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An Analysis of Physico-Chemical Properties of the Next Generation Biofuels and Their Correlation with the Requirements of Diesel Engine

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/53685>

1. Introduction

There is a pressing need to hasten developing advanced energy technologies to reduce dependency on crude oil and climate protection. Biofuels – liquid and gaseous fuels derived from organic matter – can play an important role in reducing of carbon dioxide (CO₂) emissions in the transport, and can raise the energy security. By 2050, biofuels could provide 27% of total transport fuel. The use of biofuels could avoid around 2.1 gigatonnes (Gt) of CO₂ emissions per year when produced sustainably. To meet this vision, most conventional biofuel technologies need to improve conversion efficiency, cost and overall sustainability. Conventional biofuel technologies include well-established that are already producing biofuels on a commercial scale. These biofuels, commonly referred to as first-generation, include sugar- and starch-based ethanol, oil-crop based biodiesel and straight vegetable oil, as well as biogas gained through anaerobic digestion. The International Energy Agency has undertaken an effort to develop a series of global technology road maps covering 19 advanced technologies, commonly referred to as second- or third-generation. This new technologies are still in the research and development (R&D), pilot or demonstration phase [1]. Significant decrease of fossil fuels and lack of new ones becomes the basis for the Olduvai theory, published by R.C. Duncan [2]. The theory postulated that in the years 2012-2030, because of shortage of energy, the world would go through an economic crisis. This crisis would lead to collapse of industrial civilization. So, there is a need to look for alternative, renewable sources of raw materials.

According to the current EU Directive on promoting the use of energy from renewable sources [3], petrochemical companies are obliged to market fuel containing biocomponents (2009/28/EC). Biomass means the biodegradable fraction of products, waste and residues from biological origin, from agriculture, forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal wastes. Assuming biomass as the basic source of materials for the production of biofuels, two main material pathways and the suiting material processing technologies have been considered in the European definition. That is 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).

Biofuels are 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 first and second generation biofuels having been introduced in this Communication for the first time. However, an idea of “synthetic biofuels” has been introduced and defined as “synthetic hydrocarbons or mixtures of synthetic hydrocarbons produced from biomass, for example SynGas produced from gasification of forestry biomass or SynDiesel.”

2. Classification of biofuels

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

1. Liquid biofuels:

- Bioethanol got from biomass 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 (“pure vegetable oils”), RME (“rapeseed methyl esters”), FAME (“fatty acid methyl esters”)] produced from vegetable oil, animal oil or recycled (for example 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 ingredient;
- BioETBE, that is 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%;
- BioMTBE, that is Methyl-tertio-butyl-ether produced from biomethanol, used for the same purposes as those of the BioETBE and added to petrol at a percentage rate of 36%;
- BtL, that is Liquid fractions or mixtures of liquid fractions produced from biomass, for use as biofuels or fuel ingredients;

- Pure vegetable oils (PVO) produced through pressing, extraction or similar, inclusive of refining, but chemically unmodified, which can be used as biofuel when compatible with the engine involved and when meeting the matching environmental protection requirements.
2. Gaseous biofuels:
 - BioDME transport fuels gained from Renewable Energy Sources (RES), that is Dimethylether produced from biomass, for direct use as biofuel for compression-ignition engines;
 - Biogas, that is Biofuel produced from biomass 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, that is Biofuels not named above, originating from sources as defined in Directive 2001/77/EC and suitable to power transport.

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 the report titled "Biofuels 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 got through hydrolysis and fermentation from raw materials such as cereals, sugar beets.;
- Pure vegetable oils, got through cold pressing and extraction from seeds of oil plants;
- Biodiesel, consisting of RME or FAME and fatty acid ethyl esters (FAEE) of higher fatty acids of other oily plants and gained as the result of cold pressing, extraction and transesterification;
- Biodiesel, consisting of methyl and ethyl esters and gained as the result of transesterification of post-frying oil;
- Biogas, got by purification of wet landfill or agricultural biogas;
- BioETBE, got by chemical processing of bioethanol.

The idea of second generation biofuels development is based on an assumption. Feedstock to be used for producing 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. The second generation ("advanced") biofuels includes:

- Bioethanol, biobutanol, and blends of higher alcohols and derivative compounds, got as the result of advanced of hydrolysis and fermentation of lignocellulosic biomass (excluding the feedstock for food production purposes);

- Synthetic biofuels, being products of biomass processing and gained by gasification and proper synthesis into liquid fuel ingredients (BtL) and products of process biodegradable industrial and municipal wastes, including carbon dioxide (WtL);
- Fuels for compression-ignition engines, got from biomass through Fischer-Tropsch, inclusive of synthetic biodiesels got by blending of lignocellulosic products;
- Biomethanol, got as the result of lignocellulose transformation, inclusive of Fischer-Tropsch synthesis, as well as with the use of waste carbon dioxide;
- Biodimethylether (bioDME), got by thermochemical processing of biomass, inclusive of biomethanol, biogas, and synthetic biogases being derivative products of biomass transformation;
- Biodiesel as biofuel or a fuel ingredient for compression-ignition engines, got by hydrorefining (hydrogenation) of vegetable oils and animal fats;
- Biodimethylfuran (bioDMF), obtained from sugar transformation, inclusive of transforming cellulose in to thermochemical and biochemical processes;
- Biogas as synthetic natural gas (SNG) or biomethane, obtained in result of lignocelluloses gasification, correct synthesis, or purification of agricultural, landfill, and sewage sludge biogas;
- Biohydrogen got in result of gasification of lignocellulose and synthesis of the gasification products or as the result of biochemical processes.

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 gain and introduction of such fuels may be developed in 2030s or even later, according to the estimates. Preliminarily, biohydrogen and biomethanol have been classified in this group. The third generation biofuels may be obtained by the methods similar to those used in 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 changes is to improve the conversion of biomass into biofuels (biohydrogen, biomethanol, biobutanol) by for example cultivation of trees of low lignin content, development of crops with enzymes incorporated as required, etc.

Separating a new, fourth generation of biofuels was proposed because of the need to close the carbon dioxide balance or to cut out the environmental impact of this compound. Therefore, the fourth generation biofuel technologies should be developed with considering the CCS ("Carbon Capture and Storage") at the raw material preparation and biofuel production stages. The raw materials used for production of such fuels should be the plants of increased CO₂ assimilation rates at the plant growing stage and the technologies applied must be devised considering the capture of carbon dioxide in proper geological formations by causing the carbonate stage to be reached or the storage in oil and gas exploitation cages.

3. The main directions of advanced fuel technology's development

Within the planned perspective of the production and use of biofuels, the fuels are required: to be available in enough large quantities; to have acceptable technical and energy characteristics for being suitable for fueling engines or heating; to be inexpensive at both the production and sale stages; to cause smaller environmental hazard in comparison with the conventional fuels; to improve energy independence.

Based on the experience and on results of the research work carried out, we should strive in the nearest future to get biofuels as hydrocarbon blends produced by definite pathways. Such pathways will make it possible to get alternative fuels for IC engines with simultaneous closing of the CO₂ cycle. Therefore, the advanced biofuels should be:

- Synthetic biofuels made as blends of hydrocarbons produced in result of biomass gasification and pyrolysis [4] (figures 1 and 2)

