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The Biorefinery Concept: An Integrated Approach

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1.1 Sustainability for the Twenty-First Century

The greatest challenge we face in the twenty-first century is to reconcile our desires as a society to live lives based on consumption of a wider range of articles both essential (e.g. food) and luxury (e.g. mobile phones) with the fact that we live on a single planet with limited resources (to make the articles) and limited capacity to absorb our wastes (spent articles). While some will argue that we should not be limited by our own planet and instead seek to exploit extra-terrestrial resources (e.g. mining the asteroids), most of us believe it makes more sense to match our lifestyles with the planet we live on.

We can express this in the form of an equation whereby the Earth's capacity (EC) is defined as the product of world population *P*, the economic activity of an individual *C* and a conversion factor between activity and environmental burden *B*:

$$EC = P \times C \times B.$$

Since we live in a time of growing *P* and *C* (through the rapid economic development of the mega-states of the East in particular), and if we assume that all the indicators of environmental stress (including climate change, full landfill sites,

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pollution and global warming) are at least partly correct, then to be sustainable we must reduce *B*. There are two ways to do this:

1. dematerialisation: use less resources per person and hence produce less waste; and
2. transmaterialisation: use different materials and have a different attitude to 'waste'.

While many argue for dematerialisation, this is a dangerous route to go down as it typically requires that the developing nations listen to the developed nations and 'learn from their mistakes'. While many of our manufacturing processes in regions such as Europe and North America are becoming increasingly more efficient, we continue to treat most of our waste with contempt, focusing on disposal and an 'out of sight, out of mind' attitude. We also have to face the unavoidable truth that people in developing countries want to enjoy the same standard of living we have benefited from in the developed world; pontificating academics and politicians in the West talking about the need to reduce consumption will have little impact on the habits of the rest of the world!

Transmaterialisation, as it would apply to a sustainable society based on consumer goods, is more fundamental. It makes no assumption about limits of consumption other than the need to fit in with natural cycles such as using biomass at no more than the rate nature can produce it. Transmaterialisation also avoids clearly environmentally incompatible practices (such as using short-lifetime articles that linger unproductively in the environment for long periods of time, e.g. non-biodegradable polyolefin plastic bags) and bases our consumption pattern on the circular economy model, with spent articles becoming a resource for other manufacturing [1]. This model is essentially the same as the green chemistry concept, at least in terms of the chemical processes and products that dominate consumer goods, described in more detail in Section 1.4.

1.2 Renewable Resources: Nature and Availability

We need to find new ways of generating the chemicals, energy and materials as well as food that a growing world population (increasing *P*) and growing individual expectations (increasing *C*) needs, while limiting environmental damage. At the beginning of transmaterialisation is the feedstock or primary resource and this needs to be made renewable (see Figure 1.1). An ideal renewable resource is one that can be replenished over a relatively short timescale or is essentially limitless in supply. Resources such as coal, natural gas and crude oil come from carbon dioxide, 'fixed' by nature through photosynthesis many millions of years ago. They are of limited supply, cannot be replaced and are therefore non-renewable. In contrast, resources such as solar radiation, wind, tides and biomass can be considered as renewable resources, which are (if appropriately managed) in no danger of being over-exploited. However, it is important to note that while the first three resources can be used as a renewable source of energy, biomass can be used to produce not only energy but also chemicals and materials, the focus of this book.

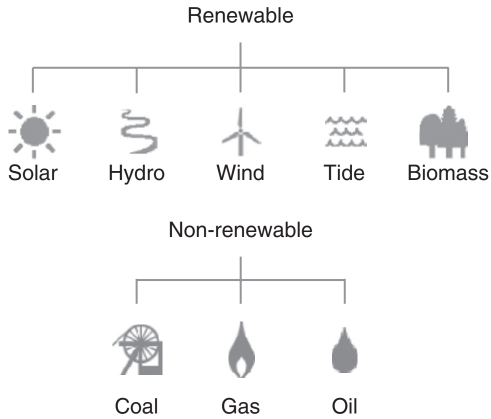

Figure 1.1 *Different types of renewable and non-renewable resources.*

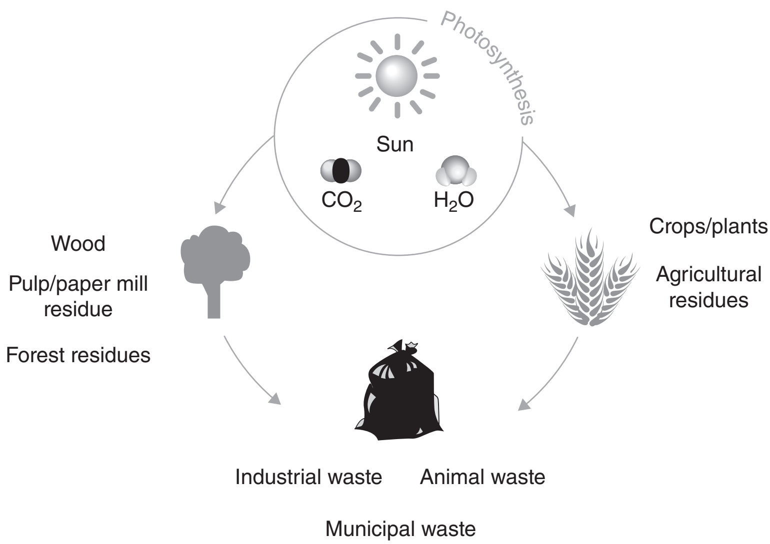

Figure 1.2 *Different types of biomass.*

By definition, biomass corresponds to any organic matter available on a recurring basis (see Figure 1.2). The two most obvious types of biomass are wood and crops (e.g. wheat, maize and rice). Another very important type of biomass we tend to forget about is waste (e.g. food waste, manure, etc.), which is the focus of Section 1.3. These resources are generally considered to be renewable as they can be continually re-grown/regenerated. They take up carbon dioxide from the air while they are growing (through photosynthesis) and then return it to the air at the end of life, thereby creating a closed loop [2].

Table 1.1 Biomass potential in the EU [5].

	Biomass potential (MTonnes oil equivalent)		
	2010	2020	2030
Organic wastes	100	100	102
Energy crops	43–46	76–94	102–142
Forest products	43	39–45	39–72
Total	186	215–239	243–316

Food crops can indeed be used to produce energy (e.g. biodiesel from vegetable oil), materials (e.g. polylactic acid from corn) and chemicals (e.g. polyols from wheat). However, it is becoming widely recognised by governments and scientists that waste and lignocellulosic materials (e.g. wood, straw and energy crops) provide a much better energy production opportunity than food crops since they avoid competition with the food sector and often do not require as much land and fertilisers to grow. In fact, only 3% of the 170 million tonnes of biomass produced yearly by photosynthesis is currently being cultivated, harvested and used (food and non-food applications) [3]. Indeed, according to a report published by the USDOE and the USDA [4], the US alone could sustainably supply more than one billion dry tons of biomass annually by 2030. As seen in Table 1.1, the biomass potential in Europe is also enormous.

1.3 The Challenge of Waste

Waste is a major global issue and is becoming more important in developing countries, as well as in the West. According to the World Bank, world cities generate about 1.3 billion tonnes (Gt) of solid waste per year, and this is expected to increase to 2.2 Gt by 2025 [6]. Globally, solid waste management costs will increase from today's $200 billion per year to about $375 billion per year in 2025. Cost increases will be most severe in low-income countries (more than five-fold increases) and lower–middle income countries (more than four-fold increases). Global governments need to put in place programmes to reduce, reuse, recycle or valorise as much waste as possible before burning it (and recovering the energy) or otherwise disposing of it.

