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Biorefineries: converting biomass into valuable products

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Biotechnology was the first technology to produce chemicals, fuels and other industrial products. Goods were produced on a large scale based on biomass as early as the 19th century. Early industrial products from biomass include pulp and paper production from wood, nitration of cellulose from guncotton and viscose silk, soluble cellulose for fibers, production of furfural for nylon and production of acetate, lactic acid, citric acid and ethanol. Later, fossil fuels set the progress of biomass-based production of industrial products on standby.

There is general concern about the current fossil-fuel system, which is largely based on finite resources that are not sustainable. In addition, the political volatility of many oil-producing countries and the rapid fluctuation of the fuel market are encouraging governments to plan long term to decouple from dependence on fossil fuels. Concern about the instability of fossil-fuel supply, limits on fossil-fuel reserves and especially environmental concerns have brought new focus on white biotechnology. White (or green) biotechnology uses biomass as feedstock instead of fossil fuels for production by biological conversion processes, bio-based fuels, chemicals, solvents etc. Using biomass as a raw material instead of fossil fuel has the advantage of working in a closed sustainable carbon cycle, in contrast to the open cycle of using fossil fuel with net release of greenhouse gases to the atmosphere (Fig. 8.1).

Numerous compounds can be produced from biomass, although only a few can be produced economically compared with present fossil fuel–based technology. Besides the interest in new chemicals, a strong interest in producing biofuels and bioenergy has brought biotechnology into focus.

Biomass

Globally, biomass resources are mainly from wood and agricultural products and waste. Agricultural residue mainly comprises lignocellulosic biomass. Lignocellulose is the term for the structural parts of plants. It consists of cellulose, hemicellulose and lignin. Cellulose is an organic polysaccharide of glucose and can be broken down by enzymes (cellulases and glucosidases), although the process is slow. Hemicellulose is a heteropolysaccharide containing mainly C-5 sugars such as xylose and arabinose and the C-6 sugar mannose. The composition of hemicellulose varies between plant species. Lignin is a term for amorphous, three-dimensional polymers that have a phenylpropane structure. Lignin is very resistant to degradation and can be used for combustion if it can be separated in dried form since it has a high heat value.

Many biofuels are derived from sugar cane, corn and wheat. Cereal straw represents the largest biomass resource from agriculture in Denmark (5.2 million tons in 2006): 26% is directly burned for household heating and in power plants, 19% for fodder and 12% for bedding; the remainder (43%) is plowed in. Other major resources in Denmark

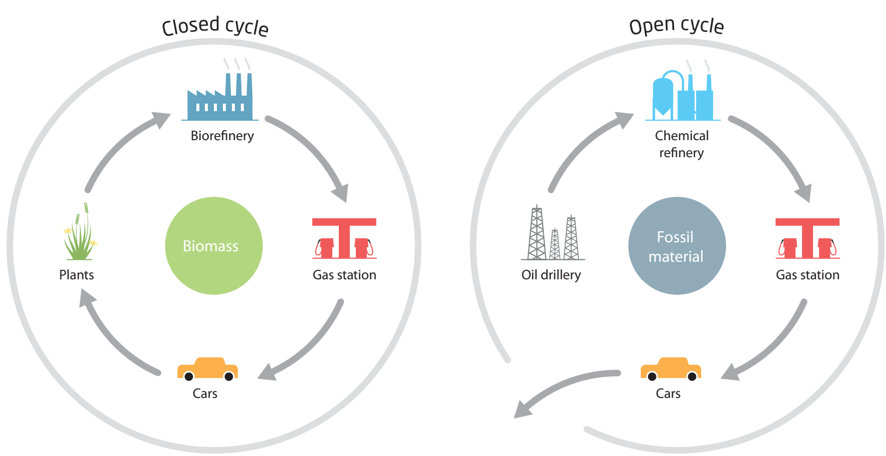

Fig. 8.1. The closed carbon cycle using biomass as raw material for fuels, chemicals and energy in contrast to using fossil fuel as raw material and releasing net carbon

