

CO-COMBUSTION OF SOLID FUELS

OPPORTUNITIES, ADVANTAGES AND APPLICATION PROSPECT



NATIONAL ACADEMY OF SCIENCES OF UKRAINE
THERMAL ENERGY TECHNOLOGY INSTITUTE
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CO-COMBUSTION OF SOLID FUELS

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IN A FOREIGN LANGUAGE»*

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The collective monograph summarises almost twenty years of experience of the Thermal Energy Technologies Institute of the National Academy of Sciences of Ukraine in theoretical and practical research on the joint thermal processing of two solid fuels. The research has been applied in boiler furnaces of various capacities, using various technologies, from pulverised coal combustion to bed combustion. The research is unique due to the wide range of fuels involved — coal of all grades and different countries of origin, biomass, petroleum coke, coal preparation waste, etc. Such research has contributed to expanding the energy sector's fuel base with local fuels, industrial and agricultural waste, reducing harmful emissions, creating distributed generation, and thus, to Ukraine's energy independence.

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LIST OF ABBREVIATIONS

CFD	—	Computational Fluid Dynamics
CHPP	—	Combined Heat and Power Plant
DT	—	Deformation Temperature
DTA	—	Differential Thermal Analysis
DTG	—	Differential Thermogravimetry Curve
EDX	—	Energy-Dispersive X-Ray
LHV	—	Lower Heating Value
SC	—	Salty Coal
SD	—	Standard Deviation
RDF	—	Refuse Derived Fuel
SFR	—	Solid Recovered Fuel
TG	—	Thermogravimetry Curve
TGA	—	Thermogravimetric Analysis
TPP	—	Thermal Power Plant
UDF	—	User-Defined Function
XRF	—	X-Ray Fluorescence

INTRODUCTION

This collective monograph reviews the theoretical and applied research related to the use of solid mixed fuels for combustion with subsequent production of electricity and/or heat. The basics of physical and chemical processes in the mixing of different types of solid fuels and their subsequent combustion are considered in terms of the advantages, problems, and technical solutions used.

Fuel compositions can be described by two terms — blend or mixture. The former refers to homogenised fuels (and is used in Chapters 1—5), while the latter refers more to the process of mixing and separate fuel supply (Chapters 7 and 8). Solid fuel mixing involves obtaining a fairly homogeneous blend of two or more solids for combustion in a combustion chamber. These solids can be coal of the same or similar grades; coal of different grades; coal with biomass admixtures such as wood, wood waste, grass and crop residues, and biomass processing waste. Blends may also include coal and a range of industrial materials and residues, including petroleum coke, coal waste such as sludge or ash, lignin, fuels derived from municipal solid waste (e.g., garbage, wastepaper, plastic), tire fuel, certain hazardous waste, and more.

Blending is designed to achieve certain general goals: economic, environmental, and technical. Economic goals are always related to the production of a useful energy product at the lowest cost. This may involve blending to produce the cheapest usable fuel or the most cost-effective fuel product, given the limitations of the available boiler or heat generator.

Coal of different grades and origins, biomass, and waste have very different cost structures. Blending makes it possible to manage the overall fuel cost per unit of energy produced, recognizing that different fuels have different heating values and chemical compositions, different slagging and pollution characteristics, and different implications for the capacity of existing power equipment.

Blending has received a significant boost for environmental reasons; the use of low-sulfur coal mixed with high-sulfur coal has allowed SO₂ emission requirements to be met without signifi-

cant capital investment, providing the least cost approach to meeting the sulfur dioxide requirements. Blending can provide a mechanism to reduce ash content and consequently particulate matter. Blending can be a means to reduce the concentration of hazardous air pollutants or make them more manageable.

The monograph summarizes the results of the longstanding theoretical research on the co-firing of two solid fossil and/or renewable fuels conducted at the Thermal Energy Technology Institute of the National Academy of Sciences of Ukraine (TETI NASU) (the former Coal Energy Technology Institute) and its practical application

The subject matter of the monograph is relevant, as leading energy companies in Ukraine and abroad have been researching and practically implementing technologies for the use of co-combustion of renewable energy sources, industrial waste, etc. for several decades to replace fossil fuels in whole or in part, given the announced and legally enshrined trend of the electricity industry development using mainly renewable energy sources and waste in the first half of this century.

