Green Chemistry, Biofuels, and Biorefinery

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Annu. Rev. Chem. Biomol. Eng. 2012. 3:183–207

The *Annual Review of Chemical and Biomolecular Engineering* is online at chembioeng.annualreviews.org

This article's doi:
10.1146/annurev-chembioeng-062011-081014

1947-5438/12/0715-0183$20.00

Keywords

biomass valorization, sustainability, platforms, environmental chemistry

Abstract

In the current climate of several interrelated impending global crises, namely, climate change, chemicals, energy, and oil, the impact of green chemistry with respect to chemicals and biofuels generated from within a holistic concept of a biorefinery is discussed. Green chemistry provides unique opportunities for innovation via product substitution, new feedstock generation, catalysis in aqueous media, utilization of microwaves, and scope for alternative or natural solvents. The potential of utilizing waste as a new resource and the development of integrated facilities producing multiple products from biomass is discussed under the guise of biorefineries. Biofuels are discussed in depth, as they not only provide fuel (energy) but are also a source of feedstock chemicals. In the future, the commercial success of biofuels commensurate with consumer demand will depend on the availability of new green (bio)chemical technologies capable of converting waste biomass to fuel in a context of a biorefinery.

GREEN CHEMISTRY: INTRODUCTION

Green or sustainable chemistry is the design, development, and implementation of chemical products and processes that reduce or eliminate the use and generation of substances hazardous to human health and the environment. Green chemistry continues to expand as a scientific discipline that is governed by the so-called 12 principles established by Anastas & Warner (1): (*a*) prevention, (*b*) atom economy, (*c*) less hazardous chemical syntheses, (*d*) design for safer chemicals, (*e*) safer solvents and auxiliaries, (*f*) design for energy efficiency, (*g*) use of renewable feedstocks, (*h*) reduction of derivatives, (*i*) catalysis, (*j*) design for degradation, (*k*) real-time analysis for pollution prevention, and (*l*) inherently safer chemistry for accident prevention.

Drivers for Change

The fundamental challenge that we face in this new century is the conversion of a society based on consumption and controlled only by demand and market forces into a sustainable society based on more realistic needs and natural resources. The reassessment of our relationship with the planet must occur while we are facing an unprecedented rate of growth in demand for resources, as the new emerging economies in Asia and Latin America move toward the standards and demands established in the past century in the West.

The chemical industry that has been so effective for much of the twentieth century is now under enormous pressure to change in almost all aspects of how it operates (2). The last years of the twentieth century saw an exponential growth in legislation affecting chemical manufacturing processes (3, 4). Manufacturing is also facing escalating costs for energy and for the disposal of hazardous waste; these costs are increasing at a rate greater than the price of their associated products. The early years of the twenty-first century have also seen a dramatic increase in concern about the human and environmental safety of products. This is largely a consequence of general concerns about the environment and reports, largely from nongovernmental organizations, on the detection of synthetic chemicals in animals and humans (as much a result of improvements in analytical science as of any increase in exposure to chemicals) (5). Throughout both of these periods we have seen a rapid increase in the price of the primary raw material of the organic chemicals industry—oil. Alternatives to oil for long-term, sustainable chemical manufacturing are essential (5–7). Thus, chemical manufacturing faces an unprecedented degree of pressure at all stages in the life cycle or supply chain of chemical products (**Figure 1**).

Product Substitution

For the first time the entire supply chain is knowingly affected by and concerned with the long-term availability of chemicals. It is impossible to predict how many currently used chemicals will fall foul of new legislation [e.g., REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) and RoHS (Restriction of Hazardous Substances)] (3), but a substantial number of products can be expected to be affected. REACH has made it clear that we will need to discover, develop, and apply greener substitutes for many important chemicals. These will include solvents, adhesives, flame retardants, and stabilizers with applications across a large range of industrial and consumer products. The record on chemical substitution is not good. For example, chlorofluorocarbons were replaced by hydrochlorofluorocarbons, which were then replaced by hydrofluorocarbons, which are now considered unacceptable; currently we use products, e.g., flammable hydrocarbons, for which we substituted other chemicals many years ago. Volatile chlorinated solvents in dry cleaning, polybrominated compounds in flame retardants, and aluminum chloride in numerous organic processes have been regarded as unacceptable for many years, but

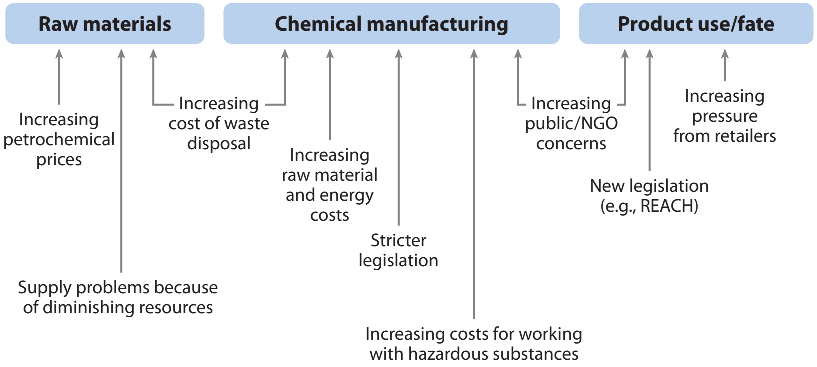

Figure 1

Pressures on the chemical industry across the life cycle. Abbreviations: NGO, nongovernmental organization; REACH, Registration, Evaluation, Authorisation and Restriction of Chemicals.

we continue to use them in large quantities owing to a lack of suitable substitutes. We need to rapidly build up our efforts in this area and especially to develop cost-effective replacements that are based on chemicals derived from alternative, renewable resources and thus will be considered green and sustainable.

Transition from Petroleum Refineries to Biorefineries

Whereas the twentieth century saw the emergence and establishment of an organic chemicals manufacturing industry based on petroleum refining, the twenty-first century will see the development of a new organics industry based on biomass refining (5–7). In both scenarios the driver is energy. The enormous demand for petroleum as a cheap, single-use fuel gave chemical manufacturing a large-volume, low-cost, and continuous supply of hydrocarbons from which the petrochemical industry was built; chemical and engineering technology for cracking, separating, rearranging, polymerizing, and functionalizing allowed us to take complex mixtures of simple chemicals and transform them into a multitude of higher-value molecules. Now, renewable sources of energy are sought with increasing vigor; biomass, a renewable source of carbon, is guaranteed a place in the new energy portfolio for the foreseeable future. The growth in the bioenergy (e.g., biomass gasification) and biofuels (e.g., biodiesel) industries will add to the consumption of renewable carbon by the food industries (7). The term biofuel or biorenewable fuel refers to any solid, liquid, or gaseous fuel derived from biomass (terrestrial or aquatic carbon-containing matter). Food production is wasteful; from crop residues (e.g., wheat straw), through processing (where substantial losses occur), to sale and consumption, we throw away approximately one-third of the food we produce. However, what is waste to food manufacturing can be feed to the chemical, energy, and other industries. Straws, for example, contain significant quantities of valuable compounds such as fatty alcohols and alkanes, and the lignocellulosic residue can be used to make paper or ethanol (8). Rice husks from rice farming can be burned to yield energy, and the residues are rich in silica (9) that could be used as a binder. Used food oils can be used to make biofuels, e.g., biodiesel (10).