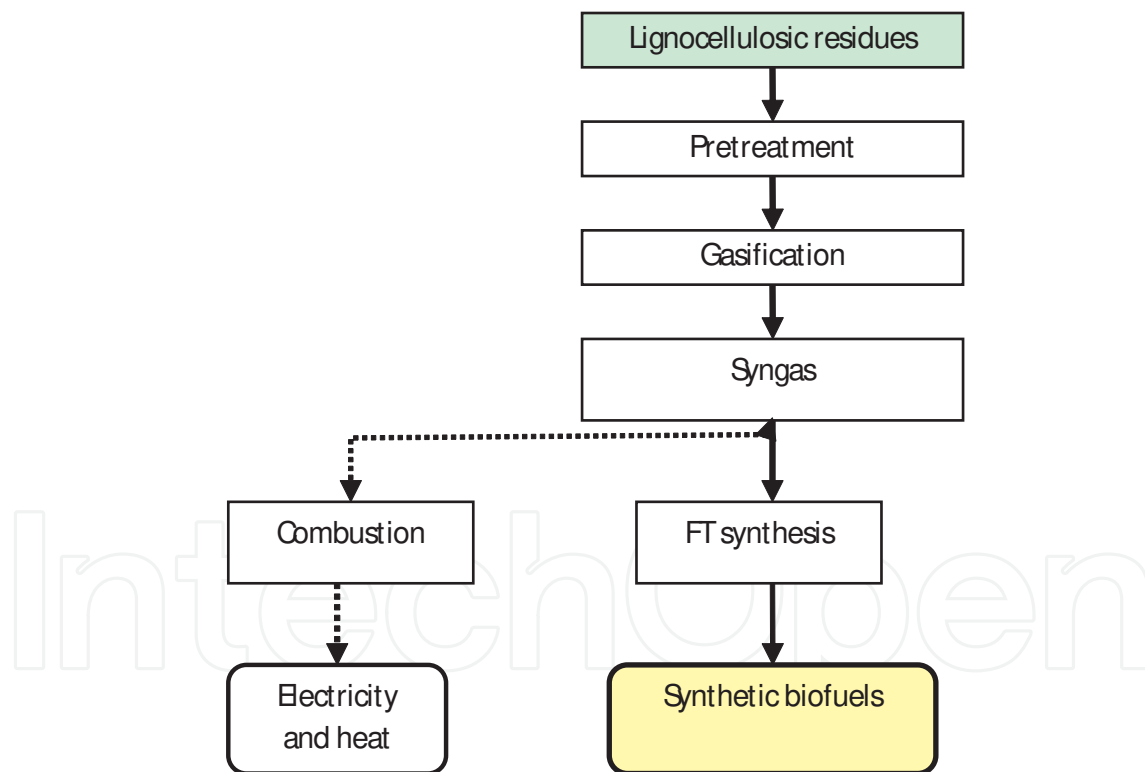


Figure 1. Schematic diagram of biomass to liquid process in Choren, Germany.

The main piece of biomass gasification technology is the patented Carbo-V process that allows to produce tar-free synthetic gas, a breakthrough for biomass to energy change. The gas consisting mainly of CO and H₂ can be used as a combustion gas for the generation of electricity, steam or heat, or for the make of transport fuels (BtL). Compared with fossil die-

sel, the combustion of BtL diesel reduces PM's (particulate matters) emissions by 30 to 50% and hydrocarbon emissions by up to 90 %. It achieves superior combustion characteristics while no engine adjustments are needed. But perhaps its most important feature is the ability to recycle atmospheric CO₂ into the fuel thus closing the sustainability cycle.

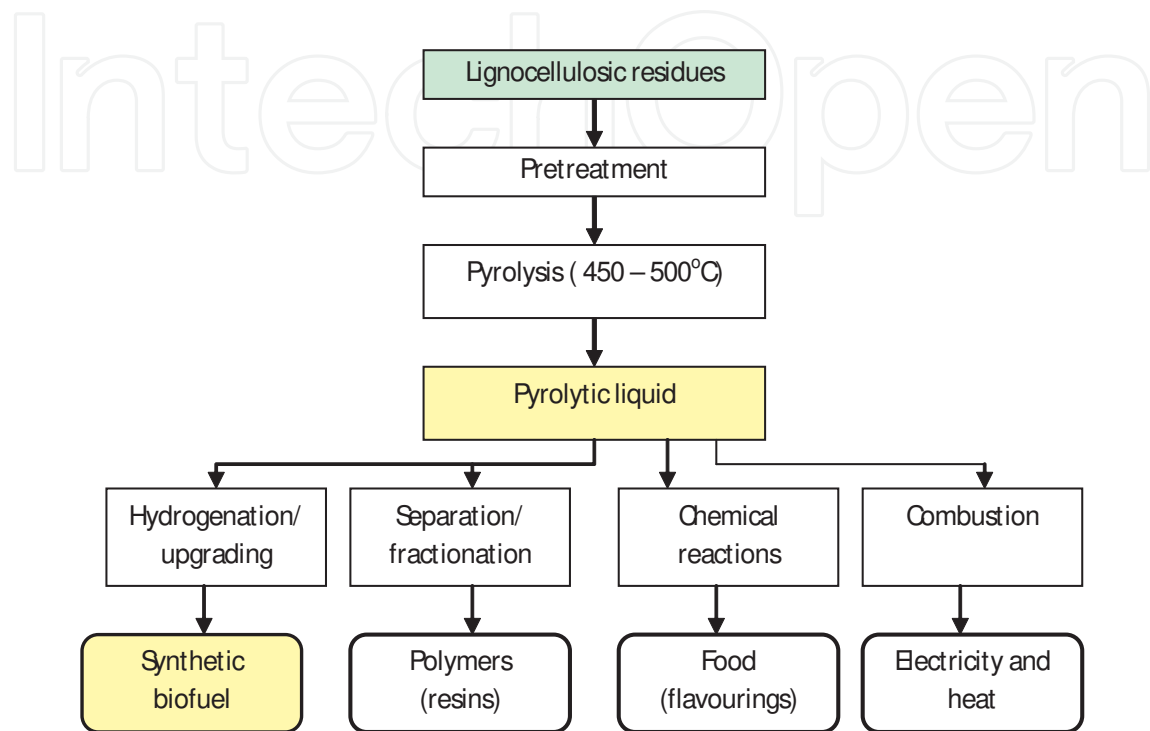


Figure 2. Schematic diagram of Rapid Thermal Processing (RTP) TM technology in Ontario, Canada (owner Ensyn). It is commercial installation.

Another promising technology is related to pyrolysis. Rapid Thermal Processing (RTP) is a fast thermal process where biomass is rapidly heated without oxygen. The biomass is vaporized and rapidly cooled to produce high yields of pyrolysis oil. The pyrolysis oil is fractionated into chemicals for engineered wood products (resins) and fuel for thermal applications. The resulting char and gases are used for energy. RTP™ typically yields 65 to 75wt% pyrolysis oil from dried woody biomass.

- Biofuels earned from biomass in result of other thermochemical processes, such as pyrolysis or processes of depolymerisation and hydrogenation of biomass decomposition products (hydrothermal upgrading-HTU processes);
- Fuel blends composed of hydrocarbons gained from biomass, including those directly or indirectly obtained from sugars in result of biological or chemical processes,
- Biofuels being other sugar derivatives;
- Biomethane and other gaseous fuels got from biomass gasification processes or agricultural, landfill, and sewage sludge treatment processes;

- Bioethanol and higher alcohols -biobutanol and their derivatives, obtained from biomass in result of biochemical or catalyzed thermochemical processes (figure 3);

