



LIQUID BIOFUELS OF THE FIRST AND SECOND GENERATION – THE METHOD OF PREPARATION AND APPLICATION

Ewa Rostek

*Motor Transport Institute, Centre of Materials Testing and Mechatronics
Jagiellońska Street 80, 03-301 Warsaw, POLAND
tel. +48 22 438 53 25, fax: +48 22 438 54 01
ewa.rostek@its.waw.pl*

Krzysztof Biernat

*Automotive Industry Institute, Department of Fuels and Renewable Energy
Jagiellońska Street 55, 03-301 Warsaw, POLAND
phone.: +48 22 7777 225, fax.: +48 22 7777 020
kbiernat@pimot.org.pl*

Abstract

Sustainable economic and industrial growth requires safe, sustainable energy resources. Unfortunately, first-generation biofuels are fuels produced from organic matter, which can also be used to produce food or feed. Only second-generation fuels are based on the need for sustainable development and are produced using processes such as pyrolysis, Fischer-Tropsch synthesis or hydrotreating. This paper presents the method for obtaining the first- and second-generation biofuels. Also discussed the possibility of their application.

Keywords: *biomass, liquid first- and second-generation biofuels, biodiesel, bioethanol, pyrolysis*

1. Introduction

Under the name of biofuels lie all fuels that are produced from biomass. As biomass and, in accordance with the applicable European Directive 2009/28/EC [4], it is biodegradable fraction of products, waste and residues of biological origin from agriculture, forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industrial and urban areas. For the production of biofuels used primarily sugar beets, grains, corn, sugarcane, oilseeds such as rapeseed, palm or jatropha and straw and wood waste, sewage sludge, compost, garbage or food scraps. Biomass plant, from which biofuels are produced, is a storehouse of solar energy.

The use of biofuels is a way to reduce imports and consumption of fossil fuels and reduce carbon dioxide emissions into the atmosphere [8,15]. This is achieved through a closed loop cycle of carbon dioxide that is emitted during the combustion of biofuels, but also absorbed by plants during photosynthesis.

2. First-generation liquid biofuels

First-generation biofuels are fuels produced from organic matter that can be used also for

production of food or feed. First-generation biofuels are produced using conventional methods do not require large energy inputs (such as fermentation, esterification). The use of raw materials such as sugar cane, wheat or corn sugar beets, which can produce food for human and pet food makes its production competes with food production and do not always have enough material for both processes [10]. Tab. 1. shows the transformation of biomass into first-generation liquid fuels.

Tab. 1. The transformation of biomass into first-generation liquid fuels

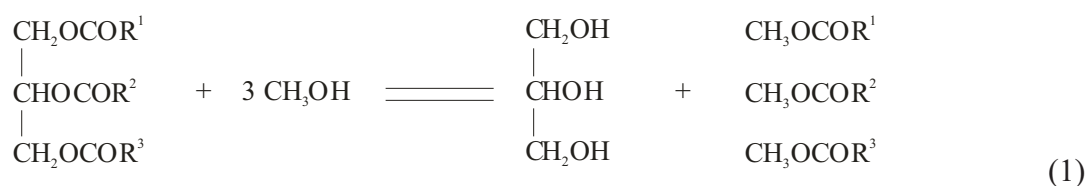
	BIOMASS		
conversion processes	cold pressing and extraction	transesterification	enzyme hydrolysis
			fermentation
product	pure vegetable oils (PVO)	Biodiesel	Bioetanol

2.1. Conversion processes for first-generation liquid biofuels

Biodiesel (rapeseed oil methyl esters (RME) or methyl esters (FAME) and ethyl (FAEE), higher fatty acids other oil crops) is obtained by cold-pressing process, the extraction and transesterification [12]. Esterification can be carried out in a homogeneous or heterogeneous phase. Raw materials for the transesterification of vegetable oils are homogeneous, used vegetable oils, fatty acids, animal fat and methanol or ethanol. The catalyst may be alkaline (sodium hydroxide, potassium hydroxide) or acid (sulfuric acid).

