EXPERIMENT 30

BIOFUELS

Instructors

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LITERATURE (in Polish):
1. R. T. Morrison, R. N. Boyd: *Chemia organiczna*, tom 2 (rozdz. 33: Tłuszcze) PWN, Warszawa 1985.
2. S. Bredsznajder, W. Kawecki, J. Leyko, R. Marcinkowski: *Podstawy ogólne technologii chemicznej*, PWN Warszawa 1973.
3. S. E. Manahan: *Environmental Chemistry*, Brooks/ Cole Publishing Company, 1984.
4. H. Koneczny: *Podstawy technologii chemicznej*, (rozdz. V: Paliwa i ich przerób), PWN, Warszawa 1973.
5. R. Bogoczek, E. Kociołek-Balawejder: *Technologia chemiczna organiczna*, rozdz. 2, WAE, Wrocław 1992.
6. *Spalanie i paliwa* praca zbiorowa pod red. J. Kordylewskiego, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2005.
7. J. Ciborowski: *Inżynieria chemiczna. Inżynieria procesowa,* WNT, 1973.

Requirements

Definitions: energy and conversion of energy, biofuels (bioethanol, biodiesel), heat/thermal capacity, diffusion, simple and complex lipids (classification), fats and vegetable oils, fatty acids and their esters, triglycerides (triacylglycerols), waxes, FAME (fatty acid methyl esters), viscosity, numbers characterizing fats.
1. Combustible materials (flammable substances). Fuels – definition and classification. Combustion processes, chain reactions, heat of combustion and calorific value , explosions, explosion limit, spark-ignition engine, compression-ignition engine (Diesel engine, diesel).
2. Technical analysis of physicochemical parameters of fuels and biofuels: density, kinematic and dynamic viscosity, relative viscosity, flash point (ignition temperature) and fire point, freezing temperature (setting point), distillation temperature, volumetric dilatation (temperature, thermal), octane number, cetane number (CN).
3. Oil plants and their application. Examples and composition of vegetable oils, methods of production, parameters characterizing fats (iodine number, acid number, peroxide value), correlation between composition, structure and freezing point of fats.
4. Transesterification: mechanism and kinetics.
5. Knowledge on the procedures of synthesis, purification and analysis of biofuels, described in this manual.

INTRODUCTION – THEORY

The definition of a fuel is wide – it includes ***any substance which, through physical and chemical changes provides significant amounts of heat, which is used for technical and households (like domestic heating) purposes***. Such definition is much broader than the old one, according to which the fuels were "*solid / liquid / gaseous organic substances which reacted with oxygen to form carbon dioxide and water vapour releasing large amounts of heat*". Fuels are a source of energy in the sense that chemical energy is converted into heat energy as a result of chemical processes.

Based on the criterion of fuel origin, fuels can be divided into two main groups:
  a) natural fuels (hard coal = coal, brown coal = lignite, petroleum, natural gas, peat, biomass, wood),
  b) synthetic fuels which result from less or more complicated transformation of natural fuels (e.g. coke, petrol) or from chemical synthesis of high-energy substances (e.g. rocket propellant - nitromethane, a mixture of hydrogen peroxide and methanol) as well as nuclear fuel.

Taking into account other criteria we can distinguish, depending on the state of matter: solid and fluid (liquid and gaseous) fuels or, depending on the origin, fossil fuels and biofuels. Depending on the application, we can distinguish fuel for heat production and fuel for transportation, and depending on the calorific value[1] we can divide fuels into low-calorie and high-calorie fuels (low energy and high energy fuels).

In most cases fuels are combustible substances it means the substances capable to exothermic reaction with air after the initiation (ignition). For commonly used fuels we use parameters which allow to compare the amount of energy that can be released by this reaction. **The calorific value** is a measure of the amount of heat obtained by combustion of unit of mass (or volume) of fuel. The calorific value of organic substances containing carbon, hydrogen, sulfur and oxygen is described by the following empirical equation:

$$W_u = 33900C + 121000\left(H_2 - \frac{O_2}{8}\right) + 10500S - 2500\left(W + \frac{9}{8}O_2\right) \qquad \left[\frac{\text{kJ}}{\text{kg}}\right]$$

where: C, H_2, O_2, S are mass participation of these elements, respectively, and W is contents of water (humidity of material).

When combustion is total, and the reaction products are brought into the standard state (at constant volume), the heat obtained in this process is called the **heat of combustion**. The process should be **total** (stoichiometric, without loss of substance, no evaporation) and **complete** (to the thermodynamically most stable product). Measurements of heat of combustion is carried out in a bomb calorimeter, in thermochemistry the heat is measured in [kJ / mol] units and in energetic a basic unit is [kJ / kg].

The heat of combustion is called the **upper calorific value**, since it corresponds to the total heat produced from the fuel. In combustion processes taking place in furnaces and engines water vapor is produced, which is not condensed. Mostly it is "entrained" with the other flue gases, which prevents the use of energy released during its condensation. Therefore, to evaluate the quantity of the resulting heat another parameter is more appropriate a **lower calorific value**. This is the amount of heat (expressed in kJ / kg) released by complete combustion of unit mass of fuel in a bomb calorimeter, when the combustion products cool off to the initial fuel temperature (at constant volume), but assuming that water is not condensed.

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[1] In physics and energetics a term *calorific value* is used whereas a term *caloric value* is in use in medicine.

An example of the solid fuel is wood. The dry weight of wood contains about 50% carbon, 6.3% hydrogen and 44.2% oxygen. During the combustion of wood we obtain relatively small (0.3-1%) amount of ash. Wood is classified as **biomass** and it is reproducible energy resource, unlike fossil fuels, which are admittedly of plant origin, but the process of their formation is so long that you can not talk about the reproducibility of fossil fuels in the biological sense. **Solid fossil fuels** are peat, brown coal (lignite), hard coal and anthracite. The calorific value of peat is within 18 000 to 25 500 kJ / kg range. Hard coal called anthracite, which includes the least of volatile substances and the most of elemental carbon, has the highest energy value (37 000 kJ / kg). As a result of combustion of fossil fuels ash (slag) - consisting of Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO - is produced.

Fluid fossil fuel are mainly petroleum (calorific value is an average 44 000 kJ / kg) and natural gas, of which calorific value is the most varied - depending on:
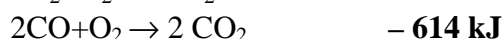- deposits associated with petroleum (so-called wet natural gas and dry),
- contents of individual hydrocarbons (CH_4 to C_5H_{12} fractions),
- amount of nitrogen and hydrogen sulfide.

Combustion in the presence of oxygen from the air (79% N_2 + 21% O_2, disregarding the content of water and CO_2) may proceed with an excess of oxygen or deficit of oxygen. It should be also remembered that the fuel can react with oxygen-containing substances (eg. H_2O, CO_2), which are externally suppli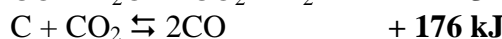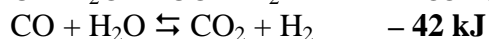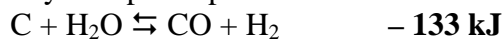ed or which are produced during combustion. Combustion with oxygen insufficiency (lack of oxygen) is described by the equations:

$$2C + O_2 \rightarrow 2CO \qquad \textbf{– 219 kJ}$$
$$2H_2 + O_2 \rightarrow 2\,H_2O \qquad \textbf{– 476 kJ}$$

however, with enough amount of oxygen:

$$C + O_2 \rightarrow CO_2 \qquad \textbf{– 395 kJ}$$
$$2H_2 + O_2 \rightarrow 2\,H_2O \qquad \textbf{– 476 kJ}$$
$$2CO + O_2 \rightarrow 2\,CO_2 \qquad \textbf{– 614 kJ}$$

Oxygen-carrying substances may also participate in the combustion reaction:

$$C + H_2O \leftrightarrows CO + H_2 \qquad \textbf{– 133 kJ}$$
$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \textbf{– 42 kJ}$$
$$C + CO_2 \leftrightarrows 2CO \qquad \textbf{+ 176 kJ}$$

Combustion (for heat production) should be carried out with enough amount of air, but introducing too much excess of air is not preferred because it decreases the temperature of the exhaust gases. Reduction of the amount of exhaust gases (flue gases, exhausts) can be achieved by the use of oxygen-enriched air.

Combustion processes of gaseous, fluid and solid fuels undergo in different ways. Mixing the gaseous fuel with air and combustion at the burner nozzle is a process that occurs in the **kinetic zone** and thus it depends on the rate of chemical reaction. In contrast, when the combustible gas is mixed with air in the reaction zone (furnace) – the process of mixing will be the reaction rate limiting factor and combustion process will take place in the **diffusion zone**.

The advantages of gaseous fuels include: ease of transport (pipelines), the ease of bringing gas to the furnace (combustion chambers), the formation of gaseous products of combustion process without solid or liquid residues, the ability to pre-heat the fuel, resulting in a higher temperature of exhausts (i.e. the formation of larger temperature gradient during heat exchange).

Combustion of fluid fuels is associated with conducting a process in a biphasic system fuel / air. Appropriate mixing of the reactants is to spray the fuel in the combustion chamber (the liquid particles of formed aerosol pass rapidly into a state of steam). This process

depends on temperature, particle fragmentation, type of fuel. During combustion process no solid or liquid residues are formed.

Solid fuels burn in multiphase system – apart from the gas-solid phase boundary, a combustible gas fraction can be released at high temperatures. The combustion process **occurs at the interface (phase boundary)**, so, development of the surface and the way of mixing fuel with air is very important. In contrast to the combustion of liquids and gases, products of solid fuel combustion are not only gases but also residues such as ash and slag.

