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GREEN FUELS

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Contents

1. Introduction

Green fuels are of particular interest to us in the early part of the 21st century for two reasons - the traditional fossil fuels such as gasoline and gas that we have used are running out and becoming far too expensive - also the carbon dioxide emissions from these fuels is now widely believed by scientists to be causing an increase in the greenhouse effect, and therefore global warming and climate change.

Clearly, as this century unfolds the emphasis is going to be increasingly upon different, 'green' fuels that are renewable and that do not contribute to further climate change. Obviously, this change is not going to happen overnight, but it would be helpful if we all understood what might be happening in the near future.

The main types of fuels to talk about are the so called biofuels. These fuels might be termed green fuels because they are renewable and they are carbon neutral i.e they do not, overall, add extra carbon dioxide to the atmosphere. The reason for both of these things is that biofuels are made from plant material. Obviously plants are renewable - they are not going to run out! Also since they make all of their own molecules from carbon dioxide absorbed from the atmosphere by photosynthesis - when these molecules are burned to release this carbon dioxide back into the atmosphere it has not added overall to the level of atmospheric carbon dioxide.

These biofuels take the form of ethanol and biodiesel. Ethanol is produced from sugar, produced from plants through the process of fermentation. Ethanol is an excellent fuel - it gives rise to no acidic gases on combustion and does not have to be compressed as it is already in a liquid form. Ethanol has been used as a fuel in Brazil for many years and is starting to be mixed in with gasoline in Europe - up to about 5%. Biodiesel is made from similar vegetable oils to those used to make margarine and cooking oil.

The disadvantage of using these types of green fuels made from sugar, grain and seeds is that this usage inevitably pushes up the price of the foodstuffs traditionally made from them. This has certainly happened in Europe as biodiesel and ethanol have become more commonly used.

2. Biogas

2.1 Introduction

Biogas is a mixture of gases obtained in the process of methane fermentation. Reactions leading to its formation occur with participation of microorganisms in anaerobic conditions. Methane fermentation involves anaerobic biochemical processes, in which macromolecular organic substances (carbohydrates, proteins, and fats) decompose to alcohols or lower organic acids and to methane, carbon dioxide and water. Methane is 21 times more effective in triggering the greenhouse effect than CO_2. It is produced mainly by anaerobic bacteria in the process of organic substance decomposition, and emitted in a natural way (oceans, surface water, bogs), or artificially (mining and combustion of fossil fuels, landfill sites, animal droppings and rice production).

Biogas in the EU countries Based on the EUobserver Barometer data we can assess the development of biogas production and its use across the EU. When reviewing the 2004 - 2007 data, we can see a considerable increase (reaching 27% on average) in biogas production in all European Union countries. Fig. 2.1 illustrates biogas production in EU, whereas Table 2.1 shows the biogas production in Europe in 2007.

Germany and Great Britain are leading biogas producers, together generating almost 70% of total biogas production in the EU. Until now, in the European Union, including Poland, this type of energy has an insignificant share.

According to the Barometer data, the driving factors in the two countries are agricultural biogas works built (especially in Germany) adjacent to medium-size cattle and poultry farms. It is estimated that in the coming years agricultural biogas can be the driving force across all European Union countries, as a result of development of the market for energetic plants such as corn, wheat or sunflower seeds. In addition, Germany has favourable renewable energy legislation in place: the Renewable Energy Act of 2004. It ensures the sale of biogas energy at guaranteed price until 2020, with additional bonus system available for those producing heat and electricity in cogeneration, or using energetic plants.

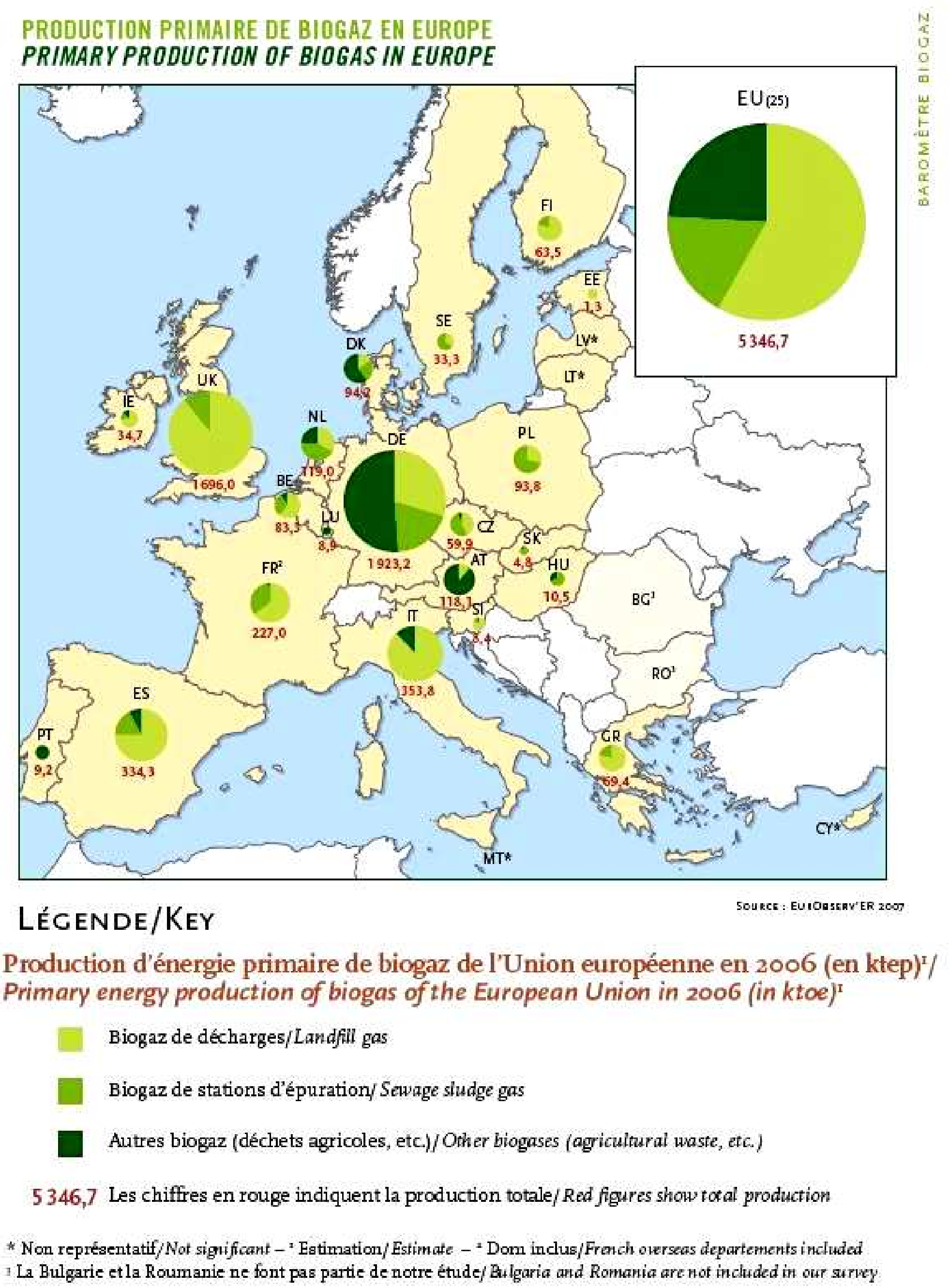


Fig. 2.1 Biogas production in EU, *Source: EUobserver*

Table 2. 1. Production of biogas in the EU in 2007, *Source; EUobserver*

Country	Landfill biogas	Sludge biogas	Other types of biogas	Total
Germany	416.1	270.2	1 656.5	2 383.1
Great Britain	1,433.1	191.1		1 624.2
Italy	357.7	1	47.5	406.2
Spain	269.6	49.1	21.3	330
France	161.3	144.2	3.7	309.2
Holland	43.2	48	82.8	174
Austria	10.7	2	126	139.1
Denmark	14.3	21	62.6	973
Belgium	48.1	18	12.5	78.6
Czech Republic	29.4	32.1	17	78.5
Poland	19.1	43	0.5	62.6
Greece	38	9.8	0	47.8
Finland	26.4	10.3	0	36.7
Ireland	23.9	7.9	1.7	33.3
Sweden	9.2	17.1	0.3	27.1
Hungary	2.1	12.4	5.7	20.2
Portugal	0	0	15.4	15.4
Slovenia	7.6	0.6	33	12
Luxembourg	0	0	10	10
Slovakia	0.5	7.6	0.5	8.6
Estonia	3.1	1.1	0	4.2
Lithuania	1.6	0.8	0	2.2
Cyprus	0	0	0.2	0.2
UE	2,905.3	887.3	2 108.9	5 901.5

Table 2.2 Biogas production per capita in the EU countries in 2007 (tons/1,000 inhabitants)
Source; EUobserver

Country	**tons/ 1,000 inhabitants**
Germany	29
Great Britain	26.7
Luxembourg	21
Denmark	18
Austria	16.8
Holland	10.6
Ireland	7.8
Czech Republic	7.6
Belgium	7.4
Spain	7.4
Finland	6.9
Italy	6.9
Slovenia	5.9
France	4.9
Greece	4.3
Estonia	3.1
Sweden	3
Hungary	2
Poland	1.6
Slovakia	1.6
Portugal	1.5
Lithuania	0.7
Cyprus	0.2
EU	**11.9**

The January 2009 amendment to the act promotes small local biogas plants, by increasing subsidies for 1 MWh of energy produced. Another development-inducing direction on the German market is the inclusion of the produced biogas into local gas supply system. This measure aims at reaching 10% consumption of biomethane with natural gas by 2030. The effect of policies supporting environment protection and renewable energy can be seen in statistics – there are currently over 3,500 agricultural biogas plants in operation in Germany. This number grows at a steady pace.

A completely different production profile was adopted in Great Britain, where the raw material is produced mainly from landfill biogas (88% of total output). Interest in this type of renewable energy is generated by the ‘green’ system of certification applied to all sources of renewable energy, and the highest profitability in producing electric power among all alternative methods.

Similar situation is observed in Austria where biogas production was increased by 67% in the period from 2004 to 2007. Rapid development in the production of this raw material in Austria was possible thanks to municipal sewage treatment plants operating small-volume fermentation chambers, and environment-friendly policy of the government. For nearly 15 years, biogas plants have been promoted by introduction of changes in legislation: rates/prices were set up for introduction of biogas into the gas supply system, and subsidies were granted to compensate the differences between the market price of electric power and the cost of its production (Green Electricity Act). One way to become independent of agricultural waste supply is to diversify the sources of substrates: over 60% of the raw material is the energetic plant, with animal droppings and organic waste being the remaining part. Austria is currently one of Europe's biggest producers of biomethane as expressed in production per capita.

An interesting solution for using biogas was implemented in Sweden: approx. 20% of the total output is used as transport biofuel. Following fermentation the gas is purified and compressed under pressure - CNG (Compressed Natural Gas) – and it then fuels car and bus engines. The municipal transport systems in many cities e.g. in Linkóping and Uppsali are based solely on biogas fuel. In addition, the development of biogas as a fuel in Sweden is supported by state subsidies, surplus of its production, and a cheaper price of electricity.

2.2 Formation of biogas – Methane fermentation.

The methane fermentation process occurs in specific conditions and depends on its environment (pH, temperature, proper alimentary substances and inhibitors) and the type of microorganisms.

Three types of microorganisms take part in the process: acidogenic bacteria, methanogenic bacteria and acetogenic bacteria. The first two stages are dominated by obligatory and facultative anaerobes (*Bacillus, Pseudomonas, Clostridium, Streptococcus, and Enterobacterium*) and strict anaerobes (*Areobacter, Clostridium, and Micrococcus)* Acetogenic bacteria (*Syntrophomonas and Syntrophobacter*) process the acid phase products into acetates and hydrogen, which can subsequently be used by methanogenic bacteria (i.e. strict anaerobes). Even small amounts of oxygen effectively inhibit the activity of methanobacteria. Methanogenic bacteria occur in the form of rods

(*Methanobacterium*) circular shapes/Cocci (*Methanococcus*) and spirillum bacteria (*Methanospirillum*).

Due to the temperature in which the fermentation is carried out, the following types can be distinguished:

- Psychrophilic fermentation - optimal temperature in the range 5-25°C
- Mesophilic fermentation - optimal temperature in the range 25-45°C
- Thermophilic fermentation - optimal temperature in the range 45-60°C

The mesophilic temperature range is the one used most often. The bacteria participating in individual phases have different pH reactions. An optimal pH for hydrolysing and acidogenic bacteria is 4.5 to 6.3. In the case of bacteria producing acetic acid and methane, the pH reaction must be in the range 6.8-7.5.

The substrates for biogas production can be obtained from:

- agriculture (animal droppings as well as plant, grain and vegetable waste),
- municipal waste (sludge),
- industrial waste (waste from food, dairy and biochemical industries etc.).

Such waste products usually contain a number of elements required for bacteria growth. The crucial ones include: carbon compounds, nitrogen, phosphorus, sulphur, trace elements, and soluble forms of potassium, sodium, iron, magnesium, manganese and calcium. Acetogenic bacteria additionally need zinc, magnesium and manganese. Hydrogen sulfide, present in the sludge water, is a strong inhibitor hindering access to these trace elements. Hydrogen sulphide forms with metals sparingly soluble sulphides, thus making them unavailable for microorganisms.

Ammonia is also a strong inhibitor, found in animal droppings. Thinning of biomass or adding substances increasing the ratio C/N (e.g. adding biomass with high carbon content, such as straw) are used in order to reduce ammonia content. Other substances disturbing the entire process of fermentation include antibiotics found in animal droppings as well as copper, nickel and chromium.

The process of methane fermentation can be divided into four successive stages. Specific bacteria groups are related to each stage.

Stage 1 – hydrolysis:

Enzymes of hydrolytic bacteria (lipase, amylase and protease) decompose organic substances to simple amino acids, fatty acids, glycerol and monosaccharides.

Stage 2 – Acid fermentation:

Fermentative bacteria convert hydrolysis products to short-chain organic acids (propionic, butyric and formic acids), ethanol and gas products. The resulting gas contains approx. 80% CO_2 and 20% H_2.

Stage 3 – acetogenesis:

Acetogenic bacteria convert fatty acids to acetic acid, CO_2 and H_2, which can be transformed into methane.

Stage 4 – methanogenesis:

during which, acetic acid is converted to methane and CO_2.

Biogas is the end product of an anaerobic decomposition of organic substance.

Fig.2.2 shows the mechanism of biogas formation.

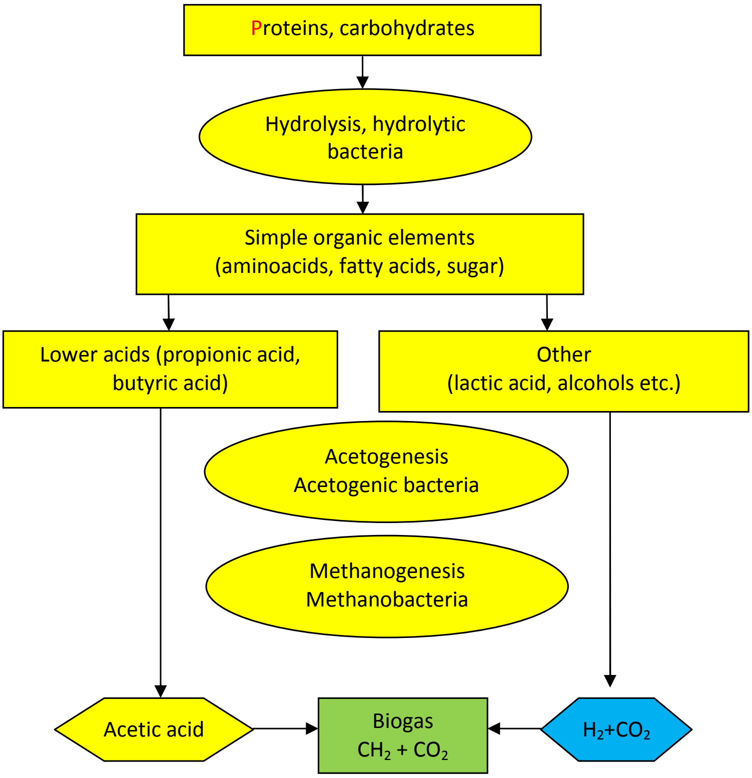


Fig.2.2 The mechanism of biogas formation.

2.3 Types of biogas

Types of biogas can be distinguished by type of applied production installation: biogas produced in agricultural biogas plants or fermentation chambers in sewage treatment plants, and biogas occurring spontaneously, the so-called landfill biogas.

The biogas from sewage treatment plants is very frequently utilized by power infrastructure of the plant. Biogas from such sources can be used as energy source only in the case of modern sewage treatment plants designed for minimum 50,000 inhabitants. The biogas is produced in closed fermentation chambers. First, the sludge from biological blocks is directed to settling tanks and there suspended matter is separated from the activated sludge. The treated sludge is transported to a discharge channel, while condensed primary sludge is pumped to separated fermentation chambers, in which biogas forms under anaerobic conditions. The gas is stored in special low-pressure tanks and from this apparatus it is pumped to a power-generating unit. It is estimated that calorific value of such biogas is approx. 6-7 kWh/m^3 and is closely related to its methane content.

Heat and electric power generated in this way are utilized by the treatment plant itself, and a surplus can be sold.

Landfill gas occurs spontaneously as a result of decomposition of organic waste in the site. Approx. 200 m^3 of gas can be produced from 1 ton of dry matter organic fraction. The speed of gas formation depends on the quality of waste, humidity and temperature. If the gas is released from the site in an uncontrollable manner, it can pose a serious threat to safety
of people and environment, due to flammability of methane. Measures taken to reduce emissions to the atmosphere include sealing of the site and installation of special devices for removing and burning methane in a safe way (torches). When burnt, biogas produces waste gas which contains nitric oxides, carbon oxides, furanes and dioxins.

The formation of dioxins is promoted by the presence of chlorine and chloroorganic compounds. Both in sludge and in landfill sites, the content of chlorine and its compounds is high enough to result in emission of poisonous substances at levels significantly exceeding permissible limits. Waste segregation and strict control of combustion conditions are recommended to reduce the formation of such substances.

Landfill gas can be used directly as furnace fuel, engine fuel or in the production of heat and electric energy.

Biogas from agricultural biogas works is produced from animal droppings biomass: liquid manure (liquid mixture of feces and urine, slurry (urine), and dung (animal droppings together with straw). Complementary substances increasing the efficiency of fermentation process may include industrial-origin organic waste (from processing of food, dairy, sugar, as well as pharmaceutical and cosmetic industry etc.). Liquid manure is the most widely used one – the less it is thinned the more biogas is produced. Due to its consistence, slurry (too low content of dry matter) and dung (solid substance) are only an additive to the fermentation process. A typical biogas production installation consists of a livestock building (where production material forms e.g. a barn), a raw material tank (where animal droppings and organic waste are stored and mixed/stirred), a fermentation chamber (bioreactor – where the fermentation process and biogas formation occur), a storage tank, as well as equipment for purifying biogas and producing electric energy or heat (gas generators of electricity and gas furnaces).

2.4 Biogas purification methods

Before transforming biogas into fuel it must be enriched, purified, dried and desulphurised. Biogas enrichment is achieved by removing CO_2. There are several methods which enable removal of that compound from biogas. One of the processes is adsorption in which CO_2 is washed out with cold water (in which it is readily soluble). Amines, KOH and NaOH (chemisorption) can be used instead of water. Adsorption is a process in which CO_2 is absorbed on the surface of a deposit (activated carbon, diatomaceous earth). The deposit is then regenerated with water vapour. The enrichment methods are also applied in purifying biogas from impurities settling on the adsorption deposit, or ones that are washed out by the absorbing agent.

Desulphurization of biogas is a very important process. It consists in removal of sulphur compounds, mainly H_2S, whose content depends on the types of substrates and may even reach up to 3% mass. Small amounts of hydrogen sulphide are removed together with CO_2 in the above-mentioned enrichment processes. The methods applied include those with a solid deposit and with alkaline solution, as well as chemical and biological methods. In the biological method, microorganisms absorb hydrogen sulphide and produce elementary sulphur. This conversion may occur directly on the fermented substrate. Unlike the desulfurization using bog iron ore, this method is not very effective. Bog iron is a sedimentary rock with scarce contents of iron. Biogas is purified using cleaners filled with bog iron ore or directly iron oxides (catalytic oxidation). These are cylindrical vessels containing wooden grates. The gas separated into several streams goes through layers of the ore at the rate of 3-9 mm/s. Fixation of hydrogen sulphide takes place while the gas flows through the ore rich in iron oxides. To put it simply, it can be described using the following reaction:

$2Fe(OH)_3 + 3H_2S \longrightarrow FeS_3 + 6H_2O + 42{,}3\ kJ$

The effectiveness depends on porosity, humidity and the content of iron oxides in the ore.

Wet desulfurization consists in spraying biogas with a sodium hydroxide solution, and it can be described using the following reaction:

$2H_2S + CO_2 + 3NaOH \longrightarrow 2NaHS + NaHCO_3 + 2H_2O$

In a used/spent lye, sulphur is fixed with sodium acid sulphate. The lye undergoes aeration enabling NaHS to oxidize to Na_2SO_4.

There are several methods of desulfurization and enrichment of biogas (e.g. desulfurization using catalysts – Mobil Oil Corp., as processed by Sulferox-Shell Development Company). They usually involve adsorption, most often applying carbon, non-organic and mixed adsorbents.

2.5 Composition of biogas

The main components of biogas are: methane, CO_2, and in much smaller amounts N_2, H_2, and mercaptans. The biogas composition depends on the type of decomposed substance, duration of the fermentation and the applied technology.

Table 2.3. Contents of individual components of biogas (%)

Biogas component	CH_4	CO_2	H_2O	H_2S	N_2	H_2	O_2	Mercaptans and other trace elements
Content (%)	50-75	25-50	2-7	0-2	0-2	0-1	0-1	0-1

Literature

1. De Baere L. Anaerobic digestion of solid waste; state-of-the-art. In II Int. Symp. Anaerobic Digestion Solid Waste. Barcelona, June 15–17, 1999.
2. Oleszkiewicz J. A. and Peggi-Valardo. High-solids anaerobic digestion of mixed municipal and industrial wastes. J. Environ. Eng., 1997, 123, 1087–1092.
3. Chynoweth D.P., Earle, J.F.K., Bosch G. and Legrand R., Biogasification of processed MSW. Biocycle. 1990, 31, 50-51.
4. O Keffe, D. M. Chynoweth D.P., Barkdall A.W. Sequential bath anaerobic composting of municipal solid waste (MSW) and yard waste. Wat. Sci. Tech., 1993, 27, 77-86.
5. De Baere L. Anaerobic digestion of solid waste: state-of-art. Wat. Sci. Tech., 2000, 41(3), 283-290.
6. Fruteau de Laclos H. Desbois S. and Saint Joly C. Anaerobic digestion of municipal solid organic waste: Valorga full-scale plant in Tilburg, the Netherlands. Wat. Sci. Tech., 1997, 36(6-7), 456–462.
7. Ten Brummeler E.. Ful scale experience with the Biocel process. Wat. Sci. Tech., 2000, 41(3), 299-304.
8. Vellinger A., Wyder K and Metzler A. E. Kompogas-a new system for the anaerobic treatment of source separated waste. Wat. Sci. Tech., 1993, 27(2), 153-158.

