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Bioinformatics

CHEMICAL TECHNOLOGY: RAW MATERIALS AND ENERGY CARRIERS

Edited by Grażyna Gryglewicz

Wrocław 2011

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Wrocław University of Technology

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Preface

This textbook is intended particularly for students who will attend the laboratory course *Chemical technology: raw materials and energy carriers*. Its scope has been limited to the subject of the laboratory work. Thus, the textbook provides the background knowledge on coal, crude oil and biomass necessary to follow the laboratory work with understanding. The laboratory classes include determinations of the selected properties of coal, biomass, crude oil and diesel oil, performed according to the ISO standards, aimed at evaluating their quality and suitability for various applications.

The textbook is divided into six chapters. The topics of the chapters are strictly connected with the laboratory work. Chapter 1 covers the proximate analysis of coal and biomass. The main components of these raw materials, including moisture, mineral matter and organic matter are discussed. A brief account of the origin, formation and classification of coal is included. Chapter 2 deals with coal and biomass used as energy carriers. The methods of calorific value determination and the factors influencing this value are presented. In Chapter 3, the problem of sulfur in coal is considered. Comprehensive information is given on the sources of sulfur in coal, the sulfur forms and their determination, the impact of sulfur on coal processing, and finally the methods of sulfur removal was given. Chapter 4 deals with the coking properties of coal that determine production of coke of high mechanical strength in the lump form. The methods of determining the plastic properties, caking power and swelling ability of hard coals are described. The author of Chapter 5 provides a summary on the genesis, extraction, composition, properties and processing of crude oil. Particularly, the properties applied as criteria for classification of crude oil were emphasized. Chapter 6 explains the composition of diesel fuel and its production process. The selected properties of diesel fuel, among many of them being regulated by ISO standards, are described. The problem of diesel vehicle emissions and the methods of their reduction are also discussed.

Grażyna Gryglewicz

1 Coal composition

Ewa Lorenc-Grabowska

1.1 Introduction to coal

Coal is a carbonaceous rock formed by the decomposition and alteration of vegetation by temperature, compaction and pressure. It is a complex material that exhibits a wide range of physical and chemical properties.

One of the earliest reports of using coal as a fuel is from the geological treatise *on stones* by Greek scientist Theophrastus (371-287 BC) [1]. Outcrop coal was used in Britain during the Bronze Age (3000-2000 BC), where it has been detected as forming part of the composition of funeral pyres [2]. In Roman Britain (200 AD) as well as in ancient China coal was used as a fuel by the 4th century AD [2,3]. The *black earth* was also known in mediaeval Europe (500-1500 AD). The invention of the steam engine that led to the Industrial Revolution induced the large-scale use of coal. Nowadays coal is used as a source of energy and a chemical feedstock from which such compounds as dyes, oils, pharmaceuticals and pesticides can be derived. It is widely used in the production of coke for metallurgical processes. Coal is a major source of energy in the production of electric power using steam generation. Moreover the gasification and liquefaction processes produce gaseous and liquid fuels that can be easily transported or stored in tanks.

The utility of coal is strongly dependent on the coal rank and coal purity. In contrast to the coal purity that can be improved, the coal rank cannot be changed. There are two kinds of coal classification. The first called *scientific* is concerned with the origin, constitution and basic properties of the coal. The second system called *commercial* concerns the trade, utilization and technological properties.

1.1.1 Coal genesis

Coal is a fossil fuel that was formed from the remains of plants that had lived and died about 100-400 million years ago. The energy we recover from coal today derives from the sun energy absorbed by plants millions of years ago. Most of the hard coal deposits were formed in the Carboniferous era. The brown coal was formed mainly in the Tertiary period. Fig. 1.1 shows the scheme of the coal formation which is called the coalification process [4]. The first stage of coal formation was the accumulation of dead plant debris on the bottom of swamps where the peat was formed. The aerobic decay led to a significant reduction of the peat volume.

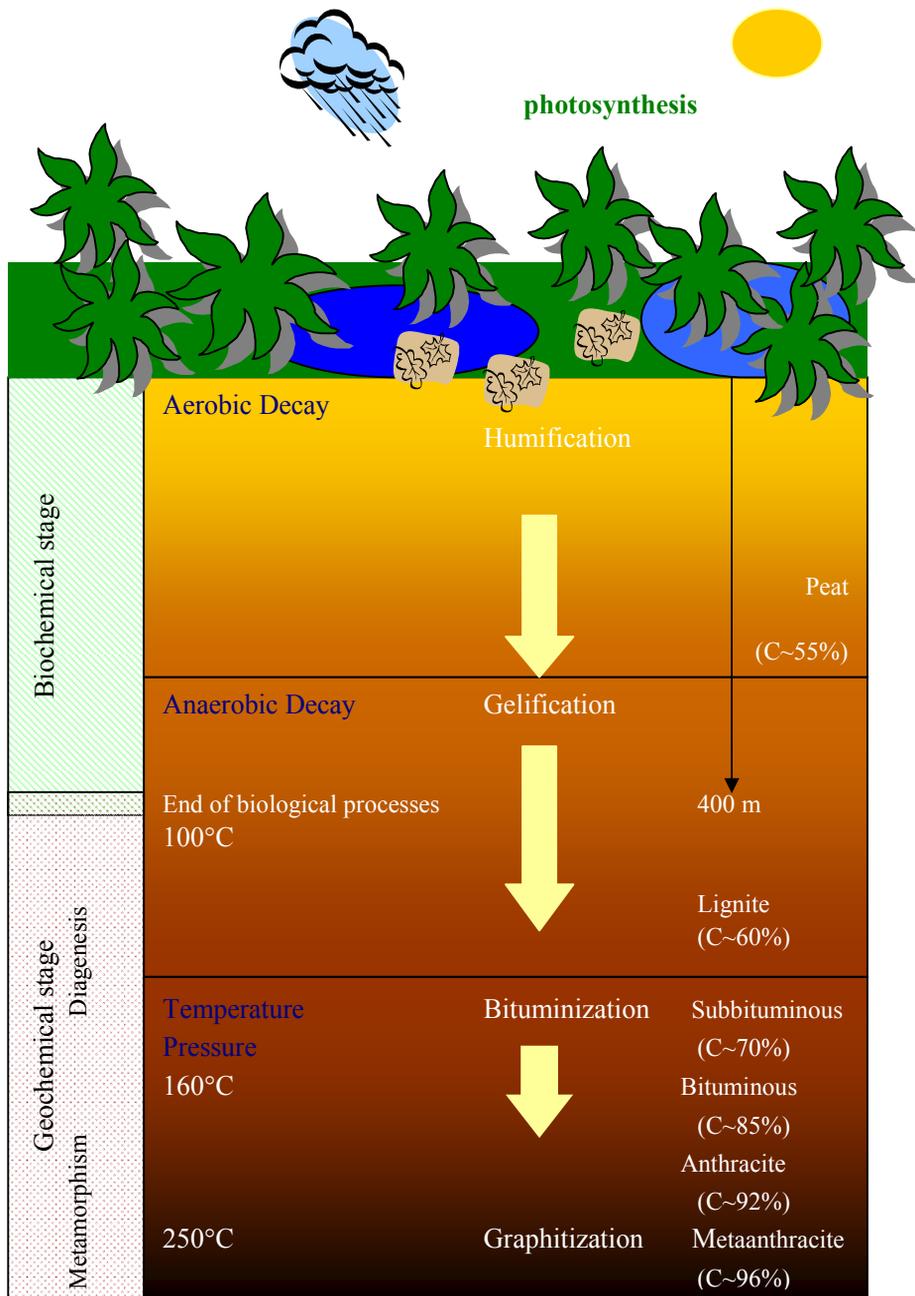


Fig. 1.1. Scheme of coal formation.

This stage is called *humification*. Afterwards the peat was buried under sedimentary accumulations and water and started to sink deeply into the earth. This stopped the aerobic decay and the anaerobic bacteria continued the decaying processes. While bacterial decay was in process, thermal processes took over for the final stage. When the peat was buried by at least 400 m of the sediment, the temperature reached 100°C, the pressure increased and the *bituminization* process began. It was followed by dehydration, the elimination of the oxygen functional groups and the increase in the carbon content [4]. The degree to which bituminization went determined the coal rank. The last stage of coalification is *graphitization*. The carbon content increased during the coalification process from 55 wt% for peat to 98 wt% for anthracite.

The coalification degree of coal can be expressed by the carbon content (C_{daf}), the volatile matter content (V_{daf}) and average random reflectance ($\overline{R_r}$).

1.1.2 Coal classification

The necessity of coal classification arose from the need of physical, chemical, petrographic and geological properties systematization. The beginning of coal classification started in the 19th century when the industrial revolution extorted the division of coal by its technological utility. The oldest parameter that had been taken into account was the appearance of the residue of the coal decomposition in the absence of air. Later the volatile matter, heat of combustion and elemental composition were considered. The coal may be classified in several ways: by rank, grain size and ash content. The most popular classification is by rank (type) that reflects the coalification degree of coal. Nowadays three kinds of tests are used.

Chemical analysis

Two kinds of chemical analysis can be distinguished. The *proximate analysis* gives the overall composition of the coal determined as moisture, volatile matter, ash, and fixed carbon content. The calorific value is often reckoned to the proximate analysis. Table 1.1 shows the proximate analysis of different solid fossil fuels.

The *ultimate (elemental) analysis* gives the amount of principal chemical elements in coal (C, H, N, S, O). Fig. 1.2 presents, as an example, the composition of Polish subbituminous coal as determined.

Table 1.1. The proximate analysis of different solid fossil fuels, wt%.

Type of fuel	Anthracite	Bituminous coal	Subbituminous coal	Lignite	Peat
Moisture	1-2	2-10	10-15	15-70	70-90
Volatile Matter	2-14	15-35	35-45	45-70	>70
Fixed carbon	75-86	50-70	30-57	25-30	
Ash	3-15	3-15	3-15	3-15	

Technological assay

The technological assay describe the behavior of the coal on heating in the absence of air. Four tests are applied: crucible swelling number determination (swelling index), dilatometer test of Audibert-Arnu, the Roga test and the Gray-King assay. For a detailed description of these tests, see Chapter 4.

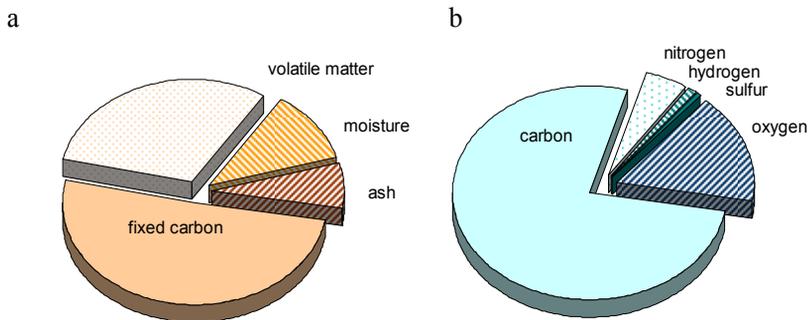


Fig. 1.2. Proximate (a) and elemental (b) analyses of subbituminous coal.

Petrographic analysis

Two tests should be mentioned: the light reflectance of the main petrographic component (vitrinite) which is the rank parameter, and the petrographic composition, as coal contains various constituents called *macerals* that are analogues to the minerals in inorganic rock. The macerals are optically homogenous organic matter in coal. We can distinguish three main groups of macerals, i.e. vitrinite, liptinite (exinite) and inertinite, which include 14 macerals. The reflectance is measured on a polished surface of vitrinite, as its reflectance changes gradually with increasing coal rank.

The standards of coal classification differentiate and depend on the country it was mined. This is due to historical aspect, as well as the complexity of the characteristics of the coal originating from different regions.

The traditional Polish classification is given in Table 1.2. The volatile matter content (V_{daf}), Roga index (RI), swelling index (SI), dilatation (b) determined by Audibert-Arnu test and the calorific value ($Q_{Gr,v,ad}$) are used to classify hard coals [5].

Table 1.2. Polish classification by rank [5].

Coal type		Classification parameters				
Name	Code	V_{daf} wt%	RI	b	SI	$Q_{gr,v,ad}$ kJ/kg
Flame coal	31.1	>28	≤5	n.s.*	n.s.	≤31000
	31.2					>31000
Gas-flame coal	32.1	>28	5-20	n.s.*	n.s.	n.s.
	32.2		20-40			
Gas coal	33	>28	40-55			
Gas-coking coal	34.1	>28	>55	No dilatation or <0	n.s.	
	34.2			≥0		
Orthocoking coal	35.1	26-31	>45	>30	>7.5	
	35.2A	20-26		>0	≤7.5	
	35.2B					
Metacoking coal	36	14-20	>45	>0	n.s.	
Semicoking coal	37.1	20-28	≥5	n.s.	n.s.	
	37.2	14-20				
Lean coal	38	14-28	<5			
Semianthracite	41	10-14	n.s.	n.s.	n.s.	
Anthracite	42	3-10				
Metaanthracite	43	<3				

*not standardized

The new coal classification by the ISO (International Organization for Standardization) standard is based on the average random reflectance ($\overline{R_r}$), vitrinite

content (vol%) and ash content (A_d). Table 1.3 presents the examples of coal classification according to the ISO standard [6]. According to the ASTM (American Society for Testing and Materials) classification, coal comes in four main types: lignite, subbituminous coal, bituminous coal and anthracite.

Table 1.3. Example of coal classification according to the ISO standard [6].

$\overline{R}_r, \%$	Vitrinite content, vol%	$A_d, \text{wt}\%$	Descriptive name
1.30	33	8.0	Medium-rank B, low-vitrinite, low ash content
2.70	95	3.0	High rank C, high-vitrinite, very low ash content
0.70	50	15.0	Medium-rank C, medium-vitrinite, medium ash content
0.38	35	25	Low rank C, medium-vitrinite, high ash content

The types can be additionally divided into groups. The classification is according to the volatile matter content (V_{daf}), fixed carbon value ($C_{fix,ad}$), the calorific value ($Q_{Gr,v,ad}$) and coal's agglomerating character. Table 1.4 shows the division of solid fossil fuels proposed by ASTM [7] and Polish standards [6]. Table 1.5 gives the short description of each type of coal, including the peat [8, 9].

Table 1.4. Division of solid fossil fuels in ASTM and Polish classifications and parameters of coalification degree.

	ASTM	Poland	$V_{daf}, \text{wt}\%$	$\overline{R}_r, \%$	
Peat	Peat	Peat	>60		
Brown coal	Lignite	Lignite	> 45	0.2 0.4	
Hard coal	Subbituminous	Hard brown coal	45-48	0.5	
		Flame coal	40-45		
	High volatile bituminous coal	Gas-flame coal	43-42	0.6	
		Gas coal	32-38		
	Medium volatile bituminous coal	Gas-coking coal	28-36	1.1	
		Orthocoking coal	22-30		
		Low volatile bituminous coal	Metacoking coal		18-23
			Semicoking coal		14-18
Lean coal	10-14				
Anthracite	Semianthracite	Semianthracite	8-18	>2.0 4.0	
	Anthracite	Anthracite	3-8		
		Metaanthracite	1-3		

In coal technology, an additional classification concerning the coal utility is used. The coal is divided into *steam* coal (coal for energy production) and *coking* coal (coal for coke manufacturing).

Table 1.5. Description of different solid fossil fuels.

Type	Picture	Description
Peat		It is considered to be a precursor of coal. It has an importance as a fuel in some regions.
Lignite		It is a crumbly and rather soft material. Its color varies from light brown to very dark brown. It is also called brown coal. It is the lowest rank of coal. Two types can be distinguished: soft brown coal and hard brown coal. It is used almost exclusively as a fuel for electric power generation.
Subbituminous coal		It is quite friable black material. It is mainly used as a fuel for electric power generation.
Bituminous coal		It is smooth coal often with well-defined bands of bright and dull material. Used mainly as a fuel and in coke manufacturing. Its characteristic property is the plasticity it undergoes under the heat treatment in the absence of air.
Anthracite		It is very hard, deeply black coal. It looks almost metallic due to its glossary surface. Nowadays is used mainly in carbon material production. Previously it was used for residential and commercial space heating.

1.2 Main components of coal

The three main analytical components that are distinguished in different types of coal are: *moisture, mineral matter and organic matter*.

1.2.1 Moisture

There are several sources of water in coal. Water is present in most mines, where groundwater circulates through coal seams. After mining, coal is often washed with water and, when stored in an open place or during transportation, is subjected to rain and snow. This type of water held on the surface of the coal particles, easy to remove by drying in air at room temperature, is called *adventitious moisture* or *surface moisture*. This moisture is lost during an attempt to bring the coal sample into equilibrium with the atmosphere in the sample preparation room. The moisture left in the coal after drying in air at ambient temperature is called *residual*, whereas the coal sample is called *air-dried*. The residual moisture data is used for the calculation of the other analytical results to *dry basis*. The moisture held within the coal itself is called *inherent moisture*. This moisture may occur in the following forms:

- *Hygroscopic moisture* - water held by capillary action within the porous structure of the coal,
- *Decomposition moisture* - water liberated during decomposition of organic compounds of the coal,
- *Mineral moisture* - water which is combined with mineral constituents of coal, such as clays and gypsum.

There are the standard methods designed to determine various types of moisture. For the determination of total moisture and residual moisture, two basic methods are designed. The first one is the gravimetric method, based on the determination of the weight loss of coal sample during heating at various temperatures and atmosphere. The second one is the volumetric method, in which the water is determined by azeotropic distillation using toluene or xylene.

In the case of the hard coal, the residual moisture is equal to the hygroscopic moisture, whereas in the case of lower rank coals the residual moisture depends strongly on the humidity of the room it is stored. The amount of moisture ranges from 2-15 wt% in bituminous coal to more than 45 wt% in lignite. A characteristic change in the hygroscopic moisture is observed for hard coals (Fig. 1.3a). The hygroscopic moisture is correlated with the porosity of coal (Fig. 1.3b). The moisture content decreases with coal rank reaching a minimum for bituminous coals. In the case of high rank coals, due to the developed ultramicroporosity, a slight increase in the moisture content is observed.

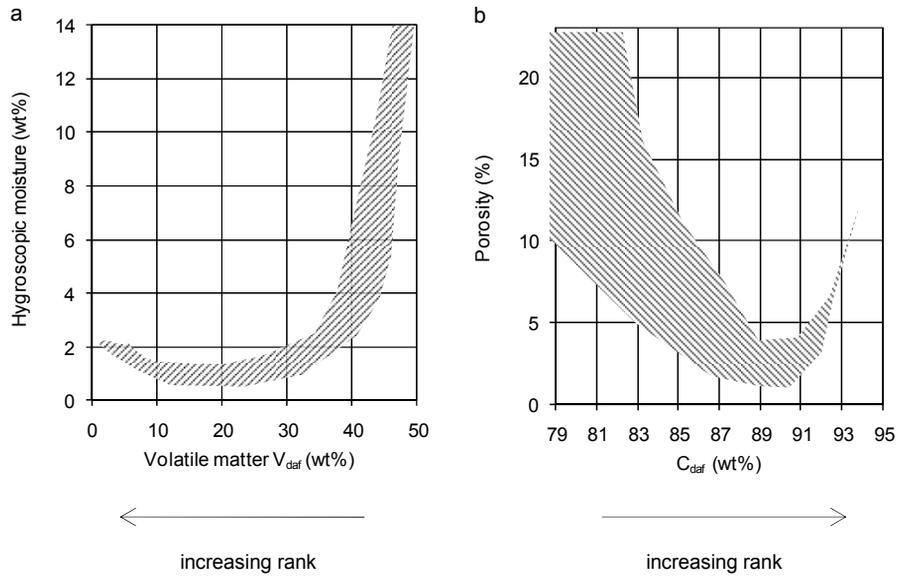


Fig. 1.3. Changes in hygroscopic moisture (a) and porosity (b) with coal rank [10].

No absolute method for determining the true moisture content in coal by heating has been devised due to the wide variance in the temperature at which different forms of moisture (including surface, inherent, chemically combined to coal) and water of minerals hydration are liberated.

Moisture is generally considered as disadvantageous as it increases the cost of transportation or trade. In combustion, high moisture content reduces the amount of heat obtained from a coal, as some of the liberated heat is used to evaporate water. In coking processes, coal with high moisture content requires more heat for the vaporization of water. This leads to longer coking cycles and lower production efficiency. Other approaches like drying and pulverizing depend on surface moisture since wet coal is very difficult to pulverize.

1.2.2 Mineral matter

The mineral matter refers to the inorganic constituents of coal that originate from coal forming vegetation and from mineral rock, sand, soil that have been transported and deposited during coalification. There are several sources of mineral matter found in coal [11-13]:

- The residues of inorganic constituents of plants from which the coal derived.
- Detrital materials (quartz, clays) which have settled into the deposit.
- Mineral deposits introduced from outside sources by erosion (both water and wind) into the decaying vegetation.

- Mineral deposits introduced into the coal seam from outside sources by percolation through cracks or fissures.
- Products of decomposition of these minerals and interactions between themselves and the coal substance.

The minerals that were introduced during coal formation are called *syngenetic*. The term *epigenetic* is used for these introduced after seam formation. Another classification of mineral matter distinguishes the *extraneous* mineral matter and the *inherent* mineral matter.

The *inherent mineral matter* is strongly associated with the coal substance and originates mainly from coal-forming vegetation. It occurs in the form of humic acid, waxen or resinous salts of calcium, magnesium, and sodium. The inherent mineral matter can be removed only by chemical methods.

The *extraneous mineral matter* (adventitious) is not associated with the coal structure and can be readily separated by the physical method, such as size reduction (Fig. 1.4.) followed by flotation and gravity methods. It mainly consists of clays, carbonates, sulfides, sulfates, silicates minerals and others.

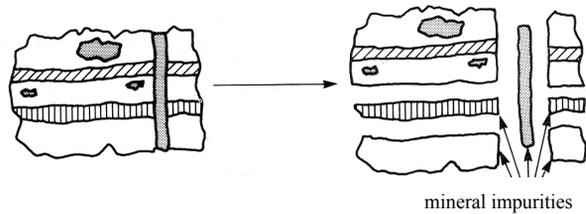


Fig. 1.4. Liberating the weakly bonded minerals by the size reduction method [14].

It is impossible to determine directly the content of mineral matter, hence it is evaluated indirectly by the determination of ash content. The mineral matter is the main source of elements that make up the ash when coal is burned. The ash content is always lower than the mineral matter content for a given coal because the minerals undergo a series of different reactions during ashing. Table 1.6 shows the main mineral groups in coal and their changes during combustion.

The mineral matter is found to be undesirable and detrimental in coal utilization. Its presence affects almost every aspect of mining, preparation, transportation and utilization.

Table 1.6. Mineral matter in coal [12,13].

Inorganic species	Minerals	Behavior on heating in air
Clay minerals (aluminosilicates)	Kaolinite	Release of H ₂ O
	Illite	$Al_2O_3 \cdot 2SiO_2 \cdot xH_2O \rightarrow Al_2O_3 \cdot 2SiO_2$
	Montmorillonite	$+xH_2O$
Carbonates	Calcite (CaCO ₃)	$CaCO_3 \rightarrow CaO + CO_2$
	Magnesite (MgCO ₃)	$CaO + SO_2 \rightarrow CaSO_3 \rightarrow CaSO_4$
	Siderite (FeCO ₃)	Decomposed with loss of CO ₂ . The
	Dolomite (CaMg(CO ₃) ₂)	calcium oxide might react with SO ₂ to form calcium sulfate
Sulfides	Pyrite (FeS ₂)	$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
	Marcasite (FeS ₂)	Burns to metal oxide and sulfur dioxide
	Sphalerite (ZnS ₂)	
Quartz	SiO ₂	SiO ₂ → SiO ₂ It is the only major minerals found in coal that is inert during burning
Chlorides	NaCl	Inorganic chlorides decompose to HCl and metallic oxide
	KCl	
	MgCl ₂	
Oxides	Rutile (TiO ₂)	Remains in ash unchanged
	Hematite (Fe ₂ O ₃)	

In combustion, the heat released from coal is reduced when highly mineral matter contaminated coal is used. It also leads to a problem of the handling and disposal of larger amounts of ash produced during combustion, clinker formation, fly ash, slagging and boiler tube corrosion.

Minerals have a remarkable effect on the yield of coking process, as well as on the structure and reactivity of produced coke. The higher ash of coal, the higher ash of coke. An enhanced ash content in coke results in a reduction in mechanical strength.

On the positive side, ash can be utilized as a construction material and be a source of refractories. Additionally some mineral might play a role of catalysts in gasification or liquefaction.

Coals with high mineral matter content need to be cleaned. The cleaning processes can improve the economics of most coal-utilization processes. The method used for improving the quality of coal depends on the concentration and composition of mineral matter. Coal is generally cleaned through physical separation. Physical separation is a process of sorting based on the differences in density between organic coal and associated minerals, or the differences between their surface properties.

1.2.3 Organic matter

The coal organic matter is mainly composed of C, H, N, S and O. The elemental composition of organic matter changes characteristically with the increasing rank of coal. The content of C, H, N and S is determined directly using an elemental analyzer. The oxygen content is usually calculated from the difference assuming that the sum of the content of these five elements is 100%. Other parameters that are used to characterize the organic matter are the volatile matter and fixed carbon value calculated to a proper base. Fig. 1.5 shows the relationship of the different analytical bases to various coal components [8].

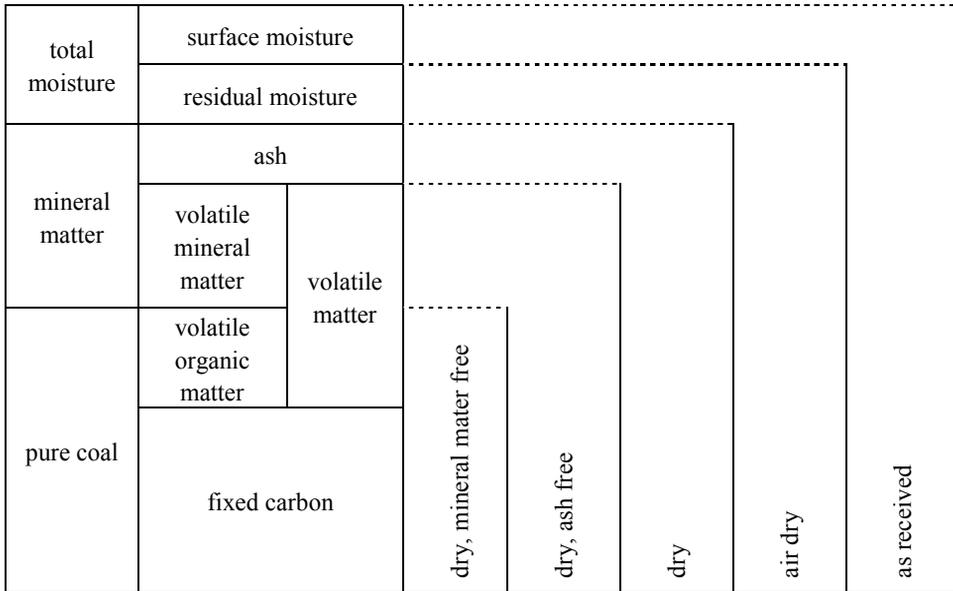


Fig. 1.5. Relationship of different analytical bases to various coal components.

1.2.3.1 Volatile matter

The term *volatile matter* in coal represents the components of coal's decomposition (except for moisture) which are liberated at high temperature in the absence of air. This is usually a mixture of short chain hydrocarbons, aromatic hydrocarbons and H₂S, NH₃, CO, CO₂, H₂, HCl etc. For the different rank of coal, the composition of volatile matter evolved varies significantly. The volatile matter of coal is determined under rigidly controlled conditions according to standards. However there are various national standards that differ in temperature (850-1050 °C), duration of heating (3-20 minutes) or the material the crucible is made of [11]. The volatile matter content is the main parameter of coal classification which is why

attention must be paid on the standard method used. The content of volatile matter for different rank coals is given in Table 1.1.

The mineral matter may also contribute to the volatile matter due to the loss of water from the clay, CO₂ from carbonate minerals, H₂S from pyrite, or HCl from chloride minerals and other various reactions that may occur within the minerals [14]. Therefore, the volatile matter is expressed on *dry ash free basis*.

The yield of volatile matter is used not only as a classification parameter. It can also be an indicator of the amount of smoke released during coal burning. The residue after the volatile matter determination will give some information about the coking properties. If the coal has the coking property, the received residue will be sintered. Otherwise, the residue will be a powder.

