos Santos Milessi TS, Antunes FAF, da Costa Freitas WL, das Gracas Almeida Felipe M, da Silva SS (2012) J Biomed Biotechnol, Article ID 989572. doi:10.1155/ 2012/989572

- Centemero M, Ricci M, Giavini M, Dall'Anna D, Campagnol J, Longu G (2015) Annual report of the Italian composting and biogas association. http://www.renewablematter.eu/partners/CIC/ CIC%20annual\_report2015eng.pdf. Accessed 7 Mar 2016
- Chiellini E, Solaro R (2003) Biodegradable polymers and plastic. Springer Science+Business Media, New York. doi:10.1007/978-1-4419-9240-6. https://books.google.it/books?id= CdLiBwAAQBAJ&pg=PA386&lpg=PA386&dq=biodegradable+polymers+based+on+ polyhydroxy+acids&source=bl&ots=-z098-XF69&sig=JFr0gSZjp1uHN74niYdHm4GY1 HM&hl=it&sa=X&ved=0ahUKEwjp18OqwajJAhXEKw8KHUuiDOIQ6AEIS-zAG#v= onepage&q=biodegradable%20polymers%20based%20on%20polyhydroxy%20acids&f=false. Accessed 7 Mar, 2016
- Clark J (2007) J Chem Technol Biotechnol 82:603-609
- Clark J, Deswarte F, Farmer TJ, Mascal M (2014) In: Introduction to chemicals from biomass, 2nd ed. Copyright © 2015 Wiley, NJ. Published online: 26 Dec 2014. doi:10.1002/9781118714478. ch4. http://onlinelibrary.wiley.com/doi/10.1002/9781118714478.ch4/summary. Accessed 7 Mar 2016
- CP Manufacturing (2012) Solid waste management equipment. http://www.cpmfg.com/materialrecovery-facility/municipal-solid-waste-recycling/solid-waste-management-equipment/. Accessed 3 Mar 2016
- David M, Joshi T, Negin D, Tan KY, Fagan JM (2010) Indus-trial biodegradable waste with primary focus on food waste. https://webcache.googleusercontent.com/search?q=cache:MT3tHA7\_Oa4J; https://rucore.libraries.rutgers.edu/rutgers-lib/37176/pdf/1/+&cd=1&hl=it&ct=clnk&gl=it. Accessed 6 Mar 2016
- Deganello F, Tummino ML, Calabrese C, Testa ML, Avetta P, Fabbri D, Bianco Prevot A, Montoneri E, Magnacca G (2015) New J Chem 39:877–885
- Department for environmental food and rural affairs (2013) Incineration of municipal solid wastes. https://www.gov.uk/government/uploads/system/uploads/attachment\_data/file/221036/pb13889incineration-municipal-waste.pdf. Accessed 3 Mar 2016
- Diffen (2016) Chemical fertilizer vs. organic fertilizer. http://www.diffen.com/difference/ Chemical\_Fertilizer\_vs\_Organic\_Fertilizer#Cost. Accessed 7 Mar 2016
- Dinuccio E, Biagini D, Rosato R, Balsari P, Lazzaroni C, Montoneri E (2013) Adv Anim Biosci 4 (Special Issue 2):515
- du Jardin P (2015) Sci Hortic 196:3-14
- Ebay (2016) Leonardite. http://www.ebay.it/itm/LEONARDITE-5-Kg-CONCIME-PIANTE-SIEPI-FIORI-ORTO-GIARDINO-CACTUS-BONSAI-/270841276887. Accessed 7 Mar 2016
- eBiochem (2016) Wholesale 2,1,3-benzothiadiazole, http://www.ebiochem.com/product/2-1-3benzothiadiazole-71535. Accessed 7 Mar 2016
- Ensinger Gmbh (n.d.) Tensile strength at break. http://www.ensinger-online.com/ru/technicalinformation/properties-of-plastics/mechanical-properties/tensile-strength-at-break/. Accessed 11 Oct 2016
- European Bioplastics (2016) Bioplastics facts and figures. http://www.google.it/url? sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0ahUKEwiymt7lrq7LAhXCbRQKHSBs-BMMQFggnMAE&url=http%3A%2F%2Fwww.muoviteollisuus.fi%2Fdocument.php%2F1% 2F156%2Feuropean\_bioplastics\_-facts\_and\_figures%2Fb4313531b6f32c56e3b4a4d3d5fdd15c &usg=AFQjCNGRZsjgqlXbzlwgl2n\_uTKZx51RfA&sig2=d\_G6fqLgWyJL82H-GWbVsw. Accessed 7 Mar 2016