3. Gas fuels used in transport

Gas and liquid fuels used to feed combustion engines have been characterised below.

3.1. Hydrogen

Hydrogen is commonly recognised as the fuel of the future, owing to its unquestionable advantage, i.e. its combustion is related to no negative effects on the environment.

From among the number of currently contemplated methods of acquiring hydrogen considerable practical importance is attached to the methods based on hard and brown coal gasification.

Their important feature is the availability of technologies proven at industrial scale. Coal gasification technologies stimulate considerable interest owing to the nature of available raw materials. Gases produced as by-products may also provide a potentially important source of hydrogen.

The prospect of using hydrogen to feed vehicle engines relies predominantly on its ecological purity, unlimitedness and accessibility to its resources, low transportation costs and, finally, its properties. It provides an opportunity for its wide application to feed contemporary engines, without their fundamental retrofit/upgrade. As engine fuel hydrogen is characterised by several advantageous properties. However, the use of hydrogen requires performing a relevant analysis and assessment of the engine working cycle. Hydrogen is one of the fuels with the highest energy capacity. Its calorific value is almost three times higher than the value of hydrocarbon fuels, amounting to $120 \bullet 10^3$kJ/kg.

Hydrogen does not experience problems associated with liquid fuels, such as vapour lock, cold wall quenching, inadequate vaporization, poor mixing, and so forth. The other significant feature of hydrogen in the present day context is the “clean-burning” characteristics of the fuel. When hydrogen is burned in air, the main product is water.

Hydrogen combustion produces lower quantity of toxic products such as hydrocarbons, carbon monoxide, oxides of sulphur, organic acids and carbon dioxide. Acid rain and the CO_2 greenhouse effect are eliminated. Some oxides of nitrogen are generated and our experiments show that it is possible to get the concentration of NO_x drastically reduced by monitoring the engine operation. The basic advantage of hydrogen combustion is that the greenhouse gas carbon dioxide (CO_2) is not formed at all when hydrogen is burned. This clean-burning property can promise an accelerated entry of hydrogen into the existing transportation sectors, as well as several energy consuming sectors, of the developing countries. Like CNG, hydrogen engine fuelling also needs an entirely different approach from that of liquid fuelling.

Some of the properties of hydrogen that are relevant to its employment as an engine fuel are listed in Table 3.1. These are compared to the corresponding values of methane and gasoline.

Table 3.1. Some comparative physicochemical properties of hydrogen and gasoline

Properties	hydrogen	gasoline
Density at 1 atm and 27 ^{o}C [kg/m^3]	0.08	0.71-0.76
Kinematic viscosity at 27 ^{o}C [mm^2/s]	110	1.18
Minimum ignition energy [mJ]	0.02	0.25
Quenching distance [cm]	0.06	>0.25
Flash-point [°C]	630	530
Flammability limits [%] (by volume)	4.7-74.2	0.59-5.0
Diffusion coefficient [cm^2/s]	0.63	0.08
Flame rate [cm/s]	-270	-30
Calorific value [kJ/kg]	$120\cdot10^3$	$44\cdot10^3$
Stoichiometric air/(1 kg) fuel ratio [kg/kg]	34.2	14.95
Calorific value of the mixture at λ=1:		
for the mixture with air [kJ/m^3]	3180	3710
for the mixture with oxygen [kJ/kg]	$1.34\ 10^4$	-

Hydrogen has some remarkably high values of the key properties for transport processes in comparison to those of the other fuel. Such differences together with its extremely low density and low luminosity help to give hydrogen its unique diffusive and heat transfer characteristics.

The present contribution focuses primarily on hydrogen applications in conventional spark ignited piston engines. There is also much information available and development work relating to hydrogen-fuelled compression ignition engines of the dual fuel type homogeneous charge compression ignition engines, commonly known recently as HCCI engines and engines where ignition is effect of either through surface or catalytic ignition.

Hydrogen, over wide temperature and pressure ranges, has very high flame propagation rates within the engine cylinder in comparison to other fuels. These rates remain sufficiently high even for very lean mixtures that are well away from the stoichiometric mixture region.

The fast burning characteristics of hydrogen permit much more satisfactory high-speed engine operation. This would allow an increase in power output with a reduced penalty for lean mixture operation. Also, the extremely low boiling temperature of hydrogen leads to fewer problems encountered with cold weather operation.

3.2. Application of biogas in transport

Following purification and enrichment biogas can be converted to heat or electric energy. The calorific value changes when methane is thinned, and varies within the range 16.7-23 MJ/m^3. After CO_2 is removed, biogas is converted to biogas similar to natural gas.
There are many methods for converting biogas into electric energy: combustion of biogas in a combustion engine with spark-ignition, Diesel engine, or in a power boiler where the produced steam propels a turbine connected to a generator.

The biogas obtained in the process of methane fermentation can be used as car engine fuel, following its prior purification.

Gas fuels such as biogas or compressed natural gas represent real and significant alternatives for the conventional fuel. They are characterized by a high octane number and high calorific value, as presented in Table 2.4.

The application of biogas as a basic fuel for a motor vehicle results in expenses that have to be incurred to upgrade and adapt the engine to gas fuel, or a purchase of a car with a factory-assembled gas installation. Since biogas and compressed natural gas have a similar composition, the existing compressed natural gas installations can be used for biogas.

The use of a gas fuel vehicle involves considerable limitations including the number of available filling stations, filling time, safety issues (the fuel tanks, under high pressure, are usually placed under the vehicle floor), as well as optimization of driving and engine.

Combustion of biogas occurs at a negative carbon dioxide balance. Biogas-driven vehicles compared with the gasoline-driven ones emit up to 90% less carbon monoxide, 80% less hydrocarbons – the main factor responsible for smog, and 50 to 80% less nitric oxides.

Table 3.2. Comparison of selected features of fuels driving combustion engines, *Source: A. Sowa, Car Gas Installations, Kraków 2007 (in Polish)*

Item	**Gasoline**	**CNG**	**LPG**	**Diesel oil**
Energy value, MJ/kg	43.6	55.5	50.4	45.1
Calorific value, MJ/kg	43.5	47.1	46.3	42.8
Octane number	98	110-120	100-115	–
Ignition temperature, ^{o}C	220-270	650	481 (propane) 430 (butane)	220
Density, kg/m^3	0.72-0.76	0.74	2 (propane) 2.7 (butane)	0.86

They reduce to minimum levels the emissions of sulphur compounds and soot, thus considerably contributing to reduction in their emissions to the environment, and improvement of the microclimate in large urban agglomerations (Table 3.2.)

Table 3.2**.** Reductions in emissions from vehicles fuelled with biogas compared to vehicles on conventional fuel *Source: Traffic biogas production, resources, environmental impacts,*
in the EU, A. Lampinen, Biomass 8 Bioenergy conference, Tallin 2008

Pollutant	Bus: diesel → biogas	Car: diesel → biogas	Car: gasoline → biogas
CO_2+ CH_4+ N_2O	-96%	- 95%	- 96%
PM	-94%	- 100%	-67%
SO_2,	-100%	-100%	-100%
NO_x,	-39%	-88%	-57%
VOC	-70%	-33%	-79%

The selection of an engine's gas fuel system is the key element of the entire process of a vehicle's modification, enabling optimization of its operation and an actual reduction in pollution emissions. From among gas installations, the following two can be distinguished by type of feeding method: Monovalent and Bivalent.

The Monovalent allows driving a vehicle using only gas fuel (e.g. CNG, compressed biogas). The system is characterized by controlling the time of injectors' opening and the ignition advance angle, as well as detecting breaks in ignition. In such engine, each cylinder is equipped with an injection valve before the suction valve, thus providing an optimal distribution of the gas-air mix. A controller keeps a steady value of the gas fuel pressure. The mechanism of action is similar to that of a combustion engine. A volatile gas is compressed in the cylinder chamber, and ignited by a spark from an ignition plug. The resulting pressure creates a piston stroke which makes the crankshaft move. A number of successive mechanisms drive a vehicle using gas.

The Bivalent (Bi-Fuel) installation allows feeding a vehicle not only with gas fuel but gasoline as well. Switching to the other type of fuel can be done while driving. In this installation the fuel is supplied in a volatile form to the cylinder through suction valves, using one of Generation 4 systems.

I – the simplest system - gas is sucked into the cylinder by negative pressure dependent on the engine's revolutions. The system does not allow regulation of the volume of the gas sucked in by the engine, thus reducing its efficiency.

II – single point injection – continuous controlling of the mixture composition using electronic sensors located on the engine, thus increasing dynamics and efficiency of driving and reducing emissions of exhaust gas.

III – multi point injection – allowing supply to each cylinder of a specific amount of the mixture formed before the suction valve. The gas is supplied separately to each suction valve; a controller equipped with injection maps controls dosing of the gas to the injectors.

IV – sequential injection – the moment an injector opens and the duration of gas injection for are controlled by computer for each cylinder. The sequential injection of gas enables compliance with the strictest exhaust gas emission standards, minimum consumption of the fuel.

Production of biogas is also significant from economical, social and business/economic perspective. In a way, it complements the ecological cycle which combines waste management with the production of green energy and transport biofuel. A considerable limitation in the development of biogas-fuelled engines or CNG, is the very insufficient number of gas filling stations, which is a big obstacle for common car users.

3.3. Natural gas as a vehicle fuel

Natural gas is one of the fuels that meet the “green fuel” requirements and its documented world resources are several times larger than those of petroleum. By the time pressurized hydrogen is used on a mass scale, natural gas will remain the basic alternative to gasoline and diesel oil.

Basic terms concerning gas:

- natural gas – NG.
- compressed natural gas – CNG.
- liquefied natural gas – LNG (temp. 112K – minus 161.15°C)
- liquefied gas (propane-butane) – LPG (Liquefied Petroleum Gas).

Natural gas is predominantly used as a raw material in the power industry and, on a smaller scale, as a raw material in the chemical industry mainly as raw material for hydrogen production, among others, helium is isolated from some of its forms). Natural gas with a high methane content is a very good engine fuel. During combustion in the vehicle engine the emission of toxic compounds is 3 times lower than in the case of gasoline, smoking does not occur, solids are not produced and the noise generated by the engine operation decreases by 10 Db. Methane fuel is safer in operation than gasoline, whereas natural gas is cheap and easily available. In order to increase the amount of energy per unit volume the gas is compressed and stored in pressurised cylinders. About 5 million vehicles in the world are fed with natural gas. Vehicles fed with natural gas are referred to as NGV (Natural Gas Vehicles).

Natural gas is a natural fossil fuel. Methane is the basic component of natural gas. An exemplary composition and parameters of natural gas at a gas refilling station are as follows:

- CH_4 – 96.6 % of volume,
- C_2H_6 – 1.1 % of volume,
- O_2 – 0.1 % of volume,
- CO_2 – 0.1 % of volume,
- N_2 – 2.1 % of volume,
- Gross calorific value – 39 302 kJ/m^3,

- Calorific value – 35 364 kJ/m^3,
- Relative density in air – 0.570 kg/m^3,
- Standard density – 0.735 kg/m^3
- Wobbe index – 52 057 kJ/m^3,
- Hydrogen sulphide content – 0.08 mg/m^3,
- Sulfur content – 0.15 mg/m^3,
- Dew point – 80°C.

The use of CNG (compressed natural gas) as fuel for combustion engines requires deep gas drying to the dew point - 30°C in order to fully safeguard the gas installation in the vehicle.

This process is necessary, because as a result of pressure reduction the gas becomes considerably colder (about 3°C/10 bar) which at a very low temperature in winter may cause formation of hydrates (crystalline combination of hydrocarbons and water) or ice and interrupt the inflow of gas to the engine. The water content in gas should not exceed 10 mg/m^3.

Natural gas is used as engine fuel in the form of:

- compressed natural gas CNG.
- liquefied natural gas LNG.

Compressed natural gas, CNG, for feeding vehicles is a natural fuel which before its use in engines does not require any technological processing, apart from drying and compressing. In the vehicles fed with natural gas it is stored mainly in the compressed form. The disadvantage of this system is a low density of stored energy per unit volume (despite considerable gas compression to the pressure of about 20 MPa), which requires the use of high capacity and heavy weight containers. Recent research works have led to the development of light containers, making use of new technologies. CNG has been successfully used to power vehicles of various ranges, starting from light delivery trucks to full size urban buses. All these applications have generally been based upon conversions of existing engines to run on both gasoline and CNG. Compressed natural gas is stored in containers securely fitted to the vehicle. Single refilling of medium-size containers (depending on the so-called water capacity) makes it possible to do the mileage of about 300 km. Containers occupy more space than a traditional fuel tank.

The difference between the operation of the conventional gasoline fuelled and CNG engine system arises from the physical and chemical properties of the two fuels. It is well-known that petroleum fuels are liquid at room temperature and CNG remains in a gaseous state at much lower temperatures (−161°C). Moreover CNG has a lower density as compared to gasoline. Due to some of its favourable physico-chemical properties CNG appears to be an excellent fuel for the S.I. engine. CNG has a very high octane number (120–130) compared to that of gasoline (90–98). The engine can be operated at a relatively higher compression ratio, without any abnormal combustion problems. e.g. detonation. Higher self ignition temperature (SIT) of CNG (540°C) compared to gasoline (257°C) results in a lower risk of inflammation or explosion in the event of leakage. Since CNG is a gas, it requires an altogether different approach of fuel induction mechanism at all normal temperatures and pressures. CNG has been routinely used as a fuel for S.I. engines. which are designed to run on petroleum fuels. Considerable operating experience with CNG-operated engines does already exist in a variety of applications. Similarly several investigators of hydrogen fuelling of S.I. engines have carried out some research and development work. A detailed discussion on all aspects of such studies is beyond the scope of this paper. In spite of excellent combustion characteristics (Table 2) of both the gaseous fuels (CNG and hydrogen), it has been observed that they often pose some problems like backfiring during suction, knocking at a higher compression ratio with advanced spark timing.

Table 3.3. Physico-chemical properties of CNG, gasoline and hydrogen

Item	Requirements	Natural gas	Hydrogen	Gasoline
1	Compositions	Methane 82.2; ethane 6.1;propane 2.4; isobutene 1.0; isopentane, n-butane 0.4; nitrogen 7.7; CO_2 and oxygen 0.2	H_2	C_8H_{18}

2	Stoichiometric composition in air, vol %	9.48	29.53	1.76
3	Lower calorific value, MJ/kg	44.24	119.93	43
4	Auto ignition temperature, °C	540	585	257
5	Adiabatic flame temperature, K	2148	2318	2470
6	Minimum energy required for ignition in air, MJ	0.29	0.02	0.24
7	Volumetric efficiency	less	more	more

Liquefied natural gas, LNG

The application of liquefied natural gas, listed alongside hydrogen as an alternative fuel of the future, makes it possible to eliminate the drawbacks related to the density of stored energy, weight of containers and problems connected with high pressures occurring in the CNG systems. During liquefaction natural gas is cooled to the temperature of –161.15°C, and concurrently, its volume is reduced 630 times. Owing to the above the "energy density" of liquefied natural gas is very high. One fourth of natural gas traded on the world market is transported in such form. Liquefaction of natural gas involves its meticulous purification from carbon dioxide, nitrogen, propane-butane and moisture etc. It is then a thoroughly clean fuel having an octane number of 130. After another change into the gaseous state there remains hardly any impurities, the gas is dry – devoid of moisture. Due to low temperatures liquefied natural gas (LNG) requires a cryogenic tank.

The first generally accessible LNG refilling station was started up in Bloomfield, US, in 1995. In Germany there are installations for liquefying natural gas in order to supply it to natural gas refilling stations.

Depending on the equipment in the refilling station both ordinary natural gas powered vehicles (so-called CNG 200 bar) and liquefied natural gas powered vehicles can be refuelled (LNG – under slight pressure, but requiring a cryogenic tank).

The world market for natural gas experiences a fast and dynamic development, because of its ecological and economic advantages as well as the safety of its use.

Owing to its physical and chemical properties the gas with a high methane content is defined as a good and ecological engine fuel. Natural gas is generally accessible, therefore there is no need for its storage, it is cheaper than liquid fuels, after treatment it is devoid of corrosive substances, and it has all indispensable properties of engine fuel, which decide about, among others, easy engine start-up at low temperatures and engine lifetime. This fuel is lighter than air – its density to air density ratio is 0.55-0.58 depending on the composition. In the case of leaks in the natural gas supply system in the vehicle gas escapes to the atmosphere, whereas liquid fuel spills over the surface and the propane-butane mixture (heavier than air) accumulates over the ground surface.

Table 3.4 Comparison of the density of different gases and stored energy in relation to gasoline

ANALYSED PARAMETER	CNG	LNG	LPG
Relation of energy stored in gas to gasoline	3.94 to 1.25% at 20 MPa	1.55 to 1.66%	1.36 to 1.74%
Gas density in the liquid phase	160 g/l at 20 MPa	422g/l	520g/l

Table 3.5 Comparison of chosen properties of engine fuels

PARAMETER	**NATURAL GAS** WITH A HIGH METHANE CONTENT	LIQUEFIED PETROLEUM GAS, **LPG**	**MOTOR SPIRITS**	**DIESEL OIL**
Octane number	115-130	125	90-98	25
Gross calorific value, MJ/kg	53.9	49.8	46.7	44.8
Autoignition point, ^{o}C	630-640	500	320-360	550-600
Autoignition limits in air (% of fuel by volume in air)	5-15	1.8-9.0	1.4-7.6	0.6-5.0

3.4. LPG as engine fuel

The propane-butane mixture (in the liquid phase, LPG) is a popular fuel used to power spark-ignition engines. The popularity of this fuel can be attributed to its following characteristics:

- high octane rating for 50%/50% propane/butane mixture RON = 104.
- calorific value for the stoichiometric mixture with air W = 3.65+3.66 MJ/m^3.

This feature opens up opportunities for obtaining a similar power of the engine fed with LPG and gasoline.

- Possibility of transporting and storing the LPG mixture in the liquid state, taking into account relatively low pressures of saturated vapours at ambient temperatures encountered in our climate. This pressure ranges from about 1 bar to about 10 bar within the temperature range -10+50°C.
- More favourable composition of exhaust gas, characteristic for gas fuels.

The discussed characteristics of LPG fuel provide the grounds for the possibility of using this fuel in diesel engines with a relatively low compression ratio, since:

- calorific value of the stoichiometric mixture of diesel oil with air W = 3.66+3.83 MJ/m^3 similar to the abovementioned value for LPG creates also an opportunity for obtaining a comparable power of the engine fed with LPG and diesel oil.
- fuel can be transported and stored in the liquid state, under the pressure of about 10 bar.
- high octane rating makes it possible to compress the propane-butane mixture with air in the diesel engine with a relatively low compression ratio, without being concerned about the occurrence of premature ignition, and after igniting the flammable mixture promises correct and knock-free combustion of this fuel.

Liquefied petroleum gas (LPG) is a mixture of liquefied gases containing – as basic components – hydrocarbons: propane, n-butane and iso-butane, but also some admixtures of other hydrocarbons: methane, ethane or pentanes. It contains also unsaturated hydrocarbons: ethylene, propylene and butenes – few % (*m/m*) in total. In order to counteract the formation of ice crystals in LPG methanol can be added to it, at the concentration of up to 2000 mg/kg. It is admissible to include corrosion inhibitors in the LPG composition. Since the composition of LPG is quite complex, it is tested and assessed according to the procedures and requirements analogous to those adopted in the case of hydrocarbon fuels. The use of LPG as fuel for spark-ignition engines requires the installation of a specifically designed supply system, the so-called dual fuel system, enabling the engine to work with both gasoline and LPG. The engine is started up with gasoline. The transition to LPG supply takes place by way of manual or automatic switchover. Several generations of LPG supply systems can be distinguished.

Literature

1. Kreith F., 2004 – Fallacies of a Hydrogen Economy: A Critical Analysis of Hydrogen Production and Utilization. J. of Energy Resour. Technol., vol. 126, pp. 249–257.
2. Surygała J., 2006 – Obecne i perspektywiczne metody otrzymywania wodoru. Przemysł chemiczny t. 85 (8–9), 661, (in Polish).
3. Moore T.A., Pearce S., 2006 – Hydrogen from coal. International Journal of Coal Geology vol. 65, 171–172.; HIGMAN C., van der BURGT M., 2008 – Gasification. Elsevier.)
4. Rezaijan J., Cheremisinoff N.P., 2005 – Gasification Technologies. Taylor & Francis Group.
5. Rose JW, Cooper JR. Technical data on fuels. Edinburgh, UK: Scottish Academic Press, 1977.
6. Klimstra J., Performance of lean-burn natural-gas-fuelled engines — on specific fuel consumption, power capacity and emissions, SAE Paper No. 901495
7. Peschka W., Hydrogen: the future cryofuel in internal combustion engines., Int. J. Hydrogen Energy, 23, 1 (1998).
8. Karim GA. Klat SR. Hydrogen as a fuel in compression ignition engines. J. Mech. Eng. ASME, 1976;98:3439. M. Ikegami. K. Miwa and M. Shioji . A study of hydrogen fuelled compression ignition engines. Int. J. Hydrogen Energy 7 (1982). pp. 341–353]
9. Shioji M. Ishayama T. Feasibility of the high speed hydrogen engine. International Symposium on Hydrogen Energy, Osaka, Japan, January 2002, p. 1–9.

4. Properties of fuels

4.1.Gas fuels

Natural gas usually accompanies oil deposits and is mined together with oil. There are also numerous deposits in which gas occurs separately. Natural gas found in deposits is under high pressure, which is why, having drilled a bore-hole to the deposit and having it cased with pipes, the gas flows up carried by its own pressure.