A biorefinery can be considered to be an integral unit that can accept various biological nonfood feedstocks and convert them into a range of useful products including chemicals, energy, and materials (**Figure 2**) (11, 12). The challenge is to use green chemical technologies to ensure maximum conversion efficiencies and minimal waste so that we can credibly say that the products of the biorefinery are green and sustainable. The biorefinery concept that has emerged is analogous to today's petroleum refineries. However, many focus on single technologies and feedstocks such

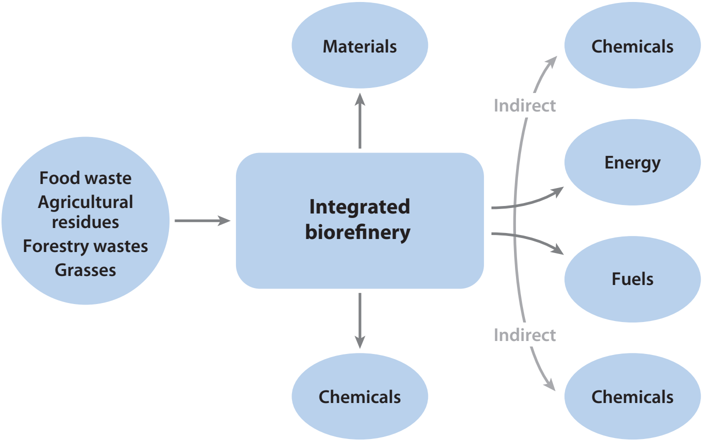

Figure 2

The integrated biorefinery as a mixed feedstock source of chemicals, energy, fuels, and materials.

as starch or vegetable oils that could compete with food or feed (13). We need to create flexible, zero-waste biorefineries that can accept a variety of low-value local feedstocks. Biorefineries will then be able to compete with existing industries.

The main biorefinery technologies can be classified as extraction, biochemical, and thermochemical processes. An integrated, close-to-zero-waste system would exploit a sequential process of extraction followed by a combination of biochemical and thermal processing that includes internal recycling of energy and waste gases (**Figure 3**). Extraction of valuable chemicals prior to their destruction during biochemical and thermal treatments can significantly increase the overall financial returns (14).

Biochemical processes have the advantage of low processing temperatures and high selectivity of products generated. However, they normally require preprocessing stages (15), long processing times, poor space-time yields, and difficult downstream processing, such as distillation, that can be energy intensive (16). Alternative thermochemical routes include gasification, pyrolysis, and direct combustion to produce oils, gas, char, or ash. These are fast but also nonspecific and generally require high operating temperatures (>500°C), which reduce their energy efficiency and increase capital investment. Biochemical and thermochemical processing complement each other, and in an integrated system they can deliver significant advantages in terms of specificity of products, flexibility, and efficiency.

For example, current flour mills operate at 70–80% grain-to-flour yields; the balance is various waste and by-product streams including bran, germ, and endosperm. These by-products contain a high proportion of starch (25–30%) that could be used for microbial bioconversion to produce valuable chemicals including succinic acid (SA). SA has become a popular biochemical in the past 1–2 years; companies including Bioamber, DSM-Roquette Freres, Myriata, BASF, and Mitsubishi all have enhanced their involvement in its manufacture. SA-producing fermentations have also been carried out recently using a range of feedstocks including wheat- and corn-derived media and hydrolysate of rapeseed meal. These lignocellulosic residues are a cheap source of chemicals, but their effective pretreatment is essential (17). This currently involves a first stage of acid treatment, e.g., rapeseed meal can be treated with dilute acid followed by enzyme hydrolysis to yield sugar (18). In the second stage, sugars are converted to SA or other target molecules; wheat-derived media, for example, can be a cost-effective medium for the bioprocess. Thus, a yield as high as 64 g SA

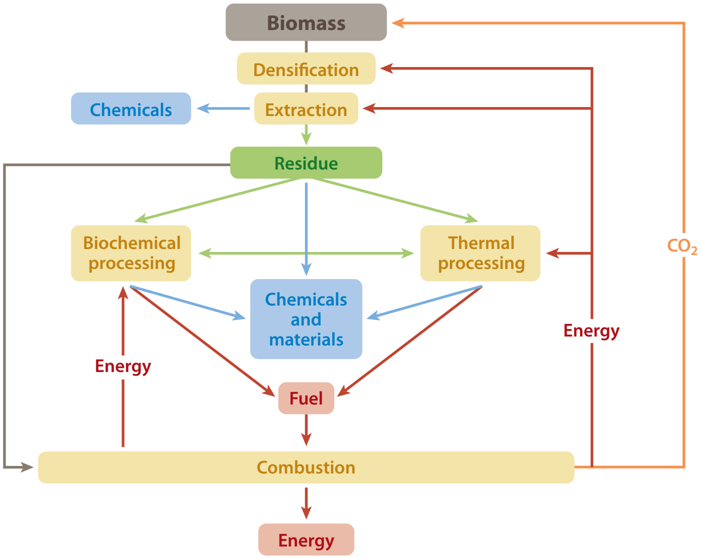

Figure 3

A model for integration of extraction, biochemical, and thermochemical processes that includes recycling of the energy and extraction solvent(s).

liter^{-1} has been obtained by using only the carbon- and nitrogen-rich stream processed via solid-state fermentation (19). In an interesting variation on this, seawater can act as an effective mineral source in SA-producing fermentations (20); approximately 45 g SA liter^{-1} could be produced using 50% seawater and 50% wheat-derived media. SA-producing fermentations have also been used to demonstrate the in situ downstream conversion of SA to other molecules, which avoids the need for a wasteful and energy-demanding separation step. These chemical catalysis reactions work unusually well in aqueous systems and in the presence of impurities (17); they rely on the unique mesoporous nature of novel polysaccharide-derived acidic carbonaceous Starbon^{TM} materials that can efficiently esterify carboxylic acids in bulk water (21).

The first stage of an integrated biorefinery is the extraction of valuable secondary metabolites. Traditionally, these are extracted from biomass using volatile organic solvents, which are environmentally problematic and rather unselective. Furthermore, strict limitations on acceptable solvents may exist, including when the chemicals can be classified as natural (a powerful financial benefit for applications in areas such as cosmetics). In the European Union (EU), only water, carbon dioxide, and (bio)ethanol can be used as solvents in the processing of natural products, although interest is increasing in the use of other green solvents for extractions (22). CO_2 combines effective isolation and fractionation of extracts with low environmental impact. For example, the waxy cuticle layer of straw can be selectively extracted using supercritical CO_2 (scCO_2) (8). scCO_2 extraction leaves no solvent residue, which means that products are suitable for use in, for example, food and pharmaceutical applications; this gives scCO_2 major commercial advantages over traditional extraction methods. Industrial-scale scCO_2 has already been employed commercially for hops extraction, decaffeination of coffee, and dry cleaning (23, 24).

scCO_2 extraction at a range of temperatures and pressures has been studied in comparison with hexane, a solvent of similar polarity (25). Similar yields and composition (**Table 1**) were observed for both solvents. Although the useful compounds extracted from wheat straw and other biomass are similar, CO_2 extractions give fewer unwanted coextracted components such as pigments, polar

Table 1 Some of the main compounds found in hexane- and supercritical CO_2-extracted wheat straw

Compound name	Group of compounds	Application
6,10,14-Trimethyl, 2-pentadecanone Palmitic acid Linoleic acid Oleic acid Stearic acid	Fatty acids	Soaps, detergents, lubricating grease/oils, cleaning compounds/ polishes
Nonacosane Hentriacontane	Alkanes	Paraffin waxes
14,16-Hentriacontanedione	Diketones	Metal chelators
14,18-Tritriacontanedione		
Octacosanyl hexadecanoate	Wax esters	Hard polishes, coatings, cosmetics, plasticizers

lipids, and free sugars. Although $scCO_2$ extraction is an energy-intensive process, a biorefinery should preferably have a plentiful supply of CO_2 so that any losses are inexpensive, and low-cost energy may be available, for example, from burning residues to minimize running costs.

The pyrolysis of biomass such as cereal straws faces challenges in terms of biofuel application owing to unfavorable properties such as high acidity as well as high water and alkali metal contents, which makes such biomass difficult to exploit as fuels. These properties can also make downstream conversion to valuable chemicals more difficult. We need new clean and efficient biomass conversion technologies to complement bioprocessing and extraction.

Microwave technology has been shown to be an energy-efficient method for chemical processing, and a good body of evidence suggests that microwaves can cause specific molecular activations (26). Although the use of microwaves to activate biomass dates back to the 1970s, more recent work based on low-temperature microwave processes has begun to reveal spectacular improvements in the quality of products produced (27). The low-temperature microwave activation of wheat straw provides a novel, energy-efficient route to bio-oils with excellent key properties for use as biofuels, including low sulfur, acid, and alkali metal contents. The microwave oil also contains large percentages of a few compounds with value as fuel and chemical intermediates. Simple additives can be used to further change the oil properties and composition. Clearly, microwaves offer an interesting alternative to nontraditional methods of biomass processing within an integrated biorefinery based on green chemical technologies.