- European Commission (2013) Innovation, how to convert research into commercial success story? http://ec.europa.eu/research/industrial\_technologies/pdf/how-to-convert-research-into-commercialstory\_en.pdf. doi:10.2777/10737. Accessed 7 Mar 2016
- European Commission (2014) Horizon 2020—Work programme 2014–2015, general annexes G, technology readiness lev-els (TRL), extract from part 19—Commission Decision C(2014) 4995, http://ec.europa.eu/research/participants/data/ref/h2020/wp/2014\_2015/annexes/h2020-wp1415-annex-g-trl\_en.pdf. Accessed 7 Mar 2016
- European Commission (2015) Environment, biodegradable waste. http://ec.europa.eu/ environment/waste/compost/. Accessed 3 Mar 2016

- European Commission (2016) REACH, http://ec.europa.eu/growth/sectors/chemicals/reach/index\_ en.htm. Accessed 7 Mar 2016
- European Compost Network (2010) Country report of Germany. http://www.compostnetwork. info/germany.html. Accessed 7 Mar 2016
- European Environmental Agency (2013) Managing municipal solid wastes. EEA report. http:// www.google.it/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0ahUKEwimrm7hK7L AhVD8RQKHdJdATgQFggrMA-E&url=http%3A%2F%2Fwww.eea.europa.eu%2Fpublicati ons%2Fmanaging-municipal-solid-waste%2Fdownload&usg=AFQjCNG4-8WUDJj9wZU0H MBKSSzxm4upCw&sig2=uSgUDij0O-FDP08ub1mV3g. Accessed 7 Mar 2016
- Eurostat (2016) Farm structure statistics. http://ec.europa.eu/eurostat/statistics-explained/index. php/Farm\_structure\_statistics. Accessed 7 Mar 2016
- FAO (2008) The state of food and agriculture, Part I: biofuels: prospects, risks and opportunities. http://www.fao.org/docrep/011/i0100e/i0100e00.htm. Accessed 7 Mar 2016
- FAO (2011) Global food losses and food waste—extent, causes and prevention, Rome. http:// www.fao.org/docrep/014/mb060e/mb060e00.pdf. Accessed 3 Mar 2016
- FAO (2015) World fertilizer trends and outlook to 2018. http://www.fao.org/3/a-i4324e.pdf. Accessed 7 Mar 2016
- Fascella G, Montoneri E, Ginepro M, Francavilla M (2015) Sci Hortic 197:90-98
- Fiedler H (1998) Sources and environmental impact of PCDD/PCDF. In: Proceedings of the subregional awareness raising workshop on persistent organic pollutants (pops), Kranjska Gora, Slovenia, 11–14 May 1998. http://www.chem.unep.ch/pops/POPs\_Inc/proceedings/ slovenia/CONTKG.html. Accessed 7 Mar 2016
- Foged H, Flotats Ripoll X, Bonmatí Blasi A, Palatsi Civit J, Magrí Aloy A, Schelde KM (2012) Inventory of manure processing activities in Europe. http://agro-technologyatlas.eu/docs/ 21010\_technical\_report\_I\_inventory.pdf. Accessed 7 Mar 2016
- Francavilla M, Beneduce L, Gatta G, Montoneri E, Monteleone M, Mainero D (2016a) Biochem Eng J 116:75–84
- Francavilla M, Beneduce L, Gatta G, Montoneri E, Monteleone M, Mainero D (2016b) J Chem Technol Biotechnol 91:2679–2687
- Franzoso F, Antonioli D, Montoneri E, Persico P, Tabasso S, Laus M, Mendichi R, Negre M, Vaca-Garcia C (2015a) J Appl Polym Sci 132(18):6006