The scientific novelty lies in the use of Ukrainian coal and local biomass, which are unique in terms of their mineral composition. The book describes studies of the combustion rates of mixed fuels and their use in the calculation of pulverized fuels, improves the methods for analyzing thermographic studies, and reveals the effects of non-additivity in the joint thermolysis of two solid fuels of different geneses, Numerical simulations of mixed fuel combustion in the ANSYS Fluent software package for various types of fuels were carried out, and the peculiarities of combustion processes, slagging effects and corrosion of heating surfaces in the case of simultaneous combustion of two solid fuels of different degrees of metamorphism were investigated. Considerable attention is also paid to the introduction of co-combustion technologies at existing boiler units of thermal power plants (TPPs), combined heat and power plants (CHPPs), and industrial boiler plants.

ROLE AND PLACE OF MIXED SOLID FUELS COMBUSTION IN THE ENERGY SECTOR

For many years, the world energy practice has been using the co-combustion of fuels of both the same aggregate state and different ones such as solid/gas, solid/liquid (e.g., coal/fuel oil and coal/natural gas) in pulverized coal boilers. New fuel is a mechanical mixture of combustible (including organic fuels) and, in some cases, combustible and non-combustible substances that have new properties compared to those of the original combustibles.

It is impossible to describe all types of existing blended fuels, their combustion technologies, and equipment for their energy use in one book. This monograph is devoted to solid blended fuels that are relevant for Ukraine and other coal-mining countries that in recent years have become indispensable for solving a number of problems such as involving local biofuels, industrial and agricultural waste, imported and non-project coal in the fuel and energy balance, combustion in boiler house of the existing boiler equipment and creation of new power plants for which such blended fuels are projected.

1.1. State of electricity production in the world and the role of solid fuels in it

Global consumption of primary energy has reached a new record with non-OECD (Organization for Economic Cooperation and Development) countries dominating both in the share and annual growth rates. Fossil fuels continue to be the foundation of their development, accounting for 84% of the energy balance.

According to the statistics of the International Energy Agency, in the OECD in June 2024, the total net electricity production reached 902.8 TWh, that is, an increase of 5.4% compared to the same period last year. Since the beginning of the year, total net electricity generation has increased by 2.9% in the first two quarters of 2024.

Electricity production from fossil fuels totaled 422.7 TWh in June 2024, which is 0.6% less than in June 2023. The largest de-

crease in fossil fuel production (−12.9%) was observed in the OECD European countries, which was due to a decrease in electricity production from natural gas (−21.0%). OECD Asia and Oceania also experienced a downward trend (−3.0%). Overall, fossil fuels account for 46.8% of the OECD electricity mix.

The European continent is the most focused on phasing out fossil fuels. The practice of using fossil fuels is more necessary for Ukraine, where the only fossil fuel that fully meets its needs is coal [1, 2]. On the one hand, in the short term, during the war and the first years of the post-war period, it will be impossible to maintain the proper level of energy consumption, especially during peak loads, without restoring coal generation [3]. On the other hand, it is impossible to restore the energy sector in the medium and long term without a significant share of renewable energy, given Ukraine's international commitments [4].

In June 2024, electricity generation from renewable sources in the OECD countries totaled 329.9 TWh, up to 14.0% compared to the same month last year. This growth was primarily driven by an increase in electricity generation from wind (28.1%), solar (18.4%), and hydropower (4.8%). The largest growth was in the Americas (17.5% or 21.5 TWh), mainly due to an increase in wind (35.8% or 11.5 TWh) and solar (30.0% or 8.1 TWh) electricity generation. The US is followed by the OECD countries, which saw a 14.6% year-on-year increase in wind (26.4% or 7.4 TWh), hydropower (10.7% or 5.4 TWh), and solar (12.9% or 4.7 TWh). Overall, during the first two quarters of 2024, electricity generated from renewable sources in the OECD countries increased by 8.5% from the beginning of the year, and in June 2024 it accounted for 36.5% of the total OECD electricity.