Few countries have a constructive waste management policy whereby a significant proportion of the waste is used in some way (see Figure 1.3); reliable data are however not easily available from developing countries, other than anecdotal evidence such as from India where many people apparently make a living from waste [7]. The increasing costs of traditional fossil reserves, along with concerns over security of supply and the identification of critical raw mineral materials by the European Union (EU) is beginning to make people realise that the traditional linear economy model of extract-process-consume-dispose is unsustainable [8].

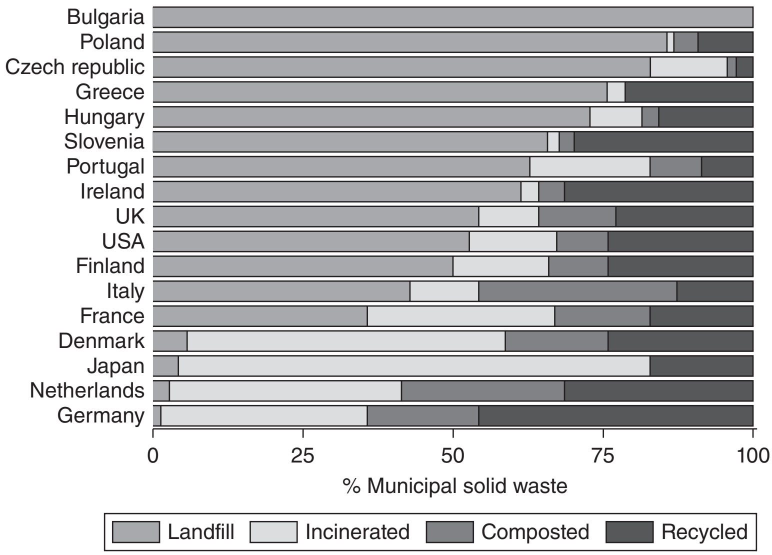

Figure 1.3 *The fate of waste in different countries.*

Rather, we must move towards a circular economy whereby we continue to make use of the resources in articles when they are no longer required in their current form. This is *waste valorisation*.

Waste produced in the food supply chain is a good example of a pre-consumer type of waste generated on a large scale all over the world. Sixty percent of this is organic matter, which can represent up to 50% of all the waste produced in a country. Food waste is ranked third of 15 identified resource productivity opportunities in the McKinsey report '*Resource Revolution*: *Meeting the World*'*s Energy*, *Material*, *Food and Water Needs*' [9]. But there are few examples that take us away from the totally wasteful and polluting landfilling or first-generation and limited-value recycling practices such as composting and animal feed production. We need to design and apply advanced methods to process food waste residues in order to produce high-value-added products including chemicals and materials which can be used in existing and future markets. Society also needs a paradigm shift on our attitude towards waste, and this needs to be steered by governments (and trans-government agencies such as the EU) worldwide. One government-driven incentive is the increasingly expensive waste disposal costs. The EU Landfill Directive, for example, has caused landfill gate fees to increase from £40–74 to £68–111 between 2009 and 2011 [10]. Improved resource utilisation can positively influence the profits of industry as well as enable new companies to start up, produce new growth and expand innovation opportunities by moving towards the ultimate sustainability goal of a zero-waste circular economy [11, 12].

1.3.1 Waste Policy and Waste Valorisation

The first significant waste policies in the EU were introduced in the early 1970s. These were aimed at developing a uniform definition of 'waste' on the basis of a range of policies and laws aimed at regulating production, handling, storage and movement, as well as treatment and disposal of waste. Their objective was to reduce the negative effects of waste generation on human health and the environment [13]. Essentially, the definition of waste is 'substances or objects that the holder discards or intends or is required to discard'. Differentiating waste from by-products and residues, as well as waste from substances that have been fully recovered, are constant issues that need to be resolved if valorisation routes additional to current first-generation practices (composting, animal feed and anaerobic digestion) are to be developed. The hierarchy for waste management places priority on preventing waste arising in the first instance, consistent with the philosophy of green chemistry (the best way to deal with waste is to avoid its formation in the first place), and relegates disposal or landfilling to the worst waste management option [14]. Among the intermediate waste management options, re-use and recycling (e.g. to make chemicals) is preferred to energy recovery; this seems sensible given the greater resource consumption and pollution associated with the production of chemicals, although the value of energy continues to grow. Significantly, a new policy approach to waste management that takes account of the whole life-cycle of products was introduced in 2008, along with an emphasis on managing waste to preserve natural resources and strengthen the economic value of waste [13].

EU Member States are required to draw up waste prevention programmes that help to break the link between economic growth and waste generation, an important development on the road to zero waste. The EU guidelines identify two main approaches to food waste prevention:

1. behavioural change; and
2. sectoral-based approaches aimed at companies, households, institutions, etc.

There is a significant directive to shift biodegradable municipal waste away from landfill by imposing stringent reduction targets on EU Member States (65% by weight by 2016 against 1995 levels, with intermediate reduction targets). Food waste is considered as biodegradable waste for the purpose of the Directive. Another factor driving the diversion of biodegradable food waste from landfill towards other waste management options is the widely recognised importance of reducing greenhouse gas (GHG) emissions to the atmosphere.

Where international transportation is contemplated for the treatment of waste, including transportation to other EU Member States, trans-frontier shipment of waste rules will also need to be considered further to the Basel Convention [15]. Shipments of waste for disposal are generally prohibited, but the rules applicable to shipments of waste for recovery depend on the classification of the waste concerned and on the destination of the waste. Waste from agro-food industries is generally found on the 'green list', subject to the condition that it is not infectious, which should enable much useful food waste to be transported. A potential policy and regulatory disincentive to the reprocessing of food wastes into chemical substances is the dovetailing of end-of-waste status and chemical substances legislation, most notably through the major new REACH (Registration, Evaluation, Authorisation and restriction of CHemicals) legislation affecting chemicals manufactured or used in the EU (see Section 1.4). The testing and administrative costs of achieving a registration under REACH are considerable; cost sharing by co-registration is only partially successful as many companies are reluctant to collaborate in areas where they are competing (e.g. over the sale of the same substance). This is a major disincentive for industry and producers in the EU, especially small and medium enterprises (SMEs) producing novel substances resulting from food waste reprocessing who may find the compliance costs of REACH legislation a major barrier to commercialising the process. With other major economies outside the EU also showing interest in adopting similar legislation to REACH (including the US, where current legislation is variable from state to state, and China), manufacturing and distribution outside of the EU will have to overcome this potential barrier.

1.3.2 The Food Supply Chain Waste Opportunity

Alternative feedstocks to conventional fossil raw materials have attracted increasing interest over recent years for the manufacture of chemicals, fuels and materials [16]. In the case of biomass as a renewable source of carbon, feedstocks including agricultural and forestry residues are converted into valuable marketable products, ideally by using a series of sustainable and low-environmental-impact technologies, so that the resulting products are genuinely green and sustainable. The facilities where such transformations take place are often referred to as biorefineries, the focus of this book [17].

Food supply chain waste (FSCW) is emerging as a biomass resource with significant potential to be employed as a raw material for the production of fuels and chemicals, given the abundant volumes globally generated and its inherent diversity of functionalised chemical components [18].

