# Biofuels as alternative energy carriers in IC engines; classification and development prospects

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Summary

A survey of perspective technologies for biofuel production has been presented in the article. Several technological routes for production of advanced biofuels have been recommended for the future utilization of carbon dioxide as a substrate. European research agenda in line with European policy on biofuels has been presented as well. Several aspects on research projects concerning biofuels carried on in Automotive Industry Institute have been presented.

#### **1. Introduction**

In Europe and the USA, biofuels are defined as liquid or gaseous fuels obtained from biomass and intended for internal combustion (IC) engines. According to the current EU Directive (2009/28/EC), "biomass" means "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste."

Directive 2009/28/EC defines biofuels in general, without dividing them into specific fuel groups. This results from both development of the biomass processing technologies, e.g. the BtL (biomass-to-liquid) processes, and search for new raw materials for the production of biofuels and alternative fuels, e.g. the WtL (waste-to-liquid) processes. The processes of these two groups are to bring about lower emissions at both the fuel production and use stages (life cycle assessment, i.e. LCA, and the "well-to-wheel" or "WtW" analysis). Therefore, taking into account the Directive provisions and our own experience acquired when carrying out our research work, we propose to adopt the following definition of biofuels: "biofuels" means

liquid or gaseous fuels for transport produced from biomass and waste substances as well as obtained from indirect or direct processes where carbon dioxide of natural and/or industrial origin is utilised."

In consideration of the development of biofuel production technologies and the promotion of development of biofuels of second and higher generations (also referred to as "advanced biofuels") and within the actions taken to introduce biofuels into large-scale use, the raw materials and technologies should be identified thanks to which the biofuels obtained from such materials and with the use of such technologies might be classified among the energy carriers whose contribution to the National Indicative Target (NIT) would be twice as high as that of the other biofuels. The future technologies have already been defined and adopted in the European Biofuels Strategic Research Agenda; they will also be defined in the "Technology Roadmap – Biofuels for Transport" being prepared by the International Energy Agency.

#### 2. Division and classification of biofuels

Assuming biomass as the basic source of materials for the production of biofuels, two main material pathways and the corresponding material processing technologies have been taken into consideration in the European definition, i.e. the processes referred to as BtL (*"biomass-to-liquid"*) or, as an alternative, BtG (*"biomass-to-gas"*) and WtL (*"waste-to-liquid"*) or, as an alternative, WtG (*"waste-to-gas"*).

The Directive mentioned above has also introduced a term "*bioliquids*," i.e. "liquid fuels for energy purposes other than for transport, including electricity and heating and cooling, produced from biomass." In the official Polish version of this Directive, the word "bioliquids" has been incorrectly translated into "biophyny," while the English equivalent of the Polish word "phyn" is "fluid" and "*bioliquids*" are confined to "*liquid*" substances and do not include gaseous energy carriers for stationary applications. Hence, the processes aimed at the obtaining of bioliquids from a definite sort of biomass as feedstock fall into the groups referred to as BtE ("*biomass-to-energy*") and WtE ("*waste-to-energy*").

Thus, biofuels are chiefly divided into groups according to their state of matter. According to Annex 1 to Communication from the Commission of the European Communities No. 34 of 2006, COM(2006)34 final, biofuels have been divided into liquid, gas, and others, with the concept of first and second generation biofuels having been introduced in this Communication for the first time. Notwithstanding this, a concept of "synthetic biofuels" has been introduced and defined as "synthetic hydrocarbons or mixtures of synthetic hydrocarbons produced from biomass, e.g. SynGas produced from gasification of forestry biomass or SynDiesel."