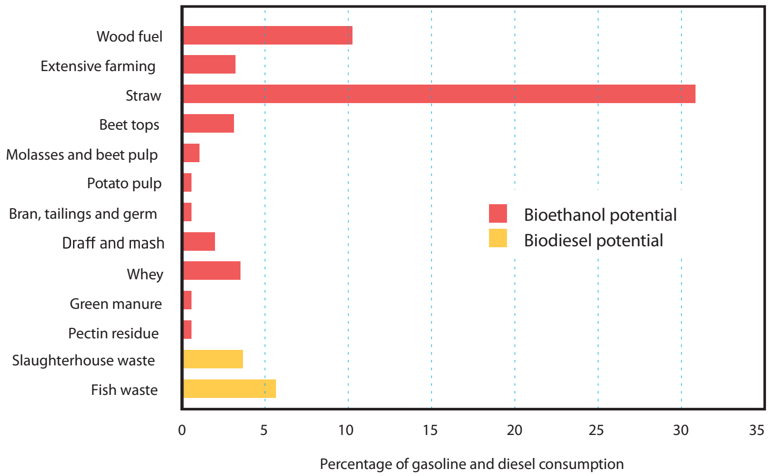

Fig. 8.2. Potential for converting biomass to transport fuels in Denmark. Both C-6 and C-5 sugars are presumed to be converted to bioethanol (source: Blume et al., 2008).

include wood, manure and organic waste from industry and households. In addition, extensive grasslands and dedicated energy crops could be considered if they can serve other additional ecosystem purposes such as landscape management, groundwater protection, biodiversity and carbon sequestration and preventing nutrient leaching. A recent report shows that converting straw from Denmark's agricultural sector into bioethanol can cover up to 30% of the existing fossil fuel consumed in transport (Fig. 8.2). Wood resources can contribute 10% and various types of waste biomass an additional 6%. Fish and slaughterhouse waste can cover up to 9% of current diesel consumption. However, if such extensive resources are used, this might have other effects on agricultural ecosystems, such as reducing soil carbon stocks and soil fertility and influencing biodiversity.

Biorefineries

A biorefinery integrates biomass conversion processes to produce fuels, electrical power and chemicals from biomass. By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock according to the market situation and biomass availability. The bulk of the products are biofuels and bioenergy, and chemicals are produced in smaller amounts. Although the amounts of other products are small, they often have much higher specific value.

Biorefinery systems and design

Biomass is complex. Plant biomass consists of the basic products carbohydrate, lignin, protein and fat and a variety of substances such as vitamins, dyes, flavors and aromatic compounds.

Many biorefinery concepts have emerged in recent years based on different feedstocks or/and different processes and products.

Four main types of biorefinery systems have been defined recently:

- lignocellulosic biorefineries, based on wood and straw;
- whole-crop biorefineries, based on such raw materials as grain and maize (whole crop);
- green biorefineries, based on grasses;
- two-platform biorefineries, with sugar and syngas (synthesis gas) platforms; and
- oily-crop biorefineries based on whole-crop utilization of oily crops.

Many of the proposed biorefinery systems focus on producing fuels for transport. However, new ideas are emerging continually, such as biorefineries based on cultivating algae, especially after the ethical quandaries of using agricultural soil for producing biofuels have emerged.

Achieving a high degree of advanced processing is theoretically possible technically. Technical, socioeconomic, political and environmental interaction plays an important role in developing biorefineries (Fig. 8.3).

Economics is often the most important factor determining the application of the technology. However, political decisions and priorities can

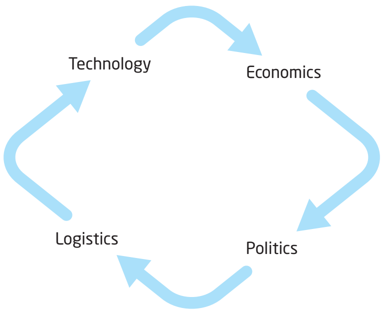

Fig. 8.3

often motivate development, which results in technologies that are more advanced and price reductions. Logistical issues and infrastructure are also important factors and depend on medium- to long-term political strategic planning.

Biorefineries based on oily crops

Significant investment has been made in the biodiesel sector in recent years. The European Union has become the world leader in biodiesel production, and demand for biodiesel fuel for cars is increasing. However, producing biodiesel competitively and sustainably is difficult. The Rapeseed Biorefinery (a project coordinated by DTU with the participation of the University of Southern Denmark, Faculty of Life Sciences of the University of Copenhagen, Aarhus University, Novozymes A/S and Emmelev Mølle A/S) will utilize the whole crop of rapeseed biomass (in contrast to the seeds only, which is the practice today) by combining seed and straw processing. Besides food and animal feed, the rapeseed biorefinery can produce a multitude of biofuels, bioenergy, fertilizers and high-value chemicals (Fig. 8.4).