Several motivating factors for the development of advanced valorisation practices on residues and by-products of food waste are available, such as the abundance, ready availability, under-utilisation and renewable nature of the significant quantities of functionalised molecules including carbohydrates, proteins, triglycerides, fatty acids and phenolics. Various waste streams also contain valuable compounds including antioxidants, which could be recovered, concentrated and re-used in applications such as food and lubricants additives. Examples of such types of wastes and associated 'corresponding target ingredient for recovery' have been used to highlight the potential of FSCW as a source of valuable chemical components [19].

The development of such valorisation routes may address the main weakness of the food processing industry and aim to develop a more sustainable supply chain and waste management system. Such routes can solve both resource and waste management problems. The important issues associated with agro-food waste include:

1. decreasing landfill options;
2. uncontrolled greenhouse gas emissions;
3. contamination of water supplies through leaching of inorganic matter; and
4. low efficiency of conventional waste management methods, notably incineration and composting.

Up-to-date and accurate data on the production of food waste (FW) at every stage of the food supply chain are difficult to obtain, but food waste is being mapped in Europe as part of the new COST (European Cooperation in Science and Technology) Action TD1203. There are strong drivers for stakeholders and public organisations in food processing and other sectors to reduce costs and develop suitable strategies for the conversion and valorisation of side streams. The development of knowledge-based strategies to realise the potential of food waste should also help to satisfy an increasing demand for bio-derived chemicals, fuels and materials, and probably affect waste management regulations over the years to come. The valorisation of FSCW is necessary in order to improve the sustainability and cost-effectiveness of food supply and the manufacture of chemicals. Together with the associated ethical and environmental issues and the drivers for utilising waste, the pressures for such changes are becoming huge.

1.3.3 Case Study: Citrus Waste

Citrus fruits are grown in many regions of the earth, including Latin and Central America and the southern USA, southern Europe, northern and southern Africa, China and India. Of the various fruit types orange is the largest in volume, representing about 95 million tonnes (Mt) annually. Major producers include Brazil, USA, China, India and southern Europe, particularly Italy and Spain. After extraction of the juice, the residual peel accounts for 50 wt% of fruit that is costly to treat and is highly regulated. However, with the high volumes of citrus production and processing, there is a real opportunity to better utilise this resource for animal feed (although it has low protein content) and essential oil extraction. Simple calculations show that the amount of organic carbon available in the peel and other residues from juicing corresponds to over 5 Mt, similar in weight to the total amount of (mostly non-renewable, typically oil-derived) carbon used by the UK for the manufacture of all of its chemicals [20].

Major components of wet orange peel are water (80% by weight), soluble sugars cellulose and hemicellulose, pectin and D-limonene. The demand for pectin (a valuable food thickener and cosmetic ingredient) and limonene (a flavour and fragrance additive for many household products and a ‘green’ solvent, e.g. for cleaning electronics where it replaces atmospherically harmful halogenated solvents) is increasing.

The production of chemical products from wet orange peel has had very limited commercial success: limonene and other oils are extracted and sold but only for a small proportion of the peel, while pectin is generally sourced from other fruit (apples and lemons). The current methods for the production of pectin requires a two-stage process involving the use of mineral acids, which generates large amounts of contaminated wastewaters (from neutralising the waste acid) adding to the cost of the final product, although there is a high demand for pectin for food and non-food applications.

One way to improve the economics of this process of is to employ an integrated technology that yields multiple products. Recent work has demonstrated that low-temperature microwave processing of citrus peel such as orange yields limonene and pectin as well as porous cellulose and other products in one process, thus offering the real possibility of developing a microwave biorefinery that could be employed wherever citrus waste is concentrated [21]. New uses for limonene have also been reported recently, notably as a solvent for organic chemical manufacturing processes where there is growing pressure to reduce the process environmental footprint and use more renewable compounds [22].

1.4 Green Chemistry

Green chemistry emerged in the 1990s as a movement dedicated to the development of more environmentally benign alternatives to hazardous and wasteful chemical processes as a result of the increased awareness in industry of the costs of waste and of government regulations requiring cleaner chemical manufacturing. Through a combination of meetings, research funding, awards for best practice and tougher legislation, the green chemistry movement gained momentum through the 1990s and into the twenty-first century. New technologies which addressed key process chemistry issues such as wasteful separations (e.g. through the use of easy-to-separate supercritical CO_2), atmospherically damaging volatile organic solvents (e.g. through the use of involatile ionic liquids), hazardous and difficult-to-separate process auxiliaries (e.g. by using heterogeneous reagents and catalysts) and poor energy utilisation (e.g. through alternative reactors such as microwave heating) were developed and promoted. The importance of metrics for measuring process greenness also became recognised and was championed by the pharmaceutical industry as well as by academics [23]. The pharmaceutical industry has led the way in many examples of green chemistry metrics in practice, including solvent selection guides and assessment of the environmental impacts of different processes [24].

The legislative, economic and social drivers for change impact all of the main chemical product life-cycle stages, resources, production and products.

Diminishing reserves and dramatic fluctuations in the price of oil, the most important raw material for chemicals, have been highlighted. However, the wider reality is of resource depletion of many key minerals and price increases for commodities affecting almost all chemical manufacturing as well as other important industries, notably electronics [25]. There has also been an exponential growth in product-focused legislation and non-governmental organisation (NGO) pressure, threatening the continued use of countless chemicals. The most important legislative driver is REACH [26]. This powerful legislation requires the thorough testing of all chemicals used at quantities of more than 1 tonne per year in Europe (including those manufactured outside of the EU and imported in). Persistence, bioaccumulation and toxicity (PBT) are the key assessments.

While there has been considerable debate on the impact of REACH on the European chemical industry due to the high costs of assessment and testing and the inevitable bureaucracy, the biggest results will ultimately be the identification of chemicals that require authorisation or restricted use. At the time of writing, the list of chemicals effectively black-listed or at least highlighted as being of serious concern (making their use very difficult due to NGO and consumer pressure) is growing and already causing alarm in industries whose own processes or supply chains rely on the same chemicals. Solvents are an area of great concern as they are widely used in many industries; several polar (e.g. N-methylpyrolloidone), polarisable (e.g. chlorinated aliphatics) and non-polar (e.g. hexane) solvents are likely to fall foul of REACH. In such cases a critical issue is suitable alternatives. While replacing some chemicals may not prove too difficult, in many cases there are no suitable alternatives. This certainly applies to solvents where currently used compounds may well have a complex set of desirable properties (liquid range, boiling point, polarity/polarisability, water miscibility, etc.); finding a suitable alternative that also has better PBT characteristics can be very difficult. This is an area where renewable products may prove to be very important. New solvents with a diverse range of properties (e.g. terpenes, esters, polyethers) can be tailored for some problematic processes, such as limonene as referred to earlier [22].

By using the low-environmental-impact technologies developed in the 1990s to obtain safe 'REACH-proof' chemicals from large-volume bioresources, we can take a major step towards the creation of a new generation of green and sustainable chemicals as well as tackle the escalating waste problems faced by modern society. Through the use of green chemistry techniques to obtain organic chemicals and materials from biomass and materials and metals from waste electronics and other consumer waste, we can help establish a life-cycle for many products that is sustainable on a sensible timescale within the human lifespan.

