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## **Bioenergy**

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## 1. Introduction

Bioenergy is the chemical energy contained in organic materials that can be converted into direct, useful energy sources via biological (including digestion of food), mechanical or thermochemical processes [1]. Over the past 150 years, fossil fuel combustion provided the energy for industrialisation and development of the modern economy. Around 1900, total energy consumption by humanity was about 20 EJ yr<sup>-1</sup> [exajoules (10<sup>18</sup> J); see Appendix for list of abbreviations and units], mainly supplied by wood [2]. By 2009, the world total primary energy supply was about 510 EJ yr<sup>-1</sup>, or the equivalent of 12 150 million Mg of oil per year (Mtoe yr<sup>1</sup>), which was almost double that of the 6 111 Mtoe supply in 1973 (Figure 1) [3]. This 2009 value is equivalent to global energy consumption by humans of 16 TW ( $16 \times 10^{12}$  W), and global energy demand is projected to increase to 23 TW by 2030 [4]. In 2011, 87% of total energy consumption was derived from fossil fuels, with only 8.5% from renewable energy sources [5]. Unfortunately, we are running out of fossil fuels, which originated from plant material produced in ancient times, and combustion of these fossil fuels leads to emissions of CO<sub>2</sub> and the consequent global warming. Current proven reserves of oil would last only 50-55 years, natural gas 60-65 years and coal 110-115 years at 2011 rates of consumption [5]. Although some experts claim that peak oil will occur in about 20 years, others argue that the world is already at peak oil production [6]. In either case, fossil fuels are created at a slower rate than they are now being consumed and cannot be considered as the world's main source of energy for more than one or two more generations. This review gives an overview of the amount of energy that can be harvested from the sun for contemporary biomass production, both for food and for bioenergy.



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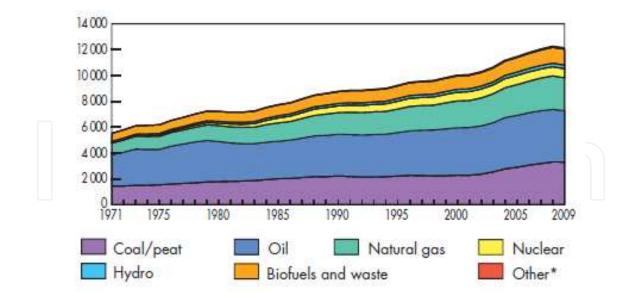


Figure 1. World total primary energy supply from 1971 to 2009 by fuel (Mtoe) [3] \*Other includes geothermal, solar, wind, heat, etc.

#### 2. Photosynthesis as a source of food and bioenergy

Oxygenic photosynthesis occurs in cyanobacteria, algae and land plants and is summarised by the equation:

$$CO_2 + H_2O + \text{light energy} \rightarrow [CH_2O] + O_2$$
 (1)

where [CH<sub>2</sub>O] indicates a carbohydrate product of photosynthesis such as sucrose or starch.

Photosynthesis is the source of global food, feed, fibre and timber production as well as biomass-based bioenergy. Each of these products of photosynthesis are renewable. Starch and sucrose are the main products of photosynthesis and sucrose is the main form of carbon translocated from leaves to other organs in plants.

The total energy from sunlight reaching the earth's surface is about 101 000 TW[8] (nearly 3 000 000 EJ per year), about 6 000 times the 2011 annual global human primary energy consumption of 500 EJ [7]. However, solar energy is geographically diffuse and this makes the efficiency of conversion of sunlight important to capture this energy in useful forms. Due to the Carnot limit, the maximum theoretically possible conversion efficiency for sunlight into electricity is 93% [8]. Photovoltaic cells have efficiencies around 15 – 20% for converting sunlight into electricity, but are limited to a maximum conversion efficiency of ~30% due to the Shockley-Queisser limit [9]. Actual solar energy conversion by photosynthesis and subsequent plant growth (biomass production) is much lower at around 2 - 4% for productive plant communities [10].

## 3. Global primary production

Earth's land plants assimilate about 10 Pmol of atmospheric CO<sub>2</sub> each year, storing (at least temporarily) nearly 5 000 EJ yr<sup>-1</sup> in sucrose, starch and other carbohydrates. For marine organisms the total may be 7-8 Pmol of CO<sub>2</sub> yr<sup>-1</sup>. Those are values of *gross primary production* (GPP) or total photosynthesis. Annual global *net* primary production (NPP), defined as GPP minus the respiration of the photosynthetic organisms, may be nearly 5 Pmol C on land (equivalent to as much as 2 000 EJ yr<sup>-1</sup>) and perhaps 4 Pmol C in the ocean [11]. NPP is critical to present life on earth because it is the organic matter (and associated energy) potentially available to all non-photosynthetic organisms for use in support of their growth, maintenance and reproduction. NPP also contains the bioenergy potentially available to society.

Land plants may have an advantage over aquatic plants as they are able to photosynthesise using leaves that can make use of the rapid diffusion of gases in air which is about 10 000 times faster than that in water [12-14]. Thus, cyanobacteria and algae in water may need to be well stirred to support rapid photosynthesis and growth [12]. Fortunately for oceanic photosynthesisers, surface waters are often vigorously mixed and where nutrients are available primary production can proceed rapidly. Since oceanic NPP is dominated by phytoplankton, most of the "plant" biomass there is photosynthetic as they do not have non-photosynthetic structures such as roots and woody stems. Those oceanic primary producers represent only about 0.2% of global (ocean + land) primary producer biomass due to rapid turnover time in the oceans (average 2 to 6 days) compared to much slower turnover on land (average of about 20 years) [11]. Large ocean area provides a significant *potential* for biomass production, though nutrients are often limiting and harvesting oceanic biomass is difficult and challenging. Because of relative ease of harvesting, and the longer life time of land plants, nearly all current bioenergy harvesting is from terrestrial plants.

## 4. Converting solar energy to biomass

To describe the component processes associated with the use of solar energy to produce biomass, Monteith's equation [15] can be used:

 $Y = 0.5 \times S_t \times \varepsilon_i \times \varepsilon_c \times \varepsilon_n$ 

Where Y is biomass energy yield (J m<sup>-2</sup> of ground); S<sub>t</sub> (J m<sup>-2</sup>) is the total incident solar radiation during the growing season;  $@_i$  is light interception efficiency (fraction of incident radiation absorbed by a plant's photosynthetic apparatus, J J<sup>-1</sup>);  $@_c$  is photosynthetic conversion efficiency, including metabolic costs of growing new biomass from products of photosynthesis (J J<sup>-1</sup>) in resulting biomass); and  $@_p$  is partitioning efficiency or harvest index (J J<sup>-1</sup>).

Photosynthetically active radiation (PAR) is approximately confined to the 400-700 nm waveband [16] which contains about 50% of total solar energy reaching Earth's surface ( $S_t$ ) [16].

(2)

Thus, about half of the incident solar energy is unavailable to higher-plant photosynthesis, which is accounted for in the coefficient 0.5 in the equation above (see Figure 3). In addition, the fraction of solar radiation absorbed by plants or  $@_i$ , depends on leaf area and orientation. A full canopy can potentially absorb about 93% of incident PAR with perhaps 92% of that absorption associated with chloroplasts [17]. Partitioning efficiency ( $@_p$ ) or harvest index is the amount of total biomass energy partitioned into the harvested portion of the crop; for a biomass crop that may approach 100%, but for a seed crop can be as low as 30%. The amount of energy in a unit mass of plant material also varies, being about 17-18 MJ kg<sup>-1</sup> for typical biomass, but as much as 35-40 MJ kg<sup>-1</sup> for oilseeds [17, 18]. During the Green Revolution, the dwarfing of the crop-plant stem improved partitioning efficiency ( $@_p$ ) [19] and selection of larger-leaved cultivars improved light interception efficiency ( $@_p$ ).