1.2.3.2 Fixed carbon

Fixed carbon is defined as a part of coal that remains after the moisture, ash and volatile matter contents are subtracted. It is the measure of the solid combustible material remaining after the volatile matter in coal has been removed. The value of fixed carbon together with ash is used as an indicator of the yield of coke production, whereas the fixed carbon calculated to dry, mineral-matter-free basis is used as the parameter in coal classification by the ASTM standard [7].

1.3 Laboratory work: proximate analysis

The aim of the laboratory work is to perform the proximate analysis of a given coal. The analysis consists of the determination of moisture, ash and volatile matter and the calculation of fixed carbon value. The determinations will be carried out according to the PN-ISO standards [15-20].

The coal sample used for the proximate analysis is grounded to pass a sieve of 0.2 mm aperture. The sample should remain in moisture equilibrium with the laboratory atmosphere.

Moisture determination

The 1 ± 0.1 g of coal sample is heated at 105-110 °C in an electric oven. The percentage mass fraction of moisture (M_{ad}) is calculated from the loss of the weight in the test portion according to the equation given below:

$$M_{ad} = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \quad (1.1)$$

where,

m_1 - the mass of the empty vessel and the lid, g

m_2 - the mass of the vessel and lid with the sample, g

m_3 - the mass of the vessel and lid with the sample after drying, g

Ash determination

The 1 ± 0.1 g of coal sample is heated at a specific rate up to a temperature of 815 ± 10 °C in air atmosphere, in a muffle furnace, until the mass becomes constant. The ash (A_{ad}) is calculated based on the mass of the residue after incineration according to the equation given below:

$$A_{ad} = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \quad (1.2)$$

where,

m_1 - the mass of the empty dish, g

m_2 - the mass of the dish with the sample, g

m_3 - the mass of the dish with the ash, g

Volatile matter determination

The 1 ± 0.1 g of coal sample is heated out of contact with air at 900 °C for 7 min in a muffle furnace. The percentage mass fraction of volatile matter (V_{ad}) is calculated from the loss in the weight of the test portion after deducting the loss of mass due to moisture according to the equation given below:

$$V_{ad} = \frac{100 \times (m_2 - m_3)}{m_2 - m_1} - M_{ad} \quad (1.3)$$

where,

m_1 - the mass of the empty crucible and the lid, g

m_2 - the mass of the crucible and the lid with the sample, g

m_3 - the mass of the crucible and the lid and the residue after heating, g

M_{ad} - the moisture in the air-dried coal sample, wt%

The final result, expressed as a percentage by mass, is calculated to the dry, ash free basis according to the equation below:

$$V_{daf} = V_{ad} \times \frac{100}{100 - (M_{ad} + A_{ad})} \quad (1.4)$$

where,

M_{ad} - the moisture in the air-dried coal sample, wt%

A_{ad} - the ash of the air-dried coal sample, wt%

Fixed carbon calculation

The fixed carbon ($C_{fix,ad}$), expressed as a percentage by mass, calculated to the air-dry basis is given by the following equation:

$$C_{fix,ad} = 100 - (M_{ad} + A_{ad} + V_{ad}) \quad (1.5)$$

where,

M_{ad} - the moisture in the air-dried coal sample, wt%

A_{ad} - the ash of the air-dried coal sample, wt%

V_{ad} - the volatile matter of the air-dried coal sample, wt%

References

- [1] The Oxford handbook of engineering and technology in classical world, ed. J.P. Oleson, Oxford University Press, Oxford 2008.
- [2] Science and civilisation in China, ed. J. Needham, Cambridge University Press, Cambridge 1999.
- [3] Read T.T., The earliest industrial use of coal, vol. 20, Transaction of Newcomen Society, 1939.
- [4] Taylor G.H., Teichmüller M., Davis A., Diessel C.F.K., Littke R., Robert. P., Organic petrology, Gebrüder Borntraeger, Berlin 1998.
- [5] PN-82-G-97002: 1982. Types of hard coal.
- [6] PN-ISO 11760: 2007. Coal classification.
- [7] ASTM D 388:2007. Classification of coals by rank.
- [8] Van Krevelen D.W., Coal: Typology - physics - chemistry – constitution, Elsevier; Amsterdam 1993.
- [9] Roga B., Tomków K., Chemiczna technologia węgla, WNT, Warszawa 1971.
- [10] Węgiel kamienny, ed. Czaplinski A., Wydawnictwo AGH, Kraków 1994.
- [11] Speight J.G., Handbook of coal analysis, Wiley-Interscience, New Jersey 2005.
- [12] Analytical methods for coal and coal products, ed. C. Karr, Jr., vol. II, Academic Press, London 1978.
- [13] Chemia i fizyka węgla, ed. S. Jasieńko, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 1995.
- [14] Couch G. R., Advanced coal cleaning technology, IEA Coal Research, UK, London 1991.
- [15] ISO/FDIS 17246: 2010. Coal-Proximate analysis.
- [16] ISO 589: 2007. Hard coal-Determination of total moisture.

- [17] PN-80/G-04511:1990. Solid fuels-Determination of moisture.
- [18] ISO 1171:2010. Solid minerals fuels-Determination of ash.
- [19] ISO 562:2010. Hard coal and coke-Determination of volatile matter.
- [20] ISO/Wd 1170:2004. Coal and coke-Calculation of analyses to different bases.

2 Calorific value of solid fuels

Piotr Rutkowski

2.1 Introduction

The development of new technologies and the increase in the world's population followed by the need to raise the standard of living increases energy consumption, and thus fuel sources. This, together with the need to reduce greenhouse gas emissions into the atmosphere, forces the rational management of fuels. Various sources of energy are used for heat and power generation, including fossil fuels, biomass, solar energy, wind energy and hydro energy.

Coal is the most important solid fuel that may be utilized in different ways depending on its type. The most significant uses of coal are electricity generation, steel production and cement manufacturing. Coal is one of the world's most important primary energy sources. It plays a crucial role in electricity generation worldwide. Statistically, coal-fired power plants currently fuel 41% of global electricity. In many countries, including Poland, coal is the dominant fuel used in electricity generation (see the list below). Moreover, it is expected that coal will play a dominant role in electricity generation worldwide, reaching 44% of global electricity in 2030 [1].

Coal in electricity generation in selected countries [2]:

South Africa 93 %	Poland 92 %	PR China 79 %
Australia 77 %	Kazakhstan 70 %	India 69 %
Israel 63 %	Czech Rep 60 %	Morocco 55 %
Greece 52 %	USA 49 %	Germany 46 %

Different types of biomass (including wood, straw, landfill wastes, organic wastes) can be used for heating, electricity production and for transportation in the form of biofuels (biodiesel, bioalcohol). Nowadays, biomass, one of the renewable energy sources, plays an important role in heat and electricity production globally. Biomass accounts for ~15% of the primary energy consumption in the world and for around half (44 to 65%) of all renewable energy used in the European Union [3], Fig. 2.1.

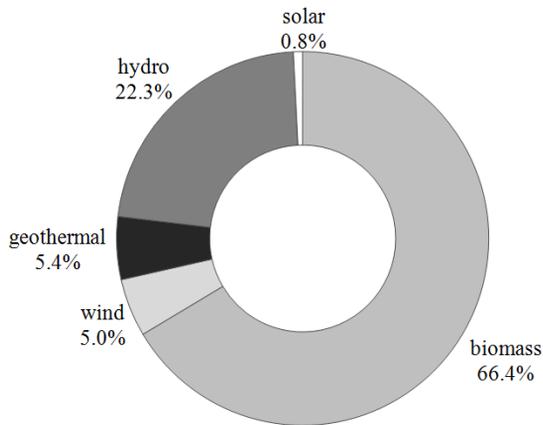


Fig. 2.1. The share of renewable energy in primary energy production in the EU.

In 2008, renewable energy supplied 10.3% of the gross final energy consumption in all of the 27 European Union countries. [4]. About 98 Mtoe of primary biomass was consumed in Europe in 2007 [5]. Much of this energy (61 Mtoe) is related to heat production, both for households and industrial processes. Therefore, the contribution of biomass to electricity production is much smaller.

2.2 Solid fuels

Fuel can be shortly described as an energy carrier intended for energy conversion. Depending on the origin, physical state and thermal properties of fuels, the different conversion methods for heat and power production can be applied. Taking into account the thermochemical processes, fuels are mostly converted by combustion for usable energy production.

Due to the differences in nature, origin or physical state of fuels, a more detailed classification can be made. Combustible fuels can be divided into three groups due to their physical state (Fig. 2.2), i.e. solid, liquid and gaseous fuels. Because of the way of receiving the fuels, they are divided into natural (primary) and synthetic (secondary) ones. The natural solid fuels group includes wood, peat, lignite, coal and anthracite. The group of synthetic solid fuels includes products of fuel processing, i.e. semi-coke, coke and charcoal.

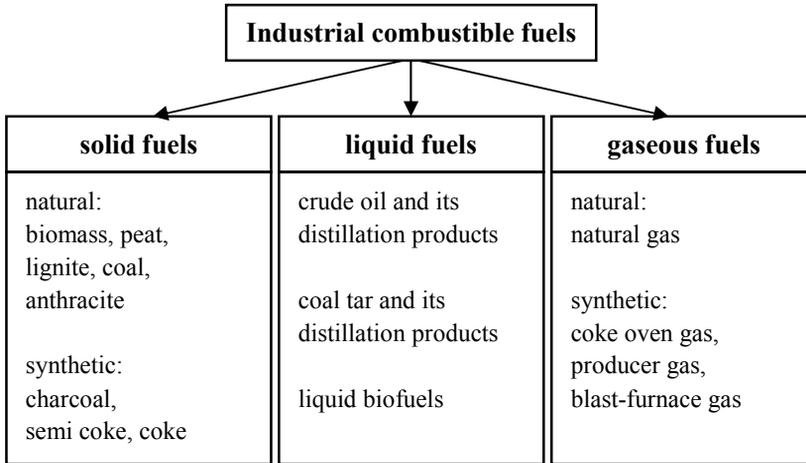


Fig. 2.2. Combustible fuels divided due to their physical state [1].

Combustible fuels can also be classified as renewable or non-renewable ones. Renewable fuels are those derived from biomass produced by the conversion of solar energy into chemical energy (energy of chemical bonds). Non-renewable fuels are those derived from fossil sources (coal, oil, natural gas).

Coal

Fossil fuels comprise of three main groups, i.e. coal, petroleum and natural gas. These fuels provide most of the energy consumed in the world for producing heat and electricity. For the combustion process, coal is the most important.

Coal can be described as a sedimentary rock of organic origin. It is the energy carrier formed by transformations of living matter by biochemical activity such as aerobic and anaerobic processes, and geological activity, such as temperature and pressure over a long period of time. As defined by IUPAC, coalification is a geological process of the formation of materials by increasing the content of the element carbon from organic materials that occurs in the first, biological stage into peats, followed by a gradual transformation into coal by action of moderate temperature (up to around 250 °C) and high pressure in a geochemical stage. Coalification is a dehydrogenation process with a reaction rate slower by many orders of magnitude than that of carbonization [6].

The utilization fields of coal depending on its properties are given in Fig. 2.3.

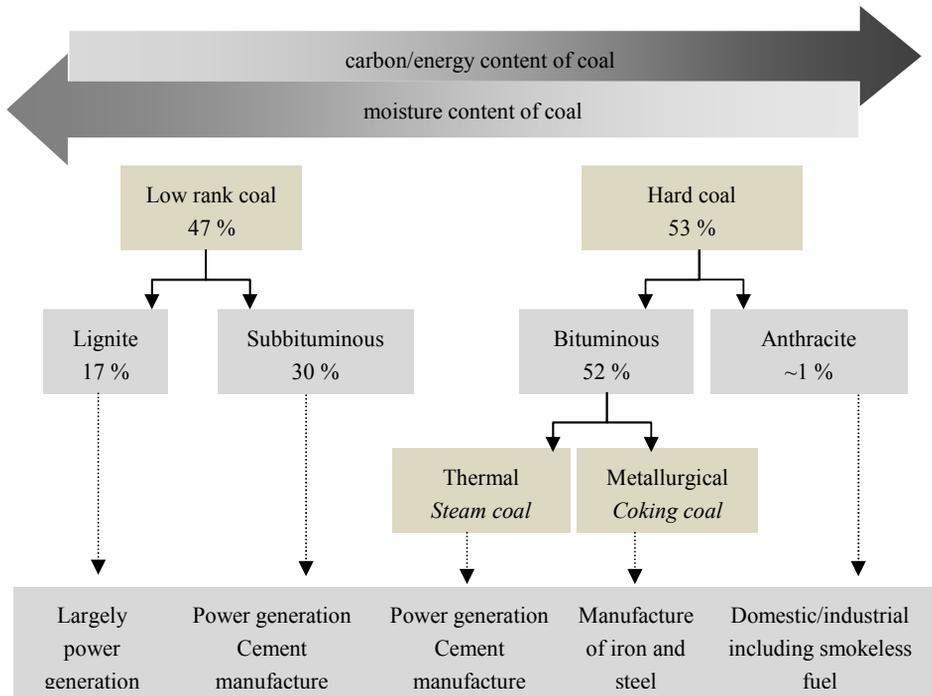


Fig. 2.3. Types of coal and their potential way of utilization [1].

Biomass

Biomass is one of the renewable energy sources. By definition, we can assume that this is a specific quantity of organic matter produced by living organisms, both plants and animals [7]. If biomass is used as an energy resource, it can be defined as a biofuel. The term *biomass* refers to all living organisms.

Biomass fuels are produced by the photosynthetic conversion of sunlight into plant matter as presented in Fig. 2.4. These may be used directly as fuels or converted into more usable forms such as gas (biogas), liquid (alcohols, biodiesel) and solid (char) fuels [8]. There are several types of biomass used for energy purposes including wood, straw, animal wastes, sewage sludge and municipal waste.

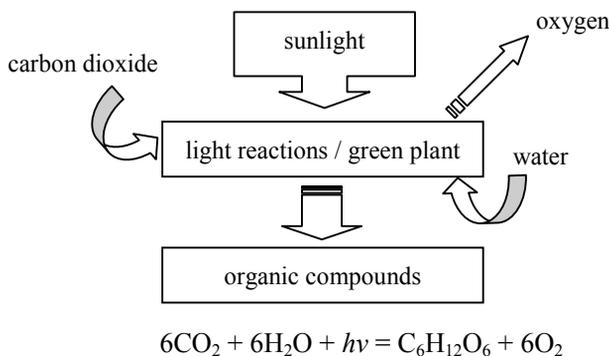


Fig. 2.4. General scheme of photosynthesis.

The advantage of biomass utilization for energy purposes is a closed carbon cycle. In fact, the process of fuel combustion is the opposite to photosynthesis. Carbon dioxide produced by combustion of biomass or biofuel is re-assimilated by plants in their growth phase through the process of photosynthesis, which makes the theoretical total CO_2 balance equal zero. The EU Commission's recent report on the sustainability of biomass concluded that the most common types of biomass energy applications reduce CO_2 emissions from 55 to 98% compared to fossil fuels [3].

2.3 Composition of solid fuels

Solid fossil fuels and biomass are composed of three major components, i.e. organic matter, mineral matter and water. They are linked both physically and chemically. The type and amount of individual components of the fuel determines its properties and suitability for processes including combustion. The chemical composition of fuels is defined by their ultimate and proximate analysis. The ultimate analysis includes the quantitative determination of carbon, hydrogen, nitrogen, sulfur, and oxygen. The determination of moisture (M), volatile matter (V), ash (A) and fixed carbon (FC) belongs to the proximate analysis of fuel. The proximate analysis of biomass and coal is described in detail in Chapter I. The knowledge about the elemental composition of fuels is important because of the possibility of estimation of technological parameters, such as calorific value and the yield of coking products. The comparison of basic properties of biomass, coal and industrial-domestic coke is given in Table 2.1 and Fig. 2.5.

Table 2.1. Comparison of example properties of natural solid fuels [9,10].

	Straw	Wood	Peat	Lignite	Coal	Anthracite	Coke*
M_{ad} , wt%	15	30	70-90	15-70	2-18	1-2	-
A_{ad} , wt%	3	1	2-10	3-15	3-10	4-15	max. 12
V_{daf} , wt%	83	85	>70	45-70	15-45	2-14	max. 2.5
$Q_{Gr,v,ad}$, MJ/kg	12-15	10-15	12	20	25	20-28	min. 29

*values may vary depending on the characteristics of coal and the coking process parameters

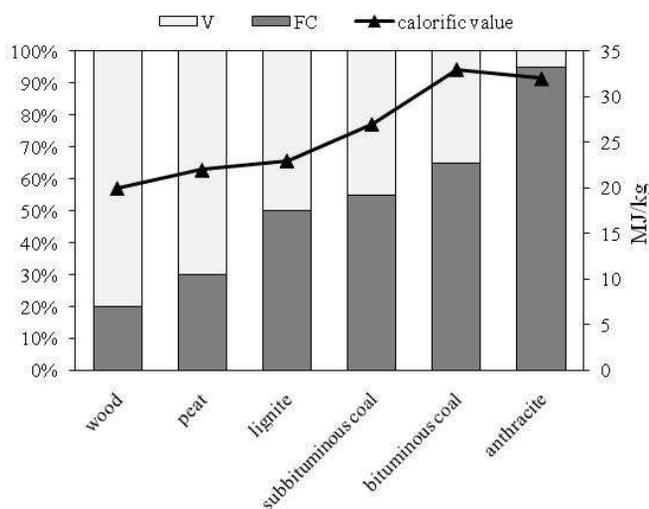


Fig. 2.5. Typical fixed carbon (FC), volatile matter (V) and calorific value for wood, peat and coal on a moisture and ash free basis [11].

Taking into account the elemental composition of organic matter, fossil fuels and biomass are composed primarily of carbon, hydrogen and oxygen accompanied by nitrogen and sulfur.

Only trace amounts of other elements, e.g. chlorine and phosphorus, are present in fuels. Shares of individual elements, i.e. carbon, hydrogen and oxygen in solid fuels are different and depend on the type of fuel and its coalification degree, as shown in Fig. 2.6. With the increase of fuel coalification degree, the carbon content increases steadily from 49% in biomass to the extreme value of 95% in anthracite. Simultaneously in these fuels, the hydrogen decreases from about 6.0% to about 2.0%. Similarly, oxygen content clearly decreases.

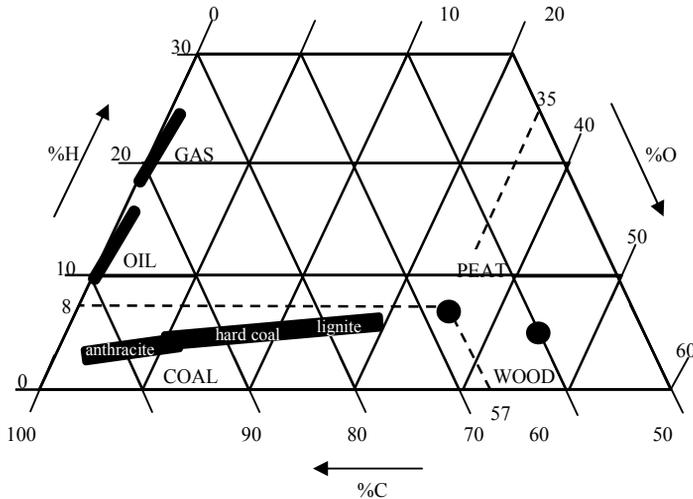


Fig. 2.6. Coalification degree in relation to the chemical composition [12].

2.3.1 Coal

Depending on the degree of coalification, solid fossil fuels can be divided into the following groups: peat, lignite (brown coal), hard coals (subbituminous and bituminous) and anthracite. Fuels are characterized by different elemental composition accompanied by different chemical structure in relation to the maturation stage, as presented in Table 2.2 and Fig. 2.7.

Table 2.2. Ultimate analysis of solid fossil fuels [13].

Fossil fuel	C	H	O	N	S	P
Peat	~ 59	~ 5.4	~ 33	3.3		
Brown coal	~ 70	~ 5.4	~ 23	1.0		
Hard coal	~ 80	4.7	~ 17			
Flame coal						
Gas-flame coal		↓	↑	~ 1.5	~ 1	< 0.3
Gas coal		↑ 5.4				
Gas-coking coal	85					
Orthocoking coal		4.7				
Metacoking coal	89					
Semicoking coal						
Lean coal						
Semianthracite						
Anthracite	↓ ~ 92	~ 3	~ 2			

The higher degree of coalification, the higher carbon content and the lower oxygen content is observed. Peat, which is characterized by the lowest carbon content, is

converted into brown coal (lignite). During the next millions of years, the temperature and pressure leads to further changes of organic matrix transforming it into hard coals with higher carbon content, followed by a decrease in the oxygen content.

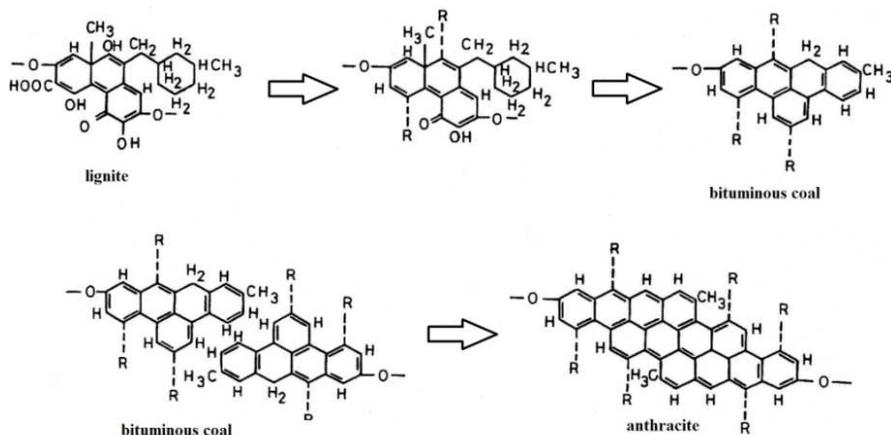


Fig. 2.7. The change of the chemical structure of coal in relation to the degree of coalification [10].

Finally, the progressive increase of coal maturation results in the anthracite formation. The fuel characterized by the highest carbon content and the lowest hydrogen and oxygen content is formed.

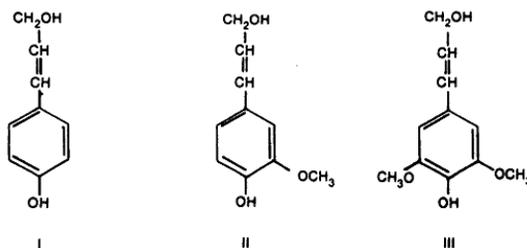
2.3.2 Biomass

In terms of biomass structural components, in most cases we can distinguish the following three groups: cellulose, hemicellulose and lignin (Table 2.3).

Table 2.3. The contents of cellulose, hemicellulose and lignin in common agricultural residues [14].

Lignocellulosic material	Cellulose, wt%	Hemicellulose, wt%	Lignin, wt%
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Nut shells	25-30	25-30	30-40

alcohols and phenolic compounds such as *p*-coumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III). The irregular structure of lignin is cross-linked by the chemical bonds such as ether, ester and methylene bridges.



2.4 Calorimetry

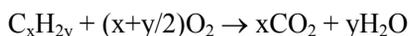
Calorimetry is the science dealing with the measurement of the amount of heat. The term is derived from the Latin *calor* meaning *heat*, and the Greek *metry* meaning *to measure*. It can be argued that any process that results in release or absorption of heat (in other words: the heat exchange with the environment during the process) may be the subject of a calorimetric study. The purpose of each calorimetric measurement is to measure the thermal effect accompanying the physical process and/or the chemical reaction. The relationship between the heat of transformation and the thermodynamic functions that characterizing it is very close. Therefore, such measurements are important in physical chemistry. Although calorimetry is a field which has a variety of applications, we are to concentrate on the measurements of the heat of reaction. This is also extremely important from a practical point of view, e.g. when the calorific value of fuel is evaluated.

The First Law of Thermodynamics says that energy under normal conditions cannot be created or destroyed, but simply transformed from one type of energy to another one. Therefore, during the thermal conversion of biomass or fossil fuel, chemical energy is transformed into new chemical energy (chemical bonds in products) and thermal energy. The latter one can be converted into mechanical energy or other usable forms.

2.4.1 Heat of combustion

Combustion is a chemical reaction involving the oxidation of the substance combined with the thermal effect and often accompanied by flame or glowing. Different types of combustion can be distinguished, depending on the reaction occurring and the products formed. Mostly, we can write about complete and incomplete combustion. In complete combustion, only heat and simple products are

formed, such as CO₂, H₂O, NO_x, and SO_x. General reaction characteristic for the complete combustion of hydrocarbon fuel is:



Taking into account the stoichiometry of reaction, the incomplete combustion of substance takes place when there is not enough oxygen to react completely. Hence, the reaction is inefficient and produces both the products that would be formed in complete combustion and other products, i.e. carbon monoxide and carbon.

If *heat of combustion* is considered as a term in the physical chemistry field, it is defined as the amount of energy in the form of the heat evolved when a unit amount/weight/volume of the substance is completely burnt in oxygen under standard conditions. It can be described as ΔH_c^0 and may be expressed in different units, i.e. J/mol, J/g and J/cm³.

In practice, the synonymous terms, i.e. *heat of combustion* or *calorific value* or *heating value*, correspond to the amount of the heat released during the complete combustion of fuel. Additionally, it is also assumed that gaseous products are cooled down to the starting temperature of fuel. Solid fuels contain moisture. Therefore, it should be noted that the calorific value may be expressed in two different ways on account of the moisture in the fuel, i.e. *gross calorific value* (formerly higher heating value) and *net calorific value* (formerly lower heating value). The gross calorific value of fuel is the amount of heat released during the complete combustion of solid fuel in a bomb calorimeter in the oxygen atmosphere related to the temperature of 25 °C per mass unit of fuel. When fuel is combusted, the moisture evaporates taking away some heat of combustion which is not available for use. Net calorific value is the heat of combustion calculated from the gross calorific value by subtracting the heat of the vaporization of water that is contained in the fuel and formed during combustion. In this case any water is treated as vapor.

From the practical point of view, fuels should be compared based on the net calorific value. It is related to the fact that the differences in hydrogen content or moisture content can be relatively high. In some cases the difference between the gross calorific value and net calorific value can reach even 50%.

2.4.2 Bomb calorimeter

Calorimeter is a device for the measurement of the heat of a physical process or chemical reaction. There is a variety of calorimeter types and measurement basis and each is adapted to its destination. The most important types of calorimeters are: adiabatic, non-adiabatic, isothermal and non-isothermal depending on the exchange of the heat of reaction and temperature changes during the combustion. Depending

on the type of test substances and processes, calorimeters are classified as: the calorimetric bomb, the Junkers calorimeter and the reaction calorimeter.

In this laboratory textbook we are concerned with the oxygen bomb calorimeter (calorimetric bomb) of constant volume, which is the standard instrument for measuring the calorific value of solid combustible fuels, e.g. coal and biomass. The bomb calorimeter provides the most suitable and accurate apparatus for the determination of the calorific value of solid and liquid fuels [16]. In general, a calorimetric measurement of calorific value includes three stages i.e. enclosing the sample in a calorimeter, initiation of the reaction, and measurement of the temperature changes observed during the reaction. The combustion of fuel takes place in the explosive-proof steel container that is submerged in water that absorbs the heat of combustion. It is assumed that the heat transfer from the calorimeter and water is complete and no corrections of heat evolved during the combustion are necessary. Nevertheless, corrections due to the heat of formation of nitric and sulfuric acids must be determined.

The heat of combustion measured under constant volume (Q_v) is described by the following general equation:

$$Q_v = C \times \Delta T, \quad (2.1)$$

where C is the calorimeter constant, ΔT is the increase of temperature. During fuel combustion, the temperature changes versus time are monitored and may be plotted as presented in Fig 2.8.

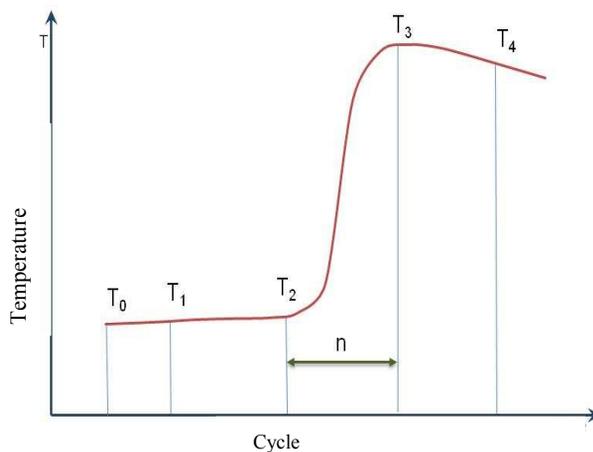


Fig. 2.8. Graphic representation of temperature changes during a measurement in the calorimetric bomb.