In our opinion, biomass is underutilized in electricity production in the OECD countries, although everyone knows the advantages in terms of its environmental neutrality. However, there are some examples of the complete conversion of coal-fired power plants to biomass in Europe. The Drax Power Station, England, 6 units of 600 MW each, fully converted to pellets. Prominent examples of co-firing include Fiddler's Ferry Power Station and Drax Power Station, which are pioneers in the UK in burning a variety of biomass fuels, both locally and imported from abroad. Drax has completed the conversion of all its boiler units to burn only biomass and has recently been selected as a key research station for Bioenergy with Carbon Capture and Storage (BECCS) to provide carbon-negative electricity for the future.

In the Netherlands, the Amer 9 Power Plant and Eemshaven Power Plant co-fire mainly wood pellets with a 80% and 15% replacement rate, respectively. Both plants plan to increase their biofuel combustion by the mid-decade.

The Amager power plant in Denmark operates with a biomass in coal-fired boiler. It has been fully converted to biomass boilers for electricity generation and district heating.

The Avedøre and Studstrup power plants in Denmark have been converted to only biomass firing with the option to burn coal if required. The Rodenhuijze power plant is a large-scale 1300 MW multifuel power plant located in Belgium, capable of burning coal, gas, and biomass for combined heat and power generation [6].

The same can be said about the use of biomass in Ukraine, where, according to [7], at peacetime we have the opportunity to use 35665 ktoe/year of technically achievable biomass (including Donbas and Crimea).

The use of coal/biomass blending is widespread around the world, especially in Asia and the Pacific. Co-firing of biomass with coal began in Europe and North America in the late 1990s. It has been proven to be a relatively fast and cost-effective way to partially decarbonize coal-fired power generation in the short to medium term. Co-combustion in coal-fired power plants can contribute to some of the UN Sustainable Development Goals. Co-firing with biomass also helps extend the life of coal-fired power plants during the transition to other low-carbon generation types. Although Canada and much of Western Europe are phasing out coal-fired power, which will reduce opportunities for biomass co-firing, coal remains an important fuel for power generation in Asia and Eastern Europe. Co-firing activity is growing in these regions, and the work on the development of co-combustion technologies is ongoing.

During the martial law period, it was of particular importance to restore the operation of coal-fired CHPPs as soon as possible to ensure energy independence, supply heat and electricity to the population, and, if possible, carry out low-cost modernization with improved economic and environmental performance, given their low capacity compared to TPPs.

Without abandoning the global goal of the "green transition", enshrined in the legislation of Ukraine and the world in numerous legislative acts, it is already understood in most countries and by the most authoritative global energy organizations [8] that the global energy sector will face a rather long transition period of 20—30 years when heat and electricity will be generated from both fossil and renewable fuels [9].

Although many countries are phasing out fossil fuels, global coal consumption reached a staggering 164 exajoules (EJ) of energy in 2023, a record high for any year. Coal will provide 26% of the global energy in 2023, more than all non-fossil fuels combined. The only energy source that contributed more to the global energy mix was oil. Here is a breakdown of this consumption by region (Table 1.1).

Coal consumption has declined in many regions. For example, in 2023, both North America and Europe reduced their energy consumption from coal by 16%. However, the strong dependence on coal in the Asia-Pacific region means that global coal consumption has remained virtually unchanged over the past 10 years. In 2023, China increased its coal consumption from 88 EJ to almost 92 EJ, accounting for 56% of global coal consumption. This has largely contributed to the Asia-Pacific region becoming the global leader with a staggering 83% of global coal consumption.

Easy access to existing infrastructure and reasonable prices have not only sustained global coal consumption over the past 10 years but have paved the way for growth. Many developing countries are currently expanding their coal consumption.

For example, according to the Statistical Review of World Energy 2024, Bangladesh and Colombia saw double-digit percentage growth in coal consumption between 2022 and 2023 compared to the previous year: 41 and 53% respectively.

Coal continues to play a crucial role in the global energy mix, especially in developing countries, where its availability makes it the preferred energy source for them at present.

