Review

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Second-generation biofuels and local bioenergy systems

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Abstract: First-generation biofuels, mainly from corn and other food-based crops are being used as a direct substitute for fossil fuels in transport. However, they are available in limited volumes that do not make them serious replacements for petroleum. Second-generation biofuels from forest and crop residues, energy crops and municipal and construction waste, will arguably reduce net carbon emission, increase energy efficiency and reduce energy dependency, potentially overcoming the limitations of first-generation biofuels. Nevertheless, implementation of second-generation biofuels technology will require a sustainable management of energy, or development of local bioenergy systems. This study aims at identifying second-generation biofuel feedstock. It also provides information on the available technologies to produce second-generation biofuels. Finally it discusses the development of local bioenergy systems vs sustainable use of second-generation biofuels. Locally produced second-generation biofuels will exploit local biomass to optimize their production and consumption. © 2008 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: second-generation biofuels; feedstock; technology; local bioenergy systems; biomass waste

Introduction

The use of biofuels for transport is becoming of increasing importance for a number of reasons, such as environmental concerns relating to climate change, depleting fossil fuel reserves, and reducing reliance on imports.[1,2] This is leading to international, national and regional focus on alternative energy sources. In the EU, transport is responsible for an estimated 21% of all greenhouse gas (GHG) emissions.[3,4] More than 90% of the total transport emissions are due to road transport.[5] A range of actions is being taken to reduce emissions from transport. In 2003, the Biofuels Directive set the objective of replacing 2% of vehicle fuel supply by 2005, rising by 0.75% each year to 5.75% by 2010.[1] The 2005 target was not met and it seems unlikely that the 2010 target can be reached. Nevertheless, in 2007, the EU target for biofuels was increased to an ambitious 10% level by 2020, under the conditions of being sustainable and second-generation technologies being commercially available.[5] Despite the fact that the first targets were missed, production of biofuels in the EU and imports from third countries has increased, and there are concerns regarding additional environmental pressures inside and outside the EU. These concerns are mainly due less-than-optimal use of biomass resources, the finite nature of resources, poor energy efficiency, consequences of the intensification of biofuel

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production on arable land (increasing pressures on soil, water and biodiversity), the import of biofuels, and the difficulties in achieving and monitoring sustainable production of biomass outside of Europe.

Biofuels, processed from biomass, a renewable resource, are suggested as a direct substitute for fossil fuels in transport (Table 1). Thus, current research and development drivers are the identification of potential renewable energy sources or biomass feedstock and their processing in order to produce alternatives to fossil fuels in transport, such as bioethanol, biodiesel, biomethanol and hydrogen.[6,7] The relatively young biofuel industry is showing the first signs of consolidation, despite unproven business models.[8] First-generation biofuels derived from corn, sugarcane and oilseed are currently available and are seen as an intermediate step to reduce GHG emissions and to diversify transport energy sources among other alternatives. However, they are available in limited volumes that do not make them serious replacements for petroleum.

Under the concept of 'carbon negative', bioenergy is produced with a 'net negative carbon balance'. This means that the carbon dioxide released (due to the biofuel production process, and during the combustion/use of the biofuel) is much less than the carbon dioxide that is captured/consumed (during feedstock cultivation or during biofuel production). For example, it has been reported that coconut biodiesel can yield reductions of 81 to 109% in net CO_2 emissions relative to petroleum diesel.[9] Carbon-neutral energy

Table 1. List of selected liquid and gaseous biofuels, technology, status and engine applications.

Biofuels	Description	Technology	Status	Engine application
Bioethanol	Ethanol produced from biomass and/or the biodegradable fraction of waste	Microbial	Industrial	Pure/blend
Biodiesel	A methyl-ester produced from vegetable oil, animal oil or recycled fats and oils of diesel quality, for use as biofuel	Physical/chemical (enzymatic)	Industrial (Laboratory)	Pure/blend
Biomethanol	Methanol produced from biomass, for use as biofuel	Thermochemical/ microbial	Pilot plant	Pure/blend (MTBE/biodiesel)
Bio-Ethyl-tertio-butyl-ether	Produced from bioethanol. The percentage by volume of bio-ETBE that is calculated as biofuel is 47%	Chemical/microbial	Industrial	Blend
Bio-Metyl-tertio-butyl-ether	Produced from biomethanol. The percentage by volume of bio-MTBE that is calculated as biofuel is 36%			
Pure vegetable oil	Oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, which can be used as biofuel when compatible with the type of engine involved and the corresponding emission requirements			
Bio-dimethyl-ether	Produced from biomass, appropriate biofuel for power generation.			
Biogas	A fuel gas produced from biomass and/or the biodegradable fraction of waste, which can be purified to natural gas quality	Microbial	Industrial	Pure/blend
Biohydrogen	Produced from biomass and/or the biodegradable fraction of waste for use as biofuel	Microbial	Laboratory	Bioethanol (syngas)/pure
Synthetic biofuels	Synthetic hydrocarbons or mixtures of synthetic hydrocarbons which have been produced from biomass	Microbial and physical (gasification) to produce syngas Fisher-Tropsch process to produce synthetic biofuel	Industrial	Gas turbine

Source: Adapted from *An EU Strategy for Biofuels*[3] and *Biofuels from microbes*.[37]

options, such as wind, solar, and hydro, have zero net carbon dioxide emissions. Fossil fuels are classified as 'carbon-positive energy'.[10] Nevertheless, there is controversy over the energy balance of biofuels production. Some studies indicate that it takes more energy to make ethanol than is contained in the ethanol itself, while other studies indicate that the energy balance is positive.[11]

Currently, renewable energy sources represent about 14% of primary-energy consumption in the world, with biomass being the major contributor (i.e., about 10%). Bioethanol is, by far, the most widely used biofuel for transport,[4,6] and Brazil stands as the world's leading producer of sugarcane bioethanol, supplying about half of the global market.[12,13] In fact, in 2005, Brazil produced 282 000 barrels of bioethanol a day, up from 192 000 barrels in 2001.[14]