We must make better use of the primary metabolites in biomass. Cellulose, starches and chitin need to be used to make new macromolecular materials and not simply act as a source of small molecules; this can include composites and blends with synthetic polymers as we move towards a sustainable chemical industry. The small molecules that we obtain in this way need to become the building blocks of that industry: compounds such as lactic acid, succinic acid and fatty acids, glycerol and sugars, as well as ethanol and butanol are all needed to feed the industry, using green chemistry methods to convert them into replacements for the very large number of organic chemicals in current use. This includes developing synthetic pathways starting from oxygenated, hydrophilic molecules, but we must avoid wasteful and costly separations from dilute aqueous fermentation broths. A wider range of chemistry in water including more water-tolerant catalysts is needed, as are other important synthetic strategies such as the reduction in the number of process steps through telescoped reactions. The future green chemistry toolkit needs to be flexible and versatile as well as clean, safe and efficient [27, 28].

1.5 The Biorefinery Concept

1.5.1 Definition

A biorefinery is a facility or a network of facilities that converts biomass including waste (Chapter 2) into a variety of chemicals (Chapters 4 and 5), biomaterials (Chapter 6) and energy (Chapter 7), maximising the value of the biomass and minimising waste. This integrated approach is gaining increased commercial and academic attention in many parts of the world [29, 30]. As illustrated in Figure 1.4, advanced biorefineries are analogous in many ways to today's petrorefineries [31].

Similarly to oil-based refineries, where many energy and chemical products are produced from crude oil, biorefineries produce many different industrial products from biomass. These include low-value high-volume products such as transportation fuels (e.g. biodiesel, bioethanol), commodity chemicals and materials and high-value low-volume products or specialty chemicals such as cosmetics or nutraceuticals [32]. Energy is the driver for developments in this

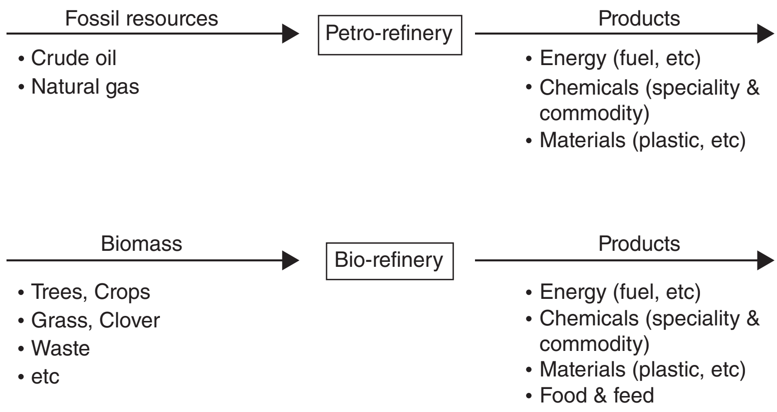

Figure 1.4 *Comparison of petrorefinery v. biorefinery.*

area, but as biorefineries become more and more sophisticated with time, other products will be developed. In some types of biorefinery, food and feed production may also be incorporated.

According to the Joint European Biorefinery Vision for 2030 [33], a significant proportion of the overall European demand for chemicals, energy and materials will be met using biomass as a feedstock by 2030:

- 30% of overall chemical production is expected to be bio-based in nature by this date (for high-added-value chemicals and polymers, the proportion might even be >50%);
- 25% of Europe's transport energy needs will be supplied by biofuels, with advanced fuels (and in particular bio-based jet fuels) taking an increasing share; and
- 30% of Europe's heat and power generation will be derived from biomass.

1.5.2 Different Types of Biorefinery

Three different types of biorefinery have been described in the literature [34, 35]:

- Phase I biorefinery (single feedstock, single process and single major product);
- Phase II biorefinery (single feedstock, multiple processes and multiple major products); and
- Phase III biorefinery (multiple feedstocks, multiple processes and multiple major products).

1.5.2.1 Phase I Biorefinery

Phase I biorefineries use only one feedstock, have fixed processing capabilities (single process) and have a single major product. They are already in operation and have proven to be economically viable. In Europe, there are now many phase I biorefineries producing biodiesel [36]. They use vegetable oil (mainly rapeseed oil in the EU) as a feedstock and produce fixed amounts of biodiesel and glycerine through a single process called transesterification (see Figure 1.5). They have almost no flexibility to recover investment and operating costs. Other examples of phase I biorefinery include today's pulp and paper mills and corn grain-to-ethanol plants.

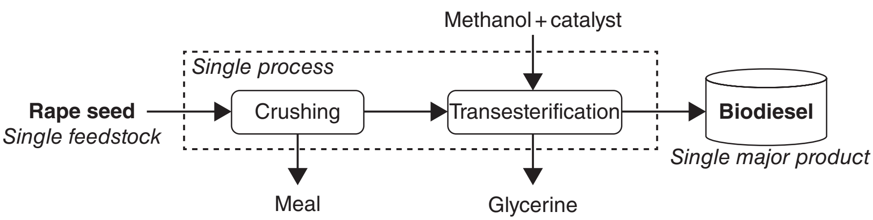

Figure 1.5 *The biodiesel process: an example of a phase I biorefinery.*

1.5.2.2 Phase II Biorefinery

Similarly to phase I biorefineries, phase II biorefineries can only process one feedstock. However, they are capable of producing various end-products (energy, chemicals and materials) and can therefore respond to market demand, prices, contract obligation and the operating limits of the plant.

Recent studies have revealed that a biorefinery integrating biofuels and chemicals offers a much higher return on investment and meets its energy and economic goals simultaneously [37]. For instance, Wageningen University performed a study in 2010 in which 12 full biofuel value chains – both single-product processes and biorefinery processes co-producing value-added products – were technically, economically and ecologically assessed. The main overall conclusion was that the production costs of the biofuels could be reduced by about 30% using the biorefinery approach [38].

One example of a phase II biorefinery is the Novamont plant in Italy, which uses corn starch to produce a range of chemical products including biodegradable polyesters (Origi-Bi) and starch-derived thermoplastics (Mater-Bi). Another example of this type of biorefinery is the Roquette site of Lestrem in France that produces a multitude of products including polyols, native and modified starches, proteins and derivatives, cyclodextrins, organic acids and resins (see Figure 1.6).

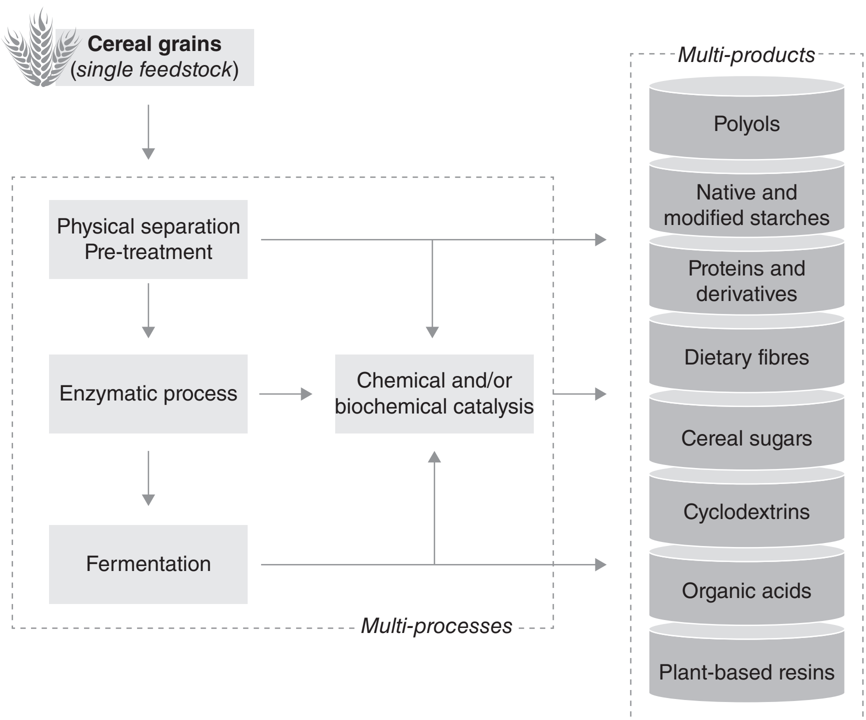

Figure 1.6 *Roquette site in Lestrem, France: an example of a phase II biorefinery.*

Roquette produces more than 600 carbohydrate derivatives worldwide and is now leading a major programme (the BioHub™ programme) aiming to develop cereal-based biorefineries and a portfolio of cereals-based platform chemicals (e.g. isosorbide) for biopolymers as well as specialty and commodity chemicals production.