As a result of esterification of fatty acids are derived fatty acid methyl esters [12]. It was created in the process of the concentration of the glycerin can be sold as a technical glycerin (80%), which is widely used the pulp industry, the synthesis of dyes, nitroglycerin, dynamite, and also in pharmaceutical and food industries. The resulting fatty acid methyl esters are subjected to neutralization treatment and drainage. They can then be formulated into diesel or, after processing with special additives, used as a self-contained biofuel.

Esterification in a heterogeneous phase with a catalyst, which is zinc oxide on alumina allows to obtain fatty acid methyl esters of high purity and pharmaceutical grade glycerine. Esterification process is as follows:



The solid acid catalyzed biodiesel production by simultaneous esterification and transesterification of low quality oil containing high FFA (free fatty acid) was performed by Kulkarni et al. [9]. The reaction mechanism of simultaneous esterification and transesterification using Lewis acid takes place between free fatty acids (RCOOH) and methanol (CH₃OH) whereas transesterification takes place between triglyceride (RCOOR') (taken as representative of triglycerides in this case) and methanol adsorbed on acidic site of catalyst surface. The interaction of the carbonyl oxygen of FFA or monoglyceride with acidic site of the catalyst forms carbocation. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate. During esterification the tetrahedral intermediate eliminates water molecule to form one mole of ester (RCOOCH₃). The transesterification mechanism can be extended to tri- and di-glyceride. It is well

known that transesterification is a stepwise reaction. In the reaction sequence the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and glycerol when tri-, di- and monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester (RCOOCH_3) in each step. In cases, esterification and transesterification produce methyl ester, the same final product. Also the catalyst is regenerated after the simultaneous esterification and transesterification reactions. Use of excess alcohol favors forward reaction and thus maximizes the ester yield [9].

The speed of the above reaction is dependent on process temperature, pH and substrate quality. The advantages of this type of fuel are very good lubricating properties and the lack of sulfur in the flue gas, and the disadvantages: the possibility of dissolving the seals and hoses made of certain types of rubber and plastic, not very good low temperature properties, and problems with the proper metering of fuel to the engine which is connected with the changing of some physical properties of esters with increasing temperature.

Bioethanol is ethanol derived from plant products containing sugar (sugar cane, wheat, sugar, fruit, juice, palm, etc.) or starch (wheat, barley, rice, corn, potatoes, cassava) can be used as fuel in specially adapted engines or the as an additive to gasoline [14]. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ has in its structure, in addition to carbon and hydrogen, the oxygen atom, so that addition of ethanol to gasoline increases the octane of fuel and reduces the concentration of hydrocarbons and carbon monoxide in the exhaust.

Ethanol production relies mainly on the fermentation and distillation. Production of fuel in this way carries with it high costs of production. Reduce production costs can be achieved using other substrates such as cellulosic wastes (lignocellulosic) - fuel derived from this process is the second-generation biofuels.

Basically, for the production of ethanol by fermentation in anaerobic conditions, are used by enzymes produced in yeast. The enzymatic hydrolysis proceeds in two steps. Chemical structure of starch consists of long chain polymer of glucose. The macromolecular starch cannot be directly fermented to ethanol by conventional fermentation technology. The macromolecular structure first broke down in to simpler and smaller glucose. In this process, starch feedstocks are grounded and mixed with water to produce a mash typically contained 15–20 % starch. The mash is then cooked at or above its boiling point and treated subsequently with two enzyme preparation. The first enzyme hydrolyzes starch molecules to short chains to glucose. The first enzyme is amylase, amylase liberates "maltodextrin" ligosaccharides by liquefaction process. The dextrin and oligosaccharides are further hydrolyzed by enzyme such as pullulanase and glucoamylase in a process known as saccharification. Saccharification converts all dextrans to glucose, maltose and isomaltose. The mash is then cooled to 30 °C and yeast is added for fermentation [11].