## 5. Potential and actual photosynthetic conversion efficiency

The observed minimum quantum requirement of 9-10 mol photons per mol  $CO_2$  assimilated in C3 photosynthesis represents an absolute limit on biofuel production from sunlight, in spite of claims for biomass production (usually by algal systems) that would correspond to significantly smaller quantum requirements [20]. That range corresponds to C3 photosynthesis in the absence of photorespiration, which in the current atmosphere increases minimum quantum requirement to about 14 mol mol<sup>-1</sup>. But due to light saturation, and other factors (below), biomass production, especially over an annual cycle, cannot approach limits set solely by minimum quantum requirements [17, 20].

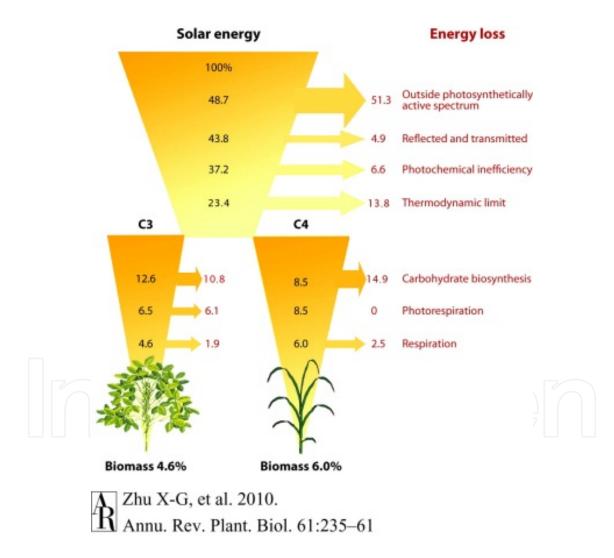
The potential maximum efficiency of converting solar energy to biomass energy is estimated at about 4.5% for algae [12, 20], 4.1-5.3% for C3 land plants and 5.1-6.0% for C4 land plants at 20-30°C and present atmospheric  $[CO_2]$  (see Figure 2) [10, 17]. C4 plants can be more efficient than C3 plants because they are able to suppress photorespiration through a combination of biochemical and anatomical innovations that arose relatively recently in plant evolution. These innovations presumably were a response to declining global atmospheric  $[CO_2]$  during the past 100 million years.

Actual maximum conversion efficiency is generally lower than the calculated potential efficiency at around 3.2% for algae [12], 2.4% and 3.7% for C3 and C4 crops [10], respectively, across a full growing season (see Figure 3) due to insufficient capacity to utilise all radiation incident on a leaf, and photoprotective mechanisms that impair efficiency. The actual photosynthetic efficiency of mature C3 forest stands was also calculated to be between 2.2 to 3.5% [21]. Of course, plants are self-regenerating and self-maintaining whereas photovoltaic cells are not.

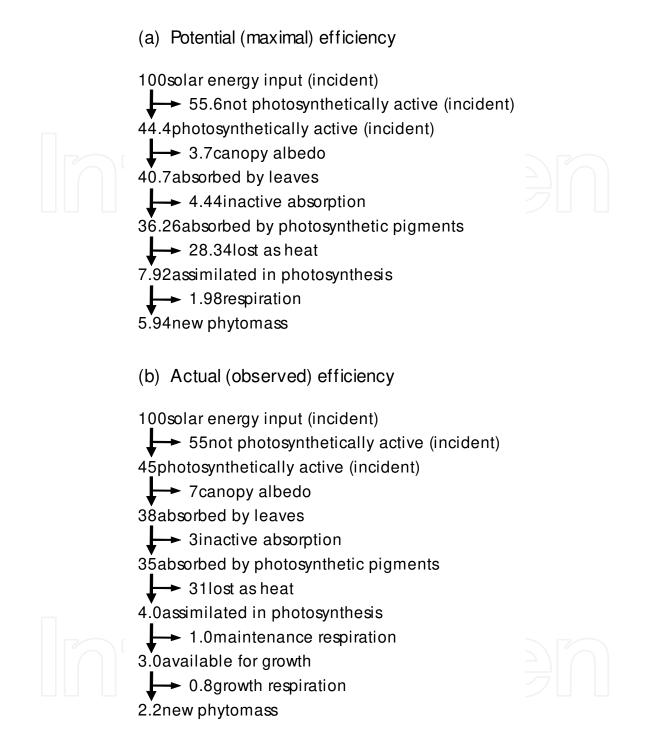
The low yields from biomass energy production are frustrating compared with photovoltaic cells that have efficiencies of up to 20%, and this is due to the following limitations in plants [10, 12, 17, 20, 22]:

1. Two photosystems (Photosystems I and II in series);

- 2. Dependence on photons limited to the approximate waveband 400–700 nm;
- 3. Inherent inefficiences of enzymes and biochemical processes;
- **4.** Light saturation under bright conditions and associated photoinhibition in Photosystem II;
- **5.** Respiration, an absolutely essential process for life and growth [23], which consumes 30-60% of the energy contained in the products of photosynthesis; and
- 6. Plants are living organisms that spend about half of each day in the dark, when they need to use previously generated carbohydrate stores to keep themselves metabolically active and growing.



**Figure 2.** Minimum energy losses associated with biomass production. Wedges show the percentage of energy from solar radiation remaining (inside arrows) and percentage losses (at right) from an original 100% calculated for several stages of photosynthetic and biosynthetic energy transduction from sunlight incident on a plant community to new plant biomass [18]. This analysis indicates that a theoretical maximal photosynthetic energy conversion efficiency is 4.6% for C3 and 6.0% for C4 plants at 25-30 °C.



**Figure 3.** estimates of (a) potential efficiency (theoretically maximal) and (b) actually efficiency for biomass production of a healthy crop [17]. These results are still generally applicable.

The current bioenergy enterprises are focussing on C4 crops such as sugarcane, maize, sweet sorghum, switchgrass and miscanthus presumably due to the higher energy conversion efficiency. However, this advantage of C4 over C3 will disappear as atmospheric  $[CO_2]$  approaches 700 µL L<sup>-1</sup>.

## 6. Improving energy conversion efficiency

Due to the apparently low actual energy conversion efficiency in whole-plant photosynthesis (i.e., 2-4%), much discussion has focused on improving photosynthesis to improve crop yield potential including [17, 18, 24, 25]:

- 1. Engineering C3 crops to use C4 photosynthesis. This would potentially suppress photorespiration and increase net photosynthetic efficiency by as much as 50% and increase both water and nitrogen use efficiencies [26, 27]. There is an ongoing ambitious research program, led by the International Rice Research Institute (IRRI), to convert the normally C3 rice to a C4 system by transforming rice to express Kranz anatomy and the C4 metabolic enzymes [28].
- 2. Improving both rubisco's catalytic rate of carboxylation ( $k_{cat}$ ) and specificity for CO<sub>2</sub> relative to O<sub>2</sub> ( $\tau$ ). This would improve the efficiency of rubisco as a catalyst of CO<sub>2</sub> assimilation [18, 24]. Unfortunately,  $\tau$  and  $k_{cat}$  are inversely related across many rubiscos found in nature [29]. Another complication for engineering an improved rubisco is that it is composed of eight large chloroplast-encoded subunits and eight small nuclear-encoded subunits, and assembling modified subunits in chloroplasts remains a challenge [30].
- **3.** Minimising, or truncating, the chlorophyll antenna size of chloroplast photosystems. This would potentially improve solar conversion efficiency by up to 3-fold in high light, which normally saturates photosynthesis [31]. Individual cells or chloroplasts would have a reduced probability of absorbing sunlight, allowing greater transmission to leaves lower in a canopy and a more uniform distribution of light across leaves within a canopy, hence reducing dissipation and loss of "excess" photons in non-photochemical quenching (NPQ).
- 4. Improving the recovery rate from the photoprotected state. This would potentially increase carbon uptake by crop canopies in the field [32]. The xanthophyll photoprotection system protects plants from damage from absorption of excess light (the reduction of photosynthesis by dissipation of photons by NPQ). High-yielding rice are reported to recover more quickly from photoinhibition than traditional varieties [33].