Combustion of solid fuels can be arranged in several ways. Fuel can be burnt on a movable or stationary fire grate and air can be supplied from below. The air goes through a layer of fuel and combustion occurs in a manner dependent on the fuel particle size, method of their arrangement, air velocity, fuel capacity for sintering, the amount and method of removal of generated ash. It is hard to keep a smooth combustion of solid fuel. The second method of the combustion of solid fuels involves the use of pulverized coal in specially constructed cyclone furnaces, where the effective mixing of dust from the air takes place. Large development of the surface makes this method rapid, complete and efficient. Dust generated during the combustion is blown from the combustion chamber and separated from the exhausting gases in cyclones, filters and electrofilters.
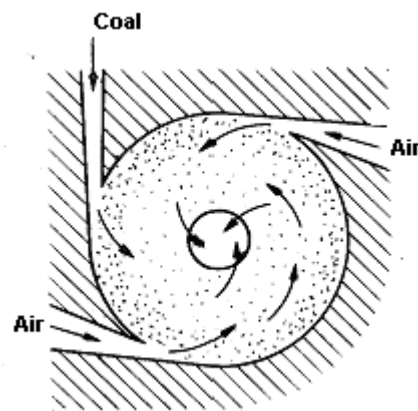

Figure 1. Scheme of the cyclone furnace for combustion of solid fuels (by S. Bredsznajder, R. Kawecki, J. Leyko, R. Marcinkowski: *General fundamentals of chemical technology*, OWN Warsaw 1973).

Ash produced after combustion of solid fuels is a residue of: (i) inorganic compounds contained in the fuel, (ii) the ingredients of plants of which coal was formed (about 1% of fuel) or (iii) geological contamination introduced into the coal (which may be up to 30% of total weight). The ash contains Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO and small amounts of other inorganic substances. Melting or sintering of ash, accompanied by combustion, is very unfavorable process leading to the slag formation which flood and block fire grate.

Combustion

Combustion is a dynamic (non-equilibrium, depending on the time) oxidation process involving the atoms, molecules, radicals that are in one phase or at the phase boundary. The rapid exothermic reactions cause the release of energy also in the form of light (flames, glowing, sparks) or the formation of gradients that are the reason of heat and mass flow (the flow of chemical individuals), thus, the flames are moving in uncoordinated ways.

If the amount of combustible gas in a mixture with air (oxygen) gradually increases, a minimum value is reached above that a mixture becomes combustible . This minimum fuel content is called the **lower combustion limit**. If the contents of gaseous fuel is further increased, then upper a certain value of the mixing it will be inflammable. This is the **upper combustion limit**. These parameters are strongly dependent on the temperature - the higher

temperature of the mixture, the bigger is difference between upper and lower limits. For some mixtures, within the lower and upper combustion limit we can distinguish the areas of explosion - when the rate of flame spread reaches a detonation (explosion) rate. This problem will be discussed later.

The flames (formed during combustion of stoichiometric mixtures of air with the generally used fuel) reach temperature 2000 K. When the composition of mixture changes reaching the limits of flammability, flame temperature drops to 1400 K.

Table 1. Combustion temperatures of selected gases.

Gas (fuel)	Oxidant	Fuel participation /% vol.	Temperature / °C
H_2	air	31.6	2045
H_2	O_2	78	2660
CO	air	20	1650
methane	air	10	1875
ethane	air	58	1895
propane	air	4,15	1925
butane	air	3,2	1895
acetylene	air	9	2325
acetylene	O_2	33	3007
ammonia	air	21	1700
$CO + N_2$	air	47,3	1675
$CH_4 + N_2$	air	17,5	1725
$9CH_4 + H_2$	air	10,5	1880

Combustion have to be initiated with ignition. This might be **spontaneous ignition**,[2] when the amount of heat provided or dissipated inside the system is greater than allowed to discharge the heat. The second type of ignition is the **spark ignition** when the flame is initiated in one place (e.g. by a spark), and from this place it is spreading to the rest of the system.

Heating of combustible liquids, including liquid fuels (even at temperatures below the boiling point) leads to increased evaporation of the liquid, and, if they are non-volatile it can lead to secretion of volatile and flammable substances derived from their decomposition. **Flash point**[3] is the lowest temperature at which the tested substance (heated in a specific way), emits a sufficient amount of gaseous products to produce with air a mixture which can be ignited being close the flame (i.e. as a result of the ignition point). If under the same conditions ignited vapour burns without external source of flame for at least 3 seconds, then this temperature is called **temperature of burning**.[4] Temperature of combustion is usually about 20-60 ° C higher than the ignition temperature.

Explosions

When the rapid exothermic reaction occurs in a limited space and when as a result of this reaction gaseous products are produced, the pressure suddenly (which is uncontrolled) jumps (increases) and this is called explosion. The amount of heat discharged is less than the

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[2] Also called spontaneous ignition or autoignition.
[3] Ignition temperature.
[4] Fire point, temperature of combustion.

amount of heat generated, resulting in an increase of temperature and, according to the Arrhenius kinetic equation, we observe acceleration of the reaction. Self-accelerating reaction will take place faster and faster until one of the reactants runs out. For mixtures of air (or oxygen) with hydrogen, hydrocarbons, vapors of sulfur, phosphorus, carbon disulfide and other organic solvents, such a process has a radical chain mechanism.

Whether the mixture is explosive, depends on the type of substance, mixture composition, temperature and pressure. **Explosion limits** (combustibility, ignition) are characteristic features of combustible mixtures:

– **lower explosive limit (LEL)** is the lowest concentration of fuel in the mixture of air / oxygen / oxidizing agent, when the mixture is still capable to produce a flash fire; below that concentration no ignition is possible with any initiating factor.

– **upper explosive limit (UEL)** is the highest concentration of fuel in the mixture of air / oxygen / oxidizing agent when the mixture is still capable to produce a flash fire; above that concentration ignition or spread of flame is not possible.

Outside these limiting concentrations an ignition of mixture does not occur even if the ignition source has an infinitely large energy. Limits of explosion expressed in concentrations are identical with the ignition limits, however, limits of explosion are dependent on the pressure and temperature, so we can talk about the temperature and pressure limits of explosion. Figure 2 presents chart of ability of hydrogen / air mixtures to explode. The parameters of susceptibility to explode for selected combustible gases and organic solvents are presented in Tables 2 and 3.
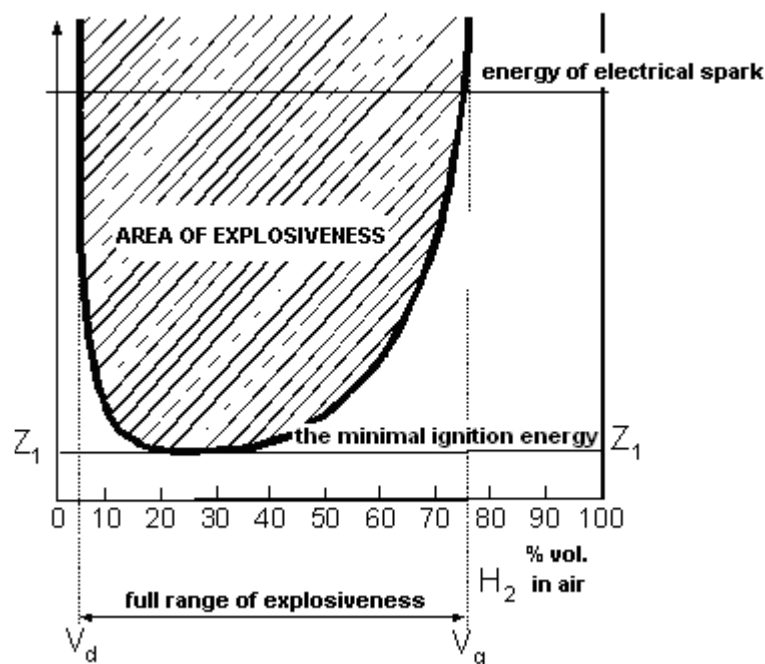

Figure 2. Dependence of ignition energy on the composition of hydrogen - air mixture: Z1 - the minimal ignition energy, $E_{min} = 0.019$ mJ, V_d - lower explosion limit, V_g - upper explosion limit.

Table 2. Values of lower (LEL) and upper (UEL) explosive limits for mixtures of combustible gases with air or oxygen.

Gas	% gas content in the air		% gas content in the oxygen	
	LEL	UEL	LEL	UEL
Hydrogen	4,1	74,2	4,0	94,0
Carbon monoxide	12,5	74,2	15,5	94,0
Methane	5,3	14,0	5,1	61,0
Ethane	3,2	12,5	3,0	66,0
Propane	2,4	9,5	2,3	55,0
Butane	1,9	8,4	1,8	48,0
Acetylene	2,5	80,0	2,5	98,0
Coke oven gas[a]	5,6	31,0	---	---
Water gas[b]	6,2	72,0	---	---
Natural gas[c]	4,5	17,0	---	---
Town gas[d]	35,0	74,0	---	---

[a] Industrial fuel obtained by heating of coal at a temperature above 1000 ° C in a specially constructed furnace, in the absence of oxygen. [b] Combustible gas formed during the reaction of coal or natural gas with steam in the presence of suitable catalysts. It is a mixture of carbon monoxide and hydrogen (it also contains a few percent of carbon dioxide, nitrogen and hydrocarbons). [c] Fossil fuel of organic origin which is collected in the crust of the Earth. [d] Other names: city gas, gasworks gas.