Natural gas is a mixture of light alkanes. The composition of natural gas varies considerably depending on a particular deposit, but methane is always its main component. The content of methane in natural gas ranges from 50 to 98 %. The remaining components are ethane, propane, and butane as well as small amounts of higher alkanes. Some sorts of the gas contain a significant admixture of nitrogen, and others – small amounts of helium. Virtually all helium currently produced across the world is separated from natural gas. There are also gas deposits under exploitation, which contain as much as several dozen percent of hydrogen sulphide – this component is processed into elementary sulfur.

Natural gas mined from a deposit always needs to be purified, especially from hydrogen sulphide and other sulphur compounds. These are very undesirable components in fuel gas, because when burnt they produce sulphur dioxide, which – after it gets to the atmosphere – causes dangerous contamination of the environment. Such gas is not suitable for chemical syntheses, as sulphur compounds 'contaminate' i.e. deactivate many catalysts. Hydrogen sulphide separated from the gas can be processed into elementary sulphur. In the case of gases containing considerable admixture of H_2S, the production of sulphur can even be the main purpose of their exploitation.

Purified natural gas, containing over 90 % of methane and ethane, is used as a raw material in chemical industry or as (furnace) fuel. Two heavier hydrocarbons i.e. propane and butane separated from the gas, form the so-called liquid gas increasingly used as fuel for specially adapted cars – vehicle gas systems are increasingly popular among Polish users, representing an excellent alternative for gasoline and Diesel fuels. The propane-butane mixture not only contributes to a considerable reduction in the cost of vehicle use, but it ensures purity of exhaust gases as well.

Fast degradation of natural environment has resulted in increased interest in sources of "pure energy". Natural gas in motor industry is considered to be the best source of such energy. Until the present time however, it is not widely used to fuel vehicles due to problems with storage and the lack of tank refilling network. This is why the attention of both engine and vehicle manufacturers and car users focused on propane-butane gas (LPG). It is already widely used as an alternative fuel in cars, delivery vans, and increasingly in urban buses, and even in trucks. Advantages of the gas-fuelled engines are evident in urban traffic – no smoke while starting and accelerating. The use of gas fuel helps eliminate smoke, sulphur oxides and aldehydes. It also radically reduces the content of carbon monoxide (by approx. 80%) in exhaust gas.

Liquid gases are produced from crude oil and from subsequent processing of semi-finished refinery products involving gasoline reforming processes, cracking of vacuum oil, hydrocracking, desulfurization of petroleum tar as well as pyrolysis of various types of gasolines and gases.

Liquid gas is stored and transported in pressure vessels in liquid state, but it is used in the gaseous state.

Properties of liquid gas:

- high calorific value,
- good combustible characteristics,
- wide range of applications,
- possibility of transporting and storing in locations with no natural gas distribution networks,
- excellent ecological characteristics.

Table 4.1. Composition of propane–butane gas

Composition	
Content of C_3, %	18.0 – 55.0
Content of C_4, min, %	45.0
Content of hydrogen sulphide	none
Calorific value, min, kJ/kg	45,220
Gas density relative to air	0.9
Vapour pressure, MPa	
- at temp. - 15°C, min	0.100
- at temp.70°C, max	2.55

4.2. Motor gasolines

Gasoline is used as fuel for combustion engines. Gasolines are fractions of oil obtained by its separation through fractional distillation, with their boiling range from 35 to 200^{0}C, or obtained through non-conservative processes (secondary processes) including cracking, reforming, isomerisation, hydrocracking, pyrolysis, alkylation, polymerization etc. The output of gasolines obtained from distillation reaches up to 25%, depending on the raw material used.

Individual groups of motor gasolines, with assigned operational properties in the oil industry, can be composed using the following fractions from various processes: base gasoline from distillation, butane fraction (improving starting capacity), a fraction with boiling point of up to 65 ^{0}C (pentane – hexane), light distillate 65 – 90 ^{0}C, reformate (full fractional), reformate (with xylene removed), rafinate of reformate (remaining after extraction), reformate (dearomatisated), gasoline from cracking or its part (divided from the start of boiling to 90 ^{0}C and before 90 ^{0}C – depending on the type of charge in the catalytic converter and cracking conditions, it contains from a dozen or so up to approx. 50% olefins), gasoline from hydrocracking, post-pyrolysis hydrogenated gasoline, alkylates (various) and isomerizates.

All these fractions are constituents used when composing motor gasoline. Blended in specific proportions, they turn into gasolines with desirable operation properties.

Table 4.2 presents generally applied requirements for unleaded premium gasoline, whereas Table 4.3 and 4.4 show admissible contents of oxygen compounds and the composition of liquid fuels.

Table 4.2. Requirements for unleaded premium gasoline.

Properties	octane number RON	octane number MON	benzene content % vol.	density (15^oC) kg/m^3	sulfur content %	induction period min.	present gum content mg/100ml
Range	min 95	min 85	5.0	725-780	max. 0.05	360	5

Table 4.3. Admissible contents of oxygen compounds in gasoline

Item	Requirements	Share % vol.
1.	Share of alcohols, not more than:	
	methyl alcohol	3
	ethyl alcohol	5
	isopropyl alcohol	5
	tert-butanol,	7
	isobutanol	10
2.	Content of ethers containing 5 or more atoms of carbon in a molecule, not more than:	15
3.	Content of other organic compounds containing oxygen, not more than:	10
4.	Total content of oxygen in gasolines containing organic oxygen compounds, not more than:	2.8
5.	Acetone	0.8

Table 4.4. Composition of liquid fuels

Type of fuel	C [% mass]	H [% mass]
Gasoline	max. 85.7	14.3

Petroleum	max. 86.0	14.0
Diesel oil	max. 86.4	13.6
Fuel oil	max. 88.0	8.0

The standards for individual sorts of motor gasoline must be observed to ensure their proper quality. Any gasoline failing to meet the standard requirements is not cleared for distribution/use. The requirements of the particular standard mainly describe the way a gasoline behaves while evaporating and combusting in an engine.

The selection of a type of fuel for an engine must be based on requirements the particular fuel must meet. Both efficiency and economical operation of an engine, as well as the rate at which its parts wear out largely depend on the quality and operational value of the fuel.

The modern-design and more stressed engines with a high degree of compression, higher power and high engine speed, always require superior quality fuel than the less stressed older-design engines.

The type of fuel used in a particular engine should strictly conform to the guidelines given by manufacturers in their instruction manuals.

Technical and economic requirements to be met by fuels, depend mainly on the design of an engine and its operation under various specific conditions. The use of an unsuitable fuel may result in faster wear and tear of an engine, reduced dynamic characteristics of a vehicle and engine’s shortened life.

Motor gasolines used to fuel spark-ignition engines must meet the following general requirements:

- ✓ They should quickly and efficiently produce a homogeneous fuel-air mixture of required quality, which is chiefly influenced by density, viscosity, fractional composition and fuel vapour pressure;
- ✓ They should ensure normal, knock-free combustion of the blend in an engine, in all known operation conditions, which is dependent upon proper knock resistance of a fuel (good anti-knocking properties);
- ✓ They should not produce large amounts of tar or other kinds of build-up (e.g. carbon deposit), which may disturb normal operation of an engine;

- ✓ They should provide stability of their properties in storage, transport and operation;
- ✓ They should not promote corrosion of the metals an engine is made from;
- ✓ They should be characterized by adequately low freezing temperature and resistance to separation in low temperature, so as to ensure steady supply of fuel to the engine;
- ✓ They should contain neither mechanical impurities nor water.

The deciding factors in meeting all above-mentioned requirements are physical and chemical properties of a fuel. They form a basis for both an assessment of fuels' value in use and their identification. These properties are determined using a dozen or so generally accepted numerical factors, specified in respective standards. Some of the indicators allow direct assessment of a particular fuel's value in use, i.e. they specify they way the fuel will behave when burning in an engine (octane number); they can identify susceptibility to produce excessive tar deposits (content of present gums) or corrosion effect on engine parts (corrosion test).

Other indicators – such as for instance initial boiling point and the boiling points of various fuel fractions – enable determination of a fuel's fractional composition, which may also indirectly allow assessment of a fuel's operation properties.

The process of fuel evaporation and mixing its vapours with air begins in carburettor chamber (carburettor engines), and ends in engine cylinders. In order to ensure efficient operation of an engine, the entire process of fuel evaporation should end before the mixture is ignited.

In today's engines fuel evaporation and creation of the mixture lasts very shortly (below 0.1 second). To enable gasoline to evaporate in this very short time, it must be atomized in the smallest possible drops. The smaller the drops, the larger evaporation surface and subsequently the faster conversion of liquid into vapour.

The degree of fuel evaporation depends, to large extent, on the temperature in the suction pipe. When heating the mixture, the speed of gasoline evaporation increases. It must be remembered that excessive heating of the mixture leads to a decrease in the cylinders' filling rate and reduction in engine power.

Apart from the above-mentioned factors, a considerable influence on the efficiency of mixture production is exerted by physical and chemical properties of a fuel, such as density, viscosity, fractional composition and fuel vapour pressure.

Density

Fuel density affects the process of dosing the mixture in the carburettor. The quantity by weight, i.e. the mass of fuel flowing through the nozzle outlets per unit time is directly proportional to its density. For example, when under the same operating conditions of the carburettor the used gasoline has the same viscosity but different density, the combustion chamber will receive more higher-density gasoline, resulting in a richer mixture and increased fuel consumption.

Viscosity

Fuel viscosity affects the speed of its flow through the nozzle outlets. Namely, the higher the fuel viscosity, the slower the rate of its flow through the nozzle outlets, and vice versa.

When the temperature drops, both viscosity and density of fuel increase, but viscosity increases much faster than density. For example, in the case of a temperature drop from 20° to -20°C gasoline density will increase by approx. 4%, and its viscosity by 50%. Increased fuel viscosity causes formation of a poorer mixture, which in the specified temperature range (from +20 to -20°C) manifests itself as a 10% depletion of the mixture.

This phenomenon must not be underestimated during the operation of vehicles, because during annual temperature fluctuations of between 50-60°C the composition of the mixture may change by 18-20%. Consequently, if the carburettor is not regulated before the onset of winter, increased fuel viscosity will slow down heating of the engine and its power, and will cause irregular engine operation.

Also, if one type of fuel is replaced with another, viscosity and density of both fuels must be examined and, if needed, the carburettor must be readjusted.

Fractional composition of fuel

Fractional composition of fuel is a very important indicator of its operational value. The fractional composition of fuel enables assessment of its volatility, which affects the speed of starting the engine, but also its tendency to form vapour locks, which cause breaks in the engine operation. Additionally, knowledge of the fractional composition of fuel enables approximate assessment of its use, and even forecasting of the rate of wear of the engine, in particular its pistons and cylinder bearing surfaces.

The fractional composition of fuel is determined by distillation method, performed in accordance with the requirements of the standards. In the majority of cases, the distillation process determines:

- ❑ the initial boiling (distillation) point, which is characterised by volatility, i.e. the ability to evaporate fuel, and the conditions under which there is a danger of its ignition;

- ☐ boiling point of 10% of fuel, which is used to assess the ease of starting the engine and the fuel tendency to form vapour locks in the engine's fuel delivery system;
- ☐ boiling point of 50% of fuel, which enables assessment of average evaporative power of fuel affecting the heating rate and the regularity of operation of the engine;
- ☐ boiling point of 90% of fuel and the temperature at the end of distillation, which show the quantity of heavy, hard-to-evaporate fractions, which negatively affect engine operation.

It is sometimes difficult to say which fractional composition of fuel ensures efficient and economical operation of the engine. Some of the requirements are contradictory. For example, starting the engine becomes easier the lighter the fuel, i.e. the lower the temperature at which 10% of fuel is distilled. It should be noted, however, that lighter fuel poses a greater danger of formation of vapour locks.

Nevertheless, there is no doubt that fuels with increased content of light fractions should always be used in winter operating conditions, at low ambient temperatures. Fuel volatility changes rapidly with a drop in temperature. For example, while 8-12% of automotive gasoline is evaporated at a temperature of 15°C, only 2-3% is evaporated at a temperature of -15°C.

Gasoline should also be selected taking into account the boiling point of 90% of its components and the temperature at the end of distillation. As those temperatures get lower, there are fewer less-volatile, heavier fractions in fuel, resulting in more complete fuel evaporation, more even filling of each cylinder, and, consequently, less fuel consumption.

Vapour locks are formed when light gasoline with high vapour pressure begins to intensely evaporate at the operating temperature of the engine and passes through the nozzle in the form of foam made of liquid gasoline, its vapours, and many air bubbles. In terms of weight, the amount of gasoline decreases rapidly, the mixture becomes much poorer, the engine starts to throttle down and may stop working.

Vapour locks are formed more easily in summer than in winter, especially in the areas located high above the sea level because with the falling atmospheric pressure gasoline starts to boil at lower temperature. In some countries the range of gasoline products takes into account regional climatic changes and there are different types of gasoline for the summer and winter seasons.

The most favourable conditions for the formation of vapour locks arise when the engine is stopped during hot weather. As a result, the fan stops, the air temperature under the engine cover quickly increases, the gasoline beings to strongly evaporate, and vapour locks are formed, which to a large degree make it more difficult to start the engine even in the case of a relatively short stoppage. The ambient temperature at which vapour locks may form (t_p) is related to the distillation temperature of 10% of fuel ($t_{10\%}$) and this relationship can be described with the following formula:

$$t_p = 2\, t_{10\%} - 93$$

Table 4.5. presents the temperature values, calculated on the basis of the above formula, at which vapour locks begin to form, when using gasoline of different volatility.

Table 4.5. Effect of gasoline volatility on the formation of vapour locks.

Distillation temperature of 10% of gasoline, [^{o}C]	Temperature, at which vapour locks begin to form, [^{o}C]
50	7
60	27
70	47
80	67

The temperature of formation of vapour locks can be calculated on the basis of known vapour pressure of fuel.

$$T = 260 – 77.8 \lg P$$

where:

T – the temperature at which vapour locks begin to form

P – vapour pressure of gasoline determined by the Reid method.

Knocking resistance of fuels

The knocking tendency of a fuel depends to a large degree on its chemical composition. This includes both the group composition and the structure of individual hydrocarbons making up the composition of the respective groups.

Resistance of fuels and individual hydrocarbons to knocking combustion is determined by means of the octane rating, where the greater the octane number of a fuel, the higher its resistance to knocking.

Generally speaking, resistance of the respective hydrocarbon groups to knocking combustion progresses in the following order (starting with least resistant)

n-paraffins → olefins → naphthenes → aromatics

For a quantitative illustration of this relationship, table 6 presents octane numbers of hydrocarbons with six carbon atoms belonging to different hydrocarbon groups. However, those general rules are not strict, because within respective hydrocarbon groups the resistance to knocking combustion changes very significantly, depending on the number of carbon atoms and the structure of a given molecule (isomerism).

The knocking resistance of aliphatic hydrocarbons, i.e. parafins and olefins, decreases as the chain length increases. In the case of a chain containing one carbon (CH_4 – methane) the knocking resistance expressed in octane number units equals 125; in the case of a hydrocarbon with seven atoms it equals zero; and hydrocarbons with more than seven carbon atoms have negative octane numbers. Branching of chains significantly increases the octane number. Resistance of a hydrocarbon to knocking improves with increased branching, greater proximity of branches to the molecule centre, and a more symmetrical branching distribution.

Cyclic (naphthenic and aromatic) hydrocarbons have greater octane numbers than paraffin hydrocarbons. The knocking resistance of highly branched paraffin hydrocarbons (isoparafins) matches the most resistant aromatic hydrocarbons.

Table 4.6. Octane numbers of hydrocarbons of various groups having 6 carbon atoms.

Name	**Chemical formula**	**Type of hydrocarbon**	**Octane number**
Hexane	C_6H_{14}	paraffin (alkanes)	45
Hexene	C_6H_{12}	olefin (alkene)	69
Cyclohexane	C_6H_{12}	naphthenic (cyclic)	87
Benzene	C_6H_6	aromatic (arenes)	96

The knocking resistance of gasoline, as a mixture of typically over a hundred hydrocarbons, is a product of octane numbers of the respective hydrocarbon components (they depend on the volumetric share and the octane number of the components). In the engine, in cases where no conditions are created to evaporate the whole fuel, the created mixture has the same knocking resistance as the evaporated components. Overall, gasoline from paraffin-base crude oil has lower knocking resistance than gasoline from crude oil having naphthenic – aromatic character. Technological processes, which results in the formation in gasoline of a large number of aromatic compounds, such as cracking and reforming, give gasoline with high knocking resistance.

Methods for determining the knocking resistance of fuels

The knocking combustion was first observed when increasingly higher compression ratios started to be used in order to obtain the greatest possible power per unit of cylinder volume. Unsurprisingly, the compression ratio was the first criterion for the assessment of the knocking resistance of fuels because low-resistance fuels burnt in the detonation process already at relatively low compression ratios, whereas high-resistance fuels ‘withstood’ even high degrees of compression. The assessment was carried out on a single-cylinder laboratory engine with variable compression ratio, operating under standardised conditions.

The critical compression ratio, i.e. the highest compression ratio at which fuel burnt without knocking, was a measure of fuel resistance to knocking combustion. That method had several disadvantages, the main one being the subjectivity of assessment of the start of detonation determined aurally and the uniqueness of the results. It turns out that even in very careful measurements we are not able to perfectly reproduce the same operating condition of the engine, therefore the obtained results will be different.

Since an absolute method of measuring the knocking resistance failed, the problem was tackled by means of a relative measurement. If the same operating conditions of the engine cannot be perfectly recreated, the knocking resistance should be related to the standards and the knocking resistance of fuel should be examined together with standard resistance. Any change in the conditions for the examined fuel will be accompanied by a change in the conditions for the standard, whose knocking resistance is known to us.

Method for determining octane numbers

Two hydrocarbons have been adopted as standards: isooctane (2,2,4-trimethylpentane) and n-heptane. Isooctane is more resistant, and heptane less resistant, than normally used fuels. The octane rating has been based on those two standards. According to the rating system, the knocking resistance of isooctane is conventionally designated with the octane number of 100, and of heptane – with the number of 0. The resistance interval was divided into 100 parts to provide a scale of octane numbers. The ***octane number*** defines the percentage, by volume, of isooctane that must be added to n-heptane so that the received mixture, used in a standardised laboratory engine and under standardised conditions, behaves like the examined fuel.

The laboratory research engine used for determination of the octane number is an overhead-valve, single-cylinder engine, in which the compression ratio can be changed during operation. The cylinder is cast as a single unit with the head. It can be moved relative to the piston by means of a special worm gear, which changes the volume of the combustion chamber and, consequently, the compression ratio. This shift is measured with a micrometer graduated in compression ratio units. The head has a built-in device that can measure the intensity of detonations. This process uses a sharp increase in pressure (bouncing pin, piezoelectric quartz sensor, magnetostrictive sensor) or in temperature (thermocouple).

The internal combustion engine is connected via belt transmission to the power receiving device, i.e. the synchronous electric motor. That motor is also used to start the internal combustion engine.

The internal combustion engine has three fuel tanks (one for the examined fuel and two for the standards) and is powered by a special carburettor with three float chambers. In order to maintain constant measurement conditions, the engine is fitted with a column for the cooling of the incoming air and devices for temperature control of cooling water and oil.

The octane number is measured as follows. A parent engine is started on the examined fuel. After some operating time has elapsed, the conditions can be obtained that correspond to the measurement standard (temperature of air, cooling water, and oil). After standardised measurement conditions have been obtained, the compression ratio is changed until the knocking combustion reaches the required intensity. Next, without changing the compression ratio, the examined fuel is replaced with reference fuels. When the engine is powered with pure isooctane, the knocking combustion disappears, so the knocking resistance of isooctane should be deteriorated with the addition of heptane. When the knocking combustion returns with the same intensity as previously for the examined fuel, it will mean that the mixture chosen from reference fuels is equivalent to the examined fuel with respect to the knocking resistance. The percentage content of isooctane in such mixture equals the fuel octane rating. Serial measurements use secondary standards, i.e. gasoline with known octane numbers.

CFR, BASF and IT-9 engines are universally recognised parent engines.

The most commonly used measurement methodologies are the ***motor*** **method** (**MM**) and ***research*** **method** (**RM**). The two methods differ as to the number of revolutions at which the engine operates during the measurements. In the case of octane measurement with the motor method, the number of revolutions is 900 rpm, and in the case of octane measurement with the research method it is only 600 rpm. The measurement conditions are less strict in the case of the research method than in the case of the motor method. Octane numbers determined with the research method are always higher than the ones determined with the motor method.

The difference between the octane number determined with the research method (ON/RM) and the octane number determined with the motor method (ON/MM) may amount to between a few and more than a dozen units. That difference is referred to as sensitivity to the measurement conditions. Paraffin-type gasoline is least sensitive, naphthene-type gasoline has intermediate sensitivity, and olefin–type and aromatic-type gasolines are most sensitive.

When there are two types of gasoline with the same octane number determined by the motor method (MM) but different research octane numbers (RM), the type that behaves better is the one with the higher octane number RM, i.e. the gasoline with higher sensitivity.

There are three main directions in raising the octane numbers: technological, preparation of mixtures with high-octane fuels and addition of antiknock agents.

Technologically, the octane number is increased by the process of reforming. In this process low-octane gasoline components, i.e. mainly straight-chain paraffin hydrocarbons are converted into cyclic (mostly aromatic) or isoparaffin (branched chain) hydrocarbons. The formed hydrocarbons have high octane numbers.

Gasoline from the reforming process, i.e. reformates, are typically used as high-octane components for the preparation of mixtures with gasoline from distillation (base). This process may involve gasoline from other processes having high octane numbers, such as e.g. gasoline from catalytic cracking, alkylation, and isomerization.

Base gasoline can also be mixed with aromatic hydrocarbons and alcohols.

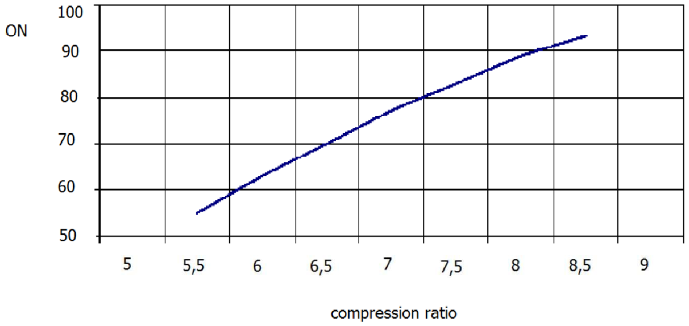


Fig. 4.1 The required octane number of gasoline for engines

Ethyl alcohol significantly increases the octane number of fuel and has low freezing point (-114.5 ^{0}C), but its ability to mix with gasoline is limited and depends on the chemical composition of gasoline (the higher the content of aromatic compounds in gasoline, the better the miscibility). The gasoline-alcohol mixtures (PA) easily break under the influence of even very small quantities of water and therefore mixing is only done with anhydrous alcohol. Much better properties are obtained by preparation of ternary mixtures: gasoline – alcohol – benzene (PAB). In those mixtures ethyl alcohol ensures low freezing point, and benzene, as an aromatic hydrocarbon, facilitates dissolution of alcohol in gasoline and reduces fuel tendency to breaking, i.e. it has a homogenizing effect.