Second-generation biofuels

According to a UN report on biofuels, 'second-generation biofuels are made from ligno-cellulosic biomass feedstock using advanced technological processes'.[15]

The goal of second-generation biofuels is to extend the amount of biofuel that can be produced sustainably by using biomass comprised of the residual non-food parts of current crops, as well as other crops that are not used for food purposes and also municipal, industrial and construction waste. Second-generation biofuels are expected to reduce net carbon emission, increase energy efficiency and reduce energy dependency, potentially overcoming the limitations of first-generation biofuels. Additionally, and although outside the scope of this review, it should be mentioned that research on third-generation biofuels (e.g., algae and cyano-bacteria) and fourth-generation biofuels (e.g., biohydrogen and bioelectricity using photosynthetic mechanisms) is also being explored.[6,16]

The challenges include cost, technological breakthroughs and infrastructure needs. Relatively high production costs mean that second-generation biofuels cannot yet be produced economically on a large scale. Additionally, key developments are needed on enzymes, pre-treatment and fermentation in order to make processes more cost- and energy-efficient. The commercialization of second-generation biofuels will also necessitate the development of a whole new infrastructure for harvesting, transporting, storing and refining biomass.

For the biofuel industry to succeed, supply of biomass feedstock should be available at a low cost and on a very large scale, so it will have a meaningful impact on energy and sustainability challenges. It is widely recognized, for example, that production of cellulosic crops, such as short-rotation coppices, winter cover crops or perennial grasses, could have substantially more positive environmental attributes than production of corn, soy or other annual row crops.[6,13] The biofuel industry could also benefit from other biomass feedstock, such as solid waste including green waste, food waste and biodegradable fractions of municipal solid waste (MSW).[17] Cellulose and polymeric hemicelluloses (mainly xylans) are the main components that constitute these lignocellulosic materials, and their bioconversion require a pre-treatment process.[18,19] The pre-treatment and hydrolysis of lignocelluloses can be carried out physically (e.g., steam treatment), chemically (by acid or alkaline hydrolysis) and enzymatically (using cellulases, hemicellulases and ligninases from various fungi), or using a combination of these methods.

Biomass feedstock

Biomass feedstock toward second-generation biofuel production is still an unresolved question. The next generation of feedstock is being developed mainly from agricultural wastes, but other biomass feedstock is also under consideration (Table 2). Waste to energy may play a very important role where the most critical issues and influences include biodegradable-waste-diversion targets, energy and climate change, fiscal incentives, potential future markets for byproducts and planning and land use. Barriers to waste to energy include public perception, inefficient use of heat, regulatory constrains and lack of suitably skilled personnel to design, build and then operate the plants.

Energy crops

Energy crops can be divided into two types: herbaceous energy crops and short-rotation coppice (SRC). Herbaceous energy crops are mostly types of grasses that could be harvested as hay or fresh (e.g., grass, rye, switchgrass), while

Table 2. Selected second-generation biomass feedstocks.

Energy crops	Agricultural and wood residues	Organic waste	Traditional breeding and genetically modified crops	Vegetable oils
Amaranth	Barn	Animal fats	Miscanthus	Calophyllum inophyllum
Bamboo	Citrus waste	Food waste	Switchgrass	Corn oil
Energy maize	Corn stover	Municipal solid waste	Willow	Castor bean
Eucalyptus	Green waste	Olive pulp	etc.	Cottonseed
Grass	Industrial waste	Recycled cooking oil		Jatropha
Miscanthus	Sugarcane bagasse	Wastewater from pulp and paper industry		Palm
Oilseed rape	Sawdust	Wastewater from tofu or sugar factory		Pogamia Pinnata
Poplar	Wheatstraw	etc.		Rapeseed
Salix	Waste ricestraw			Soybean
Sugarbeet	Wood			Sunflower
Sweet sorghum	Wood chips			etc.
Switchgrass	etc.			
Willow				
Winter tritricade				
Winter wheat				
Wood				
Wood chips				
etc.				

SRCs are species that have been grown for producing fiber for the pulp industries and, more recently, for producing biomass for energy purposes (e.g., eucalyptus, Salix, poplar and bamboo).[22] A recent four-year field trial conducted on one site in south-western Germany compared and evaluated the biomass and energy yield performance of six important energy crops.[23] The systems were short-rotation willow coppice, miscanthus, switchgrass, energy maize and two different crop-rotation systems including winter oilseed rape, winter wheat and winter triticale. The effect of three specific nitrogen application levels were additionally investigated in the two-crop rotation systems. Results provided evidence of the superiority of the annual energy crop maize with peak values at the highest nitrogen application level. The highest yielding perennial crop was miscanthus followed by willow at the highest nitrogen application level, whereas switchgrass showed the lowest yields of the perennial crops. The yields of the two-crop rotation systems did not differ significantly. Regarding energy use efficiency, willow was the most efficient whereas the two-crop rotation systems presented the lowest energy. Overall, energy maize gave the best energy yield performance but at a relatively high energy input, whereas willow and miscanthus as perennial energy crops combined high yields with low inputs.[23]

Perennial energy crops currently supply the energy that fuels approximately 100 million ruminant animals on US farms with a total estimated economic value of $39 billion.[24] Additionally, the lignocellulose in forage energy crops (e.g., switchgrass, reed canarygrass and alfalfa) represents a second-generation of biomass feedstock for conversion into energy-related end products. An advantage of using forages as energy crops is that farmers are familiar with their management and already have the capacity to grow, harvest, store, and transport them. Forage crops offer additional flexibility in management because they can be used for biomass or forage and the land can be returned to other uses or put into crop rotation.[25]

In fact, energy crops are most promising for second-generation biofuels because:[15,20,21]

- They have a more favourable GHG balance. Cellulose ethanol could produce 75% less CO_2 than normal petrol, whereas corn or sugarbeet ethanol reduces CO_2 levels by just 60%. As for diesel, Biomass-to-Liquid (BtL) technology could slash CO_2 emissions by 90%, compared with 75% for currently available biodiesel.
- They are able to use a wider range of biomass feedstocks, and might not compete with food production.