Table 3. Parameters characterizing selected organic solvents.

	Ignition temperature (flash point) °C	LEL*	UEL*	minimum temp. of autoignition °C	maximum pressure of explosion kPa	Explosiveness Group
ethanol	11	3,1	20	425	634	IIA
methanol	11	5,5	36,5	470	625	IIA
acetone	-19	2,1	13	540	772	IIA
isopropanol	12	2,0	12	400		IIA
dichloromethane		13	18	660		IIA
methyloamine	-17,8	4,9	20,7	430		IIA
toluene	4	1,3	7	570	566	IIA
ethyl eter	-40	1,6	48	160	801	IIB
ethyl acetate	-4	2,2	11,5	460	752	IIA
dioxane	12	2	22	180		IIB

* Values of lower (LEL) and upper (UEL) explosion limits.

When the combustion is performed in order to obtain heat - a process is carried out in furnaces or boilers. Then, the thermal energy can be converted into mechanical work e.g. in steam turbines. A more direct and more effective way to convert chemical energy into mechanical work is the use of internal combustion engines (more specifically, heat engines

with internal combustion). In reciprocating engines[5] the energy is converted into the work of piston or pistons moving in a cylinder (cylinders). This movement is converted into the torque of the crankshaft.

In **spark-ignition engines** (Figure 3) combustion is initiated by a spark of the spark plug. Fuels used in this type of engines may be natural gas, light fractions of petroleum (liquid gas, petrol, leaded petrol) as well as flammable and volatile organic substances (e.g. methanol, ethanol). Spark engines have light constructions and simple design and they easily receive high speed, high power gain, and they are easy to start.
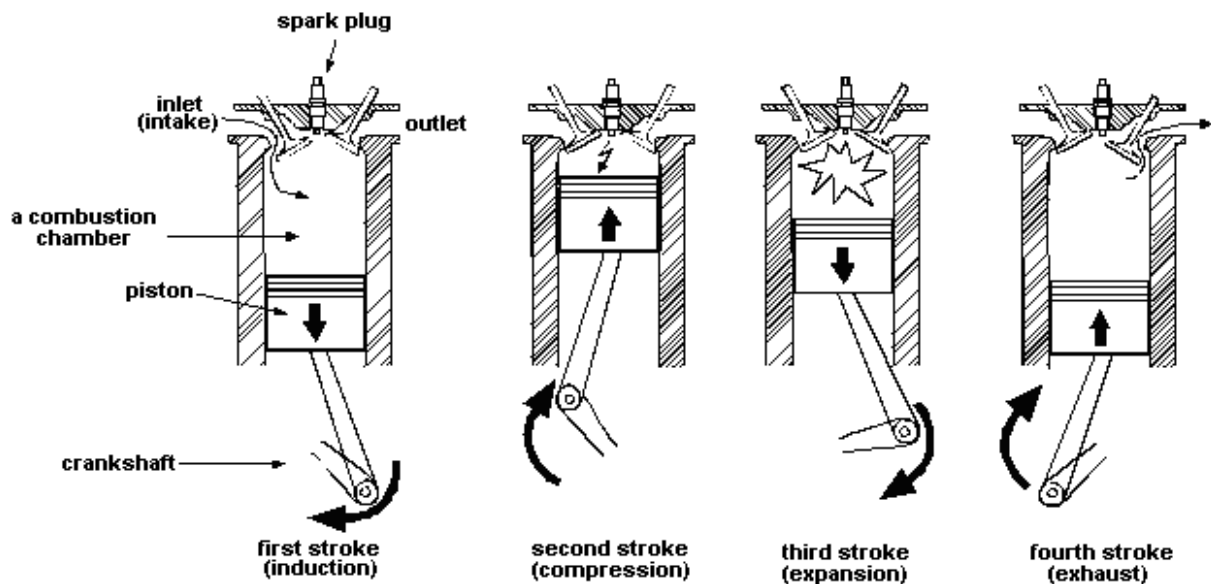
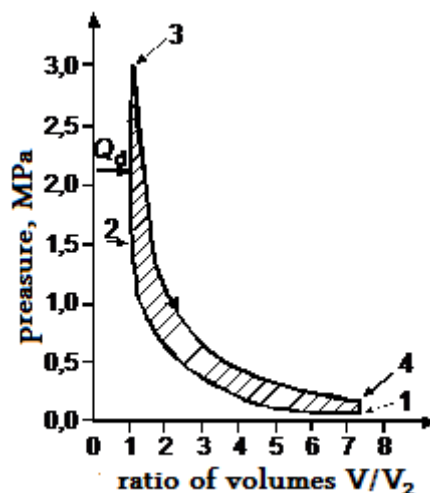Figure 3 Scheme of four-stroke engine (four-cycle engine) with spark ignition.

Figure 4. Spark-ignition engine cycle (according to *Combustion and fuels* edited by J. Kordylewski, Publishing House of Wroclaw University of Technology, Wroclaw, 2005).

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optional material

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[5] A reciprocating engine (or a piston engine) is a heat engine using one or more reciprocating pistons to convert pressure into a rotating motion.

Motor efficiency, η, refers to the amount of useful work dW that we can get from a definite quantity of supplied heat, dQ_h. Since the useful work (d$W = - pdv$) is the difference between the heat absorbed (d$Q_h < 0$) and heat discharged (d$Q_c > 0$), we have:

$$\eta = \frac{-dW}{-dQ_h} = \frac{-dQ_h - dQ_c}{-dQ_h} = 1 - \frac{dQ_c}{-dQ_h} = 1 + \frac{dQ_c}{dQ_h}$$

The efficiency of reciprocating combustion spark-ignition engine is given by:

$$\eta = 1 - \varepsilon^{1-\kappa}$$

where ε is the compression ratio (the ratio of cylinder volume to the harmful volume V_1/V_2, see Figure 4, position 1 and 2) and $\kappa = C_p / C_v$. Compression ratio in combustion engines is in the 8:1 to 11:1 range, but above 8.5:1 the combustion with engine knocking may occur (on the course of explosive), leading to the destruction of the piston, rings and bearings.
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Engine knocking combustion[6] is due to self-ignition of the mixture, and this effect is strongest for the stoichiometric mixture of fuel and air. A measure of resistance to detonative combustion of the motor fuel for spark-ignition engines is the **octane number (ON).** This parameter is equal to the percentage of isooctane (2,2,4-trimetylopentane) in a mixture of *n*-heptane / isooctane, which produces the same number of knocks in the tested engine as in analyzed fuel. ON for motor fuels is between 80-98 and this ON value is obtained by addition of **anti-knock** agents, in the past the organic lead compounds were used like tetraethyl lead. Today in lead-free petrol (lead-free gasoline) some alcohols like methanol, ethanol, and *tert*-buthanol are used and some ethers (methyl *tert*-butyl ether or methyl *tert*-amyl ether), and their amount, regulated by standards, may reach 10%. Role of anti-knock agents is suppression of uncontrolled combustion by introducing radicals into the system, which in non-explosive way initiate the combustion process at a lower temperature, and at the same time they recombine with an excess of radicals generated during spontaneous ignition.

Spark engines have some disadvantages (less efficiency and less durability) if compared to **diesel engines** (**compression-ignition engines**). Diesel engines are also internal combustion engines with piston, but the ignition of fuel-air mixture occurs as a result of increasing temperature exceeding the flash point. Diagram of the diesel engine is shown in Figure 5A.
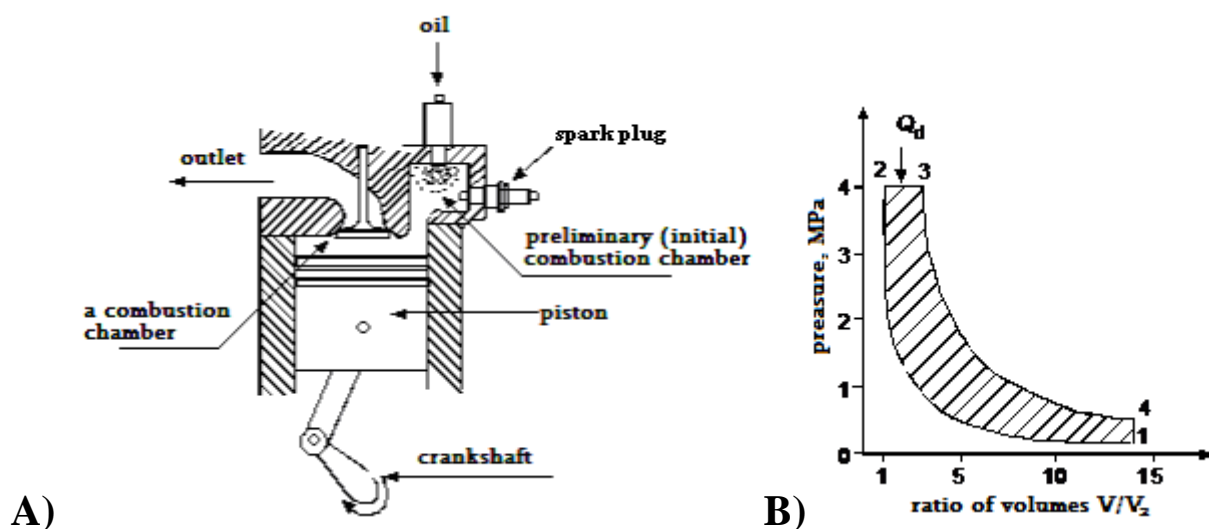

Figure 5. A) Scheme of the self-ignition engine, and B) Diesel engine cycle (according to *Combustion and fuels* edited by J. Kordylewski, Publishing House of Wroclaw University of Technology, Wroclaw 2005).