- Franzoso F, Causone D, Tabasso S, Antonioli D, Montoneri E, Persico P, Laus M, Mendichi R, Negre M (2015b) J Appl Polym Sci 132(18):5803. doi:10.1002/app.41909
- Franzoso F, Tabasso S, Antonioli D, Montoneri E, Persico P, Laus M, Mendichi R, Negre M (2015c) J Appl Polym Sci 132(4):1301. doi:10.1002/app.41359
- Franzoso F, Vaca-Garcia C, Rouilly A, Evon P, Montoneri E, Persico P, Mendichi R, Nisticò R, Francavilla M (2016) J Appl Polym Sci 133(9):2110. doi:10.1002/APP.43009
- Fresco LO (2003) FAO spotlight/2003, fertilizer and the future. http://www.louiseofresco.com/pdf/ FAO/2003%20-%20FAO%20Spotlight%20-%20Fertilizer%20and%20the%20future.pdf. Accessed 7 Mar 2016
- Gomis J, Bianco Prevot A, Montoneri E, Gonzalez MC, Amat AM, Martire DO, Arques A, Carlos L (2014) Chem Eng J 235:236–243
- Green Facts (2015) Liquid biofuels for transport prospects, risks and opportunities. http://www. greenfacts.org/en/biofuels/1-3/4-environmental-impacts.htm. Accessed 7 Mar 2016
- Hu Z, Wen Z (2008) Biochem Eng 38:369-378
- Huffington Post (2013) Food waste: Half of all food ends up thrown away, 10 Jan 2013. http:// www.huffingtonpost.co.uk/2013/01/10/food-waste-half-of-all-fo\_n\_2445022.html. Accessed 6 Mar 2016
- Isagro SpA (2014) Efficacia biologica di Compost forniti dall'Università di Torino (Unpublished confidential report delivered to the author). www.isagro.com
- Ispra (2012) Banche dati, environmental data yearbook. http://annuario.isprambiente.it/pdf/ environmental-data-yearbook-2012. Accessed 7 Mar 2016
- Ji F, McGlone JJ, Kim SW (2006) J Anim Sci 84:2482–2490
- Jindřichová B, Burketová L, Rosso D, Montoneri E (2016) (to be published)

- Kanellos M (2009) Bioplastics close in price to regular plastic and trader Joe's coconut packages. https://www.google.it/#q=83.%09Kanellos+M%2C+Bioplastics+Close+in+Price+to+Regular +Plastic+and+Trader+Joe%E2%80%99s+Coconut+Packages. Accessed 7 Mar 2016
- Kelly V, Crawford E (2007) Policies and actions to stimulate private sector fertilizer marketing in sub-Saharan Africa. Agricultural management, marketing and finance occasional paper 15. http://www.fao.org/3/a-a1136e.pdf. Accessed 7 Mar 2016
- Key to Metals AG (2014) Engineering stress-strain curve. http://www.totalmateria.com/ Article107.htm
- Kolanu RT, Kumar S (2007) Greening agriculture in India an overview of opportunities and constraints. http://www.fao.org/docrep/article/agrippa/658\_en00.htm#TopOfPage. Accessed 7 Mar 2016
- Lerda D (2011) Polycyclic aromatic hydrocarbons (PAHs) fact sheet. https://ec.europa.eu/jrc/sites/ default/files/Factsheet%20PAH\_0.pdf. Accessed 7 Mar 2016
- Liew NL (2011) Solid-state anaerobic digestion of lignocellulo-SiC biomass for biogas production. Master thesis, The Ohio State University. https://etd.ohiolink.edu/!etd.send\_file? accession=osu1306870552&disposition=inline. Accessed 7 Mar 2016
- Lingle J (2008) Examination of the sources of polycyclic aromatic hydrocarbons (PAHs) in urban background soil. http://yosemite.epa.gov/sab/sabproduct.nsf/F334E867D04350FB85257E27 0059D7F0/\$File/EPRI-1015558-Sources+of+PAHs+in+Urban+Background+Soil-2008.pdf. Accessed 7 Mar 2016