- They could use less land. For example, a new genetically modified variety of sugarcane is able to produce up to 200 tonnes of biofuels per hectare.[20] In this case, plant science could triple production volumes per hectare of land.
- They could be produced at cost-competitive prices, especially if low-cost biomass is used.
- They offer a better quality of fuel than first-generation biofuels.

Agricultural and wood residues

The use of agricultural and wood residues may result in a lower overall cost in the biofuel process as compared to the cost of producing a tonne of specially cultivated energy crops, where inputs must be invested to cultivate, fertilize and harvest them. Agricultural residues such as bagasse and residues from the production of cereals, including maize, wheat, barley, rice and rye, are among the feedstocks that can be used to generate bioethanol. However, only about 15% of total residue production would be available for energy generation after accounting for needs related to soil conservation, livestock feed and factors such as seasonal variation.[26] Agricultural residues may become more important biofuel feedstock as bioenergy production increases, and their availability could increase through improved management practices.

The wood industry produces large amounts of sawdust, wood chips and other wood residues that can be obtained from the forest. In 2005, 3.5 billion m^3 of wood of 434 billion m^3 of growing stock were removed from the forest, of which 60% was industrial round-wood and the rest fuel wood.[27] Plantations already provide 25% of the world's wood fiber supply; in New Zeeland, *Pinus radiate* plantations are on average 20-fold more productive than natural forest, whereas plantations of *Eucalyptus hybrids* in Brazil are 40-fold more productive.[28] Trees provide potentially higher calorific values for biofuel production than agricultural crops. In fact trees can achieve a lignocellulosic energy conversion factor of 16 (compared with 1–1.5 for corn and 8–10 for sugarcane), and can be grown in marginal agricultural land, reducing competition for space with food crops.[29] The development of high-output plantations to meet the increased demand for wood sustainably, and the natural forests for meeting carbon mitigation objectives while continuing to provide important ecosystem services such as clean water, or biodiversity, as well as delivering traditional forest products and services, have to be balanced.[27,30] Today, only a small proportion of liquid biofuels are forest-based, but the development of an economically viable process for producing cellulosic liquid biofuels could lead to the widespread use of forest biomass in the transport sector.

Organic waste

Organic waste from the paper industry, animal fats and byproducts, recycled cooking oils and many other sources are underused as an energy resource. Additionally, MSW represents an important source of biomass toward the production of biofuels.[17,31] Unprocessed MSW in the EU consists predominantly of paper/card, kitchen waste, garden waste, textiles, fines and miscellaneous (combustibles and others). Additionally, around 80% of MSW may be biodegradable to a given extent, averaging 65% biodegradability.[17] The biodegradable fraction present in MSW may be considered an alternative sustainable source of biofuel (i.e., bioethanol, biogas).[32] Conversion of waste materials to biofuel raises fewer environmental issues than to energy crops, and therefore the use of MSW to produce biofuel may be advantageous. Moreover, conversion of MSW will further save the land by decreasing material flows to landfill, and little or no resource investment except for MSW collection and separation will be required. Hence, potential drivers for advanced treatment sites of waste to energy are that they operate on a smaller scale and therefore have a smaller land requirement and smaller overall carbon footprint. They are potentially suitable for industry to treat waste onsite, use the energy for their process and sell any excess to the grid. They may also be easier to gain planning permission for, as they are likely to be in existing industrial areas and require fewer vehicle movements, cutting down on concern over traffic and amenity impact. For example, in Northern Ireland, bioethanol is produced from potato peelings from chip plants which have been identified as a potential fuel source.[33]

Traditional breeding and genetically modified crops

The use of genetically modified crops (GMC) is another option that could increase the plant net energy production in a number of ways, including: (i) increasing solar energy transformation by manipulating photosynthetic pathways; (ii) increasing resistance to pests and diseases; (iii) resistance to drought to adapt energy crop plant to the effects of global warming; (iv) resistance to cold for adaptation of high efficiency plants to temperate climates; (v) cultivation in marginal lands such as saline or contaminated land to resolve environment problems and obtain a profitable activity; (vi) reduction of management energy inputs such as tilling, harvesting and transport; (vii) reduction of fertilizer application by using engineering plant for N_2 fixation or increasing the efficiency of minerals capitation; (viii) modification of lignin content could also increase the biomass transformation to biofuels; and (ix) multiproduct production such as, for example, the cellulase production by maize which could reduce the cost of high-value enzymes for the biofuel conversion of cellulose.[13,16,34] Some of these could be achieved by traditional breeding at a lower cost, but require longer periods of time. Furthermore, domestication and breeding of crop species for biofuels production could be a positive method of increasing biomass production. Plants have not been domesticated for modern biofuel production, and the quickest, most efficient, and often the only way to convert plants to biomass feedstock is biotechnologically.[16] With this technology the natural diversity could be screened to look for plants with high aptitudes for bioenergy, such as yield production, that could be improved by molecular modification and breeding to speed up the domestication process. Miscanthus and switchgrass are two bioenergy crops with a low level of domestication and selection that could benefit from the technology and research of the related maize and sorghum.[35] However, the risk of introducing modified crops to the environment will need further investigation, as their use for energy crops is encouraged while their use for food crops is not yet fully understood to be safe for human consumption, and public perception is one of the greatest barriers.