For first-generation liquid biofuels are among the so-called PVO - pure vegetable oils - pure vegetable oils obtained from cold pressing process and the extraction of oilseeds. These oils can be used both as a food and fuel applied directly (without esterification) cannot be used in normal diesel engines. Their destiny is determined mainly by quality. Those with better quality are used for cooking. In most vegetable oils are used as an intermediate for the production of biodiesel.

3. Second-generation liquid biofuels

Raw first generation, which is produced biofuels compete with food, so the ideal solution is cellulosic products such as wood, straw, long grass or wood waste. Fuels produced from these raw materials are called second-generation biofuels [6, 22]. They can meet the demand for fuel in a fair and environmentally beneficial way. The advantage of second generation biofuels is the ability to use the whole plant (including stem, leaves and peels), and not just its parts (for example grains), as is the raw material first generation. Second-generation fuel can also produce, with plants of

which no part is edible, such as jatropha and switchgrass (a type of tall grass growing in South America), cereal grains contain very little, waste from wood processing and pulp of the fruit.

The main problem in the production of second generation biofuels are processes to break down the structure of lignocellulose and the release of simple sugars.

3.1. Conversion processes for second-generation liquid biofuels

Liquid biofuels from biomass can be obtained through thermochemical processing or by chemical treatment. Thermo-chemical treatment comprises thermal decomposition and chemical transformation of substrates by the action of the temperature in the presence of various concentrations of oxygen. The advantage of thermal treatment in relation to the chemical is able to convert all organic ingredients, not just the polysaccharides, as is the case with chemical treatment [6]. Tab. 2. shows the transformation of biomass into liquid biofuels second generation.

Tab. 2. The transformation of biomass into second-generation liquid biofuels

	BIOMASS				
type of biomass	forest residue	lignocellulosic			vegetable oils, fatty acids
conversion processes	extraction of valuable chemical	gasification	pyrolysis	enzyme hydrolysis	hydrotreating
		condensation		fermentation	
				distillation	
product	Bio-oil	FT-oil	Bio-oil	Bioethanol	Green diesel

The physical transformation of raw materials into liquid biofuels include [14, 20]:

- mechanical extraction - crude vegetable oils are recovered from the oil seeds by applying a mechanical pressure using screw press (expeller). Screw press can be applied in two ways: prepressing and full pressing. In pre-pressing, only part of the oil is recovered and the partially de-oiled meal (cake with 18–20% oil) is further treated by solvent extraction. Combined pre-pressing and solvent extraction is commonly applied for oilseeds with high oil content (30–40%). Full pressing requires 95,000 kPa to squeeze out. as much oil as possible;

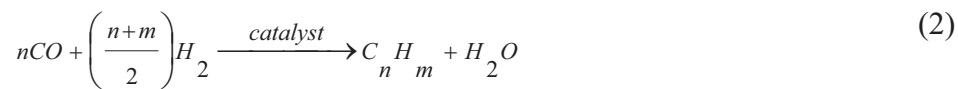
- briquetting of biomass - compaction of waste biomass from agricultural production or forestry residues takes place in closed chambers compression process combining crushing and maceration; Some time these two processes are combined, in pressing there is a close correlation of an increase in density with an increase in applied pressure in the early stage of compression, but the rate of increase in density fall rapidly as the density of pressed material approaches the density of water. There is no such close correlation of density change and degree of maceration, which may be chopping, grinding, and pulverizing. A coarse chopping of some materials may be as effective as ultrafine grinding.

- distillation - the most important method for extracting essential oil and relies on the evaporation of the more volatile constituents of a blend to separate them from the nonvolatile parts. Biomass is first crushed, then the distillation of essential oils evaporate and are condensed and condensed back into liquid.