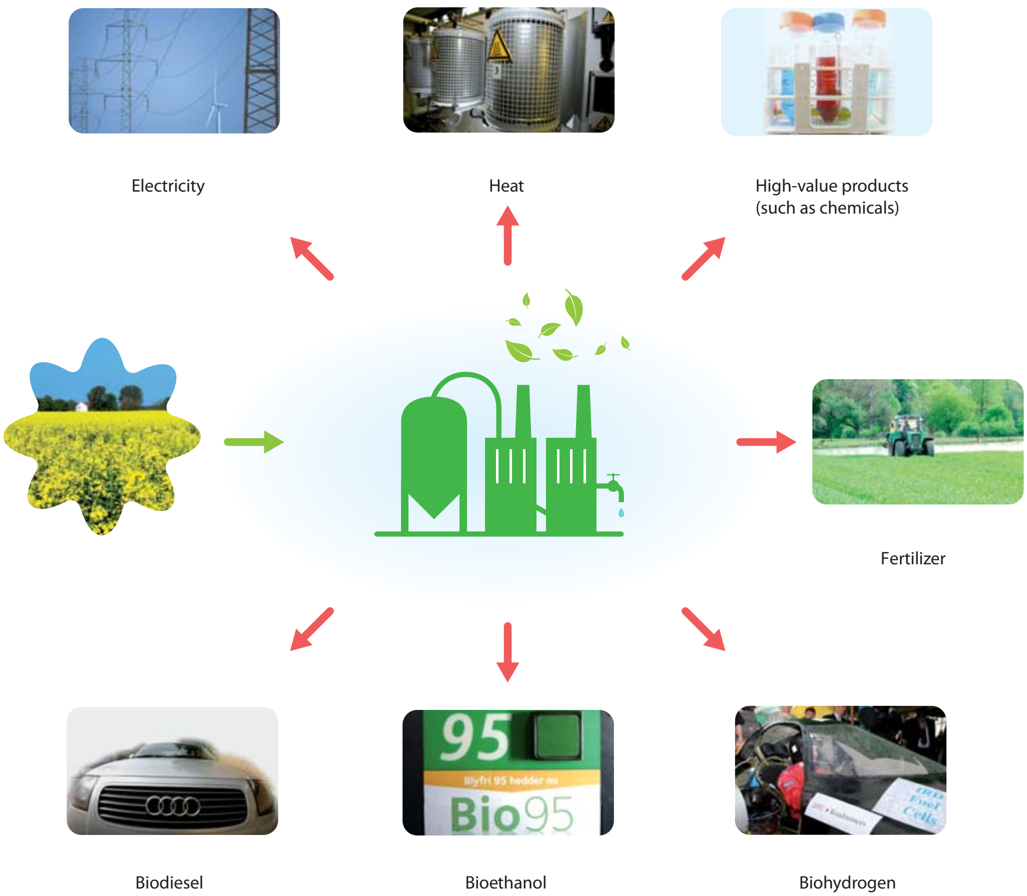

Fig. 8.4. The DTU rapeseed biorefinery

The rapeseed plant is divided into two streams: the seeds and the straw.

The seeds are treated by an innovative enzymatic process (hemicellulase), resulting in four fractions (hulls, oil, sugar and protein). Biodiesel is produced from the oil fraction by transesterification with methanol. High-value chemicals (phospholipids, tocopherols, sterols, dicarboxylic acids and epoxidized oleochemicals) are also derived. The glycerol released in biodiesel production as a byproduct can also be used for producing high-value-added products. Alternatively, extremely thermophilic microorganisms can be used to convert glycerol to ethanol or butanol.

High-value products such as antioxidants, glucosinolates, anticancer pharmaceuticals and high-quality protein rich in lysine and methionine can be recovered from the other parts (hulls, syrup and protein).