Vegetable oils

Vegetable oils, extracted from oil seeds, crops, nuts, fruits and leaves, can be used as fuels for diesel engines (e.g., biodiesel or straight vegetable oil), but they are relatively expensive if grown as dedicated energy crops. A group of oilseed-bearing shrubs, such as *Jatropha*, castor bean, *Pogamia Pinnata* and *Calophyllum inophyllum*, have been used as first-generation biofuels.[16] *Jatropha* may be the most highly promoted oilseed crop,[36] although there is very little information available about this perennial shrub and its oil-bearing seed plant.[16] *Jatropha* may grow in extremely marginal (e.g., arid) sites, but high yield will be only obtained on fertile sites or with input of water and fertilizers. Castor bean was initially promoted over half a century ago for specialty lubrication uses and for plastics, and now it is being reintroduced as a biodiesel crop, especially in Brazil.[16] Various other perennial shrubs bearing seeds with high oil content, such as *Pogamia Pinnata* and *Calophyllum inophyllum*, are being promoted, especially in India.[16,37] In Europe, rapeseed oil methyl ester (RME), produced from oilseed rape is the main substitute fuel, while soybean oil is used in the USA and canola oil in Canada. Different oilseed-bearing shrubs will result in higher yields than others, for example *Calophyllum inophyllum* yields about twice as much oil per hectare as *Jatropha*.[37] Although the aforementioned oilseeds may add to second-generation biofuels, there are many issues that need to be considered before full-scale industry can be developed. So far most of the abovementioned crops are grown using manual labor, and they have not been domesticated to a point of human safety (i.e., they have poisonous substances).[37] Future research should be oriented toward domestication of oilseed-bearing shrubs, in order to increase the harvest index (seed yield divided by biomass), to facilitate mechanical harvesting, and to suppress the formation of toxic substances, and thus used as second-generation biomass feedstock.[16]

British companies BP and D1 Oils have formed a joint venture called D1-BP Fuel Crops to accelerate the planting of *Jatropha curcas*, as a raw material source for biodiesel. The companies claim that the oilseed is a desirable biodiesel feedstock because it does not compete with food crops for good agricultural land or adversely impact the rainforest.[38] Waste oil made up of old cooking oil, expired oil from grain depots and waste oil from animal fats can also be use for biodiesel. Argent Energy's biodiesel plant at Newarthill, Motherwell, Scotland is one of the first in the UK to use waste cooking oil, produced by the fast food and catering industry, as feedstock for biodiesel.[33]

Table 3. Technologies used to produce biofuels from biomass feedstocks.

Process	Product	Applications	
Anaerobic digestion	Fuel gas	Boiler, gas engine, gas turbine, fuel cell	Heat power, heat.
Fermentation, extraction	Liquids	Oil burners, liquid motor fuels, fuel cells	Power, heat, transport
Combustion	Hot exhaust gas	Boiler, steam engine	Space heating, process heat, hot water, power, heat
Gasification	Fuel gas	Boiler, gas engine, gas turbine, fuel cell	Heat power, heat.
	Synthesis gas	Synthetic natural gas, liquid motor fuels, chemicals, heat	Heat, transport
Pyrolysis	Gas fuel	Engine	Power, heat
	Liquid (fuel oil), char (solid fuel) boiler engine		Power, heat

Source: Adapted from Awang *et al.*[55]

Technology

At present, the immediate factor impeding the emergence of an industry converting lingocellulosic biomass into liquid fuels on a large scale is the high cost of processing, rather than the cost or availability of feedstock.[6] The processes for developing second-generation biofuels are much more complex than those used for first-generation fuels and both the technologies and the logistics are still at a very early stage. While with first-generation biofuels, natural oils are extracted from the plants to produce fuel, second-generation processes, working with waste and 'woody' materials require complex catalysis and chemical alteration procedures to create the oils in the first place.[15] New techniques have been devised for the utilization of second-generation biomass feedstock for energy production, including thermochemical conversion (i.e., combustion, gasification, pyrolysis, liquefaction, hydrothermal upgrading), biochemical conversion (i.e., fermentation and anaerobic digestion) and extraction of vegetable oils (Table 3). Direct combustion involves the employment of a wide variety of systems, including the most common pile burners, stocker (or grate-fired) combustors, and fluidized-bed combustors. Gasification involves the partial oxidation of the biomass in order to convert it into a gaseous fuel. Pyrolysis is the thermal destructive distillation of biomass in the near absence of oxygen at a temperature of around 500^0C, and yields charcoal. Conventional slow pyrolysis is commonly applied for the production of charcoal, with a huge conversion-efficiency range. Liquefaction is a low-temperature, high-pressure thermochemical process using a catalyst. Hydrothermal upgrading converts biomass, at a high pressure and moderate temperatures, in water, to biocrude, and it is still in a pre-pilot-plant phase. Another approach is to develop a technology or process that works universally for all feedstock, converting carbon-based feedstock into hydrogen (H_2) and carbon monoxide (CO) and remaining components. This could use coal or natural gas and turn it into liquid fuels combining microbes that turn the 'synthesis gas – syngas' (a CO/H_2 mixture from gasified biomass) straight into ethanol. Fermentation is an anaerobic process by which yeast converts sugars, such as glucose, fructose and sucrose, into ethanol and carbon dioxide (CO_2). The anaerobic digestion process consists of three steps: a hydrolysis step in which organic compounds, such as polysaccharides, proteins, and fat are hydrolyzed by extracellular enzymes; an acidification step in which the products of the hydrolysis are converted into H_2, formate, acetate and higher molecular weight volatile fatty acids; and a third step in which biogas, a mixture of CO_2 and methane (CH_4), is produced from H_2, formate, and acetate. The complete methanogenic conversion occurs by mixed microbiological communities yielding CH_4 as the sole reduced organic compound. Only bioethanol and biodiesel are presently produced as fuel on an industrial scale. Including ethyl-tertio-butyl-ether (ETBE) partially made with bioethanol, these fuels make up more than 90% of the biofuel market.[39]

Production of bioethanol

There are various available technologies to produce bioethanol from lignocellulosic feedstock (Fig. 1), some of them are

