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Sustainable Development Strategies: An Overview

Vincenzo Piemonte[1,*]*, Marcello De Falco*[1]*, and Angelo Basile*[2]
[1]*Faculty of Engineering, University Campus Bio-Medico of Rome, 00128 Rome, Italy*
[2]*CNR-ITM, c/o University of Calabria87030 Rende (CS), Italy*

1.1 Renewable Energies: State of the Art and Diffusion

Energy is a crucial challenge that scientific and technological communities face with more to come in the future. The environmental impact of fossil fuels, their cost fluctuations due both to economical/political reasons and their reducing availability boost research toward the development of new processes and technologies, which are more sustainable and renewable, such as solar energy, wind, biomass and geothermal.

Governments have facilitated renewable energy production diffusion by means of incentive schemes as the feed-in tariff (FIT) and Green Certificates (GCs), achieving unforeseeable success. In fact, the change in the world energy politics is substantially modifying the energy production network. The European Union target to increase the share of renewable energy sources (RES) in its gross final consumption of energy to 20% by 2020 from the 9.2% in 2006, which seemed unlikely up until recently, is now almost there thanks mainly to the strong increase of wind power, photovoltaics and plant biomass installations, together with the implementation of more efficient energy-consuming technologies in domestic, industrial and transport sectors, able to reduce global energy consumption.

The following charts in Figures 1.1–1.3 report wind power, photovoltaic and biomass-fired power station (by wood, municipal solid wastes and bio-gas) electrical energy production trends in recent years in EU-27 (Ruska and Kiviluoma, 2011): it is a worthy

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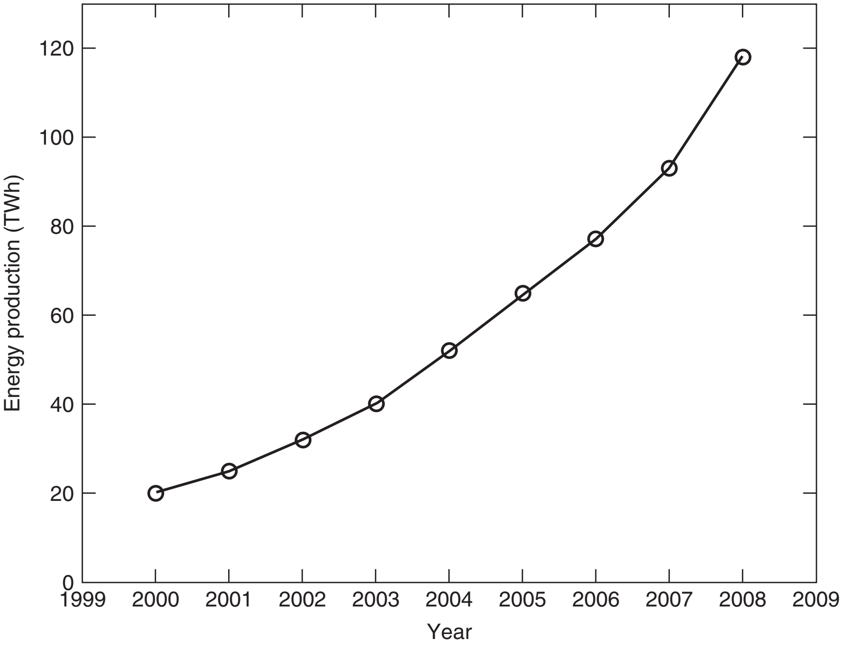