The process of formulation of gasoline mixtures with high-octane components requires introduction of large amounts of the latter to significantly increase the octane number (typically 10 – 40% vol.). So, high octane ingredients have a volumetric effect.

From the first encounters of the knocking combustion, there has been an ongoing quest for compounds that, added to gasoline in even small quantities, would very significantly increase the fuel resistance to knocking. There are such compounds, belonging to organometallic compounds, i.e. compounds in which the organic molecule has an in-built atom or several atoms of metal. The operational effectiveness of such compounds is associated with the presence of metal atoms in the molecules. They inhibit chain reactions that cause knocking combustion. Compounds which, when added to fuel in very small quantities, significantly increase knocking resistance, are called *antiknock agents.*

The most commonly used antiknock agent is lead tetraethyl with the summary chemical formula $Pb(C_2H_5)_4$.

Effect of qualitative and service parameters of fuels on emission of toxic substances

The introduction of the category of low emission vehicles (LEV) and transitional low emission vehicles (TLEV) has changed the existing attitude to the problem of emissions of toxic substances. According to LEV guidelines, restrictions on emissions are no longer limited to total hydrocarbons (THC) as the measurements should also cover non methane organic (NM-OG). Therefore, the amount of emissions from combustion of hydrocarbon fuels is no longer the only criterion of their eco-friendliness.

In order to meet standards for exhaust gas toxicity, 'clean' fuels must be introduced, such as:

- alcohols (methanol, ethanol),
- LPG (Liquefied Petroleum Gas)
- CNG (Compressed Natural Gas)
- reformulated gasoline.

Effect of gasoline composition on exhaust emissions

Depending on the components of engine fuels, the exhaust gases contain various chemical compounds. The research carried out as part of the American program AQUIP (Research Programme for the Improvement of Combustion Processes of Motor Car Fuels) on gasoline reformulated in cars with catalytic converters lead to certain conclusions regarding that problem.

1. It was concluded that a reduction in the number of aromatic hydrocarbons in fuel, leads to a reduction of the benzene content in exhaust gases, but causes increased emissions of aldehydes. No substantial impact was noted with respect to emissions of carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x).
2. The addition of MTBE (methyl tert-butyl-ether) reduces the content of carbon monoxide (without increasing NO_x) and causes increased emissions of aldehydes.
3. A reduction in the amount of olefins in the fuel slightly increases the presence of HC (hydrocarbons) in exhaust gases, but lowers NO_x.
4. Adjustment of the shares of fuel components gives different CO_2 content in exhaust gases, which is important due to the greenhouse effect. The higher the ratio of C/H in a hydrocarbon molecule included in the fuel, the more CO_2 is created.
5. A reduction in the sulfur content from 466 ppm to 49 ppm leads to a reduction in hydrocarbon emissions by an average of 16.2%.

6. A lowering of the boiling end point of fuel components causes a reduction of hydrocarbons and all unlimited toxic substances in exhaust gases. There is a linear relationship between the course of distillation and the emission of hydrocarbons. In the case of olefin-rich fuels (butene, pentene) emission is greater than in the case of gasoline with a large share of aromatic hydrocarbons.
7. Participation of burnt fuel components also affects the potential of smog development as a result of formation of tropospheric ozone and its binding by hydrocarbons contained in exhaust gases. The NM-HC/NO_x (non-methane hydrocarbons) ratio determines the number of hydrocarbons capable of transformations as a result of oxidative action of ozone formed from photochemical reactions.

Those relationships are characterised by the following amounts, determined in a research contracted by the California Air Resources Board:

- maximum incremental reactivity (MIR) – determines how many grams of ozone can be created as a result of photochemical reactions (involving NO_x and air) and can be bound under specific conditions with 1 gram of the respective components of the unburnt fuel without methane; MIR is used to assess the state of atmosphere during smog;
- ozone forming potential (OFP)

Ethanol

Anhydrous ethyl alcohol was the first substitute of motor-car gasoline. In 1937 in Europe 13 million tons of gasoline with admixture of 2.3 million tons of substitutes (17.7%) were used, of which 22% constituted ethanol with the average participation in gasoline of approx. 4%. Already in 1977, half a million tons of ethanol was used in Brazil as a 20-percent component of gasoline and it was planned that some of the sugar factories, producing 94 kg of sugar and 13 litres of ethanol from each ton of sugar, would be switched over to production of 67 litres of ethanol without sugar production.

Physicochemical properties of ethanol with respect to gasoline have been presented in table 4.6. The above date show the following features of ethanol as a fuel:

- large oxygen share and low calorific value, which causes increased fuel consumption per unit of road covered by a vehicle;

- high heat of evaporation (ethanol - 210 kcal/kg, gasoline 80 kcal/kg), which results in better cylinder fill, but requires heating of the fuel/air mixture and structural alterations of the engine if ethanol is used as autonomous fuel;
- high octane number;
- low demand of air for combustion, which necessitates structural changes of the engine and enrichment of the fuel/air mixture if ethanol is uses as autonomous fuel;
- low vapour pressure causing difficulty in starting at low temperatures, which precludes use of ethanol as an autonomous fuel and makes it necessary to use a composition containing at least 10 to 15% of light gasoline, which improves starting properties.

Theoretically, ethanol can be used as an autonomous fuel provided it is used in double fuel engine, which starts with gasoline and runs with ethanol. In practical terms, ethanol can be used exclusively as a gasoline component. The relative calorific value of the gasoline/ethanol mixtures decreases with the growing share of ethanol, causing increased consumption per unit of road covered by the vehicle.

Table 4.6. Comparison of the ethanol and gasoline properties.

Specification		Ethanol	Base regular gasoline (Etylina 94)
bulk chemical composition	carbon	0.52	0.86
	hydrogen	0.13	0.14
	oxygen	0.35	0.00
calorific value MJ/kg		26.8	45.5
octane number	by the research method	111.0	91.0
	by the motor method	94.0	82.0
air demand, kg air/kg fuel		9.0	14.7
vapour pressure by the Reid method, kPa		21	70-80
heat of evaporation at a temp. of 20^0C, kJ/10^3 kJ of calorific value		33.7	92
boiling point ^{o}C		78	30-215

Table 4.7. Comparison of the properties of gasoline/ethanol mixtures and gasoline

Specification		Mixture of 20% ethanol /80% gasoline	Gasoline
toxic exhaust components g/test	CO content	112.0	112.0
	HC content	9.2	9.6
	NO_x content	4.0	12.0
fuel consumption g/test		409.0	410.0
fuel consumption	consumption of fuel equivalent, g/test	377.0	410.0
	energy saving %	8.0	-

Table 4.8. Mileage comparison of a car powered either by gasoline or by a mixture of gasoline and ethyl alcohol with the composition of 10% ethanol and 90% gasoline.

Vehicle speed, mil/h	10	20	30	40	50	60
gasoline mileage, mil/USgal	20.7	20.5	19.4	17.6	15.9	13.9
mixture mileage, mil/USgal	21.5	21.5	19.6	18.0	16.0	14.0
gain in mileage, %	3.9	5.0	1.0	2.3	0.6	0.7

Change in the distillation curve of gasoline with the growing share of ethanol augments starting problems.

Pure, hundred percent ethanol mixes with water and gasoline hydrocarbons at any ratio. However, mixtures with gasoline hydrocarbons are hygroscopic, which creates significant difficulties during storage, warehousing and transport, and operation, because even minimum quantities of water cause breaking of the homogeneous gasoline/alcohol mixture and its separation into the water/alcohol layers and the gasoline layer. This means than only the ethanol used for mixtures with gasoline must be anhydrous, but special attention must be also given to anhydrous condition during the storage, transport, and refuelling of mixtures to the vehicle tank. The risk is reduced when the mixtures are operated exclusively at positive temperatures (e.g. in Poland only as a seasonal, summer fuel) or when anti-breaking substances are added (so-called solubilisers). The data show significant ethanol usability as a factor improving the anti-knocking properties of fuel (the octane number).

The addition of alcohol increases the research octane number to a greater degree than the motor octane number.

Because of quicker progression of the wave of flame during combustion of the ethanol/air mixture and broader ignition boundaries than in the case of the gasoline/air mixture, the energy effect of ethanol use is positive, especially considering the fact that alcohol enables use of higher compression rates in engines.

A positive aspect of use of the gasoline-ethanol mixtures is the lowering of emission of toxic substances in exhaust gases. The results of the engine test bed studies of emission as well as fuel and energy consumption in passenger cars are presented in table 4.7

As early as over 50 years ago it was observed during road operation that fuel consumption increased by 6% relative to gasoline with the use of a mixture containing 10% ethanol. Those data were confirmed during the measurement of fuel consumption with the 10% ethanol content in 12 cars at different driving speeds; savings were found at low driving speeds and none were found at higher speeds, as shown in table 4.8.

4.3. Diesel fuels

Compression-ignition engines have compression ratio of around 13-20, i.e. almost two and half times higher than spark-ignition engines. The fuel/air mixture created directly in the cylinder has the excess air ratio of 1.4-2.0 whereas in the spark-ignition engine the excess air ratio ranges from 0.85 to1.2.

In high-speed compression-ignition engines the method of feeding fuel to the cylinder, the formation of the fuel/air mixture, and the combustion process itself are more complicated than in modern engines with spark-ignition engines.

Diesel fuels must have good spraying capacity, good miscibility with air, and must enable easy start of the engine, which depends primarily on their volatility (fractional composition) and viscosity.

In the combustion process it is extremely important that the ignition starts easily and the combustion is complete, and takes place in a rhythmic manner, where the decisive role is played by the self-ignition temperature of the fuel, defined by the so-called cetane number.

As in the case of gasoline fuels, it is expected that diesel fuels will not form excessive amount of deposits, will not corrode engine parts, will not accelerate the wear of the supply system or other engine systems, and will maintain sufficient stability under storage and transport conditions.

High-speed compression-ignition engines use fuels called diesel fuels. The boiling point of diesel fuels is in the range of 150-350°C.

In a diesel engine the time required to spray fuel and produce mixture with the same engine speed (2 000 rpm) is only -0.002-0.003 seconds, i.e. it is ten times less than in a spark-ignition engine.

Efficient production of a mixture in a compression-ignition engine depends on many factors, of which the most important include: temperature and pressure in the combustion chamber, the degree of fuel atomisation at injection and the fuel jet speed, as well as the physicochemical fuel properties, in particular viscosity and volatility.

Viscosity

Viscosity influences very strongly the free flow of fuel through injection pump filters, lines, and inlets as well as the degree of fuel atomisation and the jet scope. Viscosity is an important indicator of the operational value of diesel fuels because it characterises their liquidity at the selected measurement temperature.

The higher the viscosity of a fuel, the more difficult is its flow through lines, filters, and other elements of the supply system and, as a result, the more energy is wasted to overcome flow resistance, which consequently reduces engine power. When fuel viscosity exceeds the permissible limit for a given compression-ignition engine, the fuel jet breaks and the fuel delivery system stops.

Too low viscosity of diesel fuels is also undesirable because in compression-ignition engines fuel also acts as a lubricant for injection pump plungers. Consequently, if lubrication of those elements is insufficient due to too low fuel viscosity, they wear out faster and do not achieve the planned operational mileage.

Low-viscosity fuels are also prone to leaking through gaps in injection pumps and injectors, which impedes steady flow of fuel to the cylinders. There are some cases of leakage of fuel through injection nozzles and cocking of their outlets due to incomplete combustion of fuel.

Because of all those reasons, the viscosity of diesel fuels must be regulated within strictly defined limits, depending on the type of engine design.

Diversification of viscosity in summer and winter fuels is caused by their changing viscosity depending on temperature. Whereas in the range of above-freezing temperatures from 0 to 20^{o}C the changes in diesel fuel viscosity are small, as the temperature falls below 0°C their viscosity begins to increase very rapidly.

Table 4.9. shows a sample course of change in diesel fuel viscosity in relation to temperature.

Table 4.9. Change in diesel fuel viscosity depending on the temperature of two kinds of diesel fuel (summer and winter). Fuel viscosity is expressed as kinematic viscosity in centistokes.

Fuel type	Temperature ^{o}C			
	20	0	-10	-20
	Kinematic viscosity cSt			
Summer diesel fuel	6.36	12.94	20.59	50.92
Winter diesel fuel	4.26	8.36	-	20.60

Effect of fuel viscosity on the degree of its atomisation and the jet scope

Another issue is the impact of fuel viscosity on its jet scope. If the flow range is too small, all fuel will burn close to the injection nozzle outlets with the participation of a small amount of air. Insufficient air in the mixture causes incomplete fuel combustion and, consequently, loss of engine power and a reduction of its efficiency. If the jest scope is excessive, fuel will be deposited on the walls of the combustion chamber and the piston head, where it will burn down to from carbon deposits.

Fuels with lower viscosity and lower specific gravity spray better, but they have a smaller jet scope and evaporate faster; on the other hand, the better the fuel viscosity, the deeper it penetrates the compressed air layer and the lower its evaporation due to the higher boiling point.

When diesel oils with higher viscosity are used, the injection pressure must be increased to obtain better atomisation.

The fuel jet injected into the combustion chamber is heterogeneous and consists of a large number of drops of various sizes, which disperse at different speeds. The drops in the middle of the jet, which is most concentrated area, have the largest diameter, and as the distance from the centre increases their diameter diminishes.

All other conditions being the same, the size of drops of the sprayed fuel is directly proportional to the fuel viscosity. As the diesel fuel viscosity increases, the degree of jet atomisation decreases, which, in turn, disrupts the rhythm of mixture formation and contributes to its incomplete combustion.

Diesel fuels of increased viscosity are burnt up already during the expansion stroke, which contributes to increased unit consumption of fuel and increased degree of exhaust smoke.

Too low fuel viscosity is undesirable because lubrication of injection pump plungers can then be inadequate, causing their faster wear.

Fractional composition of fuel and mixtures

Evaporation is influenced to a large degree by the degree of atomisation and the fractional composition of the fuel that characterises its volatility. Fuels with lighter fractional composition, i.e. with lower boiling point limits, will evaporate faster, whereas heavier fuel components will not evaporate within the specified period of time. Fuel will then burn already during the expansion stroke, and its unburnt parts will be evacuated through the exhaust pipe.

Less volatile fuels with heavier fractional composition can only power compression-ignition engines with a precombustion chamber or a turbulence chamber.

The boiling point of fuel with optimal fractional composition should fall within the range of 150-350°C.

Diesel fuel with a wide range of boiling points and heavy tails is undesirable because it does not burn completely (which can be determined by the large amount of smoke in exhaust gases) and, moreover, during combustions creates excessive amounts of carbon deposits and tar, which build up on the injector tips.

Insufficient amount of light fractions in fuel makes it more difficult to start the engine at low temperature. The boiling point of the individual fuel components characterises to some extent the starting properties of diesel fuel due to the relationship between the value of that temperature and the fuel viscosity.

Disruptions in the operation of compression-ignition engines in winter

Water may be diluted in diesel fuels or it may form a certain type of emulsion. Although only very small amounts of water dissolve in fuel, just its presence in fuel increases the cloud point and the freezing point of fuel, which is very undesirable during winter operation.

If fuel contains water in the form of emulsion, it loses transparency and becomes cloudy.

Water dissolved in fuel in a state of very fine suspension does not constitute a serious danger to the operation of injection pumps and injectors during summer. However, the use of watered fuel in winter, at a temperature below 0°C, is especially dangerous because emulsified water freezes, releasing ice crystals that settle on the fuel filter mesh and clog it up. As a result, fuel flow to the cylinders is broken and the supply system becomes air locked.

Rheological properties of fuel.

Difficulties in the supply of compression-ignition engines at low ambient temperatures are caused not only by excessively high freezing point of fuels, but especially by their inappropriate rheological properties, as evidenced by excessive increase of viscosity at decreasing temperature.

Due to a significant increase in viscosity, diesel fuel can no longer flow through the filter at a temperature that is between a few to more than a dozen degrees higher than its freezing point. The ability of a fuel to flow through filters, at a temperature higher than its freezing point, is determined mostly by viscosity that is achieved by that fuel at a given ambient temperature.

With falling temperatures the viscosity of a fuel increases at a slower or higher rate depending on its chemical composition and structure. The ability of fuel to flow through filter rapidly decreases near the starting temperature for crystallisation.

Criteria for assessing liquidity of fuels at low temperature

Both the cloud point and the freezing point are primary indicators of the ability of fuel to flow at low temperature.

Fuel becomes cloudy due to its release of small, hard crystals of paraffin hydrocarbons. The temperature at which this phenomenon takes place is called the cloud point.

If the engine is powered with diesel fuel whose cloud point is higher than the ambient temperature, the paraffin crystals begin to fall out of fuel and deposit on the filter mesh, which may cause interruptions in the supply of fuel to the cylinders. Cases of interruption of fuel supply due to filter clogging with paraffin crystals occur most often during the start and warming of the engine, when the air temperature under the engine housing is still relatively small. Once the engine has warmed up, the risk of clogging of the filter meshes is significantly reduced.

In order to ensure normal fuel supply to the cylinders during cold weather, the diesel fuel should be used with the cloud point lower by 3-5°C than the ambient temperature.

The freezing point is the temperature at which diesel fuel completely loses its liquidity.

The freezing point is determined according to the requirements of the standards by the so-called test tube method. The freezing point is assumed to be the temperature at which the meniscus of the examined fuel in a test tube does not change over the period of 1 minute after the test tube has been tilted by 45°.

The freezing point of diesel fuels is usually 5-15°C lower than their cloud point. Therefore, in order to ensure normal engine operation at low temperatures, the fuel should be used whose freezing point is at least 15°C below the ambient temperature.

Cetane number and the functional properties of fuel

Self-ignition temperature of fuel, assessed by means of the so-called cetane number, has a direct and substantial impact on the character of the combustion process in a compression-ignition engine.

The higher the cetane number of a fuel, the better its self-ignition ability, the shorter the ignition delay period, and the more regular the course of the combustion process.

The cetane number specifies volumetrically the percentage ratio of cetane to α-methylnaphthalene in such reference mixture of those two components, which at standardised conditions in a single-cylinder parent engine burns in the same way as the examined fuel.

It has been assumed that cetane ($C_{16}H_{32}$) is characterised by a short ignition delay period, has the cetane number equal to 100 units, and for α-methylnaphthalene ($C_{11}\,H_{10}$), with high self-ignition temperature, the cetane number equals 0.

There are several methods of determining the cetane number, which different from each other with respect to the method of measurement of fuel ignitability.

The cetane number can be calculated on the basis of average boiling point of diesel fuel according to the formula:

$$\mathrm{LC} = \frac{t_{śr} - 58}{5 \times q}$$

where:

t_{avr} – average boiling point of fuel [^{o}C],

q – fuel density at 20^{o}C [g/cm^{3}].

The difference between the calculated cetane number value and the value determined on the parent engine varies on average between 2÷5 units.

Optimum cetane number values of the fuels for ignition-compression engines should fall within the range of 45÷70 units. Too low cetane numbers (less than 45 units) deteriorate engine operation and increase fuel consumption. Increasing cetane numbers over 70 units increases the engine tendency to rough running.

The cetane number, as an indicator of fuel ability to self-ignite, also defines other operational properties of the engine connected with combustion, in particular the starting characteristics and the tendency to form deposits and smoke. The higher the cetane number, the more the above properties improve.

The value of the cetane number is related to the group composition of diesel fuel. The biggest cetane numbers belong to paraffin hydrocarbons with long and simple chains, containing a lot of carbon. Aromatic hydrocarbons have the smallest cetane numbers. Naphthenic hydrocarbons are characterised by average value of cetane numbers.

Paraffin hydrocarbons are most desirable in diesel fuel, but due to high freezing point and cloud point they are undesirable in the conditions of winter operation. Therefore, diesel fuels are a mixture of paraffin and naphthene groups, selected at a ratio ensuring sufficiently high cetane number and low freezing point.

In order to increase the cetane number, fuels derived from crude gasolineeum are enhanced with additives in the amount of 1÷2%. The operational effectiveness of an additive depends on the chemical composition of a fuel. Additives are found to be more effective in the case of diesel fuels derived from crude oil distillation, than in the case of diesel fuels derived from cracking.

Effect of diesel fuel quality on the formation of carbon deposits and engine corrosion

During fuel combustion in compression-ignition engines carbon deposits are formed on valves, pistons, injectors, and in the combustion chamber. Carbon deposits disrupt normal engine operation by causing overheating of the engine, cocking of atomiser holes, and seizing of piston rings.

Carbon deposits are a product of oxidation and thermal decomposition of hydrocarbons constituting components of fuel and lubricating oil.

The amount of carbon deposits depends on the degree of engine compression, the intensity of heat evaporation from the combustion chamber, the quality of fuel atomisation, and, above all, on the type of fuel.

The higher the compression ratio and the lower the temperature of the piston head, the greater the intensity and amount of the formed carbon deposits.

The amount of carbon deposits increases if fuel contains unsaturated hydrocarbons, gums, sulphur compounds (mostly mercaptans) or organic acids. During the combustion of high-sulphur fuels the formed carbon deposits are harder and denser, which is one of the reasons for more intensive engine wear.

Free sulfur and its compounds as well as acids and bases contained in diesel fuels may cause corrosion of engine parts. Corrosion intensity depends mainly on the temperature of the engine units. At low temperatures condensed water vapour reacts with sulfur dioxide and sulfur trioxide (fuel combustion products) by forming acids, which cause intensive corrosion of pistons, cylinder bearing surfaces, and the exhaust system.

At high temperatures over 300°C gas corrosion is formed. Thus, acid corrosion will occur most frequently at engine start and stop, while gas corrosion will take place in high-speed stressed engines running at constant conditions.

Diesel fuel additives

Due to the need to improve engine efficiency and thus reduce CO_2 emissions, there is a noticeable growth in the popularity of compression-ignition engines, used mostly with direct injection. Their use has always been characterised by high cost-effectiveness and lower CO_2 emissions. However, considering future Euro standards, actions are being taken to improve diesel fuel characteristics by means of:

- lowering of sulfur content,
- increasing the cetane number value,
- lowering the content of aromatic hydrocarbons,
- improving low-temperature properties.

There are four alternative ways to improve the quality of diesel fuels:

- selective composition,
- aromatics extraction,
- hydrocracking,
- hydrodesulfurisation.