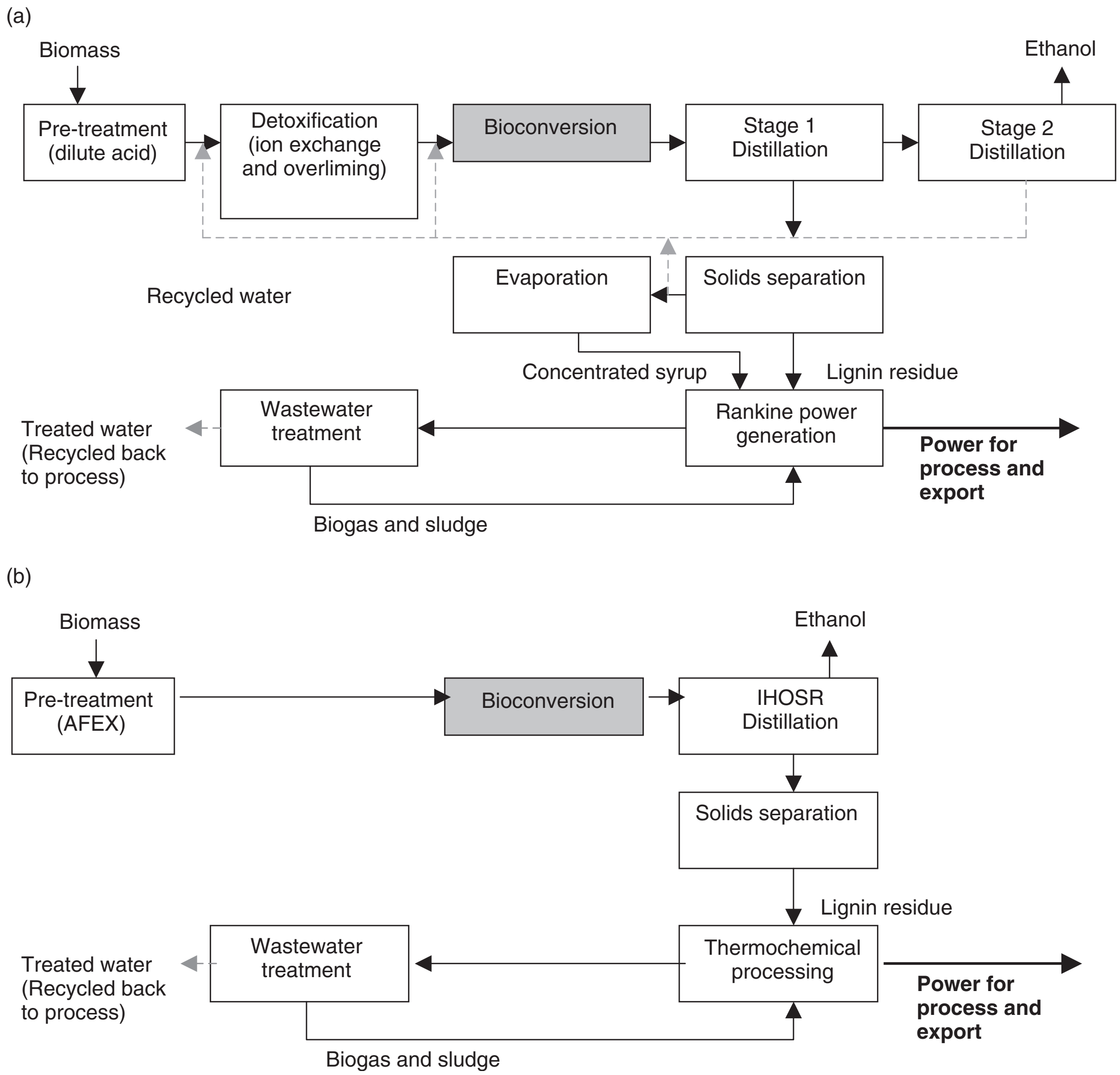

Figure 1. Biofuel production processes with (a) and without (b) detoxification steps. Note: AFEX, ammonia fiber expansion; IHOSR, intermediate via heat pump and optimal sidestream return. Adapted from Lynd *et al*.[6]

currently used by companies (Table 4). Yeast fermentation of free sugars (e.g., glucose) is the easiest and most efficient way to produce bioethanol.[39] Enzymatic hydrolysis followed by yeast fermentation presents low efficiency but can be applied to multiple substrate feedstock types, which may be necessary to achieve the desirable large-scale bioethanol production.[17,40] The production of bioethanol by fermentation of syngas is also possible.[39] Process studies have been reported to define more specific technical opportunities to lower bioethanol production costs and estimate the resulting cost of the production.[6, 21] Previous research on bioethanol production has focused on the development of pre-treatment technologies and genetically engineered organism using agricultural residues and forest products.[41] Other studies have investigated the feasibility of using paper waste and garden waste to produce bioethanol.[42] Nevertheless, scarce information is available regarding the use of MSW as a waste biomass for bioethanol production.[17] With the advantages of low cost and large quantity, MSW feedstock is very likely to become more economically attractive, and thus more research needs to be done to optimize bioethanol processes and technologies for the conversion of MSW to bioethanol production. Previous research into bioconversion of lignocellulosic materials (i.e., agricultural residues, woods,

Table 4. Technologies used to produced bioethanol from lignocellulosic feedstocks.