The measurement cycle includes the following stages:

- Turning on the calorimeter (T_0) and stabilizing the temperature inside.
- The preliminary interval - registration of temperature T_1 and a time segment metering before initiating the reaction.
- The main time interval - registration of T_2 and the ignition temperature of the sample in a bomb calorimeter.
- The final interval – registration of temperature T_3 (maximum temperature read).
- Registration of temperature T_4 and the end of the measurement.

Before the calculation of the calorific value of fuel, there is a need to know the heat capacity of the calorimeter (calorimeter constant). The heat capacity is the amount of heat needed to raise the temperature of the entire calorimeter by 1 °C. This can be determined by the measurement of the calibration substance, e.g. benzoic acid.

2.5 Thermal properties of biomass and coal

Solid fuels, including biomass and fossil fuels, are designed for industrial and economical processes of the chemical energy conversion for heat and power production. Taking into account the thermal properties, fuels are materials that produce high amounts of heat on the mass unit during the combustion process. Moreover, the mixture of gases that is a product of the fuels oxidation process, may be used as a heat source. Finally, fuel should be a readily available material that is characterized by the properties allowing for an easy, efficient and economical combustion [17].

Solid fuels should have suitable thermal properties, which define the usefulness of these materials for the utilization in heat and electricity production processes. The calorific value of fuel is one of the most important parameters that influences the economics of the power plant operation. It gives the information on the amount of energy released in the form of heat while the fuel is combusted. Also, the calorific value of fuel provides information on the amount of fuel needed to produce a unit of heat or electricity. Although a higher calorific value increases the price of the fuel, the costs of logistics and storage are reduced.

The calorific value of fuel is a basic parameter to assess the suitability of fuel for energy purposes. It is the heat liberated by its complete combustion with oxygen. The calorific value of solid fuel is mostly influenced by carbon and hydrogen contents. Other elements present in the fuel, such as sulfur and nitrogen, can also contribute a little to the changes in the calorific value. The calorific value is a complex function of the elemental composition of the fuel as given in Fig. 2.9.

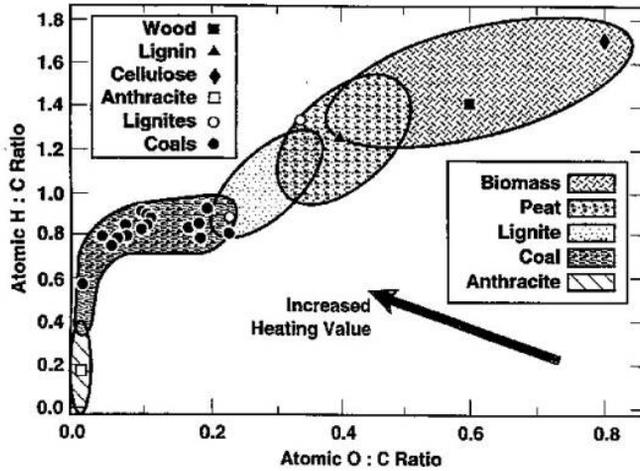


Fig. 2.9. Solid fuels and their chemical composition [18].

Coal

The calorific value of different rank coals is strictly related to the coalification degree followed by the elemental composition of the fuel. Hydrogen is the element characterized by the highest heat of combustion and carbon is an element found in the largest percentage of solid fuels. The role of oxygen is opposite to hydrogen and carbon, i.e. it decreases the calorific value of fuel. Changes in the calorific value of hard coals with coal rank described by volatile matter, as shown in Fig. 2.10a. The relationship between the hydrogen and oxygen contents and the volatile matter content in coal is given in Fig. 2.10b.

As can be seen in Fig. 2.10, the coals which are characterized by volatile matter content of around 20 wt% show the highest heat of combustion. Hard coals with lower and higher content of volatile matter are characterized by a lower calorific value. This observation can be explained by the differences in the chemical composition of coals of different rank. Low rank coals show a relatively low carbon content and high hydrogen and oxygen contents. Medium rank coals show similar hydrogen content but higher carbon content and lower oxygen content compared to low rank coals. This is the reason of the highest calorific value for these coals. A further increase of the coalification degree leads to the lowering of calorific value due to a large decrease of hydrogen content. The increase of carbon content and the decrease of oxygen content do not compensate for this drop of the calorific value.

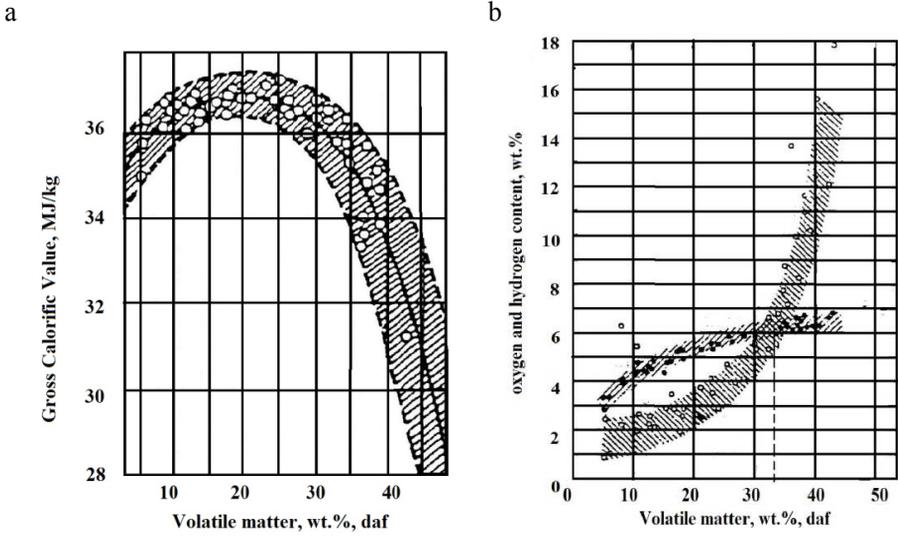


Fig. 2.10. Changes in calorific value (a) and hydrogen and oxygen contents (b) as a function of coal rank [19].

Biomass

The energy value of various types of biomass depends on the chemical and physical properties of the biomass components [20]. The main characteristics of biomass, relevant to the process of using it as an energy source, are: the moisture content, the calorific value, the volatile matter and fixed carbon content, the content and composition of ash, the alkali content and the ratio of cellulose/lignin [6]. Fig. 2.11 shows how moisture and ash affect the calorific value of biomass.

The decision on the form of biomass can be utilized for energy purposes is made based on several factors, including the most important ones which are: the ratio of energy contained in biomass into energy needed for its cultivation and acquisition, the ability to collect solar energy and conversion efficiency of liquid and gaseous fuels, and namely the flexibility to use it as an energy source. Hence, the ideal energy crop characteristics are: high efficiency (the maximum production of dry matter per hectare), low energy investment in production, low cost, minimum contamination and low nutrient requirements [21].

The calorific value of fuels is dependent not only on its chemical composition but also on its proximate properties, i.e. ash and moisture contents. For example, the increases of both the moisture content and the ash content in biomass leads to the lowering the calorific value [22,23], as given in Fig. 2.11.

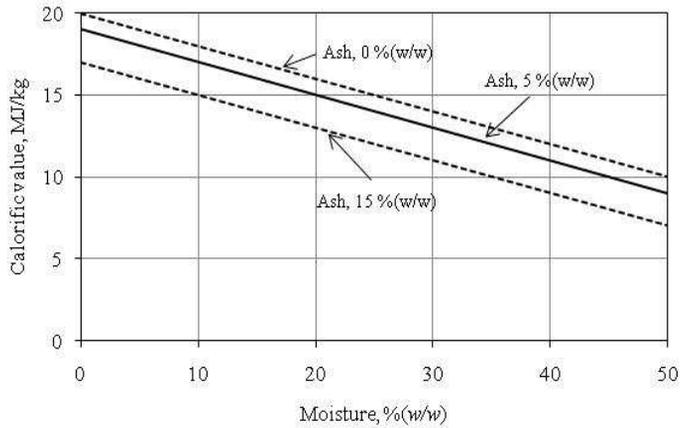


Fig. 2.11. Calorific value of biomass in relation to moisture and ash content [24].

2.6 Classification of steam coals

Classification by rank

Hard coals can be divided into steam coals and coking coals. Steam coals are used mainly for energy production in the combustion process. As far as the coal rank is concerned, different rank coals can be classified as steam coals.

Low rank coals are the most important fuel for heat and electricity production worldwide including:

- Flame coal
- Gas-flame coal
- Gas coal

The second group of coals used for energy purposes is represented by high rank coals, including:

- Lean coal
- Semi-anthracite
- Anthracite

Classification by class

Taking into account other parameters, the characteristics for coal, i.e. calorific value, ash content and sulfur content, coals can be grouped into different classes. Each class of coal is described by three numbers as in the example given below:

Example: numbers 25/08/04 describe a coal characterized by a calorific value of at least 25 MJ/kg, ash content higher than 8% and sulfur content equal to or lower than 0.4%.

Classification by grade

Depending on the size of the coal grain, different grade classes of coal can be distinguished, i.e. nut coal, pea coal and fine coal. As an example, the description of coal being explored in the Polish mine “Bogdanka” and its characteristics are given below.

Coal type: gas-flame (32.2); *Coal grade:* pea coal; *Class:* 27/07/12:

- calorific value > 27 MJ/kg
- ash content < 7 wt%
- sulfur content < 1.2 wt%
- grain size 16.5-31.5 mm
- total moisture < 8.5 wt%

2.7 Laboratory work: determination of calorific value

The purpose of the laboratory work is to determine the calorimeter constant and the calorific value of solid fuel. Calorimetric measurement consists of two independent experiments carried out under specified conditions. The first measurement is the burning of the calibration substance (benzoic acid) followed by the determination of all corrections required for the proper calculation of the calorimeter’s constant (C) according to the following equation:

$$C = \frac{Q_{BA} \times m_{BA} + c_1 + c_N}{D_t - k} \quad (2.2)$$

where Q_{BA} is calorific value of benzoic acid, m_{BA} is the mass of benzoic acid, c_1 is the correction for heat evolved due to the combustion of wire [J], c_N is the correction for heat of formation of nitric(V) acid [J], D_t is the overall temperature rise, k is the correction for the calorimeter heat exchange with environment [°C].

The second measurement consists in the combustion of fuel (biomass, coal, coke) followed by the determination of all corrections required for the proper calculation. Gross calorific value ($Q_{Gr,v,ad}$) and net calorific value ($Q_{Net,v,ad}$) of air-dried sample measured under constant volume should be calculated according to the following equations:

$$Q_{Gr,v,ad} = \frac{C \times (D_t - k) - c}{m} \quad (2.3)$$

$$Q_{Net,v,ad} = Q_{Gr,v,ad} - 24.42 \times (M_{ad} + 8.94 \times H_{ad}) \quad (2.4)$$

where c is the sum of corrections due to additional thermal effects [J], m is mass of sample [g], 24.42 is the heat of the vaporization of water at 25 °C related to 1% of the water in fuel [J/g], 8.94 is the conversion factor for the calculation of water from hydrogen content, H_{ad} is the hydrogen content in fuel (air dried basis), wt%, M_{ad} is the moisture content in air dried fuel, wt%.

The determination of the calorific value of fuel by the calorimetric method is performed according to the ISO 1928:2009 standard [25]. The standard specifies a method for the determination of the gross calorific value of a solid mineral fuel at constant volume and at the reference temperature of 25 °C in a bomb calorimeter calibrated by combustion of certified benzoic acid. It involves measuring the exact amount of heat generated during the combustion of a known amount of fuel in a calorimetric bomb in oxygen, under pressure, when the products are cooled down to room temperature. The procedure allows for further calculations of net calorific value of fuel and all related corrections. The detailed procedure of the laboratory work is given in the lab instruction.

References

- [1] The coal resource: A comprehensive overview of coal. World Coal Institute, London 2009.
- [2] Mills S.J., Prospects for coal, CCTs and CCS in the European Union. London: IEA Clean Coal, London 2010.
- [3] European Commission, Report from the Commission to the Council and the European Parliament on sustainability requirements for the use of solid and gaseous biomass sources in electricity, heating and cooling, Brussels 2010.
- [4] Eurostat. Statistics in focus: Renewable energy statistics, European Union 2010.
- [5] European Biomass Statistics, A statistical report on the contribution of biomass to the energy system in the EU 27, AEBIOM, Brussels 2007.

- [6] McNaught A.D., Wilkinson A., IUPAC Compendium of chemical terminology, The Gold Book, Blackwell Science, 1997.
- [7] Directive 2001/77/EC of the European Parliament and of the Council on the promotion of electricity produced from renewable energy sources in the internal electricity market, Brussels 2001.
- [8] Demirbas A., Progress in Energy and Combustion Science 2004, 30, 219-230.
- [9] Chemia i fizyka węgla, ed. S. Jasińko, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 1995.
- [10] Węgiel kamienny, ed. A. Czaplński, Wydawnictwo AGH, Kraków 1995.
- [11] Borman G.L., Ragland K.W., Combustion engineering. WCB McGrawhill, Boston 1998.
- [12] Termochemiczne przetwórstwo węgla i biomasy, eds. M. Ściążko, H. Zieliński, IChPW and IGSMiE, Zabrze-Kraków 2003.
- [13] Roga B., Wnękowska L., Ihnatowicz A., Chemia węgla, PWT, Warszawa 1955.
- [14] Sun Y., Cheng J., Bioresource Technology 2002, 83, 1-11.
- [15] Hatakeyama T., Hatakeyama H., Thermal properties of green polymers and biocomposites, Kluwer Academic Publishers, 2005.
- [16] Speight J.G., Handbook of coal analysis, Wiley, New Jersey 2005.
- [17] Analytical methods for coal and coal products, ed. C. Karr Jr., Vol. I, Academic Press, London 1978.
- [18] Baxter L.L., Biomass Bioenergy 1993, 4, 85–102.
- [19] Roga B., Węgiel kamienny, przeróbka i użytkowanie, PWT, Stalinogród 1954.
- [20] Klass D.L., Biomass for renewable energy, fuels and chemicals, Academic Press, San Diego 1998.
- [21] McKendry P., Bioresource Technology 2002, 83, 37-46.
- [22] Sheng C., Azevedo J.L.T., Biomass Bioenergy 2005, 28, 499-507.
- [23] Demirbas A., Fuel 1997, 76, 431–434.
- [24] Report on energy use of peat. Contribution to U.N. conference on new and renewable sources of energy, Nairobi 1981.
- [25] ISO 1928:2009, Solid mineral fuels – determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value.

3 Sulfur in coal

Grażyna Gryglewicz

3.1 Chemical structure of coal organic matter

Organic matter of coal is composed of five principal elements, i.e. carbon, hydrogen, oxygen, nitrogen and sulfur. The elemental composition of coals of different rank is given in Chapter 2. Carbon atoms form a skeleton which is combined mostly with hydrogen atoms. Both aliphatic and aromatic CH groups can be distinguished in the coal structure. The free spaces left are filled with oxygen, nitrogen and sulfur atoms. There are also carbon atoms which are located in the inferior of aromatic condensed ring structures. With increasing coal rank the contribution of the latter carbon in the structure of coal increases.

The oxygen functionalities in coal are divided into two groups: reactive and non-reactive ones. Reactive oxygen functionalities comprise of methoxyl (-OCH₃), carboxylic (-COOH), hydroxyl (-OH) and carbonyl (-C=O) groups. Methoxyl groups are present in peat and brown coal only. Non-reactive oxygen occurs in the form of ether groups and heterocyclic species, i.e., furan-containing structures. With increasing coal rank the contribution of reactive oxygen decreases which is accompanied by increase in the non-reactive oxygen.

Nitrogen in hard coals occurs mainly in the form of heterocyclic species such as pyrrole, pyridine, and quaternary nitrogen functionalities. Amine and amide groups are present in peat and brown coal and only small amounts are to be found in low rank hard coals.

As coal rank rises, the aromaticity f_a of coal increases, from 0.66 for lignite, 0.82 for medium volatile bituminous coal up to around 0.95 for anthracite [1]. The f_a corresponds to the fraction of the total carbon content that is aromatic in nature. The aromaticity of coal can be determined by ¹³C NMR (Nuclear Magnetic Resonance) spectroscopy. Maturation of coal is associated with the elimination of water, oxygen functionalities and non-aromatic CH groups followed by progressive growth of the aromatic ring systems. As a result, the number of aromatic rings in the structural unit of coal increases.

The complexity and heterogeneity of coal make it impossible to determine the structure of a *coal molecule*. The first model of the chemical structure of coal was proposed by Fuchs in 1942. Since that time at least several models have been elaborated by researchers, e.g. Van Krevelen (1954), Given (1960), Wisser (1975),

Solomon (1980), Spiro and Kosky (1982) and Shinn (1984). The model developed by Wisler is given in Fig. 3.1 that illustrates the aromaticity, functionalities and composition of bituminous coal.

Wisler's model also emphasizes the nature of binding (i.e. methylene, ether and sulfidic bridges) of basic structural units which are composed of 2-5 aromatic rings. The space structural models of coals of different rank, developed by Spiro and Kosky [3] are shown in Fig. 3. 2.

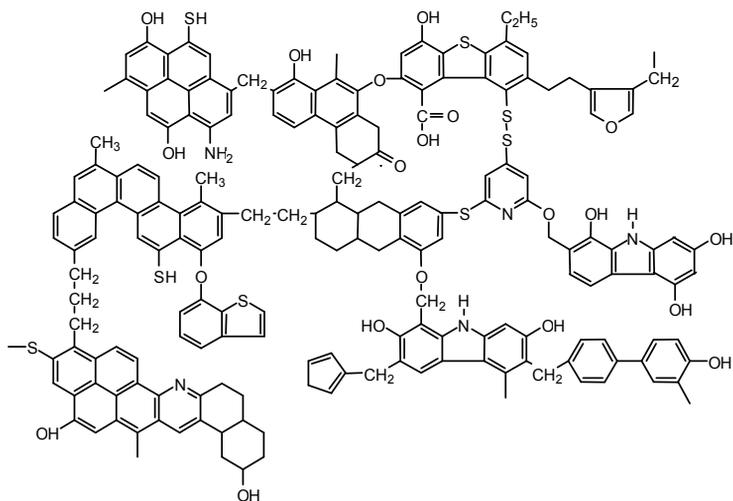


Fig. 3.1. Model of chemical structure of bituminous coal elaborated by Wisler [2].

3.2 Occurrence of sulfur in coal

The sulfur content in coals varies greatly from 0.5 wt% to even 11 wt%, but mostly it does not exceed 4 wt%. Coals with less than 1 wt% of sulfur are usually classified as low-sulfur coals. Sulfur content in the coals extracted in the Upper Silesia Basin (Poland) ranges from 0.8 to 1.8 wt%. In the U.S., the coals contain sulfur in a wide range, depending on the region, i.e. between 0.4 and 4.5 wt% in the Eastern part and between 0.1 and 2.2 wt% in the Western part of the country [4]. Australian's coals are characterized by a relatively low sulfur content, ranging from 0.3 to 1.3 wt%. Sulfur in coal has become an important determinant for coal marketability. Every coal contract includes specifications of coal sulfur and penalties imposed if the total sulfur or sulfur form limit is exceeded. Generally, the lower total sulfur content, the higher price coal is.

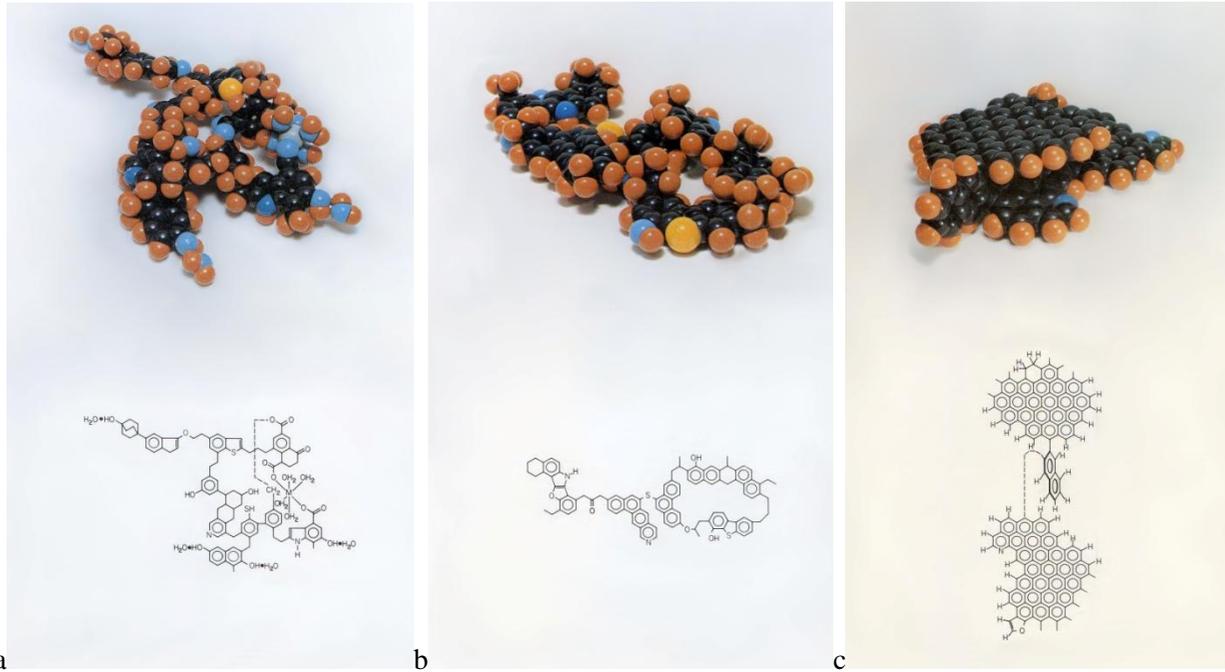
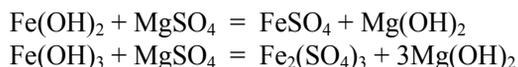


Fig. 3.2. Space-filling model for coals of different rank proposed by Spiro and Kosky [3]. a, subbituminous coal; b, bituminous coal; c, anthracite.

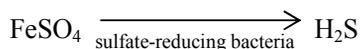
The world production of hard coal was 6000 million tons and the one of lignite about 900 million tons in 2009. For Poland, it was 77 and 56 million tons, respectively. Both fossil fuels were responsible for over 60% of sulfur emissions from human activities. The main sources of SO₂ are: power plants, refineries, domestic heating and smelting [5]. The total worldwide SO₂ emission arising from power generation is about 55 million metric tons per year. On combustion, SO₂ emissions are released from coal mainly in proportion to the content of sulfur in the coal.

3.3 Origin of sulfur in coal

The sulfur content depends on the deposition environment of the coal. The most crucial factor is whether the original peat bed that transformed to coal seam had been in contact with seawater while forming [6]. Seawater is rich in dissolved sulfates, predominantly in the form of magnesium sulfate. The sulfates are considered to be the primary source of the sulfur in coal. Iron is the second component necessary for the formation of pyrite. Iron was transported by fresh water at different stages of the coal bed formation, starting with the deposition of the parent substance. The accessibility of iron source was dependent on the permeability of the roof rock. Having sulfates coming from seawater and iron compounds from fresh water, the following reactions can proceed:



In the next step, iron sulfates were converted to hydrogen sulfide, with the contribution of sulfate-reducing bacteria. This reaction is favorable in an alkali medium under a reducing atmosphere.



Finally, H₂S reacted with iron sulfates to form pyrite (FeS₂) and elemental sulfur according to the following reaction:



The elemental sulfur could react with the substance of peat to produce the various organic sulfur functionalities. This means that the elemental sulfur which is a by-product of the pyrite formation plays an important role in the formation of organic sulfur in coal. Thus, the sulfur in high-sulfur coals is derived primarily from the bacterial reduction of sulfates contained in sea water that invades a peat during the early diagenesis stage, at which the peat is converted to humic material.

If the coal formed in a fresh water environment, the plants that formed the peat are the main source of sulfur [7]. Plants and microorganisms have sulfur containing aminoacids, such as methionine and cysteine. As a result, the coal will contain a small amount of sulfur. The coal which was in contact with both seawater and freshwater during its formation will have a high sulfur level.

Pyrite which was formed contemporaneously with the coal in the original peat swamp is called syngenetic. The syngenetic sulfides are the response to the geochemical environment during or immediately following the peat formation, which was approximately 300 million years ago for coal of the Carboniferous age. The sulfides which were formed within the coal seam subsequent to the first stages of coalification are called epigenetic. The most common form of epigenetic iron sulfide in coal is pyrite deposited in cleats of coal seam [8].

3.4 Forms of sulfur in coal

The sulfur present in coal is classified into inorganic and organic sulfur. The inorganic sulfur comprises of pyritic sulfur, sulfates and elemental sulfur. Pyritic and organic sulfur together account for the large majority of sulfur in coal. Normally, the pyritic sulfur is the dominant form. It is uncommon for the organic sulfur to be dominant.

3.4.1 Inorganic sulfur

Pyritic sulfur

The inorganic sulfur is embedded in the coal, mainly as loose pyrite. Iron sulfide (FeS_2) can occur, next to pyrite, in coal in the form of marcasite. Pyrite and marcasite are dimorphs, i.e. they are identical in their chemical composition, but have different crystalline form. Pyrite has a cubic crystal structure, while marcasite crystals are orthorhombic. The two minerals can be differentiated using only the X-ray diffraction method (XRD). Pyrite is more common so that pyrite and marcasite are referred to as pyritic sulfur. The two forms of FeS_2 differ insignificantly in the physical and chemical properties. The specific density is 5.0 and 4.87 for pyrite and marcasite, respectively. Pyrite is more stable and slightly less reactive than marcasite. Marcasite can be slowly converted into the less reactive pyrite by heating to 450 °C [6].

The wide range of sizes and forms of pyrite and marcasite is due to the different geochemical environment that affected their formation in the coal during the whole coalification period. Pyritic sulfur generally accounts for approximately 50-70% and 30-70% of the total sulfur in Polish coals and U.S. coals, respectively [9]. Pyrite inclusions can take many forms and have particle sizes ranging from 0.1 μm

to 1000 μm . The morphology of the individual pyrite particles varies from massive nodules with dimensions reaching a meter to minuscule inclusions such as submicron single crystal, dendritic, framboids (clusters of submicron crystals, resembling a raspberry) and replacements of plant tissue. The pyrite inclusions are illustrated in Fig. 3.3.

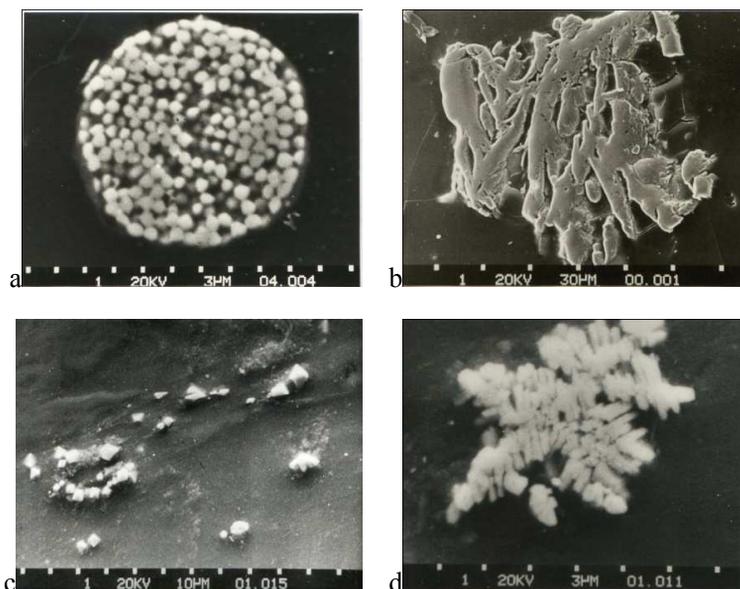


Fig. 3.3. Forms of pyrite occurring in coal. a, framboidal pyrite; b, fusinite filled with pyrite; c, pyrite crystals (euhedral pyrite); d, dendritic pyrite.

In a few coals, significant amounts of other inorganic sulfides, e.g., galena (PbS), chalcopyrite (CuFeS_2), arsenopyrite (FeAsS) and sphalerite (ZnS), which normally occur only in trace amounts, may be present [8].