Figure 1.1 *Wind energy production in EU-27 (2000–2008)*

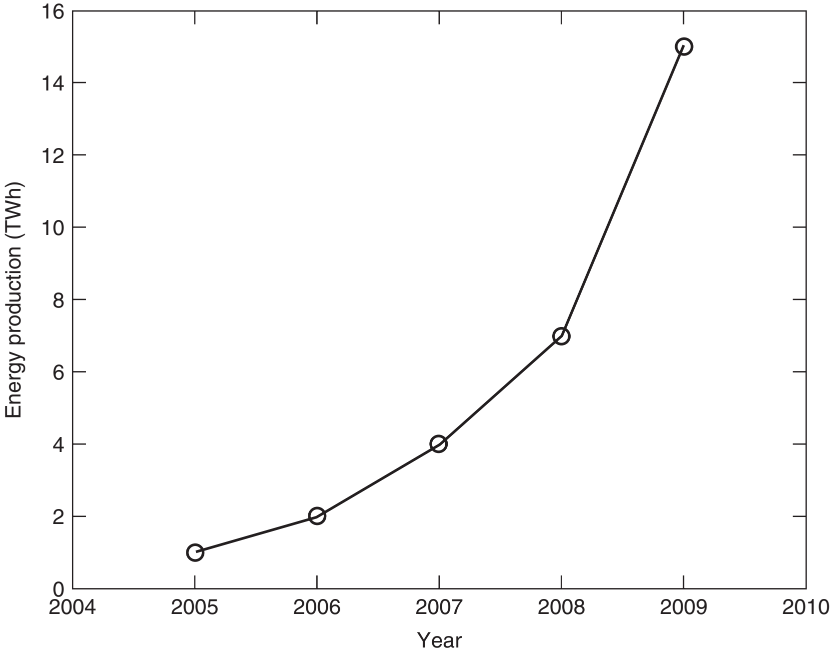

Figure 1.2 *PV energy production in EU-27 (2000–2008)*

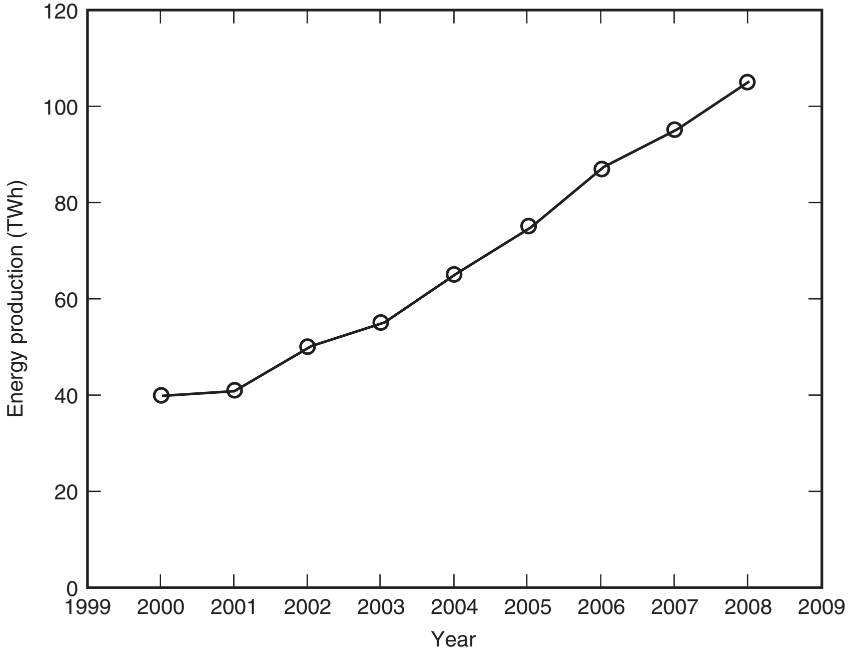

Figure 1.3 *Biomass plant energy production in EU-27 (2000–2008)*

assessment that the diffusion of such technologies follows an exponential profile. The total renewable installed capacity (hydropower, wind, biomass-fired power stations, geothermal plants, photovoltaics) was 200 GW in 2008 and it is continuously increasing.

The International Energy Outlook (*Bloomberg*, 2009) estimates that more than 42% of the new electrical power capacity to be installed up to 2020 will be based on renewable energies, with an average annual growth rates of 4.1%. By 2020 it is foreseen that US$150 bn will be invested worldwide on renewable energies. In Europe, €35 bn has been devoted to clean energy investment in 2008 (http://www.newenergyfinance.com, 2019–2013), and capital expenditure needed to achieve the EU objectives will be approximately €70 bn per year until 2020 in order to reach the 20% target.

From all these data, it is clear how the renewable energy market is becoming mainstream both from technical and financial points of view. Surely, public incentives must be one of the main reasons for renewable penetration in the energy sector, since they have allowed convenient investment when the technologies were not competitive. The increase of investors' interest on this market has pushed industrial production, with the effect of a strong reduction in prices. Taking the PV sector as an example, polycrystalline modules had a cost of about 3000 €/kW in 2009, while now the average price is 700–800 €/kW in 2011 thanks to the development of numerous modular manufacturing industries in Europe and China.

But, concerning the perspectives of renewable energies market in the next years, two crucial aspects have to be considered:

- The economic crisis is stimulating a debate about renewable energy public incentives, which have an increasing effect on the energy bills. The next target is the 'grid parity', that is, the point at which generating electricity from alternative energy produces power at a levelled cost equal to or less than the price of purchasing power from the grid.

- The penetration of renewable energy and the increase in its contribution to total electricity input in the grid lead to the problem of electricity network overload due to clean energy production fluctuations. PV and wind energy production depends on environmental conditions: during sunny and windy days renewable production could invoke serious problems for the grid. This problem stimulates the development of smart grid technologies, able to control and manage grid overloading and electricity storage systems.

Solving both these problems, which have the potential stop renewable energy use, is the main scientific and technological challenge for the future. In this context, proposing, developing and implementing new technologies able to reduce installation costs reaching grid parity and managing energy production is absolutely necessary in order to assure a clean energy future and further enhance its share in energy total production.

The EU assists innovative technology research and development process by allocating many resources to renewable energy projects funding. Figure 1.4 summarizes the organization of the RES financing programmes within the EU (ECOFYS project, 2011) for a total funding amount devoted to energy projects equal to about €4 bn for the next two years.

Thanks to EU support and to the expertise and creativity of worldwide scientific community, the next issues of renewable energy sector can be suitably overcome, allowing the implementation of a 100% clean energy system and achieving the objective of total decarbonation of economies and industries.

1.2 Process Intensification

Following Gorak and Stankiewicz (2011), process intensification (PI) is commonly considered to be one of the most promising development paths for the chemical process industry and one of the most important progress areas for chemical engineering research nowadays.

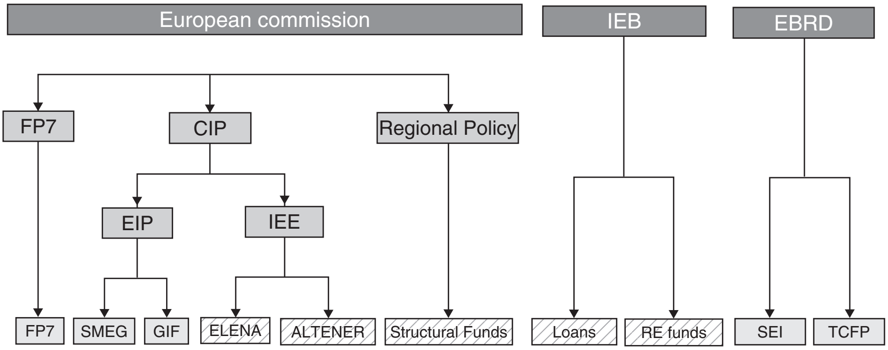

Figure 1.4 Financial organization of renewable energy in Europe

When introduced in the 1970s as a general approach, PI suggested a design strategy which aspired to the reduction in processing size of existing technology without any reduction in process output and quality. From that time, PI meaning has been changed several times and many definitions have been proposed, which, despite to their common point of view on innovation, were often different in substance. In 2009, Gerven and Stankiewicz (2009) defined the fundamentals of PI, suggesting that PI should follow a function oriented approach distinguishing four main principles:

- maximize the effectiveness of intra and intermolecular events;
- give each molecule the same processing experience;
- optimize the driving forces at every scale and maximize the specific surface area to which these forces apply;
- maximize the synergistic effects from partial processes.