Feedstocks	Technology	Company, location
Corn stover, wheatstraw, milo stubble, switchgrass	Enzymatic hydrolysis; fermentation; thermochemical	Abengoa, Madrid
Wood, citrus waste, urban green waste	Thermochemical; gasification; fermentation	ALICO, Florida
Urban green waste, wood chips, car tyres, plastics	Thermochemical; gasification; fermentation	Bioengineering Resources, Arkansas
Wood construction waste	Enzymatic hydrolysis; fermentation (Klebsiella oxytoca and *Escherichia coli*)	Bioethanol Japan, Osaka
Hay, grass, manure fibers, straw, paper	Enzymatic hydrolysis; fermentation	Biogasol, Lyngby
Urban trash, rice and wheatstraw, wood waste	Concentrated acid hydrolysis, fermentation	BlueFire Ethanol, Irvine
Corn stover	Enzymatic hydrolysis; fermentation	China Resources Alcohol Coorporation, ZhaoDong City
Cellulosic biomass	Gasification	CHOREN
Sugarcane bagasse	Thermochemical; gasification; modified Fischer-Tropsch	ClearFuels Technology, Hawai
Waste ricestraw, rice hulls	Enzymatic hydrolysis; fermentation	Colusa Biomass Energy, California
Spent pulping liquor	Alcohol sulfite cooking liquor to fractionate softwood chips; fermentation	Flambeau River Biorefinery, Wisconsis
Wheatstraw, barleystraw, corn stover switchgrass, ricestraw	Enzymatic hydrolysis; fermentation (Trichoderma reesei)	Iogen, Otawa
Wood chips, corn stover, switchgrass	Enzymatic hydrolysis; fermentation	Lignol Innovations, Burnaby
Switchgrass, wood	Enzymatic hydrolysis; fermentation (Thermoanaerobacterium saccharolyticum)	Mascoma, Cambridge, Massachusetts
Corn fiber, corn cobs	Enzymatic hydrolysis; fermentation	Poet/DuPont, Delaware
Wood and vegetative wastes	Thermochemical	RangeFuels
Paper	Gasification	UPM, Findland
Sugarcane bagasse, wood	Enzymatic hydrolysis; fermentation	Verenium, Cambridge, Massachusetts

Source: Adapted from Bartacek *et al.*[8]

residues from pulp and paper industry, urban lignocellulosic wastes) to bioethanol in the last two decades due to its large availability and immense potential. Pre-hydrolysis treatment and enzymatic hydrolysis of MSW are of crucial importance during the bioconversion of MSW to bioethanol, and thus their optimization will result in beneficial environmental and economic practices.[41,43] For that purpose, physical, physicochemical, chemical and biological pre-treatment processes have been applied to several cellulosic materials to enhance their enzymatic digestibility.[44] The combination of dilute strong acid and steam treatment using different fractions of MSW to produce bioethanol is feasible.[17, 45, 46] In a low-cost, pre-treatment process – the MixAlco process[47] – the biomass is first pre-treated with lime, and then a mixed culture of acid-forming anaerobic micro-organisms produces carboxylate salts, which are subsequently concentrated and thermally converted to mixed ketones and finally hydrogenated to mixed alcohols. The advantages of this process include that it does not require the use of a sterile environment or the need for enzyme addition, but requires long residence times (one month).[47] Another process consists of simultaneous hydrolysis and fermentation in the same reactor, which has attracted more and more researchers, because it can reduce the capital cost by reducing the number of reactors, limiting the mid-product inhibition, and shortening the residence time. However, since the enzyme and yeast have different optimal temperature ranges (45–50^{0}C and 30–35^{0}C, respectively), it is difficult to find a best temperature for both using simultaneous hydrolysis/fermentation process. Another promising pre-treatment technology is ammonia fiber expansion (APEX), which reduces the production of inhibitory compounds and nutrient addition due to ammonia, and no liquid stream is produced after pre-treatment.[48] A different process consists of the fermentation of syngas to bioethanol based on *Clostridium ljungdahlii*, and has already been developed at industrial scale.[39] During this process, MSW is gasified and cooled down to fermentation temperature (while using the waste heat to produce electricity) and is blown into the fermenter. The bioethanol produced by the organisms is then separated by distillation.

Production of biodiesel

Biodiesel is a monoalkyl ester of fatty acids from vegetable oil and is presently produced by catalytic transesterification with petrochemically derived methanol and a catalyst.[39] Other ways of modifying vegetable oils and fats to use them as biodiesel, such as pyrolysis, dilution with hydrocarbons and emulsification, have been considered.[49] A non-catalytic supercritical methanol method that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids, and requires lower reaction time and lower energy use has also been developed to produce biodiesel.[49,50] At present the microbiology of biodiesel degradation is a concern because of bacterial oxidation during storage as well as the unavoidable water content leading to corrosion problems. Furthermore, the glycerol produced during transesterification creates a deposit problem in some areas.[39] Microdiesel may be a potential future fuel completely produced by engineered *Escherichia coli*.[51] Nevertheless, the technology of microbial contribution to the production of biodiesel is almost nil at present, and the use of enzymes of biological systems in transesterification is yet to be developed.[39]

Nevertheless, the German firm, Choren Industries, is focused on gasifying woody biomass to yield biodiesel. The company's two-stage gasification scheme converts the biomass into coke and then synthesis gas. A Shell-developed Fisher-Tropsch process uses a cobalt catalyst to convert the gas into a paraffinic wax, which is cracked to yield biodiesel and naphtha.[52]