Sulfates

The sulfate sulfur content is usually less than 0.1 wt% in the pristine coal. Sulfate sulfur occurs chiefly as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and iron sulfates, the latter normally resulting from the oxidation of pyrite during the storage of coal. Pyrite and marcasite oxidize rapidly when exposed to moist air forming different phases of ferrous and ferric sulfates, e.g. szomankite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and jarosite ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$). The level of iron sulfates content can be used as an indication of the extent of weathering of coal since the amount of sulfate sulfur increases upon weathering.

Elemental sulfur

The elemental sulfur content in the pristine coal is very small, less than 0.001 wt% [10]. When the coal is exposed to the atmosphere, elemental sulfur is formed by the oxidation of the pyrite present in the coal. Therefore, weathered coals can contain a reasonable amount of elemental sulfur, even up to 0.3 wt% [8]. Moisture significantly increases its rate of formation. Elemental sulfur can also be formed by bacteriological actions.

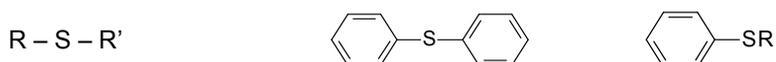
3.4.2 Organic sulfur

Organic sulfur comprises of all the sulfur which is bonded to the organic matrix of coal. It occurs in coal in four functional groups:

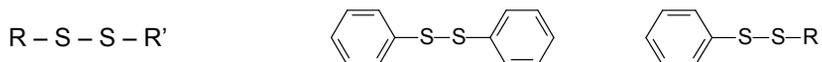
Alkyl and aromatic thiols



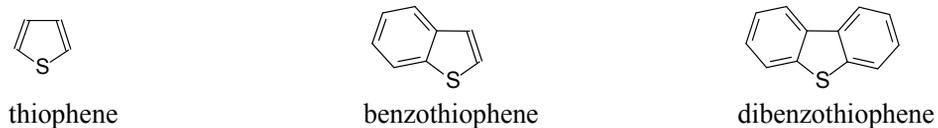
Alkyl, aromatic and mixed sulfides



Alkyl, aromatic and mixed disulfides



Thiophenes



where R and R' are designated to alkyl group.

The knowledge of organic sulfur in coal has been gained mainly based on the analysis of the degradation products of coal on pyrolysis and liquefaction. The distribution of organic sulfur functionalities in the coal matrix is related to the coal rank [11,12]. The majority of the organic sulfur in low rank coals is thiolic and

sulfidic, while most of the organic sulfur in high rank coals is thiophenic. The content of thiols is significantly higher in lignite than in high volatile bituminous coal [13]. The disulfides are present only in a reasonable amount in lignite. Summarizing, non-thiophenic sulfur is predominant in lignite, subbituminous coal and high volatile bituminous coal. Thiophenic sulfur is the dominant form in medium and low volatile bituminous coals and anthracite. The contribution of thiophenic sulfur to the total organic sulfur increases with the rank of coal, reaching over 90% for anthracite [11]. For low rank coals, the ratio of non-thiophenic to the organic sulfur amounts to about 70%.

The most informative method of characterizing the organic sulfur functionalities in coal is atmospheric pressure-temperature programmed reduction (AP-TPR) [14]. The technique is based on the fact that each form of organic sulfur is reduced to H_2S at a particular temperature on heating under a hydrogen flow. Fig. 3.4 shows an example of the H_2S evolution for lignite.

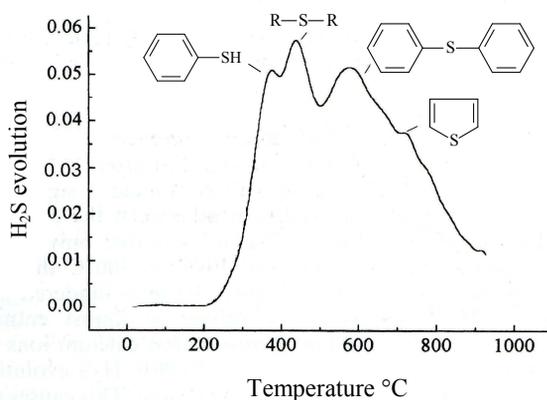


Fig. 3.4. AP-TPR kinetogram of lignite

3.5 Behavior of sulfur during coal processing

The presence of sulfur in coal is undesirable whether coal used is in a raw state or is being subjected to processing. The most relevant coal conversion processes are combustion and coking. Nearly all of the brown coal extracted is used for power generation. In case of hard coals, about 10% of the world production is used for coke making, the rest is mostly consumed for power and heat generation. In recent years, the gasification of coal has gained significance for the production of methane and synthesis gas.

Combustion

All sulfur forms contribute to sulfur emissions during coal combustion. Therefore, the knowledge of the total sulfur content in coal allows for the evaluation of the potential hazard for the environment. When coal is burnt it emits sulfur oxides (mainly SO₂ and a small amount of SO₃) and nitrogen oxides (NO_x). These gases are precursors to acid rain, which has a harmful effect on human health, lakes and vegetation. Sulfur oxides lead to the corrosion of metallic parts of boilers. If the temperature of combustion is lower than 1000 °C, a portion of SO_x can be retained in ash by calcium minerals. The latter are decomposed to form CaO which combines the SO_x evolved giving calcium sulfates (IV) and (VI) in the ash.

Coking

The sulfur compounds originally present in coal are decomposed on heat treatment and may react with the products of coal pyrolysis. As a result, a portion (45-65%) of the sulfur remains in the coke, while the rest passes into the tar and gas. It is estimated that about 25-45% of coal sulfur goes with the gas and the rest passes to the tar. The sulfur content in the gas amounts to 5-7 g/m³. H₂S constitutes around 95-98% of sulfur in the gas. The rest of the sulfur-containing compounds are CS₂, COS, and alkyl thiols. The gas is subjected to desulfurization to a sulfur level lower than 0.5 g/m³ after which it is used for industrial purposes. Thiophene and its derivatives are the major components of the tar.

The distribution of sulfur on pyrolysis depends on the coal rank, the type and the content of sulfur forms and finally, the type and content of inorganic constituents of coal. The removal of sulfur from low rank coals during pyrolysis is easier than from high rank coals due to a lower contribution of thiophenic species in the organic matrix [15].

Regardless of coal rank, the pyrite is decomposed to non-stoichiometric pyrrhotite FeS_{1+x} and elemental sulfur at a temperature between 350 and 600 °C [16]. The nascent elemental sulfur may incorporate into the char via reaction with the hydrocarbon matrix to form stable organic sulfur groups [17]. At 700 °C the conversion of pyrite to FeS (troilite) is nearly complete.

The organic sulfur functionalities of coal are decomposed during pyrolysis mainly to H₂S and other volatile sulfur compounds. Thermally stable organic sulfur groups, such as aryl sulfides and thiophenes, and FeS occur in high temperature coke [18]. Taking into account the coking yield, the sulfur content of coke is slightly lower than that of the coal.

The presence of sulfur in coke is undesirable in all processes in which coke is utilized. When coke fed to the blast furnace contains excess sulfur, the quality of

pig iron is decreased. Therefore, relatively large amounts of additives such as lime and more coke must be added to the blast furnace to insure that the sulfur content of pig iron is maintained at a low level. This implies an enhanced amount of slag produced per ton of pig iron. In the foundry industry, the sulfur in coke leads to lowering mechanical properties of cast iron. The presence of sulfur in smokeless fuel is also undesirable due to SO₂ emissions during combustion.

3.6 Sulfur removal from coal

The two most important forms of sulfur in coal are pyritic and organic sulfur. Sulfates and elemental sulfur have a small contribution in coal sulfur. Pyrite can be removed from coal by physical methods without altering the structure of coal. This assures preserving the chemical, physical and technological properties of coal. Whereas the removal of organic sulfur implies the degradation of the organic structure of coal, and as a consequence, of its properties.

In the case of using the coal for power generation, there are two basic options for controlling sulfur emissions from a coal-fired power plant. The first option is to remove the sulfur from the coal before it has burnt (*precombustion*). The alternative is to “scrub” the sulfur oxides from the combustion gases after the coal has burnt (*postcombustion*). The reduction of sulfur emissions can be reached by several methods:

- Physical removal of pyritic sulfur from coal before combustion.
- Use of flue-gas scrubbers to remove sulfur oxides from the plant gas emissions after combustion.
- Use of fluid-bed combustion with the addition which absorbs sulfur oxides during combustion.

Precombustion desulfurization includes physical and chemical methods for removing sulfur from coal. In current industrial application, density-based concentration methods are the most effective for removing pyritic sulfur from coal due to the large specific gravity difference between coal and pyrite. The specific gravity of coal is approximately 1.5, while pyrite has a specific gravity of 5.0. Therefore, gravity forces will tend to concentrate dense pyrite at the bottom of the coal containers. The gravity separators, including the various types of jigs, spirals and tables, are fed with suspended coal in water [9]. Grinding the coal to fine particles facilitates the separation process. If the pyrite is present as reasonably coarse particles, the separation is simple. When the particles are smaller than approximately 10 μm, the separation becomes very difficult.

The sharpest density-based separation tools are the heavy-media techniques. A suspension of fine, dense particles (magnetite) in water, organic heavy liquids

(halogenated hydrocarbons) and high density solutions of salts (e.g. zinc chloride) in water have been used as the heavy media. A specific gravity of heavy media is between the density of coal and waste. Unfortunately, organic heavy liquids and dissolved salts in water are very toxic. Therefore, a slurry of finely ground magnetite in water is most commonly used in industrial separators.

Removal of the organic sulfur requires chemical desulfurization techniques, many of which can also remove pyrite. The chemical methods are applied exclusively in a laboratory. Their use leads to breaking the coal structure to some extent because a portion of the coal is removed along with the associated organic sulfur. The most successful processes developed to date for the removal of organic sulfur from coal utilize oxidation or displacement reactions using strong alkali. However, chemical desulfurization is not profitable under current economic conditions.

In case of *postcombustion desulfurization*, the sulfur oxides that are produced during coal combustion are removed from the combustion gases using an absorptive chemical, such as CaO. Postcombustion absorbers capture the sulfur in a solid form suitable for disposal. There are two basic approaches to remove the sulfur oxides from the gases. The first approach is based on using a device called the scrubber that is separated from the combustor. The scrubber receives the gases from the coal burner and selectively removes the sulfur from the gases. The most common absorbents are lime (Ca(OH)_2) and limestone (CaCO_3) slurries. The second approach is based on the direct injection of a sulfur absorbent along with the fuel to the combustor. In both approaches sulfur is captured after it has already reached the flue gases. Commercially installations of the flue gas desulfurization (FGD) on coal-fired plants remove currently 72–90% of sulfur from the flue gas [9].

Fluid-bed combustion is a commercially applied solution that minimizes the release of sulfur from the combustion step. The combustor burns pulverized coal mixed with a bed material, e.g. sand mixed with a sulfur absorbent, which is fluidized by air being blown upward through the bed. The mostly used limestone-based sulfur absorbents absorb the sulfur oxides as the coal burns. Due to a solid sulfates formation, the sulfur is not released into the flue gases. Solid sulfates are discarded along with the combustor ash. The combustion process in a fluid-bed reactor is carried out at temperatures of 800-900 °C. These temperatures are low enough for the calcium sulfate to be stable. Up to 90% of the SO_2 can be captured during the combustion for a calcium/sulfur ratio of approximately 2 [19].

3.7 Methods of sulfur analysis

Sulfur analysis is needed to monitor the quality of the coal being produced and the products from coal processing. The design of the coal desulfurization process for a

particular coal requires the knowledge of the sulfur content as well as its forms. In the coal analysis the following sulfur forms can be distinguished:

Combustible sulfur S_c	Total sulfur S_T	Inorganic sulfur S_{inorg}	Pyritic sulfur S_p
			Sulfate sulfur S_{SO_4}
Non-combustible sulfur S_A		Organic sulfur S_o	

The procedures for determining the forms of sulfur in coal are described in the ISO 157 and ASTM D-2492 standards. In these standards, the sulfate and pyritic sulfur are determined directly, and the organic sulfur is referred to as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur. Determination of the pyritic sulfur and sulfate sulfur is based on the fact that, in contrast to the sulfates, the pyrite is not soluble in hydrochloric acid, but does dissolve in nitric acid.

In the case of coke, the analysis of sulfur forms is not approved by standards. The sulfur in coke occurs in the form as shown below.

Total sulfur S_T	Inorganic sulfur S_{inorg}	Sulfidic sulfur S_s
		Sulfate sulfur S_{SO_4}
Organic sulfur S_o		

3.7.1 Total sulfur

The customary methods for the determination of the total sulfur are the combustion methods. There are a few techniques of measuring the total sulfur in coal approved by the ISO and ASTM standards. The total sulfur content can be determined by the wet-chemical gravimetric (*Eschka method*, *Bomb washing method*) and high-temperature combustion methods.

Eschka method

The procedure consists of mixing coal with the Eschka mixture (1 part anhydrous Na_2CO_3 and 2 parts calcined MgO) and heating it in a porcelain crucible in a muffle furnace at 800 °C (ISO 334, ISO 351, ASTM D-3177). The crucible is held at this temperature until oxidation is complete. The sulfur compounds evolved during the combustion react with MgO and Na_2CO_3 to form sulfites and sulfates.

After the oxidation of sulfites with hydrogen peroxide (H_2O_2), the sulfates are precipitated with barium chloride (BaCl_2) in a hot solution such as barium sulfate (BaSO_4). After filtering and washing, BaSO_4 precipitate is heated at $815\text{ }^\circ\text{C}$ to a constant mass. The total sulfur content in coal is calculated based on the mass of BaSO_4 .

Bomb washing method

The bomb washing procedure is convenient for laboratories that perform frequent calorimetric determinations on coal (ASTM D-2015, ASTM D-3286). After being cooled and vented, a bomb used for a calorific determination is thoroughly washed with water, and the washings are collected. After determining the acid correction for the heating value, the solution is treated with ammonium hydroxide (NH_4OH) to precipitate iron ions such as ferric oxide ($\text{Fe}(\text{OH})_3$). The latter is removed by filtration and the sulfate is precipitated with BaCl_2 and determined gravimetrically.

High-temperature combustion method

In the high temperature combustion method (ISO 352, ISO 587, ASTM D-2361, ASTM D-4208), the coal is first burnt in a tube furnace in a stream of oxygen at $1350\text{ }^\circ\text{C}$, to completely convert the sulfur into gaseous oxides. The amount of the sulfur oxides produced by burning the sample can be determined by the three alternative methods, i.e. the acid-base titration, iodometric titration and the infrared absorption. The acid-base titration is most often used to finish the high-temperature combustion method. In this procedure, the combustion gases are bubbled through a H_2O_2 solution in a gas absorption bulb. The sulfuric acid, which is formed on the reaction of sulfur oxides with H_2O_2 , is determined by titration with a standard base solution. An adjustment must be made for the chlorine which is present in coal. Chlorine-containing compounds yield hydrochloric acid in the H_2O_2 solution, increasing its acidity.

The gravimetric methods are time-consuming and require a high level of skills. The high-temperature combustion methods are more rapid. In recent years, various commercially available automated sulfur analyzers based on high-temperature combustion have been used for a simultaneous determination of carbon, hydrogen, nitrogen and sulfur contents. The analysis of these four elements takes less than 20 min, however, it requires calibration with a standard reference material.

3.7.2 Sulfur forms

Sulfate sulfur

The coal sample is treated with a 20% HCl at boiling temperature for 20 min in order to determine the sulfate sulfur (PN-G-04582:1997). After filtering and

washing, the undissolved coal may be retained for the determination of pyritic sulfur. The extracted sulfates are precipitated as BaSO₄ for a gravimetric determination.

Pyritic sulfur

The residue remained after the sulfate sulfur extraction is leached with a 18% HNO₃ at 65 °C for 1 h to dissolve the pyrite (PN-G-04582:1997). This treatment oxidizes iron species to Fe (III) and pyrite-derived sulfur to sulfate. After filtering, the concentration of iron in the filtrate is most often determined by the atomic absorption spectroscopy (AAS). If the residue from the sulfate determination was used, the iron determined corresponds to the pyrite iron and based on its amount the pyritic sulfur is calculated.

The main use of pyritic sulfur data is connected with the cleaning of coal because pyrite can be removed from coal to a high extent by the gravity separation methods. Therefore, pyritic sulfur concentration can be used to assess how much sulfur can be removed from coal.

Elemental sulfur

Since the elemental sulfur is an oxidation product, it is not an important factor in pristine coals. Therefore, the ISO methods as well as ASTM methods for sulfur forms analysis assume that only three sulfur forms are present in coal. As a consequence, there are only the standard analytical procedures for determining the pyritic, sulfate and organic sulfur. The organic sulfur is determined in an indirect way, i.e. by subtracting the sum of pyritic and sulfate sulfur from the total sulfur. Hence, if the elemental sulfur is present in coal, it is included in the so-called organic sulfur. This implies that in some cases an overestimation of the organic sulfur content may take place. One of the non-standardized methods of determining elemental sulfur consists of its extraction with cyclohexane and its subsequent quantitative analysis in the extract by GC-MS [20].

Organic sulfur

Direct determination of the organic sulfur is difficult because it is present in many different organic functional groups and is dispersed throughout the organic matrix. The method used to determine the total organic sulfur is an indirect one. According to PN-G-04582:1997 and ASTM D2492 procedures, the organic sulfur S_o is determined by the following difference:

$$S_o = S_T - (S_p + S_{SO_4})$$

where the total sulfur (S_T), pyritic sulfur (S_p) and sulfate sulfur (S_{SO_4}) are determined directly by approved ISO and ASTM methods. The accuracy of the value assigned to the organic sulfur depends on the accuracy of the determination of S_T , S_p and S_{SO_4} . The total error may be quite significant if the errors arising from the individual determinations accumulate, affecting the final value of the organic sulfur.

Sulfidic sulfur

The sulfidic sulfur occurs in char and coke. It is formed on the decomposition of pyrite during coal pyrolysis. To determine the sulfidic sulfur, the sample is treated with a 20% HCl solution (PN-G-04587). The H_2S released is captured with a $(CH_3COO)_2Cd$ solution as cadmium sulfide (CdS). The amount of precipitated cadmium sulfide is determined iodometrically by titration with a 0.1M sodium thiosulfate ($Na_2S_2O_3$).

3.7.3 Combustible and noncombustible sulfur

When coal is burnt, the different forms of sulfur are split up into combustible and noncombustible sulfur. *Combustible sulfur* includes the total amount of volatile sulfur. This is the sulfur removed as SO_x during the complete combustion of coal. *Noncombustible sulfur* is the sulfur left in the ash after the coal is completely burnt, mainly as calcium sulfate. The sum of the combustible and noncombustible sulfur gives the total sulfur in coal [21].

3.8 Laboratory work: determination of total sulfur and combustible sulfur

The aim of the laboratory work is to determine the total sulfur and the combustible sulfur of coal in order to evaluate the potential risk for the environment due to sulfur oxides evolved during coal combustion.

For this purpose, the total sulfur in coal (PN-ISO 352) and the sulfur in coal-derived ash (PN-G-04581) were determined by a high-temperature combustion method with acid-base titration. The sample is burnt at 1350 °C under a flow of oxygen. The sulfur oxides evolved are absorbed in 3% H_2O_2 solution to produce sulfuric acid which is determined by titration with 0.05M NaOH using methyl red as indicator. An adjustment is made for the hydrochloric acid which is formed during combustion from the chlorine-containing compounds present in coal.

The *total sulfur* ($S_{T,ad}$) content in coal (air-dried basis), expressed in wt%, is calculated according to the following equation:

$$S_{T,ad} = \frac{0.0008 \times (V_1 - V_2 - V_3)}{m} \times 100 \quad (3.1)$$

where:

V_1 - the volume of 0.05M NaOH used in the determination, cm^3

V_2 - the volume of 0.05M NaOH used in the blank test, cm^3

V_3 - the volume of 0.05M $\text{Hg}(\text{NO}_3)_2$ used in the determination of chlorine correction, cm^3

M - the mass of the coal sample, g

0.0008 - the mass of sulfur corresponding to 1 cm^3 0.05M NaOH, g/cm^3 .

The *sulfur content in ash* (S_{ash}), expressed in wt%, is calculated according to the following equation:

$$S_{ash} = \frac{0.0008 \times (V_1 - V_2)}{m} \times 100 \quad (3.2)$$

where:

V_1 - the volume of 0.05M NaOH used in the determination, cm^3

V_2 - the volume of 0.05M NaOH used in the blank test, cm^3

m - the mass of the ash sample, g

0.0008 - is the mass of sulfur corresponding to 1 cm^3 0.05M NaOH, g/cm^3 .

For the above determination, the ash was produced by the ashing of the analyzed coal at 815 °C in the standard conditions according to ISO/FDIS 1171:2020(E) for ash.

The *noncombustible sulfur* ($S_{A,ad}$) of coal (air-dried basis), expressed in wt%, is calculated according to the following equation:

$$S_{A,ad} = \frac{S_{ash} \times A_{ad}}{100} \quad (3.3)$$

where:

S_{ash} - the sulfur content in ash, calculated in wt% from the equation (3.2)

A_{ad} - the ash content in coal, wt%.

The *combustible sulfur* ($S_{c,ad}$) of coal (air-dried basis), expressed in wt%, is calculated based on the difference between the total sulfur and the noncombustible sulfur of coal as follows:

$$S_{c,ad} = S_{T,ad} - S_{A,ad} \quad (3.4)$$

where:

$S_{T,ad}$ - the total sulfur content in coal, wt%

$S_{A,ad}$ - the noncombustible sulfur content in coal, wt%

References

- [1] Van Krevelen D.W., Coal. Typology-physics-chemistry-constitution, Elsevier, Amsterdam 1993.
- [2] Chemia i fizyka węgla, ed. S. Jasińko, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 1995.
- [3] Spiro C.L., Kosky P.G., Fuel 1982, 61, 1080-1084.
- [4] Baruya P., McConville A., Coal sulfur content – impact on coal markets, IEA Coal Research 1997.
- [5] Adams D.M.B., Smith I.M., Sulfate, climate and coal, IEA Coal Research, London 1995.
- [6] Tsai S.C., Fundamentals of coal beneficiation and utilization, Coal Science and Technology 2, Elsevier, Amsterdam 1982.
- [7] Casagrande D.J., Sulfur in peat and coal. In: Coal and coal-bearing strata: recent advances, ed. A.C. Scott, Geological Society Special Publication, Oxford, 1987.
- [8] Gluskoter H.J., Energy Sources 1977, 3, 125-131.
- [9] Komar Kawatra S., Timothy C. Eisele, Coal desulfurization. High-efficiency preparation methods, Taylor & Francis, 2001.
- [10] Stock L.M., Wolny R., Bal B., Energy Fuels 1989, 3, 651-661.
- [11] Gryglewicz G., S. Jasińko, Fuel Processing Technology 1988, 19, 51-59.
- [12] Maes I.I., Gryglewicz G., Machnikowska H., Yperman J., Franco D.V., Mullens J., Van Poucke L.C., Fuel 1997, 76, 391-396.
- [13] Attar A., Sulfur groups in coal and their determinations. In: Analytical methods for coal and coal products, vol. III, ed. C. Karr, Jr. Academic Press, New York 1979, pp. 585-624.
- [14] Yperman J., Maes I.I., Van den Rul H., Mullens S., Van Aelst J., Franco D.V., Mullens J., Van Poucke L.C., Analytica Chimica Acta 1999, 395, 143-155.
- [15] Maes I.I., Yperman J., Van den Rul H., Franco D.V., Mullens J., Van Poucke L.C., Gryglewicz G., Wilk P., Energy Fuels 1995, 9, 950-955.
- [16] Gryglewicz G., Wilk P., Yperman J., Franco D.V., Maes I., Mullens J., Van Poucke L.C., Fuel 1996, 75, 1499-1504.
- [17] Gryglewicz G., Jasińko S., Fuel Processing Technology 1988, 19, 51-59.
- [18] Yperman J., Franco D.V., Mullens J., Van Poucke L.C., Gryglewicz G., Jasińko S., Fuel 1995, 74, 1261-1266.
- [19] The problem of sulfur, IEA Coal Research, London 1989.

- [20] Gryglewicz G., Gryglewicz S., *Fresenius' Journal of Analytical Chemistry* 2001, 370, 60-63.
- [21] *Analytical methods for coal and coal products*, vol. I, ed. C. Karr, Jr. Academic Press, New York 1978.

4 Coking properties of coal

Krzysztof Kierzek

4.1 Coking coals

The coking coals occupy the middle position in the coalification scale. These coals are included in ISO classification in the reflectance range between 0.6 and 1.7% [1]. According to the Polish terminology, they are named gas coal (type 33), gas-coking coal (type 34), orthocoking coal (type 35), metacoking coal (type 36) and semicoking coal (type 37).

When heated to progressively higher temperatures in an absence of air, coal will decompose, evolve water, chemically complex tarry matter and a mixture of gases, and leave a solid residue. The composition and properties of the residue depend upon the maximum temperatures to which it was exposed. If the process is conducted at the final temperature below 700 °C (low temperature carbonization), a *char* or *semicoke* is obtained. Soaking at the temperature above 900 °C (high temperature carbonization) is effective to produce the solid residue called *coke*. The coking coals are able to transform to a plastic state during heating, which is necessary to produce a hard and porous coke in lump form.

The coke is used on a large scale as fuel and reactant in blast furnace where an iron ore is turned into metal. Other metallurgical procedures based on the composition of steel or thermal processing of non-iron metals also involve a lot of coke.

The parameters of the coking process are adjusted to obtain the highest yield of coke of high mechanical strength and the required reactivity. Besides the heating rate, final temperature and soaking time, a rank of coal used as the raw material has a crucial role for producing good quality coke. In practice, coal blends were used as a batch in a coking plant rather than a single coal. High rank coals or coke breeze are included in the coal blend (5-10 wt%), as leaning additives to decrease the volatile matter of the coal blend, which entails better mechanical properties of the final coke. An example of the composition of coal blends for producing metallurgical coke: gas-coking coal (20-40 wt%), orthocoking coal (60-75 wt%) and coke breeze (1-3 wt%).

The average volatile matter content in the coking blend varies in the range of 25-27 wt%. Also the content and composition of ash has an influence on the suitability of coal for coke making. Higher than 10-12 wt% of mineral matter in coal lowers its

caking power significantly and such raw material is usually rejected by coke makers [2].

4.2 Thermal decomposition of hard coal

The thermal decomposition of coal is very complex. A simplified scheme of coking can be graphically presented as shown below (Fig. 4.1). In the pre-softening stage, moisture, trapped gases, CO₂ and H₂S are evolved. Small amounts of tar and light hydrocarbons can also appear around the coal softening point. Coal is transformed to a plastic state at above 350 °C and starts swelling as a result of the evolution of gases that are generated by the cracking processes. The expansion of the charge limited by the walls of the coke oven results in an increase of pressure inside the chamber. Elevated pressure is profitable as it helps to fill all the void spaces by the high-viscosity plastic phase and to join the non-softened particles together. However, the swelling process must be controlled by the batch composition, due to a risk of damaging the ceramic coking oven. As the temperature around 500 °C has been reached, polymerization and cross-linking reactions occur that causes an increase of viscosity and, finally, the resolidification of the plastic mass. The gases are trapped in a bulk of semicoke and form a primary porous texture. At a temperature above 500 °C, the process runs further in a solid state. In the temperature range of 670-720 °C, the shrinking of semicoke is observed. This phenomenon is connected with the secondary degassing stage, when the hydrogen and methane evolutions occur. The degassing in solid states generates a lot of mechanical stresses that lead to a network of cracks. Both shrinking and cracks are advisable to some extent because they may facilitate removing coke from a coking chamber.

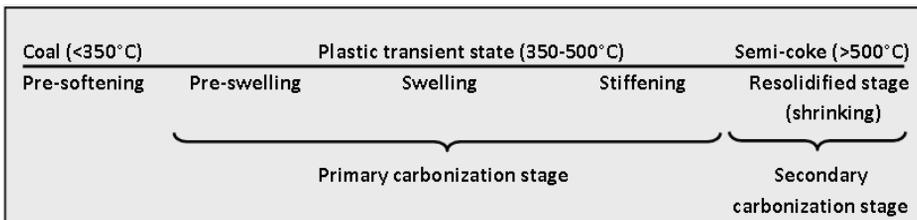


Fig. 4.1. Characteristic carbonization temperatures and stages during coke formation.

Summarizing, three main stages can be distinguished in the coking process:

- I. The release of moisture between 100 and 150 °C.
- II. Primary decomposition of coal between 350 and 500 °C followed by tar evolution. The formation of the plastic phase can occur.