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[6] Also called knock, detonation, spark knock, pinging or pinking.

In this engine, the air is sucked and compressed and during the compression process a temperature strongly increases. Compression ratio ε in diesel engines ranges from 14:1 to 23:1. After the piston reaches the top position, it is followed by injection, spraying and immediate evaporation of fuel, which in contact with hot air is ignited. The piston moves down and when reaches lowest point (dead position), the exhaust valve opens and exhausts fly out of the cylinder.

The efficiency of a diesel engine is described by the formula:

$$\eta = 1 - \frac{\varepsilon^{1-\kappa}}{\kappa} \frac{\varphi^{\kappa} - 1}{\varphi - 1}$$

where φ is a degree of engine load (volumes ratio V_3/V_2, see Figure 5B, volume corresponding to positions 3 and 2). The diesel engine works with a greater compression ratio (ε) than the spark-ignition engine, so its efficiency is higher than the efficiency of the spark-ignition engine. Other advantages of diesel engines are lower failure (break-down) and greater durability of the engine, achieving greater power and bigger torque. The disadvantages of diesel engines compared to the spark-ignition engines are higher production costs, the greater mass of diesel engines, higher emissions of nitrogen oxides and solid particles, and some difficulties with start at lower temperatures.

Due to different mechanism of action and the conditions in spark-ignition engine and diesel, we use different fuels. Instead of gasoline the higher fractions of crude oil (petroleum) are used – diesel fuel and heavy oil (black oil, mazout). The basic parameter characterizing the fuel for diesel engines is **the capacity for spontaneous combustion - the Cetane Number, CN**. CN is determined by comparing the time of ingnition of reference fuel and analyzed diesel fuel. The reference fuel is a mixture of cetane (hexadecane, $C_{16}H_{34}$, for which CN = 100) - which possesses a very short time of ignition - and α-methylnaphthalene. Pure cetane has CN = 100, while a mixture of cetane and α-methylnaphthalene (1:1) has CN = 50. Unbranched (straight) saturated hydrocarbons (paraffins) are characterized by a cetane number from 70 to 110, worse properties are observed for branched paraffinic hydrocarbons (20 < CN < 70), and CN for aromatic hydrocarbons is from 0 to 60. Generally, light fractions of petroleum have low cetane number comparing to higher fractions (but their low content is beneficial for starting a diesel engine). The minimum CN value, according to the Polish Norms, equals 51. In addition to CN, other properties are also important i.e. lubricating properties of fuel (oil) for diesel engines.

BIOFUELS

Since the time of energy crisis in 1970's the energy sources alternative to fossil fuels (petroleum, natural gas and coal) have been strongly demanded and are still being searched. The amounts of fossil fuels estimated on the basis of all previously known supplies is presented in Table 1.

Table 4. World supplies of fossil fuels (based on S. E. Manahan: Environmental Chemistry, Broks/ Cole Publishing Company, 1984).

Fuel name	Estimated amount	Energy value
shale oil	30×10^{12} liters	$0,32 \times 10^{15}$ kWh
tar-sand oil	48×10^{12} liters	$0,51 \times 10^{15}$ kWh
liquid petroleum	32×10^{14} liters	$3,25 \times 10^{15}$ kWh
natural gas	$2,8 \times 10^{14}$ m^3	$2,9 \times 10^{15}$ kWh
coal and lignite	$7,6 \times 10^{12}$ tons	$55,9 \times 10^{15}$ kWh

Fossil fuels are called non-renewable energy sources, which means that their amount is still decreasing because of intensive exploitation. Rising prices of fuel and climate changes associated with intensive use of fossil fuels are the reason for search for alternative energy sources, which currently are classified as:
- **hydroelectricity**
- **wind energy**
- **geothermal energy**
- **energy of tides (a kind of hydroenergy)**
- **solar energy**
- **photovoltaics**
- **biogas (from cogeneration processes)**[7]
- **biomass (from cogeneration processes)**
- **heat energy transformed by solar devices**
- **biofuels from vegetable oils**
- **biogas fuel from fermentation of whole plants**
- **new generations of biofuels**
- **passive utilization of solar energy**
- **new solar technologies.**

Energy exists in many forms, which can be transformed from one to another. Conversion of electricity in the light energy carried out in traditional light bulbs (with resistant wire inside) yields 5% while the remaining 95% is lost as transformed into hear. The efficiency of coal power plants (coal → steam → electricity) is about 40%. The efficiency of convertion of heat energy into mechanical energy, which occurs in steam turbines, is described according to the Carnot Cycle and the second law of thermodynamics as an inequality:

$$\eta = \frac{W}{Q} \le \frac{T-T'}{T} = 1 - \frac{T'}{T}$$

thus, the efficiency depends on the initial (T) and final (T') temperature. A typical steam turbine engine works within the range of temperatures T = 810 K and T' = 330 K, so its maximum theoretical efficiency would be 59%. At the beginning of the twentieth century

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[7] **Cogeneration** (also **combined heat and power**, **CHP**) is the use of a heat engine or a power station to simultaneously generate both electricity and useful heat.

temperature of produced steam was 550 K, and the maximum efficiency was 40% (total efficiency was a few percent!). In modern power plants, using new, more durable construction materials, steam temperature reaches about 830 K. Heat losses and temperature fluctuations cause a further decline in the efficiency of convertion of heat into mechanical energy to 47% and taking into account the stage (step) of producing a hot, pressurized steam (chemical energy → steam) the total efficiency drops to 40%.

The efficiency of nuclear power plants is limited by the maximum achievable temperature (reactor core may not exceed a certain temperature, typically 620 K) and therefore the efficiency of conversion of nuclear energy in electricity is about 30%. Energy loss (60% in the conventional power plant and 70% in nuclear power plant) is dispersed, contributing to the heating up the atmosphere (it is called thermal pollution).

In the twentieth century, the efficiency of coal power plants has increased from 4 to 40%, and the replacement of steam locomotives by internal combustion (diesel engines) contributed to 4- fold increase in the efficiency of conversion of chemical energy into mechanical energy. Efficiency of conversion of several types of energy is presented in Table 5. Loss of energy is very large compared to the total energy production. This problem is related to production methods and ways of its conversion in devices used by people as well as access to various sources of energy and minimizing of pollution generated during the conversion process.

Tabela 5. Examples of energy conversion.

ENERGY	świetlna	chemical	thermal	mechanical	electric	kinetic
light	-	photosynthesis, W<0,6%			solar cell, W=10% light bulb, W=4%	
chemical	chemiluminescence	-	Home gas furnace, W=85%		batteries = storage cell	
thermal (heat)			-	Steam turbine	thermoelement (thermocouple), W=7% Electric heater W=100%	
mechanical				-	Power generator, W=98%	↥ Jet engine
electric			↥Steam boiler, W=88%	Electric motor, W=60-90%	-	power generator in fly-wheel
kinetic						-

In accordance with EU directives (directive 30/2003/EC) participation of alternative fuels should systematically increase from 2% in 2005 to 5.75% in 2010 and 10% in 2020. The use of hydro, solar, tidal, wind and geothermal powers is dependent on geographical and geological conditions and is not always possible or profitable. Similarly, the application of advanced technologies in order to use the photovoltaic effect has not reached cost-effectiveness threshold that would allow to utilize these energy sources on a large scale. In the countries of the moderate climatic zone, biomass is basic and widely accessible energy source. The concept of biomass is defined in different ways.

By **definition 1**, they are *biodegradable fractions of products, waste and residues from agro-*

food industry (including substances of plant and animal origin), from forestry and derivative industries, as well as the biodegradable fractions of municipal and industrial waste. According to **definition 2** these are *all kinds of substances formed during biological and biochemical processes occurring in nature, being a potential source of energy for specific applications.*

Efficiency of solar energy conversion by plants is small, usually a fraction of a percent (in sugarcane conversion efficiency reaches a maximum value of 0.6%), however, in the natural environment the scale of biomass production is so great that it is potentially the largest source of energy.

The primary renewable resource is wood - a material that is 75% composed of polysaccharides, including cellulose, and many substances can be extracted from wood, among others tannins, pigments, terpenes, sugars, starch, pectin, resins, adhesives, hydrocarbons, carboxylic acids, steroids, ethers, fats and waxes. The wood is used on a large scale to produce a whole range of other useful products - boards, plywoods, chipboards, paper, methanol, cellophane, plastics, rayon, terpne oils. Methanol is called an alcohol timber because in the past most of this compound was obtained by pyrolysis of wood. In developing countries a combustion of wood is still the primary source of heat.

Fuels made from biomass are called biofuels. Like biomass, biofuels are among the renewable energy sources. The use of biofuels as additives to fossil fuels reduces petroleum consumption and contributes to a more favorable balance of carbon dioxide on a global scale, because the carbon dioxide released during combustion derives from biomass which previously bounded the same amount of CO_2 in the process of photosynthesis. Furthermore, compared with the exploitation of fossil fuels, the use of biofuels reduces the amount of sulfur and nitrogen oxides emitted to the atmosphere. Although the group of solid biofuels includes such types of biomass as granulated or briquetted straw, industrial sawdust and other processed vegetable wastes, later we will focus on liquid and gaseous biofuels only.