## 7. C3 photosynthesis

C3 crops include wheat, rice, cotton, barley, soybean, bean, chickpea, algae, palm and peanut. C3 photosynthesis of  $CO_2$  forming fructose 6-P can be summarised by:

$$6 \text{ CO}_2 + 18 \text{ ATP} + 12 \text{ NADPH} \rightarrow \text{fructose } 6\text{-P} + 18 \text{ ADP} + 17 \text{ Pi} + 12 \text{ NADP}$$
 (3)

In principle, the ATP and NADPH required to assimilate one CO<sub>2</sub> molecule can be produced during absorption of eight photons of PAR. Because 8 mol photons (PAR) contain on average

1.75 MJ, and because about 0.47 MJ of energy per mol C is stored in carbohydrates, the potential efficiency of converting *absorbed* PAR to biomass approaches 27% for C3 photosynthesis (or about 13% for total solar radiation). That efficiency occurs only in low light, however; under a bright sun, C3 photosynthesis becomes light-saturated. In addition, the process of photorespiration, which is relatively rapid in C3 plants, especially at higher temperature, is a significant constraint on  $CO_2$  assimilation in C3 plants. As much as one third of the C assimilated in C3 photosynthesis can be almost immediately lost to photorespiration with present atmospheric  $CO_2$  concentration (higher  $CO_2$  concentration not only stimulates photosynthesis, but inhibits photorespiration). In sum, at about 20°C, the efficiency of converting *absorbed* PAR into carbohydrate may be about 18% in C3 plants, accounting for photorespiration, but ignoring light saturation. Moreover, that efficiency does not account for plant respiration, and some respiration is essential for growth and maintenance processes.

#### 8. C4 photosynthesis

C4 plants include maize, sugarcane, sorghum, millet, miscanthus and switchgrass. The C4 system involves the specialised metabolism and Kranz leaf anatomy to concentrate  $CO_2$  in the bundle sheath cells. Normal C3 photosynthesis takes place in the bundle sheath cells in C4 plants, but because the CO<sub>2</sub> concentration there is quite high, photorespiration is greatly suppressed. The C4 cycle, which concentrates the CO<sub>2</sub> in bundle sheath cells, requires two ATP to assimilate a  $CO_2$  in the mesophyll, release it in the bundle sheath and regenerate the  $CO_2$ acceptor in the mesophyll. Some  $CO_2$  leakage from the bundle sheath is inevitable, and this requires that the C4 cycle operates more quickly than the C3 cycle in C4 plants. Hence, C4 photosynthesis may require at least 2.2 ATP CO<sub>2</sub><sup>-1</sup> more than C3 photosynthesis, based on a modest  $CO_2$  leak rate of 10% from bundle sheath cells [17]. In spite of the extra energy cost of the C4 cycle, C4 photosynthesis responds better to bright sunlight and to higher temperatures than C3 photosynthesis because of suppressed photorespiration. At cooler temperatures (e.g., 10-15°C), however, C3 photosynthesis is superior because photorespiration operates slowly at low temperature. In addition, many C4 plants are sensitive to low temperature. The C4 plant miscanthus (*Miscanthus* × giganteus) is relatively tolerant of low temperature, and it may be a good source of germplasm for improving the low temperature tolerance of other C4 plants [34]. In terms of efficiency, C4 photosynthesis might retain as much as 16-17% of the energy in absorbed PAR in carbohydrate products, again before any required respiration and ignoring light-saturation. That efficiency is relatively insensitive to temperature, at least over the normal range experienced by typical C4 crops during daylight hours.

## 9. CAM photosynthesis

Commonly cultivated CAM (crassulacean acid metabolism) plants include agave (*Agave* spp.), Opuntia (*Opuntia* spp.), pineapple (*Ananas comosus*), *Aloe vera*, and vanilla (*Vanilla planifolia*). CAM plants are well adapted to arid and semi-arid habitats. They open their stomata at night and take up  $CO_2$  in the dark to form malic acid, which is then metabolised to release  $CO_2$  for photosynthesis during the following day, but with their stomata closed [35, 36]. By closing the stomata during the day, less water is lost, resulting in high water use efficiencies with a tradeoff of lower growth rates. CAM imposes an additional metabolic cost of ~10% compared with the standard C3 pathway due to the transport of malic acid into the vacuole at night and conversion of C3 residue back to the level of storage carbohydrate during the daytime [37]. CAM plants have been suggested to have potential for food, fibre and biofuel production in dry marginal lands [38, 39].

## 10. World food energy demand

The energy contained in food consumed per person is only about 10 MJ day<sup>-1</sup> (equivalent to 2 500 kcal per day, 10 000 Btu or 120 W) [40]. Hence, the food energy needed to feed the world's current seven billion persons is ~25 EJ yr<sup>-1</sup>, which is only about 5% of the world's ~510 EJ of annual energy consumption, but more than 10% of global land NPP. The world's food production system consumes about 95 EJ yr<sup>-1</sup> and hence, it takes about 4 units of fossil energy to produce 1 unit of food energy [41]. In the United States, the overall energy input/food output ratio is even larger, around 7 to 1 [42]. Most of the energy consumption (~80%) occurs after the farm gate, during transportation, processing and retail. Globally, one third of food, around 1.3 billion Mg, is discarded (including spoilage) each year, and a similar share of the total energy inputs are embedded in these losses [41].

Global population is projected to increase to 9-10 billion within 40-50 years [43]. In developing countries, food consumption per person is rising with increased consumption of animal protein with the livestock revolution [44]. Average annual meat consumption is projected to rise from 32 kg person<sup>-1</sup> in 2011 to 52 kg person<sup>-1</sup> by 2050 [45]. Grazing livestock already occupy a quarter of the world's land surface, and the production of livestock feed uses a third of arable cropland [44]. With future increases in global population and per capita food consumption, global food production will have to increase by as much as 70% to meet the increased demand in 2050, an annual growth rate in food supply of 1.1% yr<sup>-1</sup> [46]. In principle, this means that by 2050 the energy consumption for global food production may increase by 162 EJ yr<sup>-1</sup> from today's 67 EJ yr<sup>-1</sup> assuming the energy conversion efficiency remains constant.

In ancient civilisations, most of the energy used for farming was provided by animals and the nutrients were derived from animal manure. During and after the Green Revolution, dependence on non-renewable fossil fuels resulted in a conversion of fossil energy into food energy, but in an inefficient way. Agriculture uses about 4% of the global fossil fuel energy of which 50% is used for the production of nitrogen fertiliser from natural gas and atmospheric N<sub>2</sub> using the Haber-Bosch process [45] with a stoichiometry of about 60 MJ kg<sup>-1</sup> N [47]. The dependency of agriculture on fossil fuels has resulted in commodity (food) prices being closely linked with global energy prices [48]. Hence, food prices tend to fluctuate and trend (upwards) in parallel with energy prices. It is instructive to compare maize production in Mexico using human labour (with a hoe and sickle) returning 10.7 times as much energy in the harvested crop as

used in production of that crop with a return of less than 4 times for mechanised maize production in the United States (Table 1). The U.S. crop was, however, more than nine times as productive.