III. Secondary decomposition with a maximum at around 700 °C followed by hydrogen evolution.

4.3 Industrial coke production

The standard oven designed for coke production on an industrial scale is shown in Fig. 4.2. The oven is 12-18 m long, 4-8 m high and 0.4-0.5 m wide, equipped with doors on both narrow sides. Current assemblies may contain up to 80 ovens in a battery. The heat energy for the coking process is produced from coking gas by combustion. The walls of the oven are heated by exhausted gases circulated in heating ducts. The wasted heat energy is transferred to the air streams by a special regenerator system. The pre-heated air is used as an oxidant in the burners. This system allows to significantly improve the heat efficiency of the whole battery. There are two systems of oven charging. In most cases, the ovens are charged from the top by gravity. Another system is stamp-charging which improves the charge density. The coal blend compacted is charged horizontally through one doorway in a metal box. The coking process takes place in completely sealed ovens. As the process is finished, the oven doors are opened and a special ram pushes the hot coke into a quenching car. The coke is transported to the sloping wharf for cooling and drying. The liquid and gas byproducts are collected and separately processed.

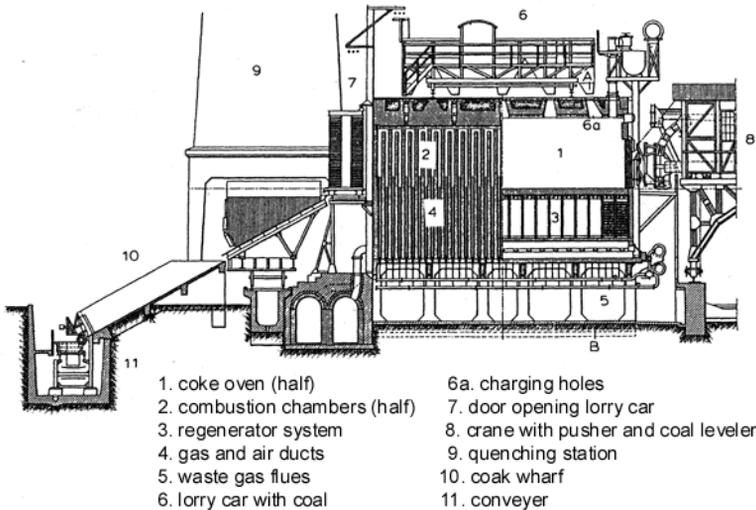


Fig. 4.2. The scheme of standard coke oven [3].

Because of the significant oven wideness and poor thermal conductivity of the charge, a huge temperature gradient occurs inside the oven during coking. The elementary processes (softening, swelling, resolidification etc.) take place

sequentially in a limited zone which is moved from an exterior-bottom to an interior-top of the oven. The example temperature profile of the oven as a function of time is shown on Fig 3.

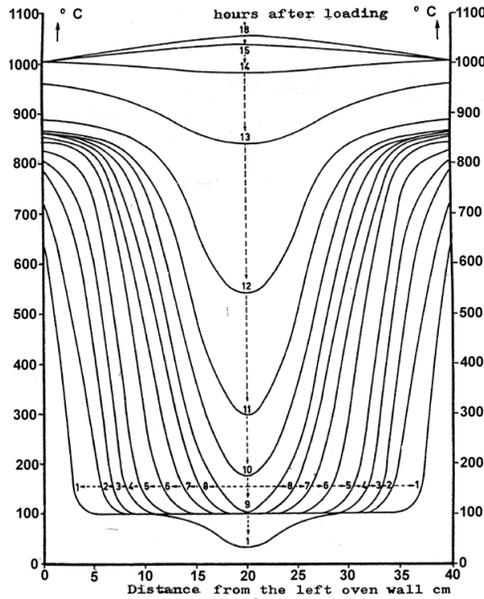


Fig. 4.3 Typical temperature profile in the coke oven of 0.4 m width as a function of time [3].

The final coking temperature is usually limited to around 1000 °C. It allows the obtaining of a product of desired quality. The entire process takes place over a long period of time, between 12-24 hours. The coke yield strongly depends on the coal rank but it is usually in the range of 75-80%.

4.4 Methods of coking properties determination

The suitability of coal or coal blends for the coking process can be evaluated in the laboratory by the determination of the coking properties, including plasticity, caking power and swelling ability.

4.4.1 Plastic properties

The coal behavior in the plastic state can be directly assessed by standardized plastometric and dilatometric methods.

Gieseler test

The apparent fluidity of plastic coal is evaluated with a constant-torque Gieseler plastometer (Fig. 4.4).

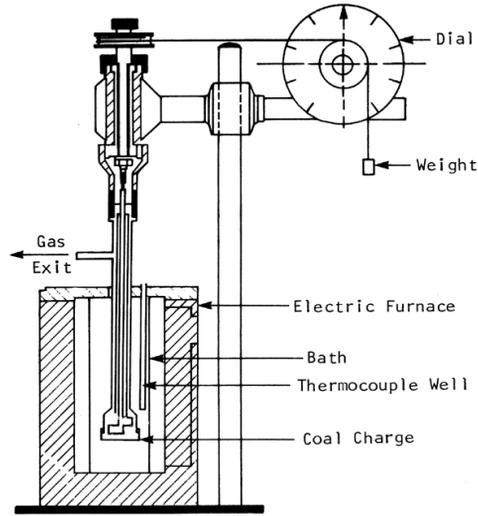


Fig. 4.4. The schematic of Gieseler plastometer [2].

This instrument measures the rotation of a rabble-armed stirrer in a compacted coal charge heated ($3\text{ }^{\circ}\text{C}/\text{min}$) in the absence of air between $300\text{--}550\text{ }^{\circ}\text{C}$. When the coal is in the solid state, the stirrer is not rotated. At a certain temperature, the stirrer begins to rotate and its speed increases with increasing temperature, reaching a maximum (F_{max} , dd/min). Afterwards, the rotation of the stirrer starts decreasing and finally, the stirrer stops. The Gieseler plastometer records the fluidity in dial division per minute (dd/min). The softening temperature (T_s), the temperature at which maximum fluidity is observed (T_m), the maximum fluidity (F_{max}) and the temperature at which the charge resolidifies (T_r) are determined from the curve of *fluidity*=*f*(*temperature*) recorded. T_s and T_r are usually equated with the temperatures at which the fluidity equals 20 dd/min, and the width of the plastic range is defined by difference $T_r\text{--}T_s$. A typical Gieseler curve is shown in Fig. 4.5. In this case, the stirrer starts to rotate at about $380\text{ }^{\circ}\text{C}$ and reaches a maximum speed of 6500 dd/min at $447\text{ }^{\circ}\text{C}$. Above this temperature, the resolidification of coal begins and at $480\text{ }^{\circ}\text{C}$ the viscosity of charge reaches a value, which was enough to stop the stirrer.

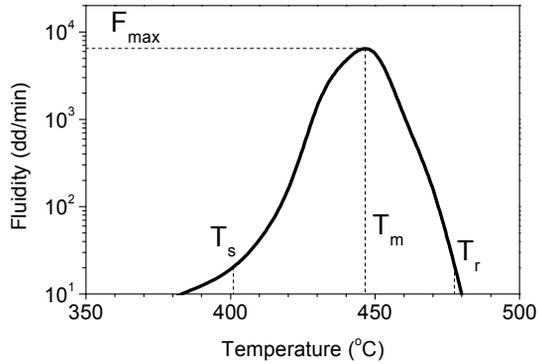


Fig. 4.5. Typical Gieseler fluidity curve.

Characteristic temperatures of bituminous coals as a function of volatile matter (V_{daf}) are given in Fig. 4.6.

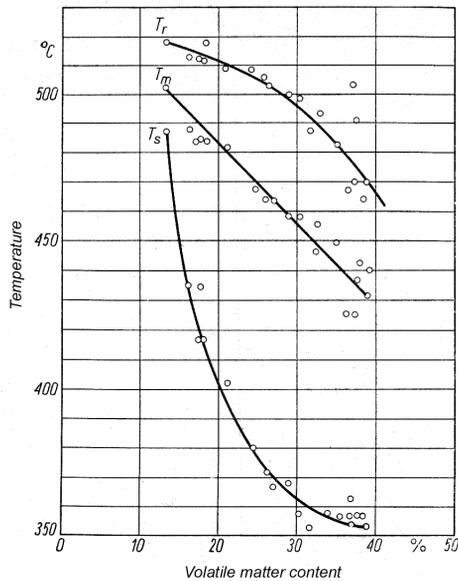


Fig. 4.6. Plasticity temperatures range determined by the Gieseler method for coals of different rank [4].

The fluidity reaches a maximum (F_{max}) when the volatile matter content is in the range of 27-33 wt%. The temperatures of softening, maximum plasticity and resolidification rise continuously with coal rank. The plasticity range ($T_r - T_s$) of coals has been a guide for blending coals for coke making.

Audibert-Arnu test

The changes of the volume of coal in the plastic range are commonly measured with the Audibert-Arnu dilatometer (Fig. 4.7).

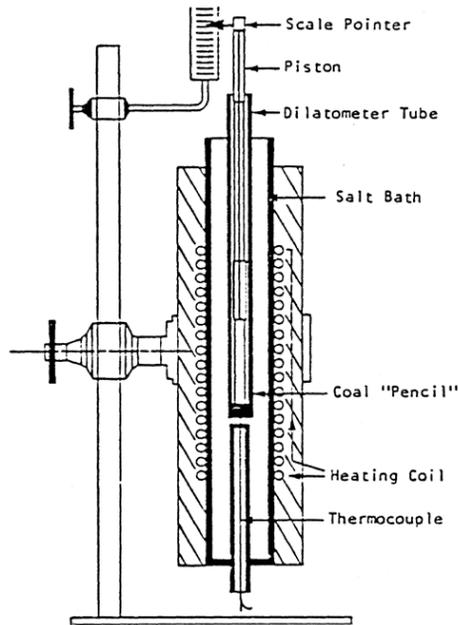


Fig. 4.7. The schematic of the Audibert-Arnu dilatometer [2].

The instrument records the vertical displacement of a piston that rests on a compacted coal charge. The dimensional change of charge is measured as a function of temperature rise at a constant rate ($3\text{ }^{\circ}\text{C}/\text{min}$) in the range of $330\text{--}500\text{ }^{\circ}\text{C}$. The traces recorded under such conditions characterize the coal by defining the extent of contraction (a), dilatation (b) as well as the temperatures at which these changes begin and end. The classification of typical dilatometer curves is shown in Fig. 4.8.

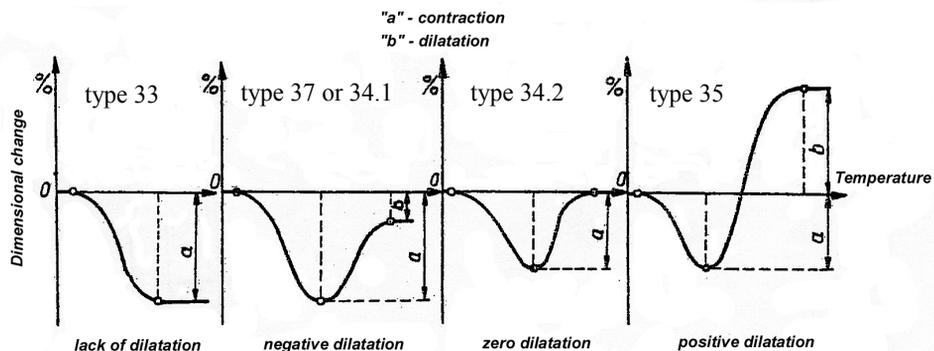


Fig. 4.8. Classification of dilatometer curves of coal [5].

4.4.2 Caking power

Two standardized methods have been elaborated to assess the caking properties of coal in a laboratory scale: Roga test and Gray-King test.

Roga test

The Roga test is to determine to which degree the softened coal is capable of binding particles of inert substance during heating, to give a solid and coherent coke. The Roga index is evaluated based on the mechanical strength of the crucible coke obtained by the carbonization of mixture 1 g of coal and 5 g of standard anthracite at 850 °C for 15 min under standardized conditions [6]. The Roga index (RI) lies between 0 and 90. The higher RI, the stronger caking power the coal has. The relationship between the RI and the coalification degree of hard coal is given in Fig. 4.9.

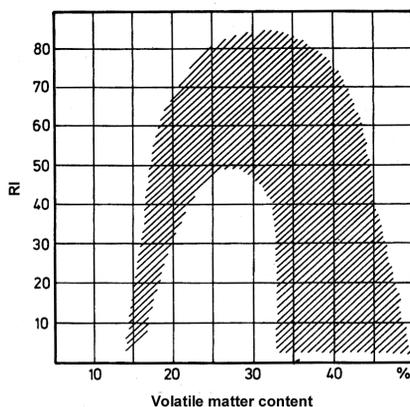


Fig. 4.9. Relationship between the RI and volatile matter content of hard coals [7].

RI values strongly depend on coal rank. The subbituminous coals have low caking power. The Roga Index of anthracite is 0. The highest caking power (RI > 75) is observed for the coals with a volatile matter of 25-30 wt%.

Gray-King test

Gray-King test is based on comparing the solid residues of coal heated (5 °C/min) in a standard quartz retort to a final temperature of 600 °C with a set of standard cokes designated from A to G (Fig. 4.10). If the coke residue produced is so swollen that it fills the cross-section of the retort tube, the determination is repeated with the coal admixed with a suitable quantity of electrode carbon or equivalent material. The cokes from the blend are designated G₁, G₂ etc., where subscripts indicate how many parts of the electrode carbon in 20 parts of the mixture cause the G-type residue after the final test.

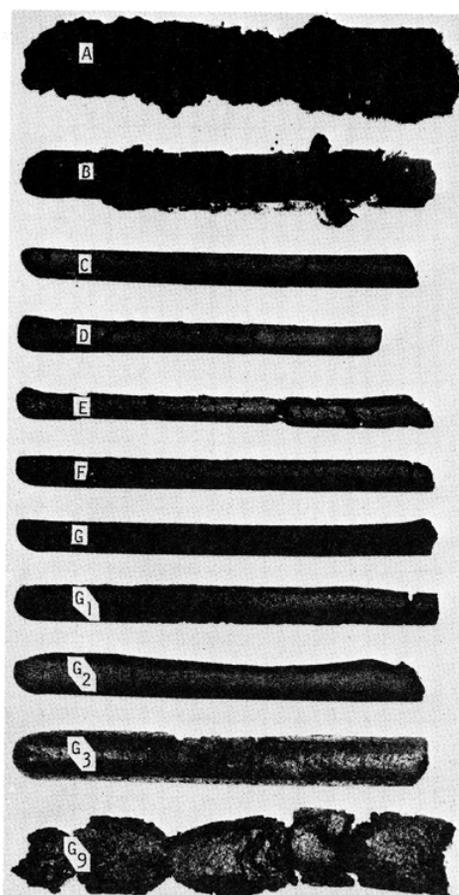


Fig. 4.10. Classification of Gray-King coke types [8].

The correlations between Gray-King coke designation and coal type are given in Table 4.1.

Table 4.1. Gray-King test results for selected coal types.

Gray-King test	Polish classification
A	31, 42
B – D	32, 33, 37
E – G	34
G ₁ – G ₈	35, 36

4.4.3 Swelling ability

The swelling properties of coal are commonly determined by the free-swelling test, also called the *crucible swelling test*. In this method, 1 g of coal without appreciable packing is heated in a covered silica crucible to 820 °C for at least 180 s. During this test, the coal softens and the particles fuse. The evolution of volatiles causes the viscous mass to swell and after resolidification the residue (coke) is larger in volume than the original sample. The extent of swelling depends on the fluidity of the plastic state. The resultant sample coke is compared with the series of standard profiles (Fig. 4.11). A non-coherent residue is assigned a swelling index (SI) of 0. Higher values, up to 9, are related to coal of superior swelling ability. A flat top of profiles of index higher than 6 is caused by the deformation of the charge by the lid.

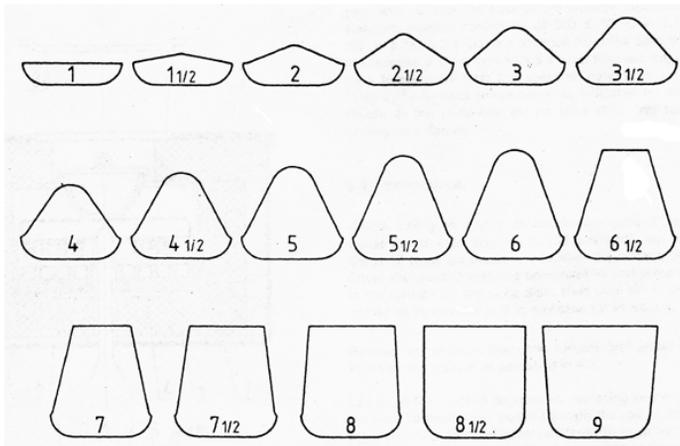


Fig. 4.11. Scale of reference profiles for crucible swelling test [9].

Fig. 4.12 shows the variation of the SI with coal rank. As can be seen, the SI values may vary with coal rank considerably. The values for the lower-rank coals are less than those for bituminous coals, while anthracite does not fuse and shows no swelling value. The maximum SI is reached for the coals with a volatile matter of 25-30 wt%.

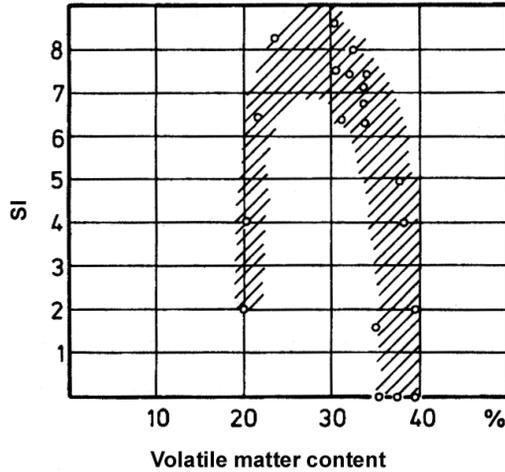


Fig. 4.12. Relationship between the SI of hard coals and their volatile matter content [7].

For industrial coking, the determination of coking pressure is very important, particularly in the case of using the so-called *dangerous coals*. When coal swells due to the gas evolution in the plastic stage, the charge exerts a certain pressure against the walls of the oven chambers. Certain coals show such high coking pressure that can lead to damage of the coke oven. Two types of methods for determining the coking pressure can be distinguished. The first method is based on the measurement of the coking pressure of coal when heated in the sealed vessel of limited volume. The second one is a movable-wall oven test, the object of which is to measure the coking pressure directly.

4.5 Laboratory work: determination of Roga index and crucible swelling index

The scope of the laboratory work comprises the determinations of the Roga index (RI) and the swelling index (SI) for a given coal. Based on the obtained results, the potential suitability of coal as a component of the coal blend for coke making will be estimated.

Roga index determination

For the RI determination, 1 g of coal and 5 g of standard anthracite is placed in a porcelain crucible. The content is mixed, steel weight is placed on the surface and the blend is pressed. The crucible is covered with the lid and inserted to the hot furnace (850 °C) for 15 min. The resultant coke is transferred to the drum and rotated for 5 min at a speed of 50 rev/min. The time and speed of rotating have a strong influence on the abrasive effect and must be absolutely restricted. After the rotating stage, the coke is removed from the drum and sieved through the 1 mm round hole sieve. The coke remaining on the sieve is reweighed and returned back to the drum. The abrasion procedure, sieving and reweighing of the oversize is repeated two more times, exactly as before. The Roga index is given by equation 4.1.

$$RI = \frac{100}{3 \times Q} \left[\frac{a + d}{2} + b + c \right] \quad (4.1)$$

where

Q - mass of the coke after pyrolysis, g

a - mass of coke remaining on the sieve before the first drum test, g

b - mass of coke remaining on the sieve after the first drum test, g

c - mass of coke remaining on the sieve after the second drum test, g

d - mass of coke remaining on the sieve after the third drum test, g

Swelling index determination

In this determination, the heat condition inside the test chamber are precisely imposed. The temperature at the base of the crucible must be increased to 800±10 °C in 90 s and 820±5 °C in 180 s from the time of inserting the crucible into the chamber.

The mass 1 g of coal is placed into the silica crucible. The crucible is lightly tapped about 12 times on the bench to level the surface of coal. Next, the crucible is covered with the lid and placed in the furnace for 180 s or longer if the volatile matter causes to be evolved. The crucible is removed from the furnace, cooled down to room temperature and the residue is examined. Five tests must be carried out in succession using another clean crucible each time.

If the residue is not coherent, i.e. mostly loose powder, no further examination is needed and the result shall be designated swelling index 0. If the residue is a coherent coke button but is not swollen, it should be placed on the flat surface and weighed by a mass of 500 g. If the button supports the weight without breaking into more than two or three hard pieces, it can be designated swelling index 1. If it is crumbled or disintegrated, then the swelling index is ½. If the coke button is swollen, it must be compared with the standard numbered profiles (Fig. 4.11). The

final result of crucible swelling index determination is the mean of the five tests to the nearest $\frac{1}{2}$ unit.

References

- [1] ISO 11760:2005. Classification of coals.
- [2] Berkowitz N., An introduction to coal technology. Academic Press, San Diego 1994.
- [3] Van Krevelen D.W, Coal: Typology - physics - chemistry – constitution, Elsevier, Amsterdam 1993.
- [4] Karcz A., Koksownictwo – część I, Wydawnictwo AGH, Kraków 1991.
- [5] ISO 349:1975. Hard coal - Audibert-Arnu dilatometer test.
- [6] ISO 15585:2006. Hard coal – Determination of caking index.
- [7] Roga B., Kopalne paliwa stałe, Wydawnictwa Geologiczne, Warszawa 1958.
- [8] ISO 502:1982. Coal - Determination of caking power - Gray-King coke test.
- [9] ISO 501:1981. Coal – Determination of the crucible swelling number.

5 Classification of crude oil

Rafał Łużny

5.1 Introduction

Crude oil (or petroleum) is a naturally occurring liquid mixture of many different substances, mainly hydrocarbons (80–95 wt%), sulfur- and nitrogen-containing compounds, and trace metals which are mainly bounded with complex organic compounds. It can be found in pools in sedimentary rocks usually beneath the earth's surface. Nowadays crude oil is the one of the most important energy sources in the majority of developed countries. After refining and separating in the oil refineries, it is used as a fuel for cars (gasoline and diesel fuel) and airplanes (jet fuel). Besides that, petroleum is an important raw material for petrochemical industry which produces plastics, synthetic rubbers and fibers (e.g. polyester, nylon etc.), fertilizers, dyes, paints, detergents, medicines and many others.

5.1.1 Origin of crude oil

According to the most widely accepted theory, crude oil is derived from the organic matter of dead organisms which lived millions of years ago. The oldest known petroleum deposit discovered near Irkutsk (Russia) is about 950 million years old. The majority of deposits are, however, much younger. About 50% of the world's oil resources was formed from about 180 to about 1 million years ago, i.e. from the Jurassic to late Quaternary period [1].

Formation of crude oil occurred in shallow seas or lakes which had an abundance of zooplankton and algae. Dead organisms sank to the bottom of the sea or lake and if the bottom of the water basin was stagnant, consecutive layers of organic matter were accumulated in the mud. Inorganic sediments, such as sand and stone built up at the bottom of water reservoir, burying and compressing organic residues under its weight. The increasing pressure and temperature initiated the transformation of organic matter into crude oil.

Generally, the formation of crude oil consists of two stages. First stage, called diagenesis, occurred at temperatures less than 50 °C and a depth of about 10 m. At this step, microbial activity was a key contributor to the breakdown of organic compounds such as carbohydrates, proteins and lipids. Products of organic matter decomposition were polymerized with waxes, resins and hydrocarbons creating insoluble in organic solvents substance called kerogen, of which the hypothetical molecule is presented in Fig. 5.1.

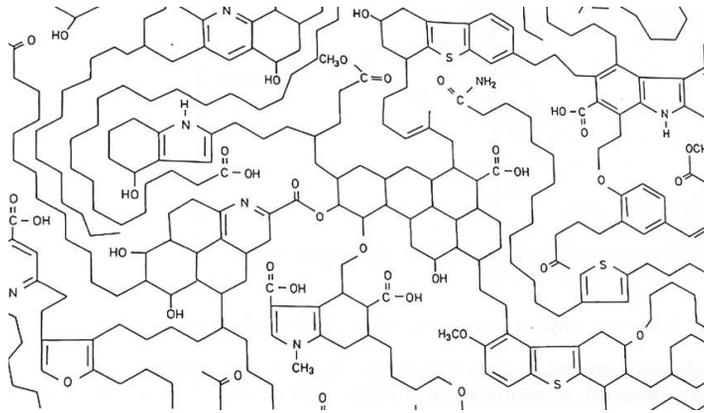


Fig. 5.1. Fragment of hypothetical molecule of kerogen [1].

Depending on the starting organic matrix from which kerogen was formed, three types of kerogen are distinguished (Table 5.1). Algal and liptinitic kerogen participated in crude oil formation, while humic kerogen was transformed into coal.

Table 5.1. Classification of the kerogen [1].

Type	Name	Source
I	algal kerogen	mainly algae
II	liptinitic kerogen	mainly plankton, some contribution of algae
III	humic kerogen	mainly higher plants

The second stage of crude oil formation, which is called catagenesis, occurred at the depth where the temperature was in the range of 60 to 170 °C. At this step, about 80–95% of liquid hydrocarbons were formed. Under the high pressure and temperature conditions, the chemical bonds in kerogen were broken down generating liquid hydrocarbons which are the main components of crude oil. At the end of this temperature range, the secondary cracking of hydrocarbons could generate methane and ethane – the main components of natural gas which are usually found together with crude oil. The conversion degree (maturity) of the kerogen is determined by the Carbon Preference Index (CPI) which is defined as a ratio of the mass of *n*-alkanes with an odd-number of carbon atoms to the mass of *n*-alkanes with an even-number of carbon atoms [2]. Immature kerogen is characterized by the CPI from 2 to 5 while the CPI of the crude oil is in 0.9–1.3 range. This phenomenon is caused by thermal decomposition of *n*-alkanes with an odd-number of carbon atoms, which are predominant in the organic matter of dead organisms, as the kerogen bed continues to descend into the earth's crust [1].

5.1.2 Crude oil reserves and extraction

Crude oil is usually found in places remote from source rocks (fine-grained sedimentary rocks e.g. clays, shales and carbonates) in which the transformation of kerogen to liquid hydrocarbons took place. It is because of the crude migration caused by gravitational forces, hydraulic and hydrostatic pressure, capillary forces and tectonic movement [1].

The release of oil from the solid particles of kerogen and its movement in the narrow pores and capillaries of the source rock is called *primary migration*. The *secondary migration* takes place through the wider pores of carrier beds (e.g. sandstones and carbonates) after the hydrocarbons are expelled from the source rock. As they are less dense than water, which usually filled the pores of permeable rocks, they migrated upwards. The oilfields and gas fields are formed where an impermeable layer of rock of the right shape stops the migration of oil and natural gas, allowing them to gradually accumulate [1,3,4]. The major class of crude oil traps are structural traps. They are formed by movement of the earth's crust during which plates can be rippled (anticline trap) and sheared (fault trap) (Fig. 5.2) or by upward movement of salt masses from deeply buried evaporite beds [3].

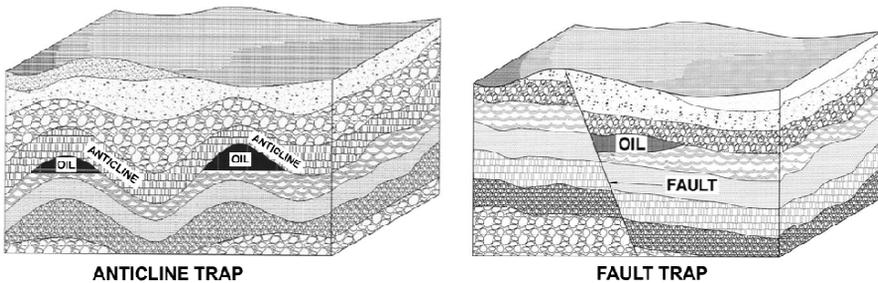


Fig. 5.2. The types of structural traps [5].

A second major class of oil traps are the stratigraphic traps. They are laterally limited reservoirs sealed by impermeable strata. Stratigraphic traps can be formed from deposits of alluvial or submarine fans, fluvial sands, channel and bar sands, carbonate shoals or carbonate reefs [6].

There are many methods which help geologists locate crude oil deposits, unfortunately none of them has proven 100 percent effective. One of the best techniques is seismic exploration which utilizes either shock waves or radio waves to obtain information about possible deposits. Fig. 5.3 represents the principles of seismic exploration.

