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# **Introductory Chapter: Prospective Biofuels**

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Krzysztof Biernat

Additional information is available at the end of the chapter

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## **1. Introduction**

The development and modifications of the drives of modern engines therefore require appropriate fuels for these drives, so that the main requirements set out above are met. These requirements are defined by engineers and vehicle manufacturers, while guaranteeing the durability and reliability of engines powered by appropriate fuels. To ensure the correct quality of fuels for spark-ignition and self-ignition engines meeting the requirements of internal combustion engines and environmental protection, leading global car concerns have established World-Wide Fuel Charter (WWFC) [1, 2]. Due to the increasingly stringent environmental requirements, the fifth edition of the WWFC was introduced, which introduced, in addition to the current four, additional, fifth categories of both motor gasolines and diesel oils. In the fifth edition of the WWFC, in the same way for all five motor gasolines categories, it is permissible to add up to 10% (v/v) of ethanol, with the ban on methanol being sustained, and for diesel oils, the permissible addition of up to 5% (v/v) FAME to fuels in categories 1–4, while in the top category 5, the content of this biocomponent is not allowed. In Category 5 of diesel oils, it is permissible to use other biocomponents originating from “hydrotreated vegetable oil” (HVO) and “biomass to liquid” (BtL) processes, provided that the resulting mixture meets all normative requirements for conventional diesel fuels.

## **2. Types of biofuels**

It is anticipated that the prospective raw materials for the production of biofuels will be all waste substances (biodegradable at the beginning), including waste biomass (lignocellulosic feedstock) and in the long-term waste carbon dioxide, and even water vapor. Due to environmental conditions, we should carefully approach energy crops as a raw material.

The modern state of knowledge defines as relatively safe crops (cultivations) of *Jatropha*, *Arnica*, halophytes, and algae, which can be raw materials for biofuels. The need to look for new raw materials necessary for the production of biofuels (as well as bioliquids—energy carriers for industrial applications) is particularly important in European countries. In these countries, the need to introduce biofuels has been legally sanctioned, and at the same time, there has been a development of waste biomass recycling technology. Taking into account significant environmental conditions, limiting the use of all biomass for industrial purposes, it is necessary, especially in European countries, to import biofuels and raw materials for their production.

From many tests, including engine tests, it is clear that use as additives (first-generation biocomponents) is not beneficial for the operation of combustion engines, and fuels with biocomponents cannot be practically stored, and in some cases, the use of biofuels. The first generation not only does not close the balance of carbon dioxide, but unfortunately it is characterized by the positive emissivity of this gas. In addition, the use of food for energy purposes is considered to be unethical (“food competition”), and in turn, energy crops can cause disturbances in “biodiversity” and the occurrence of scarcity of land for cultivation for the agri-food industry, the so-called “land hunger” (“ground competition”). Therefore, it should be considered technical, operational, and environmental, as the right way to replace first-generation biofuels with second-generation and higher-generation biofuels [3–7].

In the second generation of biofuels, as before, the following fuels are located:

- bioethanol, biobutanol, and mixtures of higher alcohols and their derivatives obtained as a result of advanced processes of hydrolysis and fermentation of lignocellulose derived from biomass (excluding raw materials for food);
- synthetic biofuels that are products of biomass processing through gasification and appropriate synthesis for liquid fuel components in BtL processes and resulting from the processing of biodegradable industrial and municipal waste, including carbon dioxide in WtL processes;
- fuels for self-ignition engines derived from the processing of lignocellulose from biomass in Fischer-Tropsch processes, including synthetic biodiesel derived from the composition of lignocellulosic products;
- biomethanol obtained as a result of lignocellulose transformation processes, including Fischer-Tropsch synthesis and also using waste carbon dioxide;
- biodimethylether (bio-DME) obtained in thermochemical processes of biomass processing, including biomethanol, biogas, and synthesis gases being derivatives of biomass transformation processes;
- biodiesel, as a biofuel or fuel component for self-ignition engines obtained as a result of hydrogen refining (hydrogenation) of waste, derived from waste vegetable oils and animal fats;
- biodimethylfuran (bio-DMF) derived from sugar processing processes, including cellulose in thermo- and biochemical processes, derived from the processing of waste raw materials;

- biogas as synthetically produced natural gas—biomethane (SNG), obtained as a result of lignocellulose gasification processes, and appropriate synthesis as a result of agricultural biogas, landfill, and sewage sludge treatment processes [8];
- biohydrogen obtained as a result of gasification of lignocellulose and synthesis of gasification products or as a result of biochemical processes.