From straw, hexoses can be converted to bioethanol by yeast and pentoses can be converted to biohydrogen. Alternatively, pentoses can be converted to bioethanol by extremely thermophilic bacteria. The effluents from different processes will be treated anaerobically to stabilize them and to produce methane. Finally, the treated effluents will be used as biofertilizer.

By using the whole rapeseed crop (seeds and straw), energy production will increase from 28% of the total plant energy content (by using the seeds only) to 49% (by using the whole crop producing second-generation biofuels) along with the production of high-value-added products and biofertilizer.

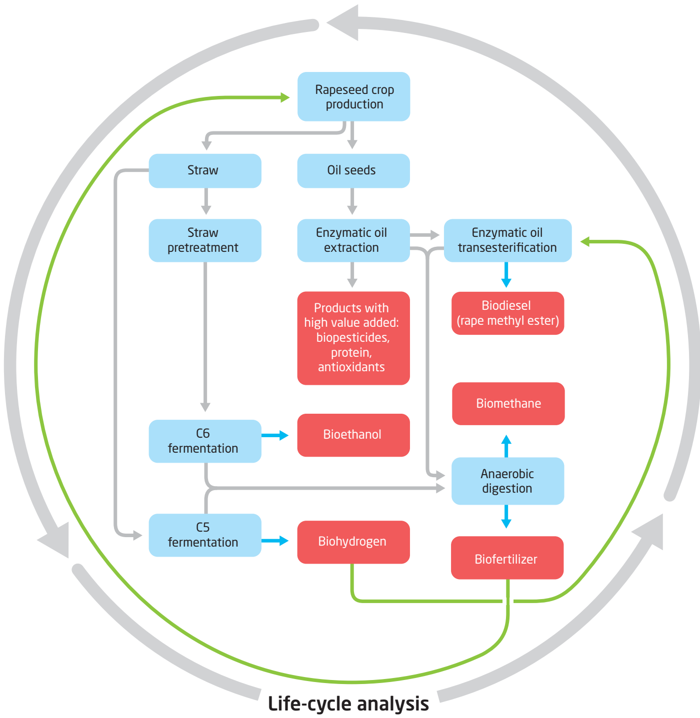

Fig. 8.5. The DTU rapeseed biorefinery concept

Converting lignocellulosic matter to bioethanol

Diesel and gasoline constitute the main fuels used for transport. The world's main oil reserves are found in a small part of the world, mainly in Middle Eastern countries, which reduces the security of energy supply for many other countries. Domestic production of fuels, such as bioethanol, reduces dependence on oil-producing countries. In addition, oil reserves are limited and alternative renewable energy sources are therefore required eventually. Environmental awareness and the threatening climate change have resulted in extreme interest in biofuels. Finally, bioethanol is a renewable energy source that can be directly implemented in the established transport systems as an additive to gasoline.

The use of ethanol for road vehicles is not new. Already in 1908, Henry Ford used ethanol to run his motor vehicle, believing it would be the fuel of the future. Ethanol later proved not to be economically competitive with fossil oil as this sector matured and more-abundant resources were identified.

Mature technologies for bioethanol production are based on using substrates such as sugar cane juice or cornstarch. These are also called first-generation technologies. Since the cost of raw materials can exceed 50% of the cost of bioethanol production, and because of the recent competition between producing food or biofuel on scarce land, recent efforts have focused on using lignocellulosic biomass.

Lignocellulosic biomass is the most abundant type of biomass on earth. Large amounts of lignocellulosic biomass are wasted today as agricultural residue, such as corn or rice stover, biofiber,

Fig. 8.6. Process steps for producing bioethanol from lignocellulosic biomass

woodchips, waste etc. However, in contrast to the established first-generation technology, technologies for lignocellulosic ethanol production (also called second-generation technologies) have not yet been fully developed. The first-generation technologies mainly include fermentation and distillation, whereas new process steps are needed for the second generation (Fig. 8.6).

Fig. 8.7. summarizes the main differences between first- and second-generation ethanol production.

Although using lignocellulosic biomass for producing biofuels has obvious advantages, the process is also facing significant challenges that need to be addressed to enable second-generation bioethanol production:

- biomass pretreatment;
- new effective enzymes are needed;
- utilization of the hemicellulose part of the sugar (mainly consisting of pentoses); and
- disposal of effluents.