Biomass can be converted into energy during the process of thermo-chemical or biological. Thermochemical processes include direct combustion, gasification, liquefaction and pyrolysis. Heating biomass in a lack of oxygen leads to the production of synthesis gas which consists primarily of hydrogen and carbon monoxide. This gas can either be burned directly or converted to other products of gas or liquid.

Direct combustion of biomass is to produce heat and leads to obtain carbon dioxide and water. Combustion of this should be done in well ventilated areas. Emissions of sulfur is in this case lower than for conventional fuels and combustion is at a level of 0.05 - 0.2% (m/m) [11].

Gasification of biomass is in the creation, in an atmosphere of oxygen, air or water vapor, the gas mixture (H₂, CO, CO₂, CH₄ and N₂) called synthesis gas or syngas and residual mineral in the form of ash. Gasification can be conducted in the presence of a catalyst at about 900 °C or without catalyst at a temperature of about 1300 °C. During the implementation process can also create by-products - tar. Syngas can be converted into electricity and heat or, using the Fischer-Tropsch process, to convert synthesis gas to aliphatic hydrocarbons and water [2]. The resulting product is free from sulfur and nitrogen. The FT reaction is given below:



where:

- n average length of hydrocarbon chain
- m the number of hydrogen atom per carbon.

All the reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are main parts. In FT one mole of CO reacts with two mole of H₂ in the presence of catalyst to form a hydrocarbon chain:



Depending on the process and especially the used catalyst in the FT process can get synthetic diesel oil (cobalt catalyst), synthetic gasoline (catalytic iron) and biomethanol (copper-zinc catalyst supported on alumina).

The pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. Properties of the products depend upon temperature, process time, the atmosphere of the process as well as the characteristics of the material subjected to pyrolysis. During the process of biomass pyrolysis is a thermal conversion, in the absence of oxygen. Depending on the conditions of this process can be divided into conventional pyrolysis, fast and flash [13].

Conventional pyrolysis occurs under a slow heating rate (0.1–1 K/s) and residence time is 45–550 s and massive pieces of wood. In the first stage of biomass decomposition which occurs in between 550 and 950 K is called pre-pyrolysis. During this stage, some internal rearrangement such as water elimination, bond breakage, appearance of free radicals, formation of carbonyl, carboxyl and hydroperoxide group take place. The second stage of solid decomposition corresponds to the main pyrolysis process. It proceeds with a high rate and leads to the formation of pyrolysis products. During the third stage, the char decomposes at a very slow rate and it forms carbon rich solid residues.

In the process of fast pyrolysis of biomass, fine particles (<1 mm), low humidity are heated with a heating rate of 10 to 200 K/s to a temperature of 850 ÷ 1250 K. The duration of fast pyrolysis is 0.5 to 10 s. The result of this process is liquid product - Bio-oil with calorific value of

about 16 to 19 MJ / kg. Small amounts are also formed gas and charcoal, which are immediately burned and provide heat for the pyrolysis process.

Fast pyrolysis produced 60–75 % of Bio-oil, 15–25 % solid char and 10–20 % non-condensed gases depending upon feedstocks [18].

Bio-oil is a dark brown viscous, corrosive and sour liquid with a characteristic "smoky" smell, which can be used as fuel in furnaces, gas turbines and diesel engines. The Bio-oil includes, among other things: aliphatic alcohols/aldehydes, furans, benzene and pyrene derivatives, fatty acids and hydrocarbons of high molecular weight. These compounds can be extracted from Bio-oil by means of selective solvents.

Flash pyrolysis it differs strongly from that of conventional pyrolysis, which is performed slowly with massive pieces of wood. It occurs in the temperature range of 1050–1300 K, fast heating rate (>1000 K/s), short residence time (<0.5 s) and very fine particle (<0.2 mm). The conversion of biomass to crude oil can have an efficiency of up to 70 % for flash pyrolysis process. The so called bio-crude can be used in engines and turbines. Its use as feedstocks for refineries is also being considered [3].