In the European classification, the following biofuels have been separated due to the state of matter:

- 1. Liquid biofuels:
  - Bioethanol obtained from biomass and/or biodegradable waste fractions, possible for use as biofuel E5 of 5% ethanol and 95% petrol contents or as biofuel E85 of 85% ethanol and 15% petrol contents;
  - Biodiesel containing methyl-esters (PME, RME, FAME) produced from vegetable oil, animal oil or recycled (e.g. post-frying) fats and oils, meeting the requirements of relevant quality standards for B5 diesel oils of 5% ester and 95% petroleum-based diesel contents, B30 diesel oils of these proportions being 30% and 70%, respectively, and B100 exclusively consisting of pure esters of properties meeting the relevant standard specifications;
  - Biomethanol produced from biomass, for use as biofuel or a fuel component;
  - Bio-ETBE, i.e. ethyl-tertio-butyl-ether produced from bioethanol, used as a petrol additive to increase the octane rating and to reduce knocking and added to petrol at a percentage rate of 47%;
  - Bio-MTBE, i.e. methyl-tertio-butyl-ether produced from biomethanol, used for the same purposes as those of the Bio-ETBE and added to petrol at a percentage rate of 36%;
  - BtL, i.e. liquid fractions or mixtures of liquid fractions produced from biomass, for use as biofuels or fuel components;
  - Pure vegetable oils produced through pressing, extraction or similar processes, inclusive of refining, but chemically unmodified, which can be used as biofuel when compatible with the type of engine involved and when meeting the corresponding environmental protection requirements.
- 2. Gaseous biofuels:
  - Bio-DME transport fuels obtained from RES, i.e. dimethylether produced from biomass, for direct use as biofuel for compression-ignition engines;
  - Biogas, i.e. biofuel produced from biomass and/or the biodegradable fractions of waste, purified to natural gas quality;
  - Biohydrogen as biofuel produced from biomass or the biodegradable fractions of waste.
- 3. Other renewable fuels, i.e. biofuels not specified above, originating from sources as defined in Directive 2001/77/EC and suitable to power transport facilities.

As mentioned previously, the assumed principles of division of biofuels into first and second generation biofuels have been specified in the same Communication. This division resulted from the reasons discussed above, in particular from assessment of the usability of specific fuels in the present-day engine technologies, availability of the feedstock needed, and environmental impact of the fuels. The formal division of biofuels into specific generations has been published in a report entitled "Biofueels in the European Union, a Vision for 2010 and Beyond". According to this report, biofuels have been divided into first generation biofuels, referred to as "conventional biofuels," and second generation biofuels, referred to as "advanced biofuels." The first generation ("conventional") biofuels include:

- Bioethanol (BioEtOH, BioEt), understood as conventional ethanol obtained through hydrolysis and fermentation processes from raw materials such as cereals, sugar beets etc.;
- Pure vegetable oils (PVO), obtained through cold pressing and extraction processes from seeds of oil plants;
- Biodiesel, consisting of rape oil methyl ester (RME) or methyl esters (FAME) and ethyl esters (FAEE) of higher fatty acids of other oily plants and obtained in result of cold pressing, extraction and transesterification processes;
- Biodiesel, consisting of methyl and ethyl esters and obtained in result of transesterification of post-frying oil;
- Biogas, obtained by purification of wet landfill or agricultural biogas;
- Bio-ETBE, obtained by chemical processing of bioethanol.

The second generation ("advanced") biofuels include:

- Bioethanol, biobutanol, and blends of higher alcohols and derivative compounds, obtained in result of advanced processes of hydrolysis and fermentation of lignocellulosic biomass (excluding the feedstock for food production purposes);
- Synthetic biofuels, being products of biomass processing and obtained by gasification and appropriate synthesis into liquid fuel components (BtL processes) and products of the processing of biodegradable industrial and municipal wastes, including carbon dioxide (WtL processes);
- Fuels for compression-ignition engines, obtained from biomass through Fischer-Tropsch processes, inclusive of synthetic biodiesels obtained by blending of lignocellulosic products;
- Biomethanol, obtained in result of lignocellulose transformation processes, inclusive of Fischer-Tropsch synthesis, as well as with the use of waste carbon dioxide;
- Biodimethylether (bio-DME), obtained by thermo-chemical processing of biomass, inclusive of biomethanol, biogas, and synthetic biogases being derivative products of biomass transformation processes;
- Biodiesel as biofuel or a fuel component for compression-ignition engines, obtained by hydrorefining (hydrogenation) of vegetable oils and animal fats;
- Biodimethylfuran (bio-DMF), obtained from sugar transformation processes, inclusive of the transformation of cellulose in thermo-chemical and biochemical processes;
- Biogas as synthetic natural gas (SNG) or biomethane, obtained in result of the processes of lignocelluloses gasification, appropriate synthesis, or purification of agricultural, landfill, and sewage sludge biogas;
- Biohydrogen obtained in result of gasification of lignocellulose and synthesis of the gasification products or in result of biochemical processes.