BIOFUELS

Economic, Environmental, and Societal Drivers for Change

The beginning of the twenty-first century is gripped by several interlinked global economic and environmental crises that, unless mitigated, represent an unsustainable future. Ensuring a secure future energy supply is one such response to the crisis. Crude oil (and fossil fuel) continues to be our cornerstone for energy and feedstock chemicals. However, its future supply is limited, as oil is not an infinite resource. At the end of 2010, world proven crude oil reserves stood at 1.5 trillion barrels; of this, the Organization of Petroleum Exporting Countries (OPEC) contributes 1.2 trillion barrels (80%). OPEC produced 29.2 million barrels (mb) day^{-1} (41.8%) of crude oil from a world total output of 69.7 mb day^{-1} in 2010 (28). As emerging economies become more successful and industrialization and urbanization increase, the International Energy Agency (IEA) predicts oil production to rise to approximately 96 mb day^{-1} by 2035 (29); OPEC estimates

105.5 mb day^{-1} by 2030 (30). Future oil production will not be able to meet demand; thus, the situation is unsustainable.

Furthermore, oil as an energy source has a negative social and environmental image. For example, in 2010, approximately 5 mb of oil leaked from the BP Deepwater oil platform in the Gulf of Mexico, which resulted in adverse global publicity. Oil and fossil fuels are significant net contributors of CO_2. Economically, oil is an unstable commodity, and prices fluctuate for many reasons. For example, the current political unrest in major oil-producing regions (Middle East and North Africa) caused oil prices to increase owing to threatened security of future supply (31). The price of Brent crude rose from approximately US$90/barrel at the beginning of 2011 to US$110–$120/barrel in May 2011, the highest level since August 2008. Consequently, President Obama's "Blueprint for a Secure Energy Future" address in March 2011 announced that the United States would become less reliant on oil imports; the aim is to reduce oil imports by one-third by 2025 and increase support for technologies that can assist in that transition (32). In June 2011, IEA member states released 60 mb of oil from their reserves, whereas the United States sold 30 mb from its Strategic Petroleum Reserve; this was the largest release ever from the nation's emergency energy stockpile (33). To this effect, alternative energy [solar, wind, hydroelectric, (bio)renewable, etc.] is attracting considerable global interest to meet our future energy demand. In 2008, the Intergovernmental Panel on Climate Change estimated that renewable energy generated 12.9% of the total 492 EJ of primary energy produced. Biomass (10.2%) was the largest contributor to renewable energy (34).

Biofuels are an important form of renewable energy and making significant inroads toward a sustainable transport sector (land, air, and sea) (35). Examples of liquid and gaseous biofuels include biodiesel, bioalcohols (biomethanol, bioethanol, biobutanol, and isobutanol), bio-dimethyl ether (bio-DME), bio-oil, biogas (a mixture of CH_4 and CO_2), biohydrogen, and landfill gas (predominantly CH_4). Unlike their petroleum counterparts, biofuels are deemed CO_2 neutral because they absorb CO_2 from the atmosphere during photosynthesis and release the same amount when burnt. In addition, many biofuels are oxygenated (e.g., bioalcohols) and help reduce particulate and NO_x emissions from combustion. Conversely, certain bioalcohols (e.g., bioethanol) have a lower energy density than gasoline; a liter of bioethanol produces 65–70% of the energy equivalent (~21 MJ liter^{-1}) of a liter of gasoline (~32 MJ liter^{-1}) (35). Bioethanol also increases exhaust emissions of acetaldehyde and is hygroscopic, which leads to corrosion problems. Furthermore, biofuels are not carbon neutral over their entire life cycle. Energy is put in and CO_2 is emitted during each stage of production, from farm to pump, prior to vehicle use. However, with respect to other forms of alternative or renewable energy, biofuels are the only type capable of producing downstream enabling chemicals and products as well as energy, thus mimicking a conventional petroleum refinery, i.e., a biorefinery (11, 12).

The ideal biofuel needs to be produced cheaply from nonfood feedstocks, to be readily available throughout the year, to serve as a drop-in replacement into existing infrastructure, and to be as energy dense as gasoline (petrol) or diesel (36). An increasing number of cars can operate using a 10–25% (E10–E25) blend of bioethanol with gasoline. New flex-fuel vehicles are capable of burning any level of blended bioethanol, including 100% hydrous bioethanol (E100) (37). Similarly, biodiesel can be blended at any level; biodiesel blends range from 2% to 5% (B2–B5) and are set to rise to 10% (B10) and 20% (B20) in the future. Compared with bioethanol (~21 MJ liter^{-1}), biodiesel contains more carbons and can deliver a similar energy density (~33 MJ liter^{-1}) as conventional diesel (~36 MJ liter^{-1}) (35). The high production cost, especially the price of raw material, is a limiting factor to higher blending rates at present.

Despite their recent and predicted future success, the concept of biofuels is not new but rather predates the discovery of petroleum in 1859, as (bio)ethanol was mixed with turpentine to yield a fuel oil in the late 1830s. In 1900, Rudolf Diesel demonstrated a compression engine operating on peanut oil at the Paris World's Fair (38). The Model T Ford (the world's first mass-produced car) was designed to run on bioethanol (39).

Globally, bioethanol comprises approximately 80% of the current biofuel market, the remainder credited to biodiesel production. In 2010, 120 billion liters (bnl) of biofuel (bioethanol, 100 bnl; biodiesel, 20 bnl) for transport were produced, almost double the amount in 2005. The market is dominated by first-generation biofuels that are based mostly on sugarcane (Brazil) and corn (United States), and to a much lesser extent on canola, sunflowers, and other agricultural feedstocks. The United States is the largest producer of bioethanol, delivering 49 bnl (57%), with Brazil in second place, producing 28 bnl (33%) of the total global output. By the end of 2011, the United States is expected to supersede Brazil as the largest exporter of bioethanol. The EU leads in biodiesel production with a market share of 53% of all biodiesel produced in 2010. Total global biofuel production is forecast to reach 200 bnl (bioethanol, 155 bnl; biodiesel, 45 bnl) by 2020, but this will demand new biofuel production technologies (second-generation or advanced fuels, see below) at commercial scale (40).

The growth and future expansion of biofuels are supported by numerous national and multinational policies and mandates. For example, the United States' 2007 Energy Independence and Security Act targets production of 60 bnl of biofuel by 2022, in the process reducing greenhouse gas (GHG) emissions by 20%. The United States Renewable Fuel Standard (RFS-2) mandate stipulates consumption of 1 billion gallons of biodiesel [3.15 Mtoe (million tons of oil equivalent)], 3.5 billion gallons of noncellulosic advanced biofuels (7 Mtoe), and 15 billion gallons of conventional biofuels (30 Mtoe) by 2020. The U.S. bioethanol industry receives US$0.45/gallon blenders' credit incentive from the government, which also imposes a US$0.54/gallon import tariff. In the EU, the Renewable Energy Directive (RED) (Directive 2009/28/EC) commits to raising the share of transport fuels from renewable sources to 10% by 2020 (41). RED also incorporates a set of sustainability criteria for biofuels that in the future will minimize negative impacts on land use and biodiversity. The RED targeted biofuels to deliver GHG savings of approximately 35% by the end of 2010 and 50% in 2017. The European Parliament resolution of February 4, 2009, titled "2050: The future begins today—Recommendations for the EU's future integrated policy on climate change" [2008/2105(INI)] advocated that the EU and member states should invest in research on advanced biofuels, among other technologies (41).

However, implementation of RED and its not-so-ambitious 10% from renewable fuels target, coupled with sustainability criteria, have impacted Europe's biofuel industry negatively. There appears to be general malaise across the EU biofuels industry owing to lack of favorable incentives and overregulation. For example, in 2010, Britain scrapped its biofuel subsidies for producers (42). The Paris renewable energy group EurObserv'ER reported growth in the use of renewable fuels in the EU at 1.7 Mtoe in 2010, down 1 Mtoe from the 2009 rate of increase (43).