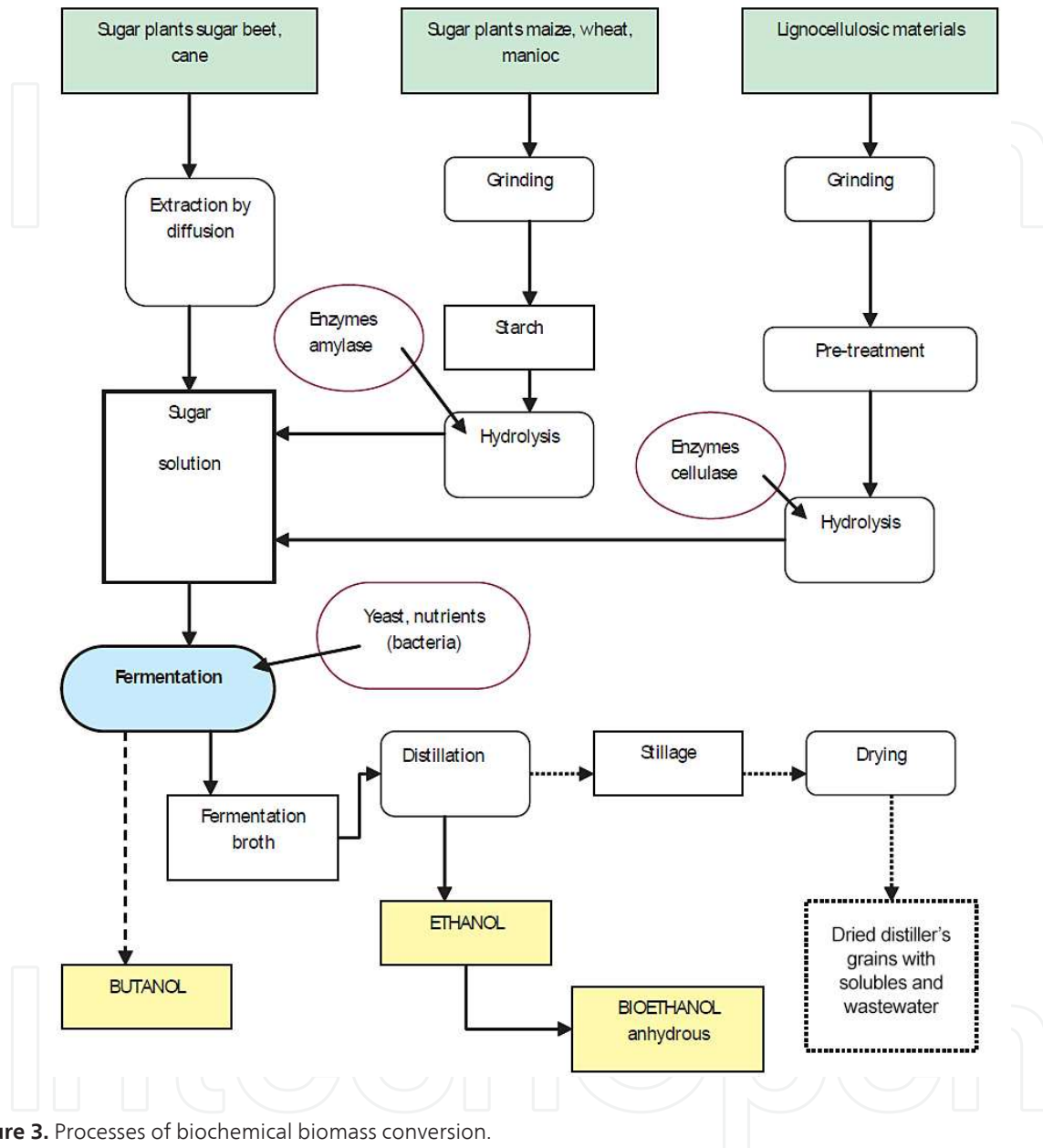


Figure 3. Processes of biochemical biomass conversion.

- Biofuels obtained by utilization of carbon dioxide for production of microorganisms or by direct or indirect synthesis of carbon dioxide of natural origin in thermochemical and biochemical;
- Biofuels obtained from synthetic gas produced as a product of direct or indirect (through methanol) conversion of biomass or GHG;
- Biofuels (HVO, hydrogenated vegetable oils) got by hydrogenation of waste vegetable and animal fats.

4. Application of selected types of biofuels of the first and second generation

Among the proposed alternative fuels, vegetable oils have received much attention in recent years for diesel engines owing to their advantages as renewable and domestically produced energy. The major disadvantage of pure vegetable oils is their inherently high viscosity, leading to poor fuel atomization, incomplete combustion, coking of fuel injectors, ring carbonization, and accumulation of vegetable oil in the lubricating oil. Several methods are consequently being used to reduce vegetable oil's viscosity. Blending of vegetable oils with an alcohol of lower viscosity is one of the methods [5, 6].

Main alcohols used as a fuels ingredient are: methanol, ethanol and n-butanol. These alcohols have different properties. Some of them are presented in Table 1. They are compared to conventional engine fuels.

Fuel	Energy density	Heat of vaporization	Kinematic viscosity at 20°C
Diesel	38.6 MJ/l	0.47 MJ/kg	>3 cSt
Gasoline	32.0 MJ/l	0.36 MJ/kg	0.4–0.8 cSt
Butanol	29.2 MJ/l	0.43 MJ/kg	3.64 cSt
Ethanol	19.6 MJ/l	0.92 MJ/kg	1.52 cSt
Methanol	16.0 MJ/l	1.20 MJ/kg	0.64 cSt

Table 1. The properties of different alcohols and engine fuels

It is interesting the butanol has similar energy density as petrol. Butanol is good solvent of heavy hydrocarbons (such diesel fuels). The mixture of these components is homogeneous and doesn't separate after several months. In contrast, ethanol is slightly soluble in diesel fuel. It is important the water is nearly insoluble in butanol, in contrast to ethanol which dissolves water in any proportion.

The old and new technology of butanol production is known as an ABE process (Acetone-Butanol-Ethanol) and the second generation process using lignocellulosic waste materials, respectively. The conventional ABE fermentation process is based on sugar's material (cane or beet) or starch (wheat, corn or rice) which is easily broken down into sugars. During the fermentation formed the three components: acetone, n-butanol and ethanol (in ratio of 3:6:1) as main products. The process is performed by anaerobic gram- positive bacteria of the genus clostridia (mainly *Clostridium acetobutylicum*, but also *C. Beijerinckii*, *C. butylicum* and others). The ABE process is not profitable because of low productivity and poor selectivity. One of the courses covers metabolic engineering issues, that is modification of metabolic pathway to increase resisting clostridia bacteria to higher concentrations of fermentation products, and improve the efficiency and selectivity. Low yield of the fermentation of butanol synthesis requires research on butanol recovery techniques. There are

many separation techniques of fermentation products, e. g. liquid-liquid extraction, perstraction, pervaporation (membrane separation with gaseous permeate discharge) combined with immobilization of bacterial cells, adsorption or reversed osmosis. It is estimated that effective solutions development can help to increase of profitability up to 40-50%.

The ideal feedstock for bioconversions could be waste biomass, for example straw, wood chips and paper pulp effluent. Also crops specially grown for their high biomass production rate (kenaf, miscanthus and short rotation woody crops). Such sources of raw materials can be described as “cellulosic biomass” because of their high cellulose and hemicellulose content. The feedstock used in fermentation determines the selection of strains and process conditions. The company Green Biologics is developing biobutanol production from glycerol and other wastes from industry and agriculture, using genetically modified thermophilic bacteria of the genus *geobacillus* and sells derived fuel named Butafuel (figure 4).

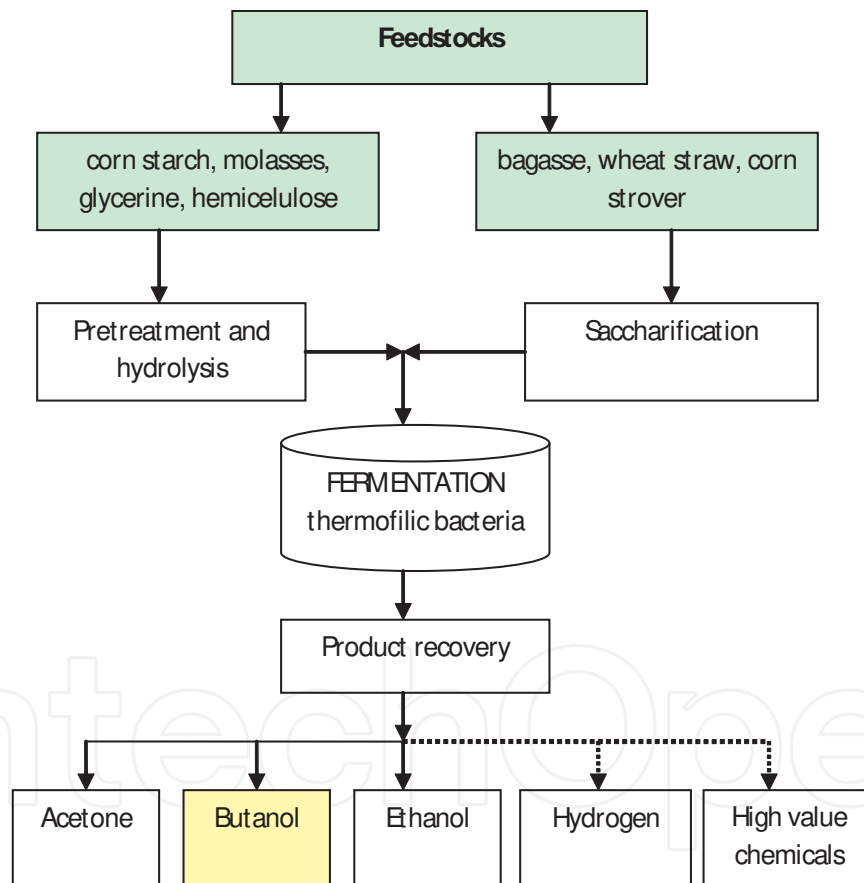


Figure 4. Schematic diagram of GBL’s technology, Green Biologics Ltd. Biobutanol used to produce fuels, paints, coatings, resins, polymers and solvents.