In particular, the PI principles refer to all scales existing in chemical processes, from molecular to meso- and macro-scales and represent the targets that an intensified process aims to reach.

By applying these principles the PI offers, to an industrial company, many opportunities which can be summarized using only four words: smaller, cheaper, safer and slicker. Indeed, PI leads to the reduction of both investment (reduced equipment or integrated processing units) and operating costs (raw materials and utilities) and less waste. Moreover, by reducing the size of process equipment and the amount of raw material it is possible to ensure a safety benefit, especially in the nuclear/oil industry.

Generally, the PI can be divided in two domains: (1) *process intensifying equipment*, which considers equipment for both carrying out chemical reactions and not involving chemical reactions; and (2) *process intensifying methods*, which takes into account unit operations and is classified furthermore into four different areas (Stankiewicz and Moulijn, 2000).

1.2.1 Process Intensifying Equipment

As mentioned previously, this domain includes both equipment for carrying out the reaction such as the spinning disk reactor, spinning mixer reactor, static mixer catalyst, microreactors and heat exchange reactors, and equipment for non-reactive operations such as the static mixer, compact heat exchangers, rotor/stator mixers and so on.

As a classic example of process intensifying equipment already used in industrial processes, the static mixer reactors must be mentioned, due to their capability in combining mixing and intensive heat removal/supply (Thakur *et al.*, 2003). Moreover, they require less space, low equipment cost and good mixing at low shear rates. On the contrary, one of the most important drawbacks is their sensitivity to clogging by solids. It must also be said that this problem can be partially avoided by developing an open-crossflow-structure catalyst, a structured packing with good static-mixing properties and at the same time, used as catalytic support. The best known of this family is the so-called Katapak, commercialized by Sulzer, and characterized by both good mixing and radial heat-transfer (Stringaro *et al.*, 1998; Irandoust *et al.*, 1998). Usually, Katapak can be applied in catalytic distillation as well as in some gas-phase exothermic oxidation.

Heterogeneous catalytic processes can be intensified by using monolithic catalysts (Kapteijn *et al.*, 1999). Among their many features, it is possible to distinguish some very important benefits such as low pressure drop, high mass transfer area, a low space requirement, low cost and better safety. Another interesting example of process intensifying equipment is the microreactor, used for highly exothermic reactions or for toxic or explosive reactants/products. This device is a small reactor characterized by a structure that has a considerable number of layers with micro-channels. The layers perform various functions such as: mixing, catalytic reaction, heat exchange, or separation (Charpentier, 2007).

1.2.2 Process Intensifying Methods

Process intensifying methods can be divided into four areas: multifunctional reactors, hybrid separation, alternative energy sources and other methods. In the first two categories, the PI is expressed by the novelty of the processing methods in which two or more operations are combined, such as reaction/separation or separation/heat exchange and so on.

A well-known example of a multifunctional reactor is the membrane reactor, in which separation and reaction take place in the same tool. This alternative device represents a real model of intensification showing a higher efficiency compared to both conventional separation and reaction operations. An extensive discussion on these membrane reactors will be given in Chapter 6.

Another example of multifunctional reactors widely studied is the reverse-flow reactor, in which the reaction is combined with the heat transfer in only one unit operation (Matros and Bunimovich, 1996). The idea is to couple indirectly the energy necessary for endothermic reactions and energy released by exothermic reactions, without mixing both endothermic and exothermic reactants in closed-loop reverse flow operation. Usually, this reactor is used for SO_2 oxidation, total oxidation of hydrocarbons and NO_x reduction (Matros and Bunimovich, 1995).

Reactive distillation is another one of the best known examples of reaction and separation combination used commercially (De Garmo *et al.*, 1992). In this case, the reactor consists of a distillation column filled with catalyst. The aim of the distillation column is to separate the reaction products by fractionation or to remove impurities or undesired species. The main benefits of reactive distillation are reduced energy requirements and lower capital investment. Moreover, the continuous removal of reaction products allows us to obtain higher yields compared to conventional systems (Stadig, 1987). Nowadays, this device has been used on a commercial scale even if the potential of this technique has not yet completely exploited.

Reactive extraction is the combination of processes such as reaction and solvent extraction. The main benefit of this integration results in fewer process steps overall, thereby reducing capital cost. Moreover, this combination allows the enhancement of both selectivity and yields of desired products consequently reducing recycle flows and waste formation (Krishna, 2002).

Multifunctional reactors can also combine reaction and phase transition, and the reactive extrusion represents an example of such combination. Currently, this reactor is used in polymer industries, which enables the processing of highly viscous materials without requiring large amounts of solvents (Minotti *et al.*, 1998; Samant and Ng, 1999). Also hybrid separations are characterized by coupling of two or more different unit operations, which lead to a sustainable increase in the process performances owing to the synergy effects among the operations. The most important category in this area is represented by the combination of membranes with another separation unit operation.

Membrane distillation is probably the best known of hybrid separation (Lawson *et al.*, 1997; Godino *et al.*, 1996). It consists of the permeation of a volatile component contained in a liquid stream through a porous membrane as a vapour and condensing on the other side into a permeate liquid. In this process, the driving force is represented by the temperature difference. This technique is widely considered as an alternative to reverse osmosis and evaporation. In comparison with other separation operations, membrane distillation shows very important benefits, such as a complete rejection of colloids, macro-molecules and non-volatile species, lower operating temperature and pressure, and therefore lower risk and low equipment cost, and less membrane fouling due to larger pore size (Tomaszewska, 2000).