Production of biobutanol

Compared to the traditional biofuel, ethanol, higher alcohols may offer advantages as gasoline substitutes because of their higher energy density, lower hygroscopicity, and being less volatile.[53] Since 1916, it's been known that microbes, such as *Clostridium acetobutylicum,* can ferment sugar to produce butanol, acetone and ethanol – the ABE process, exploited mainly for its acetone during the First World War. In this process, acetone was produced together with butanol and ethanol (ABE 3:6:1), although butanol had no value at the time.[54] Yet microbial breweries were discarded by the 1980s in favor of a cheaper petrochemical route, via the reaction of carbon monoxide and hydrogen with propylene.[55] Nevertheless, biobutanol has been in almost continuous production since 1916, and most of the time as a solvent as well as a basic chemical. Today, new uses of biobutanol are emerging, for example, as a diesel and kerosene replacement, and there is a great interest in bacterial butanol fermentation.[41] Nevertheless the main difficulty is that bacteria are poisoned by the butanol they produce once its concentration rises above about 2%. To overcome this difficulty, the recombinant gene technology of the butanol metabolic pathway may be used. In fact, it has recently reported that engineered *Escherichia coli* can produce C_3–C_5 alcohols from glucose, improving butanol tolerance and yield.[56,57] With engineered *Escherichia coli*, the 2-keto acid intermediates from the amino acid synthesis are diverted into alcohol production, where they are first converted to aldehydes by 2-keto acid decarboxylases and then to alcohols by alcohol dehydrogenases. The biosynthetic pathway produces 1-butanol, isobutanol, and other alcohols depending on the choice of the amino acid pathway. Then the fermentation process with *Clostridium acetobutylicum* produces 1-butanol. It has been suggested that because the amino acid biosynthetic pathway is universal, this process can be transferred to other microorganisms that degrade cellulose or fix CO_2.

Oxfordshire-based Green Biologics (GBL) has developed a superior butanol producing microbial strain using genetic engineering which can be integrated into a novel fermentation process. GBL intends to use waste plant material as the feedstock for the production of its Butafuel™ product. In the USA, Environmental Energy Inc., and Ohio State University have co-developed a process for the anaerobic fermentation of butanol using *C. tyrobutyricum* which obviates the ABE process and reportedly makes butanol production competitive with other fuels, both economically and in terms of energy production. Elsewhere, Swiss company Butalco GmbH uses a proprietary technology to modify yeasts in order to produce butanol instead of ethanol. DuPont and BP are working together to develop an advance butanol-based biofuel from sugarbeet feedstock. A butanol fuel demonstration plant is being built alongside the bioethanol plant which DuPont and BP are jointly developing with Associated British Foods.[33]

Production of biogas

Anaerobic digestion of biomass is a process that results in the cost-effective production of biogas. Biogas has been produced commercially, employing animal manure, sewage sludge and the organic fraction of MSW, in conventional anaerobic digesters or two-phase anaerobic fermentation. For example, anaerobic digestion is used to stabilize the sewage sludge and convert part of the volatile compounds into biogas. Currently, anaerobic digestion of sewage sludge is mainly applied at large and medium-sized wastewater treatment plants, and an interest is observed in small-sized plants.[58] Manure is a resource readily available in many farms but provides a limited production rate and yield of biogas and requires a high investment cost, which makes the production of biogas from manure uneconomical.[59] Thus, the production of biogas can be greatly improved by introducing energy-rich co-substrates (e.g., energy crops, green waste) to the anaerobic digester, which can result in a better environmental and economic situation.[60] In fact, it has recently been reported that maize and grass energy crops allow a net production of biogas together with a significant reduction in fossil-energy-related CO_2 emission.[59] The potential of semicontinuous mesophilic anaerobic digestion for the treatment of a mixture of organic wastes including solid slaughterhouse waste, fruit-vegetable wastes, and manure in a co-digestion process to produced biogas has recently been evaluated, and it has been reported that the digestion of mixed substrates was in general better than that of the pure substrates.[61] The production of biogas from organic fractions of MSW and an anaerobic thermophilic approach had also been investigated, and it has been reported that the nature of organic substrate has an important influence on the biodegradation process and methane yield, where food waste showed the smallest waste biodegradation and a high biogas production, and organic fraction of MSW showed the highest waste biodegradation and a low biogas production.[62]

Production of biohydrogen

Hydrogen can be produced from biomass by pyrolysis, gasification, steam gasification, steam reforming of bio-oils and enzymatic decomposition of sugars,[49] but the yield of hydrogen from biomass is relatively low, 16–18% based on dry biomass weight.[63] Fermentative H_2 production has been presented as a novel aspect of anaerobic digestion, and two main biological processes to produce biohydrogen are suggested.[7] One is dark fermentation, which is a special type of anaerobic digestion comprising only hydrolysis and acidogenesis, and leads to the production of H_2, CO_2 and some simple organic compounds. Another process to produce H_2 consists of light-driven processes (e.g., direct biophotolysis, indirect biophotolysis, and photofermentation). Direct biophotolysis uses solar energy to convert water to oxygen and hydrogen, and in indirect biophotolysis oxygen evolution and hydrogen evolution are temporally and spatially separated. During photofermentation, photosynthetic bacteria produce H_2 through the action of their nitrogenase system.[7] Systems for fermentative hydrogen production usually consists of one acidogenic reactor and one methanogenic reactor. Generally a low amount of biomass feedstock is transformed into hydrogen (5–10%), and thus the second step utilizes the remaining organic matter.[7]Completely stirred tank reactors (CSTR) are most often used due to their simplicity of building and operation.[64] Additionally, biomass immobilization is widely used for hydrogen-producing micro-organisms, such as upflow anaerobic sludge blanket (UASB).[65] Practical applications of biological H_2 production remain few, and no full-scale applications have yet been reported.[7] The low efficiency of H_2 production remains the main limiting factor, and this is why H_2 needs to be coupled with a second-step methane production. Biohydrogen can only be formed from carbohydrates, and thus an effective method to substrate pre-treatment should be developed in order to expand the number of usable substrates. The required quality of the H_2 gas produced depends on the type of utilization and gas treatment to remove mainly hydrogen sulfide, siloxanes, water, ammonia and CO_2 may involve several steps (physicochemical and biological methods).[7] Genetic modification of H_2-producing bacteria to improve its production is also under consideration. Double H_2 production rate has been obtained with modified *Escherichia coli* strain HD701 in comparison with the parent strain MC4100.[66] Additionally, a 2.8-fold higher hydrogen production rate has been obtained with modified *Escherichia coli* strain SR13.[67]

Biorefinery

There are many definitions for the biorefinery concept. In 1993, the US National Renewable Energy Laboratory, the earliest user of the term, suggested that 'In addition to fuels, a biorefinery could produce a wide range of chemicals and materials through microbial conversion of renewable resources.' Subsequent efforts to be more specific tended to focus on particular feedstocks, such as green crops or vegetable oils. Another accepted definition is that 'Biorefinery is the sustainable processing of biomass into a spectrum of marketable products.'[68] Biorefineries are only at the beginning of a developing process and their output may find competing uses as food as well as chemicals and fuels.