Crop	Country	Tillage	Yield (Mg ha <sup>-1</sup> )	Inputs (MJ ha <sup>-1</sup> )	Output (MJ ha <sup>-1</sup> )	Energy ratio
Groundnut	USA	Mechanised	3.72	45 817	64 051	1.40
Maize	Mexico	Human	1.94	2 687	28 881	10.70
Maize	Mexico	Oxen	0.94	3 222	13 982	4.34
Maize	USA	Mechanised	8.66	33 961	130 396	3.84
Rice	Borneo	Human	2.02	4 327	30 626	7.08
Rice	Philippiines	Carabou	1.65	7 638	25 126	3.29
Rice	Japan	Mechanised	6.33	34 405	96 163	2.80
Rice	USA	Mechanised	7.37	49 542	110 995	2.24
Soybean	USA	Mechanised	2.67	12 609	40 197	3.19
Wheat	USA	Mechanised	2.67	17 740	35 354	2.13

Table 1. Energy use in grain and legume production [49].

In developing countries, populations tend to have a cereal-based diet and are effectively at a lower trophic level in the food chain, while populations in developed countries tend to consume more meat and operate at a higher trophic level. Production of livestock, on average, may require 4 kg of wheat for the production of 1 kg of meat [40, 50]. Therefore, in developed countries where 400 kg of cereal and 100 kg of meat are consumed per year, the total need for food and feed is 800 kg of cereal per person per year [40]. Overfishing of the ocean predators (e.g., killer whales, tuna, salmon) at high trophic levels has also led to the decline in ocean fisheries yield [51]. It is important that cereal crops supply 70% of the calories consumed by humans on the global scale with the remainder supplied by potatoes, beans and other crops, with marine animals now contributing only 2% of the human food supply [52]. To increase the energy efficiency of our primary food production system, we should focus on primary production in agriculture (e.g., cereals) and aquaculture (e.g., algae, phytoplankton) rather than secondary production (e.g., livestock, fish).

#### 11. Biofuels

In addition to providing food and feed, plants are an important source of fuel. Indeed, biofuels are not a new concept. In 300 B.C., the Syrian city of Antioch had public street lighting fuelled by olive oil. More recently, the German inventor Rudolph Diesel demonstrated his engine that ran on peanut oil at the 1900 World Fair in Paris. In simple terms, the nearly 5 000 EJ contained

in annual global NPP is about 10 times current global energy demand (~ 510 EJ) [53]. That NPP, however, includes vast amounts of biomass that cannot be physically or economically harvested (including national parks). In 2009, biomass, including agricultural and forest products and organic wastes and residues, accounted for nearly 10% of the world's total primary energy supply [3], with fraction less than 10% in developed countries, but as high as 20-30% in developing countries [1]. Replacing fossil fuels with renewable energy sources derived from sunlight, such as solar, hydro or biomass is very challenging as these energy sources have a lower energy density than fossil fuels and are generally more expensive [54]. In some developing countries, as much as 90% of total energy consumption is supplied by biomass [54]. Solid biomass such as firewood, charcoal and animal dung represent up to 99% of all biofuels [54].

Since the beginning of civilisation, humans have depended on biomass for cooking and heating, and many developing countries in Asia and Africa are still dependent on traditional sources of biomass. Liquid biofuels account for only 2% of total bioenergy, and they are mainly significant in the transportation sector. Transportation accounts for 28% of global energy consumption and 60% of global oil production, and liquid biofuels supplied only 1% of total transport fuel consumption in 2009 [3]. The automative industry currently uses relatively energy inefficient internal combustion engines to burn liquid fuels (e.g., gasoline and diesel). Electric car motors have a 7.5 times higher energy efficiency than internal combustion engines, but the lightness and compactness of liquid fuels still have a fifty-fold higher energy storage than the best available batteries [1]. Hydrogen fuel cells may replace electric motors in the future but this is still in the developmental phase. In the meantime, liquid biofuels are the transition renewable alternative to fossil fuels. Globally, liquid biofuels can generally be classified into three production sources; maize ethanol from the United States, sugarcane ethanol from Brazil and rapeseed biodiesel from the European Union. In 2010, Brazil and the United States produced 90% of the 86 billion L of global bioethanol and the European Union produced 53% of the 19 billion L of global biodiesel [55]. For the rest of this chapter, we use the term biofuels to refer to liquid biofuels. First generation biofuels refer to the traditional or conventional supply chains based on food crops, whereas second generation biofuels require more complex and expensive processes and are generally operating in pilot plants and not yet widely available on the market.

## **12. First generation biofuels**

The first generation of biofuels is produced from starches, sugars and oils of agricultural food crops, including maize, sugarcane, rapeseed and soybean. Carbohydrates are fermented to bioethanol, which is mixed with gasoline as a transporation fuel. Bioethanol, produced mainly from sugarcane, replaced 40% of gasoline used in Brazil in 2008, with the introduction of flex-fuel vehicles allowing high-blending of bioethanol with petrol (all petrol blends in Brazil contain 25% bioethanol) [56]. In the United States, up to 40% of the maize crop was used for bioethanol production in 2011. If all the main cereal and sugar crops (wheat, rice, maize, sorghum, sugar cane, cassava and sugar beet) representing 42% of global cropland were to be hypothetically converted to ethanol, this would correspond to only 57% of total petrol use in 2003 [57], and would leave no cereals or sugar for human consumption, although the reduced sugar in the human diet would have health benefits. Oils/fats (i.e., a mixture of triglycerides,

free fatty acids, and/or phospholipids) are converted to biodiesels, potentially competing with food and feed production from oilseed crops such as rapeseed (including canola) and soybean. Biodiesel, a supplement or replacement to traditional diesel, is also produced from animal fats (tallow).

## 13. Second generation and advanced biofuels

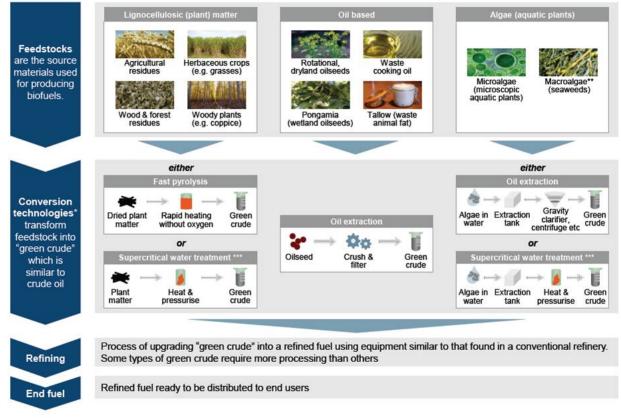
Due to food and energy security concerns, many countries are promoting bioenergy crops that can be grown on land not suited for food production, so that the two systems are complementary rather than competitive [58, 59]. Second generation biofuels refer to the range of feedstocks (e.g., dedicated energy crops such as miscanthus, switchgrass, jatropha, pongamia, agave, Indian mustard, sweet sorghum, algae, carbon waste), conversion technologies (e.g., fast pyrolysis and supercritical water), and refining technologies (e.g., thermo-chemical Fischer-Tropsch methods) used to convert biomass into useful fuels (Figure 4) [60]. There is a fine line between a first and second generation biofuel. For example, sugarcane is a first generation biofuel feedstock (sucrose) but co-generation for electricity using sugarcane residue (bagasse) as a fuel is also possible, and sugarcane residues may serve as future feedstocks in second generation ligno-cellulosic bioethanol production [61]. Ligno-cellulosic bioethanol is based on the conversion of lignocellulosic compounds, made up of chains of about 10 000 glucose and other small organic molecules, into sugars with sophisticated methods of acid or enzymatic hydrolysis. Those sugars can then be converted to fuel using tradiational methods. This means that non-food products such as cereal and wood residues can be converted to ethanol instead of remaining as a waste by-product. These lignocellulosic residues are mainly cell walls that make up 60-80% and 30-60% of the stems of woody and herbaceous plants, respectively, and about 15-30% in their leaves, and consists of around 40-55% cellulose, 20-50% hemicelluloses and 10-25% lignins [1]. There are a few examples of commercial ligno-cellulosic plants. For example, Swiss company Clariant opened a ligno-cellulosic plant in Germany in 2012 that can produce up to 1 000 Mg of cellulosic ethanol from 4 500 Mg of wheat straw [62]. Where lignin cannot be converted to small sugars easily through biochemical processes, it can be burnt for co-generation of bio-electricity.