Ultimately, all phase I biorefineries could be converted into phase II biorefineries if methods of upgrading the various side streams could be identified. For example, a phase I biodiesel processing plant could be turned into a phase II biorefinery if the operator started to convert the (crude) glycerol into valuable energy and/or chemical products (see Chapter 4 for potential chemical products from glycerol). It is in fact recognised that energy or biofuel generation will probably form the initial backbone of numerous phase II biorefineries. Indeed, crude oil refining also started with the production of energy; it now employs sophisticated process chemistry and engineering to produce complex materials and chemicals that 'squeeze every ounce of value' from each barrel of oil [31].

1.5.2.3 Phase III Biorefinery

Phase III biorefineries correspond to the most developed/advanced type of biorefinery. They are not only able to produce a variety of energy and chemical products (as phase II biorefineries do), but can also use various types of feedstocks and processing technologies to produce the multiplicity of industrial products our society requires. The diversity of the products gives a high degree of flexibility to changing market demands (a current by-product might become a key product in the future) and provides phase III biorefineries with various options to achieve profitability and maximise returns [33]. In addition, their multi-feedstock nature helps them to secure feedstock availability and offers these highly integrated biorefineries the possibility of selecting the most profitable combination of raw materials [39, 40]. Although no commercial phase III biorefineries exist, extensive work is currently being carried out in the EU, the US (the present leading player in this field) and elsewhere on the design and feasibility of such facilities. According to a recent report from the Biofuels Research Advisory Council, full-scale phase III (zero-waste) biorefineries are not expected to become established in Europe until around 2020 [5].

Currently, there are five phase III biorefinery systems being pursued in research and development, which will be discussed in more detail in the following sections:

1. lignocellulosic feedstock biorefinery;
2. whole-crop biorefinery;
3. green biorefinery;
4. two-platform biorefinery; and
5. marine biorefinery.

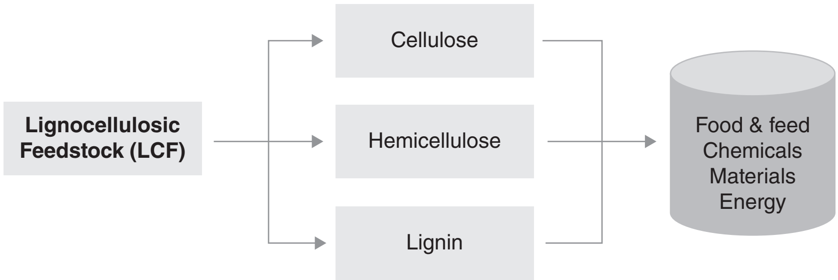

Figure 1.7 *Simplified diagram of a lignocellulosic feedstock biorefinery.*

1.5.2.3.1 Lignocellulose Feedstock Biorefinery

A lignocellulose feedstock biorefinery will typically use lignocellulosic biomass such as wood, straw and corn stover. The lignocellulosic raw material (consisting primarily of polysaccharides and lignin) will enter the biorefinery and, through an array of processes, will be fractionated and converted into a variety of energy and chemical products (see Figure 1.7).

In the US, ZeaChem is currently developing its first commercial lignocellulose feedstock biorefinery at the Port of Morrow in Boardman, Oregon. Located adjacent to their demonstration facility, the 25 million gallons per year integrated biorefinery is expected to produce bio-based fuels, C2 chemicals (acetic acid, ethyl acetate, ethanol and ethylene) and C3 chemicals (propionic acid, propanol and propylene) from nearby woody biomass and agricultural residues using a hybrid process of biochemical and thermochemical processing.

Another example of an imminent lignocellulosic feedstock biorefinery is SP Processum in Sweden, which corresponds to an integrated cluster of industries converting wood into energy, chemicals and materials (see Figure 1.8). This is probably one of the best examples of industrial symbiosis in the world, with one industry using the waste or by-product of another as a raw material [41]. Among the member companies are AkzoNobel Surface Chemistry (production of thickeners for water-based paints and the construction industry), Domsjo Fabriker (production of dissolving pulp and paper pulp), Ovik Energy (energy production and distribution) and Sekab (production of ethanol, ethanol derivatives and ethanol as fuel).

In reality, while the sole products of existing pulp and paper manufacturing facilities today are pulp and paper (phase I biorefinery), these facilities are geared to collect and process substantial amounts of lignocellulosic biomass. They therefore provide an ideal foundation on which to develop advanced lignocellulose feedstock biorefineries. Additional processes could be built around pulp mills, either as an extension or as an ‘across-the-fence’-type company.

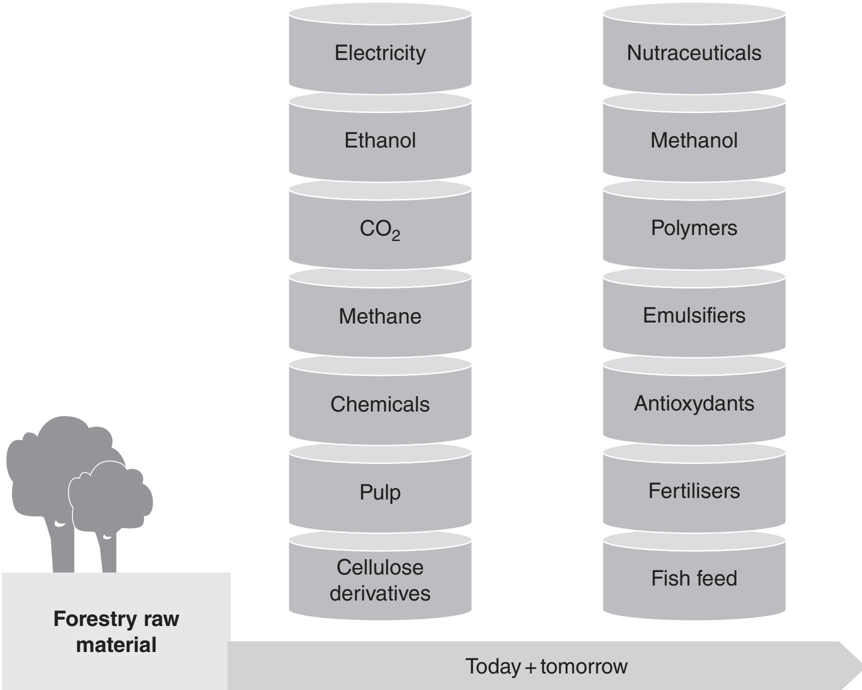

Figure 1.8 Processum biorefinery in Sweden: an example of a lignocellulosic feedstock biorefinery.