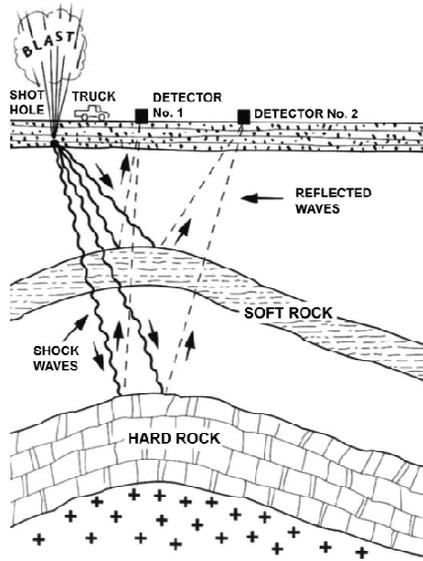


Fig. 5.3. Principles of seismic exploration [5].

To check that the located reservoir contains crude oil, a well must be drilled. Drilling operations are limited only by technical ability. Currently it is possible to drill wells with a depth exceeding 10 km [5] and to drill horizontal wells that allows the reaching of deposits that are not directly underneath the point of entry [7]. An example of directional drilling is shown in Fig. 5.4.

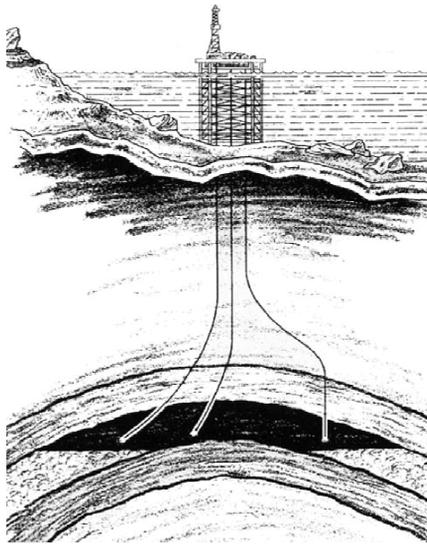


Fig. 5.4. Directional drilling from a platform [5].

The world's total oil resources are estimated to roughly 9 to $13 \cdot 10^{12}$ barrels (1.4 to 2.1 trillion m^3). Only about 30% of that amount falls to conventional crude oil resources. The remaining 70% makes up heavy oil, extra heavy oil and bitumen (see Fig. 5.5) [8].

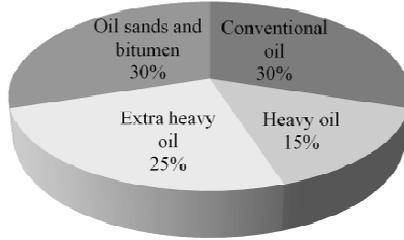


Fig. 5.5. Total world oil reserves [8].

The amount of crude oil which can be extracted from an oilfield depends on the reservoir characteristic and limitation of the existing petroleum extraction technologies. Because of that, only a fraction of the total estimated quantity of crude oil in the oilfield can be recovered. The ratio of the recoverable oil reserves to the total amount of crude oil is called *recovery factor* and varies greatly among oil fields. The part of the recoverable quantity of crude oil which extraction is commercially viable is referred to as oil reserves. According to the World Factbook [9], the world's proved crude oil reserves amount to about 1.378 trillion barrels (one oil barrel is equal to about 150 dm^3). Table 5.2 presents the crude oil reserves for selected countries.

Table 5.2. Proved crude oil reserves for selected countries (2010) [9].

Rank	Country	Crude oil reserve, mld barrels
1	Saudi Arabia	264.6
2	Canada	175.2
3	Iran	137.6
4	Iraq	115.0
5	Kuwait	104.0
6	United Arab Emirates	97.8
7	Venezuela	97.8
8	Russia	79.0
9	Libya	47.0
10	Nigeria	37.5
71	Poland	0.096

5.1.3 Petroleum refining

Raw crude oil is not generally useful, therefore it must be processed into other products in oil refineries. Refineries are typically large industrial complexes with characteristic extensive piping which delivers streams of fluids to large chemical processing units. They are processing about a hundred thousand to several hundred thousand barrels of crude oil a day.

The crude oil can be processed into many products which are shown in Fig. 5.6. All these petroleum products are usually divided into three groups: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt).

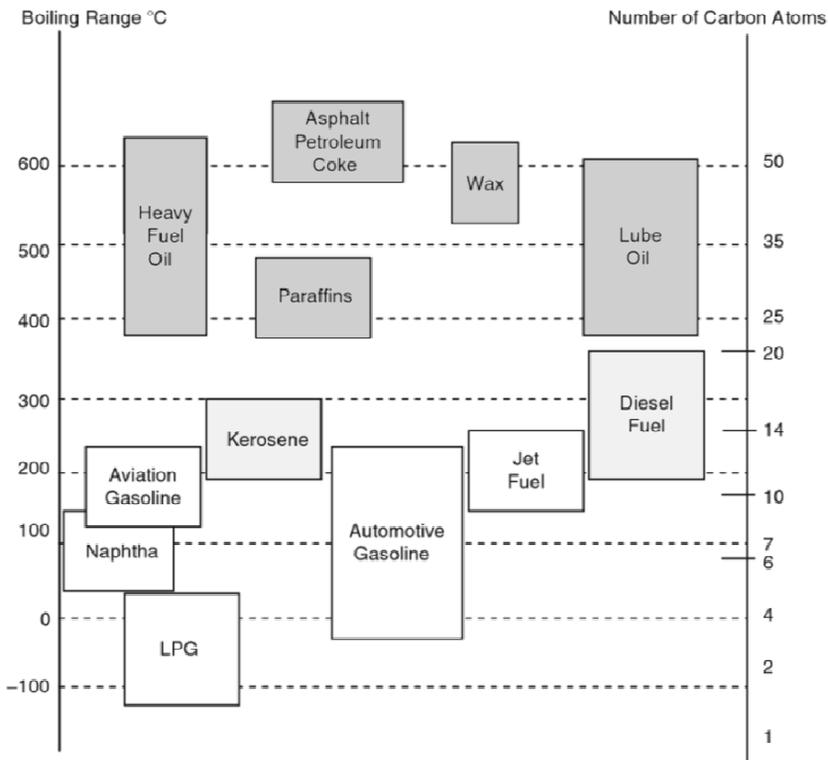


Fig. 5.6. Principal petroleum products with carbon numbers and boiling range [10].

Each refinery is adapted to a specific range of petroleum feedstock from which a desired distribution of products is obtained. Refining processes can be classified into two major groups: physical separation and chemical conversion (Table 5.3).

Table 5.3. Major refining processes in modern refineries [10].

Physical separation	Chemical conversion	
	Catalytic	Thermal
Distillation	Reforming	Delayed coking
Solvent deasphalting	Hydrotreating	Flexicoking
Solvent extraction	Hydrocracking	Visbreaking
Solvent dewaxing	Alkylation	
	Isomerisation	

5.2 Crude oil composition

The crude oil is a mixture of hydrocarbons and other non-hydrocarbon compounds of various molecular weights. Inorganic sediments and water may also be present. The molecular composition is closely connected with the age of crude oil. In older deposits, the light hydrocarbons are predominant, while relatively young deposits mostly consist of heavy hydrocarbons, condensed polycyclic aromatic hydrocarbons and asphaltenes. The elemental composition of crude oil varies over fairly narrow limits, as can be seen in Table 5.4.

Table 5.4. Chemical constitution of crude oil [11].

Element	Content, wt%
Carbon	83–87
Hydrogen	10–14
Nitrogen	0.1–2
Oxygen	0.1–1.5
Sulfur	0.5–6
Metals	<0.1

Hydrocarbons in crude oil can be divided into three main types: alkanes, cycloalkanes and aromatic hydrocarbons. Asphaltenes, which occur mainly in the heaviest fractions of crude oil, are rated by some researchers among hydrocarbons (Table 5.5).

Table 5.5. Average and range of hydrocarbons contents in crude oil [12].

Hydrocarbon	Range, %	Average, %
Alkanes	15–60	30
Cycloalkanes	30–60	49
Aromatics	3–30	15
Asphaltenes	residues	6

Other researchers create a separate group for asphaltenes and resins, due to their incompletely defined chemistry [13].

5.2.1 Hydrocarbons

Hydrocarbons molecules contain only carbon and hydrogen. According to their structure they are grouped into many chemical families. All structures are based on the quadrivalency of carbon [14]. Alkenes, which molecules contain one double bonds, are practically absent or in trace amounts in crude oil, therefore, they will not be described below.

a. Alkanes

Alkanes (usually called *paraffins*) are the second most occurring group of hydrocarbons in crude oil (Table 5.5). They are saturated (i.e. have not multiple bonds) hydrocarbons with straight or branched chains. Branched alkanes are called *isoparaffins* or *isoalkanes*. The hydrocarbon chains consist of carbon atoms linked to four other atoms which can be either carbon or hydrogen. Their general formula is C_nH_{2n+2} where n is the number of carbon atoms. Depending on the oilfield, the crude oil can consist mostly of n -paraffins. There are also crudes with equal concentration of both types of hydrocarbons, n -paraffins and isoparaffins.

The alkanes found in crude oil have generally from 1 to 60 carbon atoms per molecule. Because of branching, the number of isomers (molecules with exactly the same number of atoms, but different structure) is huge, and it is practically impossible to identify each compound occurring in crude oil. For example, octadecane ($C_{18}H_{40}$) has over 60 000 isomers, but for pentacosane ($C_{25}H_{52}$), the number of isomers exceeds 36 millions.

Due to lower boiling point than other types of hydrocarbons, alkanes occur mostly in the low-boiling fraction of crude oil. The boiling point of the paraffins increases with the number of carbon atoms. For molecules of low carbon number, the addition of a carbon increases the boiling point of about 25 °C. Further addition results in a smaller increase [13]. Isoparaffins have boiling points lower than normal paraffins with the same number of carbon atoms. Table 5.6 gives some physical properties of selected paraffins.

b. Cycloalkanes

Cycloalkanes (called *naphthenes*) occur in crude oil at an average concentration of about 50 wt% (Table 5.5). They contain cyclic structure in all or part of the skeleton. Naphtenes, which are found in crude oil, mostly have one carbon ring consisting mainly of 5 or 6 carbon atoms, but the compounds with more rings also

can be found. In these rings, each hydrogen atom can be substituted by an alkyl chain that is either a straight chain or branched. Cycloalkanes have similar properties to alkanes, but have a higher boiling point and higher specific gravity than alkanes with the same number of carbon atoms (Table 5.7). Some of the four and five ring cycloparaffins serve as biochemical markers, due to retained in part the structure of living matter at the crude oil's origin (steranes and hopanes) [13].

Table 5.6. Physicochemical characteristic of selected alkanes [13].

	Overall formula	Structural formula*	Molecular weight	BP, °C, (1atm)	SG_4^{15}
methane	CH ₄	C	16.0	-161.5	0.260
ethane	C ₂ H ₆	C—C	30.1	-88.6	0.377
propane	C ₃ H ₈	C—C—C	44.1	-42.1	0.508
<i>n</i> -butane	C ₄ H ₁₀	C—C—C—C	58.1	-0.5	0.585
isobutane	C ₄ H ₁₀	$\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} - \text{C} \end{array}$	58.1	-11.7	0.563
<i>n</i> -pentane	C ₅ H ₁₂	C—C—C—C—C	72.1	36.1	0.631
<i>n</i> -heptane	C ₇ H ₁₆	C—C—C—C—C—C—C	100.2	98.4	0.688

* Hydrogen atoms are omitted to simplify illustration, BP – boiling point, SG_4^{15} – specific gravity.

Table 5.7. Physicochemical characteristics of selected cycloalkanes [13].

	Overall formula	Structural formula*	Molecular weight	BP, °C, (1 atm)	SG_4^{15}
cyclopentane	C ₅ H ₁₀	$\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \quad \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{C} \end{array}$	70.1	49.3	0.750
methylcyclopentane	C ₆ H ₁₂	$\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \quad \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{C} \quad \text{C} \end{array}$	84.2	71.8	0.753
cyclohexane	C ₆ H ₁₂	$\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \quad \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{C} \quad \text{C} \end{array}$	84.2	80.7	0.783
methylcyclohexane	C ₇ H ₁₄	$\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \quad \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{C} \quad \text{C} \end{array}$	98.2	100.9	0.774

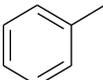
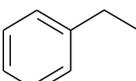
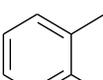
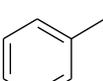
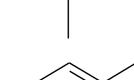
* Hydrogen atoms are omitted to simplify illustration, BP – boiling point, SG_4^{15} – specific gravity

a. Aromatic hydrocarbons

The third group of hydrocarbons which occurs in crude oil in concentration below 15 wt% are aromatic hydrocarbons. Those compounds have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached. Each of these hydrogen atoms can be substituted in the following ways [13,14]:

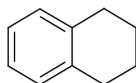
- by alkyl groups to give alkyl-aromatics (e.g. toluene, xylenes etc.) The prefixes *ortho*, *meta* and *para* are used to show the position of substitutes on the ring (see Table 5.8).

Table 5.8. Physicochemical characteristic of selected aromatic hydrocarbons [13].

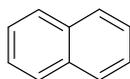
	Overall formula	Structural formula*	Molecular weight	BP, °C, (1atm)	SG_4^{15}
benzene	C_6H_6		78.1	80.1	0.884
toluene	C_7H_8		92.1	110.6	0.871
ethylbenzene	C_8H_{10}		106.2	136.2	0.871
<i>o</i> -xylene	C_8H_{10}		106.2	144.4	0.884
<i>m</i> -xylene	C_8H_{10}		106.2	139.1	0.868
<i>p</i> -xylene	C_8H_{10}		106.2	138.4	0.865

* Hydrogen atoms are omitted to simplify illustration, BP – boiling point, SG_4^{15} – specific gravity.

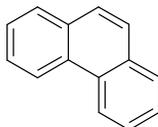
- by naphthenic ring forming a naphthene aromatic such as tetralin



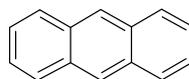
- by other aromatics giving condensed polynuclear aromatics



naphthalene



phenanthrene



anthracene

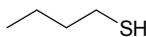
5.2.2 Non-hydrocarbon compounds

Except for hydrocarbons, crude oil consists of other components such as heteroatom (sulfur, oxygen and nitrogen) and trace metals (iron, nickel, vanadium, cobalt, copper and magnesium) -containing compounds. The majority of those components (especially trace metals) are bounded with the structure of asphaltenes and resins.

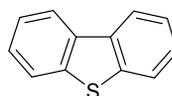
Sulfur is the heteroatom most frequently found in crude oil. Its concentration varies from 0.1 to more than 8 wt% [13]. The sulfur content is correlated with the gravity of the crude oil and therefore, its quality. Sulfur might be present in crude oil in inorganic forms (i.e. elemental S, hydrogen sulfide H_2S , carbonyl sulfide COS) and bounded with organic molecules (sulfides, disulfides, thiols, mercaptans thiophenes and their derivatives). The knowledge of these compounds is important due to their undesirable attributes, such unpleasant odor, catalyst poisoning etc. The example of sulfur compounds found in crude oil is given below.



hydrogen sulfide



n-butyl mercaptan
(butanethiol)

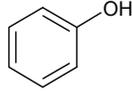


dibenzothiophene

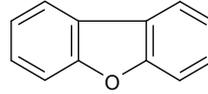
Concentration of oxygen compounds in crude oil is generally smaller than sulfur compounds. Oxygen is present in crude oil in the form of phenols, furanes and benzofuranes, carboxylic acids and esters.



acetic acid

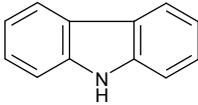


phenol

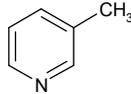


dibenzofurane

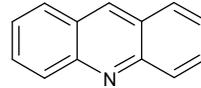
Nitrogen is found in lighter fractions of crude oil as basic compounds and in heavier fractions as non-basic compounds. Nitrogen types include amides, amines, carbazoles, and pyridines.



dibenzopyrrole



2-methyl pyridine



acridine

5.2.3 Other compounds

Asphaltenes constitute a general class of aromatic-type substances which are defined as the *n*-heptane-insoluble, toluene-soluble component of a carbonaceous material such as crude oil, bitumen or coal. The portion that is soluble in *n*-heptane is named maltenes (Fig. 5.7).

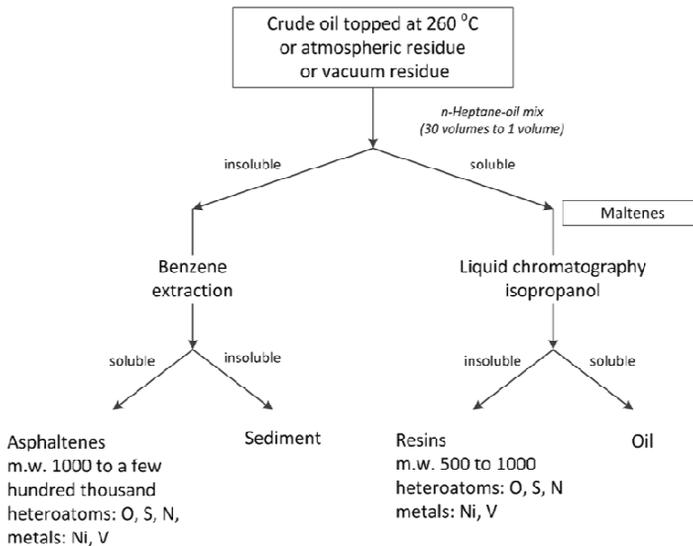


Fig. 5.7. Separation procedure for heavy fractions [13].

An average molecular mass of asphaltenes, which occur in crude oil, exceeds 3000 units. The structure of those compounds is complex and difficult to determine. It is assumed that they constitute of condensed polynuclear aromatic layers linked by saturated chains (Fig. 5.8).

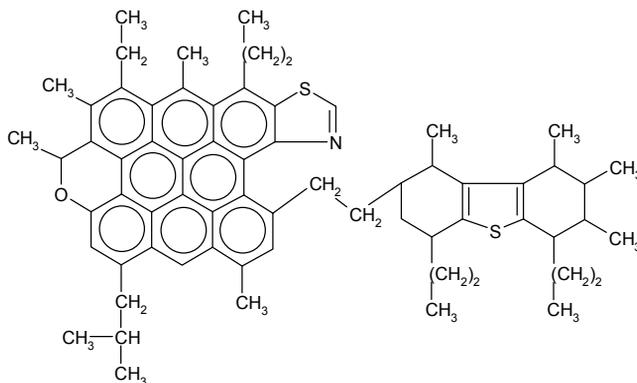


Fig. 5.8. Fragment of hypothetical molecule of asphaltenes [1].

Due to high concentrations of heteroatoms in asphaltenes, which causes pollution problems (e.g. catalyst poisoning, corrosion) the refining industry seeks either to eliminate asphaltenes or to convert them to lighter materials. To eliminate the asphaltenes from oil, propane and butane are used. As a result of this process, deasphalted oil and asphalt are obtained [13].

Resins are part of the maltenes eluted during liquid chromatography by the more polar solvents (Fig. 5.7). They have generally aromatic characteristics and contain heteroatoms (N, O, S) and occasionally Ni and V. It is believed that the resins are responsible for dissolving and stabilizing the solid asphaltene molecules in crude oil by surrounding and suspending them in liquid oil [12].

5.3 Properties of crude oil

Because of the complex composition of crude oil, its physical and chemical properties vary depending on the oilfield from which crude oil comes. The differences between the various types of crude oil arise from its density, viscosity, appearance, sulfur content and molecular structure. The vast number of possible variations of the above mentioned properties may also influence the suitability of the different types of the crude oil for specific products and the resulting quality of these products. Refiners often mix selective crude oils to optimize a product which requires careful examination of the various crude assays and modeling the refinery operation to set the crude oil mix and its operation parameters.

The crude oil assay is a detailed report which describes the properties of the whole crude, as well as the major fractions into which crude is distilled at the refinery. The data obtained in laboratories and pilot plants are the basis of crude oil classification [15]. Crude oil assay should contain at least a distillation curve and a specific gravity curve. Most assays, however, contain yields generated from the physical distillation, specific gravity, composition determined by gas chromatography, sulfur, nitrogen, viscosity and others. The most important tests, due to crude oil classification, are the measurements of density and viscosity, fractional distillation and determination of sulfur content, which are discussed below.

5.3.1 Density and API gravity

The API gravity scale has been universally adopted and commonly used in the crude oil industry worldwide since about 1921. The API gravity is an arbitrary scale developed by the American Petroleum Institute (API) as a measure of the density of petroleum liquids at 60 °F (15.56 °C) relative to the density of water at 60 °F. The values of API gravity are expressed as degrees API and denoted as °API. The scale is calibrated such that most petroleum liquids will have API gravities between 10 and 70 °API. The API gravity is inversely related to the density of the petroleum liquid which means that the higher the API gravity, the lower the liquid density. Density of the crude oil is strictly connected with its chemical constitution. Crudes with a predominance of lighter paraffins are characterized by lower density than crudes with a high concentration of aromatic hydrocarbons. Higher concentration of sulfur, nitrogen and asphaltenes implies an increase of density. Average densities of common crude oils are in the 0.8–1.0 g/cm³ range.

5.3.2 Viscosity

Crude oil's viscosity is one of its most important properties which influences crude mobility during pipeline transportation, pumping operation etc. Knowledge of the relationship between viscosity and temperature is crucial during the calculation of pressure drop in pipelines and refinery tubulation and during the design of pumps and heat exchangers.

Viscosity is a key parameter in case of any flow measurements of fluids such as liquids, semi-solids, gases and even solids are carried out. Viscosity describes the fluid's internal resistance to flow and may be thought of as a measure of fluid friction. There are actually two main quantities being called *viscosity*, namely: *dynamic viscosity* (also called absolute viscosity or just viscosity), and *kinematic viscosity*. SI physical unit of the former quantity is the Pascal-second (Pa·s). Kinematic viscosity is defined as a ratio of dynamic viscosity of liquid to its

density. The SI unit of kinematic viscosity is square meter per second (m^2/s). However, because of its magnitude the more common unit of kinematic viscosity is the square centimeter per second (cm^2/s), called *stokes*.

Kinematic viscosity is a measure of the resistive flow of a liquid under the influence of gravity. It is frequently measured using a device called capillary viscometer, an example of which is the Ubbelohde-type capillary tube viscometer.

5.3.3 Fractional distillation

As mentioned before, crude oil consists of a vast number of compounds, mostly hydrocarbons. Before it can be used, these compounds must be sorted into batches (fractions) of compounds with similar properties. This is accomplished in the crude distillation units in refinery. Normally there are two complementary units which separate crude oil into fractions: an atmospheric unit and a vacuum unit. Typical product streams leaving the refinery are: liquefied petroleum gas (LPG), gasoline (also known as petrol), naphtha, kerosene (jet fuel), diesel fuel, fuel oils, lubricating oils, paraffin wax, asphalt, tar and petroleum coke.

Fractional distillation is also one of the laboratory methods which is used to characterize and classify crude oil. The distillation is carried out under the atmospheric pressure in a relatively simple apparatus consisting of a heated flask connected to a water cooled condenser, which condenses the rising vapors. The fraction distilled is collected in a graduated cylinder. The temperature of the rising vapours is recorded at a specific interval of the collected distillates. The obtained data can be used to plot a distillation curve which represents the relation between the temperature and volume of product at a given temperature (Fig. 5.). As can be seen, at low temperatures the light crude oils are characterized by a higher volume of the distilled fraction than heavy crudes. For example, at 400 °F (about 204 °C*) one can obtain about 35 cm^3 of the distilled fraction from 100 cm^3 of Bonny light crude oil, and only about 12 cm^3 from the same amount of Western Canada heavy crude.

5.3.4 Sulfur content

The concentration of sulfur in crude oil varies from 0.1 to 8 wt% [13]. Knowledge of its concentration is very important due to the difficulties which can be caused by sulfur components during refining crude oil. In crude oil, both corrosive and non-corrosive sulfur compounds are found.

* to convert Fahrenheit degrees to Celsius degrees you should use the following equation: $[\text{°C}] = 5/9 \cdot ([\text{°F}] - 32)$

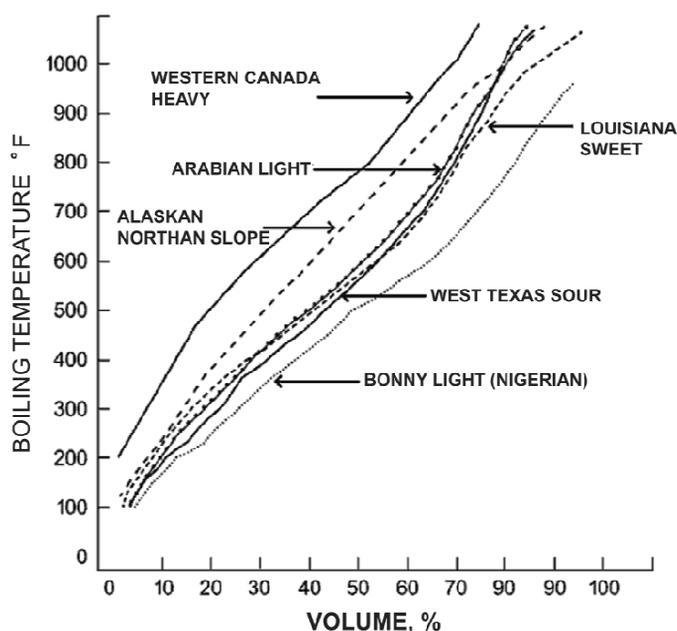


Fig. 5.9. Distillation curves of crude oil [16].

These compounds in many cases have noxious or harmful effects and must be removed or converted to less harmful compounds during the refining process. Sulfur compounds (e.g. hydrogen sulfide) contribute to the corrosion of metal, poisoning of catalysts (especially those with noble metals like platinum) and have a negative effect on the quality of refinery products, such as gasoline or diesel fuel. After the combustion of sulfur containing fuels, the sulfur oxides (SO_x) are emitted. The predominant form of SO_x found in the lower atmosphere is SO_2 . This compound together with other sulfur oxides (e.g. SO_3) is a precursor to acid rains because it dissolves readily in water present in the atmosphere to form sulfurous acid (H_2SO_3). SO_2 causes lung function reduction, irritation of the eyes, nose and throat, and premature mortality. Moreover sulfur oxide emissions cause a negative impact to vegetation, including forests and agricultural crops.

At a time when sulfur content restrictions on the use of fossil fuels are causing shortages and making it more difficult for industry to achieve air quality standards, data are needed regarding the quality of available world crude oil supplies. There are many methods for sulfur content determination. The methods based on gas chromatography, spectrophotometry and titration are the most popular. In case of titration, a sample of crude oil is burnt and sulfur oxides are absorbed in 3 vol% H_2O_2 solution. To ensure that all sulfur is converted to sulfur oxides, the Wickbold combustion apparatus is used which uses the oxygen-hydrogen flame to sample

decomposition. The Wickbold apparatus is particularly suited for trace compounds (such as chlorine, sulfur, mercury etc.) analysis by virtue of good combustion characteristics, high sample introduction rate, and a system isolated from atmospheric contaminants.

5.4 Classification of crude oil

The complex composition of crude oil affects its physical (density, viscosity) and chemical (content of sulfur, nitrogen, trace metals, proportion of the various hydrocarbon fractions etc.) properties. These properties affect the ease with which the refineries can process various crude oils into the different products required by the consumers. From the refinery point of view the most valuable crude oils are those which are characterized by a high concentration of lighter hydrocarbons and with low sulfur and other non-hydrocarbon impurities content. The aim is to turn the crude oil into as much of the lighter, higher priced products and as little of the heavier, lower priced products as is cost-effectively possible. Because of that described above, desirable types of crude oils have a higher price than crude oils which have high concentration of heavy hydrocarbons, asphaltenes and impurities.

There are many criteria on which crude oils are classified. The most common classifications are based on API gravity, sulfur content, light fraction content and the oil markers, also known as the crude oil benchmarks.

a. API gravity

The different crude oils are graded by their density or specific gravity and assigned an API gravity. The API gravity can range from 8.5 for very heavy crude oils to 44 for light crudes.

- Light crudes – API gravity higher than 38 °API (less than 835 kg/m³).
- Medium crudes – API gravity between 38 °API and 29 °API (835–882 kg/m³).
- Heavy crudes – API gravity between 29 °API and 8.5 °API (882–1011 kg/m³).
- Very heavy crudes – API gravity below 8.5 °API (> 1011 kg/m³) [10].