Of the presented options, the most practical, but also the most expensive one, is hydrodesulfurisation.

The research on the impact of diesel fuel components on emissions from compression-ignition engines shows that:

1. There is a linear relationship between diesel fuel density, the S content, and particulate matter (PM) emissions.
2. An increase in the cetane number causes a reduction of PM and nitrogen oxides NO_x in exhaust gases, with this effect being dependent on the type of engine.

3. the use of improvers has a positive effect on emissions of particulate matter, hydrocarbons, and carbon monoxide; no relationship was found regarding NO_x emissions.
4. The use of diesel fuels with different chemical compositions also changes such operating parameters of engines as:
   - value of torque obtained,
   - fuel consumption per unit,
   - combustion process,
   - course of start-up of cold engine.

Positive results of improvement of combustion quality and lowering of emissions of toxic exhaust components can be obtained by using additives to standard diesel fuel. Fuel improvers are intended to reduce smoke emissions and emission of CO, HC, NO_x and SO_2. The main additives are organometallic or organic compounds containing weakly bound oxygen. The most frequently used organometallic compounds are salts of barium, iron, aluminium, and zinc.

The action of organometallic compounds involves:

- ❑ inhibiting agglomeration of soot particles, facilitating their aftercombustion,
- ❑ lowering of the self-ignition temperature of soot,
- ❑ catalytic effect on the combustion process, which accelerates fuel oxidation,
- ❑ catalytic effect accelerating decomposition of water vapour, which results in the formation of hydroxyl radicals that accelerate oxidation of carbon.

The action of organic compounds, containing weakly bound oxygen, involves mainly its quick release during the ignition delay period and acceleration of the pre-flame reactions. The effectiveness of the impact of organometallic compounds is several times greater that the effectiveness of organic compounds.

Additives raising the cetane number of diesel fuels

It has been concluded that additives break down fairly quickly under the influence of water and long-term storage of fuels, and the cetane number is again lowered. Consequently, the choice of a proper additive is difficult and complicated.

Table 4.10.. The effect of additive use on the value of the fuel cetane number.

Type of additive	Percentage amount of the additive					
	0	0.5	1.0	2.0	3.0	4.0
	Value of the cetane number of fuel					
Acetone peroxide	33	41	45	51	57	63
Butyl peroxide	33	43	48	55	57	60
Methyl acetate	33	40	44	50	55	60
Isoamyl nitrate	33	39	41	49	54	58
Ethyl nitrate	33	39	44	49	53	57

On the basis of research, a relationship has been determined between the cetane number (CN) and the octane number (ON) of fuel:

$$\mathrm{CN} = \frac{ON}{2}$$

According to the formula, the higher the cetane number of fuel, the lower its octane number and vice versa. Therefore, the higher temperature of the surrounding air contributes to knocking combustion in a spark-ignition engine, but reduces the tendency of a combustion-ignition engine to rough running.

At low temperatures there is less knocking tendency in a spark-ignition engine, but conditions are created for rougher running of a compression-ignition engine.

Literature

1. Gasoline FAQ - Part2 of 4, Bruce Hamilton, Industrial Research Ltd. (IRL), a Crown Research Institute of New Zealand.
2. http://www.turborick.com/gsxr1127/gasoline.html
3. Gary, J.H. and Handwerk, G.E. (2001). Petroleum Refining Technology and Economics, 4th Edition. Marcel Dekker, Inc.. ISBN 0-8247-0482-7.
4. James Speight (2008). Synthetic Fuels Handbook, 1st Edition. McGraw-Hill, p 92-93.

5. David S.J. Jones and Peter P. Pujado (Editors) (2006). Handbook of Petroleum Processing, 1st Edition. Springer.
6. John Mc Ketta (Editor) (1992). Petroleum Processing Handbook. CRC Press.
7. http://www.bodrum-hotels.com/slide/i2ttp-s8erv8era17c3arl8etona17c3a/2b-gasoline-and-diesel-properties.html
8. http://www.oilandnaturalgasproperties.com/
9. A.J.Pahnke and W.E. Bettoney , Role of Lead Antiknocks in Modern Gasolines, SAE Paper 710842 (1971) 32p.
10. I.S. Al-Mutaz, How to implement a gasoline pool lead phase down, Hydrocarbon Processing , February 1996, 63-69p.
11. Abdel-Rahman, A.A., Osman, M.M., 1997. Experimental investigation on varying the compression ratio of SI engine working under different ethanol–gasoline fuel blends. International Journal of Energy Research 21, 31–40.
12. Alexandrian, M., Schwalm, M., 1992. Comparison of ethanol and gasoline as automotive fuels. ASME papers 92-WA/ DE-15.
13. Aulich, T.R., He, X.M., Grisanti, A.A., Knudson, C.L., 1994. Gasoline evaporation ethanol and nonethanol blends. Journal of Air and Waste Management Association 44, 1004–1009.
14. Bata, R.M., Elord, A.C., Rice, R.W., 1989. Emissions from IC engines fueled with alcohol–gasoline blends: a literature review. Transactions of the ASME 111, 424–431.
15. Chandler, K., Whalen, M., Westhoven, J., 1998. Final result from the state of Ohio ethanol-fueled light-duty fleet deployment project. SAE Paper 982531.
16. Furey, R.L., Perry, K.L., 1991. Composition and reactivity of fuel vapor emissions from gasoline-oxygenate blends. SAE Paper 912429.
17. Naegeli, D.W., Lacey, P.I., Alger, M.J., Endicott, D.L., 1997. Surface corrosion in ethanol fuel pumps. SAE Paper 971648.
18. Rice, R.W., Sanyal, A.K., Elrod, A.C., Bata, R.M., 1991. Exhaust gas emissions of butanol, ethanol and methanol– gasoline blends. Journal of Engineering for Gas Turbine and Power 113, 337–381.
19. George E. Totten, Steven R. Westbrook Rajesh J. S Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing (Astm Manual Series, Mnl 37) Publisher: ASTM International

5. Alternative fuels

There is a growing interest in non-petroleum-derived fuels. Fig. 5.1. shows classification of alternative fuels.

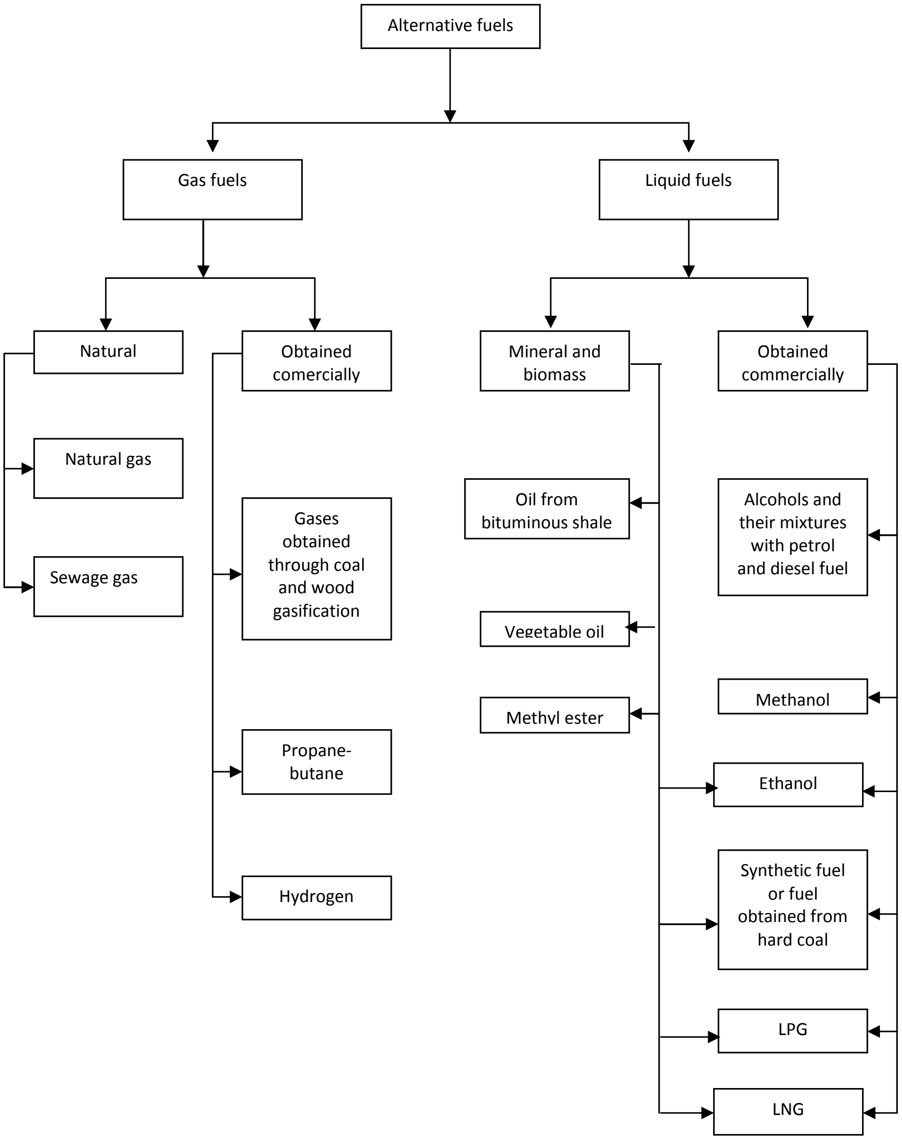


Figure 5.1. Classification of alternative fuels.

An interesting characterisation of the properties of conventional and alternative fuels can be found in table 5.1

Table 5.1. Comparison of the properties of conventional and alternative fuels

Fuel parameters	Unit	Gasoline super RON 98	Diesel fuel	Heavy oil	Methanol	Ethanol	Vegetable oil	Liquefied petroleum gas	Methane	Biogas	Hydrogen
Calorific value, CV	MJ/kg MJ/m^3	41.0 30.8	43 35.8	41.3 39.25	19.7 15.5	26.8 21.2	37.1 34.5	45.84 24.75	50.00 21.20	17.50 0.0215	120 8.52
Energy density	MJ/m^3	3.75	3.865	3.657	3.438	3.475	3.504	3.725	3.223	3.17÷3.25	2.97
Flammability limit from…to λ	-	0.4 1.4	0.48 1.35	0.5 1.35	0.34 2.0	0.3 2.1		0.4 1.7	0.7 2.1	0.7 2.3	0.5 10.5

RON/MON R- research M- motor	- -	98 98			114.4 94.6	111.4 94.0		100 95	140		
Methane share	-							18	100	65	0
CN	-		45÷55	34÷44			40÷50				
H C O N	- - - -	0.15 0.85 0 0	0.137 0.863 0 0	0.14 0.85 0 0.01	0.125 0.375 0.5 0	0.13 0.52 0.35 0		0.177 0.823 0 0	0.25 0.75 0 0	0.09 0.44 0.47 0	1.0 0 0 0
Gram-molecular weight	kg/mol	98	170	198	32	46		51	16	27	2
Distillation temp.	^oC	30÷190	170÷350	175÷450	65	78	180÷360	-30	-162	-128	-253
Heat of vaporization	kJ/kg	420	300		1119	904		353	510		450
Vaporisation pressure	bar	0.45÷0.9			0.37	0.21					
Density of: liquid gas	kg/m^3	730÷780	815÷855	950	795	789	930	540 2.06	424 0.72	1.2	71 0.09
Theoretical air demand, L_t	kg/kg	14.7	14.5	14.6	6.46	9.0	12.7	15.5	17.2	6.1	34

Biofuels

More and more attention is given to the growing role of biofuels, mainly for economic reasons and because of new raw materials for their production, which are substitutes for crude petroleum.

An important role in promoting those raw materials is played by their ecological properties, i.e. the high degree of biodegradability and the ability to lower emissions of toxic components in exhaust gases. Production and use of biofuels significantly reduce carbon dioxide emissions compared to diesel fuel and gasoline, which is extremely important due to the worsening of the greenhouse effect (biofuel production will result in the use of fallow land to plant crops). The European Commission predicts that biofuels will be applied in all engine fuels. It is assumed that mainly three types of biofuels will be produced, i.e. bioethanol, biogas, and biodiesel.

Bioethanol – ethanol is used as a component of engine fuels and a raw material for the production of ETBE (ethyl tert-butyl ether) and MTBE (methyl tert-butyl-ether). Those products are used as components for lead-free gasoline. Bioethanol is produced mainly from wood (lignocellulose), cereal seeds, sugar beet, and sugar cane.

Biogas – fermentation gas obtained from household waste and municipal sewage with the participation of anaerobic bacteria. It consists of approx. 65% methane, up to 30% of CO_2, approx. 2% of hydrogen and trace amounts of nitrogen and sulphide. It is used for energy purposes, mainly on farms, and to power SI and CI engines after their modification.

Biodiesel – that fuel consists of methyl esters of rapeseed oil fatty acids. They are used alone or in combination with diesel fuel.

Rapeseed oil fuel has the following major advantages compared to diesel fuel:

- on average approx. 65% less exhaust smoke,
- lower sulfur dioxide emissions,
- 35÷40% less CO and hydrocarbon content in exhaust gases,
- on average approx. 35% less particulate matter content (mainly soot),
- biodegradability at a level of 98.3%,
- less carbon dioxide emissions (it is partially assimilated by rapeseed cultivation).

High flash point of biodiesel ($170^{o}C$) is also an advantage due to the improved fire safety. The fuel also does not form explosive mixtures with air. The main disadvantage of rapeseed oil fuel is increased emission of nitrogen oxides NO_x.

Literature

1. Elsbett L., Entwicklung eines Dieselmotors mit warmedichterem Verbrerungsraum. MTZ, nr 3, 1981.
2. Fidell T.: Liquid gold. Engine Technology International, nr 1, 1999.
3. Shaine Tyson K: Biodiesel Handling and Use Guidelines. US Department of Energy, 2001.
4. [103] Shell Lexikon, Folgę 26, MTZ, nr 7/8, 1997.
5. [104] Shell Lexikon, Folgę 27, MTZ, nr 9, 1997.
6. Sykes R., Gas works -Gas fuel systems are maturing quickly to make LPG a practical alternative to diesel and gasoline. Engine Technology International, nr 4, 1999.
7. American Coalition for Ethanol: www.cthanol.org

6. Coal derived liquid fuels

6.1. Introduction

Two basic approaches to convert coal to a liquid fuel:

- ✓ Direct Liquefaction calls for breaking coal down in a solvent at elevated temperature and pressure, followed by interaction with hydrogen gas and a catalyst.
- ✓ Indirect Liquefaction involves first gasifying coal and then making synthetic fuels from this "syngas." Using modern technology, indirect liquefaction produces environmentally compatible zero-sulfur liquid fuels that are cleaner than required under today's emissions laws and regulations.

Technology has come a long way since the first coal-derived liquid fuel (a synthetic crude oil) was produced through direct liquefaction in the early 1900s. In 1925, Franz Fischer and Hans Tropsch used an indirect liquefaction process, which still bears their name, to produce excellent transportation fuels. Germany had 25 liquefaction plants that, at their peak in 1944, produced more than 124,000 barrels daily and met 90 percent of the nation's needs.

In the 1950s, South Africa, through its SASOL Co., developed a commercial coal liquids industry to produce transportation fuels (gasoline and diesel) using synthesis gas produced by the gasification of coal. Modern research has further developed this technology, and SASOL has produced more than 700 million barrels of synthetic fuels from coal since the early 1980s. About 85 percent of the coal consumed in South Africa is used as synfuels feedstock or to produce electricity.

Advantages of Coal-to-Liquid Fuels

- ➢ Improves national and economic security by lessening dependence on foreign oil and substituting plentiful, more affordable U.S. coal.
- ➢ Uses domestic resources and produces more jobs for Americans.
- ➢ Provides positive influence on balance of trade and economy.
- ➢ Provides environmental benefits, including cleaner fuels that reduce nitrogen oxide and particulate emissions, enabling use of higher efficiency engines.
- ➢ Is capable of capturing carbon dioxide (CO_2) emissions and serving as a bridge to a hydrogen fuel future through.

- Polygeneration (linking multiple types of plants into one, such as co-production of liquid fuels, electricity, hydrogen, etc., embodied in initiative).

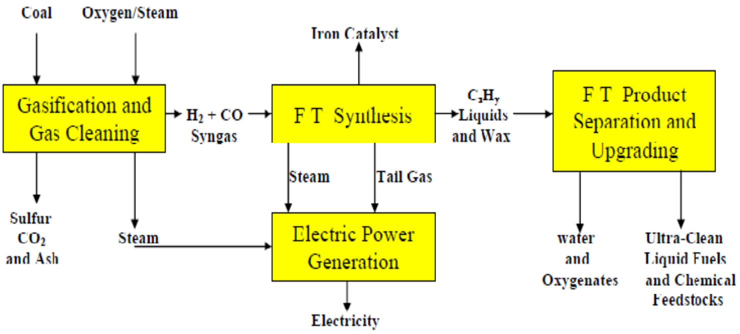


Figure 6.1. One method of producing liquid fuels from coal is the Fischer-Tropsch indirect liquefaction process, which yields high quality transportation fuels, among other products (SOURCE: FT Solutions LLC).

In addition to synthetic oil and diesel fuels, numerous additional liquid products can be derived from coal, including these examples from the Fischer-Tropsch indirect liquefaction process.

6.2 Fischer – Tropsch (F-T) Liquids

The Fischer-Tropsch process can produce fuel out of syngas. It also offers a way to recover "stranded" natural gas (resources that would be uneconomical to transport in gaseous form). While diesel fuel is easily produced, the lighter components can be processed into gasoline with substantial refining. Fischer-Tropsch processes are widely used in South Africa to produce liquid fuels from coal.

Fischer-Tropsch liquids can be transported through the existing infrastructure and used in existing engines. They offer a substantial opportunity to reduce dependence on petroleum, and offer modest environmental benefits. In a 1998 study, emissions from trucks were measuring using California diesel and Fischer-Tropsch diesel. F-T emissions were lower by 12% for NOx, 24% for PM, CO by 18%, and hydrocarbons by 40%. Fischer-Tropsch diesels are also very low in aromatics, a class of compounds that includes hazardous chemicals such as benzene. However, life-cycle CO_2 emissions from Fischer-Tropsch liquids are higher than for petroleum-derived fuels unless sequestration is employed.

Indirect coal liquefaction through the Fischer-Tropsch process provides a "safety valve" against oil price shocks or supply disruptions. Its emission characteristics are superior to conventional diesel, and its cost may be competitive.

Fischer-Tropsch diesel does not have the infrastructure problems. Price, however, remains a problem and, as with cellulosic ethanol, someone will have to take the risk with the first several pioneer plants. Also, particulate matter, while lower than conventional diesel, is still high enough to be a significant concern for both global warming (black carbon) and direct human health impact. Finally, until sequestration is demonstrated to be politically, economically, and environmentally viable on a large-scale, neither F-T diesel or DME will make sense from a global warming perspective.

6.3. Coal to liquid - Coal-Derived Products

Coal can be converted into liquid fuels like gasoline or diesel by several different processes.

- ✓ The Fischer-Tropsch process of indirect synthesis of liquid hydrocarbons was used in Nazi Germany, and for many years by Sasol in South Africa - in both cases, because those regimes were politically isolated and unable to purchase crude oil on the open market. Coal would be gasified to make syngas.
- ✓ Coal-To-Liquids, Indiana Center for Coal Technology Research - a balanced purified mixture of CO and H_2 gas, and the syngas condensed using Fischer-Tropsch catalysts to make light hydrocarbons which are further processed into gasoline and diesel.
- ✓ Syngas can also be converted to methanol: which can be used as a fuel, fuel additive, or further processed into gasoline via the Mobil M-gas process.
- ✓ A direct liquefaction process Bergius process (liquefaction by hydrogenation) is also available but has not been used outside Germany, where such processes were operated both during World War I and World War II. SASOL in South Africa has experimented with direct hydrogenation.
- ✓ Several other direct liquefaction processes have been developed, among these being the SRC-I and SRC-II (Solvent Refined Coal) processes developed by Gulf Oil and implemented as pilot plants in the United States in the 1960's and 1970's.

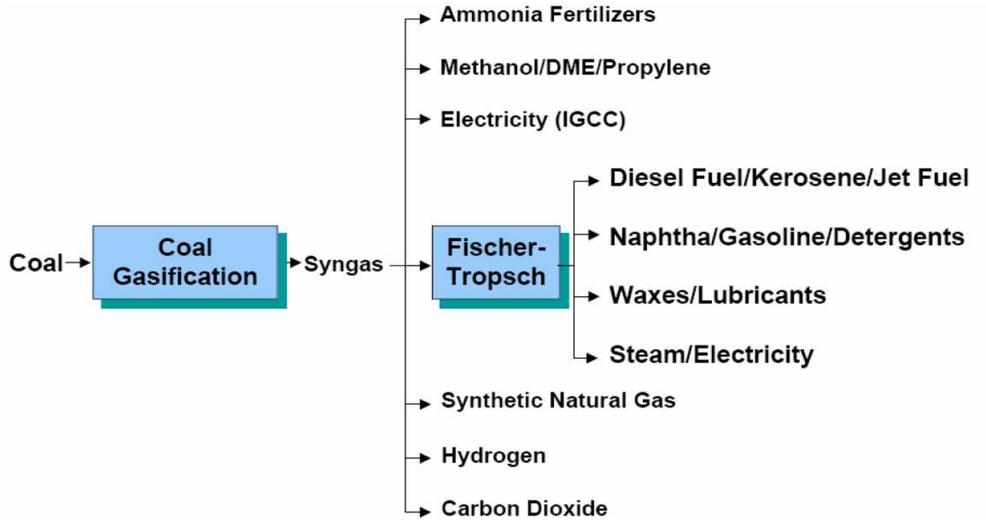


Figure 6.2 The possibility convert coal

Syngas can be used for power generation (IGCC) or for making fertilizers, methanol, synthetic natural gas, hydrogen or CO_2. Syngas could alternatively be sent throught the Fischer-Tropsch process to produce diesel fuels etc.

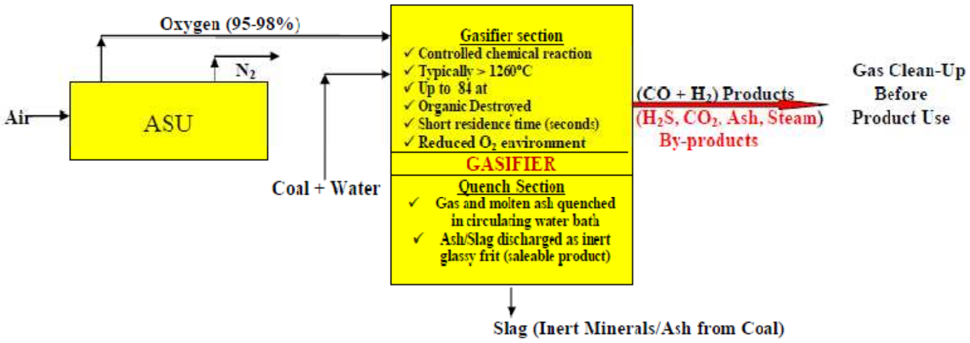


Figure 6.3. Scheme of syngas manufacturing.