Brazil has been at the forefront of national and multinational policies promoting an in-house biofuel economy ever since the first oil crisis of 1973. In 1974, Brazil introduced the National Alcohol Program (PROALCOOL, decree 76.593), which offered public sector subsidies and tax breaks to kick-start the program. In addition, the Common External Tariff of Mercosur protects Brazil's biofuel industry by stipulating import duties on bioethanol (20%) and biodiesel (14%). Tariffs have been relaxed recently amid a sugarcane crisis; see below. Today, bioethanol accounts for approximately 70% of the fuel that Brazilians pump into their vehicles (predominantly flex-fuel vehicles) (44). At the start of 2011, Brazil's bioethanol blending obligation was set at 25% (E25) for gasoline (petroleum) but was reduced mid-year to 20% (E20) owing to a bioethanol (sugarcane-derived) shortage as dry weather cut sugar content and Brazilian mills focused on production of sugar rather than ethanol. Consequently, during the period of June to August 2011, the price of bioethanol rose by 27%. For only the second time in its history of bioethanol production, Brazil is expected to import up to 650 million liters of ethanol during 2011/2012 (45) and temporarily lifted bioethanol import tariffs until the end of 2011 (46) to meet shortfalls in production. In the current round of EU-Mercosur discussions, tariffs are being renegotiated, either to be eliminated or significantly reduced. As a net importer of first-generation biofuel agricultural commodities and biofuels from the Mercosur countries, the EU requests free or freer trade to be considered (47).

Similarly, Brazilian biodiesel production is regulated and incentivized. In 2004, the national program for the production and use of biodiesel set blending mandates for biodiesel at B2 by 2008 and B5 by 2013. In January 2010, the mandated blend requirement for biodiesel in Brazil was increased from B2 to B5, three years ahead of initial scheduled targets. The Brazilian biodiesel industry is now lobbying government to increase the mandate to B20 by 2020. With Brazil's considerable experience, now the best part of 35 years, in developing itself as a global leader in biofuels, Moraes (48) provides an insightful overview of some lessons learned from the Brazilian biofuel story that other countries should heed: government intervention, supply chain management, flexibility, scale, environmental factors, and private investment all play important roles.

First-Generation Biofuels

The current commercial success of biofuels (bioethanol and biodiesel) is based on first-generation biofuel technologies that utilize agricultural commodities [sugarcane, corn, wheat, grains, oilseeds, vegetable oils, and rendered animal fats]. Pure plant oil is also available via direct crushing and excising of oil from the native plant but its use is limited at present.

First-generation bioalcohols (bioethanol) are produced via yeast (*Saccharomyces cerevisiae*) fermentation of plant sugars and starches from crops such as sugarcane (*Saccharum* sp.), sugar beet, and corn (*Zea mays*). Brazilian bioethanol production utilizes sugarcane, which is rich in directly fermentable sucrose, whereas the U.S. bioethanol industry is based on corn. Unfortunately, corn or starch crops cannot undergo direct fermentation to bioalcohols but require pretreatment (liquefaction followed by saccharification with amylolytic enzymes) prior to fermentation. Bioethanol production from sucrose-containing feedstocks is easier and more efficient than that from starch-based feedstocks.

First-generation biodiesel is produced from chemical modification (base-catalyzed transesterification with methanol) of plant oils such as rapeseed (*Brassica napus*), palm tree fruits (*Elaesis guineensis*), and soybean (*Glycine max*); used vegetable oils; and rendered animal fats to yield biodiesel [fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE, when transesterified with ethanol)] (49). For a full account of the production of first-generation biofuels, see Naik et al. (50); see Vyas et al. (51) for a review on FAME production processes.

However, the future success of first-generation biofuels is limited because they are socially and environmentally unsustainable. Raw materials used in the production of first-generation biofuels compete directly with food/feed production. Although stable at present, the price of many commodity foods increased sharply a couple of years ago as agricultural food was diverted to fuel (52). First-generation biofuels negatively impact GHG emissions, biodiversity, land use, water usage, and water fouling (35). Increased use of fertilizer to grow crops for biofuels has led to increases in the amounts of nitrogen and phosphorus entering ground and surface waters. The expansive, annual algal blooms in the Gulf of Mexico are a direct result of fertilizer-rich farm runoff seeping into the Mississippi River and eventually into the Gulf (53). With a caveat for sugarcane ethanol, the future success of biofuels will depend on nonfood feedstocks (54). To this effect, new technologies are coming to the fore that are based on converting municipal solid waste, lignocellulosic crops and residues, and algae (micro and macro) into advanced biofuels (or second- and third-generation biofuels) and that afford improved GHG savings [although these are still debatable owing to differing methodologies and the impact of indirect land use changes (55)], better land use, reduced water requirements and drainage (except for algae), and independence from the fuel versus food/feed debate (56).

Advanced Biofuels: Second-, Third-, and Fourth-Generation Biofuels

Advanced biofuels (second, third, and possibly fourth generation) derived from lignocellulosic materials, biowaste, and algae are still at the developmental stage but are expected to become commercial within the next 15–20 years as intense research and scale-up activities driven by government, public, and private intervention are actively pursued (56–58). For a full account of the production of second-generation biofuels, see Naik et al. (50). Exciting opportunities and potential for advanced biofuels have already been demonstrated. For example, Formula 1 advocates the use of at least 5.75% biofuel for all Formula 1 fuel, and team Ferrari was the first to use lignocellulosic fuel (52). The aviation industry has demonstrated the use of a 50/50 blend of biodiesel (derived from *Camelinas sativa*, an inedible mustard crop) with conventional jet fuel in passenger airplanes and, more recently, in F-22 Raptor fighter jets (56). In 2011, the U.S. government announced a three-year, US$510 million investment package in partnership with the private sector to fast-track production of advanced drop-in aviation and marine biofuels to power military and commercial transportation.

Advanced liquid biofuels are expected to yield greater than 90% fewer GHG emissions than traditional diesel or gasoline, compared with 25–70% for first-generation biofuel technologies. However, a rigorous assessment still needs to be undertaken once commercial advanced biofuel plants are fully operational. At present, data are limited to pilot and demonstration scale plants and do not represent a true picture. The IEA predicts that 90% (26 EJ) of all liquid biofuel (29 EJ) used for transportation in 2050 will be derived from advanced biofuel technologies, thus mitigating 2 gigatonnes of carbon dioxide emission (28, 59). Currently, conservative estimates predict that approximately 5 EJ (17% of 29 EJ) of transportation fuel is derived from liquid biofuels, but this is predominantly from first-generation biofuels.

Agricultural and forestry residues are the feedstock of choice in the initial stage of advanced biofuel production because of their availability and lack of requirement for additional land cultivation. An estimated 5 billion dry tonnes of agricultural residues are produced globally. The IEA estimates that approximately 160 Mha of land dedicated to energy production will be needed to produce the required volumes of second-generation biofuels in 2050 (60).

There are two main conversion routes to advanced biofuels (61):

1. Biochemical conversion is based on enzymatic hydrolysis of lignocellulosic material to sugars, which are subsequently fermented and distilled to give cellulosic ethanol.
2. Thermochemical (biomass to liquid, BTL) conversion is based on, for example, gasification and pyrolysis of the feedstock under high temperature into a synthesis gas (syngas), which can then be transformed into different types of liquid or gaseous fuel, so-called synthetic biofuels [e.g., BTL-diesel, biosynthetic natural gas (bio-SNG), biomethanol, bioDME]. Traditional gasification (high-temperature heating in the presence of oxygen to give syngas as a precursor for Fischer-Tropsch fuels) and pyrolysis (high-temperature heating in the absence of oxygen to yield bio-oil, a mixture of hydrocarbons) as well as their subsequent refinements [e.g., low-temperature microwave-assisted pyrolysis (26, 27)] also can be used to produce hydrocarbon-based bio-oils. The resultant bio-oil usually requires further

> processing or upgrading into a biofuel using catalytic technologies. An American start-up company, Allenotech, has developed an in situ process that pyrolyzes biomass to bio-oil to hydrocarbons (benzene, toluene, and xylene), which can be blended into fuels for high-performance cars that utilize a higher percentage of toluene in the blend (36).