Other examples of hybrid separation are membrane absorption and stripping, in which the membrane serves as a permeable barrier between the gas and liquid phases (Jansen *et al.*, 1995; Poddar *et al.*, 1996).

Adsorptive distillation represents a hybrid separation process not involving membranes (Yu *et al.*, 1996). In this technique, a selective adsorbent is added to a distillation mixture which allows us to increase separation ability. Adsorptive distillation can be used for the removal of trace impurities in the manufacturing of fine chemicals or it can present an attractive option in separation of azeotropes or close boiling components. Also alternative energy sources can be considered as an example of PI. Indeed, for instance, alternative forms of energy, such as microwaves, can accelerate chemical processes by hundreds of times compared to the conventional unit operation.

However, other techniques not belonging to the three aforementioned areas can also be considered as intensified processes, such as supercritical fluids and cryogenic techniques. In particular, supercritical fluids are currently applied in mass transfer operations, such as extraction (McHugh and Krukonis, 1994) and for chemical reactions (Savage *et al.*, 1995; Hyde *et al.*, 2001) owing to their high diffusion coefficient; instead, the cryogenic technique, combining distillation with adsorption, is used for industrial gas production but it can present a future option for separation operations in fine chemical industries (Jain and Tseng, 1997; Stankiewicz, 2003).

Anyhow, despite the benefits arising by application of PI principles and by considering that some PI technologies have already been implemented, PI industrial applications on a large scale are faced with several barriers. These obstacles are represented by an insufficient PI knowledge and know-how among process technologists, no pilot plant or possibility to use an existing pilot line, both technical and financial risk in the development of first industrial prototype and the implementation of PI modules in existing production plants and low awareness of potential benefits of PI technologies at the management level.

Only a broad action plan including not only technical factors (technological R&D, upscaling and industrial implementation), but also social and economic factors, can ensure the fast and successful implementation of PI.

1.3 Concept and Potentialities of Bio-based Platforms for Biomolecule Production

Around the world significant steps are being taken to move from today's fossil based economy to a more sustainable economy based on biomass. The transition to a bio-based economy has multiple drivers:

- the need to develop an environmentally, economically and socially sustainable global economy;
- the anticipation that oil, gas, coal and phosphorus will reach peak production in the not-too-distant future and that prices will climb;
- the desire of many countries to reduce an over dependency on fossil fuel imports, so the need for countries to diversify their energy sources;
- the global issue of climate change and the need to reduce atmospheric greenhouse gases (GHG) emissions.

The production of bio-based chemicals is not new, nor is it an historic artefact. Current global bio-based chemical and polymer production (excluding biofuels) is estimated to be around 50 000 000 tonnes (Higson, 2011). Notably, examples of bio-based chemicals include non-food starch, cellulose fibres and cellulose derivatives, tall oils, fatty acids and fermentation products such as ethanol and citric acid. However, the majority of organic chemicals and polymers are still derived from fossil based feedstocks, predominantly oil and gas.

Historically, bio-based chemical producers have targeted high value fine or speciality chemical markets, often where specific functionality played an important role. The low price of crude oil acted as barrier to bio-based commodity chemical production and producers focussed on the specific attributes of bio-based chemicals, such as their complex structure, to justify production costs.

The recent climb in oil prices, the consumer demand for environmentally friendly products, population growth and limited supplies of non-renewable resources have now opened new windows of opportunity for bio-based chemicals and polymers. Bio-based products (chemicals, materials) can be produced in single product processes; however, the production in integrated biorefinery processes producing both bio-based products and secondary energy carriers (fuels, power, heat), in analogy with oil refineries, probably is a more efficient approach for the sustainable valorization of biomass resources in a future bio-based economy (Kamm, 2006; World Economic Forum, 2010).

However, the main driver for the development and implementation of biorefinery processes today is the transportation sector. Significant amounts of renewable fuels are necessary in the short and midterm to meet policy regulations both in- and outside Europe. A very promising approach to reduce biofuel production costs is to use so called biofuel-driven biorefineries for the co-production of both value-added products (chemicals, materials, food, feed) and biofuels from biomass resources in a very efficient integrated approach.

From an overall point of view, a key factor in the realization of a successful biobased economy will be the development of biorefinery systems that are well integrated into the existing infrastructure. Through biorefinery development, highly efficient and cost effective processing of biological raw materials into a range of bio-based products

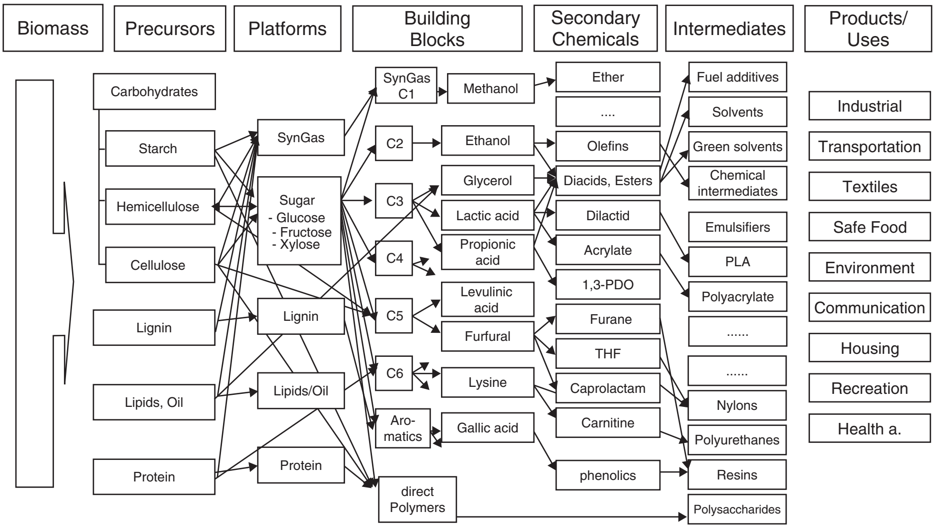

Figure 1.5 *Biorefinery system scheme (Kamm et al., 2006). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

can be achieved. On a global scale, the production of bio-based chemicals could generate US$10–15 bn of revenue for the global chemical industry (World Economic Forum, 2010).