Rich in isoparaffins "Green diesel" produced in the process of hydrotreating raw materials containing triglycerides and fatty acids in the presence of a cobalt-molybdenum or nickel-molybdenum. Isomerization resulting "Green diesel" has a composition similar to the composition of a typical diesel fuel, has a high cetane number, good low temperature properties and a sulfur content below 1 ppm. Compared to FAME's properties do not depend on the quality of raw and hydrogenated biodiesel is readily miscible with diesel [7].

Conversion of lignocellulosic biomass to ethanol is a more involved process than obtaining bioethanol from starch and consists of pretreatment, acid or enzymatic hydrolysis, fermentation and distillation.

Lignocellulosic biomass is mainly composed of cellulose (crystalline biopolymer of glucose), hemicelluloses (amorphous polymers of xylose and arabinose) and lignin or large poly-aromatic compounds. Enzymatic hydrolysis of cellulose is slower than the hydrolysis of starch due to the presence of bonds β -1,4-glucosidic linkages in the molecule of the biopolymer (starch present in the binding of α -1,4-glycosidic bonds).

The pretreatment processes separate xylose and lignin from the crystalline cellulose. The steam explosion process is an efficient pre-processing method for converting lignocellulosic biomass. In this process biomass sample is placed in a pressure vessel (i.e. digester) and vaporized using saturated steam for a short time at a temperature 473–543 K and high pressure 14–16 bar. The pressure in digester is then dropped quickly by opening the steam and the material is exposed to normal atmospheric pressure to cause explosion which disintegrate lignocellulosic biomass [19].

Steam explosion causes the hemicellulose and lignin from the wood to be decomposed and converted into low molecular weight fractions which can be easily extracted. Therefore most of the water soluble fraction of hemicellulose can be removed by water extraction. At the same time, a part of the low molecular weight fraction of lignin is also extracted. The xylose can be fermented to ethanol and the lignin can be further processed to produce other fuels. The crystalline cellulose remains solid after the pretreatment and later break down to glucose by enzymatic hydrolysis process. The glucose is further fermented to alcohol and the hemicellulose fraction is converted to xylose. The conversion of xylose to ethanol is a difficult process, therefore, pretreatment is necessary to reduce the crystallinity of cellulose to lessen the average polymerization of the cellulose and hemicellulose–lignin sheath that surround the cellulose and to increase available surface area for the enzyme to attack [19].

Ethanol can be blended with gasoline to produce an oxygenated fuel with lower hydrocarbon and greenhouse gas emissions, certain aldehydes are increased. Automobiles can be operated on ethanol/gasoline blends from 5% to 25% without any alterations in engine equipment's or setting.

The major engine operation issue with alcohol blended fuels is fuel quality, volatility, octane number, cold start, hot operation, and fuel consumption.

In order to extract bio-oil from oil seeds solvent extraction can be done (usually as the solvent used is hexane) followed by distillation. Extraction refers to a process in which the desired substance is selectively removed from the raw materials by allowing the desired substance to dissolve into the solvent, and subsequently recovering the substance from the solvent. To remove the particular substance from biomass, extraction and separation are both essential.

Typically biomass (wood, wheat straw, aromatic grasses, etc.) contains high volume of macromolecular compounds (polysaccharide, cellulose, hemicellulose, and lignin) called primary metabolite. The other low volume and high value biochemical molecules like terpenoids, waxes, resins, sterols, and alkaloids are known as secondary metabolites or extractive biomass. In the biorefinery process these chemicals are initially extracted from biomass by using solvent extraction or supercritical fluid extraction.

The extraction can also be performed using CO₂ or supercritical water. A supercritical fluid is defined as a substance that is at temperature and pressure conditions which are above its vapour liquid critical point (for water it is 644 K and 22 MPa; for CO₂ it is 304 K and 7.4 MPa) [16]. At supercritical conditions a fluid is neither liquid nor gas as it can not be made to boil by decreasing the pressure at constant temperature, and it would not condense by cooling at constant pressure.