As part of the developed documents characterizing further perspectives in the development of biofuels, it was also proposed to separate the next generation of biofuels, i.e., the third one, which would contain biofuels obtained from genetically modified biomass, in order to facilitate conversion processes with known technologies. The fourth category would include biofuels produced from biomass, whose genetic modification would additionally increase the absorptivity of carbon dioxide in the photosynthesis process. In the available literature, biofuels obtained from algae are very often included in the third generation of biofuels. It is definitely not correct, because the division of biofuels into the third and fourth generation has been clearly defined by the former Directorate General for Energy and Transport of the European Commission [9]. Based on previous experience, it turned out that there is a need to develop more efficient ways to obtain biofuels, which resulted in the separation of third-generation biofuels, obtained by similar methods as second-generation fuels, but from a properly modified raw material. The raw material for the production of third-generation biofuels should be made of biomass, modified at the stage of cultivation, among others by means of molecular biological techniques. The purpose of these modifications is to improve the conversion of biomass to biofuels by, for example, growing trees with low lignin content, growing crops with enzymes built in. Biofuels that are completely obtained by biochemical methods such as biohydrogen, biomethanol, or biobutanol can also be included in this generation of biofuels.

A prospective fourth generation of biofuels has been separated due to the need to close the carbon dioxide balance or to eliminate its impact on the environment. Therefore, the fourth-generation biofuel technologies should take into account carbon capture and storage (CCS) processes, i.e., carbon capture and storage at the stage of raw materials and production technologies of these biofuels. So, raw materials for the production of biofuels of this generation can be plants with increased, even genetically assimilated,  $\text{CO}_2$  during cultivation, and the technologies used must take into account the uptake of carbon dioxide in appropriate geological formations by bringing to the carbonate stage or storage in oil and gas workings. To avoid creating further divisions of biofuels that may arise in the future, the International Energy Agency proposes to group these fuels as conventional (“conventional biofuels”) and future-oriented (“advanced biofuels”). The proposed division of biofuels by IEA is increasingly used.

### 3. Perspective biofuels

Research into the processes of obtaining substitutes for previously used fuels, referred to as “alternative fuels” for motor gasolines, diesel fuels, and even aviation fuels is being conducted intensively in the world. An alternative gas fuel for SI engines is already manufactured in

the world, DME (dimethylether) or bio-DME, where DME can be produced from coal, and bio-DME from lignocellulosic biomass, and even from waste substances. Biofuels should also be included in the group of alternative fuels. It is planned to purify biogas to almost pure biomethane and compress it to form gaseous fuel with similar qualitative characteristics as compressed natural gas (CNG). In the field of liquid fuels, technologies for the production of second-generation bioethanol from lignocelluloses (waste biomass or specific energy crops) or from waste substances are being implemented. Also tested is biobutanol from fermentation processes and DMF (dimethylfuran) obtained from cellulose and starch, also considered solar fuels, obtained in the processes of thermal decomposition of biomass or waste. The processes of converting biomass into liquid fuels are referred to as “biomass to liquid” processes (BtL), and obtained from waste—“waste to liquid” processes (WtL). Alternative fuels are also considered, being properly composed mixtures of synthetic hydrocarbons obtained from various raw materials—so-called XtL processes. A prospective raw material may be synthesis gas obtained from very different thermal and thermocatalytic processes of waste substances, including biomass and energy crops, and also, what is new, derived from the synthesis of water vapor and carbon dioxide. Various types of hydrocarbons can be obtained from syngas whose compositions will correspond to the composition of gasolines, diesel fuels, or aviation fuels. Synthesis gas, in the light of recent studies, the results of which are already implemented on a demonstration scale, can also be subjected to a fermentation process, leading to the production of bioethanol, and hydrocarbons from C<sub>2</sub> to C<sub>5</sub>. In the perspective, hydrogen or biogas obtained from synthesis gas or other biomass transformation processes is referred to as a universal energy carrier, but it is envisaged to use it as a carrier in fuel cells (for example, supplying electric cars). The future of alternative fuels in the world up to 2050 was outlined in a document prepared by the International Energy Agency (“Technology Roadmap—Biofuels for Transport”). The document also presents the current division and prospects for the development of biofuels, as shown in **Figure 1**.