6.4. Fischer-Tropsch process

The **Fischer–Tropsch process** (or Fischer–Tropsch Synthesis) is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.

The process, a key component of gas to liquids technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil and as synthetic fuel. The F-T process has received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons.

Process chemistry

The Fischer–Tropsch process involves a series of chemical reactions that lead to a variety of hydrocarbons. Useful reactions give alkanes:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

where 'n' is a positive integer. The formation of methane (n = 1) is generally unwanted. Most of the alkanes produced tend to be straight-chain alkanes, although some branched alkanes are also formed. In addition to alkane formation, competing reactions result in the formation of alkenes, as well as alcohols and other oxygenated hydrocarbons. Usually, only relatively small quantities of these non-alkane products are formed, although catalysts favoring some of these products have been developed.

Other reactions relevant to the F-T process

Several reactions are required to obtain the gaseous reactants required for F-T catalysis. First, reactant gases entering a F-T reactor must first be desulfurized to protect the catalysts that are readily poisoned. The other major class of reactions are employed to adjust the H_2/CO ratio: Water gas shift reaction provides a source of hydrogen:

$$H_2O + CO \rightarrow H_2 + CO_2$$

For F-T plants that start with methane, another important reaction is steam reforming, which converts the methane into CO and H_2:

$$H_2O + CH_4 \rightarrow CO + 3\ H_2$$

Chemical mechanisms

The conversion of CO to alkanes involves net hydrogenation of CO, the hydrogenolysis of C-O bonds, and the formation of C-C bonds. Such reactions are assumed to proceed via initial formation of surface-bound metal carbonyls. The CO ligand is speculated to undergo dissociation, possibly into oxide and carbide ligands. Other potential intermediates are various C-1 fragments including formyl (CHO), hydroxycarbene (HCOH), hydroxymethyl (CH_2OH), methyl (CH_3), methylene (CH_2), methylidyne (CH), and hydroxymethylidyne (COH). Furthermore, and critical to the production of liquid fuels, are reactions that form C-C bonds, such as migratory insertion. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous F-T catalysts are poorly developed and of no commercial importance.

Process conditions

Generally, the Fischer–Tropsch process is operated in the temperature range of 150–300 °C. Higher temperatures lead to faster reactions and higher conversion rates but also tend to favor methane production. As a result, the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.

A variety of synthesis gas compositions can be used. For cobalt-based catalysts the optimal H_2:CO ratio is around 1.8-2.1. Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This reactivity can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2:CO ratios (<1).

Product distribution

In general the product distribution of hydrocarbons formed during the Fischer–Tropsch process follows an Anderson-Schulz-Flory distribution, which can be expressed as:

$W_n/n = (1-\alpha)^2\alpha^{n-1}$

Where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms. α is the chain growth probability or the probability that a molecule will continue reacting to form a longer chain. In general, α is largely determined by the catalyst and the specific process conditions.

Examination of the above equation reveals that methane will always be the largest single product; however by increasing α close to one, the total amount of methane formed can be minimized compared to the sum of all of the various long-chained products. Increasing α increases the formation of long-chained hydrocarbons. The very long-chained hydrocarbons are waxes, which are solid at room temperature. Therefore, for production of liquid transportation fuels it may be necessary to crack some of the Fischer-Tropsch products. In order to avoid this, some researchers have proposed using zeolites or other catalyst substrates with fixed sized pores that can restrict the formation of hydrocarbons longer than some characteristic size (usually $n<10$). This way they can drive the reaction so as to minimize methane formation without producing lots of long-chained hydrocarbons

Fischer-Tropsch catalysts

A variety of catalysts can be used for the Fischer–Tropsch process, but the most common are the transition metals cobalt, iron, and ruthenium. Nickel can also be used, but tends to favor methane formation.

Cobalt-based catalysts are highly active, although iron may be more suitable for low-hydrogen-content synthesis gases such as those derived from coal due to its promotion of the water-gas-shift reaction. In addition to the active metal the catalysts typically contain a number of "promoters," including potassium and copper. Group 1 alkali metals, including potassium, is a poison for cobalt catalysts but is a promoter for iron catalysts. Catalysts are supported on high-surface-area binders/supports such as silica, alumina, or zeolithes. Cobalt catalysts are more active for Fischer-Tropsch synthesis when the feedstock is natural gas.

Natural gas has a high hydrogen to carbon ratio, so the water-gas-shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower quality feedstock's such as coal or biomass.

Unlike the other metals used for this process (Co, Ni, Ru), which remain in the metallic state during synthesis, iron catalysts tend to form a number of phases, including various oxides and carbides during the reaction. Control of these phase transformations can be important in maintaining catalytic activity and preventing breakdown of the catalyst particles.

Fischer-Tropsch catalysts are sensitive to poisoning by sulfur-containing compounds. The sensitivity of the catalyst to sulfur is greater for cobalt-based catalysts than for their iron counterparts.

Promotors also have an important influence on activity. Alkali metal oxides and copper are common promotors, but the formulation depends on the primary metal, iron vs cobalt. Alkali oxides on cobalt catalysts generally cause activity to drop severely even with very low alkali loadings. C_{5+} and CO_2 selectivity increase while methane and C_2-C_4 selectivity decrease. In addition, the olefin to parafin ratio increases.

LTFT and HTFT

High-Temperature Fischer-Tropsch (or HTFT) is operated at temperatures of 330°C-350 ° C and uses an iron-based catalyst. This process was used extensively by Sasol in their Coal-to-Liquid plants (CTL). Low-Temperature Fischer-Tropsch (LTFT) is operated at lower temperatures and uses a cobalt based catalyst. This process is best known for being used in the first integrated Gas-to-Liquid (GTL) plant operated and built by Shell in Bintulu, Malaysia.

6.5. Liquefaction

Liquefaction - Change of a substance from the solid or the gaseous state to the liquid state. Since the different states of matter correspond to different amounts of energy of the molecules making up the substance, energy in the form of heat must either be supplied to a substance or be removed from the substance in order to change its state. Thus, changing a solid to a liquid or a liquid to a gas requires the addition of heat, while changing a gas to a liquid or a liquid to a solid requires the removal of heat.

In the liquefaction of gases, extreme cooling is not necessary, for if a gas is held in a confined space and is subjected to high pressure, heat is given off as it undergoes compression and it turns eventually to a liquid. Some cooling is, however, necessary; it was discovered by Thomas Andrews in 1869 that each gas has a definite temperature, called its critical temperature, above which it cannot be liquefied, no matter what pressure is exerted upon it. A gas must, therefore, be cooled below its critical temperature before it can be liquefied. When a gas is compressed its molecules are forced closer together and, their vibratory motion being reduced, heat is given off. As compression proceeds, the speed of the molecules and the distances between them continue to decrease, until eventually the substance undergoes change of state and becomes liquid.

6.6 Dimethyl ether (DME)

DME can be made from biomass, natural gas, or coal. If it is made from biomass, the life-cycle CO_2 emissions are 25% that of diesel. If it is made from natural gas, emissions are comparable to diesel. And, if made from coal, CO_2 emissions would be 90% higher than diesel if the CO_2 were vented, but could be reduced to 20% less than diesel with sequestration of CO_2 and H_2S. By one calculation, carbon sequestration might add only 15% to the cost of DME.

Used in a diesel engine, DME provides substantial reductions in particulate matter (PM) and nitrogen oxides (NOx). For DME used in a heavy duty CIE, uncontrolled emissions of NOx and PM have been measured to be 58% and 75% less than for conventional Diesel. Black carbon soot is virtually eliminated due to the absence of carbon-19 carbon bonds. However, DME is a gas at standard temperature and pressure. For use as a vehicle fuel, it would require moderate compression (similar to propane) to liquefy it for distribution. This would entail considerable infrastructure investments.

Literature

1. Uchiyama, S., Journal of Society of Automotive Engineers of Japan, 58, (11), 83 (2004).
2. Matsuo, S., Takami, K., Yamamoto, H., Journal of Society of Automotive Engineers of Japan, 58, (11), 89 (2004).
3. Ondrey, G., Chem. Eng., 111, (5), 23 (2004).
4. Skrebowski, C, Petroleum Review, 691, (58), 18 (2004).
5. Myburgh, I., Schnell, M., Oyama, K., Sugano, H., Yokota, H., Tahara, S., Prepr. SAE2003-01-1946, (2003).
6. Bisio, A., Atkinson, C, Prepr. Pap. Am. Chem. Soc, Div. Fuel Chem., 47, (2), 496 (2002).
7. Nishiumi, R., Yasuda, A., Tsukasaki, Y., Tanaka, T., SAE Tech. Pap. Ser., Soc. Automot. Eng., (2004).
8. Alleman, T. L., Mccormick, R. L., "Spec. Publ. Soc. Automot. Eng.," (2003), p. 185-204.
9. Gjirja, S., Olssone, E., Eklund, A., Proc. Int. Symp. Automot. Technol. Autom. 2000, (2000), p. 105-115.
10. Erwin, J., Prepr. Pap. Am. Chem. Soc, Div. Fuel. Chem., 37, (4), 1915 (1992).
11. Arima, Y., Jpn. Toroku Tokkyo Koho JP1999-2901047 (1999).
12. Espinoza R.L., Steynberg A.P., Jager B., Vosloo A.C., Applied Catalysis A 186 (1999) 13-26.
13. Jager B., Espinoza R.L., Advances in Iow temperature Fischer-Tropsch technology. Catalysis Today 23 (1) (1995) 17-28.
14. Dry M.E., in: J. Anderson, M. Boudard (Eds.), The Fischer-Tropsch Process, Catalysis, Science and Technology, vol. 1, Springer-Verlag, Berlin, 1981, pp. 319-343.

7. Biofuels in liquid form

7.1 Introduction

Gasoline and diesel produced from crude oil are currently the dominant automotive fuels. Liquefied Petroleum Gas (LPG), which is a byproduct of processing crude oil, Compressed Natural Gas (CNG) and Liquefied Natural Gas (LNG), both derived from natural gas, have lower CO_2 emissions but they are only used on a small scale in most European countries. Biofuels present a further alternative and are attracting increasing interest in many industrially developed and developing countries.

Several pieces of legislation have helped advance the widespread use of biodiesel. In the United States for example, the American Society of Testing and Materials (ASTM) issued a specification (D 6751) for biodiesel fuel in December 2001. ASTM is the premier standard-setting organization for fuels and additives in the United States. This development was crucial in standardizing fuel quality for biodiesel in the U.S. market and increasing the confidence of consumers and engine makers. The ASTM specification was developed so that approved fuels could be consistently manufactured using any vegetable oil or animal fat as the raw material.

Biodiesel also became the only alternative fuel in the United States to have successfully completed the EPA's Tier I and Tier II Health Effects testing under Section 211(b) of the Clean Air Act of May 2000. The Tier I testing conclusively demonstrated biodiesel's significant reductions in most currently regulated emissions as well as most unregulated emissions — especially those associated with cancer and lung disease. Tier II testing demonstrated biodiesel's non-toxic effect on health.

To date, the European Parliament has issued directives concerning biofuels. Their main points are summarised below.

DIRECTIVE 2003/30/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport

Article 1

This Directive aims at promoting the use of biofuels or other renewable fuels to replace diesel or gasoline for transport purposes in each Member State, with a view to contributing to objectives such as meeting climate change commitments, environmentally friendly security of supply and promoting renewables energy sources.

Article 2

1. For the purpose of this Directive, the following definitions shall apply:
(a) 'biofuels' means liquid or gaseous fuel for transport produced from biomass;
(b) 'biomass' means the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste;
(c) 'other renewable fuels' means renewable fuels, other than biofuels, which originate from renewable energy sources as defined in Directive 2001/77/EC (2) and used for transport purposes;
(d) 'energy content' means the lower calorific value of a fuel.

2. At least the products listed below shall be considered biofuels:
(a) 'bioethanol': ethanol produced from biomass and/or the biodegradable fraction of waste, to be used as biofuel;
(b) 'biodiesel': a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel;
(c) 'biogas': a fuel gas produced from biomass and/or from the biodegradable fraction of waste, that can be purified to natural gas quality, to be used as biofuel, or woodgas;
(d) 'biomethanol': methanol produced from biomass, to be used as biofuel;
(e) 'biodimethylether': dimethylether produced from biomass, to be used as biofuel;
(f) 'bio-ETBE (ethyl-tertio-butyl-ether)': ETBE produced on the basis of bioethanol. The percentage by volume of bio-ETBE that is calculated as biofuel is 47 %;

(g) ‘bio-MTBE (methyl-tertio-butyl-ether)’: a fuel produced on the basis of biomethanol. The percentage by volume of bio- MTBE that is calculated as biofuel is 36 %;
(h) ‘synthetic biofuels’: synthetic hydrocarbons or mixtures of synthetic hydrocarbons, which have been produced from biomass;
(i) ‘biohydrogen’: hydrogen produced from biomass, and/or from the biodegradable fraction of waste, to be used as biofuel;
(j) ‘pure vegetable oil’: oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, when compatible with the type of engines involved and the corresponding emission requirements.

Article 3

1. (a) Member States should ensure that a minimum proportion of biofuels and other renewable fuels is placed on their markets, and, to that effect, shall set national indicative targets.
(b) (i) A reference value for these targets shall be 2 %, calculated on the basis of energy content, of all gasoline and diesel for transport purposes placed on their markets by 31 December 2005.
(ii) A reference value for these targets shall be 5,75 %, calculated on the basis of energy content, of all gasoline and diesel for transport purposes placed on their markets by 31 December 2010.
2. Biofuels may be made available in any of the following forms:
(a) as pure biofuels or at high concentration in mineral oil derivatives, in accordance with specific quality standards for transport applications;
(b) as biofuels blended in mineral oil derivatives, in accordance with the appropriate European norms describing the technical specifications for transport fuels (EN 228 and EN 590);
(c) as liquids derived from biofuels, such as ETBE (ethyl-tertiobutyl-ether), where the percentage of biofuel is as specified in Article 2(2).

Given the increasing importance of biofuels, the scope of this chapter is to describe the main pathways for their production, and to examine some of the technical characteristics and economic considerations of the different production technologies, the biomasses used, and the resultant fuels. Although some biofuels may be suitable for use in fuel cell vehicles, here we will only deal with their use in combustion engines. The names and processes of some of the principal fuels are shown in Table 7.1.

Table 7.1. Biofuels for transportation

	Name of bio fuel	Name by EU directive	Production process
1st	Straight vegetable oil	Pure vegetable oil	Mechanical or chemical extraction, refining
1st	Ethanol	Bio ethanol	Sugar fermentation, starch hydrolysis and fermentation
1st	Fatty acids esters	Bio diesel	Triglycerides etherification and purification
2nd	Fischer-Tropsch (FT) diesel	Synthetic bio fuel	Gasification, gas-shift, synthesis, hydrocracking
2nd	Methanol	Bio methanol	Gasification, gas-shift, synthesis
2nd	DME	Biodimethylether	Gasification, gas-shift, synthesis
2nd	SNG from syngas	Biogas, synthetic bio fuel	Gasification, gas-shift, synthesis, CO_2H_2O-removal
2nd	Ethanol from celluloses	Bio ethanol	Advanced hydrolysis, fermentation, distillation
2nd	Pyrolysis-diesel	Synthetic bio fuel	Pyrolysis, hydro de oxygenation, refining

For fuels produced from biomass, various conversion routes are available that follow from the different types of biomass feedstocks, i.e. woody biomass, sugar-rich crops, oil crops, and wet biomass. Figure 7.1 shows the biomass to fuel conversion routes.

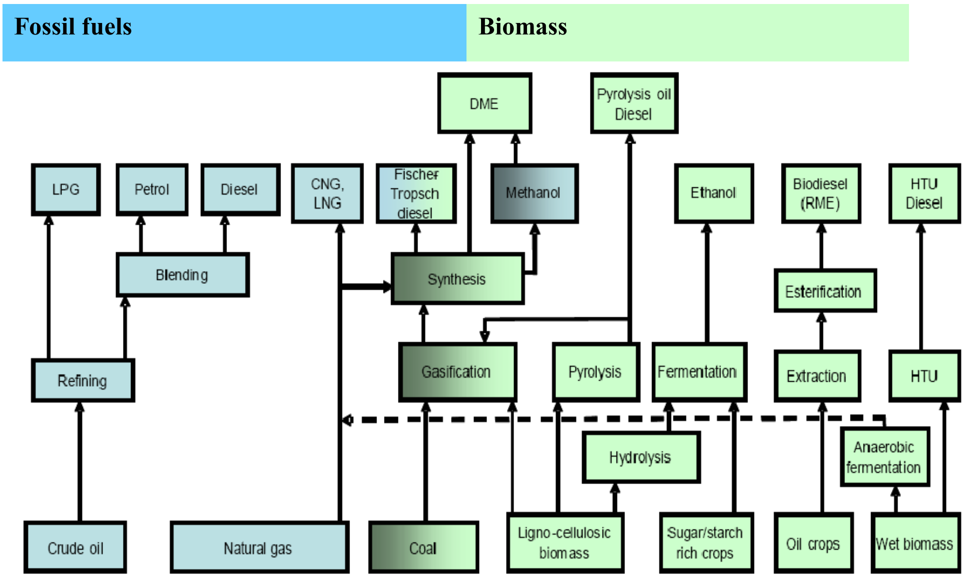


Fig. 7.1. Overview of automotive fuel conversion routes

7.2 Biodiesel from rapeseed methyl ester (RME)

Biodiesel is a renewable, clean burning, oxygenated fuel for diesel engines or boilers made from vegetable oils or animal fats. Chemically, biodiesel consists of a small number of alkyl esters. It contains no sulphur or aromatics and already meets the 2006 on-road standard for sulphur content in diesel fuel set by the Environmental Protection Agency (EPA) in the United States. Because it has properties similar to petroleum-based diesel fuel, biodiesel can be blended in any ratio with petroleum diesel and used in diesel engines without major modifications. Biodiesel is registered as a fuel and fuel additive with the EPA and meets clean diesel standards established by the California Air Resources Board (CARB).

Biodiesel used as a fuel is as old as the diesel engine. Rudolph Diesel, inventor of the diesel engine in 1892, used peanut oil as the original engine fuel. The use of petroleum fuels for diesel engines only came into widespread use in the 1920s. This fuel substitution was the result of a significant drop in the price of petroleum. Starting in the 1970s after the “oil crisis”, interest in the use of domestically produced biofuels returned.

Vegetable oils have been used as fuels for many years. Table 7.2 shows the typical oil extraction from 100 kg of oil from some of the most common oil crops. Table 7.3 shows some typical vegetable oil yields. The biodiesel yield from these = oil yield x 0.8 approx.

The conversion of biomass into vegetable oils for automotive fuel applications is similar to the production of vegetable oils for the food industry, which is a well-established process. Since, in Europe, vegetable oils for the production of biodiesel are mainly derived from rapeseed, this section will focus on this type of biodiesel, rapeseed methyl ester (RME).

The vegetable oils that are used for biodiesel production can be extracted from the seeds or the pulp of several oil crops. The most important sources for vegetable oil production are rapeseed, soybean, palm and sunflower. For the production of 1 ton of RME, about 2.5 tons of rapeseed are needed, which requires a land area of 0.77 hectares.

Table 7.2. Typical oil extraction from 100 kg of oil seeds.

Crop	Oil/100kg
Castor Seed	50 kg
Copra	62 kg
Cotton Seed	13 kg
Groundnut Kernel	42 kg
Mustard	35 kg
Palm Kernel	36 kg
Palm Fruit	20 kg
Rapeseed	**37 kg**
Sesame	50 kg
Soybean	**14 kg**
Sunflower	32 kg

Table 7.3. Typical the vegetable oil yields.

Crop	kg oil/ha	litres oil/ha
Avocado	2217	2638
Brazil nuts	2010	2392
Calendula	256	305
Camelina	490	583
Cashew nut	148	176
Castor beans	1188	1413
Cocoa (cacao)	863	1026
Coconut	2260	2689
Coffee	386	459

Coriander	450	536
Corn (maize)	145	172
Cotton	273	325
Euphorbia	440	524
Hazelnuts	405	482
Hemp	305	363
Jatropha	1590	1892
Jojoba	1528	1818
Kenaf	230	273
Linseed (flax)	402	478
Lupine	195	232
Macadamia nuts	1887	2246
Mustard seed	481	572
Oats	183	217
Oil palm	5000	5950
Olives	1019	1212
Opium poppy	978	1163
Peanuts	890	1059
Pecan nuts	1505	1791
Pumpkin seed	449	534
Rapeseed	1000	1190
Rice	696	828
Safflower	655	779
Sesame	585	696
Soybean	375	446
Sunflowers	800	952
Tung oil tree	790	940

For the production of biodiesel, vegetable oils are extracted from oil seeds by mechanically pressing or by extraction with a solvent, like hexane. The latter technology results in a higher yield. Vegetable oils can be used directly as diesel engine fuels, but this requires engine modification because some of their properties are less advantageous for this application. Two major problems are their very high viscosity and poor thermal and hydrolytic stability. Moreover, the low cetane number of vegetable oils, which varies between 33 and 43, indicates that they have less favourable ignition qualities.

7.2.1 Esterification

To overcome the problems mentioned above and make vegetable oils suitable for engines used in road vehicles, they must be adapted in such a way that they meet the requirements of current diesel engines, especially with regard to the viscosity and cetane number. This can be done through esterification. This means that the large, branched molecule structures of the oils (triglycerides) are transformed into smaller straight-chained molecules (methyl esters) that are similar to fossil diesel components. The methyl ester produced from rapeseed vegetable oil is called Rapeseed Methyl Ester (RME).

The majority of the methyl esters are produced through catalytic transesterification of the oil with methanol. Here, the triglycerides of the vegetable oil react with methanol in the presence of a catalyst, resulting in the production of methyl esters (biodiesel). This process takes place in a simple reactor system at low temperature (range 50-66ºC) and pressure (around 1.4 bars). The general steps in this conversion process are indicated in Figure 7.2.