Butanol, like ethanol, can blend well with gasoline. Biobutanol can replace gasoline in E85 fuel. Also, butanol could be a future for blending with diesel. Butanol contains more oxygen compared to the biodiesel, leading to further decline of soot. NO_x emissions can also be reduced because of its higher heat of evaporation, which results in a lower combustion tem-

perature. The butanol has more advantages than the widely used ethanol and FAME. However, the main disadvantage of butanol is low production. Biobutanol is noncorrosive and can be shipped via pipeline.

No.	Butanol isomers	Main application
1	1-butanol	Gasoline additive, solvents, plasticizers, chemical intermediate, cosmetics
2	2-butanol	Solvents, chemical intermediate, industrial cleaners, perfumes or in artificial flavors
3	iso-butanol	Gasoline additive, solvent and additive for paint, industrial cleaners, ink ingredient
4	tert-butanol	Gasoline additive for octane booster and oxygenate; intermediate for MTBE, ETBE, THBP; denaturant for ethanol; solvent

Table 2. The main application of butanol isomers. Ref. [7]

This work presents a novel way of using alcohols and pure vegetable oil as fuels for a diesel engine. It was shown the possibility of use of higher alcohols as a solvent for straight vegetable oil (the mixture was named BM). Such a mixture, after getting the density similar to the density of diesel fuel, was mixed with diesel fuel (D) giving biomixdiesel (BMD). For BMD preparation was used the n-butanol and iso-amyl (by-product of ethanol fermentation) as an alcohol, rapeseed oil and conventional diesel fuel. Another biofuels as an example of second generation were obtained by nonoxidative thermal/pyrolytic cracking of straw (nearly 200 microns) followed by biooil hydrotreating. The last one- HVO diesel was obtained by catalytic hydroconversion of vegetable oil mixtures. Hydrotreated vegetable oils do not have the harmful effects of ester-type biodiesel fuels, like increased NO_x emission, deposit formation, storage stability problems, more rapid aging of engine oil or poor cold properties. HVOs are straight chain paraffinic hydrocarbons that are free of aromatics, oxygen and sulfur and have high cetane numbers. All three biofuels were examined according to EN-590:2009 standard [8]

4.1. Experimental and results

4.1.1. Assessment of the physico-chemical properties of the BMD biofuel

To assess the quality of biofuel containing components such as higher alcohol and rapeseed oil were prepared two experimental blends based on previous works [9, 10]. Major scientific works regards diesel-biobutanol mixtures [11] and minor triple mixtures with vegetable oil. The main component of mixtures was conventional diesel (in 80% vol.), made up to 100% with two mentioned above biocomponents. Experiment was carried out with two higher alco-

hols: n-butyl alcohol and iso-amyl alcohol. First were prepared blends consisting of selected alcohol and rapeseed oil in a ratio of 2:1 (BioMix), and then received blend was introduced into diesel fuel (D). Prepared samples are marked with symbols BMD-1 (with n-butanol) and BMD-2 (with iso-amyl alcohol). Mixtures of BMD-1 and BMD-2 were clear, without haze and sediment. New biofuels stored for several days at room temperature showed no features of separation. Diesel fuel used to compose biofuels met all quality requirements according to EN-590. Table 3 shows the basic features of diesel, and Table 4 compares properties of n-butyl alcohol and iso-amyl.

No.	Property	Result
1.	Cetane number	53,0
2.	Density at 15°C, kg/m ³	836,2
3.	Flash point, °C	63
4.	Carbon residue (on 10% distillation residue), %(m/m)	<0,10
5.	Distillation	39,5
	%(V/V) recovered at 250°C,	94,9
	%(V/V) recovered at 350°C,	266,7
	50%(V/V) recovered at , °C	350,5
	95%(V/V) recovered at , °C finish boiling point, °C	362,4

Table 3. Basic physico-chemical properties of diesel fuel

No.	Property	n-butyl alcohol	iso-amyl alcohol
1.	Density at 20 °C, kg/m ³	810	814
2.	Boiling point °C	117	138
3.	Flash point, °C	30	43

Table 4. Properties of n-butyl alcohol and iso-amyl alcohol

Prepared biofuels samples were examined according with regulatory needs of the standard EN 590. The results got are presented in Table 5 and Table 6.

No.	Property	Test method	Result		Limits EN 590
			BMD-1	BMD-2	
1	Cetane number	EN ISO 5165	44,4	45,0	min 51,0
2	Cetane index	EN ISO 4264	46,8	46,9	min 46,0
3	Density at 15°C, kg/m ³	EN ISO 12185	837,9	837,8	820,0 – 845,0
4	Polycyclic aromatic hydrocarbons, % (m/m)	EN 12916	1,9	1,9	max 11
5	Sulfur content, mg/kg	EN ISO 20846	5,7	5,7	max 10,0
6	Flash point, °C	EN ISO 2719	< 40,0	45,0	above 55
7	Carbon residue (on 10% distillation residue), %(m/m)	EN ISO 10370	0,48	0,27	max 0,30
8	Ash content, %(m/m)	EN ISO 6245	< 0,001	< 0,001	max 0,01
9	Water content, mg/kg	EN ISO 12937	110	110	max 200
10	Total contamination, mg/kg	EN 12662	<6,0	9,0	max 24
11	Copper strip corrosion (3 h at 50°C)	EN ISO 2160	class 1	class 1	class 1
12	Lubricity, corrected wear scar diameter (wsd 1,4) at 60°C, µm	EN ISO 12156-1	281	339	max 460
13	Viscosity at 40°C, mm ² /s	EN ISO 3104	2,710	2,827	2,00 – 4,50
14	Distillation	EN ISO 3405			
	%(V/V) recovered at 250°C,		47,3	44,2	< 65
	%(V/V) recovered at 350°C,		261,9	261,4	min 85
	50%(V/V) recovered at , °C		349,9	349,7	max 360
	95%(V/V) recovered at , °C				
	Finish boiling point, °C				
15	Fatty acid methyl ester content, FAME, %(V/V)	EN 14078	< 1,6	< 1,6	max 7,0
16	Oxidation stability, g/m ³	EN-ISO 12205	66	39	max 25

Table 5. Comparison of the results of biofuels BMD-1 and BMD-2 according to EN 590

No.	Property	Test method	Result		Climate-related requirements		
			BMD-1	BMD-2	Summer	Spring and autumn	Winter
1	Cold filter plugging point, CFPP, °C	EN 116	-21	-21	max 0	max -10	max -20
2	Cloud point, °C	ISO 3015	-6	-6	Limits only for arctic climate		

Table 6. Comparison of low-temperature properties of fuels BMD-1 and BMD-2 to the climatic requirements of EN 590

Comparing the results of biofuels BMD-1 and BMD-2 with quality requirements for diesel fuel it is worth to note that most of the parameters meet these requirements; however, several features deviate from the normative requirements. Cetane number is similar on both biofuels and amounted 44.4 and 45.0 for BMD-1 and BMD-2, respectively and is lower than the required standard that is at least 51 units. This is because of sharing 20% biocomponents. Rapeseed oil has a cetane number about of 40-50 units and a small addition to the diesel fuel should not drastically reduce the cetane number. However alcohol is usually characterized by a high octane number, which is good in case of composing gasoline, added to the diesel fuel can degrade the diesel engine start-up parameters.

The process of starting engine and his operation is also influenced by fractional composition of fuel, particularly temperature distillation of 50% by volume of fuel, T_{50} . The lower the temperature T_{50} the easier the start, but at too low temperature ignition characteristics fuel property is worsen - cetane number decreases.