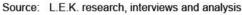
Another potential bioethanol feedstock is agave (*Agave* spp.) which is adapted to semi-arid land unsuitable for food production [63, 64]. Agaves are well-suited for biofuel production as they can be grown in sandy soil with little or no irrigation and are less likely to be weedy. Agave have above-ground productivities similar to that of the most efficient C3 and C4 crops (25-38 Mg ha<sup>-1</sup> yr<sup>-1</sup> dry biomass), but with only 20% of the water required for cultivation [38].

Sisal (*Agave sisalana*) is mainly produced in east African countries of Kenya, and Tanzania, as well as in Brazil, China and Madagascar. The sisal leaf contains about 4% by weight of extractable hard fibre (vascular tissue), the remaining 96% being water and soluble sugars which is disposed of during the decortication process into rivers and the sea, causing pollution, eutrophication and water contamination [65]. Production of ethaonol and bioenergy from sisal juice from the sisal leaves and stems is under pilot testing at the Institute for Production Innovation at the Uninversity of Dar es Salaam and Aalborg University [65]. The first field experiment of blue agave (*Agave tequilana*) as a biofuel crop was planted in 2009 in the Burdekin

River Irrigation Area of Queensland, Australia [35]. Blue agave can acheive strong growth rates by potentially switching from CAM to C3 photosynthesis if there is sufficient water supply [66]. Approximately 0.6 Mha of arid land was used to grow sisal for coarse fibres (sisal) but this has fallen out of production or abandoned due to competition with synthetic fibre [63]. In theory, this crop area (0.6 Mha) alone could provide 6.1 billion L of ethanol if agave were re-established as a biofuel feedstock without causing indirect land use change [63].

In the meantime, new and novel feedstock conversion technologies are being developed such as fast pyrolysis and supercritical water treatment that can now convert nearly any biomass feedstock, such as wood residues, agricultural residues (e.g., wheat and maize stalks), woody plants, and  $C_4$  grasses [e.g., switchgrass (*Panicum virgatum*), miscanthus and sweet sorghum] into a green biocrude that can be processed into jet fuel, biodiesel, or bioethanol [60]. Hydrogen (H<sub>2</sub>) is designated as a third generation biofuel, when it is produced from biomass by algae or enzymes [1]. H<sub>2</sub> is a fuel whose combustion produces only water, although future technological breakthroughs are needed before H<sub>2</sub> can be produced economically.





**Figure 4.** The advanced biofuels value chain [60]. \*Conversion technologies include fast pyrolysis and supercritical water treatment that transform feedstock into "green crude" which is similar to crude oil. \*\* Macroalgae are multicellular organisms (seaweeds) with low lipid content but are high in carbohydrates. \*\*\* Supercritical water treatment is a thermochemical process which involves subjecting the biomass to controlled temperature and pressure conditions in the presence of appropriate catalysts to produce a "green crude".

There is also a move to source oilseed from non-food dedicated energy crops grown on marginal land. These crops might include jatropha (Jatropha curcas), pongamia (Millettia pinnata), Indian mustard (Brassica juncea), and microalgae. The recent failure of jatropha as an energy crop in India and other developing countries due to a lack of bioenergy policy highlights the need for investment in research and policy development before starting on largescale investments [67]. Pongamia is a tropical tree legume (Fabaceae family) and is a native of India and northern Australia. It has been used as a biofuel crop in India for some time, and is well-suited to marginal land as it is regarded as both a saline- and drought-tolerant species. The seeds contain about 40% extractable oil, predominantly in the form of triglycerides; is rich in C18:1 fatty acid (oleic acid); and has relatively low amounts of palmitic and stearic acid, making it useful for the manufacture of biodiesel [68]. In India, the de-oiled cake of pongamia (i.e., the leftover component of seeds following solvent extraction, and containing up to 30% protein) is used as a feed supplement for cattle, sheep, and poultry [69]. Opportunities exist for a sustainable pongamia agroforestry program to supply biodiesel in northern Australia, although substantial infrastructure investment in processing plants would be needed [59]. Indian mustard is another potential annual oilseed crop being developed in India and Australia. It is drought-tolerant (annual rainfall 300-400 mm) and many varieties can express greater osmotic adjustment than canola [70]. Indian mustard was up to 50% more productive than canola under dry conditions, but not under normal rainfall conditions in northwest New South Wales, Australia [71]. An Indian mustard breeding program for biodiesel production was commenced in 2006 at the University of Sydney's I.A. Watson Grains Research Centre at Narrabri, Australia. Indian mustard is now part of a four year rotation at the Watson Centre.

Microalgae can be cultivated in open raceway ponds or closed photobioreactors, harvested, extracted and then converted into a suitable biofuel such as biodiesel. Raceway ponds are shallow (no more than 30 cm deep) raceways and contents are cycled continuously around the pond circuit using a paddlewheel. Most commercial algal producers are currently using open raceway ponds as these require lower capital costs to set up but may result in increased evaporation and risks of contamination [72]. Photobioreactors are closed systems which offer better control over contamination and evaporation but have higher capital and operating costs than open raceway ponds [72]. The surface area/volume ratios of photobioreactors are also almost double that of the open pond, hence doubling the energy recovered as biomass and potential productivity [73]. Surface fouling due to competitors (e.g., other algae), grazers and pathogens (e.g., bacteria) are a major problem with photobioreactors and cleaning can be a major design and operational problem [72].

Despite the development of microalgae as a feedstock for biodiesel production, there are problems scaling up from laboratories to commercial production [74, 75]. Key limitations to algal production in raceways or photobioreactors are (1) the need for stirring, (2) provision of nutrients for optimal growth and (3) very large surface areas required to capture significant amounts of sunlight [12]. Other problems are pathogen attack, ageing of algal cultures, and lack of system optimisation [76]. The need to de-water and dry the algal biomass can consume up to 69% of the energy input of the process [77]. Despite their potential productivity per unit surface area, and containing up to 30% lipids as storage products, algal biodiesel is not yet economically competitive with petroleum diesel; algal diesel was recently priced at USD 2.76 kg<sup>-1</sup> compared with petroleum-based diesel at USD 0.95 kg<sup>-1</sup> [78].

## 14. Lifecycle analysis and energy balance

Life cycle analysis (LCA) is a tool to take into account the inputs and outputs of a food or biofuel crop production system, including the growing of the crop and its subsequent processing; the technique is also used to assess the energy efficiency and impact of food and biofuel crops on greenhouse gases [79]. Ecologists can relate an LCA to a foodweb or ecosystem model that traces the fluxes of energy through the system. Net energy value (NEV) is an efficiency term calculated as the difference between the usable energy produced from a crop and the amount of energy required for the production of that crop [79].