- Luque T, Clark J (2013) Sustain Chem Process, pp 1-10
- Ma R, Xu Y, Zhang (2014), ChemSusChem 7:1-29
- Magnacca G, Laurenti E, Vigna E, Franzoso F, Tomasso L, Montoneri E, Boffa V (2012) Process Biochem 47:2025–2031
- Marketsandmarkets (2015) Surfactants market by product .... trends and forecast to 2020. http:// www.marketsandmarkets.com/Market-Reports/biosurfactants-market-493.html. Accessed 12 Oct 2016
- Marketsandmarkets (n.d.) Biostimulants market ... Global trends and forecasts to 2021. http:// www.marketsandmarkets.com/PressReleases/biostimulant.asp
- Martins O (1992) Bioresour Technol 42:103-111
- Massa D, Prisa D, Montoneri E, Battaglini D, Ginepro M, Negre M, Burchi G (2016) Sci Hortic 205:59–69
- McEntee K (2011) National compost prices. http://www.recycle.cc/compostprices.pdf. Accessed 11 Oct 2016
- Mirbagheri SA, Poshtegal MK, Parisai MS (2010) Desalination 256:70-76
- Montoneri E (2012) Efficacy of an extract obtained from gardening trimmings in pigs diet, unpublished study commissioned by Università di Torino to Cerzoo. Piacenza, Italy
- Montoneri E, Boffa V, Savarino P, Perrone DG, Montoneri C, Mendichi R, Acosta EJ, Kiran S (2010) Biomacromolecules 11:3036–3042
- Montoneri E, Mainero D, Boffa V, Perrone DG, Montoneri C (2011) Int J Glob Environ Issues 11:170–196
- Montoneri C, Montoneri E, Tomasso L, Piva A (2013) J Agriculture Sci 13:31-44
- Montoneri E, Tomasso L, Colajanni N, Zelano I, Alberi F, Cossa G, Barberis R (2014) Int J Environ Sci Technol 11(2):251–262
- Montoneri E, Rosso D, Bucci G, Berto S, Baglieri A, Mendichi R, Quagliotto P, Francavilla M, Mainero D, Negre M (2016) Chem Select 1:1613–1629
- Morone PG, Tartiu VE, Falcone P (2015) J Clean Prod 90:43-54
- Mostofa KMG, Yoshioka T, Abdul Mottalemb M, Vione D (2013) Photobiogeochemistry of organic matter. Springer, Berlin. http://www.springer.com/br/book/9783642322228. Accessed 7 Mar 2016
- Mozzetti Monterumici C, Rosso D, Montoneri E, Ginepro M, Baglieri A, Novotny E, Kwapinski W, Negre M (2015) Int J Mol Sci 16:8826–8843
- Nasa (2015) Definition of technology readiness levels. http://esto.nasa.gov/files/trl\_definitions.pdf. Accessed 7 Mar 2016

- Natale G (2012) The world market for biostimulant in crop production. http://www.biostimulants. eu/wp-con-tent/uploads/2012/12/121128\_TheWorldMarketForBiostimulants\_Natale\_def\_ LOWRES.pdf. Accessed 4 Mar 2016
- New Ag International Journal (2012) Nov/Dec, Biostimulants: What's behind the name? NewAgInternational\_excerpt\_Biostimulants-Whatsbehindthename.pdf. http://www.lawrieco. com.au/uploaded\_files/document\_uploads/2012\_11-12\_. Accessed 4 Mar, 2016
- Niemel K, Alen R, Sjçstrçm E (1985) Holzforschung 39:167-172
- Nisticò R, Evon P, Labonne L, Vaca-Medina G, Montoneri E, Francavilla M, Vaca-Garcia C, Magnacca G, Franzoso F, Negre M (2016) Chem Select 1:2354–2365
- Nova Institute (2015) Bio-based building blocks and polymers in the world. http://bio-based.eu/ download/?did=32875&file=0. Accessed 7 Mar 2016