The classification based on API gravity is not uniform. For example, according to the United States Geological Survey, there are only two types of petroleum: light crude oil with API gravity greater than 20 °API, and heavy crude oil with API gravity between 20 and 10 °API [17].

b. Sulfur content

The classification based on sulfur content distinguishes two types of crude oil [18]:

- Sweet, or low sulfur crudes with less than 0.5 wt% of sulfur.
- Sour, or high sulfur crudes, with over 0.5 wt% of sulfur.

This classification is dated from the time when the main use of crude oil was for the manufacture of lighting kerosine. Kerosine during combustion emits a nauseating smell if obtained from high sulfur crude oil. Crude quality was determined by tasting the crude. A low sulfur crude oil tested sweet, whereas crude oil with higher sulfur concentration tested sour.

Sweet crudes have the highest price in the market. Due to low percentage of wax, they are characterized by low viscosity which facilitates easy pumping and transportation of oil and reduces the chance of oil clogging while processing. Sour crudes have a lower price because of the bigger concentration of sulfur impurities and necessity of refining to obtain gasoline and kerosene.

According to the Russian classification, crudes are divided into four classes [19]:

- Class 1 - Low sulfury with sulfur content up to 0.60 wt%.
- Class 2 - Sulfury with sulfur concentration in range 0.61–1.80 wt%.
- Class 3 - High sulfury with sulfur concentration in range 1.81–3.50 wt%.
- Class 4 - Extra high sulfury with over 3.50 wt% of sulfur.

c. Content of the light fractions

Another classification takes into consideration the chemical composition of crude oil, in particular the content of light fraction (boiling point below 320 °C) which can be determined by fractional distillation. This classification distinguishes the following types of crudes:

- Crude oil with low light fractions content (below 25% of light fractions)
- Crude oil with medium content of light fractions (25–50% of light fractions)
- Crude oil with high content of light fractions (50–70% of light fractions)
- Crude oil with very high content of light fractions (above 70% of light fractions)

d. Crude oil benchmarks

The petroleum industry often characterizes crude oils according to their geographical source, e.g. Alaska North Slope Crude. Oils from different

geographical areas have unique properties. They can vary in consistency from a light volatile fluid to a semi-solid. Classification of crude oil types by geographical source has, however, flaws due to the large number of crude oil sources. According to the Energy Intelligence Group, there are 161 different blends (mixtures of crude oil from different oilfields) in total. To simplify oil market operations (e.g. oil pricing) the crude oil benchmarks were introduced. There are four primary benchmarks [20]:

- West Texas Intermediate (WTI), also known as Texas light sweet - light crude with API gravity of around 39.6 and sulfur content about 0.24 wt%.
- Brent Blend - combination of crude oil from 15 different oil fields located in the North Sea. It is characterized by API gravity of 38.3 degrees and sulfur content about 0.37 wt%.
- Dubai Crude - light sour crude oil extracted from Dubai. Dubai Crude has a gravity of 31 °API and sulfur content of 2 wt%.
- OPEC basket consists of eleven crude streams representing the main export crudes of all member countries, weighted according to production and exports to the main markets. The crude oil streams in the basket are: Saharan Blend (Algeria), Minas (Indonesia), Iran Heavy (Islamic Republic of Iran), Basra Light (Iraq), Kuwait Export (Kuwait), Es Sider (Libya), Bonny Light (Nigeria), Qatar Marine (Qatar), Arab Light (Saudi Arabia), Murban (UAE) and BCF 17 (Venezuela). The OPEC basket is characterized by API gravity of 32.7 degrees and sulfur content of 1.77 wt%.

5.5 Laboratory work: classification of crude oil

The main purpose of the laboratory work is the classification of a crude oil on the basis of density, viscosity, fractional distillation and the determination of sulfur content. The methods used in the characterization of crude oil are briefly described below.

API gravity

The determination of the crude oil density is carried out by means of the hydrometer method. A hydrometer is placed in the sample after the temperature has stabilized. A graduated scale shows how deep the hydrometer sinks in the sample. In order to calculate the density, the thermal-expansion coefficient, which describes the relation between the density and the temperature, must be taken into account. After determination of the sample density, the relative density (i.e. ratio of the sample density to the water density) and the API gravity is calculated in order to classify crude oil according to the API scale.

Viscosity

The determination of kinematic viscosity of crude oil is based on the time measurement of a sample flow between two marks on a viscometer. The time recorded is proportional to the kinematic viscosity of a liquid. The kinematic viscosity of the crude oil sample is obtained by multiplication of the measured time and the capillary constant which is provided with viscometer.

Content of the light fractions

The fractional distillation is one of the laboratory methods which is used for the characterization and classification of crude oil. The distillation is carried out under the atmospheric pressure, in a relatively simple apparatus consisting of a heated flask connected to a water cooled condenser, which condenses the rising vapors. The fractions distilled are collected in a graduated cylinder. The temperature of the rising vapors is recorded at a specific interval of the collected distillates. The data obtained are used to plot a distillation curve which represents the relation between the temperature and the volume of product distilled off. The distillation head holds a thermometer to allow the temperature of the vapors to be monitored during the distillation process.

Sulfur content

The method of determining total sulfur content is based on the mineralization of crude oil sample using the Wickbold combustion apparatus. Sulfur oxides formed during combustion are absorbed in hydrogen peroxide (H₂O₂) solution to form sulfuric acid. Sulfate ions are determined by visual titration.

References

- [1] Surygała J., Ropa naftowa a środowisko przyrodnicze, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2001.
- [2] Peters K.E., Walters C.C. Moldowan J.M., The biomarker guide: Biomarkers and isotopes in petroleum systems and earth history, Cambridge University Press, Cambridge 2005.
- [3] Encyclopedia Brytanica, <http://www.britannica.com/>.
- [4] Shah S., Crude - the story of oil, Seven Stories Press, New York 2004.
- [5] Grace R., Oil - An overview of the petroleum industry, Gulf Publishing Company, Houston 2007.
- [6] Zimmerle W., Zimmerle H., Petroleum sedimentology, Kluwer Academic Publishers, Dordrecht 1995.
- [7] http://www.naturalgas.org/naturalgas/extraction_directional.asp

- [8] Aulboldwarej H. et. al., Oilfield Review 2006, 18, 34–53.
- [9] <https://www.cia.gov/library/publications/the-world-factbook/geos/xx.html>
- [10] Fahim M.A., Al-Sahhaf T.A., Lababidi H.M.S., Elkilani A., Fundamentals of petroleum refining, Elsevier, Oxford 2010.
- [11] Speight J.G., The chemistry and technology of petroleum, Marcel Dekker, New York 1999.
- [12] Hyne N.J., Nontechnical guide to petroleum geology, exploration, drilling, and production, PennWell Corporation, Tulsa 2001.
- [13] Petroleum refining: crude oil, petroleum products, process flowsheets, ed. J-P. Wauquier, Éditions Technip, Paris 1995.
- [14] Morrison R.T., Boyd R.N., Chemia organiczna, PWN, Warszawa 2010.
- [15] Jones D.S.J., Pujadó P.R., Handbook of petroleum processing, Springer, Dordrecht 2006.
- [16] Leffler W.L., Petroleum refining in nontechnical language, PennWell Corporation, Tulsa 2000.
- [17] http://pubs.usgs.gov/fs/2006/3133/pdf/FS2006-3133_508.pdf
- [18] Riegel E.R., Kent J.A., Riegel's handbook of industrial chemistry, Kluwer Academic, New York 2003.
- [19] <http://www.vivaldosa.com/Docs/Classes%20of%20crude%20oil.pdf>
- [20] http://tonto.eia.doe.gov/ask/crude_types1.html

6 Properties of diesel fuel

Karolina Jaroszevska

6.1 Introduction

Diesel fuel is a liquid fuel used in compression ignition engines. The expansion of the internal combustion engine began in the late 19th century. By 1898 Rudolf Diesel was granted his innovative engine that uses the heat of compression to initiate ignition to burn the fuel [1]. About fifty years earlier, in the 1850s, Ignacy Łukasiewicz started to extract crude oil in Poland. In 1853 he elaborated the process of distillation of crude oil to produce lamp oil (kerosene) [2]. The demand for the petroleum as a fuel for lighting around the world quickly grew. Oil exploration in North America during the early 20th century later led to the U.S. becoming the leading producer of kerosene. Because only a fraction of the crude was a good lamp oil, producers of it had to figure out what to do with the rest of the petroleum. Rudolf Diesel, recognizing that the liquid petroleum byproducts might be a good engine fuel began to experiment with one of them. His work resulted in a successful prototype engine. Until now, both the engine and the fuel still bear his name.

The first commercial diesel engines were huge and worked at low speeds. Slow but steady progress in the mechanical design of engines was made over the next hundred years. They were originally used as a more efficient replacement for stationary steam engines. Since the 1910s, diesel engines have been used to power ships, trains, and industrial plants. In the 1930s, they slowly began to be used in a few automobiles, however, an effort to extend the engine's use to passenger cars was interrupted by World War II. After the war, diesel passenger cars became very popular in Europe, but they have not enjoyed similar success in the United States yet. As of 2007, about 50 percent of all new car sales in Europe are diesel. Their success comes from their efficiency, economy, and reliability.

6.2 Production of diesel fuel

Diesel fuel is made from crude oil. An industrial process plant where crude oil is processed and refined into more useful petroleum products (e.g. gasoline, diesel fuel, asphalt base etc.) is a refinery. Today's refinery is a highly integrated combination of interdependent processes. These processes can be divided into five basic categories [3]:

a. *Separation processes.* Distillation is the most common form of separation technique used in petroleum refineries (Fig. 6.1). Crude oil is a mixture of thousands different chemicals, generally *hydrocarbons*. Before crude oil can be used, these compounds must be sorted into batches of compounds with similar properties, i.e. *fractions*. Crude oil is heated and put into a distillation column. Different products boil off and can be recovered at different temperatures. Distillation does not change the chemical composition of the feedstock. The *diesel fuel fraction* is mixture that boils between 150 and 360 °C.

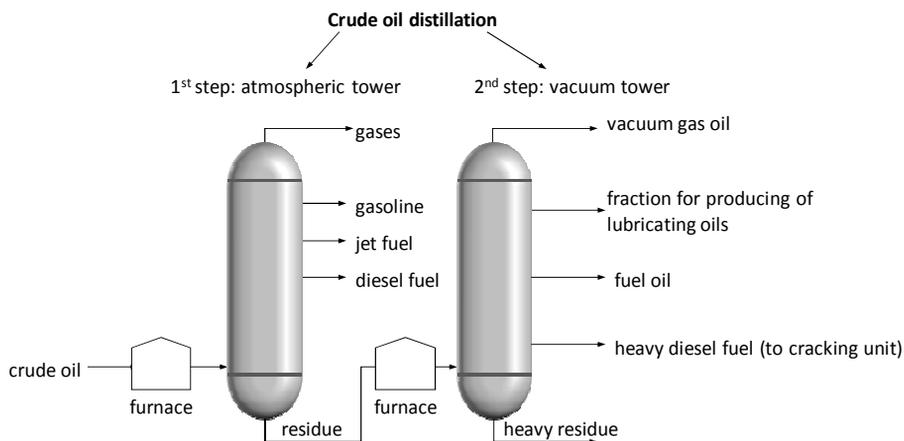


Fig. 6.1. Fractional distillation of crude oil.

b. *Conversion processes* fundamentally change the molecular structure of the feedstock, leading to different size and/or structure of hydrocarbon molecules. These processes include:

- Decomposition (dividing) by cracking and hydrocracking.
- Unification (combining) through alkylation.
- Alteration (rearranging) with isomerization and reforming.

The major conversion processes, which convert heavier fractions of crude oil into diesel fuel fraction, are catalytic cracking and hydrocracking.

c. *Upgrading processes* improve the quality of a material by using chemical reactions to remove undesirable compounds present in trace amounts. The most commonly used upgrading process for diesel fuel is hydrodesulfurization to remove sulfur [4].

d. Formulating and blending is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce the end products with specific performance properties.

e. Other refining operations include, e.g. hydrogen production, sulfur recovery, steam and power generation.

Commercial diesel fuel is produced by blending appropriate fractions of crude oil obtained in the processes of petroleum treatment i.e. from separation and conversion process. The refineries blend the available streams to meet all performance, regulatory, economic and environmental requirements. Diesel oil is a mixture of components separated from crude oil but also of some additives [5]. There are numerous additives such as: lubricity improvers, antioxidants, stabilizers and metal deactivators. Cetane improvers are also used which raise the cetane number and improve ignition quality. Biocides may be used to reduce the formation of bacteria and fungi, which helps to prevent fuel filter from plugging. At low temperatures, depressants may be added to develop cold flow properties. In some cases, deicers may also be used to prevent fuel line from freezing. Diesel fuel is widely used in: on-road transportation, agriculture, marine shipping, off-road uses (e.g., mining, construction) and military transportation.

A strong growth in diesel fuel demand is mainly driven by developments in automotive diesel, which is growing rapidly in most countries (Table 6.1). Projections for the number of passenger and commercial vehicles show that there will be an additional 550 million cars by 2030, compared to 2010 level [6].

Table 6.1. Projections of transportation fuels global demand, (million barrels per day) [6].

	2009	2015	2020	2030
Diesel fuel	24.3	27.4	29.8	34.1
Gasoline	21.2	22.0	23.4	25.0

6.3 Diesel fuel chemistry

6.3.1 Molecular components

Diesel fuel is a mixture of various petroleum-derived components: paraffins, naphthenes, aromatics and olefins, each with their own physical and chemical properties (Table 6.2) [7]. Paraffins, naphthenes and olefins are the terms used in the petroleum industry to describe hydrocarbons respectively, alkanes, cycloalkanes and alkenes. Each class is a family of individual hydrocarbon

molecules that share a common structural feature, but differ in size (number of carbon atoms) or geometry. The classes also differ in the ratio of hydrogen to carbon atoms and in the way the carbon atoms are bonded to each other.

a. Paraffins (alkanes)

There are two subclasses of paraffins: *n-paraffins* and *isoparaffins*. *n*-Paraffins have carbon atoms linked to form chain-like molecules, with each carbon – except those at the ends – bonded to two others, one on either side. Isoparaffins have a similar carbon backbone, but they also have one or more carbons branching off from the backbone. *n*-decane and 2,4-dimethyloctane (Table 6.2) have the same chemical formula, $C_{10}H_{22}$, but different chemical and physical properties. Compounds like this, with the same chemical formula, but a different arrangement of atoms, are called *structural isomers*. The paraffins in diesel fuel have chains of C_8 to C_{24} length.

b. Naphthenes (cycloparaffins, cycloalkanes)

Naphthenes have some of their carbon atoms arranged in a ring [8]. The naphthenes in diesel fuel have rings of five or six carbons. Sometimes two or more rings are fused together, with some carbons shared by adjacent rings.

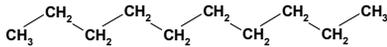
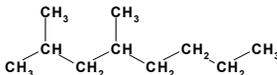
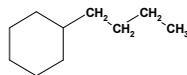
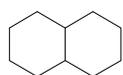
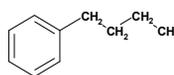
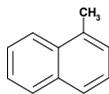
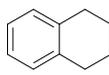
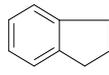
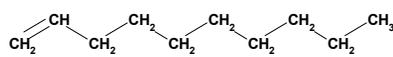
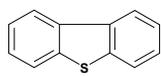
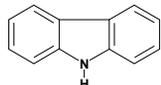
c. Aromatic hydrocarbons

Aromatic compounds of concern include benzene and its alkyl derivatives as well as naphthalene and its alkyl derivatives, and traces of polycyclic aromatic hydrocarbons (PAHs). PAHs are compounds with two or more aromatic rings. These rings are fused together, with some carbons being shared by adjacent rings [9].

d. Olefins

Olefins are hydrocarbons containing at least one carbon-carbon double bond in the chain. The olefins are classified as monoolefins (*alkenes*) and diolefins, in which the number of double bonds per molecule is, one or two. Olefins are usually formed by thermal and catalytic cracking and rarely occur naturally in unprocessed crude oil [10].

Table 6.2. Selected examples of compounds present in diesel fuel.

Name	Molecular formula	Structure	Properties
<i>n-Paraffins</i>			
<i>n</i> -decane	C ₁₀ H ₂₂		MW = 142.3 BP = 174 MP = -28
<i>Isoparaffins</i>			
2,4-dimethyloctane	C ₁₀ H ₂₂		MW = 142.3 BP = 156
<i>Naphthenes</i>			
butylcyclohexane	C ₁₀ H ₂₀		MW = 140.3 BP = 181 MP = -75
decalin	C ₁₀ H ₁₈		MW = 138.3 MP _{trans} = -31 MP _{cis} = -43 BP _{trans} = 187 BP _{cis} = 196
<i>Aromatics</i>			
butylbenzene	C ₁₀ H ₁₄		MW = 134.2 BP = 183 MP = -88
1-methylnaphthalene	C ₁₁ H ₁₀		MW = 142.2 BP = 240-243 MP = -22
tetralin	C ₁₀ H ₁₂		MW = 132.2 BP = 207.5 MP = -36
indan	C ₉ H ₁₀		MW = 118.2 BP = 176 MP = -51
<i>Olefins</i>			
1-decene	C ₁₀ H ₂₀		MW = 140.3 BP = 181 MP = -66
<i>Other compounds</i>			
dibenzothiophene	C ₁₂ H ₈ S		MW = 184.3 BP = 332 MP = 98
carbazole	C ₁₂ H ₉ N		MW = 167.2 BP = 354.7 MP = 246.3

MW, molecular weight (g/mol); BP, boiling point at 760 mm Hg (°C); MP, melting point (°C).

e. Other compounds

While carbon and hydrogen are the predominant elements in crude oil, small amounts of sulfur, nitrogen, and oxygen are also present. Molecules containing heteroatoms are not classified as hydrocarbons. Typical examples found in diesel fuel include dibenzothiophene [11] and carbazole [12]. Although these compounds are present in small amounts, they have a large influence on main diesel fuel properties.

6.3.2 Composition

Fig. 6.2 shows an example of diesel fuel composition arranged according to the molecular formula. As shown in the gas chromatogram, diesel fuel contains the hydrocarbons ranging from C_8 to C_{24} .

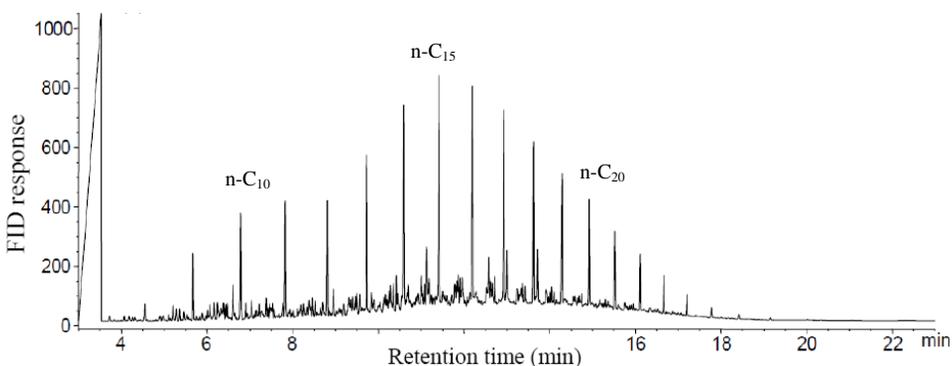


Fig. 6.2. Gas chromatogram of diesel fuel [13].

Diesel fuel consists of three groups of compounds with different concentration level, about 70% of saturated hydrocarbons (primarily paraffins including *n*-paraffins, isoparaffins, and cycloparaffins), 25% of aromatic hydrocarbons (including naphthalenes and alkylbenzenes) and 5% of other compounds (olefins and heteroatoms containing compounds) (Fig. 6.3).

Their relative distribution depends on the feedstock and fuel processing scheme. It should be noted that refineries generally vary the hydrocarbon composition of fuel to suit the demand and climate requirements. They include more components of low boiling range in cold climates and in winter, and vice-versa in hot weather [8].

Although the composition of diesel fuel is highly variable, there are some trends [14]:

- An average carbon number is 14 or 15.
- The isoparaffins are usually lightly branched with one or two side methyl groups.
- The naphthenes typically have one ring with multiple alkyl side chains.
- The aromatics are usually one ring with multiple side chains.
- There are also some two-ring naphthenes and two-ring aromatics with alkyl side chains.

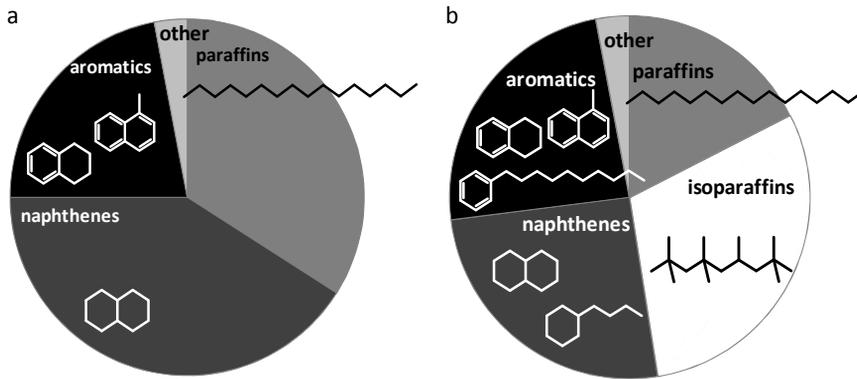


Fig 6.3. Relative amounts of hydrocarbons and representatives of these compounds in a) diesel fuel fraction separated in the distillation process and b) diesel fuel commercial product.

6.4 Properties of diesel fuel

6.4.1 Distillation characteristics

Distillation is a method of separating the mixture based on differences in the volatility of its components in a boiling liquid mixture. To separate a mixture of liquids, the liquid is heated to force the components, which have different boiling point, into the gas phase. The gas is then condensed back into liquid form and collected.

The boiling range distribution is one of the most important physical parameters defining diesel fuel. The distillation characteristics give information on the composition, the properties and the behavior of fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially vapors [15]. It affects autoignition temperature, flash point, viscosity and cetane number. High volatility promotes vapor lock and lowers the flash point. The latter has an adverse effect on safety in handling and storage. Higher volatility also causes an easier evaporation of fuel in the combustion

chamber. Consequently, low volatility components may not burn completely, thereby increasing deposits and smoke.

The basic method of distillation to determine the boiling range of a petroleum product is regulated by EN ISO 3405 [16]. In this test, a 100 cm³ sample is distilled under the prescribed conditions which are appropriate to its nature. Based on systematic observations of temperature readings and volumes of condensate, the results of the test are calculated and reported. Distillation characteristics are often presented as distillation temperature versus the amount of distillate. The distillation curve of diesel fuel indicates the amount of fuel that boils off at a given temperature. The curve can be divided into three parts (Fig. 6.4):

- The initial boiling point (IBP) and T10, which affects startability. T10 is the temperature at which 10% of the fuel distils off.
- The region around the 50% evaporated point (T50), which is linked to other fuel parameters such as viscosity and density. T50 is the temperature at which 50% of the fuel distils off.
- The heavy end, characterized by the T90, T95 and the final boiling point (FBP). For diesel fuel this is one of the most important properties, as at 360 °C almost 95% should vaporize and only 5% should remain. If the percent decreases then heavier fractions are present in the diesel fuel. The heavier components in diesel have more potential for incomplete vaporization and combustion, resulting in increased smoke or soot. Lowering high end temperatures reduces the proportion of these heavy components, giving cleaner burning. T90 and T95 are the temperatures at which 90 and 95% of the fuel distils off, respectively.

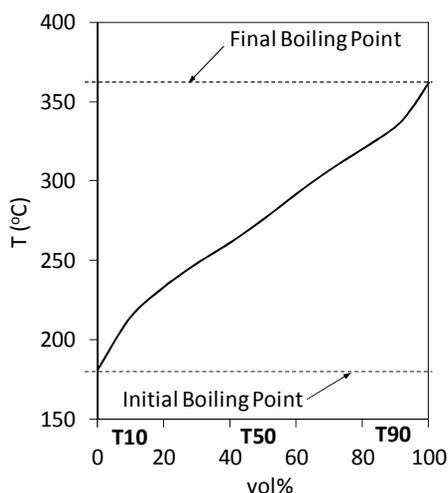


Fig. 6.4. Distillation curve for diesel fuel.

6.4.2 Density

Density (ρ) is the mass (m) of a unit volume (V) of material at a selected temperature:

$$\rho = \frac{m}{V} \quad (6.1)$$

The *SI* Metric System unit for density is kilograms per cubic meter (kg/m^3). However, grams per cubic centimeter (g/cm^3) unit is often used. Since density depends on the temperature and may be measured at various temperatures, the results are always converted to the values at standard temperature (generally $15\text{ }^\circ\text{C}$; in the U.S. $60\text{ }^\circ\text{F}$) according to the equation:

$$\rho_t = \rho_{t_0} + \gamma(t_0 - t) \quad (6.2)$$

where:

t – standard temperature, $^\circ\text{C}$

t_0 – temperature of the density measurement $^\circ\text{C}$

γ – thermal-expansion coefficient, $\frac{\text{g}}{\text{cm}^3\text{ }^\circ\text{C}}$.

The petroleum industry often uses relative density and API [16]. The relative density (D) is the ratio of the density of a material at a selected temperature (t) to the density of a reference material at a selected temperature (t_r) (equation 6.3). The relative density of petroleum crudes and products is generally defined with respect to water. The equation (6.4) relates API gravity, in degrees API ($^\circ\text{API}$), to relative density. The API gravity is inversely proportional to the density. Fuels of low API gravity will have both high density and high relative density.

$$D_{t_r}^t = \frac{\rho_{\text{sample}}(t)}{\rho_{\text{water}}(t_r)} \quad (6.3)$$

$$^\circ\text{API} = \frac{141.5}{D_{60}^{60}(\text{ }^\circ\text{F})} - 131.5 \quad (6.4)$$

The principal use of density is to convert the weight of fuel to volume or volume to weight. It is also required when calculating the volume of fuel at a temperature different from that at which the original volume was measured. Although density by itself is not a significant measure of quality, it is strongly correlated with other fuel parameters, such as cetane number, aromatics content, viscosity and the

distillation characteristics [17]. For instance, reducing the high end distillation temperatures (T95) will reduce the density by excluding the heaviest components. Moreover, fuel is injected directly into the combustion chamber in diesel engines, using in most cases a volume based metering system. The energy content of fuel is approximately proportional to the mass of fuel injected. Thus, for a constant volume injection system, variation in fuel density affects the energy content of the fuel injected. Consequently, engine power, emissions and fuel consumption may be affected. In order to optimize the engine performance and exhaust emissions, fuel density must be controlled within a fairly narrow range.

6.4.3 Cold filter plugging point

Inadequate cold flow performance will result in high viscosity at low temperatures, leading to difficulties with the starting and blockage of fuel filters. The cold filter plugging point (CFPP) indicates the temperature at which a fuel will cause a fuel filter to plug due to fuel components, which have begun to crystallize. All diesel fuels contain wax (*n*-paraffins) which normally is liquid in the fuel. However, if a fuel gets cold, the wax will crystallize. Wax crystals will continue to grow as the fuel temperature decreases, leading to plugging the filter not allowing fuel to pass through (Fig. 6.5 a). Since removing the wax during refining reduces the cetane number, the amount of wax in diesel is limited by the season.

The common alternative to diesel fuel blending in the winter is to treat diesel fuel with cold flow improver (CFI) additives. CFI additives can be very effective at improving low temperature operability without reducing the fuel's energy content. They are designed to modify the size and shape of wax crystals in order to allow the treated fuel to flow through a vehicle's fuel system (Fig. 6.5 b).

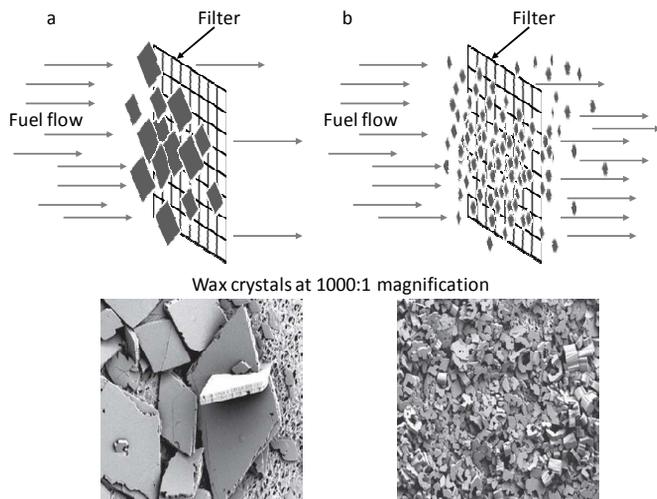


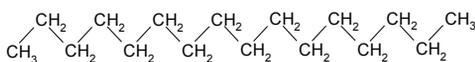
Fig. 6.5. Cold flow improvers – how do they work? a) without cold flow additive, b) with cold flow additive.