The above classification shows that the first generation biofuels having been subsequently processed cannot be considered as second generation biofuels; this means that any further processing of esters, for example by hydrogenation, will not result in the obtaining of second generation biofuels, and is technically and economically unreasonable. In general, the idea of development of second generation biofuels is based on an assumption made that the feedstock to be used for the production of such fuels should equally include biomass, waste vegetable oils and animal fats, as well as any waste substances of organic origin that are useless in the food and forestry industries.

In the past years, the European Commission Directorate-General for Energy and Transport proposed to separate third generation biofuels, defining them as those for which the technology of universal acquisition and introduction of such fuels may be developed in 2030s or even later, according to estimates. Preliminarily, biohydrogen and biomethanol have been classified in this group.

In consideration of the most important factor that forces the propagation of the use of biofuels, i.e. the necessity to reduce the emissions of greenhouse gases (GHG), chiefly carbon dioxide, the definition of third generation biofuels was made more precise and the introduction of fourth generation biofuels was proposed. Both of theses groups are counted among the "advanced biofuels." The third generation biofuels may be obtained by methods similar to those used in the case of the second generation biofuels, but from the feedstock (biomass) having been modified at the plant growing stage with the use of molecular biology techniques. The objective of such modifications is to improve the process of conversion of biomass into biofuels (biohydrogen, biomethanol, biobutanol) by e.g. cultivation of trees of low lignin content, development of crops with enzymes incorporated as required, etc.

The separation of a new, fourth generation of biofuels was proposed because of the necessity to close the carbon dioxide balance or to eliminate the environmental impact of this compound. Therefore, the fourth generation biofuel technologies should be developed with taking into account the CCS ("Carbon Capture and Storage") processes at the raw material preparation and biofuel production stages. The raw materials to be used for the production of such fuels should be plants of increased  $CO_2$  assimilation rates at the plant growing stage and the technologies applied must be devised with taking into account the capture of carbon dioxide in appropriate geological formations by causing the carbonate stage to be reached or the storage in oil and gas exploitation hollows.

In the USA, biofuels have not been categorised so far. The National Renewable Energy Laboratory (NREL) has reported that gradual development and implementation of biofuel production technologies is planned.

According to the NREL's data, the technologies of the following biofuels are being implemented at present:

• Ethanol as a biofuel component produced from cereal grain and cellulose obtained from agriculture and forestry;

• Biodiesel, being a mixture of esters of higher fatty acids obtained in result of the processes of transesterification of vegetable oils and petroleum-based diesel oil.

In the future, next biofuel technologies are to be implemented, related to the following:

- "Green Diesel and Jet Fuel," general-purpose fuel for diesel and turbine engines (chiefly for military applications), obtained from fats, waste oils, and pure vegetable oils, refined at oil refineries to very low sulphur content;
- Other products of biomass fermentation processes, such as butanol, acetates and lactates, and the like;
- Post-pyrolysis liquids, obtained in result of biomass pyrolysis processes as an alternative raw material for oil refineries or gasification processes;
- Synthetic gas obtained from biomass by means of the Fischer-Tropsch method, as feedstock for the production of methanol, dimethylether, or alcohol mixtures;
- "Algae-derivative Fuels," obtained from seaweed biomass as a source of triglycerides for the production of biodiesel and "Green Diesel and Jet Fuel" and as feedstock for the production of hydrocarbons;
- Biofuels obtained from such raw materials as jatropha, halophytes, camelina (*Camelina sativa*), to be used for the production of diesel fuels and Jet-type fuels;
- Hydrocarbon fuels as fuels of the far future, to be obtained in result of biological processes or biomass hydrogenation processes, inclusive of the fuels obtained in result of the xtL (*"anything-to-liquid"*) processes.