- Parsell T, Yohe S, Degenstein J, Jarrell T, Klein I, Gencer E, Hewetson B, Hurt M, Kim JI, Choudhari H, Saha B, Meilan R, Mosier N, Riberio F, Delgass WN, Chapple C, Kenttamaa HI, Agarwal R, Abu-Omar MM (2015) Green Chem 17:1492–1499
- Plastermat (n.d.), Bioplastics to grow to 7% of total plastics market by 2020. http://www. plastemart.com/Plastic-Technical-Article.asp?LiteratureID=1903&Paper=bioplastics-to-growto-7-per-cent-total-plastics-market-by-2020. Accessed 7 Mar 2016
- Plumer B (2012) How the U.S. manages to waste \$165 billion in food each year. The Washington Post, 22 Aug. https://www.washingtonpost.com/news/wonk/wp/2012/08/22/how-food-actu ally-gets-wasted-in-the-united-states/. Accessed 7 Mar 2016
- Provolo G, Riva E (2009) Modelli gestionali per l'uso sostenibile degli effluenti di allevamento, GEA Quaderni della ricerca n. 104, Regione Lombardia, http://www.arca.regione.lombardia.it/ shared/ccurl/409/896/GEA\_q104\_web,0.pdf. Accessed 7 Mar 2016
- Quesada J, Rubio M, Gómez D (1999) J Wood Chem Technol 19:115-137
- Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, Davison BH, Dixon RD, Gilna P, Keller M, Langan P, Naskar, Saddler JN, Tschaplinski TG, Tuskan GH, Wyman CE (2014) Science 344:1246843. doi:10.1126/science.1246843
- Ricci-Jürgensen M (2012) Bio-waste management in Italy. http://www.assobioplastiche.org/wpcontent/uploads/2012/10/Newmann-David-Bio-waste.pdf. Accessed 6 Mar 2016
- Riggio V, Rosso M, Comino E, Biagini D, Montoneri E (2016) J Chem Tech Biotechnol. doi:10. 1002/jctb.5106
- Roland-Holst D, Triolo R, Heft-Neal S, Bayrami B (2013) Bioplastics in California. http://www.calrecycle.ca.gov/publications/Documents/1469%5C20131469.pdf. Accessed 7 Mar 2016
- Rosso D, Fan J, Montoneri E, Negre M, Clark J, Mainero D (2015) Green Chem 17:3424-3435
- Rovero A, Vitali M, Rosso D, Montoneri E, Chitarra W, Tabasso S, Ginepro M, Lovisolo C (2015) Int J Agronomy Agricultural Res (IJAAR) 6:75–91
- Sanders JPM, Clark JH, Harmsen GJ, Heeres HJ, Heijnen JJ, Kersten SRA, van Swaaij VPM, Moulijn JA (2012) Chem Eng Process 51:117–136
- Savarino P, Montoneri E, Bottigliengo S, Boffa V, Guizzetti T, Perrone DG, Mendichi R (2009) Ind Eng Chem Res 48:3738–3749
- Savarino P, Montoneri E, Musso G, Boffa V (2010) J Surfactants Detergents 13:59-68
- Segre A, Gaiani S (2011) Transforming food waste into a re-source. RSC Books 2013, Royal Society of Chemistry Publishing, UK. http://www.rsc.org/globalassets/05-journals-booksdatabases/booksellers/portfolio-flyers/rsc-books-food-science-portfolio-flyer.pdf?id=13583. Accessed 6 Mar 2016
- Segre A, Falasconi L, Morganti E (2009) Last minute market, increasing the economic, social and environmental value of unsold products in the food chain. Total food sustainability of the agrifood chain. RSC, London, pp 161–167
- Sereno CK (2010) Impact of ammonia and long chain fatty acids on thermophilic anaerobic digestion of swine wastes. PhD dissertation, North Carolina State University. http://www.lib. ncsu.edu/resolver/1840.16/6147. Accessed 7 Mar 2016
- Sheldon-Coulson GA (2011) Production of levulinic acid in urban biorefineries. Master of Science thesis in technology and policy, Massachusetts Institute of Technology. https://dspace.mit.edu/ bitstream/handle/1721.1/68450/769021899-MIT.pdf?sequence=2. Accessed 7 Mar 2016