Pretreatment and enzymatic hydrolysis

Since the cellulose and hemicellulose are embedded in lignin, a pretreatment step is necessary before the polymers can be broken down to simple sugar by enzymes for subsequent fermentation. Several techniques have been developed for this purpose, including acid and alkaline hydrolysis and elevated temperature and pressure. One of these techniques, wet oxidation (high temperature and pressure with added oxygen) was originally developed within the Risø DTU National Laboratory for Sustainable Energy for extracting uranium from ore from Kvanefjeldet in Greenland. This technique also turned out to be able to break down complex organic compounds and was therefore exploited for pretreating straw. The technique is, however, quite energy-intensive and thus expensive. Other techniques such as wet explosion and treatment with hydrogen peroxide are more aggressive and more expensive. In practice, a simpler hydrothermal solution seems to be more feasible,

Fig. 8.7. Main differences between first- and second-generation ethanol production

such as that DONG Energy developed in the EU-funded IBUS (Integrated Biomass Utilization System) project. The biomass is generally heated to 150–200°C during the pretreatment step. Another important part of the pretreatment is to separate lignin from cellulose, because lignin cannot be converted to ethanol.

After the pretreatment, the cellulose and hemicellulose are hydrolyzed to monosaccharides by means of enzymes. Cellulose is broken down by cellulase followed by glucosidase. Breaking down hemicellulose requires another set of enzymes including xylanase. This enzymatic hydrolysis is normally carried out at a temperature of 50°C.

Utilization of hemicellulose

Sugar is released after pretreating lignocellulosic material. Two types are released: hexoses (the main constituent of cellulose) and pentoses. Hexose can effectively be converted to bioethanol, and the process is carried out with high yield and productivity by *Saccharomyces cerevisiae* or recombinant *S. cerevisiae*. *S. cerevisiae* is by far the best-known ethanol producer today but cannot convert pentose. No effective microorganisms for the industrial conversion of pentose (the main constituent in hemicellulose) to bioethanol have been found yet, although several promising recombinant candidates for pentose fermentation have been described and presented as future solutions. Meanwhile, these organisms have not yet proven their applicability on a large scale. These organisms often have relatively low productivity, low ethanol tolerance and high sensitivity to the inhibitors present in the hydrolysate (the liquid stream of thermal pretreatment of lignocellulose biomass) from the pretreatment step.

DTU is working in several directions to find cost-effective methods of utilizing pentose. Due to the limitations in the conversion of pentose into bioethanol, an obvious solution would be to investigate alternative methods of utilization.

Conversion of pentose to ethanol

An ideal microorganism to be used as an industrial ethanol producer for second-generation ethanol production should fulfill several requirements, such as:

- fermenting essentially all the carbohydrate present in lignocellulose;
- ethanol tolerant; and
- substrate tolerant.

Many fermentative extremely thermophilic microorganisms have the capacity to produce ethanol from pentose and hexose. DTU has screened in hot springs, anaerobic digesters, sediments and other places. Several candidates have been enriched or isolated from the screening.

One very promising microorganism has been isolated from an extremely thermophilic process (70°C) operated as a continuously mixed reactor with household waste at a retention time of 1–2 days (Fig. 8.8). This organism can be directed to produce ethanol with a high yield (>70% at low pH, about 5); at higher pH, it produces more hydrogen. This possibility for manipulating the metabolic pathway of the microorganism enables products to be altered according to the market situation and the demand for specific products.