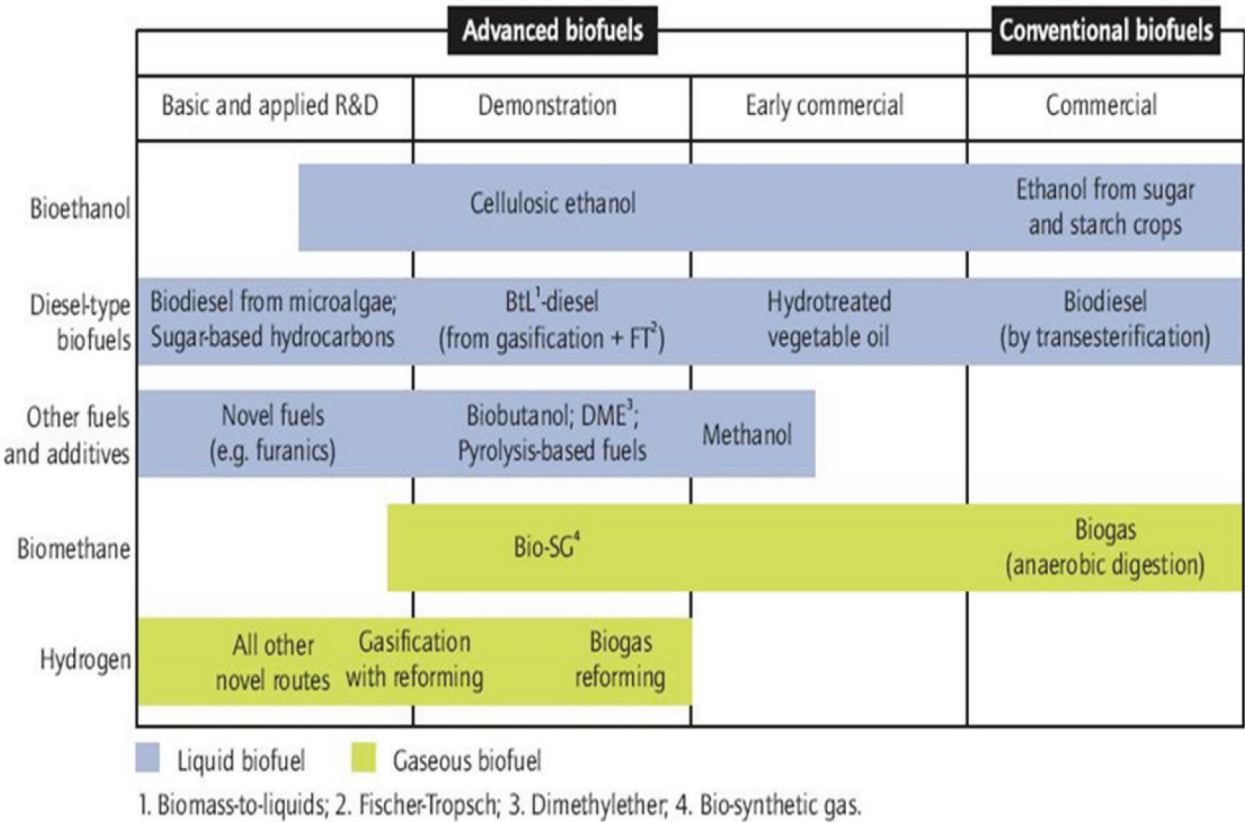
An analogous document, “Innovation Outlook: Advanced Liquid Biofuels,” was developed by the International Renewable Energy Agency (IRENA) in 2016, where the state and prospects for biofuels were also characterized with the current TRL levels. The division of biofuels according to IRENA is shown in **Figure 2**.

Therefore, taking into account environmental, operational, and logistic conditions, it is necessary to gradually pass biofuel production processes from processes using typical agro-food products to biomass, mainly waste—BtL processes, waste substances—“waste to liquid” processes (WtL), vegetable fat waste, and animal oils (frying oils), nonedible vegetable oils—HVO processes, production of biomethane from biogas using waste carbon dioxide for industrial algae breeding (microalgae). The future is the work started in the USA on the production of “solar fuels,” furan fuels, and work on the gasification of various waste substances in XtL processes, followed by the production of so-called “synthetic hydrocarbons,” i.e., biorefinery processes also in the beginning become the main European program “Bio-economy for Europe.”