The first step in this process is the mixing of methanol and the catalyst, which is usually sodium hydroxide (caustic soda) or potassium hydroxide (potash). Excess methanol is added to ensure the total conversion of the triglycerides into esters, because it first reacts with free fatty acids present in the oil, leading to soap formation. The catalyst/methanol mixture is fed into a closed reactor vessel, which prevents the loss of alcohol. Then the vegetable oil is added to the reactor. The reaction mixture is left to settle in the vessel for 1 to 8 hours. The concentrations of free fatty acids (FFA) and water in the mixture must be monitored because if these are too high they may cause problems with regard to soap formation, and the separation of the glycerine by-product.

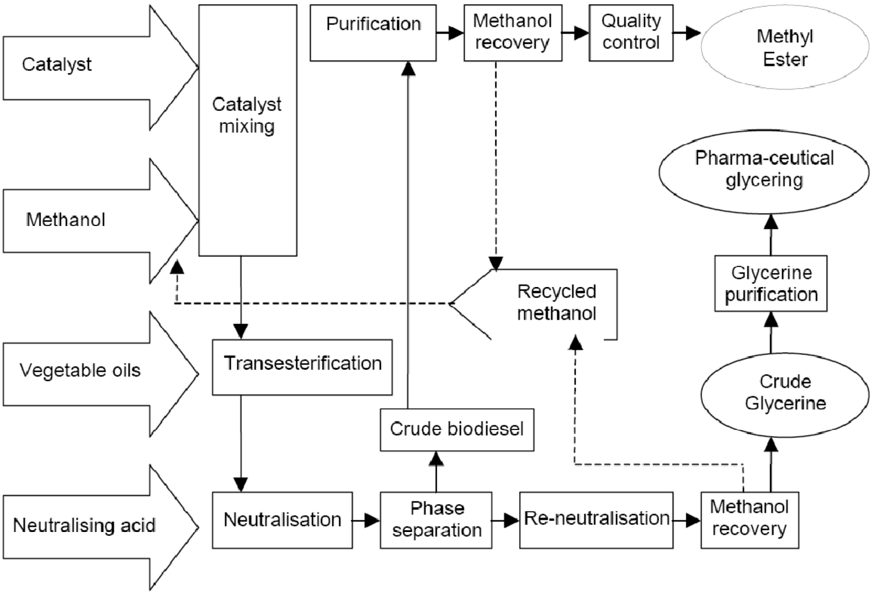


Fig. 7.2. General conversion process scheme for biodiesel production from vegetable oils

Biodiesel molecules resemble Cetane, in that they are almost the same size and have no branches. After the conversion of the vegetable oils into esters has taken place, the reacted mixture is neutralised first by adding acids. Then the methanol is removed and recovered for re-use in the process.

$\mathbf{CH_3\text{-}O\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}}$
$\mathbf{CH_2\text{-}CH_3}$
methylester
$\mathbf{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3}$
n-heksadekan (Cetane)

Fig. 7.3. View of molecule methylester and cetane

The mixture now consists of two major products: methyl esters and glycerine. These have formed two layers in the reaction vessel, because glycerine is heavier than methyl esters. The glycerine is separated from the methyl esters and the soaps present in the glycerine are neutralised. The salts resulting from this neutralisation process are sometimes recovered for use as fertiliser. The crude glycerine can be used in the cosmetic and pharmaceutical industry. After being separated from the glycerine, the methyl esters are purified. By means of a washing process, residual catalyst and soaps are removed. The purity of the esters produced in this way amounts to about 98%. This can be improved further by distillation. The end product is an amber-yellow coloured liquid with a strongly reduced viscosity. This biodiesel also has better long term storage properties than the original vegetable oils and can be used as a fuel in diesel engines.

7.2.2 Some properties of biodiesel from RME

Diesel is not one chemical compound but a mixture of a great number of different hydrocarbon compounds. These can include paraffin (or alkanes, linear and branched), olefins (linear and branched), naphthenes and aromatics. Diesel also contains larger and heavier hydrocarbon molecules than gasoline. Esterified vegetable oils are suitable for application in automotive diesel engines, as the specific gravity and cetane number of RME are similar to those of diesel. Table 2.4 compares some fuel parameters for RME with those of fossil diesel.

On Fig. 7.4.is presented biodiesel production scheme from soybean oil. As mentioned above, many of the problems found with using neat vegetable oils in diesel engines (compression ignition engines) can be overcome to a large extent by converting the oils into esters. This process results in a remarkable reduction in viscosity, namely from 50 - 86 mm^2 for vegetable oils to 7.4 mm^2/s for RME. However, the viscosity of RME is still about twice that of diesel fuel and this affects the atomisation of the fuel during injection. Below a temperature of 0ºC, problems occur with the supply of biodiesel from the tank to the engine and the cold starting behaviour of the engine. These problems can be solved by heating the fuel or adding additives such as flow enhancers. On the other hand, as we can see from Table 7.4, RME has a higher cetane number for RME compared to regular diesel. This denotes a good ignition quality, which leads to higher engine efficiency and emission reduction.

Table 7.4 Properties of commercial diesel vs biodiesel

Characteristics	**Diesel**	**Biodiesel**
Specific gravity at 15 °C	0.82	0.88
Heating Value MJ/kg	43.0	41.8
Cetane Number	40-55	48 - 60
Flash Point, °C	60 – 80	100 - 170
Stochiometric Air / Fuel Ratio	15	13.8

The stoichiometric air/fuel ratio is somewhat lower for RME, which indicates that less air is needed to burn the same quantity of fuel. A disadvantage of combustion of RME is that it produces a specific smell which some people find disagreeable.

The density of RME is somewhat higher than that of diesel. This higher density compensates for the reduced energy content (gravimetric Lower Calorific Value) of RME to some extent. This lower calorific value is due to the much higher oxygen content of RME compared to diesel. Because vehicles using RME have, on an energy basis, the same fuel consumption as those running on diesel fuel, this lower energy content leads to higher fuel consumption. RME also differs from regular diesel with respect to some properties that are not related to engine performance. One of them is the fuel flash point, which is primarily important for the safe handling of a fuel. RME needs to be heated to a higher temperature than diesel to produce a vapour/air mixture that will ignite when a flame is applied. The flash point of biodiesel is very sensitive to the alcohol content. It drops from 167°C to 35°C when the residua methanol concentration in RME is increased from 0% to 0.5%.

An ecologically favourable property of biodiesel is its high biodegradability. This is a significant advantage for use in niche markets where a high biological decomposability is an important feature, e.g. in environmentally endangered areas. However, high biodegradability also means that the fuel is less stable, which is disadvantageous with respect to storage.

Since RME has similar fuel properties compared to diesel, it can be mixed with fossil diesel in any proportion for application in conventional diesel engines. However, if 100% RME is to be used, a number of relatively minor changes in the engines are required. Material incompatibility with some engine components should be taken into account because RME shows a high chemical aggressiveness towards metallic materials, rubber seals, coatings and elastomers. Although RME can be mixed with fossil diesel in any ratio, car manufacturers often recommend not applying mixtures in their engines with a proportion of RME higher than, for example, 5%. A reason for this is that the certification level for the engine with regard to NOx emissions can be exceeded when a large proportion of RME is used. Moreover, the durability of the engine cannot be guaranteed if the engine is run with any other fuel than the one it has been constructed, tested and certified for. Many makers of diesel engines are working on an (improved) application of biodiesel.

Some car manufacturers, for example PSA Peugeot - Citroën, have produced private cars especially for the use of pure RME. Another application of biodiesel is a mixture with ethanol to esterol, which has been developed for regular diesel engines. Because RME can be mixed with fossil diesel, the fuel can be distributed and marketed using the existing diesel fuel infrastructure. However, one should take into account that the lower volumetric energy content of RME results in a larger volume to be transferred. The limited compatibility with construction materials must be anticipated here too.

Biodiesel-resistant materials should be used in fuel systems and storage tanks. When storing RME for longer periods, its low stability causes storage difficulties. Since RME degrades upon exposure to air, the fuel should be isolated from oxygen. Ingress of water should also be avoided, since water destroys the ester-linkage between alcohol and acid components in the methyl esters of biodiesel. This causes sludge formation in the fuel storage tank. RME is best stored in a dark and cool place. However, at low temperatures, biodiesel starts to crystallise and solidify. When heated up to room temperature again, the oil resumes its original form. These adverse longer-term storage effects can be reduced by using additives.

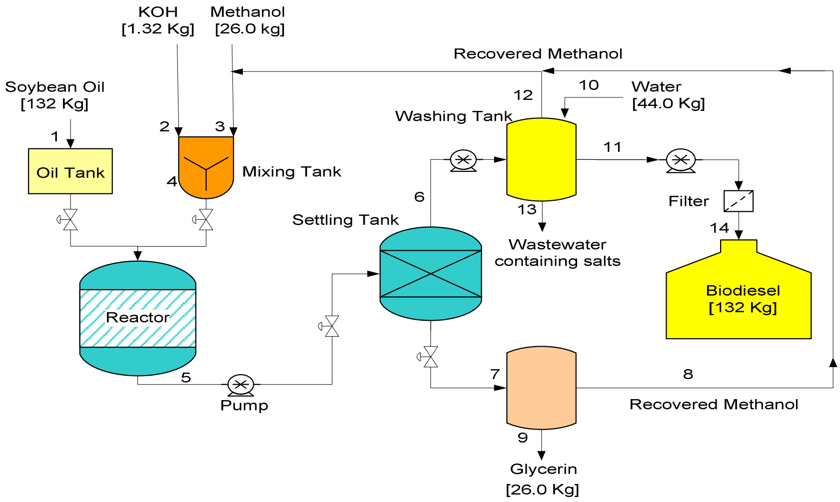


Fig. 7.4. Biodiesel production scheme

1. Soybean oil; 2. Potassium hydroxide; 3. Methanol; 4. Mixed methanol and potassium hydroxide; 5. Mixture of methyl ester and glycerin; 6. Mixture of methyl ester and methanol; 7. Mixture of glycerin and methanol; 8. Recovered methanol; 9. Glycerin; 10. H_2O; *11. Biodiesel; 12. Recovered methanol; 13. Wastewater; 14. Pure biodiesel*

When handling biodiesel, it should be taken into account that RME dissolves asphalt and makes it soft. The higher viscosity at low temperatures and the heavy foaming of RME may cause problems during refuelling. The foaming can be reduced by adding anti-foamants.

Four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits have been investigated. These are: blending with petrodiesel, pyrolysis, microemulsification (cosolvent blending), and transesterification. Transesterification is by far the most common method and will be dealt with here. Only the transesterification reaction leads to the products commonly known as biodiesel, i.e., alkyl esters of oils and fats.

7.3 Transesterification

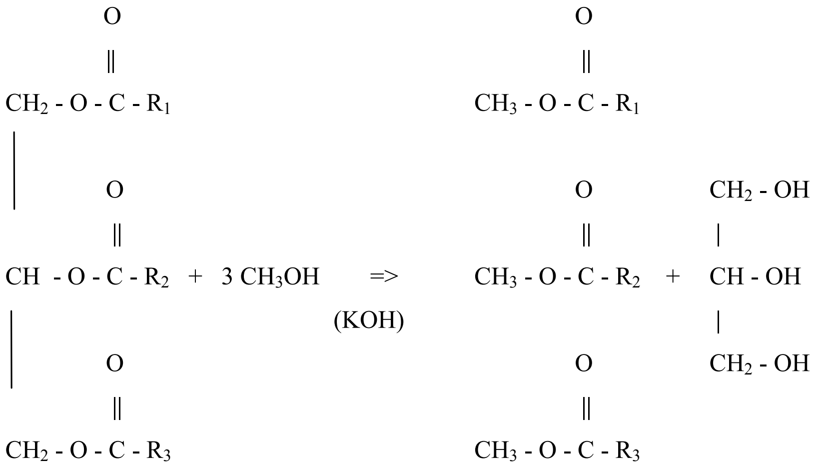
The most commonly prepared esters are methyl esters, largely because methanol is the least expensive alcohol, although there are exceptions in some countries. In Brazil, for example, where ethanol is less expensive, ethyl esters are used as fuel. In addition to methanol and ethanol, esters of vegetable oils and animal fats with other low molecular weight alcohols have been investigated for potential production and their biodiesel properties. Properties of various esters are listed in the tables. Table 7.5 contains a list of C_1–C_4 alcohols and their relevant properties. These alcohols can be used in the transesterification reaction.

Table 7.5. List of C_1–C_4 alcohols and their relevant properties.

	Formula	**Molecular weight**	**Boiling point [°C]**	**Melting point [°C]**	**Density [kg/dm^3]**
Methanol	CH_3OH	32.042	65	-93.9	0.7914
Ethanol	C_2H_5OH	46.069	78.5	-117.3	0.7893
1-propanol	$CH_2OHCH_2CH_3$	60.096	97.4	-126.5	0.8035
2-propanol (iso-propanol)	$CH_3CHOHCH_3$	60.096	82.4	-89.5	0.7855
1-butanol (n-butanol)	$CH_3CH_2CH_2CH_2OH$	74.123	117.2	-89.5	0.8098
2-butanol	$CH_3CHOHCH_2CH_3$	74.123	99.5	-	0.8080
3-methyl-1-propanol (iso-propanol)	$CH_2OHCH(CH_3)CH_3$	74.123	108	-	0.8018
3-methyl-2-propanol (tert-butanol)	$CH_2(CH_3)CHOHCH_3$	74.123	82.3	25.5	0.7887

In addition to vegetable oils and animal fats, other materials such as used frying oils can also be suitable for biodiesel production; however, changes in the reaction procedure frequently have to be made due to the presence of water or free fatty acids (FFA) in the materials. This section discusses the transesterification reaction as it is most commonly applied to (refined) vegetable oils and related work.

Di- and monoacylglycerols are formed as intermediates in the transesterification reaction. Figure 2.5 qualitatively depicts conversion vs. reaction time for a transesterification reaction taking into account the intermediary di- and monoacylglycerols.



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R_1 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-R_2 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + 3\,CH_3OH \underset{(KOH)}{\Rightarrow} \begin{array}{l} CH_3-O-\overset{\overset{O}{\|}}{C}-R_1 \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_2 \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Fig. 7.5. The transesterification reaction. R_1- R_3 is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol.

Tables 7.6-7.10 show some of the basic physicochemical properties of most common oils, as well as the established standards for vegetable oils and animal fats used as starting materials in the transesterification reaction.

Table 7.6. Biodiesel Standard EN 14214.

Property	Test method	Limits		Unit
		min	*max*	
Ester content	EN 14103	96.5		%, m/m
Density; 15°C	EN ISO3675; ENISO12185	860	900	kg/m^3
Viscosity; 40°C	EN ISO 3104; ISO 3105	3.5	5	mm^2/s
Flash point	EN ISO 3679	120		°C
Sulphur content	EN ISO20346; EN ISO 20384		10	Mg/kg
Carbon residue (10% dist. residue)	EN ISO 10370		0.30	%, m/m
Cetane number	EN ISO 5165	51		
Sulfated ash	ISO 3937		0.02	%, m/m
Water content	EN ISO 12937		500	Mg/kg
Total contamination	EN 12662		24	Mg/kg
Copper strip corrosion (3 hr,50°C)	EN ISO 2160		1	
Oxidative stability,110°C	EN 14112	6.0		hr
Acid value	EN 14104		0.50	mgKOH/g
lodine value	EN 14111		120	g I_2/100 ml
Linolenic acid content	EN 14103		12	%, m/m
Content of FAME with 4 double bonds	EN 14112		1	%, m/m
Methanol oontent	EN 14110		0.20	%, m/m
Monoglyceride content	EN 14105		0.80	%, m/m
Diglyceride content	EN 14105		0.20	%, m/m
Triglyceride content	EN 14105		0.20	%, m/m
Free glycerine	EN 14105, EN 14106		0.02	%, m/m
Total glycerine	EN 14105		0.25	%, m/m
Alkali metals (Na+K)	EN 14103, EN 14109		5.0	mg/kg
Earth alkali metals (Ca+Mg)	EN 14538		5.0	mg/kg
Phosphorus content	EN 14107		10.0	mg/kg

Table 7.7. Basic physicochemical properties of most common oils.

Oil	**Density at 150°C [kg/dm³]**	**Lower heating value [MJ/kg]**	**Kinematic viscosity at 200°C [mm²/s]**	**Cetane number**	**Melting point [°C]**	**Flash point [°C]**	**Iodine number**
Diesel	O,84	42,7	4,6	50	-	80	-
Rapeseed	0,92	37,6	74	49	0..-3	317	94..113
Sunflower	0,93	37,1	66	35,5	-16..-18	316	118..144
Soybean	0,93	37,1	63,5	38,5	-8..-18	350	114..138
Linseed (flax)	0,93	37,0	51,0	(52)	-18..-27		169..192
Olive	0,92	37,8	83,8	37,1	-5..-9		76..90
Cotton	0,93	36,8	89,4	4,1	-6..-14	320	90..117
Peanuts	0,91	37,2	71,0	(51)		340	(103)
Palm oil	0,87	35,3	21,7 (1)		14..25		7..10
Palm grease	0,92	37,0	29,4 (1)	42	27..43	267	34..61
Palm Kernel		35,5	21,5 (1)		20..24		14..22

Table 7.9. Biodiesel Standards.

Standard Specification	**EU**	**Austria**	**Germany**	**USA**
	-	ON C1191	DIN E 51606	ASTM PS121-99
Water (mg/kg)	-	< 0,8	< 300	< 500
Methanol (% w/w)	-		< 0,3	
Ester content (% w/w)	-	-	-	-
Standard / specification	EN 14214	ON C1191	DIN V 51606	ASTM D-6751
Density at 15°C g/cm	0.86 -0.90	0.85 - 0.89	0.875 - 0.90	-
Viscosity at. 40°C mm^2/s	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0
Distillation 95% °C	-	-	-	90% at 360°C
Ignition temperature°C	>120	>100	>110	>130 (150 av.)
CFPP °C (cold filter plugging point)	differs in each country	0/-15	0/-10/-20	-

Table 7.10. Biodiesel Standards

Standard	Austria	Czech Republic	France	Germany	Italy	Sweden	USA
Specification	ON C1191	CSN 65 6507	Journal Official	DIN E 51606	UNI 10635	SS 155436	ASTM PS121-99
Water (mg/kg)	< 0,8	< 500	< 200	< 300	< 700	< 300	< 500
Acid value (mg KOH/g)	< 0,20	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,8
Methanol (% w/w)	-	-	< 0,1	< 0,3	< 0,2	< 0,2	-
Ester content (% w/w)	-	-	> 96,5	-	> 98	> 98	-
Monoglycerides (% w/w)	-	-	< 0,8	< 0,8	< 0,8	< 0,8	-
Diglycerides (% w/w)	-	-	< 0,2	< 0,4	< 0,2	< 0,1	-
Triglycerides (% w/w)	-	-	< 0,2	< 0,4	< 0,1	< 0,1	-

Several reviews dealing with the production of biodiesel by transesterification have been published, and investigations of the processes have been the subject of numerous research papers. Generally, transesterification can proceed by base or acid catalysis. However, in homogeneous catalysis, alkali catalysis (sodium or potassium hydroxide; or the corresponding alkoxides) is a much more rapid process than acid catalysis.

In addition to the type of catalyst (alkaline vs. acidic), reaction parameters of base-catalyzed transesterification that have been studied include the molar ratio of alcohol to vegetable oil, temperature, reaction time, degree of refinement of the vegetable oil, and effect of the presence of moisture and free fatty acids (FFA). For the transesterification to give maximum yield, the alcohol should be free of moisture and the FFA content of the oil should be <0.5%. The absence of moisture in the transesterification reaction is important because according to the equation (shown for methyl esters),

$R\text{-}COOCH_3 + H_2O \rightarrow R\text{-}COOH + CH_3OH$ (R = alkyl)

hydrolysis of the formed alkyl esters to FFA can occur. Similarly, because triacylglycerols are also esters, the reaction of the triacylglycerols with water can form FFA.

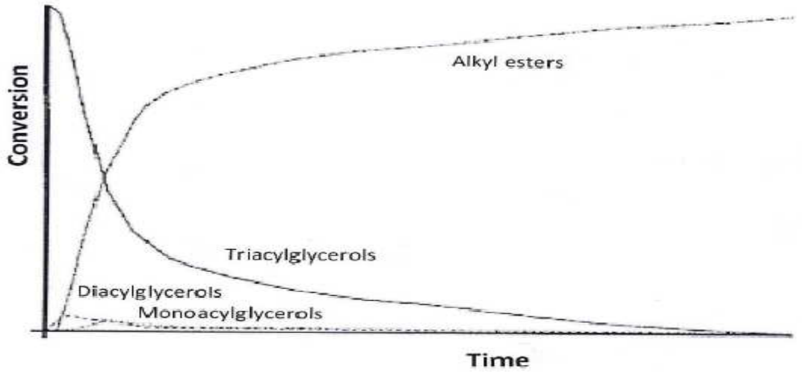


Fig. 7.6. Qualitative plot of conversion in a progressing transesterification reaction indicating relative concentrations of vegetable oil (triacylglycerols), intermediary di- and monoacylglycerols, as well as methyl ester product.

At 32°C, transesterification was 99% complete in 4 h when using an alkaline catalyst (NaOH or NaOMe). At ≥60°C, using an alcohol:oil molar ratio of at least 6:1 and fully refined oils, the reaction was complete in 1 h, yielding methyl, ethyl, or butyl esters. Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils. These parameters (60°C reaction temperature and 6:1 methanol: oil molar ratio) have become a standard for methanol-based transesterification. Similar molar ratios and temperatures have been reported in earlier literature. Other alcohols (ethanol and buthanol) require higher temperatures (75 and 114°C, respectively) for optimum conversion. Alkoxides in solution with the corresponding alcohol (made either by reacting the metal directly with alcohol or by electrolysis of salts and subsequent reaction with alcohol) have the advantage over hydroxides in that the water-forming reaction according to the equation

$R'OH + XOH \rightarrow R'OX + H_2O$ (R'= alkyl; X = Na or K)

cannot occur in the reaction system, thus ensuring that the transesterification reaction system remains as water free as possible. This reaction, however, is the one forming the transesterification-causing alkoxide when using NaOH or KOH as catalysts. The catalysts are hygroscopic; precautions, such as blanketing with nitrogen, must be taken to prevent contact with moisture. The use of alkoxides reportedly also results in glycerol of higher purity after the reaction.

Effects similar to those discussed above have been observed in studies on the transesterification of beef tallow. With this feedstock, FFA and, even more importantly water, should be kept as low as possible. NaOH has been reported as more effective than the alkoxide, which may have been a result of the reaction conditions.