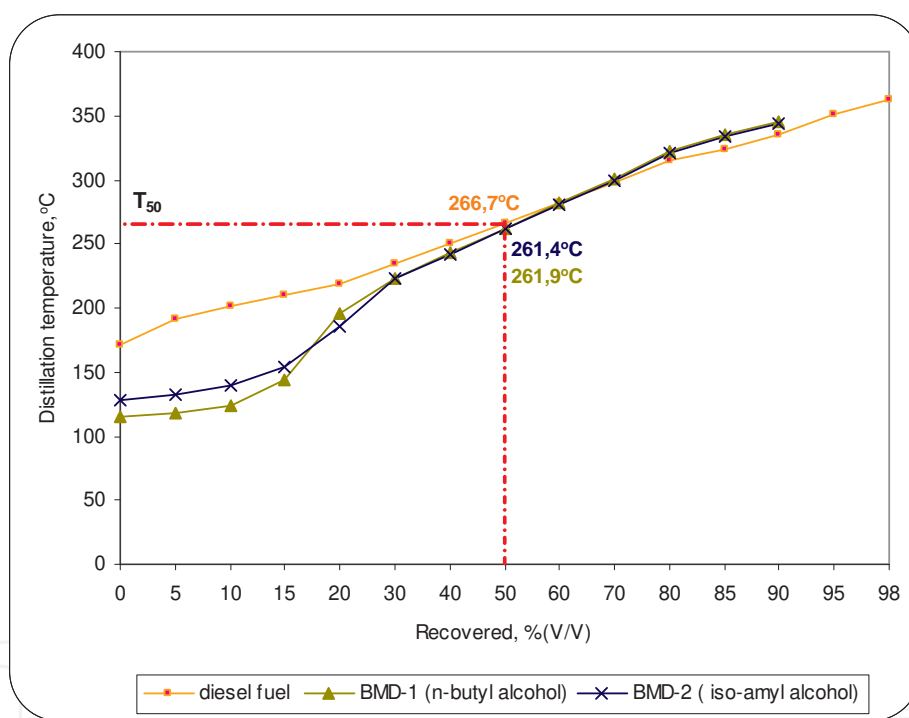


Figure 5. Distillation of diesel fuel, biofuels BMD-1 and BMD-2 comparison.

Figure 5 shows the distillation composed of biofuels compared to diesel. T_{50} temperatures for the tested biofuels BMD-1 and BMD-2 are similar and amounted 261.9 and 261.4°C, respectively and slightly differs from the T_{50} for diesel fuel - 266.7 °C. The temperature range from about 250 °C to 340 °C showed the curves of the distillation of biofuels and diesel fuels are similar. The beginning of the distillation is unusual for sample BMD-1, which begins to boil in temperature 114°C, and BMD-2 at a temperature of 127°C. Alcohol is distilled off first at the early stage of the distillation followed by hydrocarbons and rapeseed oil. Distillation points out the biofuel combustion in the engine can be irregular.

Contributing alcohol in biofuel can cause the decline of ignition temperature. Flash point of biofuel blend is determined by its flash point of the lightest ingredient, which n-butyl alcohol and iso-amyl alcohol was 37 °C, and 45 °C, respectively. Safety in transport and storage of diesel fuel requires the ignition temperature be higher than 55°C. Thus, the fuel with a lower flash point cannot be marketed and sold, could possibly be used as fuel for selected fleets.

The tested biofuel has a high tendency to form sludge and carbon deposits, which is determined by the remains of carbon residues. BMD-1 sample carbon residue value exceeds regulatory requirements by 60%, for the BMD-2 approaches the limit. Biofuel with such high carbon residues will cause form deposits in the combustion chamber, the valves, piston rings and injector parts. Sediments and carbon residues can change conditions of heat exchange, worsen the quality of fuel atomization and eventually can lead to immobilization of the vehicle.

Both samples of biofuels have good low temperature properties (Table 6). Tested cold filter blocking temperature for both samples amounted -21 °C, and the cloud temperature -6°C and slightly was different from the similar parameters of diesel. Low-temperature stability studies have shown that biofuel stored for several days at a temperature of about-10°C becomes cloudy, but segregation was not observed and had the liquid properties. Viscosity of biofuels is correct and for BMD-1 and BMD-2 were 2.710 mm²/s and 2.827 mm²/s, respectively. Proper fuel viscosity is important, because directly influence on the quality of atomization and combustion. Other biofuels quality parameters measured; do not differ from the normative requirements. The sulfur and water content, polycyclic aromatic hydrocarbons, solids, ash residue, lubricity and density are within the limits. Please note that this biofuel may not be used for long-term storage, it is unsatisfactory because of their oxidation stability. The sludge after being marked with an accelerated aging process is large, about 2 times the standard requirements. It is therefore recommended product produced in small quantities, intended for fast using.

Tested biofuels BMD-1 and BMD-2 were assessed for regulatory quality requirements. It is difficult to clearly settle, which biofuel blends is better. Features such as low cetane number, low flash point, and atypical distillation limit the usefulness of both biofuels to power the diesel engines. Preliminary experiments should be continued for improvement to compose biofuels and carry out the procedure for selecting additives. It is necessary to increase the cetane number. The proper corrosion protection should be considered because of the presence of alcohol ingredient in biofuel. To introduce new BMD biofuels still needs much research and formula improvements.

4.1.2. Emission test for BMD fuel

Based on the physicochemical properties of biofuels BMD-1 and-2 for further test was selected BMD mixture with n-butanol only. Prepared under laboratory conditions mixtures of n-butanol with diesel fuel were examined on the chassis dynamometer. In the first step the rapeseed oil was mixed with butanol as such parts to obtain a mixture having a density similar to the density of diesel fuel. This mixture is denoted as a BM (BioMix). In the second

step this fuel (BM) was mixed with conventional diesel fuel (D) to get biomixdiesel (marked as a BMD). These fluids were mixed in the following parts:

- biomix (BM) 20 % v/v,
- diesel fuel (D) 80 % v/v,

giving fuel called as biomixdiesel (BMD20). In contrast to the mixture of ethanol with rape methyl ester and conventional diesel fuel, this mixture is homogeneous. The comparison of new fuel with requirements of the standard diesel fuel is presented in Table 7.

No.	Property	Test method	Results BMD20	Limits EN 590
1	Cetane number	EN ISO 5165	44,4	min 51,0
2	Cetane index	EN ISO 4264	46,8	min 46,0
3	Density at 15°C, kg/m ³	EN ISO 12185	837,3	820,0 – 845,0
4	Polycyclic aromatic hydrocarbons, %(m/m)	EN 12916	1,9	max 11
5	Sulfur content, mg/kg	EN ISO 20846	5,7	max 10,0
6	Flash point, °C	EN ISO 2719	< 40,0	above 55
7	Carbon residue (on 10% distillation residue), % (m/m)	EN ISO 10370	0,48	max 0,30
8	Ash content, %(m/m)	EN ISO 6245	< 0,001	max 0,01
9	Water content, mg/kg	EN ISO 12937	112	max 200
10	Total contamination, mg/kg	EN 12662	<6,0	max 24
11	Copper strip corrosion (3 h at 50°C)	EN ISO 2160	class 1	class 1
12	Lubricity, corrected wear scar diameter (wsd 1,4) at 60°C, µm	EN ISO 12156-1	281	max 460
13	Viscosity at 40°C, mm ² /s	EN ISO 3104	2,710	2,00 – 4,50
14	Distillation	EN ISO 3405		
	%(V/V) recovered at 250°C,		47,3	< 65
	%(V/V) recovered at 350°C,		349,9	min 85
95%(V/V) recovered at , °C			max 360	
	Finish boiling point, °C			
15	Fatty acid methyl ester content, FAME, %(V/V)	EN 14078	< 1,6	max 7,0
16	Oxidation stability, g/m ³	ISO 12205	66	max 25

Table 7. Properties of investigated fuel

The investigations of fuel properties under working conditions were carried out with a modern diesel engine on the chassis bed dynamometer in the NEDC test (New European Driving Cycle). This test consists of two parts: UDC (Urban Driving Cycle) and EUDC (Extra Urban Driving Cycle). The first part represents urban driving, in which a vehicle is started in the morning (after being parked all-night) and driven in stop-and-go rush hour traffic. The maximum speed is 50 km/h. The second part represents extra-urban driving with a maximum speed of 120 km/h.