Efficient gasification requires good pretreatment and energy densification of biomass, for example, via torrefaction. van der Stelt et al. (62) have reviewed the merits of torrefaction, which is a thermal method (200–300°C) for the conversion of biomass under atmospheric conditions in the absence of oxygen. Torrefaction destructs the fibrous structure, increases energy density, and removes water and volatiles, which leads to mass reduction and ease of transportation.

Significant quantities of water in biomass have a negative effect on pyrolysis, as it requires a high heat of vaporization to remove. Typically, pyrolytic liquefaction liquefies biomass with a moisture content of less than 40%. Tropical grasses can contain up to 80–85% water content and aquatic species even more. To avoid unnecessary drying and the associated cost, Akhtar & Amin (63) review the merits of hydrothermal liquefaction of biomass for optimum bio-oil yield. Hydrothermal liquefaction is a technique for obtaining relatively pure biofuel from biomass in the presence of a solvent at moderate to high temperature (250–550°C) and pressure (5–25 MPa). Hemicelluloses and celluloses are favorable for bio-oil production, but high-lignin feedstocks lead to the formation of chars.

Bioethanol can be readily produced via BTL technologies (the syngas acts a progenitor for bioethanol production using anaerobic Clostridia) but has a higher fossil fuel demand than the biochemical route (39). Bio-SNG produced from a variety of biomass types is similar to natural gas and can be compressed or liquefied for use as a transport fuel in modified vehicles. The fuel-equivalent biofuel yield is higher for bio-SNG compared with cellulosic ethanol and BTL-diesel.

The greatest challenge to the success of advanced biofuels from lignocellulosic materials is cellulose recalcitrance, the inability to degrade lignin, which acts as a protective barrier against fungi and bacteria, to fermentable pentose and hexose sugars. Besides glucose, the pentose sugars D-xylose and L-arabinose are the most abundant hemicellulosic sugars and can constitute up to 30% of the lignocellulosic biomass. *Saccharomyces cerevisiae* is unable to ferment the pentose sugars and thus to use these sugars for growth. The Boles group has developed C5 technologies for the construction of industrial yeast strains able to efficiently ferment both pentose sugars, thus significantly improving the yield of existing bioethanol production using corn, wheat, or sugar cane as raw material (64).

The key steps in generating fermentable sugars from lignocellulosic material are (39) (*a*) preprocessing such as washing off of dirt and debris as well as shredding; (*b*) pretreatment, whether physical, chemical, or biological; (*c*) solid-liquid separation (hemicellulose sugars can be separated from the solid fibrous material comprising cellulose and lignin); and (*d*) cellulose hydrolysis (cellulase attack on crystalline cellulose). Pretreatment methods that can partially break down fibrous matter are important. Kumar et al. (65) have reviewed methods for treatment of lignocellulosic biomass for efficient hydrolysis and biofuel production.

Significant activity is focused on harnessing the known cellulose-degrading enzymatic pathways found in fungi that may unlock cellulose recalcitrance. Enzymatic degradation involves the concerted action of a consortium of different endoglucanases and exo-acting cellobiohydrolases (collectively termed cellulases); both enzyme classes perform classical glycoside hydrolysis through attack of water at the anomeric center of oligo/polysaccharide substrates (66). Quinlan et al. (66) report a set of glycoside hydrolases (known as CAZy or GH61) that is a unique family of copper-dependent oxidases. Copper is needed for GH61 maximal activity, and the formation of cellodextrin and oxidized cellodextrin products by GH61 is enhanced in the presence of small-molecule redox-active cofactors such as ascorbate and gallate. As part of the consortium of cellulose-degrading enzymes, GH61 action renders the substrate far more prone to attack by classical endoglucanases and cellobiohydrolases and thus provides a major breakthrough in enzymatic biomass conversion (66).

In an alternative to enzyme technologies for lignin degradation, Sergeev & Hartwig (67) report a homogenous nickel catalyst that selectively removes oxygen (selective hydrogenolysis of aryl ethers) from lignin model compounds without destroying the entire structure. Although their work is based on model compounds, according to Sanderson (68), Hartwig aims to develop a heterogeneous catalyst that works on naturally occurring lignin. Demirbas et al. (69) have also reviewed the potential of biowaste-to-biofuel as a source of second-generation biofuels. As the amount of solid waste increases owing to urbanization, industrialization, and increasing human population, waste-to-energy (WTE) technologies will become important. Advanced WTE technologies (hydrogenation, pyrolysis, gasification, and bioconversion) are capable of producing biogas (methane and CO_2), syngas, and liquid biofuels (bioethanol and biodiesel) as well as pure hydrogen. Biodiesel production from waste oils and fats has been shown to be more efficient than any related biodiesel production, regardless of the utilized feedstock (69). However, conversion of waste oils to biodiesel requires extra processing steps because of their high free fatty acid (FFA) content, which inhibits traditional base-catalyzed transesterification. Using Starbon^{TM}, Luque & Clark (70) have produced diesel-like biofuels from simultaneous transesterification/esterification of waste oils. The solid acids (Starbons^{TM}) were found to catalyze both the esterification of FFAs in the waste oil with methanol and the transesterification of the triglycerides to give biodiesel and glycerol.

Advanced fuels based on algal matter (micro- and macroalgae) and cyanobacteria (third-generation biofuels), which yield carbohydrates, proteins, vegetable oils (lipids), and, subsequently, biodiesel and hydrogen gas, are gaining considerable interest (58, 71). Researchers estimate that algae could yield 61,000 liters ha^{-1}, compared with 200–450 liters ha^{-1} from crops such as soybean and canola (72). Similarly, the microalgae *Chlorella vulgaris* and *Chlorella protothecoides* are rich sources of lipids for biofuels (73), as lipid accumulation can account for more than 50% of their biomass. The resultant bio-oil generally has a low acid value and is suitable for the synthesis of biodiesel. The competitiveness, role, and impact of microalgal biodiesel production in the twenty-first century have been reviewed by Takeshita (74), who concludes that microalgae offer significant advantages over first- and second-generation biofuel feedstocks, namely: Microalgae have significantly higher oil and biomass yields (the per unit area yield of oil from microalgae is 7–31 times greater than that of the next-best crop, palm oil) and thus require very little land. Microalgae can be cultivated in saltwater or wastewater ponds on marginal land or in specially constructed photobioreactors, and thus they have little or no competition with food production. Microalgae require less water than terrestrial crops; the amount of water needed to produce a unit of energy is estimated to be 74% smaller for microalgal biodiesel production than for rapeseed biodiesel production. However, drawbacks of microalgae include high initial capital investment for infrastructure, costly harvesting of microalgal biomass, a large space requirement, and high energy consumption during the drying of harvested microalgal biomass owing to its high water content (74).

Because second-generation biofuels can be produced from the whole plant or agricultural and forestry residues, they can have considerably reduced overall life-cycle emissions and especially emissions related to feedstock production (per unit of produced fuel). GHG savings continue to a debatable point because of a lack of standardized accounting procedures from crop to pump within any given life-cycle assessment. According to McKone et al. (75), seven grand challenges must be tackled to enable life-cycle assessment to effectively evaluate the environmental footprint of biofuel alternatives: (*a*) understanding farmers, feedstock options, and land use; (*b*) predicting biofuel production technologies and practices; (*c*) characterizing tailpipe emissions and their health consequences; (*d*) incorporating spatial heterogeneity in inventories and assessments; (*e*) accounting for time in impact assessments; (*f*) assessing transitions as well as end states; and (*g*) confronting uncertainty and variability.

Interestingly, Davis et al. (76) have used the DAYCENT model (the daily time-step version of the CENTURY biogeochemical model that simulates fluxes of C and N among the atmosphere, vegetation, and soil) to estimate the effects on ecosystem services of replacing corn ethanol feedstocks with the perennial cellulosic feedstocks switchgrass (*Panicum virgatum* L) and miscanthus (*Miscanthus* × *giganteus*) in U.S. corn-growing regions and concluded that more ethanol (+82%) and grain for food (+4%) could be produced while reducing nitrogen leaching (−15% to −22%) and GHG emissions (−29% to −43%). Even after accounting for indirect land use, conversion from a high-input annual crop to a low-input perennial crop for biodiesel production can transition the central United States from a net source to a net sink for GHGs.