Taking into account the demand for biofuels that meet the requirements of future sources of propulsion for means of transport, including air transport, as well as limiting carbon dioxide emissions, in terms of future fuels, the following biofuels will be preferred along with the technological paths of their production [1, 3–7]:



- **Fuels from BtL processes** (synthetic hydrocarbon compositions), obtained by rapid pyrolysis, biomass heating to a temperature between 400 and 600°C, followed by rapid cooling, whereby unstable compounds can be converted into liquids (HTU process) as a fuel HTU-diesel or deoxidized (HDO process), distilled, and refined for fuel compositions. The remainder of the so-called bio-char (charcoal) as a by-product can be used as a solid fuel, or used as a means for carbon sequestration and soil fertilization;
- **Diesel oil from processes BtL**, so-called FT-diesel, obtained by conversion to synthesis gas and catalytic Fischer-Tropsch synthesis (FT) in a wide range of liquid hydrocarbons, including synthetic diesel and JET biofuels;
- **Hydrotreated vegetable oil (HVO)** as fuel for self-ignition engines or fuel oil produced by hydrogenation of vegetable oils or animal fats (nonfood and waste). The first large plants were launched in Finland and Singapore, but the processes have not yet been fully commercialized;
- **Cellulosic bioethanol** produced from lignocellulosic raw materials by biochemical conversion of cellulose and hemicellulose leading to the fermentation of sugars (IEA, 2008a, [16]). Cellulose ethanol has a better energy balance in terms of greenhouse gas emissions and land-use requirements than starch ethanol;
- **Biogas** obtained through anaerobic digestion of raw materials such as organic waste, animal waste, and sewage sludge, and/or energy plants. Purified for biomethane (SNG) by



Source: Modified from Bauen *et al.*, 2009.

**Figure 1.** The division of biofuels and their advancement in production according to IEA [10].

removing carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), it can be a motor fuel or a hydrogen source, also for cell fuel;

- **Dimethyl ether (bio-DME)** as a gaseous fuel for self-ignition engines, obtained from methanol in the process of catalytic dehydration, from synthesis gas by gasification of lignocellulose and other biomass. The production of bio-DME from biomass gasification is in a demonstration phase (September 2010 in Sweden, Chemrec);
- **Biobutanol** with higher energy density and more favorable than ethanol in motor gasolines (MG). It can be distributed via the existing BS network. Biobutanol can be produced by fermenting sugars with *Clostridium acetobutylicum*. Demonstration plants operate in Germany and the USA, while others are under construction;
- **Furan fuels**, for which polysaccharides of the type cellulose and starch, constitute a raw material, obtained in defragmentation processes of multisugar chains leading to glucose, then converted into fructose, by isomerization using enzymatic catalysts. Fructose in the dehydration process changes into 5-hydroxymethylfurfural (HMF), which in the process of hydrogenolysis, in the presence of a copper-ruthenium catalyst, is converted into DMF (dimethylfuran), a fuel for spark-ignition engines with advantages over ethanol, without its disadvantages as a component fuel;
- **Solar fuels** [12] obtained by gasification of biomass for syngas using heat generated by the concentration of solar energy, which potentially improves conversion efficiency and