Three annual crop management systems, conventional (several tillage operations for weed control, seedbed preparation, seeding), conservation (reduced, minimum and no-till systems), and organic (intensive tillage for seeding, weed control) were compared in Canada and Spain [80-82]. Generally, energy inputs for the conservation system were 10% lower than for the conventional system (due to lower fuel and machinery use from reduced tillage) [80]. However, fertiliser and pesticide rates were often increased in response to increased soil water, resulting in a similar total energy use by conventional compared with conservation systems [80-82]. In contrast, there was a reduction in energy input in organic systems due to the use of organic fertilisers instead of synthetic pesticides and fertilisers [47]. In terms of energy output:input ratio, organic farming in Spain was 2.3 times more energetically efficient (5.36:1) than either the conventional or conservation systems (2.35:1 and 2.38:1, respectively) [80]. Inclusion of a leguminous forage crop (e.g., vetch, chickpea) into canola and cereal (e.g., wheat, barley) rotations increased the energy efficiency and output under all management systems [80, 83]. Legume-rhizobial associations are effective solar-energy-driven systems fixing atmospheric N<sub>2</sub> into ammonia with minimal CO<sub>2</sub> emissions compared to industrial nitrogenfertiliser production. Legumes fix nitrogen and thus reduce synthetic N fertiliser use in farming systems; they also enhance the productivity of subsequent crops through breaks in the disease cycle [84]. Pulses contribute about 21 million Mg of fixed-N per year globally, accounting for one third of the toal biological N<sub>2</sub> fixation in agroecosystems [85].

The energy efficiency of biofuels can also be termed the fossil energy ratio (FER) expressed as the ratio of the amount of fuel energy produced to the amount of fossil fuel energy required for that production [79]. An FER < 1 indicates a net energy loss, whereas an FER > 1 represents a net energy gain. Life cycle assessments for biofuels have also shown that Brazilian sugarcane, agave, and switchgrass ethanol could achieve positive energy balances and substantial greenhouse gas offsets, while maize in the United States and China offers modest or no offsets [64]. The bioenergy created in sugarcane and agave ethanol, and in palm oil, is at least four times the amount required to produce it, while maize in the United States and China release almost as much energy when they are burnt as the energy that is consumed in growing and processing them (Figures 5 and 6) [54, 86]. Sugar crops usually produce more ethanol per ha with a better energy balance than starch crops because sugar crops produce higher sugar amounts per ha than starch crops; and sugar (sucrose) can be directly fermented, whereas starch polymers have to be hydrolysed before being fermented by yeast [1]. In general the energy gain and conversion of solar energy into biomass in the sub-tropics is substantially greater than any achievable in temperate zones [87], possibly due to the longer growing season and higher levels of solar energy over an annual cycle. For example, the FER of sugarcane in Brazil was 8.1-10 in 2009, compared with 1.4 for maize-ethanol in the United States and 2.0 for sugarbeet in Europe [61]. There is already evidence of a land-grab with countries (e.g., China and the Middle East) securing their own energy and food security by acquiring large areas of subtropical land in Africa and Asia [88]. Many countries may never be able to establish a position of energy or food independence or anywhere near approaching it [88]. For example, Sweden is importing Brazilian bioethanol as its main source of renewable transportation energy, due to the climatic constraints of growing biomass for liquid fuels within Sweden [88]. FER of microalgal-based (*Chlorella vulgaris*) biodiesel produced in raceways is 0.31, which is 2.5 times as energy intensive as conventional diesel (FER of 0.83] in the United States [89]. This current negative energy balance is unacceptable unless the production chain can be fully optimised with heating and electricity inputs decarbonised [89].

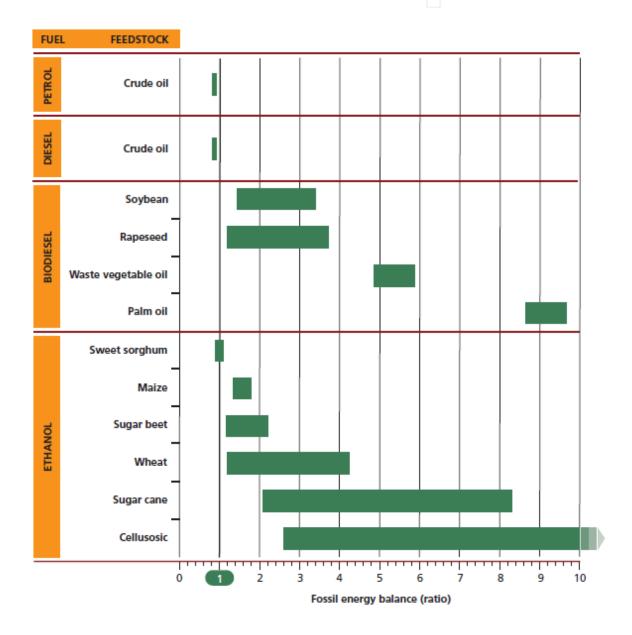
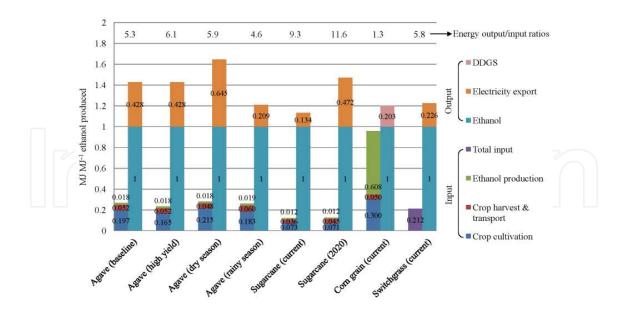


Figure 5. Estimated ranges of fossil energy ratio (FER) of selected fuel types [54, 86]. Note: The ratios for cellulosic biofuels are theoretical.



**Figure 6.** Energy input and output per MJ ethanol produced for various feedstocks including Mexican agave, Brazilian sugarcane, and United States maize (corn) and switchgrass [64]. Abbreviation: DDGS, Dried Distillers Grains with Solubles.

## 15. Carbon footprint of food and biofuels

The world's food production system is inefficient, globally taking four units of energy to produce one unit of food energy. Globally, agriculture also accounts for ~60% of nitrous oxide (N<sub>2</sub>O) and 50% of methane (CH<sub>4</sub>) emissions [90]. On-farm, N<sub>2</sub>O emissions are mainly associated with the use of nitrogenous fertiliser, while CH<sub>4</sub> emissions are mainly from digestion in ruminant livestock (e.g., cattle and sheep). The carbon footprint is the total amount of greenhouse gases (GHG) associated with the production, processing and distribution of food and biofuel crops expressed in carbon dioxide equivalents (CO<sub>2</sub>e). This can range from 0.15 to 0.20 kg CO<sub>2</sub>e per kg of wheat in New South Wales, Australia [91], to 0.46 kg CO<sub>2</sub>e per kg of wheat in Canada [83]. In Canada, legumes like chickpea, dry pea, and lentil may emit only 0.20 to 0.33 kg CO<sub>2</sub>e per kg of grain, about half that of wheat, due to biological N fixation by the legumes. As with the energy balance, durum wheat emitted 20% lower CO<sub>2</sub>e when preceded by an N-fixing crop, compared to when the crop was preceded by a cereal, highlighting the benefits of including a legume in a cereal rotation on GHG balance [83].

Since nearly 80% of the energy used in the food supply chain is in the postharvest phase [41], there is a fashionable trend for an eat-local movement to reduce `food miles`. Food miles refers to the distance a food commodity travels from the point of production to the point of consumption and the related energy and CO<sub>2</sub> emitted during transportation [92]. However, shipping food for long distances may sometimes require less energy and emit less CO<sub>2</sub>. For example, even when shipping was accounted for, New Zealand dairy products imported into the UK used half the energy of their UK counterparts, and in the case of lamb, a quarter of the energy due to grass-fed conditions in New Zealand compared with the energy-intensive

system used in the UK [93]. New Zealand was 10% more energy efficient for apples, and the energy costs of shipping of onions was less than the cost of storage in the UK, making New Zealand onions more energy efficient overall [93].