Biorefineries can be classified on the basis of a number of their key characteristics (see Figure 1.5). Major feedstocks include perennial grasses, starch crops (e.g. wheat and maize), sugar crops (e.g. beet and cane), lignocellulosic crops (e.g. managed forest, short rotation coppice, switchgrass), lignocellulosic residues (e.g. stover and straw), oil crops (e.g. palm and oilseed rape), aquatic biomass (e.g. algae and seaweeds), and organic residues (e.g. industrial, commercial and post-consumer waste). These feedstocks can be processed to a range of biorefinery streams termed platforms. The platforms include single carbon molecules such as biogas and syngas, five- and six-carbon carbohydrates from starch, sucrose or cellulose; a mixed five- and six-carbon carbohydrate stream derived from hemicelluloses, lignin, oils (plant-based or algal), organic solutions from grasses, pyrolytic liquids. These primary platforms can be converted to wide range of marketable products using combinations of thermal, biological and chemical processes.

1.3.1 Biogas Platform

Currently, biogas production is mainly based on the anaerobic digestion of ‘high moisture content biomass’ such as manure, waste streams from food processing plants or biosolids from municipal effluent treatment systems. Biogas production from energy crops will also increase and will have to be based on a wide range of crops that are grown in versatile, sustainable crop rotations. Biogas production can be part of sustainable biochemical and biofuel-based biorefinery concepts as it can derive value from wet streams. Value can be increased by optimizing methane yield and economic efficiency of biogas production (Bauer *et al.*, 2007), and deriving nutrient value from the digestate streams (De Jong *et al.*, 2011).

1.3.2 Sugar Platform

Six-carbon sugar platforms can be accessed from sucrose or through the hydrolysis of starch or cellulose to give glucose. Glucose serves as feedstock for (biological) fermentation processes providing access to a variety of important chemical building blocks. Glucose can also be converted by chemical processing to useful chemical building blocks. Mixed six- and five-carbon platforms are produced from the hydrolysis of hemicelluloses. The fermentation of these carbohydrate streams can in theory produce the same products as six-carbon sugar streams; however, technical, biological and economic barriers need to be overcome before these opportunities can be exploited. Chemical manipulation of these streams can provide a range of useful molecules (see Figure 1.6).

Six- and five-carbon carbohydrates can undergo selective dehydration, hydrogenation and oxidation reactions to give useful products, such as: sorbitol, furfural, glucaric acid, hydroxymethylfurfural (HMF), and levulinic acid. Over 1 000 000 tonnes of sorbitol is produced per year as a food ingredient, a personal care ingredient (e.g. toothpaste), and for industrial use (Vlachos *et al.*, 2010, ERRMA, 2011).

1.3.3 Vegetable Oil Platform

Global oleochemical production in 2009 amounted to 7.7 million tonnes of fatty acids and 2.0 million tonnes of fatty alcohols (ICIS Chemical Business, 2010). The majority of fatty acid derivatives are used as surface active agents in soaps, detergents and personal care products (Taylor *et al.*, 2011).

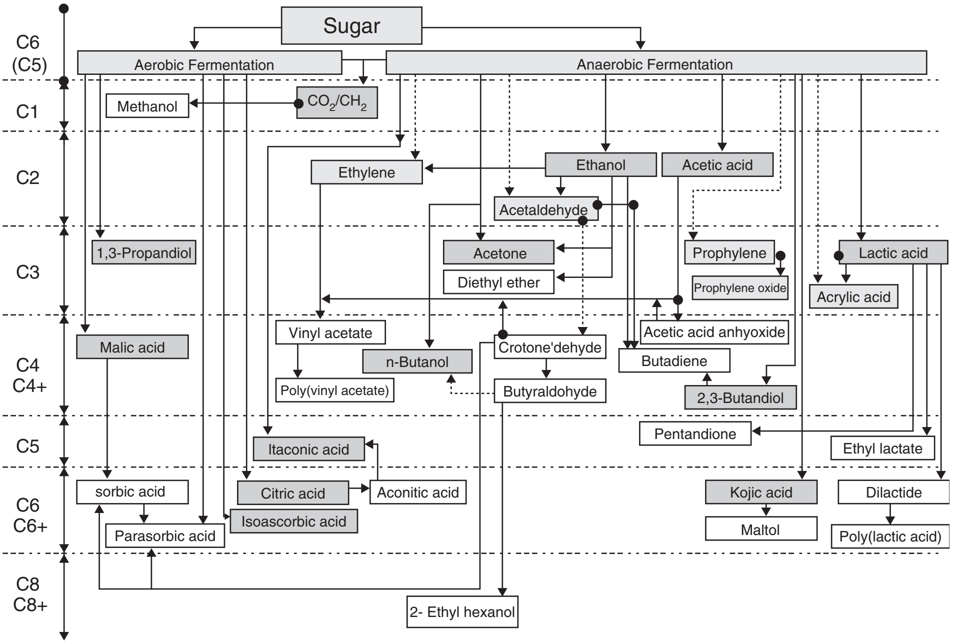

Figure 1.6 Sugar platform scheme (Kamm et al., 2006). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Major sources for these applications are coconut, palm and palm kernel oil, which are rich in C12–C18 saturated and monounsaturated fatty acids. Important products of unsaturated oils, such as soybean, sunflower and linseed oil, include alkyd resins, linoleum and epoxidized oils. Rapeseed oil, high in oleic acid, is a favoured source for biolubricants. Commercialized biofunctional building blocks for bio-based plastics include sebacic acid and 11-aminoundecanoic acid, both from castor oil, and azelaic acid derived from oleic acid. Dimerized fatty acids are primarily used for polyamide resins and polyamide hot melt adhesives.