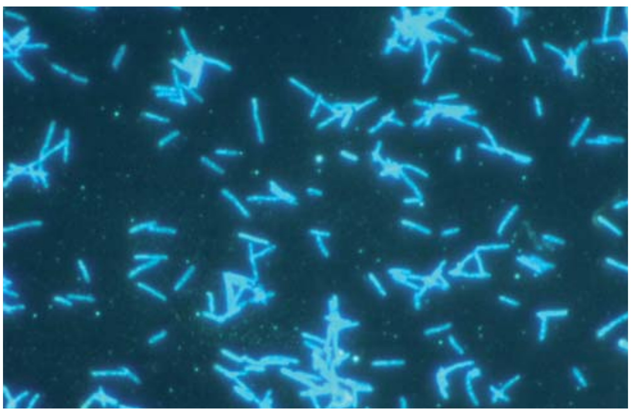

Fig. 8.8. Newly isolated organism that can convert xylose to ethanol

Converting pentose to biohydrogen

Fermentative biohydrogen production is an emerging technology and has received increasing interest in recent years as a sustainable energy source for fuel cells. The dark fermentative hydrogen process is environmentally friendly, cost-effective and sustainable. Moreover, this process is considered a promising treatment technology for organic waste and/or residue with simultaneous clean, highly efficient energy production. During the dark fermentation process, hydrogen is produced together with CO_2 in the gas phase and organic acids and solvents in the liquid phase as the end-products. Substrates that have been used for hydrogen dark fermentation are mainly carbohydrate-containing feedstock such as glucose, sucrose and starch. We have used pentose for producing biohydrogen. Cultures of extremely thermophilic bacteria have been enriched for biohydrogen production and adapted to convert hydrolysate. Hydrolysate contains most of the pentose and is a harsh environment for microbial growth because of several toxic substances formed during the thermal pretreatment process. Compounds such as furfural, hydroxymethyl-furfural and organic acids are examples. Long-term adaptation of the enriched microbial culture enabled the organic compounds in hydrolysate to be converted to hydrogen and entirely detoxified.

We have developed a two-step process in which biohydrogen is produced in a first step and methane in a subsequent step (Fig. 8.9). The process can be optimized by recycling the methane produced through the hydrogen reactor and thus reducing the hydrogen partial pressure, resulting in thermodynamically increased efficiency.

The gas mixture produced comprises CH_4 and H_2. Using this in internal combustion engines leads to many advantages in terms of combustion efficiency and engine performance due to the specific physical and chemical properties of the two fuels.

A new process was developed recently that applies a slight voltage potential in the reactor to convert the organic matter into hydrogen: electrohydrogenesis.

Biogas

The biogas process is an established technology and considered the most efficient way to convert a broad range of biomass to energy. Although biogas has mainly been used for producing electricity and heat, biogas can be upgraded for use in transport. However, infrastructure is required to use it generally in transport. Nevertheless, the biogas process is very versatile and non-selective with regard to substrate and is therefore an excellent way to remove organic matter and polish effluent streams. Codigestion of waste streams has been shown to be a way of optimizing the bio-gas process to increase substrate utilization and to decrease process inhibition. Biogas is a complex microbiological process requiring different groups of bacteria to collaborate in a balanced way for successful digestion.

Fig. 8.10 shows the anaerobic digestion process schematically.

Several groups of microorganisms are involved in the conversion process, such as hydrolytic, acidogenic and acetogenic bacteria and methanogenic Archae. Archae are distinctive from bacteria and are supposedly older evolutionary than bacteria.

We examined the distribution of Archae and

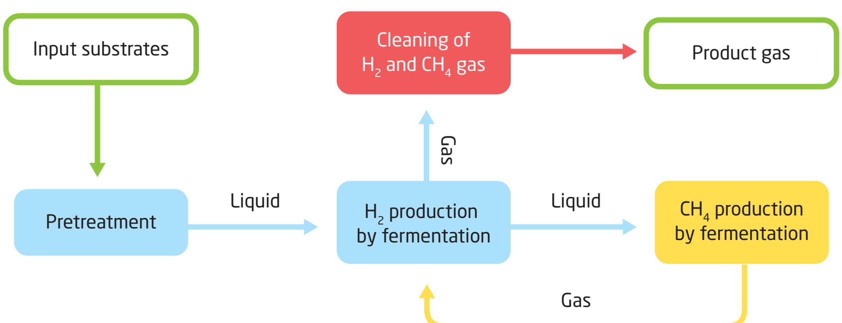

Fig. 8.9. Process for producing hythane (H_2 + CH_4 mixture)