Biofuels Outlook

Clearly, biofuels will play a major role in the suite of alternative energy technologies used to combat climate change and obviate overreliance on crude oil. White biotechnology is anticipated to offer considerable potential for the production of biofuels and feedstock chemicals. The BREW Project assessed the medium- and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources (**http://www.chem.uu.nl/brew/**). First-generation biofuel technologies are now mature but compete for the same feedstocks as are required for food. Interestingly, Betts (77) has recently reported that the expansion of sugarcane into pastureland for biofuel production produces a climatic cooling effect. With the exception of first-generation sugarcane-derived bioethanol, future expansion and development of biofuels will require second-generation [lignocellulosics, (bio)waste, municipal solid waste] and third-generation (algae and cyanobacteria) technologies that yield advanced biofuels.

Short time to commercialization is critical for the success of advanced biofuels. Advanced biofuels are still at pilot or demonstration scale because of their higher production cost compared with current commercially successful first-generation biofuels. At present there is no clear candidate for the best technology pathway, either thermochemical (BTL) or biochemical (enzymatic/fermentation) (57). Well-defined operations research models of various biofuel supply chains need to be developed so as to assess the most economically viable and also to identify gaps (78). Depending upon the type of biofuel, feedstock prices, and conversion costs, the cost of cellulosic ethanol is approximately two to three times higher than the current price of gasoline on an energy-equivalent basis (79). Biomass conversion costs need to be reduced for cellulosic ethanol, whereas feedstock costs need to be reduced for biodiesel. The IEA estimates that the cost of producing and retailing diesel and ethanol from cellulose is approximately US$1.10/liter of gasoline-equivalent, or approximately US$4/gallon. By way of comparison, corn- and sugarcane-based bioethanol are US$0.62–0.75/liter-equivalent, whereas gasoline itself is approximately US$0.54. By 2050, given sufficient investment, research, and development, the IEA estimates that cellulose-based biofuels could be produced for as little as US$0.75/liter-equivalent (56).

A second-generation biofuel industry cannot survive as a stand-alone product. It must encompass all the products available to it and act as an equivalent to a petroleum refinery, i.e., as a biorefinery (80). A biobased economy that results from a biorefinery concept will offer much needed economic benefits through delivery of biobased chemicals and products such as fine chemicals, lubricants, and solvents (81). In the long term, biobutanol or isobutanol may replace bioethanol as a transportation biofuel because of its higher energy content (90% equivalent energy with respect to gasoline, whereas bioethanol is 70%), good blending ability (EU regulations allow biobutanol to be blended at up to 15% by volume, and U.S. regulations allow 16% by volume), better air-to-fuel ratio, less likelihood of explosion, and lower hygroscopicity than bioethanol. Biobutanol has the added attraction of being a feedstock for high-value chemicals made from a base of *n*-butanol, which benefits biorefinery-based industries. Biobutanol commercialization is advancing; for example, BP and DuPont have a joint venture for the production of biobutanol that includes new facilities in the United States (Butamax^{TM} Advanced Biofuels LLC) and the United Kingdom (Kingston Research Center, soon to be operational). Gevo is also a major producer of iso- and *n*-biobutanol.

Biobutanol can be produced by traditional acetone-butanol-ethanol (ABE) fermentation, which is the anaerobic conversion of carbohydrates by strains of *Clostridium* into acetone, butanol, and ethanol. However, ABE fermentation has well-known inherent challenges such as low butanol titer, availability of compatible feedstocks, and product inhibition that still need to be addressed (82). Improvements in genetic engineering [of both Clostridia (*Clostridium beijerinckii*) and non-Clostridia organisms (*Escherichia coli*, *S. cerevisiae*, *Pseudomonas putida*, and *Bacillus subtilis*)] and integrated continuous fermentation processes with efficient product recovery techniques appear most promising (82, 83).

An ethical framework for biofuels needs to be considered. Future biofuels should be environmentally sustainable, recognize the rights of people to just reward, and have costs and benefits that are distributed in an equitable way (84). The Global Bioenergy Partnership aims for an intergovernmental consensus on sustainability criteria and indicators for bioenergy production and use. Once second-generation biofuels are produced commercially, new definitions will be required to assess the sustainable production of these new fuels. Similarly, various public and private initiatives are taking steps to develop certification schemes for biofuels; these include the Roundtable on Sustainable Biofuels (**http://rsb.epfl.ch**) and the International Sustainability and Carbon Certification (85).

A critical eye on land use always must be maintained, as advanced fuels may not always impact land use positively. For example, *Jatropha* planted on both government and private land in rural India (Rajasthan) for second-generation biodiesel has displaced grazing and forage collection. Any benefits from biofuel production have negatively impacted socioeconomic groups reliant on the previous pasture. Similar consequences may occur for other types of feedstock (e.g., *Miscanthus* × *giganteus*, switchgrass, *Pongamia*), and governmental organizations and policy makers should take heed (86). In a wider context, Harvey & Pilgrim (87) considered the competition for land arising from growing and changing demand for food with respect to the need for biofuels in the United States, Brazil, and Europe; they concluded that an integrated approach for growing regimes, adopted technology, and government policy led to the best GHG abatement and sustainability.

Agriculture accounts for approximately 70% of global freshwater withdrawals from rivers, lakes, and aquifers. Because bioenergy is largely dependent on biomass production, expected growth trends will lead to increasing competition and pressures on water resources (88). Feedstock sources such as agricultural and forestry residues that do not require irrigation should be prioritized. Production of cellulosic ethanol requires 4–8 liters of water per liter of ethanol produced. Process optimization of water consumption needs to be considered; for example, efficient cooling towers, replacement of water with air as a means of cooling, and improved water recycling may have tangible energy-saving benefits (89).

Finally, algae hold much promise as a feedstock for fuels and high-value chemicals. Because many hurdles need to be overcome, commercial reality may not be achieved for several years. Significant improvements in the efficiency, cost structure, and ability to scale up algal growth are needed (90). Algae does not require freshwater to grow. A combination of wastewater and flue gases may be the best option for reducing the environmental burden from the cultivation of algal biomass (91).

BIOREFINERIES

Basic Concepts

IEA Bioenergy Task 42 recently coined a formal definition for biorefinery as "the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals and/or materials) and bioenergy (biofuels, power and/or heat)" (**Figure 4**) (92). This means that a biorefinery can be a concept, a facility, a process, a plant, or even a cluster of facilities that obviously requires the integration of many different areas of knowledge encompassing chemical engineering, chemistry, biology and biochemistry, biomolecular engineering, and other fields (93). In this way, biorefining can provide a sustainable approach to valuable products that can also improve biomass processing economics as well as environmental footprint (e.g., GHG savings) if a fully integrated concept is developed (**Figure 5**).

The integration of bioconversion and appropriate chemical technologies is critical to the successful translation of refinery concepts to aqueous transformations. In the case of chemical technologies and chemical production, this means the use of green chemistry methods including

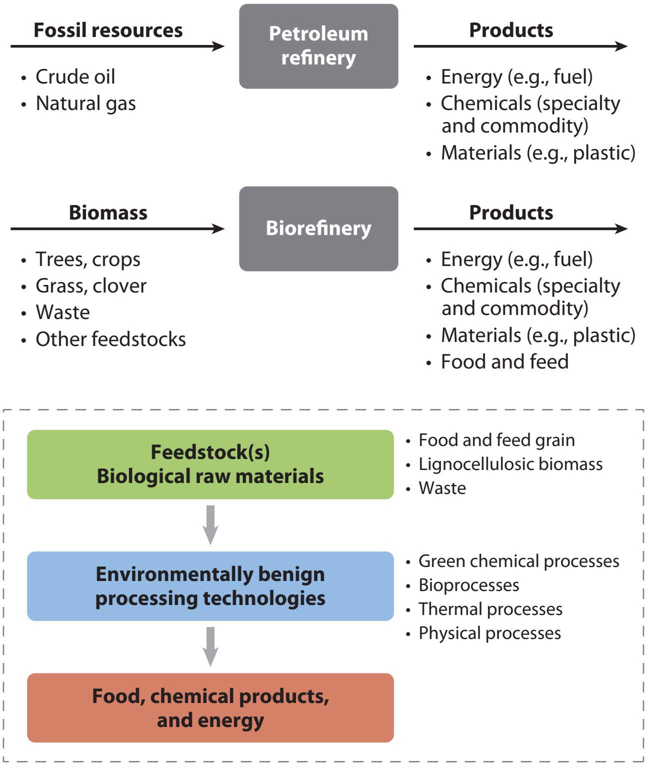

Figure 4

The biorefinery concept: from biomass to valuable products via low-environmental-impact valorization practices.