Main parameters of car engine (power, torque, specific fuel consumption) and the main exhaust gas ingredient (in this case CO, CO₂, NO_x, total hydrocarbons-THC, particulate matter-PM, THC+NO_x) and fuel consumption is evaluated and explain here in g/km. In Table 8 obtained are presented results.

Emission	Fuel	Pollutants, g/km						Fuel consumption
		THC	CO	CO ₂	NO _x	THC+NO _x	PM	g/km
UDC	BMD 20	0,1000	1,3900	163,6367	0,1933	0,2967	0,0042	6,2467
UDC	Diesel	0,0833	1,3400	162,1367	0,2000	0,2867	0,0053	6,1933
EUDC	BMD 20	0,0100	0,0367	118,7567	0,2133	0,2267	0,0064	4,4667
EUDC	Diesel	0,0100	0,0467	114,5500	0,1600	0,1700	0,0078	4,3167
NEDC	BMD 20	0,0467	0,5367	135,2933	0,2067	0,2533	0,0056	5,1233
NEDC	Diesel	0,0367	0,5233	132,1100	0,1767	0,2167	0,0069	5,0100

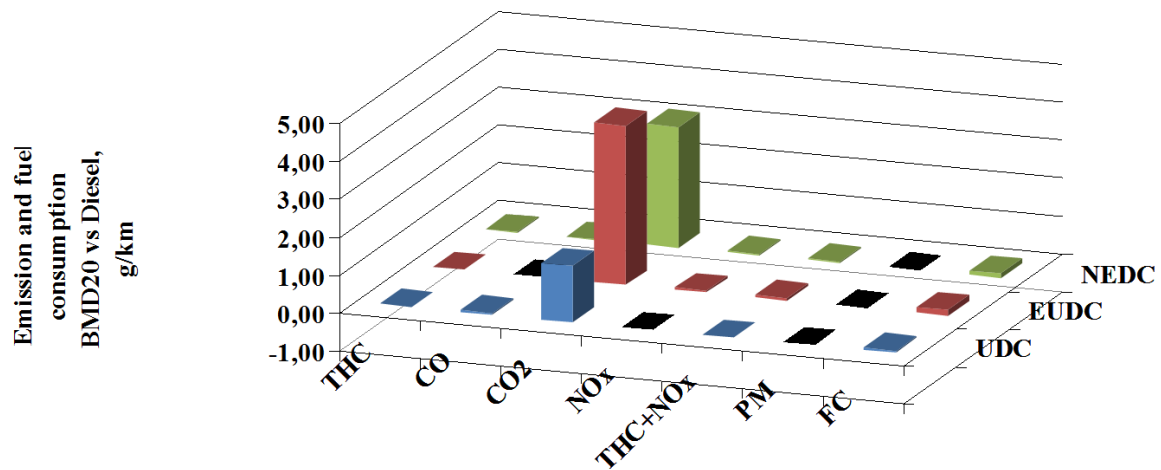
Table 8. Examples of investigations results on the car test chassis bed by NEDC test load and by fueling the engine with examined BMD20 and standard Diesel fuel

Supplying the car engine with different fuel leads to a diversity of parameters of the engine. But the differences are not so significant. Differences between the results got for the tested BMD20 fuel and diesel fuel are presented below. The results of investigations of pollutant emission are presented here as the results got by fueling the engine with the conventional diesel fuel. The results expressed in g/km are shown in Table 9.

Test	Pollutants						Fuel consumption
	THC	CO	CO ₂	NO _x	THC+NO _x	PM	g/km
UDC	0,0167	0,0500	1,5000	-0,0067	0,0100	-0,0011	0,0533
EUDC	0,0000	-0,0100	4,2067	0,0533	0,0567	-0,0014	0,1500
NEDC	0,0100	0,0133	3,1833	0,0300	0,0367	-0,0013	0,1133

Table 9. Relative changes of pollutants emission and fuel consumption by fueling the car engine with BMD20 and Diesel fuel

The results are presented in graphical form as well on the Figure 6.



Pollutants and fuel consumption (FC)

Figure 6. The differences in emission and fuel consumption during fueling the car engine with BMD20 and Diesel fuel recorded during the test bed investigation of the car

In all phases of the test, during fueling the engine with BMD20, the increase of the carbon dioxide (CO₂) is observed. Emissions of other toxic components and fuel consumption don't differ from those when the engine is fueled by conventional fuel.

Small differences in the results are becoming clear when relative changes are expressed in percentages. The results of this analysis are presented in Table 10 and pictured on Figure 6.

Test	Pollutants						Fuel consumption
	THC	CO	CO ₂	NO _x	THC+NO _x	PM	
	%						
UDC	20,00	3,73	0,93	-3,33	3,49	-20,75	0,86
EUDC	0,00	-21,43	3,67	33,33	33,33	-18,38	3,47
NEDC	27,27	2,55	2,41	16,98	16,92	-18,93	2,26

Table 10. Relative changes of pollutants emission and fuel consumption during engine fueling with BMD20 and Diesel fuel

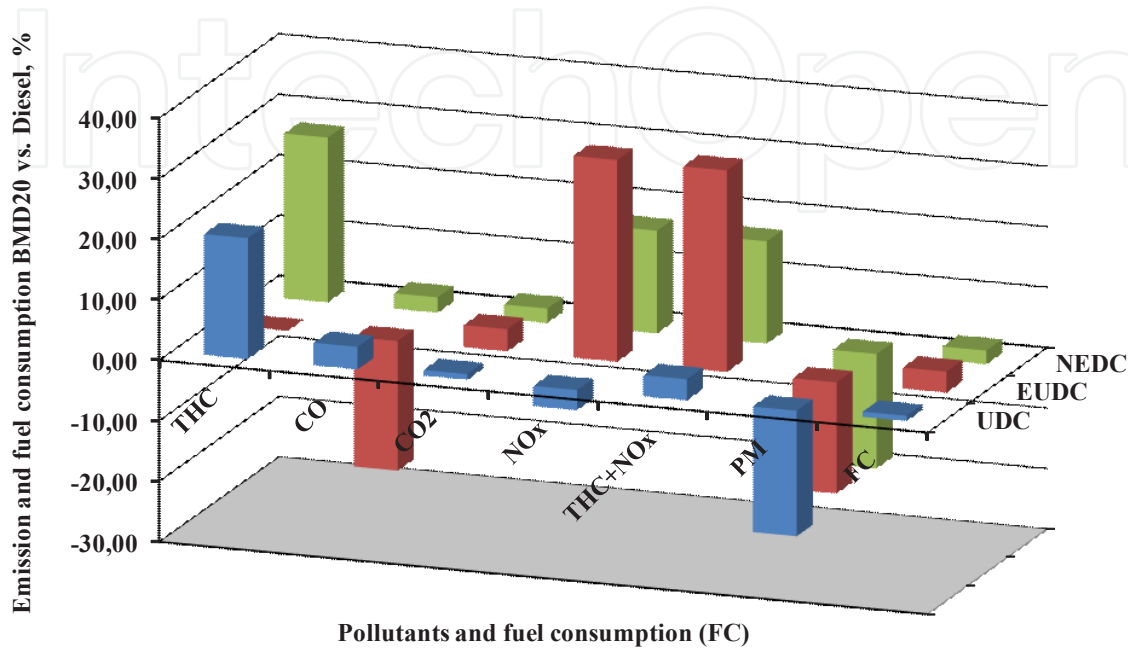


Figure 7. Relative changes of emissions and fuel consumption of the car engine fueled with BMD20 and diesel oil.

During fueling the car engine with the BMD20, the fuel consumption is not significantly different (Table 10) from that noted for Diesel fuels. The differences in emitting pollutants were dependant on the test phase (UDC or EUDC). For example the emission of THC in the EUDC phase is the same as that recorded for diesel oil, but the quantity of THC grows in UDC phase. Thus in full test (NEDC) the relative emission of THC grows. Other trend is observed for carbon monoxide (CO) emissions. In the UDC phase emission of CO slightly increases, in the EUDC phase significantly decreases (more then 21%) so, therefore in the NEDC test the emission of CO slightly grows. The emissions of NO_x grows, first, in the EUDC phase. This is understandable if we take into consideration the engine load – the higher combustion temperatures (peaks) in this phase favor to form nitrogen oxides. In the same phase the emission of THC neither increases nor decreases, so in the entire test, the summary quantity of THC+NO_x increases (the emission of THC increases in the UDC phase). It is important that, the PM emission decreases in all phases of test. The decrease is significant, about 21% in the UDC phase and more than 18% in the EUDC phase.