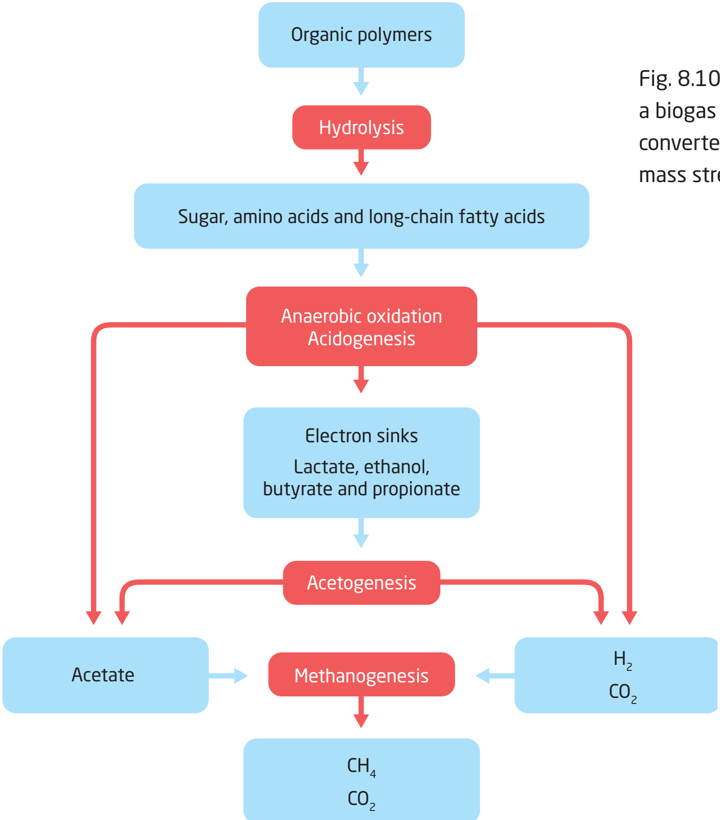

Fig. 8.10. The primary conversion processes in a biogas reactor, in which organic matter is converted to biogas, with typical relative mass streams

bacteria in biogas plants in Denmark by using specific probes targeting 16S RNA, which can produce different colors for bacteria and Archae. Fig. 8.11 shows the distribution of bacteria and Archae in the Fangel biogas plant. Understanding the factors determining the establishment of specific methanogens may enable manipulation of the microbial composition of a biogas reactor and thereby increase the efficiency of the reactors.

Sustainability of biofuels

For biofuels, the focus should be on the potential of biofuels to reduce global warming: reducing emissions of greenhouse gases (most importantly CO_2, N_2O and CH_4). Several other issues are also highly relevant such as air pollution with soot, aerosol particles, nitric oxide, carbon monoxide and ozone, which affects human health. In addition, ozone is a greenhouse gas and negatively

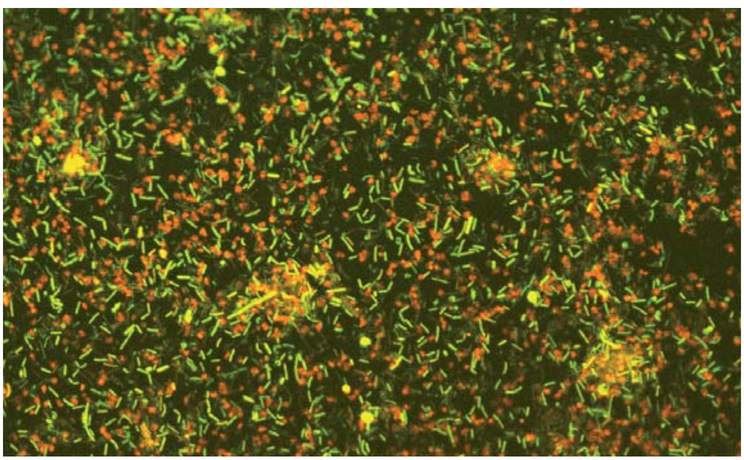

Fig. 8.11. The red microorganisms are methanogens, and the green ones are bacteria (hydrolytic, acidogenic and acetogenic)