- Sortino O, Dipasquale M, Montoneri E, Tomasso L, Avetta P, Bianco Prevot A (2013) Agron Sustain Dev 33(2):433-441
- Sortino O, Montoneri E, Patanè C, Rosato R, Tabasso S, Ginepro M (2014) Sci Total Environ 487C:443-451
- Storz H, Vorlop KD (2013) Appl Agric For Res 4:321-332
- Tabasso S, Montoneri E, Carnaroglio D, Caporaso M, Cravotto G (2014) Green Chem 16:73–76. doi:10.1039/C3GC41103F
- Tang J (2012) A cost benefit analysis of waste incineration with advanced bottom ash separation technology for a Chinese municipality Guanghan. Master of science thesis, Vienna School of International affairs. http://www.seas.columbia.edu/earth/wtert/sofos/PubDat\_210340.pdf. Accessed 3 Mar 2016
- Testa ML, Tummino ML, Agostini S, Avetta P, Deganello F, Montoneri E, Magnacca G, Bianco Prevot A (2015) RSC Adv 5:47920–47927
- The engineering toolbox (2013) Modulus of elasticity or Young's modulus and tensile modulus for some common materials. http://documents.mx/documents/elastic-properties-and-young-modulus-for-some-materialspdf.html; http://www.engineeringtoolbox.com/young-modulus-d\_417.html. Accessed 10 Oct 2016
- Twardowska I, Janta Koszuta K, Miszcsak E, Stefaniak S (2010) Occurrence and binding strength of metals in composted bio-waste and sewage sludge. In: Pawlowski L, Dudzviska M, Pawlowski A (eds) Environmental engineering III. Taylor and Francis, London. https://books.google.it/books?id=\_NXKBQAAQBAJ&pg=PA339&lpg=PA339&dq=food+waste+as+%25 +of+total+bio-waste+production&source=bl&ots=tNyLi2\_aQm&sig=MbNROoxerzh0XeK3 UGPWvOq-Tn&&hl=it&sa=X&ei=FkamVKCvEYboUtLNgOgI&ved=0CEsQ6AEwBQ#v= onepage&q=food%20waste%20as%20%25%20of%20total%20bio-waste%20production&f= false. Accessed 6 Mar 2016
- United States Department of Defense (2011) Technology readiness assessment (TRA) guidance. http:// www.acq.osd.mil/chieftechnologist/publications/docs/TRA2011.pdf. Accessed 7 Mar 2016
- US Environmental Protection Agency (2013) Global mitigation of non-CO<sub>2</sub> greenhouse gases. https:// www.epa.gov/sites/production/files/2016-06/documents/mac\_report\_2013-iii\_waste.pdf. Accessed 11 Oct 2016
- van Ree R, van Zeeland A (2014) Iea bioenergy task42, biorefining. http://www.iea-bioenergy. task42-biorefineries.com/en/ieabiorefinery.htm. Accessed 7 Mar 2016
- Vargas AKN, Savarino P, Montoneri E, Tabasso S, Cavalli R, Bianco Prevot A, Guardani R, Roux GAC (2014) Ind Eng Chem Res 53:8621–8629
- wiseGEEK (n.d.) Bending modulus. http://topics.wisegeek.org/topics.htm?bending-modulus#. Accessed 7 Mar 2016
- Wrap (2016) Compost calculator. http://www.wrap.org.uk/content/compost-calculator. Accessed 7 Mar 2016
- Zarebska A, Romero Nieto D, Christensen KV, Fjerbæk Søtoft L, Norddahl B (2015) Crit Rev Environ Sci Technol 45:1469–1521
- Zhao Q, Leonhardt E, MacConnell C, Frear C, Chen S (2010) Purification Technologies for biogas generated by anaerobic digestion. CSANR research report 2010–001. http://csanr.wsu.edu/ publications/researchreports/CFF%20Report/CSANR2010-001.ch09.pdf. Accessed 7 Mar 2016