Biodiesel production has increased significantly in recent years with a large percentage being derived from palm, rapeseed and soy oils. In 2009 biodiesel production was around 14 million tonnes; this quantity of biodiesel co-produces around 1.4 million tonnes of glycerol. Glycerol is an important co-product of fatty acid/alcohol production. The glycerol market demand in 2009 was 1.8 million tonnes (ICIS Chemical Business, 2010). Glycerol is also an important co-product of fatty acid methyl ester (FAME) biodiesel production. It can be purified and sold for a variety of uses (De Jong *et al*., 2011).

1.3.4 Algae Oil Platform

Algae biomass can be a sustainable renewable resource for chemicals and energy. The major advantages of using microalgae as a renewable resource are:

- Compared to plants, algae have a higher productivity. This is mostly due to the fact that the entire biomass can be used in contrast to plants which have roots, stems and leafs. For example, the oil productivity per land surface can be up to 10 times higher than palm oil.
- Microalgae can be cultivated in seawater or brackish water on non-arable land, and do not compete for resources with conventional agriculture.
- The essential elements for growth are sunlight, water, CO_2 (a greenhouse gas), and inorganic nutrients such as nitrogen and phosphorous which can be found in residual streams.
- The biomass can be harvested during all seasons and is homogenous and free of lignocellulose.

The main components of microalgae are species dependent but can contain a high protein content, quantities can be up to 50% of dry weight in growing cultures with all 20 amino acids present. Carbohydrates as storage products are also present and some species are rich in storage and functional lipids, they can accumulate up to 50% lipids, and in very specific cases up to 80% (the green algae *Botryococcus*) which accumulates long chain hydrocarbons. Other valuable compounds include: pigments, antioxidants, fatty acids, vitamins, anti-fungal, -microbial, -viral toxins and sterols (De Jong *et al*., 2011).

1.3.5 Lignin Platform

Up to now the vast majority of industrial applications have been developed for lignosulfonates. These sulfonates are isolated from acid sulfite pulping and are used in a wide range of lower value applications. Around 67.5% of world consumption of lignosulfonates in 2008 was for dispersant applications followed by binder and adhesive applications at 32.5%. Major end-use markets include construction, mining, animal feeds and agriculture uses.

Besides lignosulfonates, Kraft lignin is produced as commercial product at about 60 kton per year. New extraction technologies developed in Sweden will lead to an increase in Kraft lignin production at the mill-side for use as an external energy source and for production of value added applications (Öhman *et al.*, 2009) (see Figure 1.7). The production of bioethanol from lignocellulosic feedstocks could result in new forms of higher quality lignin becoming available for chemical applications. The production of more value added chemicals from lignin (e.g. resins, composites and polymers, aromatic compounds, carbon fibres) is viewed as a medium to long term opportunity which depends on the quality and functionality of the lignin that can be obtained. The potential of catalytic conversions of lignin (degradation products) has been recently reviewed (Zakzeski, 2010).

1.3.6 Opportunities and Growth Predictions

The potential for chemical and polymer production from biomass has been comprehensively assessed in several reports and papers (Shen *et al.*, 2009; US Department of Agriculture, 2008; Patel *et al.*, 2006; Bozell and Petersen, 2010; Werpy and Petersen, 2004; Nexant ChemSystems, 2008).

An international study (Patel *et al.*, 2006) found that with favourable market conditions the production of bulk chemicals from renewable resources could reach 113 million tonnes by 2050, representing 38% of all organic chemical production. Under more

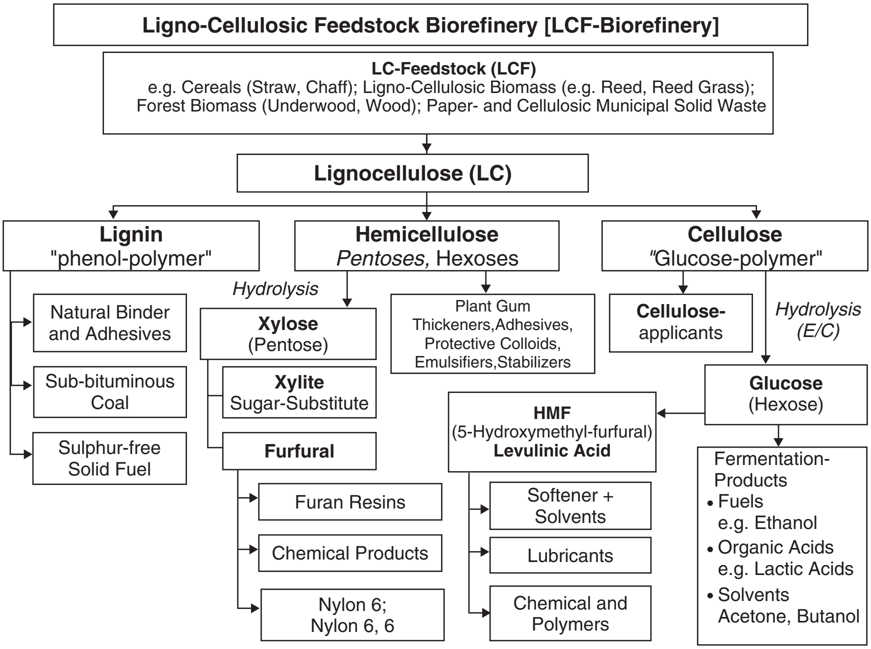

Figure 1.7 *Lignin platform scheme (Kamm* et al.*, 2006). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