Results were obtained without any change of engine control parameters (the engine control parameters were the same as during supplying the engine with conventional diesel fuel). It seems that after optimization of engine control features the results would be much better.

4.2. Assessment of the physico-chemical properties of the synthetic diesel fuel obtained by biomass depolymerization

Biomass depolymerization is a process for the reduction of complex organic materials. Under pressure and heat, long chain polymers of hydrogen, oxygen, and carbon decompose into biocrude oil. The depolymerization process for fuel production from organic materials takes two forms, thermal only or with assisted catalysts usually aluminum silicate type doped with non-precious metals for example Na, Ca. Although the thermal depolymerization has been understood for some time, human-designed processes were not efficient enough to serve as a practical source of fuel because more energy was required than was produced. Research breakthroughs in the 1980's led to efficient processes that were eventually commercialized [12, 13]. Green diesel was obtained by non-oxidative thermal/pyrolytic cracking of straw (around 200 micron) followed by biooil upgrading in hydrogen process. Fuel had a clear yellow color and has been tested in accordance with EN 590, one parameter not included in the specification standard (iodine number) was checked because of some doubts about non-saturated hydrocarbons content. It's known that if these hydrocarbons are present in significant quantity in the fuel, than it will cause polymerization and change the physico-chemical properties of the fuel.

No.	Property	Test method	Results	Limits EN 590
1	Cetane number	EN ISO 5165	58,6	min 51,0
2	Density at 15°C, kg/m ³	EN ISO 12185	815	820,0 – 845,0
3	Polycyclic aromatic hydrocarbons, %(m/m)	EN 12916	0,8	max 11
4	Sulfur content, mg/kg	EN ISO 20846	120	max 10,0
5	Flash point, °C	EN ISO 2719	43,5	above 55
6	Water content, mg/kg	EN ISO 12937	150	max 200
7	Viscosity at 40°C, mm ² /s	EN ISO 3104	3,45	2,00 – 4,50
8	Iodine number , gl/100g		8	

Table 11. The results of synthetic biofuel (Green diesel) according to EN 590.

Discussion of above parameters in Table 11 are presented below

- Cetane number - the standard EN 590 required a minimum cetane number- 51, fuels with higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed. Generally the engine is "soft", it's easier on the speed falls, helps to start the engine, slows pollution injector nozzles, limits the participation of PM in the exhausted gas and reduces engine noise. In the tested fuel cetane number was 58.8.
- The content of polycyclic aromatic hydrocarbons (PAHs) - in the test fuel PAH content amounted 0.8 and was significantly below the maximum value 11
- Density at 15 °C - has been marked below the lower limit of the density of 820 kg/m³ and amounted 818 kg/m³ for tested fuel. It could be adjusted by distillation the light fraction.
- Water content - the test fuel contained 170 mg/kg of the water and the result was below the maximum value of 200 mg/kg.
- Flash point - It was found the ignition temperature of the test fuel is below the value of 55 °C and was 43.5 °C, which was caused by the presence of a light fraction of the fuel.

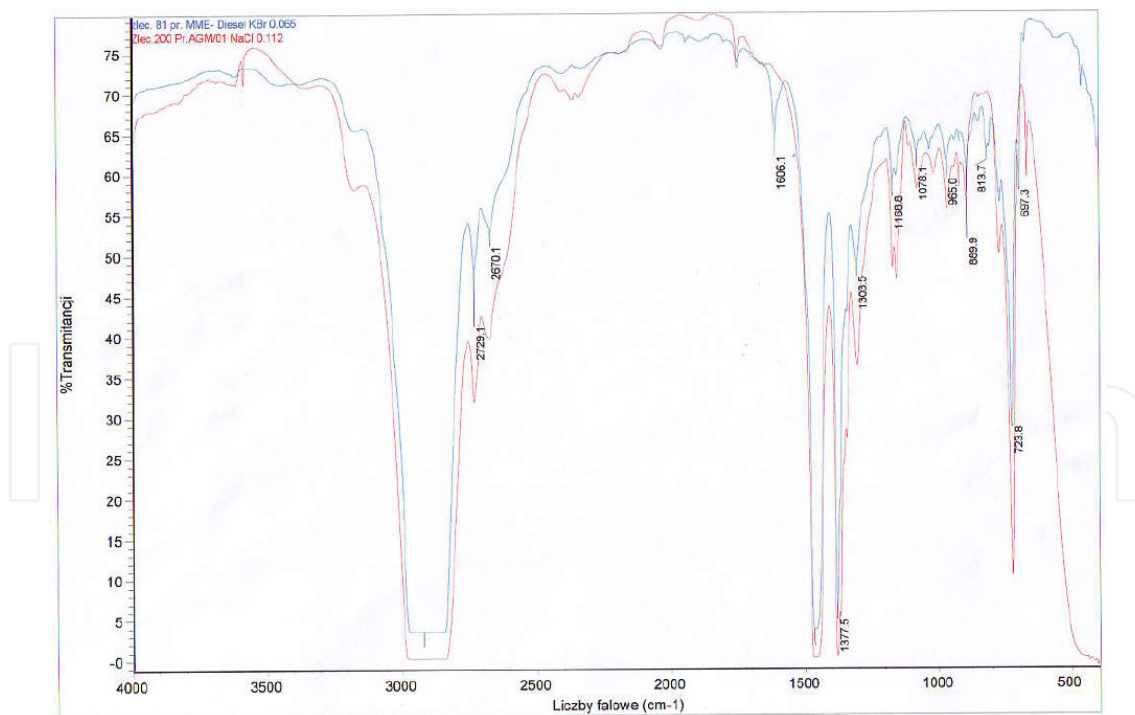


Figure 8. The comparison of IR spectrums of commercial diesel oil (red spectrum) and a sample of the green diesel (blue spectrum).

The other limits of EN 590 were not tested as the fuel is still under technological development but above results are promising. Sulfur content in fuel after preliminary hydrodesulfurization process significantly exceeded specification value of 10 ppm. Infrared spectrum of green diesel was compared with spectrum of commercial diesel oil (Figure 8).

IR spectrums of analyzed commercial diesel and green diesel were similar in appearance, what shows that both fuels contain similar chemical groups. The spectrums show little difference, that reveals the presence in the spectrum of green diesel peaks at wave number 1606 cm^{-1} and around 814 cm^{-1} . These bands can be attributed to the unsaturated bonding (alkenes, aromatics). The spectrum has also characteristic bands of the groups - CH_3 and - CH_2 alkanes, including alkanes having carbon numbers greater than four, wave number band around 723 cm^{-1} . The lower band intensity in comparison with the spectrum of commercial diesel may point out a lower content of long-chain hydrocarbon sample. Analyzes mark the tested green diesel could meet the needs for diesel EN 590 if the level of sulfur below 10 ppm, increased the density and required temperature of ignition would be achieved.

4.3. Assessment of the physico-chemical properties of the synthetic diesel fuel – HVO diesel

Hydrotreating of vegetable oils or animal fats is an alternative to esterification for producing FAME. Hydrotreated vegetable oils do not have the harmful effects of ester-type biodiesel fuels, like increased NO_x emission, storage stability problems and poor cold properties. HVOs are straight chain paraffinic hydrocarbons that are free of aromatics, oxygen and sulfur and have high cetane numbers. Examined HVO diesel oil was obtained at demonstration plant by catalytic hydroconversion of straight rapeseed oil. Selected features of HVO diesel are presented in Table 12.