6.4.4 Cetane number and cetane index

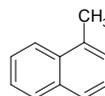
The *cetane number* (CN) of diesel fuel is a measure of a fuel's ignition delay, i.e. the time period between the start of fuel injection and start of its combustion (autoignition). In the cetane number scale, high values represent fuels that readily ignite and, therefore, perform better in a diesel engine [18]. The cetane number is determined by comparing its combustion characteristics in a test engine with those of blends of reference fuels with the known cetane number under standard operating conditions. In order to define the cetane number scale, two reference hydrocarbons were chosen:

- *n*-hexadecane (cetane), which burns well, was assigned a cetane number of 100.
- 1-methylnaphthalene (α -methylnaphthalene), which burns poorly in a diesel engine, was assigned a cetane number of 0.

n-hexadecane, CN = 100



1-methylnaphthalene, CN=0



The cetane number of a fuel is defined as the volume percent of *n*-hexadecane in a blend of *n*-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with the cetane number of 46 will perform the same in an engine as a mixture of 46% *n*-hexadecane and 54% 1-methylnaphthalene.

The cetane number of diesel fuel depends on its chemical composition [19]:

- *n*-Paraffins have high cetane numbers that increase with molecular weight.
- Isoparaffins have cetane numbers from about 10 to 80. Molecules with many short side chains have low CN, whereas those with one side chain of four or more carbons have high CN.
- Naphthenes generally have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high CN. Lower molecular weight molecules with short side chains have low CN.
- Aromatics have cetane numbers ranging from zero to 60. A molecule with a single aromatic ring with a long side chain will be in the upper part of this range. A molecule with a single ring with several short side chains will be in

the lower part. Molecules with two or three aromatic rings fused together have cetane numbers below 20.

High CN fuels will contain more *n*-paraffins. Lower CN fuels will contain more higher aromatics and heavier hydrocarbons. They are characterized by higher density, giving a lower volume of fuel for the same amount of energy.

Since measuring the cetane number requires a special engine, it is obvious that it is a difficult and expensive test. There is also another parameter that measures the ignition quality of fuel called *cetane index* (CI). There are some methods for estimating CI, which involve some combination of fuel density and distillation properties. The EN ISO 4264:2007 standard [20] provides a method for estimating the cetane number of distillate fuels from the density and distillation characteristics of the fuel. The relation is given by the following equation:

$$CI = 45.2 + (0.892)[T_{10N}] + [0.131 + (0.901)(B)][T_{50N}] + [0.0523 - (0.420)(B)][T_{90N}] + [0.00049][(T_{10N})^2 - (T_{90N})^2] + (107)(B) + (60)(B)^2 \quad (6.5)$$

where:

CI – cetane index;

$B = [e^{(-0.0035)(DN)}] - 1$;

$DN = D - 850$;

D – density at 15 °C (kg/m³) determined by test method ISO 3675;

$T_{10N} = T_{10} - 215$;

T_{10} – 10% recovery temperature (°C), determined by test method ISO 3405 and corrected to standard barometric pressure;

$T_{50N} = T_{50} - 260$;

T_{50} – 50% recovery temperature (°C), determined by test method ISO 3405 and corrected to standard barometric pressure;

$T_{90N} = T_{90} - 310$;

T_{90} – 90% recovery temperature (°C), determined by test method ISO 3405 and corrected to standard barometric pressure.

Cetane improving additives can be used to increase the CN by aiding the autoignition of the fuel. Since they do not change the parameters on which the CI is based, cetane improvers do not change the calculated CI.

6.4.5 Other properties of diesel fuel

There are other properties of diesel fuel that should be controlled by petroleum companies. They are specified in the EN ISO 590:2009 standard. These properties and their importance are given in Table 6.3.

6.5 Hydrocarbon properties

None of the hydrocarbon classes present in diesel fuel fulfill all the criteria to the same extent (Table 6.4). *n*-Paraffins, which have very good ignition performance and low smoking tendency, show poor low-temperature behavior and have a low calorific value.

Aromatics have very good cold flow properties and volumetric heating values, but very low cetane numbers. Isoparaffins and naphthenes are intermediate, with the values of these properties between those of normal paraffins and aromatics. The combination of e.g. paraffinic and aromatic structures in the molecules can reduce cold flow problems without impairing the combustion properties.

Table 6.3. Properties of diesel fuel and related influence on diesel engine performance.

Diesel fuel property	Importance
Cetane number/cetane index	Measure of ignitability, reduce knock and smoke
Density at 15 °C	Engine power, emissions and fuel consumption
Polycyclic aromatic hydrocarbons	Limits aromatic content of fuel to prevent adverse emissions impact, reduce knock and smoke
Sulfur content	To protect emissions control equipment
Flash point	Safety during fuel handling and storage
Carbon residue	Fuel system deposits, combustion chamber deposits
Ash content	Injector and fuel pump wear, piston and ring wear, engine deposits
Water content	Injector wear, increased corrosion
Total contamination	Filter plugging
Copper strip corrosion	Protect copper, brass, bronze fuel system parts
Oxidation stability	Storage
Lubricity	Injector and pump wear
Viscosity at 40 °C	Injector wear and spray pattern, pump wear, filter damage
Distillation	Deposits, wear, exhaust smoke
CFPP	Flow properties, filter plugging

Table 6.4. Properties of various hydrocarbon groups with regard to their suitability as diesel fuel [21].

Group of hydrocarbons	Ignition quality	Cold flow properties	Volumetric calorific value	Density	Smoking tendency
<i>n</i> -Paraffins	good	poor	low	low	low
Isoparaffins	low	good	low	low	low
Naphtenes	moderate	good	moderate	moderate	moderate
Aromatics	poor	moderate	high	high	high
Olefins	low	good	low	low	moderate

6.6 Diesel fuel specifications

The properties of diesel fuel must be balanced to meet the fuel quality standards related to the operability, performance, environmental objectives (emissions), fuel economy and durability of a diesel engine and related systems. In the European Union, the automotive fuel standards are developed by the European Committee for Standardization (CEN). The European fuel standard EN 590:2009: *Automotive fuels - Diesel - Requirements and test methods* embodies the latest diesel fuel quality requirements (Tables 6.5 and 6.6) [22].

The standard prescribes the required properties of diesel fuel, the methods of their determination and sets the limits for the values of these properties. These standards are used broadly in Asia and the Pacific basin countries, with modifications to fit local supply, crudes and regulations. It is worth noticing that the standards are continuously reviewed and updated when the need arises. The most common guidelines for diesel fuel in the U.S. are established by ASTM. Diesel fuel specifications in the U.S. are comparable, but not identical, to those in the European Union. For example, the minimum cetane number and cetane index in the U.S. are lower and there is not a density range requirement.

As mentioned above, diesel fuel must be suitable for a variety of climates. The cold filter plugging point is used as the criterion to predict the low temperature performance of diesel fuel. The CFPP is the lowest temperature at which fuel will still flow through a specific filter.

Table 6.5. EN 590:2009: Automotive fuels - Diesel - Requirements and test methods [22].

Diesel fuel specification parameter	Units	Limits		Test method
		minimum	maximum	
Cetane number		51.0	-	EN ISO 5165
Cetane index		46.0	-	EN ISO 4264
Density at 15 °C	kg/m ³	820	845	EN ISO 3675 EN ISO 12185
Polycyclic aromatic hydrocarbons	wt%	-	11	EN 12916
Sulfur content	mg/kg	-	10	EN ISO 20846 EN ISO 20884
Flash point	°C	> 55	-	EN ISO 2719
Carbon residue	wt%	-	0.30	EN ISO 10370
Ash content	wt%	-	0.01	EN ISO 6245
Water content	mg/kg	-	200	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper strip corrosion	rating	class 1		EN ISO 2160
Oxidation stability	g/m ³	-	25	EN ISO 12205
Lubricity	µm	-	460	EN ISO 12156-1
Viscosity at 40 °C	mm ² /s	2.00	4.50	EN ISO 3104
Distillation				
vol% recovered at 250 °C	vol%		< 65	EN ISO 3405
vol% recovered at 350 °C	vol%	85		
95 vol% recovered at	°C		360	
Fatty Acid Methyl Esters (FAME) content	vol%	-	7	EN 14078

For climate-related requirements, there are several options to allow for seasonal grades to be set at a national level. Climate-dependent prerequisites are given in Table 6.6. For temperate climates diesel fuel is classified into six CFPP grades (from A to F), and for arctic or severe winter climates into five different classes (from 0 to 4).

Table 6.6. Climate-related requirements and test methods [22].

Table 6.6.a. Temperate climates.

Property	Units	Limits						Test method
		Grade A	Grade B	Grade C	Grade D	Grade E	Grade F	
CFPP	°C, max.	+5	0	-5	-10	-15	-20	EN 116

Table 6.6.b. Arctic or severe winter climates.

Property	Units	Limits					Test method
		Class 0	Class 1	Class 2	Class 3	Class 4	
CFPP	°C, max.	-20	-26	-32	-38	-44	EN 116
Cloud point	°C, max.	-10	-16	-22	-28	-34	EN 23015
Density at 15 °C	kg/m ³	800-845	800-845	800-840	800-840	800-840	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C	mm ² /s	1.50-4.00	1.50-4.00	1.50-4.00	1.40-4.00	1.20-4.00	EN ISO 3104
Cetane Number	min.	49.0	49.0	48.0	47.0	47.0	EN ISO 5165
Cetane Index	min.	46.0	46.0	46.0	43.0	43.0	EN ISO 4264
Distillation							
vol% recovered at 180 °C	vol%, max.	10	10	10	10	10	EN ISO 3405
vol% recovered at 340 °C	vol%, min.	95	95	95	95	95	

6.7 Diesel engine

In the vast majority of motor vehicles used around the world, four-stroke internal combustion engines are employed. Diesel engines contain a reciprocating piston within a cylinder and two classes of valves: intake and exhaust [23]. Modern engines typically use direct injection of fuel into the engine cylinder. This fuel auto-ignites and does not require a spark. A high compression ratio is required to obtain the compression temperature necessary to achieve autoignition. The four-stroke operating cycle presented in Fig. 6.6 includes:

a. Intake stroke

The intake valve opens while the piston moves down from its highest position in the cylinder to its lowest position. In this process air is drawn into the cylinder.

b. Compression stroke

The intake valve closes and the piston moves back up the cylinder. This compresses the air and consequently, heats it to a high temperature, typically in excess of 540 °C. Near the end of the compression stroke, fuel is injected into the cylinder. Fuel injection begins shortly before the end of the compression stroke.

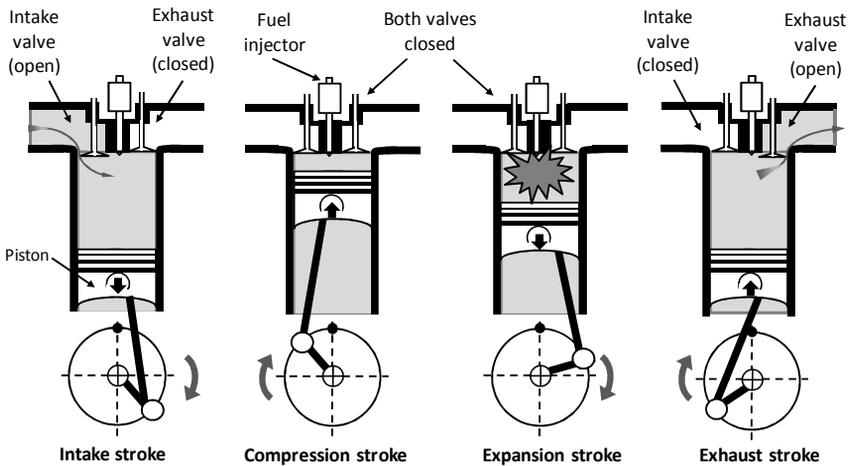


Fig. 6.6. Four-stroke cycle.

c. Expansion stroke

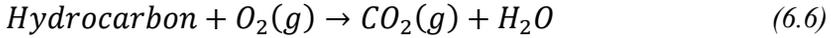
After a short delay, the fuel ignites spontaneously, a process called autoignition. The hot gases produced by combustion of the fuel further increase the pressure in the cylinder. Raising pressure causes the piston to be driven down generating power to propel the vehicle. The combustion energy is transformed into mechanical energy.

d. Exhaust stroke

The exhaust valve opens when the piston is again near its lowest position, so that as the piston once more moves to its highest position. The exhaust gases are pushed by the rising piston through the exhaust manifold, through any included after-treatment devices, and out the exhaust pipe into the atmosphere.

6.8 Diesel vehicle emissions

The combustion reaction occurs between the fuel and oxygen from the air according to the general equation (equation 6.6), creating the desirable effect of heat and pressure within the cylinder. In the case of complete combustion, the only products are water (H_2O) and carbon dioxide (CO_2). However, the reaction is not 100% efficient [24].



The air used to supply the oxygen contains about 78% of nitrogen and diesel fuel contains a small amount of sulfur containing compounds. As a consequence, trace amounts of other compounds are formed during the combustion process (Fig. 6.7).

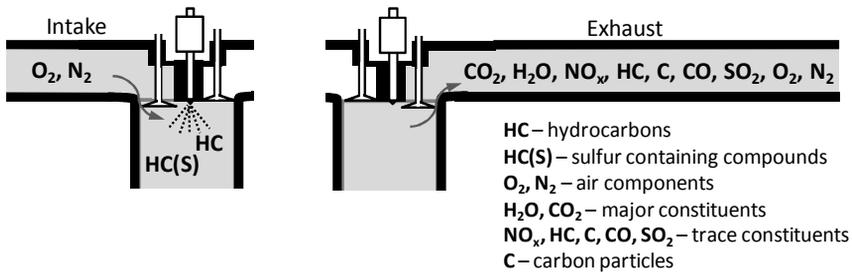


Fig. 6.7. Exhaust emissions in diesel engine.

Even the most technologically advanced vehicle engines are not ideal and they produce harmful emission output. Exhaust emission is of concern to the environment and includes [25]:

- Dry carbon particles (C).
- Unburned hydrocarbon fraction that results from the incomplete combustion of diesel fuel and engine lubricating oils and tends to adsorb or condense onto the carbon particles.
- Hydrocarbons that evaporate from the fuel system before getting into the engine to be burned (Volatile Organic Compounds – VOC).
- A gaseous component consisting mainly of carbon dioxide (CO_2), carbon oxide (CO), nitrogen oxides (NO_x) and sulfur dioxide (SO_2).

The main problem is the emission of NO_x (mainly NO) and particulate matter (soot) [26]. Both NO_x and particulates are significant environmental pollutants. The nitrogen from the air reacts with the oxygen at high temperature and pressure which occur during the combustion process. Any organic nitrogen in the fuel also

contributes to NO_x emissions, however this source is negligible compared to nitrogen in the air.

NO_x together with SO_2 can react in the atmosphere to form acidic compounds (acid rain). NO_x combines with organic compounds, e.g., hydrocarbons in the presence of sunlight to form low level ozone, a main component of smog. Diesel engines produce relatively high level of particulate emissions, often referred to as particulate matter (PM) [27]. The visible portion of PM, the black smoke, is larger carbon particles that are formed under acceleration and insufficient air conditions. However, all components of exhaust emission contribute directly to the formation of PM.

Diesel exhaust NO_x and PM are associated by the nature of diesel fuel combustion. Attempts to decrease PM by increasing combustion efficiency lead to higher combustion temperatures, thus higher NO_x emissions. Reducing NO_x formation by lowering combustion temperature leads to incomplete combustion and, thus higher PM emissions. The challenge for diesel engine designers is to reduce emissions of NO_x and PM simultaneously. There are many emissions-reducing efforts which can be divided into:

a. Advances in combustion system design. The application of higher injection pressure leads to better atomization and smaller fuel droplets, which vaporize more readily than larger droplets. The cylinder head, air intake valve, and piston head are designed to provide optimal air motion for better fuel-air mixing. In modern diesel engines, there is the Exhaust Gas Recirculation (EGR) system which involves lowering the temperature in the combustion chamber by the circulation of a portion of the exhaust gas back to the air intake manifold [28]. The maximum temperature of the combustion gas is reduced because some of the heat generated by combustion must be used to heat this recirculated gas.

b. Exhaust after-treatment technologies which are designed to remove pollutants from the exhaust gas. Particulate traps, or filters, filter the exhaust gas before it is released to the atmosphere and they remove 70 to 90% of the particulate matter. The particulates agglomerate in the traps and must be removed by burning because they are mainly carbon. To minimize NO_x emissions in Europe, the selective catalytic reduction (SCR) system is fitted to most new heavy-duty diesel engines. In the SCR system, a reducing agent such as ammonia or urea reacts with NO_x over the SCR catalyst to form nitrogen, carbon dioxide (in the case of using urea) and water [29]. Then the reaction products are released into the air. The SCR system is one of the most cost-effective technologies available to help reduce emissions. SCR can reduce NO_x emissions up to 90% while simultaneously reducing hydrocarbon and CO emissions by 50-90%, and PM emissions by 30-50%. SCR system can also be combined with a diesel particulate filter to achieve even greater reductions for PM emission [30].

c. *Advances in diesel fuel production*, e.g. limitation and control of sulfur and PAHs content in diesel fuel.

6.9 Alternative diesel fuel - biodiesel

The consumption of biofuels continues to increase as more attention is paid to the environment protection and the shortage of fossil fuel sources. Biodiesel is a fuel suitable for use in compression ignition (diesel) engines that is made of fatty acid monoalkyl esters derived from biologically produced oils or fats including vegetable oils, animal fats, recycled cooking greases or oils and microalgal oils. The quality criteria for the production of biodiesel are specified in EN 14214 [31]. Biodiesel can be used as a diesel (B100) or as a blend with petroleum derived diesel fuel, normally at 20% (B20) [32].

Vegetable oils and animal fats consist of three fatty acids – hydrocarbon chains of varying lengths, bonded to a glycerol molecule. This structure is commonly known as a triglyceride. In a process known as transesterification, triglycerides react in the presence of the catalyst with an alcohol, resulting in three fatty acids bonded to the methyl group from methanol [33]. The chemical reaction for biodiesel production is depicted in Fig. 6.8. When biodiesel is produced using methanol, fatty acid methyl esters (FAME) are produced. Biodiesel fuels can also be produced using other alcohols, for example ethanol to produce fatty acid ethyl esters, however this type of biodiesel is not covered by EN 14214. Water, unreacted triglycerides and alcohol as well as glycerin are byproducts and must be removed from biodiesel fuel.

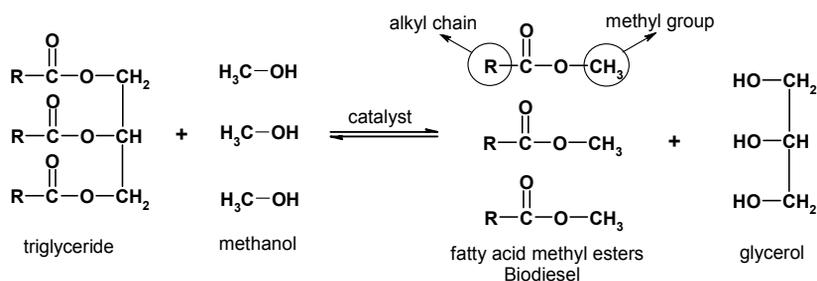


Fig. 6.8. Transesterification of triglycerides to fatty acid methyl esters (biodiesel); R - hydrocarbon chain, the length may vary from 10-30 carbons (typically 16-18).

In Europe, rapeseed oil is the largest source of biodiesel, although oil from other plants is used as well [34]. Soybean oil is the source for most of the biodiesel produced in the U.S. In countries where winters are warm, palm and coconut methyl esters are commonly used.

The major advantage of biodiesel fuel is that it is a renewable energy source and it does not pollute the environment. Since biodiesel is made from CO₂ taken out of the biosphere it adds no new CO₂. Diesel fuel is produced from a fossil source of carbon thus its combustion adds CO₂ to the biosphere. A liter of petroleum derived fuel will produce 2.73 kg of CO₂ [35]. Carbon dioxide is the most prominent greenhouse gas in the earth's atmosphere.

6.10 Laboratory work: determination of diesel fuel properties

Determination of distillation characteristics

According to the EN ISO 3405:2000 standard [16] a 100 cm³ sample of diesel fuel is distilled under conditions which are given in Table 6.7. The temperature is recorded when the first drop is collected (IBP), at recovered volume percentages of 5%, 10%, every subsequent 10% to 90%, 95%, and at the end of the test (FBP). The percent loss is calculated based on the volume of total recovery (volume of the condensate and the volume of the residue).

Table 6.7. Conditions during the procedure of determining the fractional composition of the petroleum-derived products.

Type of sample	Diesel fuel
Temperature of the cooling bath (°C)	0-60
Temperature of the receiver (°C)	±3 of the sample temperature
Period between the first application of heat and IBP (min)	5-15
Average rate of distillation (cm ³ /min)	4-5
Time from 5 cm ³ of residue in the flask to FBP (min)	≤5

The thermometer readings are corrected to 101.3 kPa by the following equations:

$$T_c = 0.0009(101.3 - p_k)(273 + t_r) \quad (6.7)$$

$$T = t_r \pm T_c \quad (6.8)$$

where:

T_c – correction to be added/deducted algebraically to the observed thermometer reading

p_k – prevailing barometric pressure at the time of the test, kPa

t_r – reordered temperature of distillation at the prevailing barometric pressure, °C

T – corrected temperature, °C

Determination of density at 15 °C

A sufficiently accurate and quick determination of density (EN ISO 3675:1998) standard may be obtained by the floating hydrometer, which allows the density of a liquid to be deduced from the depth of immersion by reading a graduated scale [36]. The basic concept of hydrometer method is that a sample being tested is placed in an appropriate glass cylinder and the hydrometer is placed in the sample. The temperature of the sample should be allowed to stabilize with the prevailing temperature. After the temperature has stabilized, the hydrometer is placed in the sample and density is read directly from the hydrometer. The reading of the hydrometer is corrected for the effect of the temperature according to the equation (6.2).

Determination of cold filter plugging point

According to the EN 116 standard [37] for determining the cold filter plugging point, a portion of the diesel fuel is cooled under the defined conditions and at intervals of 1 °C, is drawn into a 20 cm³ pipette through a standardized metal mesh filter. Testing is continued until the amount of wax throughout the solution is sufficient to stop or slow down the flow. If the time taken to fill the pipette exceeds 60 s or the fuel fails to return completely to the test jar before it has cooled by a further 1 °C, the measurement cycle ends. The temperature at which the last filtration was commenced is recorded as the CFPP.

References

- [1] Rockman H.B., Intellectual property law for engineers and scientists. Wiley-Interscience, New Jersey 2004.
- [2] Golonka J., Picha F.J., The Carpathians and their foreland: geology and hydrocarbon resources, American Association of Petroleum Geologists, 2006.
- [3] Speight J.G., The chemistry and technology of petroleum, CRC Press, Taylor&Francis, New York 2007.
- [4] Fujikawa T., Kimura H., Kiriyaama K., Hagiwara K., Catalysis Today 2006, 111, 188-193.
- [5] Parkash S., Petroleum fuels manufacturing handbook, McGraw Hill Professional, USA 2009.
- [6] World Oil Outlook, 2010.
- [7] Song, C., Hsu C.S., Mochida I., Chemistry of diesel fuels, Taylor&Francis, New York 2000.
- [8] Olah G.A., Molnár Á., Hydrocarbon chemistry, Wiley-Interscience, 2003.
- [9] Pavlova A., Petrov S., Milina R., Ivanova R., Chemistry and Technology of Fuels and Oils 2004, 40, 275-278.
- [10] Corgozinho C.N.C., Carvalho M.M.O., Barbeira P.J.S., Energy Fuels 2009, 23, 2136-2142.

- [11] Stanislaus A., M. Abdulazeem, Rana M.S., *Catalysis Today* 2010, 153, 1–68.
- [12] Li N., Ma X., Zha Q., Song C., *Energy Fuels* 2010, 24, 5539–5547.
- [13] Ogawa T., *Fuel* 2005, 84, 2015–2025.
- [14] Farrell J.T., Cernansky N.P., Dryer F.L., Friend D.G., Hergart C.A., Law C.K., McDavid R., Mueller C.J., Pitsch H., Development of an experimental database and kinetic models for surrogate diesel fuels, SAE World Congress, Detroit, MI, 2007.
- [15] Nadkarni R.A., Guide to ASTM test methods for the analysis of petroleum products and lubricants, ASTM International, 2007 – 299 USA 2007.
- [16] EN ISO 3405:2000. Petroleum products - determination of distillation characteristics at atmospheric pressure.
- [17] Speight J.G., *Handbook of petroleum product analysis*, Wiley & Sons, New Jersey 2002.
- [18] Report of the Technology Panel of the Diesel Impacts Study Committee, National Research Council, Diesel technology, National Academy, Washington 1982.
- [19] Clothier P.Q.E., Aguda B.D., Moise A., Pritchard H.O., *Chemical Society Reviews* 1993, 22, 101–108.
- [20] EN ISO 4264:2007: Petroleum products - Calculation of cetane index of middle-distillate fuels by the four-variable equation.
- [21] Elvers B., *Handbook of fuels: energy sources for transportation*, Wiley –VCH, Weinheim 2008.
- [22] EN 590:2009. Automotive fuels - Diesel - Requirements and test methods.
- [23] Tao R., Huang K., Tang H., Bel D., *Energy Fuels* 2009, 23, 3339–3342.
- [24] Fox M.A., Whitesell J.K., *Organic chemistry*, Jones and Bartlett Learning, Canada 2004.
- [25] Wallington T.J., Kaiser E.W., Farrell J.T., *Chemical Society Reviews* 2006, 35, 335–347.
- [26] Faiz A., Weaver C.S., Walsh M.P., *Air pollution from motor vehicles: standards and technologies for controlling emissions*, World Bank Publications, Washington 1996.
- [27] Hensher D.A., Button K.J., *Handbook of transport and the environment*, Elsevier, Amsterdam 2003.
- [28] Abd-Alla G.H., *Energy Conversion and Management* 2002, 43, 1027–1042.
- [29] Koebel M., Elsener M., Kleemann M., *Catalysis Today* 2000, 59, 335–345.
- [30] Knecht W., *Energy* 2008, 33, 264–271.
- [31] EN 14214, Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods.
- [32] McCormick R.L., Westbrook S.R., *Energy Fuels* 2010, 24, 690–698.
- [33] Lotero E., Liu Y., Lopez D.E., Suwannakarn K., Bruce D.A., Goodwin J.G., *Industrial and Engineering Chemistry Research* 2005, 44, 5353–5363.
- [34] Singh S.P., Singh D., *Renewable and Sustainable Energy Reviews* 2010, 14, 200–216.
- [35] Leslie D.R., Diesel emissions evaluation for the surface mining industry. In: *Environmental issues and management of waste in energy and mineral production*, eds. R.K. Singhal, A.K. Mehorata, A.A. Balkema, Rotterdam 2000, p. 211–218.
- [36] Speight J.G., *Handbook of petroleum product analysis*, Wiley Sons, New Jersey 2002.
- [37] EN ISO 3675:1998. Crude petroleum and liquid petroleum products - Laboratory determination of density - Hydrometer method.

Glossary and abbreviations

wt%	mass fraction
vol%	volume fraction
alkylation	reaction of a C ₃ /C ₄ alkane with a C ₃ /C ₄ olefin to yield a high octane <i>iso</i> -paraffin
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
B100	100% of biodiesel
B20	a blend containing 20% biodiesel and 80% petroleum diesel
catalytic cracking	breaking apart large molecules into small ones, most often in a reactor employing a fluidized catalyst bed
CEN	the European Committee for Standardization
CFI	cold flow improver
CFPP	cold filter plugging point
CI	cetane index
CN	cetane number
EGR	exhaust gas recirculation
FAME	fatty acid methyl esters
FBP	final boiling point
FID	flame ionization detector
hydrocracking	catalytic cracking of heavy molecules with addition of hydrogen
IBP	initial boiling point
ISO	International Organization for Standardization
isomerization	catalytic conversion of <i>n</i> -paraffins to isoparaffins
PAHs	polycyclic aromatic hydrocarbons
percent recovered	volume in milliliters of condensate observed in the receiving graduate, in connection with a simultaneous thermometer reading
PM	particulate matter
reforming	conversion of paraffins and cycloparaffins to branched paraffins and aromatics via dehydrogenation/dehydrocyclization
SCR	selective catalytic reduction
VOC	volatile organic compounds