Commonly used liquid biofuels are **bioethanol** in blends with gasoline, **biodiesel** containing methyl esters in blends with diesel, biomethanol (as a component or fuel derived from biomass), **bio-ETBE** derived from ethanol (ETBE: Ethyl tertiary-Butyl Ether), **bio - MTBE** obtained from methanol (MTBE: Methyl Tert-Butyl Ether) and **pure vegetable oils** meeting the requirements for their use in engines. The prefix bio- is introduced in order to put emphasis that a substance is derived from biomass. However, there is no chemical difference between, for example, synthetic ethanol and ethanol derived from biomass. Examples of gaseous biofuels are **bio-gas**, **Bio-DME** (DME: Dimethyl Ether) and **bio-hydrogen** - all derived from biomass.

Cultivation of plants from which biofuels are made (especially biodiesel and bioethanol) covers more and more agricultural areas and may cause a reduction in food production, leading to an increase in prices of basic food products. Today, biofuels are equivalent to 1.5 million barrels of petroleum a day and their production becomes competitive relating to food production (according to the World Bank production of biofuel caused 75% of the dramatic increase in food prices that occurred in 2007-2008. Further development of the area of the food crops used for biofuels production might cause a serious global food deficiency. The use of edible plants (negative factor) or waste (positive factor) is the basis for biofuels division into I, II and III generation. Taking into account the impact of biofuel production on the materials management, the division is given below.

BIOFUELS OF FIRST GENERATION :
- ethanol formed in the fermentation process,
- vegetable oils obtained by conventional methods,
- biodiesel obtained by transesterification of oils,

- biodiesel obtained by transesterification of waste fats,
- bio-gas produced from agricultural wastes,
- Bio-ETBE derived from ethanol,
- bioMTBE obtained from methanol.

BIOFUELS OF SECOND GENERATION are biofuels produced on the basis of biomass and waste materials unsuitable for the food industry, forestry, etc. They include:
- bioethanol derived from lignocellulose (advanced hydrolysis and fermentation),
- synthetic biofuels obtained as a result of gasification / liquefaction of biomass,
- biodiesel obtained by refining of waste plant oils,
- bio-gas produced by gasification of lignocellulose,
- hydrogen generated by gasification or biological processes.

BIOFUELS OF THIRD GENERATION
- methanol obtained by gasification of lignocellulose,
- hydrogen generated by gasification of lignocellulose.

According to Polish regulations on bio-components in gasoline it is forbidden to add methanol. Ethanol may be added to the fuel to reach maximally 10% by volume and higher alcohols in an amount not greater than 0.1% v / v. Gasoline with10% of ethanol emits about 2% less toxic substances and 10% less CO than gasoline with10% methyl tert-butyl ether, however, up to 14% more nitrogen oxides (NO_x) is evolved during combustion of gasoline/EtOH mixtures. Engine oils may contain maximally 5% vol. of added fatty acid esters.

FATS
(Recommended reading: Morrison, Boyd: Organic Chemistry, chapt. 33 or other Organic Chemistry textbook with section on lipids).

The definition of lipids is very general: in older definitions they are natural substances (biomolecules), soluble in nonpolar solvents (fats), such as acetone, chloroform, ether and benzene, but insoluble in water. Such a general definition includes not only the carboxylic acids (called fatty acids) and their esters but also steroids, terpenes and carotenoids.

As components of cells lipids play important functions: (i) they are construction material (in cell membranes and organelles), (ii) they provide energy reserves (also responsible for thermal insulation), (iii) they improve solubilization and transport of other food ingredients in the body, and (iv) lipids are precursors used to synthesis of other biomolecules. Some substances included in the group of lipids are an important part of the nervous system in which they act as nerve signal transducers. In addition to its role as cells components, lipids (called fats) play another important function: they are the most efficient source of energy in food. One gram of fat gives about 38 kJ while 1g of protein or 1 g of sugar provide about 17 kJ.

There are many classifications of lipids, such as the division into plant and animal lipids, the distribution in saturated and unsaturated lipids, liquid (colloquially: vegetable oils) and solid (colloquially: animal fats). Due to the chemical structure we distinguish the following lipids:

I. Simple lipids, which include:
   a) simple esters of fatty acids and alcohols including triacylglycerols (esters of fatty acids and glycerin),
   b) waxes (esters of fatty acids and long chain fatty alcohols).

II. Complex lipids:
   a) phospholipids (esters of fatty acids and glycerol containing phosphoric acid groups),
   b) glycolipids (esters of fatty acids and glycerol containing the rest of the sugar).

III. Isoprene lipids:
   a) steroid,
   b) carotenoids.

IV. Derivatives of lipids (including fatty ingredients which form lipids, so fatty acids, fatty alcohols).

The basic ingredients of most fats are triglycerides, i.e. esters of fatty acids and glycerin. The composition of fatty acids is characteristic for the fat and determines its physicochemical parameters. Typically, natural fatty acids have not branched chains and, with the exception of propanoic and pentanoic acids, have an even number of carbon atoms. Generally, we use common names: lauric, myristic, palmitic, stearic, behenic, whereas, systematic names contain the chain length + end of word (-oic) + word acid, such as octadecanoic acid, dodecanoic acid. The names of saturated fatty acids are given in Table 6.

Unsaturated fatty acids contain one or more double bonds, and the vast majority of these bonds are in the configuration E (*cis*). We use the common names of these acids, while in the systematic names there are given the numbers of carbon atoms (numbering starts from from the carboxyl group) next to which a double bond is present. Examples of names of unsaturated fatty acids are given in Table 7.
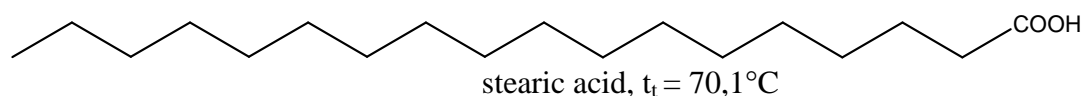
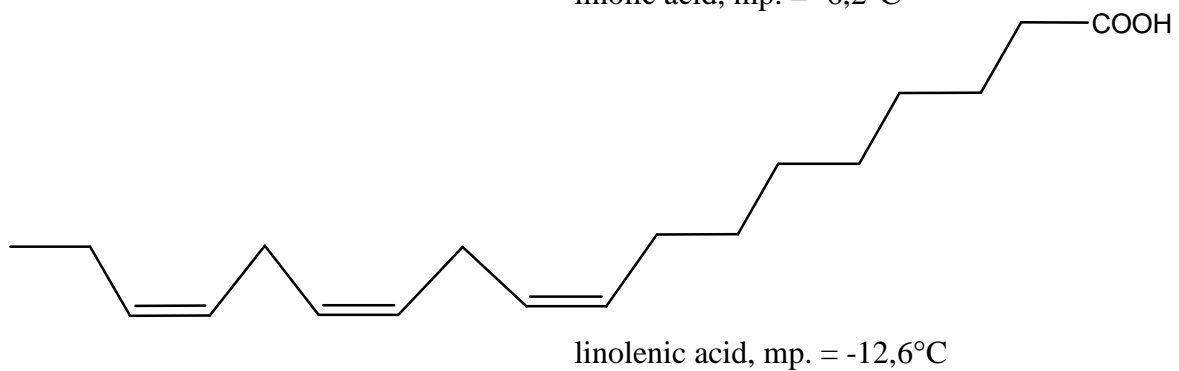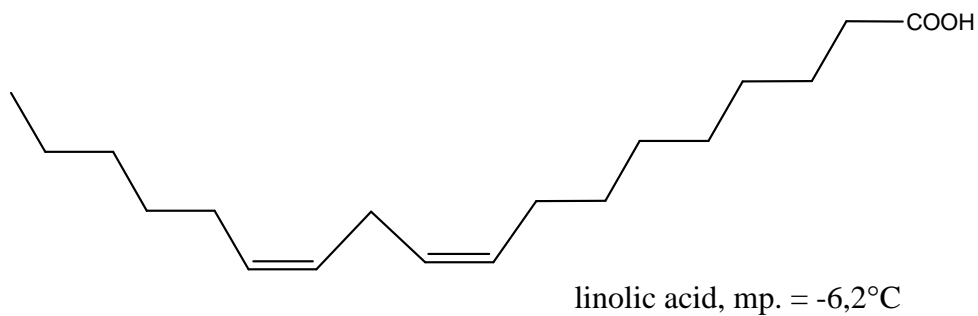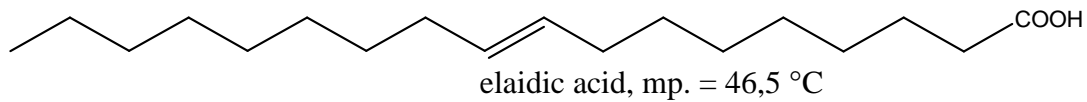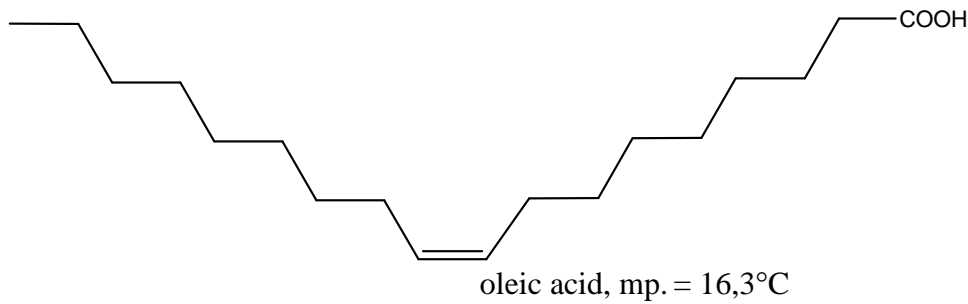Table 6. Names and symbols of saturated fatty acids.