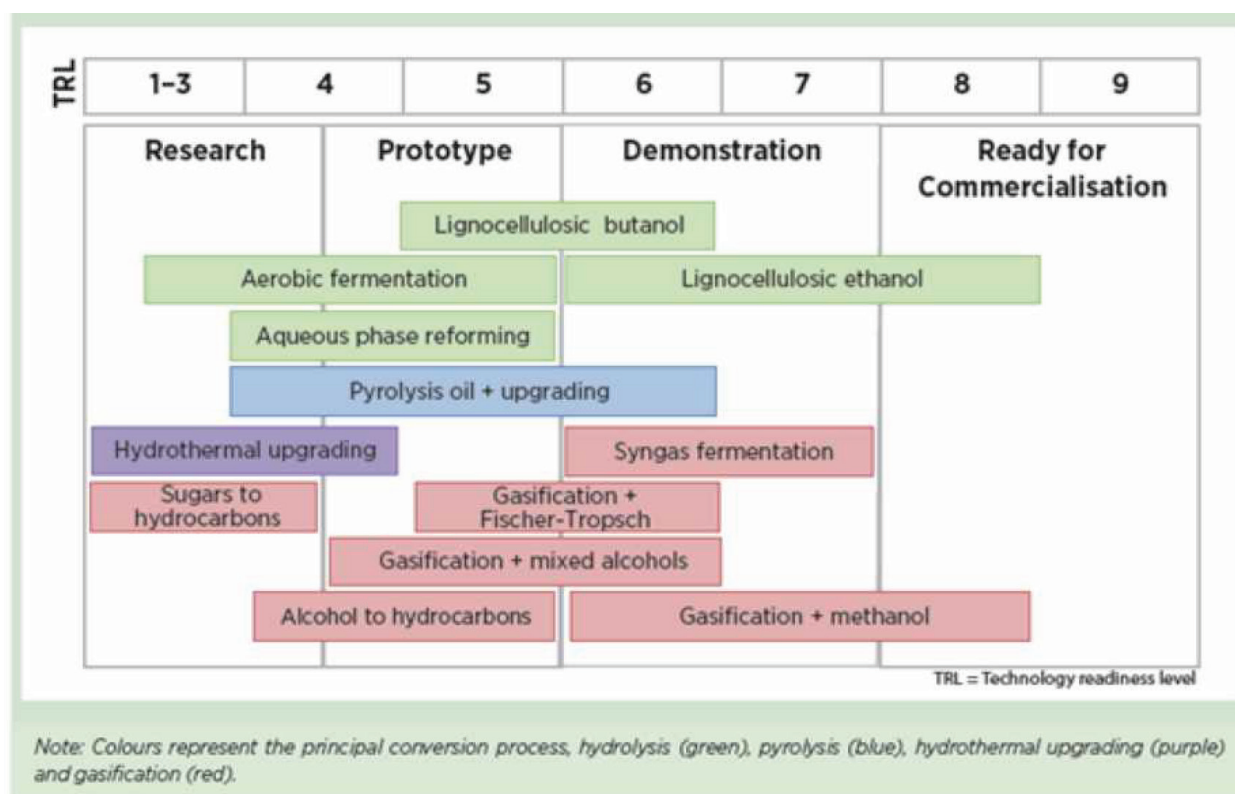


Figure 2. Division and level of technological readiness of biofuels according to IRENA [11].

ensures greater reduction of greenhouse gas emissions. They can also be obtained as a result of the decomposition of water (steam) and the use of carbon dioxide to produce synthesis gas, catalytically converted to fuel fractions. The production of these fuels may also include so-called “artificial leaf”;

- **Biorefinery systems** [13] for the production of liquid fuels and chemical intermediates. These processes are preferred in each of the five “value chains” set started in 2014. Bioeconomy for Europe, as a prospective, waste-free, biofuels, biomaterials (biochemicals).

In the area of the most promising raw materials for future biofuels, taking into account the so-called “land hunger” and requirements for reducing CO<sub>2</sub> emissions, cultivation of algae, niknik, Jatropha, and halophytes is preferred. To increase the amount of possible biomass resources to be used, technologies such as sunless (dark) photosynthesis and marine membrane systems for the production of algae, and technologies for the production of biomethanol as a raw material are also being developed.

## 4. Conclusion

The future of biofuels as alternative energy carriers for transport and bioliquids for stationary devices will depend on many factors. The main determinant is the availability of raw materials and the efficiency of both production technology and direct exploitation and, most importantly, the reduction of greenhouse gas emissions, including mainly carbon dioxide, throughout the life cycle assessment cycle (LCA). Taking into account the degree of development of various biomass waste processing technologies, it seems that the most effective and efficient gasification technologies are not only waste biomass for biofuel production in BtL processes but also gasification processes for industrial waste, mainly plastics leading to the production of alternative fuels in WtL processes [14], which prefers to jointly run XtL processes as processes significantly affecting the improvement of the environment. It seems, therefore, that future synthesis gas can be treated as a universal energy carrier. The confirmation of this thesis may be synthesis gas fermentation processes [13] enabling the production of bioethanol and other C2 to C5 hydrocarbons, i.e., acetic acid, isopropanol, dimethylketone, 2,3-butenediol, butane, isobutane, succinic acid, as well as isoprene structures important in the processes of economy on a closed circuit. In the field of alternative fuel production, with significant co-operation of the author’s team, a patented thermolysis technology for plastic waste has been developed, which under atmospheric pressure conditions allows to obtain hydrocarbon fractions that can meet components of both motor gasolines and diesel oils compliant with the quality requirements of European fuel standards as “drop in alternative fuels” [15]. The catalyzed technology for producing synthesis gas from waste carbon dioxide and water vapor, which also has a significant negative impact on climate change, can also be considered as prospective. Therefore, one should strive to develop effective technologies of gasification processes of any waste raw materials, of course with regard to biomass, to obtain energy carriers adaptable by modern engines, both transport and stationary destination.



## Author details

Krzysztof Biernat

Address all correspondence to: k.biernat@pimot.eu

Department of Fuel and Bioeconomy, Automotive Industry Institute, Warsaw, Poland

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