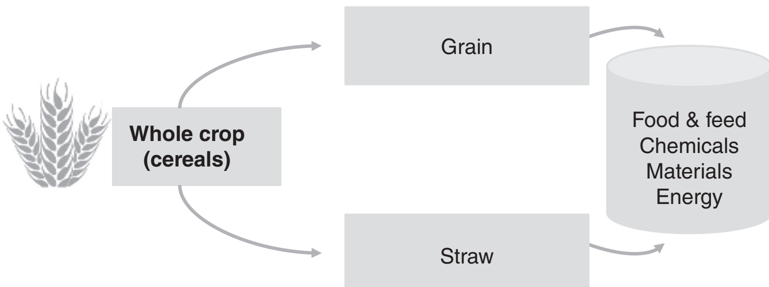

Figure 1.9 Simplified diagram of a whole-crop biorefinery.

1.5.2.3.2 Whole-Crop Biorefinery

A whole-crop biorefinery will employ cereals (e.g. wheat, maize, rape, etc.) and convert the entire plant (straw and grain) into energy, chemicals and materials (see Figure 1.9).

The first step will involve the separation of the seed from the straw (collection will obviously occur simultaneously to minimise energy use and labour cost). The seeds may then be processed to produce starch and a wide variety of products

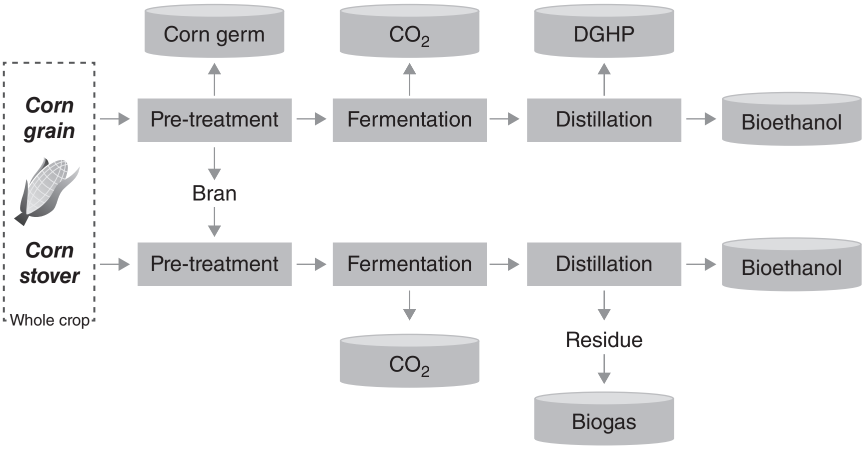

Figure 1.10 *POET-DSM advanced biofuels biorefinery, US: an example of a whole-crop biorefinery.*

including ethanol and bioplastics, as it is currently done in phase II biorefineries. In parallel, the straw may undergo various conversion processes as described in the previous section.

POET (formerly known as Broin Companies), one of the largest producers of ethanol in the world, has built a commercial whole-crop biorefinery in Iowa which started operations in 2014. Through the Liberty project (jointly funded by POET, DSM Advanced Biofuels and the US Department of Energy), a corn grain-to-ethanol plant was converted into a commercial-scale whole-crop biorefinery designed to utilise advanced corn fractionation and lignocellulosic conversion technology to produce ethanol from corn cobs, leaves, husk and some stalk (see Figure 1.10). The facility also produces a number of valuable products including corn germ and a protein-rich dried distillers grains (Dakota Gold® HP or DGHP), which can be used as animal feed.

1.5.2.3.3 Green Biorefinery

Green biorefinery is another form of phase III biorefinery which has been extensively studied in the EU (especially Germany, Austria and Denmark) over the last 10–20 years [42, 43]. It takes green biomass (such as green grass, lucerne, clover, immature cereals, etc.) and converts it into useful products including energy, chemicals, materials and feed through the use of different technologies including fermentation (see Figure 1.11). Rich in water, green biomass is typically separated into a fibre-rich press cake and a nutrient-rich green juice. The green juice contains a number of useful chemicals such as amino acids, organic acids and dyes. The press cake can be used for fodder or to produce energy, insulation materials, construction panels and biocomposites, etc.

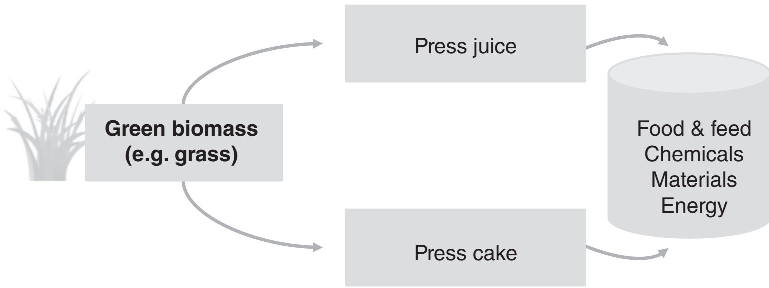

Figure 1.11 Simplified diagram of a green biorefinery.

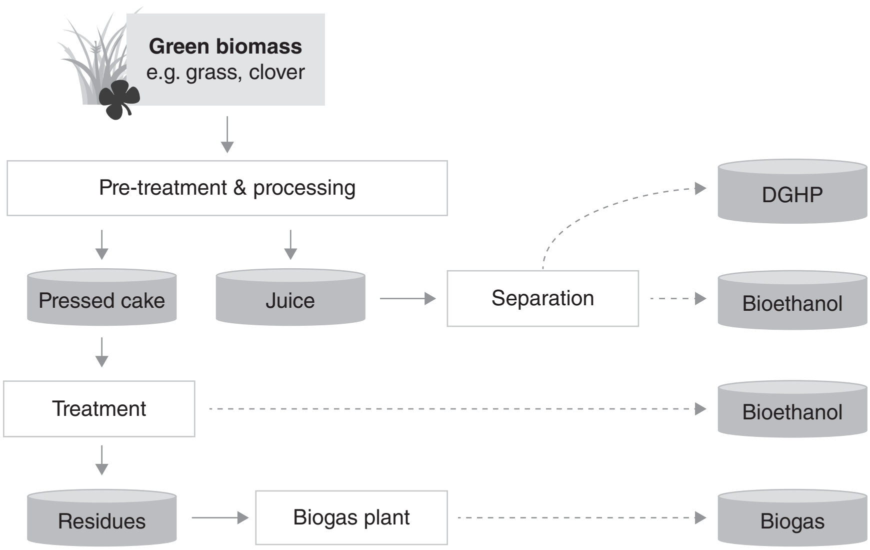

Figure 1.12 Schematic of the Austrian green biorefinery. Based on [44].

A green biorefinery demonstration plant has recently been set up in Brandenburg (Germany) and produces high-value proteins, lactic acid and fodder from 20,000 tonnes per year of alfalfa and wild mix grass. In this facility, insulating material, reinforced composites for production of plastics and biogas for heat and power are all produced from grass in an integrated process. Another example of this form of phase III biorefinery is in Austria, where the processing of green biomass from silage ensures a decentralised and seasonally independent feedstock process (see Figure 1.12). A demonstration facility based in Utzenaich currently produces a range of chemicals (e.g. lactic acid, amino acids) and fibre-derived products (e.g. animal feed, boards, insulation materials, etc.) as well as electricity and heat from grass silage.