Supercritical fluid processing of biomass to chemicals represents an alternative path to acid hydrolysis, enzymatic hydrolysis of cellulose to sugars. With acid hydrolysis acid recovery is a costly and polluting issue. Enzymatic saccharification needs pretreatment of lignocellulosic biomass. Supercritical water can quickly convert cellulose to sugar and convert biomass into a mixture of oils, organic acids, alcohol and methane. In supercritical and near critical state acid (H⁺) and base components (OH⁻) of water are separate and dissolve in the biomass. The dissolved supercritical water breaks the bonds of cellulose and hemicellulose rapidly to produce small sugar molecules, glucose, xylose and oligosaccharide [17].

4. Opportunities and plans to use liquid biofuels in the industry (including military)

In December 2009, AltAir Fuels entered into a memorandum of understanding with 14 commercial airlines (including Delta, United, US Airways, Mexicana airlines, Air Canada) for the purchase of up to 750 million gallons of sustainable jet fuel over a 10 year period. In the same year AIR FRANCE KLM Group, North Sea Group and Spring Associates, after test flight, create consortium - Sky Energy, which is responsible for the development of aviation biofuels. SkyRND (research and development) develops sustainable jet fuel for the global aviation market based on a unique low cost operating model. Sky Energy has a proven track record; it has so far supplied sustainable jet fuel to more than 15 airlines around the world on all continents apart from Africa.

The 2007 National Defense Authorization Act (NDAA 2007) required that U.S. Department of Defense produce or procure 25 percent of all energy from renewable sources by 2025 [21]. The military has in fact, moved beyond this type of broad mandate toward the creation of a new energy strategy with each service branch developing its own energy strategic plan. For example, the U.S. Air Force, the largest consumer of liquid fuels in the military, has a stated goal of acquiring half of its domestic aviation fuel from domestic, synthetic (i.e., non-petroleum) sources by 2016 [5]. U.S. Air Force also plans to test flying B-52 bomber and a transport C-17 Globemaster fed a mixture of kerosene and biofuel derived from FT synthesis (in the ratio 50:50).

The Navy (in US), which consumes daily approximately 80,000 barrels of oil at sea and 20,000 MWh of electricity on shore, has set a goal of making half of its bases net-zero energy facilities by 2020. By 2016, the U.S Navy also plans to sail the "Great Green Fleet," a carrier strike group composed of nuclear ships, hybrid electric ships running on biofuels, and aircraft flying on biofuels [1].

In Poland the production of biofuels is mainly obtained FAME and Green diesel, which are then added to a mixture of diesel fuel.

5. Conclusions

National governments strongly support the development of refineries producing biofuels on a commercial scale. The European Union aims to meet the objectives set out in Decree 20/20/20, which is to increase energy efficiency by 20 percent, reduce greenhouse gas emissions by 20 percent and ensure that 20 percent of the total energy production will come from renewable sources by 2020. This opens up tremendous opportunities for the biofuel market. From the standpoint of limiting carbon dioxide emissions reduction is an important resource pool for biofuel production to areas where effective control is possible (i.e. the European Union countries), because otherwise the use of biofuels could lead to an increase in its emissions.

According to many analyzes of second-generation biofuels could soon completely replace the first-generation biofuels made from food materials. Before doing so, we need to address the problem of very high production costs of biomass. The solution may be optimization of processing technology of various raw materials for production of biofuels and more efficient use of by-products.

Increasingly popular to enjoy the start of the third generation biofuels based on algae derived, which are not only restrict the emission of greenhouse gases during combustion, but also allow the capture of CO₂ from coal particles, and even directly from the air, and thus contribute to further increase the reduction greenhouse gas emissions. However, while the algal culture is relatively easy to have the oil extracted from them difficult.

6. References

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