Amount of carbon atoms	Systematic name	Common name	Symbol
4	butanoic	butyric	4:0
6	heksanoic	caproic	6:0
8	oktanoic	caprylic	8:0
10	dekanoic	capric	10:0
12	dodekanoic	lauric	12:0
14	tetradekanoic	myristic	14:0
16	hexadekanoic	palmitic	16:0
18	octadekanoic	stearic	18:0
20	eicosanoic	arachidic	20:0
22	dokosanoic	behenic	22:0

Table 7. Names and symbols of unsaturated fatty acids.

Amount of carbon atoms	Systematic name	Common name	Symbol
	monounsaturated		
14	*cis*-9-tetradecenoic	myristoleic	14:1
16	*cis*-9-hexadecenoic	palmitoleic (oleopalmitic)	16:1
18	*cis*-9-octadecenoic	oleic	18:1(9)
18	*trans*-9-octadecenoic	elaidic	
18	*trans*-11-tetraadecenoic	vaccenic	18:1(11)
20	*cis*-9-icosenoic	gadoleic	20:1(9)
22	*cis*-13-docosenoic	erucic	22:1(13)
22	*trans*-9-docosenoic	brassidic	
	multi-unsaturated (polyunsaturated)		
18	*cis,cis*-9,12-octadecadienoic	linolic	18:2(9,12)
18	all *cis*-9,12,15-octadecatrienoic	linolenic	18:3(9,12,15)
20	all *cis*-5,8,11,14-eicosatetraenoic	arachidonic	20:4(5,8,11,14)
20	all *cis*-5,8,11,14,17-eicosapentaenoic	timnodonic	
22	all *cis*-4,7,10,13,16,19-docosapentaenoic	clupanodonic	22:6(4,7,10,13,16,19)

The presence and configuration of double bonds has a strong influence on the melting point of fatty acid (and on the phase transition temperature of fats containing fatty acids). For example, for saturated and unsaturated octadecanoic fatty acids (eighteen carbons) the melting point changes from -13 to +70 ° C.
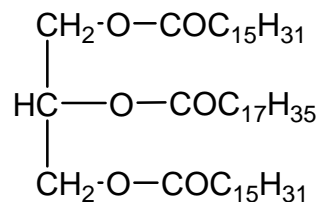

stearic acid, $t_t = 70,1°C$

oleic acid, mp. = 16,3°C

elaidic acid, mp. = 46,5 °C

linolic acid, mp. = -6,2°C

linolenic acid, mp. = -12,6°C

Esters formed by fatty acids with glycerol are called triglycerides:
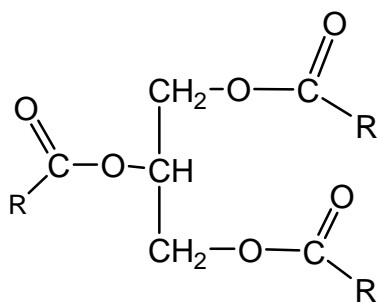
triacylglycerol (triacylgliceryde)

dipalmitoil-stearoil-glycerol
(1,3-dipalmitoil-2-stearoil-*sn*-glycerol)

Increasing amount of unsaturated fatty acids in vegetable fats causes their lower melting temperature, they are liquid at 15 ° C and usually they are called oils. Animal fats have a higher participation of saturated fatty acids and they are solid at room temperature.

The source of vegetable oils are seeds and fruit of oil plants such as rapeseed, sunflower, soybean, corn, olives, poppy, flax, cotton. Triglycerides isolated from plants

contain a few percent of saturated fatty acids, other acidic residues are derived from mono- and polyunsaturated fatty acids. High content of polyunsaturated fatty acids (including those with conjugated bonds (C = CC = C) in tung, hemp and linseed oils makes that these oils have a film-forming properties - they are called drying oils used in the manufacture of adhesives, lacquers and coatings. Name "linoleum" is derived from linseed oil, which is crosslinked in the process of oxidative polymerization.

Vegetable oils are obtained by **extrusion** or **extraction**. These methods can be combined, i.e. residue after extraction is subjected to extrusion. Seeds or fruits are deprived of their hard shells, dried, crushed or minced (before extrusion) or flaked (for extraction). Oil pressing (in a press) gives about 50% of oil, (first pressing of olive oil gives the highest quality *extra virgin oil*), then pomace (pulp) are re-crushed, heated and pressed, and additional amount of oil is obtained. Pomace (pulp)containing about 5% of fats, proteins and carbohydrates can be applied for feeding the farm animals. **The extraction method** uses low-boiling hydrocarbon solvents, which are then evaporated. Extraction is more efficient method (there is only 1% of fat in the residue).
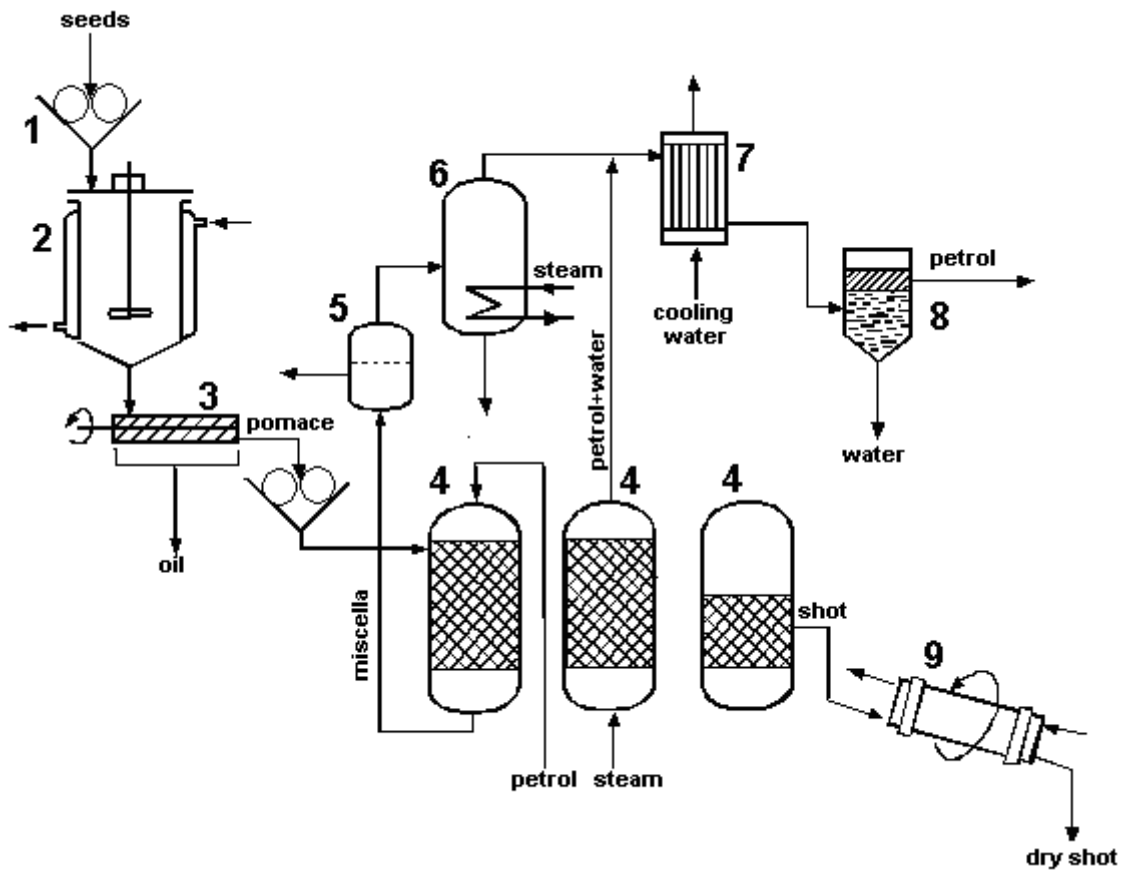

Figure 6. Scheme of oil production by the use of extraction method with preliminary pressing: 1 - crushers and rollers, 2 - heater, 3 - hot press (oil expeller), 4 - extractors, 5 - filter, 6 - distillation column, 7 - condenser (heat exchanger), 8 - separator, 9 - rotary dryer (by: R. Bogoczek, E. Kociołek-Balawejder: *Technologia chemiczna organiczna*, chapt. 2, WAE, Wrocław 1992).

Regardless the method (pressing and extraction), the oils contain many undesirable substances, such as colorants, proteins, lecithin, free fatty acids and therefore must be refined. Sequential processes are carried out such as degumming and desludging (to remove lecithin[8]

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[8] Lecithin is a phospholipid, diacylglyceride containing the rest of phosphoric acid and choline:

and other viscous substances). After desludging a de-acidification process is carried out, involving the chemical (neutralization or esterification) or physicochemical (distillation) removal of free fatty acids. The final stages are discoloration involving adsorption of coloring substances and deodorization of oils by distillation of aromatic substances in the steam distillation. Refining of technical oils does not have to meet standards as for edible oils for food purposes. For technical oil a refination with concentrated sulfuric acid is sufficient to remove the proteins, organophosphorus substances and resins.

TECHNICAL ANALYSIS OF FUELS AND FATS

Some parameters used to describe the physical and chemical properties of fuels already have been mentioned: *heat of combustion, calorific value, flash point, temperature of burning, lower and upper explosion limit, the octane number and cetane number*.