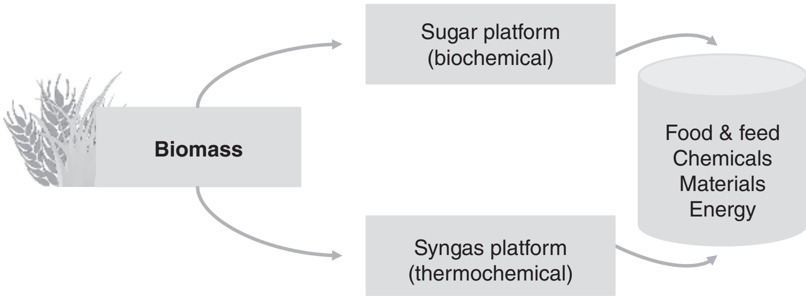

Figure 1.13 *Simplified diagram of a two-platform biorefinery.*

1.5.2.3.4 Two-Platform Biorefinery

Another form of biorefinery recently defined by the National Renewable Energy Laboratory (NREL) is the two-platform biorefinery. As depicted in Figure 1.13, the feedstock is separated into a sugar platform (biochemical) and a syngas platform (thermochemical). Both platforms can offer energy, chemicals, materials and potentially food and feed, therefore making use of the entire feedstock(s) (see Chapter 3). The sugar platform is based on biochemical conversion processes and focuses on the fermentation of sugars extracted from biomass feedstocks. The syngas platform thermolytically transforms biomass into gaseous or liquid intermediate chemicals that can be upgraded to transportation fuels as well as commodity and speciality chemicals [45].

No biorefinery of this type currently exists in Europe but sugar conversion technologies (e.g. wheat grain-to-ethanol fermentation) and gasification approach (e.g. Linde's Carbo-V® process) are independently used. Opinions vary widely on the best strategy to combine these two platforms. However, it is most likely that, as new technologies are developed, multiple biorefinery designs will emerge commercially depending on the location of the plant and the feedstock(s) used.

Importantly, the sugar platform and many other (non-thermochemical) processes likely to be incorporated into a biorefinery will almost certainly generate some waste products that will be difficult to convert into value-added materials and chemicals. Such wastes and residues could potentially represent an important source of energy within the biorefinery, and are an ideal candidate for thermochemical conversion [46].

1.5.2.3.5 Marine Biorefinery

There is considerable interest in the use of micro- and macro-algae (seaweed) as a biorefinery feedstock to produce food, feed, biofuels and chemicals. Although their potential is considerable, marine biorefineries are in their infancy compared to the other types of phase III biorefineries (based on terrestrial crops) described in the preceding sections [47].

Table 1.2 *Comparison of petrorefinery and biorefinery in terms of feedstock, conversion processes and products.*

		Petro-refinery	Biorefinery
Feedstock	Location	Rich deposits in some areas	Widely distributed
	Density	High	Low
	Availability	Continuous but finite	Seasonal but renewable
	Chemical composition	Hydrocarbons; not functionalised	Highly oxygenated and functionalised
Conversion processes		Optimised over 100 years	Require further research and technological development
Products		On the market and to high specification	Quality needs to be standardised

1.5.3 Challenges and Opportunities

Biorefinery products (energy, chemicals and materials) will unavoidably have to compete with existing and future petroleum-derived products. As seen in Table 1.2 (comparison of biorefinery and petrorefinery characteristics in terms of feedstock, process and products), the two types of refinery display major differences, which translate into a number of challenges to and opportunities for the rapid and widespread deployment of biorefineries.

1.5.3.1 Feedstock

Biorefinery feedstocks mainly consist of existing arable crops (e.g. cereals, oilseeds), dedicated biomass crops (e.g. perennial lignocellulosic crops), biowaste (e.g. agricultural and forestry residues, food and municipal wastes) and algae.

In contrast to fossil resources which are found in rich deposits ('mine mouth' or 'well head'), biomass is widely distributed geographically (multiplicity of 'farm gate' or 'waste sources') [41, 48]. As such, the economic viability of biorefineries largely depends on the availability of a reliable supply of appropriate quality biomass at fair prices [49].

Biomass is clearly not an unlimited resource. Consequently, it is critical to ensure that additional uses of biomass do not compromise the ability to produce food and feed in sufficient quality and quantity [49]. Due to limited land availability for biomass production for both food and non-food applications, the following requirements are now widely recognised.

- We must increase the productivity and output of biomass from forest and agricultural land through the development of high-yielding arable and perennial crop varieties with greater value for industrial processing (e.g. higher oil or starch content, more digestible lignocellulose) and increased tolerance to pests and diseases under changing climatic conditions [50].

- We must unlock the potential of greatly untapped resources such as waste and algae [51]. In the EU alone, unused biowaste (e.g. agriculture and forestry residues, waste water treatment sludge, organic household waste, food processing waste, debarking waste) amounts to a total of 2.8 billions tonnes per year [49].

In addition, biomass typically exhibits a low bulk density and a relatively high water content (up to 90% for grass), which makes its transport in its raw state much more expensive than the transfer of natural gas or petroleum. Reducing the cost of collection, transportation and storage through pre-processing biomass into a higher-density, aerobically stable, easily transportable material is therefore critical to developing a sustainable infrastructure capable of working with significant quantities of raw material [52].

The most common approach used to increase biomass density is grinding. By chopping bailed straw, for example, a 10-fold densification can typically be achieved. An alternative strategy that can provide a material of even higher density is pelletisation. Through conversion of ground straw into pellets, the density of the material could be further increased by a factor of three [53]. This pre-treatment also provides the added benefit of providing a much more uniform material (in size, shape, moisture, density and energy content) which can be much more easily handled (see Chapter 3). Pre-processing might be performed onsite but can also be done during harvesting. An example of technology recently developed to address the engineering challenge presented by low-bulk-density biomass such as wheat straw is a multi-component harvester that can simultaneously and selectively harvest wheat grain and the desired parts of wheat straw in a single pass [52].

Another issue associated with the use of (fresh) biomass is its perishable character or susceptibility to degradation. Taking straw as an example once more, fermentation will begin if the moisture content of baled straw is kept above 25% for a prolonged period of time, resulting in a dramatic reduction of the quality of the raw material. In some cases, spontaneous combustion in the stacks can even take place [54]. This issue is particularly important given that, in contrast to fossil resources (which are of permanent availability and are continuously pumped and mined), the availability of biomass is seasonal. In order to ensure a continuous year-round operation of the biorefinery, biomass may have to be stabilised (e.g. dried) prior to (long-term) storage. For example, the Austrian green biorefinery tackles this problem by processing not only direct-cut grasses but also silage, which can be prepared in the growing season and stored in a silo [55, 56].

In summary, it is essential that we develop versatile and sustainable biomass supply chains and cost-effective infrastructures for production, collection, storage and pre-treatment of biomass. As highlighted by Nilsson and Kadam, the economic success of large biorefineries will greatly depend upon the fundamental logistics of a consistent and orderly flow of feedstocks [54, 57]. Localised small-scale (and perhaps mobile) pre-treatment units will be necessary to minimise transportation costs and supply the biorefinery with a stabilised feedstock (e.g. in the form of a dry solid or a liquid such as pyrolysis oil) which can be stored, allowing the biorefinery to run continuously all year long [58]. Such an approach will yield the added benefits of reducing the environmental impact of transportation [55], allowing farmers to gain a greater share of the total added value of the supply chain.