For example, Novamont has developed new polymeric complexing agents derived from vegetable oils and a low environmental impact route to complexing agents for starch, and may extend beyond bioplastics to the field of renewable chemical intermediates and create a fully integrated biorefinery.[68] Although there is much interest in using plant-matter as the basis for new products, feedstock security for so-called renewable raw materials remains a major issue for the big companies. Today, the best examples of biorefineries are pulp and paper mills that can produce bioethanol from forestry products. These may evolve to large, integrated chemical plants or local biofuel stations.

Local bioenergy systems

The first large-scale schemes for biofuel production began in the early 1970s; however it is only in the last five years or so that biofuels have been given notable consideration worldwide as an alternative to fossil fuels.[33] Their greatest appeal lies in their potential to reduce GHG emissions by partial replacement of oil as a transport fuel. In a global market, energy and products are transported with a consequent waste of fossil fuels and CO_2 production. It will be naïve if biomass is produced in the USA, Brazil or South Asia and then exported to the rest of the world with the consequent CO_2 release to the atmosphere when the use of biomass is implemented to reduce CO_2 release.[69]

Additionally, it is unarguable that current approaches of biofuel production results in considerable social benefits (e.g., generation of jobs), but also in some environmental and social problems, such as soil erosion, river basins contamination, air pollution, human respiratory diseases and extremely poor working conditions.[14,70,71] More sustainable approaches should consider local production of biofuels, obtained from local feedstock and adapted to the socioeconomic and environmental characteristics of the particular region where they are developed. Thus, rural areas could develop their economy through second-generation biofuel production.[20] This could mean no more subsidies for farmers in developed countries and better quality of life in developing countries because the price of their products will be more valuable at a local level. New industries should be created to transform biomass products with the resultant increment of rural jobs and independence of long-distance factories. In fact, waste to energy could be a great source of biofuels, particularly in or near urban centers where large quantities of biodegradable fractions of MSW are produced.[17]

The production of second-generation biofuels should be economical beneficial, should produce none or minimal CO_2 or GHG emissions, and should contribute to rural development and to the production of energy at a local level as well as local distribution around villages, towns, cities and countryside. Thus, a new concept of local bioenergy system (LbES), created to understand a real sustainable energy production, and based on a simple input/output balance is introduced. This concept is based on the use of currently available or improved processes and technologies to produce biofuels, even on a small scale at the site of waste origin.

Issues that need to be addressed in the local context include mainly resource availability and competing uses, and economic access, reliability and accessibility.[20] Location of demand and supply and purchasing power versus cost are key issues. In poor rural areas a key concern is the competition of biomass energy systems with present use of biomass resources in applications such as animal feed and bedding, fertilizer and construction materials. These may be a higher priority to rural populations, as alternatives may not exist. Thus a very detailed and participatory resource assessment must be done before initiating action on bioenergy systems using existing resources. Additionally, economic access by poor rural societies to different bioenergy options is a key matter. The level of trade in fuel wood is on the increase. In remote areas or on islands, where the cost of fossil fuels are usually high due to transport costs, bioenergy systems may prove to be the most economical option.

Bioenergy options such as small- and medium-scale biogas or gasifiers and power generators operating with locally available biomass sources such as vegetable oils, biogas from manure, and agricultural and forestry byproducts can become in some areas the most economical and reliable providers of energy services. Reliability, local maintenance and monitoring capacity, and accessibility of the technologies needed to make use of these resources are in many cases the key barriers.

A well-established process at waste management facilities consisting of composting the organic fractions of MSW to produce compost could be used to apply the LbES concept. Using the same infrastructure, additional processes could be implemented for bioconversion of organic fractions of MSW to biofuel. Byproducts may include a solid waste and a liquid waste which could be used in soil conditioning or further composted to obtain high-quality compost. The biofuel generated during this process can be used for running the integrated process, including the use of biofuel in the transport of waste from households to the waste management facilities. Overall, this process will help to reduce the emission of GHGs, offering a new solution for dealing with waste by providing a solution to reduce the amount of waste. In summary, in order to successfully apply the LbES concept, one should contemplate the feasibility of the use of a wide range of biomass feedstock for the sustainable production of second-generation biofuels, as compared to biomass feedstock traditionally used for first-generation biofuels. If waste is considered as biomass feedstock, there is a potential to increase feedstock sources and thus the production of second-generation biofuels. Nevertheless, there is a present need to improve and optimize current available bioconversion technologies (i.e., cellulose treatment, cellulose conversion, and hydrolysis) of second-generation biomass feedstock to sugars, toward a lower process cost. Only then will the implementation of LbES allow the partial substitution of fossil fuels by second-generation biofuels.

Summary

The potential for second-generation biofuels to overcome some of the problems associated with the existing industry is only gradually being understood. There is no simple clear-cut transition from first- to second-generation biofuels in terms of feedstock or production process. In economic terms, some of the traditional technologies, such as fermenting of sugarcane, will stay competitive for many years. Enhancements to traditional feedstocks are likely to change the cost effectiveness and carbon footprint of crops such as corn. Meanwhile, ethanol has become a highly political subject in some countries (e.g., USA). Large multinationals in industry sectors ranging from agribusiness to oil are increasingly becoming active in the biofuels industry, but the issues are complex. The solutions are likely to come from a combination of small companies with innovative technologies and the incumbent players. Only then will the implementation of LbES allow the partial substitution of fossil fuels by second-generation biofuels. What is clear is that the potential for biofuels to contribute to the solution to energy and climate change issues should not be underestimated.

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