Physical parameters characterizing both the fats and fuel are **melting and solidification temperatures**. Since the fuel and fats are not homogeneous substances, phase transitions *liquid ⇆ solid* can take place in a much wider temperature range than transitions for the homogeneous compounds. During slow heating fats and waxes become soft, then turn into a cloudy liquid and finally into a clear liquid. Slow cooling of the liquid causes a very slow solidification, the temperature of which is not the same as melting point. Relating to these phenomena a series of temperatures is determined: softening point, the temperature of drop, melting point in the capillary, cloud point and solidification as well as hardening (curing) temperature. These parameters are helpful in fats identification, in control of curing process, and investigation of the waxes properties. Solidification temperature is an important parameter describing thermal behavior of fuels and biofuels during storage, transport (transmission by pipeline, transportation in tanks) and exploitation at low temperatures.

Another parameter is the **density** sometimes mistakenly identified with the **specific gravity** (weight to volume ratio, expressed in N / m^3). Density (ρ or d) is determined in a strictly defined temperature by the use of the areometer or the pycnometer, and the resulting density value must always be complemented with information on the temperature at which the measurement was carried out.

The volume is strongly dependent on temperature, the process of volume change occurs in the temperature range in which phase transitions do not occur as well as during these changes. **Dilation of volume** is a change of volume that occurs during the heating of a substance. Dilation of fats is determined within the limits of the melting point, when there is a phase transition from solid to liquid.

Viscosity is a parameter expressing the strength of the internal friction of the fluid particles in motion. It characterizes internal resistance of a fluid against the laminar flow(caused by shear stress or tensile stress). For a given fluid at defined temperature the viscosity is constant. It is determined based on the Newton equation (also called the equation of viscosity) according to which the shear stresses generated during the fluid motion are directly proportional to the gradient of velocity (resulting stress have the opposite return to direction of the fluid):
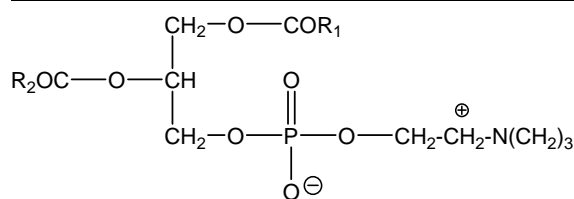
Lecithin is used as an emulsifier in the pharmaceutical and food industries (e.g. as an ingredient in chocolate).

$$\tau = -\eta \frac{du}{dx}$$

The force needed to balance shear stresses formed in the system is:

$$F = -\tau A$$

$$F = \eta A \frac{du}{dx}$$

where A is the surface area of shifting layers of fluid and η is the coefficient of **dynamic viscosity (absolute viscosity).** The unit of absolute viscosity is the poise: 1 poise (P) = $1 g \times cm^{-1} \times s^{-1} = 0,1\ N \times m^{-2} \times s^{-1} = 0,1\ Pa \times s$ (Pa $\times$ s is a unit of SI). The viscosity of water at 20 ° C under 1 atm. is 0.01 poise. Dynamic viscosity is the inverse of liquidity ($\varphi = 1 / \eta$). The ratio of absolute viscosity to the density is the **kinematic viscosity** (expressed by v), which in SI units is: $m^2 \times s^{-1}$ and in the CGS system 1 stokes ($1 St = 10^{-4}\ m^2 \times s^{-1} = cm^2 \times s^{-1}$). Viscosity coefficient is a parameter of great practical importance used to deal with many issues physicochemical, hydro-technical, technological (e.g. problems of fluids transportation, mixing of the liquid in the reactors).

The increase of pressure decreases the distance between molecules and thus increases the viscosity - for pressures to 2000 atm. increase in viscosity is linear with increasing pressure. It is different from the viscosity of solutions in which there are strong interactions between the solvent and dissolved substance. When a dissolved substance organizes the structure of the solvent (e.g. polymers, proteins and lyophilic colloids bind many solvent molecules), then generated internal structures cause an additional increase in viscosity. This is a structural viscosity, η_{struct}, which, together with normal viscosity, Newtonian (η_N) is included in the solution viscosity: $\eta = (\eta_N + \eta_{struct})$.

Newton equation is used only for the so-called Newtonian fluids, i.e. fluids of which viscosity does not depend on the velocity of motion.

Chemical analysis of fats

Modern methods of chemical analysis allow to determine the fatty acids composition quickly and precisely. Gas chromatography can be used after initial derivatization of the sample (the non-volatile triglycerides have to be converted into fatty acid methyl esters). Another analytical method is High Performance Liquid Chromatography (HPLC). Despite the widespread use of these instrumental methods, older methods of analysis are still often in use, for example, titration allows to rapidly determine the total amount of fatty acids, unsaturated fatty acids content, the quality of fat, oxidation state of mixtures, glycerol content and the content of unsaponifiable matter. Some of these basic parameters are will be concisely described.

There is always a content of free fatty acids in fat. This is the result of enzymatic or non-enzymatic decomposition of triglycerides and during the storage a concentration of free fatty acids increases. The content of free fatty acids is determined by **acid number (AN)** - the number of milligrams of potassium hydroxide needed to neutralize the free fatty acids in 1 g of the fatty substance. Determination of AN is based on alkalimetric titration of fat solution in mixture of ethyl ether with ethanol. This analysis is one of the most frequently performed measurements in analysis of fats and oils.

Unsaponifiable substances are the ingredients not reacting with strongly alkalized water (they do not form soaps). The content of such substances in natural fats should not exceed 1.5%. Determination of unsaponificable substances is based on heating under reflux a certain amount of fat with an alcohol solution of KOH until it is completely dissolved, then adding water to a concentration of 50% and extraction of water-insoluble fraction with petroleum ether. After evaporation of the ether, residue is weighted and it is the unsaponifiable fraction.

Saponification number (SN) is the amount of KOH (in milligrams) needed to the complete saponification of free and associated fatty acids contained in one gram of fatty material. It is determined by adding of potassium hydroxide excess to the fat at a higher temperature:

triglyceride + known amount of KOH → glycerol + $3R_x$-COOK + excess of KOH

and back-titration of unreacted KOH. SN contains the value consumed in the titration of free fatty acids (acid number, AN), while the number of milligrams of KOH required to react with fatty acids linked in the form of triglycerides is called **EsterNumber**, EN

SN = EN + AN.

The content of unsaturated fatty acids is expressed by characteristic parameters such as iodine number, thiocyanogen value, hexabromide number and diene value = maleic value. **Iodine number (IN)** is the number of grams of iodine reacting with 100 g of analyzed fat. This parameter indicates the total number of double bonds (in mono- as well as polyunsaturated acids). Thiocyanogen value, hexabromide number and diene value allow to measure the content of polyunsaturated fatty acids.

PRODUCTION of FATTY ACID METHYL ESTERS

The annual demand for diesel in Poland is 7,290 thousand m^3 and, according to the Directive 30/2003/EC, the participation of biofuels in oil should reach 5.75% on total diesel in 2010, which means the demand for 445 thousand m^3 of biocomponents per year. Despite the high calorific value, vegetable fats cannot be directly used as a motor fuel because the triglycerides have too high flash point, they are too viscous - their presence in fuels might cause blockage of fuel filters, seizure and destruction of the engine. Vegetable oils also should not be used in compression-ignition engines because they are less volatile than diesel fuel (at 350°C decomposition instead of evaporation occurs), the kinematic viscosity is about ten times larger than the viscosity of diesel fuels and the cetane number is 32-36 (rapeseed oil) (according to Polish standards LC have to be more than 50). Therefore, triglycerides have to be converted into fatty acid methyl esters (FAME -Fatty Acids Methyl Esters). Term biodiesel means FAME used alone or a fuel containing FAME as biocomponent. The raw material for the production of FAME is not expensive and produced, depending on geographical region, from vegetable oils: canola oil (in Poland), soybean (in U.S.), sunflower, cottonseed, corn, palm oil and from waste oils.

In Poland, the most commonly grown oily plant is rapeseed. Rapeseed oil was used in Asian countries and the Mediterranean as early as ancient times as a mean for oil lamps. Cultivation of rapeseed in Europe has been carried out since the thirteenth century, but the popularity of rapeseed oil has increased with the development of steam engines, for which it was needed as a lubricant. Canola oil was not used as a food product. The increasing rapeseed fertility, improvement of sensory properties and reduction of content of the harmful erucic acid resulted in intensification of cultivation of this plant and the increase of world oil production. Currently, rapeseed belongs to the list of five largest oil raw materials. In Poland, for food purposes the low-erucic rapeseed oil is produced (doubly improved - marked with 00 symbol meaning less than 2% of the erucic acid in total fatty acid contents). From a technical point of view, it is a precious vegetable fat with a high content of oleic acid (18:1) and is used as a food fat and technical oil applied in chemical industry as raw material for biofuel production. The fatty composition of rapeseed oil is presented in Table 8.

Fatty acid methyl esters (FAME) from rapeseed oil meet the requirements of European Standard, which specifies that:
- the sulfur content should be not more than 10 mg / kg of seed,
- iodine number of FAME should be no higher than 120,

- maximum linolenic acid content is 12%
- fatty acids with more double bonds than 4 should be less than 1% by weight.

Tabela 8. Fatty composition of rapeseed oil.[9]

Fatty acid	Percentage of fatty acids	
	winter rapeseed	spring rapeseed
Palmitic and stearic	4-6	5-6
Oleic	56-68	58-67
Linolic	18-22	18-22
Linolenic	10-12	8-11
Eicosenoic	1-2	1-2
Erucic	0-2	0-0.5

The calorific value of esters of rapeseed oil (37.5 MJ / kg) is significantly higher than the calorific value of ethanol and methanol (respectively 25.0 and 19.5 MJ / kg) and comparable to the calorific value of diesel (42.4 MJ / kg).