Coal and biomass co-combustion technologies have been actively developing for more than two decades as a partial substitution technology for fossil fuels in line with global trends. At the beginning of the 21st century, this technology became widespread in both Europe and North America [10]. For example, in 2015, the Netherlands built a demonstration power plant for energy saving and deep CO₂ emission reduction, as well as CO₂ capture, consisting of an 1100 MW supercritical pulverized coal unit + biomass combustion + CO₂ capture. The biomass utilization rate is 30% and the plant efficiency is over 47%. Finland has built the world's largest circulating fluidized-bed boiler at 550 MW. Biomass, along with, e.g., coal, sludge, wood, forest waste, etc., can be burned in any proportion in circulating fluidized-bed boilers. Such a developed country as the UK — the country with the largest use of coal co-firing technology in the last century — has almost completely abandoned such combustion and reached an installed capacity of 25,336 GW of biomass combustion in 2018 [11].

Today, due to the energy policy of these regions to completely abandon fossil fuels, biomass and coal co-combustion (BCC) is being replaced by existing thermal power plants that burn only biomass or waste (AMAGER CHPp — Denmark) [12].

However, this technology has found its second life in the Asia-Pacific region. For example, China is a large agricultural country with abundant biomass resources and great potential for the development and use of biomass energy, for which CCS is a promising choice [13]. Utilization of agricultural waste in existing coal-fired power plants is an attractive option to reduce environmental pollution and reduce the excessive use of fossil fuels [14]. Thanks to domestic measures to promote and support the development of renewable energy, investment in biomass power generation is growing rapidly, and construction of various agricultural and forestry waste-to-energy projects has already begun. China's biomass power generation technology industry is showing a general trend of accelerated development [15]. The increase in generation capacity from both fossil and renewable

Table 1.1. Coal consumption in different regions of the world (2023) [9]

Region	Consumption (EJ)	Share, %	Region	Consumption (EJ)	Share, %
China	91.9	56.1	CIS countries	5.5	3.4
Pacific Asia (excluding China)	43.8	26.7	Africa	4.1	2.5
Americas	10.0	6.1	Middle East	0.4	0.2
Europe	8.4	5.1	Total	164.0	100

sources continues to grow: in 2024, China began construction of coal-fired power plants with a total capacity of 94.5 GW. In the same year of 2024, 356 GW of wind and solar capacity was installed [16, 17]. Based on an average blending rate of 10%, the installed capacity of biomass power plants could reach 55 GW [18]. At the same time, high-efficiency, large-capacity coal-fired power plants are switching to co-firing coal and biomass, which should become the main measure to reduce carbon emissions at this stage in China.

In Asia, Japan is leading the way in co-firing efforts with commercial operations, developed in the late 2000s as a way to keep major thermal power plants connected for stable and secure power supply amid the growth of other intermittent renewable sources. The Shin Onoda power plant has been burning wood pellets and wood chips in its two 500 MW supercritical units since 2007. In 2008, the Hofu Biomass and Coal Combined Heat and Power Plant was a newly installed 112 MW TPP that co-fires wood pellets and palm shells with coal.

New TPPs, such as the Hitachinaka TPP and Taketoyo TPP, are specifically designed to co-fire different types of biomass and coal fuels as Japan's energy demand continues to grow.

R&D here is also looking at co-firing hydrogen in the form of ammonia as an additional effort to reduce greenhouse gas emissions from thermal power plants.

India is another country with a rapidly growing energy demand, which relies on TPPs for a stable and uniform energy supply. In 2021, it launched the National Mission on Biomass Utilization at TPPs, which mandated a minimum of 5% co-firing of biomass pellets in all TPPs. The main source of biomass is local agricultural residues, as India also aims to become a major exporter of biomass pellets.

In Malaysia, commercial co-firing was implemented at the 2,100 MW Malakoff Tanjung Bin power plant as a major project of the National Energy Transition Roadmap (NETR). In 2022, the trial combustion was successfully carried out at a replacement level of 0.5% of palm residues, which was followed by an increase in biomass to 2%.