Mixing has been found to be important due to the immiscibility of NaOH/MeOH with beef tallow, with smaller NaOH/MeOH droplets resulting in faster transesterification. Ethanol is more soluble in beef tallow which increases the yield, an observation that should hold for other feedstocks as well. Other studies have reported the use of both NaOH and KOH in the transesterification of rapeseed oil.

Same dates of producing biodiesel from waste frying oils employed KOH. With the reaction conducted at ambient pressure and temperature, conversion rates of 80–90% were achieved within 5 min, even when stoichiometric amounts of methanol were employed. In two transesterifications (with more MeOH/KOH steps added to the methyl esters after the first step), the ester yields were 99%. It was concluded that an FFA content up to 3% in the feedstock did not affect the process negatively, and phosphatides up to 300 ppm phosphorus were acceptable. The resulting methyl ester met the quality requirements for Austrian and European biodiesel without further treatment. In a study similar to previous work on the transesterification of soybean oil, it was concluded that KOH is preferable to NaOH in the transesterification of safflower oil of Turkish origin. The optimal conditions were given as 1 wt% KOH at 69 ± 1°C with a 7:1 alcohol: vegetable oil molar ratio to give 97.7% methyl ester yield in 18 min.

In principle, transesterification is a reversible reaction, although in the production of vegetable oil alkyl esters, i.e., biodiesel, the back reaction does not occur or is negligible largely because the glycerol formed is not miscible with the product, leading to a two-phase system. The transesterification of soybean oil with methanol or 1-butanol has been reported to proceed with pseudo-first-order or second- order kinetics, depending on the molar ratio of alcohol to soybean oil (30:1 pseudo first order, 6:1 second order; NaOBu catalyst), whereas the reverse reaction was second order. However, the originally reported kinetics has been reinvestigated and differences have been found. The methanolysis of sunflower oil at a molar ratio of methanol:sunflower oil of 3:1 was reported to begin with second order kinetics but then the rate decreased due to the formation of glycerol. A shunt reaction (a reaction in which all three positions of the triacylglycerol react virtually simultaneously to give three alkyl ester molecules and glycerol) originally proposed as part of the forward reaction was shown to be unlikely, that second- order kinetics are not followed, and that miscibility phenomena play a significant role. The reason is that the vegetable oil starting material and methanol are not well miscible. The miscibility phenomenon results in a lag time in the formation of methyl esters as indicated qualitatively in Figure 7.6. The formation of glycerol from triacylglycerols proceeds stepwise *via* the di- and monoacylglycerols, with a fatty acid alkyl ester molecule being formed in each step. From the observation that diacylglycerols reach their maximum concentration before the monoacylglycerols, it was concluded that the last step, formation of glycerol from monoacylglycerols, proceeds more rapidly than the formation of monoacylglycerols from diacylglycerols.

The addition of cosolvents such as tetrahydrofuran (THF) or methyl *tert*-butyl ether (MTBE) to the methanolysis reaction was reported to significantly accelerate the methanolysis of vegetable oils as a result of solubilizing methanol in the oil to a rate comparable to that of the faster butanolysis. This is to overcome the limited miscibility of alcohol and oil at the early reaction stage, creating a single phase. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high FFA feedstocks. However, molar ratios of alcohol: oil and other parameters are affected by the addition of the cosolvents. There is also some additional complexity due to recovering and recycling the cosolvent, although this can be simplified by choosing a cosolvent with a boiling point near that of the alcohol being used. In addition, there may be some hazards associated with its most common cosolvents, THF and MTBE.

Other possibilities for accelerating the transesterification are microwave or ultrasonic irradiation. A continuous pilot plant-scale process for producing methyl esters with conversion rates >98% was reported as well as a discontinuous two-stage process with a total methanol:acyl (from triacylglycerols) ratio of 4:3. Other basic materials, such as alkylguanidines, which were anchored to or entrapped in various supporting materials such as polystyrene and zeolite, also catalyze transesterification. Such systems may provide for easier catalyst recovery and reuse.

7.4 The processing and production of biodiesel

The chemistry described above forms the basis of the industrial production of biodiesel. It should be noted that processing and quality are closely related, and the processes used to refine the feedstock and convert it to biodiesel determine whether the fuel will meet the required specifications. This section briefly describes the processing and production of biodiesel and how these determine fuel quality. The emphasis is on processing as it is conducted in the United States, where most biodiesel is produced by reacting soybean oil or used cooking oils with methanol and the standard for fuel quality is ASTM D 6751-02.

For alkali-catalyzed transesterification, Figure 7.7 shows a schematic diagram of the process flow for biodiesel production from feedstocks containing low levels of FFA. These include soybean oil, canola (rapeseed) oil, and the higher grades of waste restaurant oils. Alcohol, catalyst, and oil are combined in a reactor and agitated for ~1 h at 60°C.

Smaller plants often use batch reactors but larger plants (>4 million L/yr) use continuous flow processes involving continuous stirred-tank reactors (CSTR) or plug flow reactors. The reaction is sometimes done in two steps in which ~80% of the alcohol and catalyst is added to the oil in a first-stage CSTR. Then, the product stream from this reactor goes through a glycerol removal step before entering a second CSTR. The remaining 20% of the alcohol and catalyst is added in this second reactor. This system provides a very complete reaction with the potential of using less alcohol than single-step systems.

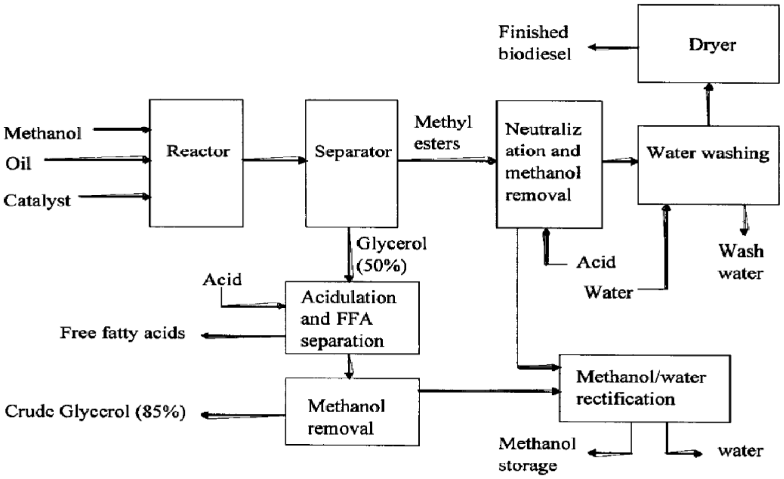


Fig. 7.7. Scheme of process flow for biodiesel production

After the reaction, glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and can be accomplished with either a settling tank or a centrifuge. The excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol.

Some researchers state that it is possible to realize reaction vegetable oil and methanol without a catalyst, which eliminates the need for the water washing step. However, high temperatures and large excesses of methanol are required. Some studies report difficulties with reproducing the results of the reaction kinetics found by other researchers, which could be attributed to catalytic effects at the surfaces of the reaction vessels. They also note that these effects would be exacerbated at higher temperatures. Not including the effect of surface reactions could cause difficulties when scaling up reactors due to the decrease in the ratio of reactor surface area to volume.

According to Figure 7.7, after separation from the glycerol, the methyl ester enter a neutralization step and then pass through a methanol stripper, usually a vacuum flash process or a falling film evaporator before water washing. Acid is added to the biodiesel product to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water-soluble salts and FFA according to the following equation:

$$\text{R-COONa} + \text{HAc} \rightarrow \text{R-COOH} + \text{NaAc}$$

Sodium soap +Acid → Fatty acid +Salt

The salts will be removed during the water washing step and the FFA will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the amount of water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. After the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

The glycerol stream leaving the separator consist only of 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the glycerol presents little value and disposal may be difficult. The methanol content requires the glycerol to be treated as hazardous waste. The first step in refining the glycerol is usually to add acid to split the soaps into FFA and salts. The FFA are not soluble in the glycerol and will rise to the top where they can be removed and recycled.

7.4.1 Acid-Catalyzed Pretreatment

Special processes are required if the oil or fat contains significant amounts of FFA. Used cooking oils typically contain 2–7% FFA, and animal fats contain 5–30% FFA. Some very low-quality feedstocks, such as trap grease, can approach 100% FFA. When an alkali catalyst is added to these feedstocks, the FFA reacts with the catalyst to form soap and water as shown in the reaction below:

$$\text{R-COOH} + \text{KOH} \rightarrow \text{R-COOK} + \text{H}_2\text{O}$$

Fatty acid + Potassium hydroxide → Potassium soap +Water

Up to ~5% FFA, the reaction can still be catalyzed with an alkali catalyst, but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or washed out during the water wash. When the FFA level is >5%, the soap inhibits separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulphuric acid can be used to esterify the FFA to methyl esters as shown in the following reaction:

$$\text{R-COOH} + \text{CH}_3\text{OH} \rightarrow \text{R-COOCH}_3 + \text{H}_2\text{O}$$

Fatty acid + Methanol → Methyl ester +Water

This process can be used as a pretreatment to convert the FFA to methyl esters, thereby reducing the FFA level (see Fig. 7.8 below). Then, the low-FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters. As shown in the reaction, water is formed and, if it accumulates, it can stop the reaction well before completion.

It has been proposed to allow the alcohol to separate from the pretreated oil or fat after the reaction. Removal of this alcohol also removes the water formed by the esterification reaction and allows for a second step of esterification; alternatively, one may proceed directly to alkali-catalyzed transesterification. Note that the methanol-water mixture will also contain some dissolved oil and FFA that should be recovered and reprocessed. Pretreatment with an acidic ion-exchange resin has been shown that acid-catalyzed esterification can be used to produce biodiesel from low-grade by-products of the oil refining industry such as soapstock. Soapstock, a mixture of water, soaps, and oil, is dried, saponified, and then esterified with methanol or some other simple alcohol using an inorganic acid as a catalyst. The procedure relies on a large excess of alcohol, and the cost of recovering this alcohol determines the feasibility of the process.

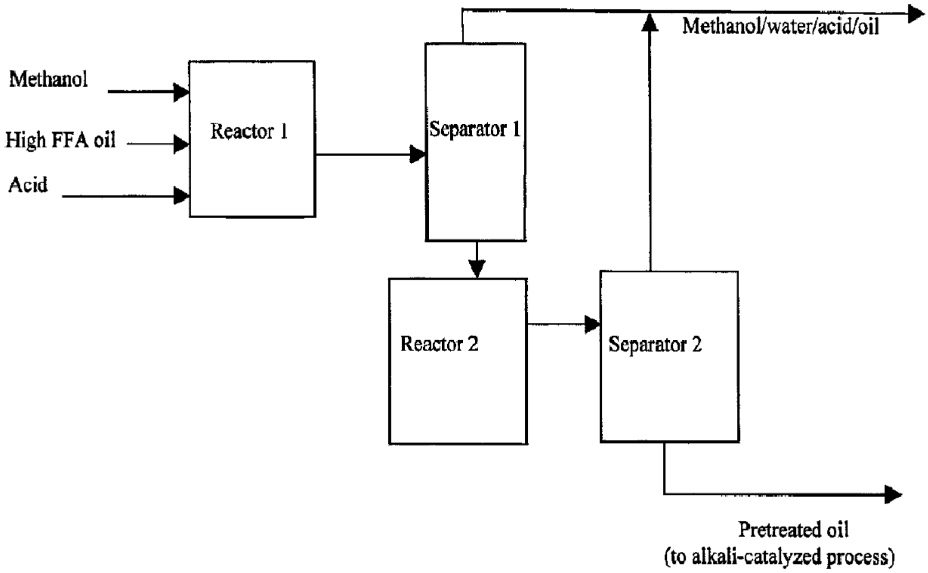


Fig. 7.8. Pretreatment process for feedstocks high in free fatty acids (FFA).

7.4.2 Fuel quality

The primary criterion for biodiesel quality is adherence to the appropriate standard. Generally, the fuel quality of biodiesel can be influenced by several factors, including the quality of the feedstock, the fatty acid composition of the parent vegetable oil or animal fat, the production process, the other materials used in this process, and postproduction parameters.

When specifications are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability. Even when used in low-level blends with petrodiesel fuel, biodiesel is expected to meet the standard before being blended. Although some properties in the standards, such as cetane number and density, reflect the properties of the chemical compounds that make up biodiesel, other properties provide indications of the quality of the production process. Generally, the parameters given in ASTM D6751 are defined by other ASTM standards and those in EN 14214 by other European or international (ISO) standards. However, other test methods, such as those developed by professional oleochemical organizations, such as the American Oil

Chemists' Society (AOCS), may also be suitable (or even more appropriate because they were developed for fats and oils and not for petroleum-derived material addressed in the ASTM standards). This section will focus on the most important issues for ensuring product quality for biodiesel as it relates to production as well as some postproduction parameters.

The most important issue during biodiesel production is the completeness of the transesterification reaction. The basic chemical process that occurs during the reaction is indicated in Figure 7.5 with the reaction proceeding stepwise from triacylglycerols to glycerol and alkyl esters with each step producing a fatty acid alkyl ester. Even after a fully "complete" transesterification reaction, small amounts of tri-, di-, and monoacylglycerols will remain in the biodiesel product. The glycerol portion of the acylglycerols is summarily referred to as *bound glycerol*. When the bound glycerol is added to the free glycerol remaining in the product, the sum is known as the *total glycerol*. Limits for bound and total glycerol are usually included in biodiesel standards. For example, ASTM D6751 requires <0.24% total glycerol in the final biodiesel product as measured using a gas chromatographic (GC) method described in ASTM D 6584. Because the glycerol portion of the original oil is usually ~10.5%, this level of total glycerol corresponds to 97.7% reaction completion. Other methods can be used to measure total glycerol such as high-performance liquid chromatography (HPLC) (e.g., AOCS Recommended Practice Ca 14b-96: Quantification of Free Glycerine in Selected Glycerides and Fatty Acid Methyl Esters by HPLC with Laser Light-Scattering Detection) or a chemical procedure such as that described in AOCS Official Method Ca 14–56 (Total, Free and Combined Glycerol Iodometric Method). However, only the GC procedures are acceptable for demonstrating compliance with standards.

Glycerol is essentially insoluble in biodiesel so that settling or centrifugation easily removes almost all glycerol. Free glycerol may remain either as suspended droplets or as the very small amount that does dissolve in the biodiesel. Alcohols can act as cosolvents to increase the solubility of glycerol in the biodiesel. Most glycerol should be removed from the biodiesel product during the water washing process. Water-washed fuel is generally very low in free glycerol, especially if hot water is used for washing. Distilled biodiesel tends to have a greater problem with free glycerol due to glycerol carry-over during distillation. Fuel with excessive free glycerol will usually have a problem with glycerol settling out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine.

7.4.3 Residual alcohol and residual catalyst

Because alcohols such as methanol and ethanol as well as the alkaline catalysts are more soluble in the polar glycerol phase, most will be removed when the glycerol is separated from the biodiesel. However, the biodiesel typically contains 2–4% methanol after the separation, which may constitute as much as 40% of the excess methanol from the reaction. Most processors will recover this methanol using a vacuum stripping process. The water washing process should remove any methanol remaining after this stripping process. Therefore, the residual alcohol level in the biodiesel should be very low. A specific value for the allowable methanol level is specified in European biodiesel standards (0.2% in EN 14214), but is not included in the ASTM standard; however, the flash point specification in both standards limits the alcohol level. Tests showed that as little as 1% methanol in the biodiesel can lower its flashpoint from 170°C to <40ºC. Therefore, by including a flashpoint specification of 130ºC, the ASTM standard limits the amount of alcohol to a very low level (<0.1%). Residual alcohol left in biodiesel will generally be too small to have a negative effect on fuel performance. However, lowering the flashpoint presents a potential safety hazard because the fuel may have to be treated more like gasoline (which has a low flashpoint) than diesel fuel.

Most of the residual catalyst is removed with the glycerol. Like the alcohol, remaining catalyst in the biodiesel should be removed during the water washing. Although a value for residual catalyst is not included in the ASTM standard, it will be limited by the specification on sulfated ash. Excessive ash in the fuel can lead to engine deposits and high abrasive wear levels. The European standard EN 14214 places limits on calcium and magnesium as well as the alkali metals sodium and potassium.

7.4.4 Water and sediment

These two items are largely housekeeping issues for biodiesel. Water can be present in two forms, either as dissolved water or as suspended water droplets. Although biodiesel is generally insoluble in water, it actually takes up considerably more water than petrodiesel fuel. Biodiesel can contain as much as 1500 ppm of dissolved water, whereas diesel fuel usually takes up only ~50 ppm. The standards for diesel fuel (ASTM D 975) and biodiesel (ASTM D 6751) both limit the amount of water to 500 ppm. For petrodiesel fuel, this actually allows a small amount of suspended water. However, biodiesel must be kept dry. This is a challenge because many diesel storage tanks have water on the bottom due to condensation. Suspended water is a problem in fuel injection equipment because it contributes to the corrosion of the closely fitting parts in the fuel injection system. Water can also contribute to microbial growth in the fuel. This problem can occur in both biodiesel and petrodiesel fuel and can result in acidic fuel and sludge that will plug fuel filters. Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation. Some biodiesel users have noted that switching from petrodiesel to biodiesel causes an increase in sediment originating from deposits on the walls of fuel tanks that had previously contained petrodiesel fuel. Because its solvent properties are different from those of petrodiesel fuel, biodiesel may loosen these sediments and cause fuel filter plugging during the transition period.

7.4.5 Storage stability

Storage stability refers to the ability of the fuel to resist chemical changes during long-term storage; it is a major issue with biodiesel. Contact with air (oxidative stability) and water (hydrolytic stability) are the major factors affecting storage stability. Oxidation is usually accompanied by an increase in the acid value and viscosity of the fuel. Often a darkening of the biodiesel color from yellow to brown and the development of a “paint” smell accompany these changes. In the presence of water, the esters can hydrolyze to long-chain FFA, which also cause the acid value to increase. The methods generally applied to petrodiesel fuels for assessing this issue, such as ASTM D 2274, were shown to be incompatible with biodiesel, and this remains an issue for research.

Antioxidant additives such as butylated hydroxytoluene and *t*- butylhydroquinone were found to enhance the storage stability of biodiesel. Biodiesel produced from soybean oil naturally contains some antioxidants (tocopherols, e.g., vitamin E), providing some protection against oxidation (some tocopherol is lost during refining of the oil before biodiesel production). Any fuel that is going to be stored for an extended period of time, petrodiesel or biodiesel, should be treated with an antioxidant additive.

Literature

1. IEA, “World energy outlook 2004” 2004.
2. Van Gerpen *et al* “ Biodiesel production technology August 2002-January 2004”National Renewable Energy Laboratory, US Department of Energy, NREL/SR-510-36244 July 2004.
3. Lal R., “World crop residues production and implications of its use as a biofuel”. Environment International, vol.31, n°4, pp.575-584. 2005.
4. Bridgwater AV, "Renewable fuels and chemicals by thermal processing of biomass", Chem Eng J. 91 (2003) 87-100.
5. Bridgwater A.V. *et al* “Fast Pyrolysis of Biomass: A Handbook Volume 2 (and Volume 1)” Edited by AV Bridgwater CPL Press 2002.
6. Mittelbach, M., Diesel Fuel Derived from Vegetable Oils, VI: Specifications and Quality Control of Biodiesel, *Bioresour. Technol., 56:* 7–11 (1996).
7. Komers, K., R. Stloukal, J. Machek, F. Skopal, and A. Komersová, Biodiesel Fuel from Rapeseed Oil, Methanol, and KOH. Analytical Methods in Research and Production, *Fett/Lipid, 100:* 507–512 (1998).
8. Cvengrosˇová, Z., J. Cvengrosˇ, and M. Hronec, Rapeseed Oil Ethyl Esters as Alternative Fuels and Their Quality Control, *Petrol. Coal, 39:* 36–40 (1997).
9. Freedman, B., R.O. Butterfield, and E.H. Pryde, Transesterification Kinetics of Soybean Oil, *J. Am. Oil Chem. Soc. 63:* 1375–1380 (1986).
10. Stavarache, C., M. Vinatoru, R. Nishimura, and Y. Maeda, Conversion of Vegetable Oil to Biodiesel Using Ultrasonic Irradiation, *Chem. Lett., 32:* 716–717 (2003).
11. Lifka, J., and B. Ondruschka, Einfluss des Stofftransportes auf die Herstellung von Biodiesel (Influence of Mass Transfer on the Production of Biodiesel), *Chem. Ing. Techn., 76:* 168–171 (2004).
12. Noureddini, H., D. Harkey, and V. Medikonduru, A Continuous Process for the Conversion of Vegetable Oils into Methyl Esters of Fatty Acids, *J. Am. Oil Chem. Soc., 75:* 1775– 1783 (1998).
13. Peterson, C.L., J.I. Cook, J.C. Thompson, and J.S. Taberski, Continuous Flow Biodiesel Production, *Appl. Eng. Agric., 18:* 5–11 (2002).
14. Cvengrosˇ, J., and F. Povazanec, Production and Treatment of Rapeseed Oil Methyl Esters as Alternative Fuels for Diesel Engines, *Bioresour. Technol., 55:* 145–152 (1996).

15. Haas, M.J., P.J. Michalski, S. Runyon, A. Nunez, and K.M. Scott, Production of FAME from Acid Oil, a By-Product of Vegetable Oil Refining, *J. Am. Oil Chem. Soc., 80:* 97– 102 (2003).
16. Van Gerpen, J.H., E.H. Hammond, L. Yu, and A. Monyem, Determining the Influence of Contaminants on Biodiesel Properties, SAE Technical Paper Series 971685, SAE, Warrendale, PA, 1997.
17. Goff, M.J., N.S. Bauer, S. Lopes, W.R. Sutterlin, and G.J. Suppes, Acid-Catalyzed Alcoholysis of Soybean Oil, *J. Am. Oil Chem. Soc., 81:* 415–420 (2004).
18. Haas, M.J., S. Bloomer, and K. Scott, Simple, High-Efficiency Synthesis of Fatty Acid Methyl Esters from Soapstock, *J. Am. Oil Chem. Soc., 77:* 373–379 (2000).
19. Haas, M.J., P.J. Michalski, S. Runyon, A. Nunez, and K.M. Scott, Production of FAME from Acid Oil, a By-Product of Vegetable Oil Refining, *J. Am. Oil Chem. Soc., 80:* 97– 102 (2003).
20. Saka S., and D. Kusdiana, Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol, *Fuel, 80:* 225–231 (2001).
21. Kusdiana, D., and S. Saka, Kinetics of Transesterification in Rapeseed Oil to Biodiesel Fuel as Treated in Supercritical Methanol, *Fuel, 80:* 693–698 (2001).