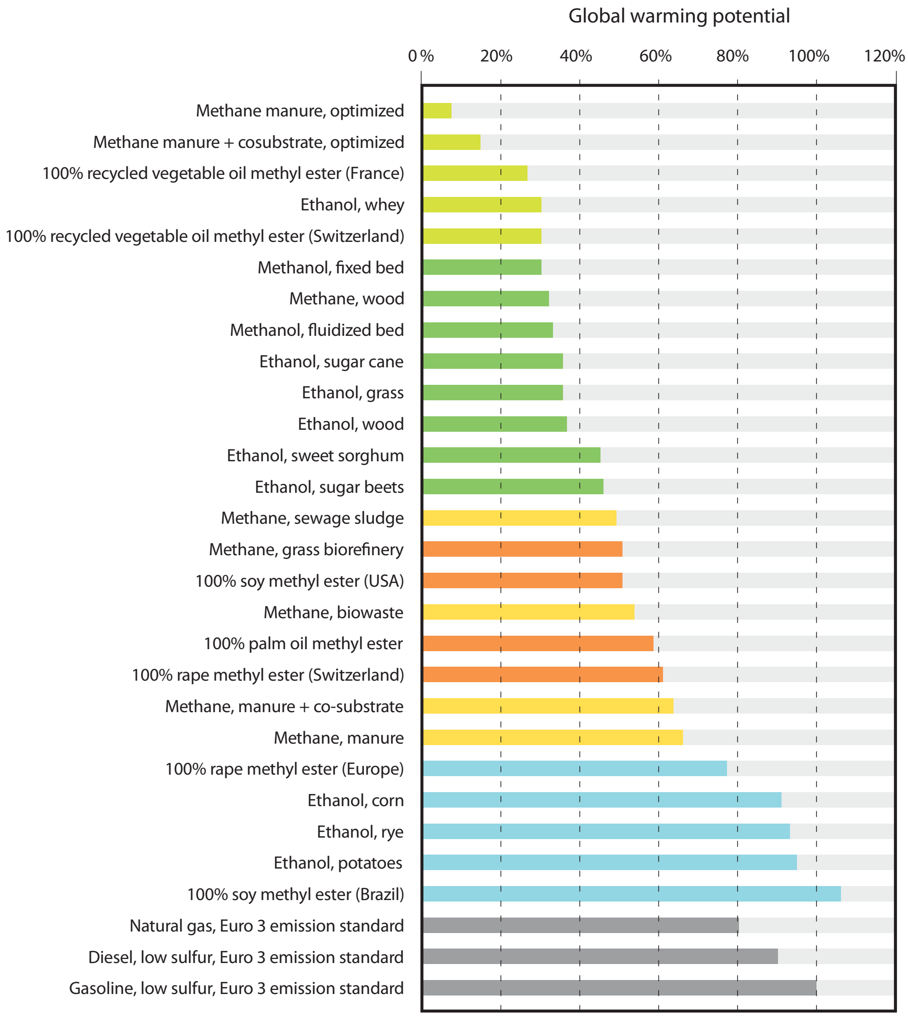

Fig. 8.12. Relative global warming potential of biofuels (source: Zah et al. 2007)

affects plant growth. The energy used to produce, handle and process the feedstock should be considered as well as the change of land use for growing fuel crops and their potential influence on food production and food prices.

Sustainability analysis is quite complicated, and comparing analyses is often difficult. An activity has therefore been started to certify biofuels using a common set of criteria.

As shown previously, a wide variety of feedstock can be used for biofuels. The task of calculating the sustainability of biofuels is not easy, and there is some controversy about exactly how much greenhouse-gas emissions are reduced depending on how many factors the analysis includes. Fig. 8.12. gives an overview of the global warming potential of various biofuels relative to gasoline. Biogas from manure has the lowest global warming potential, but lignocellulosic ethanol, which typically saves 50–80% compared with fossil fuel, is an attractive technology. Corn ethanol and biodiesel from rapeseed oil save much less, often only about 20%. However, for biodiesel only seeds were used, whereas using the whole plant can substantially change the sustainability of oil seed plants for energy production. Another benefit of bioethanol is that replacing as little as 6% of the gasoline avoids the need to add the toxic methyl tertiary-butyl ether (MBTE) to increase the octane rating.

When land-use change is considered, the greenhouse-gas balance might become negative. A recent study comparing energy solutions for transport concluded that the highest-ranking solutions were wind-powered battery-electric or hydrogen fuel cell vehicles. The lowest-ranking solutions were corn and lignocellulosic ethanol. It was even concluded that they may actually worsen climate and air pollution. The main reasons for this are that, despite the relatively high overall greenhouse-gas savings, there are other environmental issues, especially for lignocellulosic ethanol, which requires a large land footprint and results in high air pollution, increasing mortality rates.

The use of biomass for biofuels should therefore be considered carefully, and biorefineries should be justified not solely on their biofuel production but also on the production of high-value products that can substitute for fossil fuel.

More to explore

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