Over 30% of the food energy is lost through wastage in both developed and developing countries [41]. In developing countries, food is mainly lost due to pests, and spoilage due to the lack of cold storage and food-chain infrastructure. In developed countries, food safety issues have resulted in the over-reliance of `use by` dates resulting in good food being discarded in landfills (instead of being used, e.g., for animal feed or compost) [94]. This wastage can be reduced through improved education, better legislation and research in postharvest technology to reduce food wastage. We can invest in better diagnostics that monitor food spoilage such as temperature- and time-sensitive inks on food package that cause labels to change colour if the food has been exposed to the wrong temperature for too long [95]. Restaurants can stop serving super-sized portions.

GHG emissions during agricultural production of biofuel crops contribute 34-44% to the GHG balance of maize ethanol in the United States [96] and more than 80% in pure vegetable oils [1]. In theory, biofuel feedstocks remove CO<sub>2</sub> from the air and can potentially reduce greenhouse gas emissions. However, clearing of undisturbed native ecosystems such as rainforest and savanna or grassland for biofuel production also increases net GHG production due to change in land use [97]. For example, a hectare of maize grown for bioethanol can sequester 1.8 Mg ha<sup>-1</sup> yr<sup>-1</sup> of CO<sub>2</sub>e, but each hectare of forest converted to maize field has up-front emissions of 600-1100 Mg CO<sub>2</sub>e and each hectare of grassland converted to crop releases 75-300 Mg CO<sub>2</sub>e equivalents. Hence, maize-based bioethanol production might double GHG emissions over 30 years and increase GHGs for 167 years [97]. Converting lowland tropical rainforest in Indonesia and Malaysia to oil palm biodiesel crops would result in a carbon debt of 610 Mg CO<sub>2</sub> ha<sup>-1</sup>. This might take 85-90 years to repay, while sugarcane bioethanol produced on Brazilian Cerrado woodland-savanna might take 17 years to repay [98].

## 16. Water footprint of food and biofuel

Agriculture accounts for about 86% of global fresh water consumption [99]. Energy is also needed to pump water for irrigation. The water footprint (WF) of a product, such as food or biofuel, is the total volume of fresh water used for production and processing, through to eventual use of the the product [99]. In general, the WF of biofuels is up to 2-5 times larger than the WF of fossil fuels [100]. For example, water consumption of bioethanol processed from rainfed maize grain is 0.71 L km<sup>-1</sup> travelled by a light duty vehicle compared with 0.24 L km<sup>-1</sup> for fossil fuel-based gasoline [100]. Most of the water used in gasoline is for the oil refining process while most of the water used in bioethanol production is water used to grow the crop. The water footprint includes three components: green, blue, and gray WFs. Green WFs refer to rainwater transpired and blue WFs to surface and groundwater evaporated following their use in irrigation. Gray WF refers to water that becomes polluted during crop production and includes the amount of water necessary to reduce pollutants (through dilution) discharged so that water quality meets appropriate standards [101].

The global annual mean WF was 9 087 Gm<sup>3</sup> yr<sup>-1</sup> (74% green, 11% blue, 15% gray) and agricultural production contributed 92% to that total during the period 1996-2005, with the remainder accounted for by food processing and end-user consumption [102]. The average consumer in the United States has a WF of 2 842 m<sup>3</sup> yr<sup>-1</sup>, whereas the average consumer in China and India have WFs of 1 071 and 1 089 m<sup>3</sup> yr<sup>-1</sup>, respectively. The differences are mainly due to differences in meat consumption. Globally, consumption of cereals gives the largest contribution to WF of the average consumer (27%), followed by meat (22%) and milk products (7%) [102]. Approximately one third of the total WF of agriculture is related to livestock products. The average WF per calorie (or MJ) for beef is 20 times larger than cereals and starchy roots, and the WF g<sup>-1</sup> of protein for chicken meat, eggs, and milk is 1.5 times larger than for legumes [103]. The WF of any livestock product is larger than any WF of crop products of equivalent nutritional value (e.g., calories, protein, and fat) due to the unfavourable feed conversion efficiency for livestock products [103]. The weighted global average WF of sugarcane was 209 m<sup>3</sup> Mg<sup>-1</sup>; 133 m<sup>3</sup> Mg<sup>-1</sup> for sugarbeet and 1222 m<sup>3</sup> Mg<sup>-1</sup> for maize [104] for bioethanol. Incentives to switch from overhead sprinkler irrigation systems to drip irrigation can potentially use 40% less water and lower energy requirement for maize farmers by reducing energy needed to pump water, and by reducing evaporation losses [95].

## 17. Improving the energy efficiency of food and biofuel systems

The following are some suggestions to improve the energy efficiency of food and biofuel systems:

1. (i) Commercial hybrids of wheat and rice and (ii) increased crop stress tolerance. Increasing productivity during the Green Revolution was largely through a combination of crop genetic improvement through the development of  $F_1$  hybrid varieties of maize and semidwarf, disease-resistant varieties of wheat and rice; and increased use of fertiliser and irrigation [105]. Unfortunately, crop yield increases are now slowing (or have halted) and input costs such as fuel and fertiliser are increasing. Future increases in crop production will have to come mainly from increased yield per hectare, higher cropping intensity (number of crops sown in the same field per year) and to a lesser extent from cultivation of new land [46, 106]. Hybrids are the result of heterosis or the favourable combination of dominant genes by crossing two genetically different parents. In general, hybrids provide around 15% yield advantage over open-pollinated parents in maize, and around 10% over inbred parents in wheat and rice [107]. Although hybrid maize has been widely utilised, adoption of hybrids in wheat and rice (with the exception of China where O. indica hybrids cover around 60% of area) is low [108]. Hence, future adoption of hybrid wheat and rice may increase yield by around 10%. Currently, most of the major commercial genetically modified (GM) crops are based on simple insertion of a gene for protective traits such as insect toxin (e.g., Bacillus thuringiensis, Bt) and/or herbicide resistance (e.g., glyphosate tolerance). The next phase will be the development of abiotic stress tolerance genes such as DroughtGard® (drought tolerant) hybrid maize released by Monsanto in 2012. Not all crop improvement initiatives need to be GM based on transgenic biotechnology. For example, there are a number of heat tolerance breeding programs in wheat, chickpea, and cotton using conventional breeding together with marker assisted selection [109-111].