This last group of biofuels is now becoming increasingly important because, in consideration of the more and more urgent necessity to reduce carbon dioxide emissions, new ways to close the CO<sub>2</sub> balance by searching for new raw materials and raw material processing pathways must be sought.

### 3. Future (advanced) biofuel production technologies

In consideration of the estimated biomass potential and the necessity for radical reduction of carbon dioxide emissions, new forward-planned technologies are being developed in the USA and Europe:

- Biofuel production technology, covering the Jet-type fuels as well, involving the sunless growing of algae on sludge of agricultural origin, grass, and waste substances, with utilising carbon dioxide (the SOLAZYME technology);
- Plasma gasification of waste biomass as well as municipal and industrial wastes (BtG and WtG processes), followed by conversion of the gases thus obtained into liquid biofuels (diesel oils and Jet-type fuels) within a GtL process (the SOLENA technology implemented in the UK and Italy);
- Technology to utilise carbon dioxide at energy carrier production processes;

• Integrated biorefinery technologies.

Based on the experience gathered and on the development of biofuel production technologies or, to be more precise, on the technologies of production of alternative fuels from raw materials that are wastes in both biological and civilisation-related terms, efforts are chiefly made to reduce  $CO_2$  emissions or to achieve an optimum  $CO_2$  balance in the fuel production and combustion processes. Within the planned perspective of the production and use of biofuels (alternative fuels), the fuels are required:

- To be available in sufficiently large quantities;
- To have adequate technical and energy characteristics for being suitable for the fuelling of engines or heating systems;
- To be inexpensive at both the production and sale stages;
- To cause smaller environmental hazard in comparison with the fuels used hitherto thanks to lower emissions of toxic compounds and greenhouse gases during the combustion process;
- To ensure the achieving of acceptable economic indices and safety of operation of engines or boilers and lower costs of operation of such devices;
- To improve energy independence.

With respect to the above, the European Biofuels Technology Platform prepared an update to the Biofuels Strategic Research Agenda at the beginning of 2010, with taking into account the technology progress and the necessity to intensify the greenhouse gases abatement activities. Apart from this, the International Energy Agency is now preparing a Technology Roadmap – Biofuels for Transport, where the necessity for sustainable development and reduction of GHG emissions by, *inter alia*, the utilisation of carbon dioxide is taken into consideration. Similarly, the preamble to the EU Directive includes a suggestion that "The Community should take appropriate steps (...), including the promotion of sustainability criteria for biofuels and the development of second and third generation biofuels in the Community and worldwide (...)."

The biofuels meant here include:

- Synthetic fuels / hydrocarbons obtained by biomass gasification (application: transport fuels obtained from renewable energy sources (RES) for aircraft engines and compression-ignition engines);
- Biomethane and other gaseous fuels obtained by biomass gasification, used as substitutes for natural gas and other gaseous fuels (application: engine fuels and energy generation with high efficiency);
- Biofuels (bioliquids) obtained from biomass in result of other thermochemical processes such as pyrolysis (application: heating fuels, energy generation, or indirectly through xtL processes for the production of transport fuels);
- Ethanol and higher alcohols obtained from the sugar contained in biomass (application: transport fuels obtained from RES; petrol components, E85);

- Hydrocarbons obtained from the sugars contained in biomass by means of biological or chemical processes (application: renewable transport fuels for aircraft engines and compression-ignition engines);
- Biofuels obtained by utilisation of carbon dioxide for the production of microorganisms or in result of direct synthesis of carbon dioxide of natural origin in thermo-chemical and biochemical processes (application: transport fuels obtained from RES and aircraft fuels).

As it can be seen, the above definitions cover the production of biofuels the types of which have already been defined, such as bio-DME, bio-DMF and other furan derivatives, FT-diesel (based on the Fischer-Tropsch process), HTU-diesel (obtained from the hydrothermal upgrading process), or fuels made by hydrogenation of vegetable oils and animal fats unusable in the food industry.