Co-firing technologies are widely used in Indonesia, where the technology and efficiency of co-combustion are constantly evolving to reduce coal consumption [19]. The researchers of this technology focus on the behavior of biomass as the most complex fuel in the coal-biomass pair. The type of biomass and the composition of the blend used determine the boiler efficiency. The conditions for pre-mixing biomass and coal are critical factors. The properties of certain types of biomass, such as high moisture content, low calorific value, and poor grinding ability, must be taken into account [20, 21]. As a result, optimizing the biomass quality is crucial for achieving high combustion efficiency.

Another example is the Indonesian energy company PLN. Co-combustion was introduced as one of the strategic initiatives under the Green Booster Program to accelerate the achievement of the 23% RES target by 2025 using existing power plant infrastructure as well as waste-to-energy solutions. The total capacity of PLN Group's co-combustion steam power plants is 18.9 GW. Co-firing activities have been carried out at several PLN Group facilities since 2020 using diffe-

rent types of boilers. The types of biomass used include sawdust, palm shells, wood chips, wood pellets, rice husks, coconut shells, solid renewable fuel (SRF) pellets, water hyacinth, and corn cobs. Developing countries have seen a significant increase in demand for electricity in recent decades. Their coal-fired power plants were built 10–20 years ago (80%). Using their capacities for co-firing coal with biomass and waste has become the main way for these countries to fulfill their international commitments to reduce CO₂ emissions and meet the needs of industries and the population in the coming years.

Carbon storage and capture technologies, which are currently being widely researched and rapidly developed around the world, may lead to the emergence of co-fired coal and/or biomass plants with negative CO₂ emissions, given that the biomass is considered CO₂-neutral.

1.2. State of development of co-firing technologies for two solid fuels in Ukraine

In recent years, while supporting initiatives to reduce greenhouse gas emissions, Ukraine's leadership has paid insufficient attention to coal TPPs, announcing its complete closure first by 2050, then by 2035, and finally by 2030. Unfortunately, our enemies had realized the importance of the regulatory role of TPPs before we did. While a year ago, 35% of our TPP and CHPP capacities remained intact as a result of enemy shelling, and a significant part of the equipment was restored by the end of the year, the targeted shelling in February-April of 2024 has left us with less than 20% of our thermal power generation capacity. We are now covering the daily peaks in energy consumption with expensive emergency assistance from other countries. Therefore, the tasks of restoring damaged TPP and CHPP capacities and building new decentralized generating capacities, in particular solid fuel ones, have become extremely urgent, given the high cost of gas.

Both tasks require an appropriate fuel base, but as a result of the hostilities in Western Donbas, we no longer have enough domestic thermal coal, and we need to use coal that has not yet been used in the energy sector, namely, imported coal of different quality, biomass, peat, RDF/SFR, etc.

These should not be just mixtures but fuels with specified thermal properties, which for existing boiler units should meet their design requirements and, if possible, ensure a reduction in emissions of harmful and greenhouse gases, and for newly created ones — plus the absence of slagging of heating surfaces and other problems during their combustion.

This is exactly what is envisaged by the resolutions of the Presidium of the National Academy of Sciences of Ukraine on the experience in energy use of non-project fuels. In particular, one of the priority tasks of the scientific institutions of the National Academy of Sciences of Ukraine is to develop scientific foundations, provide scientific support and practical solutions to urgent scientific, engineering, and technological problems of the heat and power industry to improve the reliability and safety of heat and power generation in the war and post-war peri-

ods. It is planned to develop research on the thermal conversion of blended fuels using renewable and alternative solid fuels, as well as on the combustion of biomass together with coal in TPP and CHPP boilers to diversify energy sources and utilize industrial and agricultural waste. Here are a few examples of the results of such research and their implementation.

One of the problems with the use of the so-called salty coal in pulverized coal boilers, which is abundant in the Northern Donbas, is the impact of ash with a high alkali metal content on slagging and corrosion of heating surfaces. The composition of the ash of composite raw materials is the result of chemical reactions of its mineral components and has other properties concerning corrosion and slagging. In experiments conducted by the TETI NASU with specialized equipment, it was found that the blend of salty coal with conventional steam coal increases the slagging start temperature due to the formation of new refractory compounds such as nepheline and ultramarine. The study of various blends allowed us to establish that for fuel compositions with salty coal, the share of salty coal that does not exceed 20% is acceptable in terms of preventing slagging and corrosion [22].