The use of FAME as biocomponents leads to obtaining biodiesel fuels with high Cetane Number and better lubricating properties than traditional mineral oils. Biodiesel burns emitting less carbon monoxide and sulfur dioxide. The disadvantages are: worse biofuel properties at low temperature, interaction with elements of rubber and plastics, the possibility of corrosion of coating, susceptibility to microbial contamination, hygroscopicity, the possibility of the presence of methanol and glycerol.

FAME are obtained by transesterification of rapeseed oil with methanol.
Transesterification reaction (alcoholysis) is the equilibrium displacement of the rest of one alcohol in ester group by another alcohol:
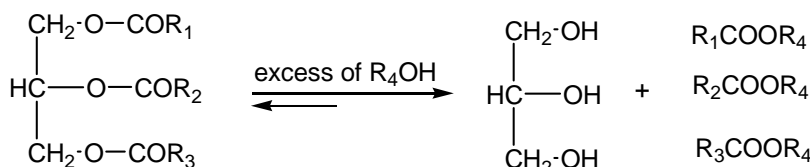

This process can also be enzymatic, catalyzed by lipases. Lipases are produced by different strains of yeast, mold or bacteria (*Candida antarctica*, *Candida rugosa*, *Candida cylindracea*, *Rhizomucor miehei*, *Aspergillus niger*, *Pseudomonas pseudomalle*, *Bacillus fluorescens*, *Bacillus piocyaneum*)[10] and the optimal conditions for transesterification is the temperature 30-37 ° C and pH 7 -8.

Transesterification can be non-enzymatically catalyzed by acid or base. In alkaline solution alcoholysis proceeds rapidly at room temperature, while in acidic solution alcoholysis requires heating the boiling point of methanol or ethanol (depending on whether methanolysis or ethanolysis iscarried out). At temperatures above 250 ° C it is not necessary to use a catalyst because the rate of the process is enough to proceed with acceptable rate.

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[9] Wałkowski T.: Growing rapeseed as a source of renewable energy, *Rapeseed -Biofuels*, edition 2, pp. 24-30, Warsaw, 2006.

[10] Lipases are used in the food industry to produce esters which affect the sensory characteristics of products. Isoamyl acetate (banana flavor), methyl butyrate (pineapple flavor), methyl propionate (fruity taste), tolyl esters (honey aroma), citronellyl acetate (rose aroma), terpinyl acetate (fruity aroma) are produced by the use of lipases. These esters give the right flavor and taste of the drinks, juices, nectars, jams and cookies. Lipases are widely used in the dairy industry - the taste and smell of hard cheese comes from the short-chain fatty acids released by lipases.

Acid catalysed transesterification proceeds through stages of protonation of the ester and connection of alcohol with the cation. Each step is reversible, so the direction of reaction depends on the molar ratio of substrates and products:
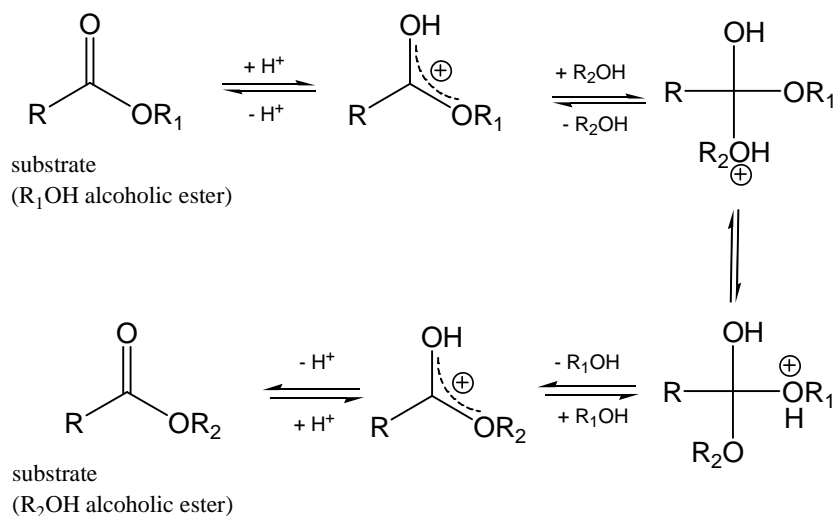
In alkaline solution ester is attacked by alcoholate (alkoxide):
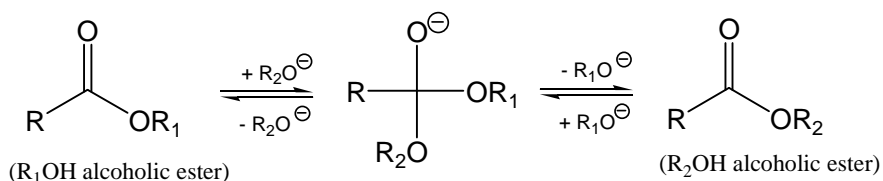
Also in this case, each step is reversible and the efficiency of the process depends on the use of excess of alcohol.

Industrial transesterification of rapeseed oil with methanol is carried out at temperature higher than ambient to improve a solubility of the mixture of oil / methyl esters /methanol. Initially, the process takes place in two phases, but after formation of certain amount of ester system becomes homogeneous. The catalyst is usually potassium hydroxide and rate of alcoholysis increases with increasing concentration of KOH.

Production of FAME by transesterification (alcoholysis) in presence of alkaline catalysts is a multistep process which includes: refining crude oil, two-step transesterification, washing with sulfuric acid, rinsing with water and drying. Because methanolysis is an equilibrium process, the yield depends on the stoichiometric ratio of methanol / triglycerides and on the amount of water in reacting system. In practice, too large excess of methanol is not used - it is better to arrange the process in two stages, each time removing the fraction containing glycerol and adding a slight stoichiometric excess of methanol. Reaction products are methyl esters, glycerol and soap. Figure 7 shows a schematic process for FAME preparation from rapeseed oil in the system of two reactors working in alternate sequence.
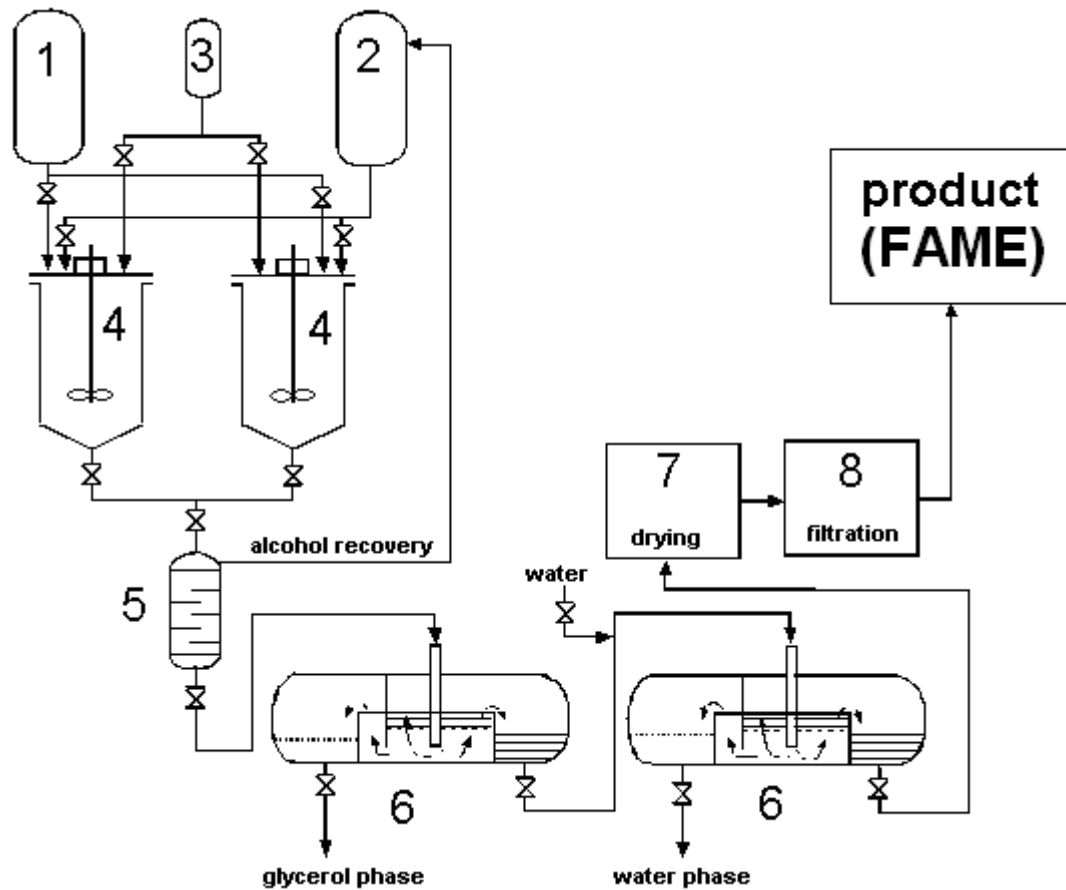
Figure 7.Scheme of continuous production of FAME (: 1-oil tank, 2-alcohol tank, 3-tank with catalyst in methanol solution (KOH or NaOH), 4-reactors working alternately, 5-distillation of the excess of methanol, 6-phase separators, water-glycerol fraction is separated in the first separator, then washed, neutralized and separated in the second separator, 7, 8 –drying block (by the use of sodium sulfate, silica gel) and filtration.