In consideration of the basic reason for the introduction of biofuels as separate fuel grades or fuel components, i.e. the necessity to reduce the carbon dioxide emissions, it is reasonable to supplement the list of prospective biofuels with the fuels produced in result of synthesis or utilisation of waste carbon dioxide in the processes of production of energy carriers for transport purposes. An example of the activities undertaken in this field may be the research work being now carried out in the USA, where synthetic gas is produced from carbon dioxide and water vapour based on a catalysed process run with the employing of solar energy as presented in Fig. 1.

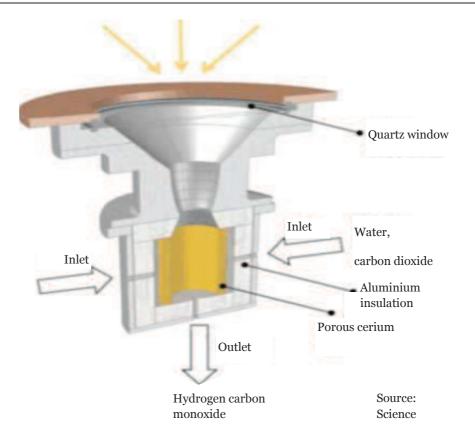


Fig. 1. Schematic diagram of the solar-driven process of obtaining synthetic gas (the Sossina-Haile technology).

The counting of biofuels (biocomponents) thus obtained among biofuels of the second or higher generations ("*advanced biofuels*") is fully consistent with the recommendations of Directive 2009/28/EC because carbon dioxide is also a waste substance of natural origin of the "bio" type.

Based on the experience gathered and on results of the research work carried out, we should strive in the nearest future to obtain biofuels as hydrocarbon blends produced in accordance with definite process pathways. Such pathways will make it possible to obtain alternative fuels for IC engines with simultaneous closing of the  $CO_2$  cycle. Hence, the biofuels of the future should be:

• Synthetic biofuels made as blends of hydrocarbons produced in result of biomass gasification and pyrolysis processes (Fig. 2);

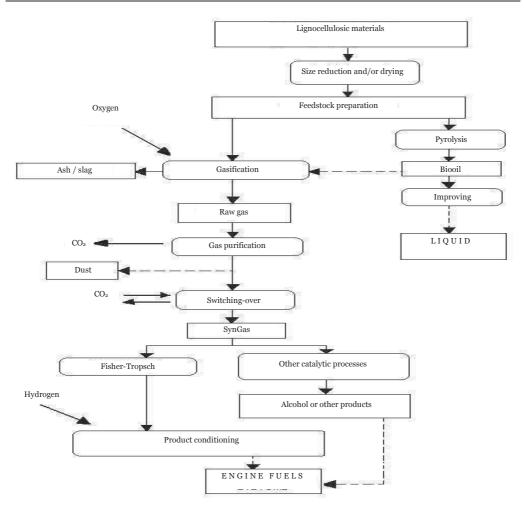


Fig. 2. Biomass gasification and pyrolysis process flowchart.

• Biofuels obtained from biomass in result of other thermo-chemical processes, such as pyrolysis or processes of depolymerisation and hydrogenation of biomass decomposition products (HTU processes, Fig. 3);

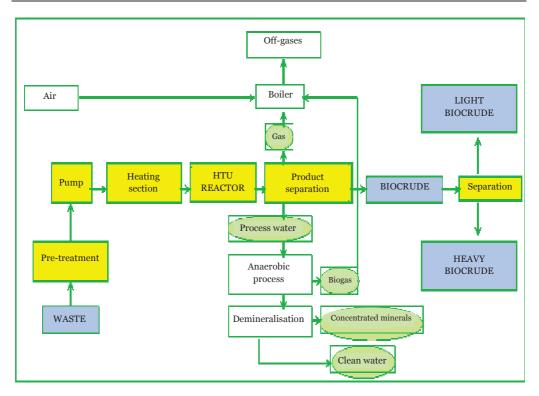


Fig. 3. HTU (hydrothermal upgrading) process flowchart.