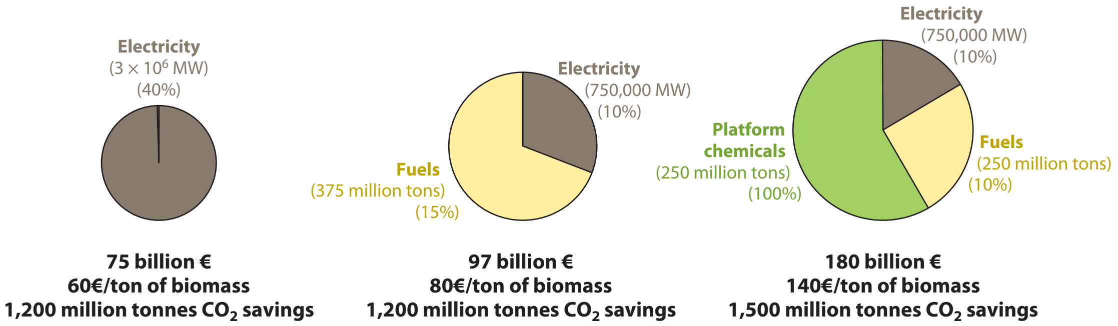

Figure 5

The advantages of a fully integrated biorefinery located in the Netherlands that bridges the gap between agriculture and chemistry. Reproduced by permission of Wageningen University and Johan Sanders.

heterogeneous catalysis and the application of green chemistry principles (94, 95). The main problem in the implementation of the biorefinery concept with regard to chemical transformations is the existing underdeveloped technologies to switch the chemistry from organic to aqueous reactions (2, 93–99). Intensive research endeavors have been carried out over the past few years in an attempt to establish local biorefinery concepts on various feedstocks and resources.

From these, different classifications of biorefineries have been proposed depending on various considerations. Some of them consider different items, which may include feedstocks, products, and processes, and may vary in focus (energy or products) (100–102). A simple overview and classification of biorefineries subdivides them into three types: Phase I, Phase II, and Phase III.

Phase I, II, and III Biorefineries

Phase I biorefineries are integrated facilities with fixed processing capabilities limited to a single feedstock (e.g., oils) that is converted into a single major product (e.g., FAMEs) (100, 101). An example is a biodiesel plant in which rapeseed or sunflower is transformed via crushing of the seeds (for oil extraction) and subsequent transesterification of the oil into biodiesel using methanol and a catalyst (**Figure 6**).

The more advanced Phase II biorefineries possess the capability to produce various end products from a single feedstock as well as far more processing flexibility depending on product demand, prices, and contract obligation (**Figure 7**). An example is a biorefinery that can generate multiple products, ranging from polymers to amino acids to biofuels, by utilizing cereal grains (e.g., wheat) as single feedstock. Last but not least, Phase III biorefineries are the most advanced, as they use

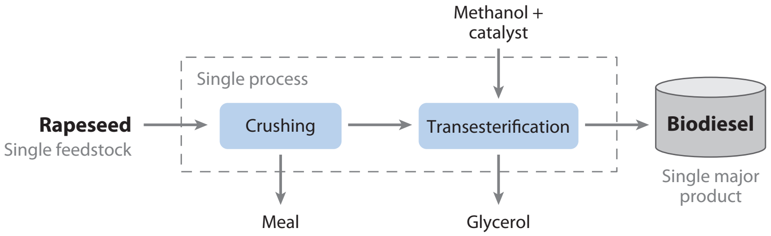

Figure 6

A biodiesel plant is the simplest example of a Phase I biorefinery.

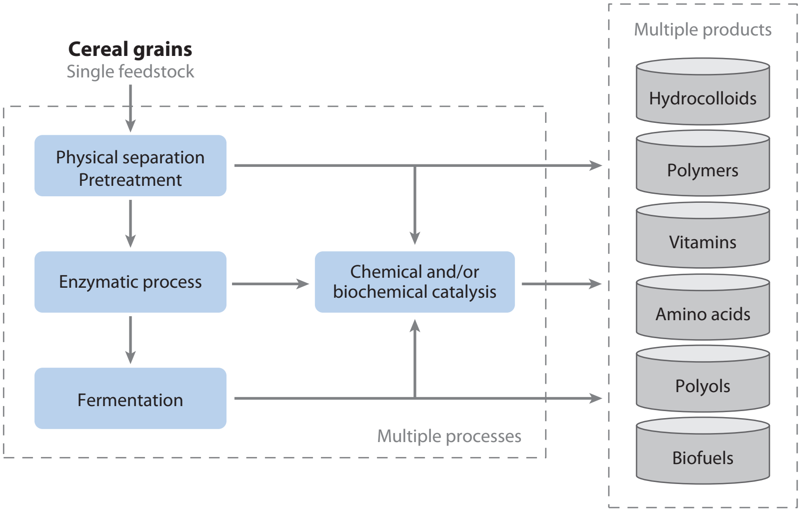

Figure 7

Example of a Phase II biorefinery. The processing of a single feedstock yields multiple valuable products.

a mix of biomass feedstocks to yield a wide variety of products by employing a combination of technologies (e.g., chemical and/or biological transformations, extractions, separations).

Examples of these types of biorefineries include whole-crop biorefineries encompassing an array of transformations of feedstocks (e.g., cereals, corn, rape) as well as the better-known and applied green biorefineries that make use of nature-wet biomass such as green grass, alfalfa, clover, and/or immature cereals; marine biorefineries that use macro- and microalgae (seaweed); and lignocellulosic biorefineries that employ lignocellulosic dry biomass feedstocks (e.g., wood, wheat straw, corn stover) that yield chemicals, fuels, energy, and other valuable outputs. Lignocellulosic biorefineries can be subclassified into various intermediate concepts including thermochemical biorefineries/syngas platforms, biochemical biorefineries/sugar platforms, two-platform concept biorefineries, and forest-based biorefineries. Phase III biorefineries are currently gaining momentum, and they are expected to expand the range and volume of bioproducts on the market as well as to improve the economics of biorefinery plants, while optimizing their energy and environmental performance to enhance the cost competitiveness of biofuels. However, the development of such advanced integrated biorefineries is expected after 2020, as most current projects are still ongoing.

Classification of Biorefineries: Platforms, Products, Feedstocks, and Processes

This classification oversimplifies the highly complex biorefinery concept and prompted scientists internationally to develop a more systematic classification approach for biorefinery systems that Cherubini et al. (100) advanced in 2009 and the IEA Bioenergy Task 42 subsequently extended in 2010 (2). Such classification relies on four main features: platforms, products, feedstocks, and processes.

1. Platforms, defined as key intermediates between raw materials and final products, were considered to be the most relevant feature of the proposed classification, as these can be used to link different biorefinery concepts. Platforms identified in energy-driven biorefineries are summarized in the Platforms Available to a Biorefinery sidebar.

PLATFORMS AVAILABLE TO A BIOREFINERY

Platforms available to a biorefinery include:

- Biogas (a mixture of mainly CH_4 and CO_2) from anaerobic digestion;
- Syngas (a mix of CO and H_2) from gasification;
- Hydrogen (H_2) from water-gas shift reactions, steam reforming, water electrolysis, and fermentation;
- C_6 sugars (e.g., glucose, fructose, galactose: $C_6H_{12}O_6$) from the hydrolysis of starch, cellulose, and hemicellulose;
- C_5 sugars (e.g., xylose, arabinose: $C_5H_{10}O_5$) from hydrolysis of hemicellulose and food and feed sidestreams;
- Lignin [phenylpropane building blocks: $C_9H_{10}O_2(OCH_3)_n$] from lignocellulosic biomass processing;
- Pyrolysis liquid (a multicomponent mixture of molecules with different sizes) from pyrolysis;
- Oil [triglycerides: $RCOO\text{-}CH_2CH(\text{-}OOCR')CH_2\text{-}OOCR''$] from oilseed crops, algae, and oil-based residues; and
- Organic juice (made of different chemicals) from the liquid-phase extract upon wet biomass (e.g., grass) pressing.