Characteristics presented in Table 12 confirmed superior properties of HVO diesel compared with commercial diesel oil. It does not contain polynuclear aromatic and has low sulfur content. HVO diesel does not exceed the limit values for water. This product has a low tendency to foam, test parameters meet the requirements of EN 590 grade F. This means HVO diesel itself, without additives has excellent winter properties. Also the HVO diesel had a high resistance to oxidation which 2.5 times exceeds the needed normative values. During the HFRR test (High Frequency Reciprocating Rig, not presented here) was indicated the lubricant film produced by the sample is unstable, which is obvious at the early stage of the test. Typical diesel oil film thickness should exceed 90%, while in the HVO diesel case was only 78%. This shows the inadequate lubricating properties of the sample and that a lubricating additive is necessary. HVO is based on the hydrotreating, which could be used not only to convert plant-derived oils such as soybean, rapeseed, and palm, but also non-edible oils, such as *Jatropha* and algal oils as well as animal fats [14]. UOP and Eni have developed the Ecofining™ based on conventional hydroprocessing technology to produce diesel-fuel ("green diesel") [15] or jet-fuel [16]. Similar technologies have been developed by Neste Oil (NExBTL Renewable Diesel) [17] and Petrobras (H-Bio process) [18].

No.	Property	Test method	Results	Limits EN 590		
1	Cetane number	EN ISO 5165	"/> 76	min 51,0		
2	Cetane index	EN ISO 4264	91,8	min 46,0		
3	Density at 15°C, kg/m ³	EN ISO 12185	776,5	820,0 – 845,0		
4	Polycyclic aromatic hydrocarbons,	EN 12916		max 11		
	mono, %(m/m)				< 6,0	
	di+, %(m/m)				< 1,0	
	tri+, %(m/m)	< 0,1				
5	Sulfur content, mg/kg	EN ISO 20846	< 3	max 10,0		
6	Flash point, °C	EN ISO 2719	71	above 55		
7	Carbon residue (on 10% distillation residue), %(m/m)	EN ISO 10370	< 0,01	max 0,30		
8	Ash content, %(m/m)	EN ISO 6245	< 0,001	max 0,01		
9	Water content, mg/kg	EN ISO 12937	20	max 200		
10	Total contamination, mg/kg	EN 12662	1	max 24		
11	Copper strip corrosion (3 h at 500C)	EN ISO 2160	class 1	class 1		
12	Lubricity, corrected wear scar diameter (wsd 1,4) at 60°C, µm	EN ISO 12156-1	313	max 460		
13	Viscosity at 40°C, mm ² /s	EN ISO 3104	2,609	2,00 – 4,50		
14	Viscosity at 50°C, mm ² /s	EN ISO 3104	2,183	---		
15	Distillation	EN ISO 3405				
	Initial boiling point, oC				190,4	--
	5 %(V/V) recovered at , oC				225,4	--
	10 %(V/V) recovered at , oC				242,6	--
	20 %(V/V) recovered at , oC				259,0	--
	30 %(V/V) recovered at , oC				267,3	--
	40 %(V/V) recovered at , oC				271,8	--
	50 %(V/V) recovered at , oC				274,9	--
	60 %(V/V) recovered at , oC				277,6	--
	70 %(V/V) recovered at , oC				280,3	--
	80 %(V/V) recovered at , oC				283,8	--
	90 %(V/V) recovered at , oC				288,2	--
	95 %(V/V) recovered at , oC				291,9	--
Finish boiling point, oC	306,1	max 360				
Recovery, %(V/V)	98,3	--				
Residue, %(V/V)	1,2	--				
%(V/V) recovered at 250oC	13,5	< 65				
16	CFPP, oC	EN 116	-19	*		
17	Cloud point, oC	ISO 3015	-18	*		
18	Pour point, oC	ISO 3016	-21	--		
19	Oxidation stability, g/m ³	ISO 12205	10,5	max 25		

No.	Property	Test method	Results	Limits EN 590
20	Heating value	PN-C-04062	43,7	--
	- lower, MJ/kg		46,8	--
	- higher, MJ/kg			
21	Composition:	ASTM D5291	14,7	--
	- hydrogen, %(m/m)		85,5	--
	- carbon, %(m/m)		0,1	--
	- nitrogen, %(m/m)			

*- depending on the climatic requirements

Table 12. Comparison of the results of synthetic biofuel (HVO diesel) with EN 590.

5. Conclusions

Blends of n-butanol, rapeseed oil and conventional diesel fuel showed promising results and what is most important the biofuel was prepared by simple blending of biocomponents with diesel oil. Nearly the same fuel consumption compared with diesel oil was noted and the emissions of main toxic compounds including PM decreased. The other two second generation Green and HVO goals met main requirements of standard specification EN 590. The use of biofuels in transport depends on few causes like: availability of raw materials, low cost production of biofuels, low selling price, the calorific value, high quality and compliance with the needs of fuels for automotive engines.

Synthetic hydrocarbon fuels, considered as the best solution replacements of fossil fuels, may be obtained by biomass gasification followed by FT process, biomass pyrolysis towards biocrude oil followed by catalytic upgrading, by novel hydrothermal upgrading (HTU) getting biocrude with low content of oxygen for further upgrading. Currently, because of promoting the use of biofuels, diesel is a mixture of petroleum hydrocarbon fractions, and fatty acid methyl esters (FAME). On the market there are the most common fuel oils with a content of 7 and 20% vol. FAME. The research results has shown that diesel fuel can be formulated using other biocomponents like higher alcohols such as biobutanol, pure vegetable oil. Biofuels should have a high cetane number, high calorific value, normal rheological properties and proper viscosity. Also important is the fuel spray and its evaporation in the engine. Biofuel quality with many of biocomponents should be thoroughly investigated, because the individual components may interact with fuel system materials. For example support of proper emulsifiers are needed in diesel fuel containing ethanol, because it allows to preserve of uniformity of fuel at low temperatures. Synthetic biohydrocarbons are chemical compounds with similar physico-chemical properties characteristic for middle distillates used in the production of petroleum diesel. By changing the conventional fuel formula one have to be aware of the requirements posed by modern fuels car engines, in this respect must be maintained full compliance requirements.

Biofuels considered in this work were compared with diesel oil from the point of view of various physico-chemical limits included in EN 590: 2009 standard and the new technical specification under development by CEN (European Committee for Standardization) under the title: Automotive fuels - Paraffinic diesel fuel from synthesis or hydrotreatment- requirements and test methods, and based on recommendations of the world's car companies members of the Committee for the Affairs of the Worldwide Fuel Charter (WWFC). Figure 9 summarized the technologies used for production biofuels discussed in this chapter. Some of them like HVO diesel (NExBTL) are already commercially available, and others are at demo stage.

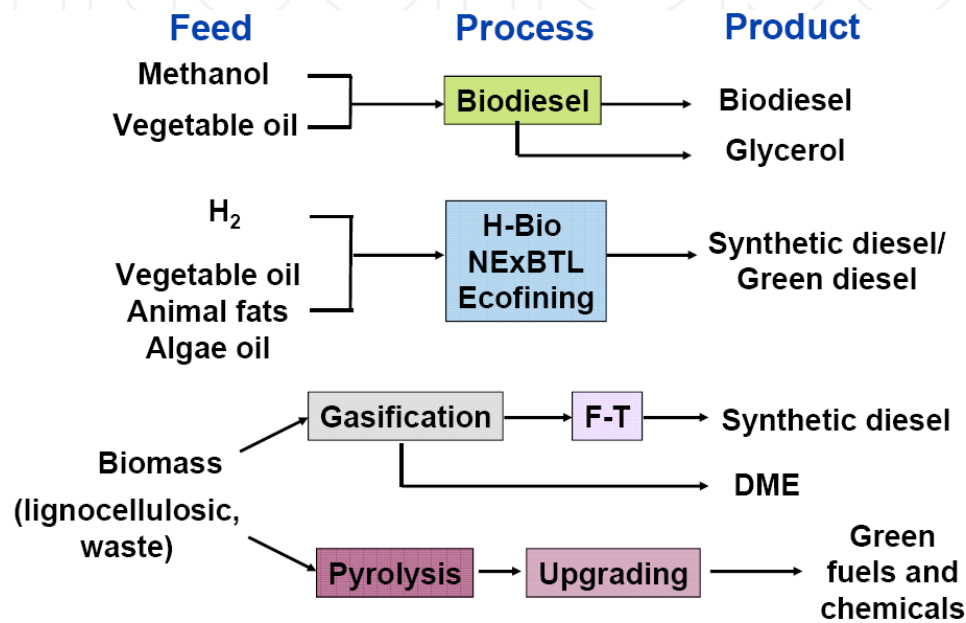


Figure 9. Current (green rectangle) and future (the blue and pink rectangles) most promising ways for producing of second generation biodiesel [19]

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