- Fuel blends composed of hydrocarbons obtained from biomass and meeting the engine fuel quality requirements, including those directly or indirectly obtained from sugars in result of biological and/or chemical processes;
- Biofuels being other sugar derivatives, inclusive of cellulose derivatives, meeting the engine fuel specifications;
- Biomethane and other gaseous fuels obtained from biomass gasification processes and/or agricultural, landfill, and sewage sludge treatment processes (substitutes for natural gas and other gaseous fuels);
- Bioethanol and higher alcohols (biobutanol) and their derivatives, obtained from biomass in result of biochemical and/or catalysed thermo-chemical processes (fig. 4);

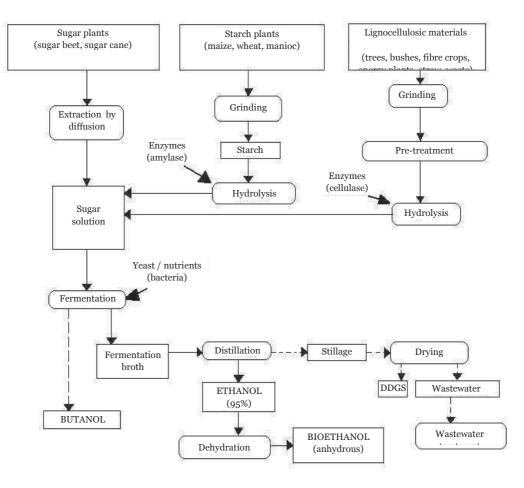


Fig. 4. Biochemical biomass conversion processes, schematic flowchart.

- Biofuels obtained by the use of carbon dioxide for the production of microorganisms or by direct or indirect synthesis of carbon dioxide of natural origin in thermo-chemical and biochemical processes;
- Biofuels obtained from synthetic gas generated as a product of direct or indirect (through methanol) conversion of biomass and/or GHG;
- Biofuels (HVO, hydrogenated vegetable oils) obtained by hydrogenation of waste vegetable and animal fats.

## 4. PIMOT's research work on biofuels

Valuable research and development work is carried out at PIMOT (Automotive Industry Institute) in the field of biofuels and other renewable energy sources. This work, done in the form of various R&D projects and other work undertaken within the scope of Institute's statutory activities, will make it possible, *inter alia*, to adapt the methods of production of biocomponents and biofuels of the first and second generation to the Poland's potential of raw material supplies and to the existing industrial base, to evaluate the possibilities of raising the Poland's energy supply capacity with the use of the raw materials suitable for the production of alternative fuels, and to work out the principles of distribution and storage of biocomponents and biofuels of the first and second generation.

The projects being currently implemented by PIMOT in the field of biofuels are dedicated to the following issues:

- Development of the method of production of second generation biofuels for transport and energy applications, produced within a process of thermal cracking of raw materials obtained from renewable energy sources and organic wastes (within an R&D project);
- Working out of a Polish technology of production and use of bioethanol biofuels for IC engines (within an R&D project);
- Development of a system of continuous monitoring of the degree and rate of the liquid fuel ageing process taking place during storage (within the Operational Programme Innovative Economy);
- Development and introduction of a dual-fuel system of the feeding of compression-ignition engines with agricultural biogas with a pilot dose of liquid fuel (within the Eureka Initiative);
- Working out of integrated technologies of the production of fuels from biomass as well as agricultural and other waste (within a strategic project);
- Research on the processes of hydro-conversion of natural oils and fats into hydrocarbons (within Institute's statutory activities).

Moreover, PIMOT is a coordinator of the Polish Technology Platform for Biofuels, which is an organisation of business entities, scientific institutions, and other units of the business environment.

The work being done at PIMOT will make it possible to develop a long-term strategy for diversification and regionalisation of the production of specific types of materials used to manufacture biofuels and for the utilisation of the existing industrial infrastructure for the implementation of biotechnologies. The establishing of a technical base for the setting up of vehicle fleets adapted for being powered with first and second generation biofuels and for the adaptation of energy system fuelling installations for the use of biofuels will be possible as well. A growth in the use of energy obtained from renewable energy sources (RES), inclusive of biofuels, as well as an improvement in the efficiency of energy generation, transmission, and distribution should be expected, which will result in increased energy efficiency of the process of energy use and in reduced environmental impact of the energy sector. The activities conducted will also help to develop the industry that manufactures machinery and equipment for the production of fuels and energy from renewable sources.

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