1.5.3.2 Conversion Processes

The major impediment to biomass use is the development of economically viable methods (physical, chemical, thermochemical and biochemical) to separate, refine and transform it into energy, chemicals and materials [29, 59]. Biorefining technologies (most of which require further research and technological development) have to compete with well-developed and very efficient processes which have been continuously improved by petrorefineries over the last 100 years; the latter demonstrate a very high degree of technical and cost optimisation. Large investments will therefore be required from the public and private sector to bring these technologies to maturity through research, development, demonstration and deployment [60, 61]. The EU and a consortium of bio-based industries have recently committed to jointly invest over €2.8 billion in research and innovation between 2014 and 2020 [62].

Priorities for research and development include the following topics.

- *Pre-processing*: there is currently no effective way to separate the major components of biomass (i.e. cellulose, hemicellulose and lignin). More sophisticated and milder pre-treatment methods therefore need to be developed [63].
- *Chemical catalysis and biochemical processes*: in contrast to fossil resources, biomass feedstocks are composed of highly oxygenated and/or highly functionalised chemicals (see Table 1.3). This means that we must apply significantly different chemistries (e.g. reduction instead of oxidation) to convert them into the valuable chemical products our society is built on and, in particular, develop new catalysts that are able to work in aqueous media [46, 64]. These include new biocatalysts (microorganisms and enzymes) being developed through the novel field of synthetic biology.
- *Thermochemical processes*: research should focus on scaling-up and integrating these processes into existing production units as well as end-product quality improvement [50].

Table 1.3 *General chemical composition of selected biomass components and petroleum. Reproduced with permission from [65]. Copyright © 2008, John Wiley & Sons, Ltd.*

Cellulose/starch	$[C_6(H_2O)_5]_n$	Gasoline	C_6H_{14}–$C_{12}H_{26}$
Hemicellulose	$[C_5(H_2O)_4]_n$	Diesel	$C_{10}H_{22}$–$C_{15}H_{32}$
Lignin	$[C_{10}H_{12}O_4]_n$		

- *Downstream processes*: biorefineries need to develop intelligent process engineering to deal with separation and separation, by far the most wasteful and expensive stage of biomass conversion and currently accounting for 60–80% of the process cost of most mature chemical processes [66]. For example, the production of chemicals (e.g. succinic acid) and fuels (e.g. bioethanol) through fermentation processes generates very dilute and complex aqueous solutions which will have to be dealt with using clean and low-energy techniques [64].

For biorefineries to flourish, enhanced cooperation between academia and industry needs to be supported and new unconventional partnerships between traditionally separate industry sectors need to be developed (e.g. agri-food businesses and chemical companies). A number of regional bioeconomy clusters bringing together industry (large and small companies), academia, investors and policy-makers have emerged across the world over the last decade to encourage these necessary collaborations (e.g. IAR in France, BioVale in UK).

Last but not least, all the processes employed in future biorefineries will have to be environmentally friendly. It is essential that we use clean technologies and apply green chemistry principles throughout the biorefinery in order to minimise the environmental footprints of its products and ensure its sustainability, as discussed in Section 1.4 and described in more detail in Chapter 3. Future biorefineries will have to be highly energy-efficient and make use of mostly zero-waste production processes [33].

1.5.3.3 Products

There are currently a number of factors driving the development and commercialisation of bio-based products. These include high oil prices, consumer preference for and corporate commitment to sustainable products, and government mandates and support for the bio-economy [38].

However, a competitive price and an equal or superior level of performance compared to their fossil-based counterparts are central to the viability of bio-based products. Although some bioplastics are cost-competitive, most are 2–4 times more expensive than conventional plastics, limiting their uptake to date [49]. Importantly, biorefineries should not limit themselves to producing existing products but instead should aim to develop new families of products, taking full advantage of the native properties of biomass and its components [29].

A major issue for biomass as a raw material for industrial product manufacture is variability. Standards and certifications therefore need to be established as new biofuels, biomaterials and bioproducts are introduced to the market to assure end-users of a bio-based product's quality, its performance and its bio-based content (see Chapter 8).

A secure and long-term policy and regulatory framework is also needed to provide certainty for companies and investors seeking to exploit biomass/biowaste as a feedstock. As with many emerging industries, new incentives will be required to stimulate market uptake and attract the necessary private investment required in the development of new bio-based products and the large-scale deployment of integrated biorefineries [36, 37]. For example, the US Federal Government set up the BioPreferred programme in 2002 to increase the purchasing of bio-based products [49].

One of the main drivers for the use of bio-based products (energy, chemicals and materials) is their potential environmental benefits compared to petroleum-derived products (e.g. carbon dioxide emission reduction, biodegradability). It is therefore essential that we assess the environmental impact of all the energy and chemical products manufactured by biorefineries (across their life cycle) to ensure that they are truly sustainable and represent real (environmental and societal) advantages compared to their petroleum-derived analogues [67]. In particular, the impacts of direct and indirect land-use change and biomass production on regional biodiversity need to be evaluated as part of this assessment [50]. Work is currently underway through a number of initiatives to reach agreement at an international level on sustainability principles, criteria and indicators [36].

1.5.4 Biorefinery Size

Biorefineries are emerging around the world in a variety of different forms and sizes and encompass a combination of large-scale facilities (which can take full advantage of the economies of scale, enjoying greater buying power when acquiring feedstocks) and small-scale plants (which can keep transport costs to an absolute minimum and take full advantage of available process integration technologies). Their optimal size, which will obviously depend upon the nature of the feedstock(s) processed, the location of the plant, the technologies employed and the demand for given products (not 'one size fits all'), will correspond to a balance between the increasing cost of transporting pre-treated biomass and the decreasing cost of processing as the size of the biorefinery increases [33, 36].

Many of these integrated biorefineries are expected to be located in rural or densely forested areas in close proximity to the biomass (e.g. POET in US, Processum in Sweden), while some are likely to emerge in large ports and refinery complexes (e.g. Nestle Oil in Rotterdam, ENI in Venice), making the most of existing infrastructures and easy access to key markets and customers.

1.6 Conclusions

Current industrial economies are largely dependent on oil, which provides the basis of most of our energy and chemical feedstocks; in fact, over 90% (by weight) of all organic chemicals are derived from petroleum [29]. However, crude oil reserves are finite and world demand is growing. In the meantime, there is increasing concern over the impact of these traditional manufacturing processes on the environment (i.e. effect of CO_2 emissions on climate change). In order to maintain the world population in terms of food, fuel and organic chemicals and tackle climate change, it has been recognised by a number of governments and companies that we need to substantially reduce our dependence on petroleum feedstock by establishing a bio-based economy [68].

For this purpose, long-term strategies that recognise the potential of local renewable resources including waste should be developed. Of paramount importance will be the deployment of biorefineries (of various size and shape) which can convert a variety of biofeedstocks into power, heat, chemicals and other valuable materials, maximising the value of the biomass and minimising waste. These integrated facilities will most likely employ a combination of physical, chemical, biotechnological and thermochemical technologies; they must be efficient and adopt the green chemistry principles in order to minimise environmental footprints and ensure the sustainability of all products generated (cradle-to-grave approach). Local pre-treatment of low-bulk-density and often wet biomass will be critical to the development of a sustainable infrastructure capable of working with significant quantities of raw material. Specific attention should therefore be paid to the development of these (local) processes. The challenge of the next decade will be to develop demonstration plants, which will require cross-sector collaborations and major investment in the construction of full-scale advanced biorefineries.

1.7 Acknowledgement

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