- 2. Reduced yield gaps. Yield gaps are the difference between realised farm yield and the potential yield that can be achieved using available technologies and management. In many irrigated cereal systems, actual yield tends to plateau at or around 80% of yield potential while, in rainfed systems, average actual yields are no more than 50% of yield potential [112]. In many instances, however, even the 80% of yield potential is not achieved, presumably due to technical, knowledge, climatic and biophysical constraints [113]. Reducing the yield gaps can potentially boost yields per unit of input, and hence, energy conversion efficiency. International aid programs such as the Gates Foundation and the Consultative Group on International Agricultural Research (CGIAR) are working to help to close these yield gaps.
- **3.** Conservation agriculture. Zero or reduced tillage and retaining crop residues can potentially reduce energy use and fuel use for farm machinery in agriculture by 66-75% [108], as well as conserve soil moisture and sequester carbon in soil organic matter. Conversion from conventional tillage to zero/reduced tillage can reduce on-farm GHG emssions by 110-130 kg CO<sub>2</sub>e ha<sup>-1</sup> per season, since soil disturbance caused by tillage increases soil organic carbon losses through decomposition (accelerated oxidation) and physical erosion [114]. Crop residues produced worldwide are estimated at 3 Pg, equivalent to more than 1 Pg carbon per year [115]. With less than 10% of the global crop land under conservation tillage, there is an opportunity for wider adoption of this practice to improve energy- and water-use efficiency [108], as well as reducing net GHG emissions.
- 4. Legume rotations and N-fixing cereals. Replacing synthetic N fertilisers with legumes and organic fertilisers (e.g., animal manures and green manure crops) can reduce the fossil fuel combusted during fertiliser synthesis as well as reduce N<sub>2</sub>O emissions. Soil microorganisms such as rhizobium N<sub>2</sub>-fixers (in legumes), arbuscular mycorrhizal fungi (AM fungi, which can improve plant P and Zn uptake) and P solubilising fungi and bacteria can form a symbiotic relationship with plant roots and act as biofertilisers and biopesticides [116, 117]. Many bacteria can produce natural plant hormones such as ethylene, cytokinins, auxins and gibberellins that can stimulate plant growth, increasing root branching, or shoot development [118]. Microorganisms can also affect gene expression and activate plant defence mechanisms through systemic acquired resistance (SAR) [119]. A challenge going forward is to boost biological N fixation to levels that can substitute for the synthetic fertilisers now used. Effective nitrogen-fixing wheat, rice, and/or maize would be boons to reducing energy input to cropping systems for food, feed, and bioenergy [120]. Past attempts to develop such symbioses are not encouraging.
- **5.** Improving overall annual solar radiation use efficiency in annual crops. In locations supporting only one crop per year, it may be possible to extend the photosynthetic period via stay-green traits to maximise annual solar energy capture [121, 122]. In other areas, it may be possible to shorten the crop cycle to fit a second or third crop into the annual rotation (i.e. increase crop intensification) [123].

- 6. Perennial crops. Perennial crops have greater potential for a more sustainable production due to their longer growing season than annuals, utilising more sunlight during the year, and reduced farming operations [1]. The development of perennial wheat by the Land Institute in Kansas provides the opportunity to crop continuously without tillage and reduce soil erosion [124]. Most LCA also show that perennial C4 biofuel crops such as miscanthus and switchgrass and CAM biofuel crops like agave can provide positive energy balances, supplement renewable energy demands, and mitigate GHG emissions [63, 79]. An important question is whether perennial wheat can attain yields of present wheats across a wide range of environments.
- 7. A lower-trophic-level society. Overall solar energy conversion efficiency in agriculture would be increased if humans consumed more crops directly, rather than after their processing through livestock. Even a modest replacement of energy-intensive meats with less-energy-intensive grains, fruits and vegetables [95] would be significant at the global scale. In marine systems, gains in sustainability could come from harvesting lower trophic level species such as algae, phytoplankton, and filter feeder organisms such as bivalves. For example, over 1.5 Tg yr<sup>-1</sup> of macroalgae (seaweed) is produced in China to be used as food for humans, feed for marine animals, and industrial raw materials [51]. A factor to be overcome is the global trend toward eating more energy-costly food as a component of economic development.

## 18. Hydrogen production and artificial photosynthesis

Hydrogen cells might be used to fuel future cars. Although H<sub>2</sub> contains three times the energy of petrol on a mass basis, 4.6 L of H<sub>2</sub>, compressed at 70 MPa, are needed to substitute for 1 L of petrol. H<sub>2</sub> is also highly flammable and it is 50% more expensive to transport than natural gas [1]. There is interest in both biotic and abiotic sytems that mimic the biological production of H<sub>2</sub> gas via the breakdown of water (analogous to its electrolysis,  $2H_2O \rightarrow 2H_2 + O_2$ , which is carried out in photosystem II using solar energy). Certain algae contain the enzymes hydrogenase or nitrogenase (a key enzyme in nitrogen fixation) which can produce H<sub>2</sub> from CO or organic waste [125]. The combination of microalgae (harvesting radiation in the waveband 400-750 nm) and purple bacteria (using the waveband 400-1100 nm) allow a more complete utilisation of the solar energy spectrum. There are still many unresolved problems in producing H<sub>2</sub> using algae and bacteria, including how to combine microalgal and bacterial biological processes [125].

Artificial photosynthesis involves mimicking natural systems using molecular photocatalytic systems for light-driven water oxidation and  $H_2$  production [126]. Artificial photosynthesis was only an academic activity until the development of the first practical artificial leaf by Nocera in 2011 [127]. The key to this breakthrough was the discovery of new, cheaper photocatalysts made from nickel and cobalt that are capable of splitting water into  $H_2$  and  $O_2$  efficiently. This artificial leaf was claimed to be potentially 10 times more efficient in photosynthesis than a natural leaf [127]. Commercialisation of artificial photosynthesis is yet to be proven.

#### **19.** Conclusions

Solar radiation is the ultimate source of renewable energy for human use, and bioenergy will continue to be a major vehicle for its use. Solar-energy conversion efficiency by even the most productive plant communities are less than 5%, however, while photovoltaic cells may approach 20%. 'Average' plant communities operate at considerably lower efficiencies, but there are opportunities to substantially increase the average efficiency in crop systems. Photosynthesis is now used extensively in agriculture to produce food, feed, fibre, and biofuels, but the current biofuels (bioethanol and biodiesel), mainly produced from first generation feedstocks (e.g., sucrose from sugarcane, carbohydrates from maize seeds, and lipids from rapeseed seeds), constitute only a small fraction (1%) of present transportation energy, and a much smaller fraction of total human energy supply. The future second generation biofuels will come from dedicated perennial energy crops (e.g., miscanthus, switchgrass, agave, pongamia), and in the near future, hydrogen gas may be produced from algae, bacteria, or artificial photosynthesis to fuel hydrogen-cell powered cars.

<b>Abbreviations</b>	and	units
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Abbreviation	Term represented		
Bt	Bacillus thuringiensis		
Btu	British thermal unit (equivalent to 1.055 kJ)		
CAM	Crassulacean acid metabolism		
CO <sub>2</sub> e	Carbon dioxide equivalents		
ε <sub>c</sub>	Photosynthetic conversion efficiency (J J <sup>-1</sup> in resulting biomass)		
ε	Light interception efficiency (fraction of incident radiation absorbed by a plants photosynthetic apparatus, J J <sup>-1</sup> )		
EJ	Exajoules (10 <sup>18</sup> J)		
ε <sub>p</sub>	Partitioning efficiency or harvest index (J J <sup>-1</sup> ).		
FER	Fossil energy ratio		
GHG	Greenhouse gas		
GM	Genetically modified		
GPP	Gross primary production		
kcal	Kilocalories		
k <sub>cat</sub>	Catalytic rate of carboxylation (reactions catalysed per second by each enzymatic site)		
LCA	Life cycle analysis		
Mtoe	be Million Mg of oil equivalent		

NEV	Net energy value	
NPP	Net primary production	
NPQ	Non-photochemical quenching	
PAR	Photosynthetically active radiation (radiation in the 400-700 nm wave band)	
Pg	Petagram (1 × 10 <sup>15</sup> g)	
Pmol	Petamole (1 × 10 <sup>15</sup> mol)	
SAR	Systemic acquired resistance	
S <sub>t</sub>	Total incident solar radiation across the growing season (J m <sup>-2</sup> )	
Tg	Teragram $(1 \times 10^{12} \text{ g})$	
TL	Trophic level	
TW	Terawatt (1 $\times$ 10 <sup>12</sup> W)	
WF	Water footprint	
Y	Biomass energy yield (J m <sup>-2</sup> of ground)	
τ	Specificity for $CO_2$ relative to $O_2$	

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