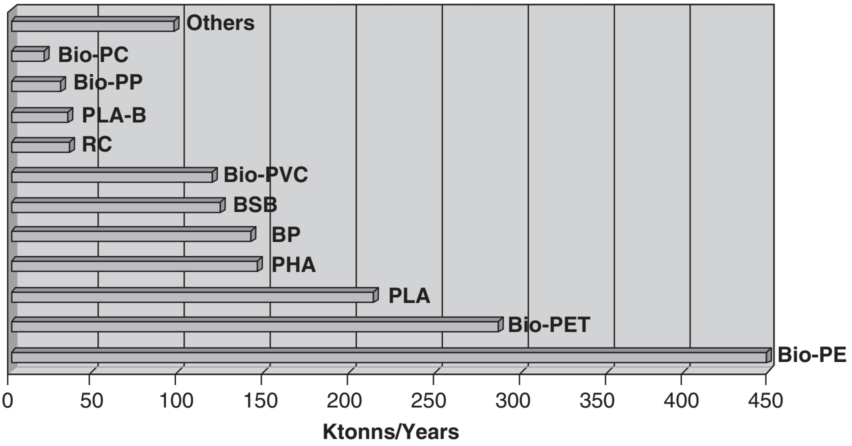

Figure 1.8 *Plastics Europe anticipated biopolymer production capacity (in tonnes/year) by 2015*

conservative market conditions the market could still be a significant 26 million tonnes representing 17.5% of organic chemical production.

Recently Plastemart (Plastemart, 2011) gave an overview of the biorenewable market which was estimated to be worth US$2.4 bn globally in 2010. This steadily growing market has experienced a compounded annual growth rate (CAGR) of 14.8%, a growth trend that is going to increase as the world resumes a more normal production pace and new bio-based chemicals such as bio-ethylene come to market (see Figure 1.8).

The platform biorenewable chemicals glycerine and lactic acid make up the bulk of biorenewable chemicals being sold in 2010, accounting for 79.2% of the market. There is a large range in market maturity for platform biochemicals, ranging from mature markets such as lactic acid to nascent markets for chemicals such as succinic acid.

Currently, commercialized biopolymers (i.e. PLA, PHA, thermoplastic starch) are demonstrating strong market growth. Market analysis shows growth per annum to be in the 10–30% range (Pira, 2010; SRI Consulting, 2012; Helmut Kaiser Consultancy, 2012). Bio-based polymer markets have been dominated by biodegradable food packaging and food service applications. It can be rationalized that the production of more stable, stronger and longer lasting biopolymers will lead to CO_2 being sequestered for longer periods and leads to (thermochemical) recycling rather than composting where the carbon is released very quickly without any energy benefits (De Jong *et al.*, 2011).

1.4 Soil and Water Remediation

One of the most urgent problems being faced worldwide is contamination of soil and water due to domestic and industrial activity. Large polluted areas have lost their eco-functionality and also often present a serious risk to human health. A policy of restoration of natural resources is thus a priority. In recent years, a range of technologies for the remediation of contaminated sites have been developed. Treatment methods are

Table 1.1 *Overview of soil remediation methods*

SOIL Remediation Techniques	Degree of Effectiveness	References
Biological treatments	Removal efficiencies >80% for mineral oil & >95% for monocyclic aromatic hydrocarbons (HC) • HC biodegradation rates under biopile–44,000 g/m3/day	Hoeppel and Hinchee (1994), Tsang *et al.* (1994), Lei *et al.* (1994), Alcade *et al.* (2006), Adekunle (2011)
Chemical treatments Remediation using actinide chelators	Potential solubility problems, stability, and pH requirements that could limit the use of chelators exist	Gopalan *et al.* (1993), Henry and Warner (2003)
Chemical immobilization	Tests results demonstrated that with chemical treatment, heavy metals mobility was drastically reduced; 82–95% metals confined	Czupyrna *et al.* (1989), Khan and Husain (2007)
Critical fluid extraction	Extraction efficiencies between 90–98% demonstrated using PCB-laden sediments • Process is complex; predicting the efficiency of such extraction is difficult	Bellandi (1995)
Oxidation • Chlorine dioxide CD • Hydrogen Peroxide HP • Photolysis P • Reductive Dechlorination RD	• Oxidation can reduce or eliminate volume & toxicity • CD best applied to aqueous phase chemicals • HP easily oxidizes organic and compound rings • UV shown to degrade PCB, dioxins, PAHs	Bellandi (1995), Aristov and Habekost (2010), Fontaine and Piccolo (2011)
In situ catalysed peroxide remediation	• Injection pressure and injection depth influenced decontamination efficiency • Nitrobenzene was reduced in concentration by >50% over 15 days	Ho *et al.* (1995), Gates and Siegrist (1994)
Photodegradation with uranium recovery	• Overall rate of photodegradation faster at pH 3.5 than 6.0	Dodge and Francis (1994), Alvarez *et al.* (2007), Marin *et al.* (2012)