2. In terms of products, biorefineries can be broadly grouped into energy-driven and product-driven biorefineries (100). The main goal of energy-driven biorefineries is the production of one of more secondary energy carriers—fuels, power, and/or heat—from biomass. Process residues are upgraded and valorized to biobased products to maximize the economic profitability of the full biomass-to-products chain. In comparison, product-driven biorefineries aim to generate one or more biobased products—chemicals, materials, food, and/or feed—from biomass. Process residues are then used for the production of bioenergy for internal/external use to maximize the economic profitability, similar to that highlighted before.
3. Feedstocks are divided into two subgroups, namely dedicated feedstocks and residues; **Table 2** provides examples of such feedstocks.
4. Several technological processes can be employed in biorefinery systems to convert biomass feedstocks into marketable products. These are subdivided into four main subgroups,

Table 2 Classification of feedstocks in biorefinery systems

Classification	Feedstock	Examples
Dedicated feedstocks	Sugar crops	Sugar beet, sugarcane
	Starch crops	Wheat, corn, sweet sorghum
	Lignocellulosic crops	Wood, short-rotation poplar, switchgrass, *Miscanthus*
	Oil-based crops	Rapeseed, soy, palm oil, *Jatropha curcas*
	Grasses	Green plant materials, grass silage, immature cereals, plant shoots
	Marine biomass	Micro- and macroalgae, seaweed
Residues	Oil-based residues	Animal fat from food industries; used cooking oil from restaurants, households, and others
	Lignocellulosic residues	Crop residues, sawmill residues
	Organic residues and others	Organic urban waste, manure, wild fruits and crops

namely mechanical/physical (e.g., pressing, pretreatment, milling, separation, distillation), biochemical (e.g., anaerobic digestion, aerobic and anaerobic fermentation, enzymatic conversion), chemical (e.g., hydrolysis, transesterification, hydrogenation, oxidation), and thermochemical (e.g., pyrolysis, gasification, hydrothermal upgrading, combustion) processes.

Application of the proposed classification to examples of actual biorefinery systems is summarized in **Table 3**. The advantage of this extended classification is the flexibility to modify and extend the different subgroups depending on future advances and developments in the biorefinery area.

Biorefineries Outlook

The development of relatively small-scale biorefinery concepts (e.g., local) that make use of local or regional biomass/waste resources seems to be the most favored method to introduce more advanced (green, whole-crop, and lignocellulosic) biorefinery processes into the market in the medium term. These concepts will require a reduced initial investment, which potentially can be an advantage for the industrial stakeholder in the introduction of new risky initiatives. Most importantly, these initiatives will change the perception of our current society, creating a new socioeconomic and environmental perspective for the future introduction of more advanced biorefinery concepts (e.g., lignocellulosic and marine feedstocks) at larger scale in the long term.

SUMMARY

Green and sustainable chemistry will play a pivotal role in this century to produce feedstock chemicals and fuels derived from biomass. White biotechnology for the conversion of fermentable sugars to chemicals is now at an advanced stage. Efficient breakdown and conversion of lignocellulosic material to chemicals and fuels remains one of the biggest obstacles currently holding back the development of successful biomass-based biorefineries that can compete with traditional petroleum refineries. Overcoming lignocellulose recalcitrance to release the locked polysaccharides is important. Several lignocellulose pretreatment technologies are under intensive investigation at the laboratory scale and in pilot plants, e.g., dilute or concentrated acid, alkali, flow-through, ammonia fiber explosion, ammonia recycle percolation, lime, steam explosion, and organosolv pretreatment. Development of a lignocellulose pretreatment featuring modest reaction conditions is highly desired; one approach is hydrothermal hydrolysis and/or liquid hot water hydrolysis (103). Super- and subcritical solvents are also been explored. Kilambi (104) reports a solvo-thermal hydrolysis process for producing furfural from xylose comprising: (*a*) mixing an aqueous xylose solution containing xylose oligosaccharides with subcritical or near-critical water to form a mixture at a first temperature and first pressure; (*b*) maintaining the mixture at the first temperature and first pressure for a first time period; and (*c*) rapidly cooling the mixture to a second temperature and second pressure, wherein furfural is produced. The process can be carried out with or without mixing carbon dioxide with the aqueous xylose solution before it is mixed with subcritical or near-critical water (104). Furthermore, Kilambi (105) also has patented an approach, described as nano-solvo thermal hydrolysis technology platform biorefineries, whereby methods of making glucose and/or furfural from biomass requiring one or more supercritical fluids may be used to process biomass, cellulose from the biomass, and/or xylose from the biomass. Supercritical fluids used in processing biomass include ethanol, water, and carbon dioxide at a temperature and pressure above the critical points for ethanol and carbon dioxide but below that of the critical point for water. For example, a supercritical fluid containing carbon dioxide and water may be used to convert cellulose to glucose

Table 3 Classification of selected examples of biorefinery systems according to the model of Cherubini et al. (100)[a]

Name	Platforms	Products		Feedstock	Processes	Source of auxiliary energy	
		Energy	Materials			Heat	Power
One-platform (C6 sugar) biorefinery for bioethanol and animal feed from starch crops	C6 sugars	Bioethanol	Animal feed	Starch crops (corn)	Hydrolysis, fermentation	Natural gas	Grid
One-platform (oil) biorefinery for biodiesel, animal feed, and glycerol from oil crops	Oil	Biodiesel	Animal feed (rape cake), glycerol	Oil crops (rapeseed)	Pressing, transesterification	Natural gas	Grid
One-platform (syngas) biorefinery for synthetic biofuels and chemicals from lignocellulosic residues	Syngas	Synthetic biofuels (Fischer-Tropsch fuels)	Chemicals (alcohols)	Lignocellulosic residues (straw)	Pretreatment, gasification, FT synthesis, alcohol synthesis	Natural gas	Grid
Two-platform (biogas and organic juice) biorefinery for biomethane, chemicals, biomaterials, and fertilizer from grasses	Biogas, organic juice	Biomethane	Chemicals (lactic acid, amino acid), biomaterials (fibers)	Grasses	Pressing, fiber separation, anaerobic digestion, upgrading	Natural gas	Grid
Four-platform (C6/C5 sugars and lignin/syngas) biorefinery for synthetic biofuels, bioethanol, and animal feed from lignocellulosic crops	C6/C5 sugars, lignin, syngas	Synthetic biofuels (Fischer-Tropsch fuels), bioethanol	Animal feed	Lignocellulosic crops (switchgrass)	Pretreatment, hydrolysis, fermentation, gasification, Fischer-Tropsch synthesis	Natural gas	Grid

[a] Reproduced with permission of the Society of Chemical Industry and John Wiley & Sons, Ltd.

or xylose to furfural. The fluid has a temperature and pressure above the critical point for carbon dioxide, but at least one of the temperature and pressure is below the critical point for water (105).

An integrated approach using best available technologies within the infrastructure of a biorefinery needs to be adopted. The BREW project (**http://www.chem.uu.nl/brew**) best summarizes the four core requirements that must be fulfilled for a biorefinery to be successful: (*a*) substantial technological breakthroughs must be realized in the bioprocess step, (*b*) major progress must be made in downstream processing, (*c*) prices for fossil fuels must be high, and (*d*) prices for fermentable sugar must be low.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

A.S.M. expresses his thanks to the University of York for the award of an Anniversary Lectureship to promote scholarly activities. R.L. gratefully acknowledges Ministerio de Ciencia e Innovacion, Gobierno de España, for the concession of a Ramon y Cajal contract (ref. RYC-2009-04199) and project CTQ2011-28954-C02-02 as well as Consejeria de Ciencia e Innovacion, Junta de Andalucia, for funding under project P10-FQM-6711. The authors are indebted to the reviewer for significant upgrading of this chapter based on given advice and guidance.

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