Table 1.1 *(continued)*

SOIL Remediation Techniques	Degree of Effectiveness	References
	• Absence of O_2, excess citric acid, and intermediate degradation products prevented uranium precipitation	
Physical treatments Capping	• Interim stabilization successful at Hanford • If uncontrolled, methane gas that migrates within cover system can balloon and possibly combust	Bellandi (1995), Henry and Warner (2003)
Cementitious waste forms sulfur polymer cement concrete (SPCC) Sulfur polymer cement (SPC)	NRC requires only 500 psi compressive strength and SPCC avg. is 4000 psi • SPC resists attack by most acids and salts, less permeable than concrete	Smith and Hayward (1993), Darnell (1994)
Electrokinetic remediation	• Results indicate optimum moisture content for soil between 14–18 weight % exists • Possibility of inducing greater flow thru fine-grained soils	Lindgren *et al.* (1994), Swartzbaugh *et al.* (1990), Krukowski (1993), Park *et al.* (2007)
Incineration technologies • Rotary kiln RK • Infrared conveyor furnaces ICF • Liquid injection LI • Plasma arc PA • Fluidized bed FB • Multiple hearth MH Feed rates (FR) Destruction and removal efficiency (DRE)	• Incineration reduces volume & toxicity • RK solid waste feed rate 160–170 g/s • ICF DRE 99.9999% for PCBs • PA efficiency at high temperatures is exceedingly high • FB enhances efficiency (larger particles remain suspended until combustion) • MH FR 9–16g/m2/s	Bellandi (1988 and 1995), Aronne *et al.* (2012)

(*continued overleaf*)

Table 1.1 *(continued)*

SOIL Remediation Techniques	Degree of Effectiveness	References
In situ grouting ISG	• ISG of shallow landfills has been used to effectively control inflow of surface water into hazardous and radioactive waste sites • Chemical grouts – high penetration potential	Spence and Tamura (1989), Karol (1990)
In situ vitrification ISV	• Reduces toxicity, mobility, and volume of waste, and residual product rendered relatively innocuous • Volume reduction of soil matrix ~20–40%	Bellandi (1995), Oma (1994), Tixier *et al*. (1992), Luey *et al*. (1992), Spalding (1994)
Soil washing	• Knowing distribution of contaminants among various particle-size fractions is key to predicting effectiveness • Mobile washing system capacity of 2–4 tons/hr demonstrated reduction in lead concentrations by factor of ~20 • Contaminants must be Hydrophobic	Bellandi (1988 and 1995), Scholz and Milanowski (1983), Masters *et al*. (1991), Griffiths (1995), Gombert (1994), Kim (1993), Wilson and Clarke (1994a,b), Berselli *et al*. (2004),Conte *et al*. (2005)
Sorting methods	Potentially contaminated soil is processed at a rate of 750 m3/ week with a volume reduction between 95–99%	Bramlitt (1990)
Stabilization/ solidification S/S	Polybutadiene resin used in S/S is durable, resists corrosion, and is impermeable to leachates	Conner (1994), Unger *et al*. (1989)
Thermal desorption	Advantage over incineration–reduced amount of gases produced, thereby reducing the size of the off-gas handling system	Bellandi (1995), Ayen *et al*. (1994), Wilson and Clarke (1994a,b)
Vapour stripping	• Large volumes can be readily treated, cleanup times short, toxic material removed and destroyed • Environmental impacts are low	Bellandi (1995), Wilson and Clarke (1994a,b), Thompson (1996)

Table 1.2 *Overview of surface and groundwater remediation methods*

WATER Remediation Techniques	Degree of Effectiveness	References
Biological treatments	• Specific environment governs success of process • Aerobic fluidized-bed had higher chlorophenol loading rates and better quality effluent than those reported	Bellandi (1989 and 1995), Wilson and Clarke (1994a,b), Jarvinen *et al.* (1994), Okonko and Shittu (2007), Cicek (2003)
Chemical treatments Electron-beam irradiation	• Low dose rates of electrons more efficient • E-beam technology has shown removal efficiencies up to 99.99% in full-scale Operation	Rosocha *et al.* (1994), Nyer (1992)
Mercury extraction	Microemulsion containing a cation exchanger reduces mercury content of aqueous phase from 500 ppm to 0.3 ppm, a 40-fold improvement over equilibrium extraction	Larson and Wiencek (1993 and 1994)
Radiocolloid treatment	In situ colloid remediation process using polyelectrolyte capture successful in laboratory column tests	Nuttall and Kale (1994), Nuttall *et al.* (1992)
Removal by sorption to organo-oxides	Advantages: can be regenerated in situ; selective removal achieved if specific surfactant that sorbs contaminant selectively is used; solute removed can be Recovered	Park and Jaffe (1994)
Physical treatments Air sparging/Air stripping In situ air sparging IAS Pump & treat P&T	• Efficiency with which O_2 is transferred to groundwater must be addressed if IAS to be proven effective • Air and steam stripping technologies most effective with VOCs and ammonia	Bellandi (1995), Wilson and Clarke (1994a,b), Cartwright (1991), Hinchee (1994), Isherwood (1993), Johnson (1994), Looney *et al.* (1991)

divided into those for soil remediation and for surface and groundwater remediation. Further categorization results in the consideration of biological (also called bioremediation), chemical, and physical treatment techniques.

The majority of techniques are categorized as physical treatments with only one process, and treatment based on biodegradation falling in the biological treatment category. Chemical treatments involve the application of agents to promote extraction of the hazardous substance, and physical treatments involve removal of the hazard through physical means. The relative benefit of the various remediation methods has dependence in large-scale applicability as well as overall cost. Techniques such as in situ vitrification can be applied only to finite areas in each application, however, because of the associated expense, multiple applications in different areas of the same waste site increase the method's cost-effectiveness.

In the following we try to give an overview of the most important processes for water and soil remediation in a schematic way, through Tables 1.1 and 1.2, which report the remediation processes applied to water and soil remediation along with the relative degree of effectiveness as well as the reference papers that the readers can refer for detailed information on each method.

As for the newest technologies now available for water and soil remediation, the reader can directly refer to the dedicated chapters (Chapters 10 and 11) in this book.

1.4.1 Soil Remediation

In the following table the most used methods for soil remediation along with their degree of effectiveness are reported. For detailed information about each method the reader can refer to the original articles (see Table 1.1).

1.4.2 Water Remediation

In the following table the most used methods for water remediation along with their degree of effectiveness are reported. For detailed information about each method the reader can refer to the original articles (see Table 1.2).

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