Co-firing of two fuels that differ significantly in characteristics requires a study of the combustion characteristics of the blends [23]. We have obtained the kinetic characteristics of the combustion rate of coal, peat, and their blends and have determined the proportion of peat at which the combustion rate of the blend becomes maximum [24].

Another technology is known for using peat as a fuel — with preliminary extraction of humic acids when used as a fertilizer, and then burning the residue as a fuel separately or together with coal [25].

Similar studies have been conducted for a blend of coal and chopped pellets from different types of biomass. The TETI has developed a preliminary design for the co-firing of coal and biomass in pulverized coal boilers at the Trypilska TPP [26]. Its implementation, which would allow adding 10–12% of biomass to the fuel base in terms of heat, improving flame ignition and burnout and reducing the generation of nitrogen oxides, sulfur dioxide, and greenhouse gas emissions, is low-cost compared to new biomass units, as it uses available equipment. Unfortunately, our legislation has not yet provided a preferential feed-in tariff for the share of clean energy produced from biomass when it is co-combusted with coal, which leaves its implementation without payback.

Another promising component of blended fuels is municipal waste, either sorted (RDF) or with specific thermal characteristics (SFR). Using numerical modeling methods, the TETI specialists have proved the possibility of co-combustion of RDF or SFR of different quality in a mixture with gas coal in the TPP-312 boiler and determined that this ensures the neutralization of harmful substances in combustion products at the required temperature and duration [27].

Complex physical and chemical processes occur during the thermal processing of another class of blends — coal and biomass. Using an example of a blend of coal with two types of biomass — wheat straw and pine pellets, a significant influence of biomass on the course of the coal pyrolysis process was established, in particular,

the degree of influence depends on the chemical characteristics of the biocomponent of the blend. During the combined thermolysis of coal and biomass in a dense layer, a synergistic effect was found, manifested in an increased conversion degree of the blend compared to the calculation according to the additivity rule and in changing composition of volatile products and the structure of solid residues [28].

The combustion of composite fuels has been widely used in dense-bed boilers. For example, sugar CHPPs have either gas-oil or anthracite boilers with a dense bed, which were later converted to natural gas. The urgency of their conversion to biomass with gas coal as a backup fuel has increased with the rise in gas prices. This is a non-trivial task, firstly, due to a decrease in the heat transfer of the furnace and an increase in heat transfer to the convection shaft of the boiler. The traditional solution — increasing the furnace volume or installing a pre-furnace — would be expensive and impossible for enterprises to implement in the short period between production seasons. Secondly, due to the high content of low-melting alkali metal oxides in the biomass ash, the slagging of the heating surfaces is so intense that it requires a shutdown every 2—3 weeks to clean them.

Here are two examples of how TETI specialists have addressed these issues. One concerns anthracite dense-bed boilers. As a result of the reconstruction of the heating surfaces, the boiler heat output is maintained when operating on sunflower husk pellets, dried sugar beet pulp, gas coal, and their blends. The other is gas-oil BKZ-75 GMA boilers, which, when converted to solid fuel, require reconstruction of the lower part of the furnace with the installation of a mechanical dense layer grate. It was possible to retain only 76% of the boiler heat output but to maintain virtually the same performance as gas-fired boilers' and even reduce nitrogen oxide emissions. Computational studies and tests have also led to new scientific results, in particular, in the redistribution of heat transfer when power plants are converted to other fuels. In total, from 2019 to 2023, with the participation of TETI specialists who developed technical solutions and supported commissioning, 20 former gas-oil or anthracite boilers with a steam capacity of 20 to 57 t/h were converted to biomass and gas coal. They replaced half a billion cubic meters of gas with biomass and coal. This experience is extremely important in creating decentralized energy capacities with cheaper and carbon-neutral biomass replacing gas.

The TETI's efforts to replace anthracite that has been in short supply or unavailable for ten years because of Russia's occupation of part of the Donetsk basin with another fuel, have played a major role in preserving the ability of the Ukrainian thermal power industry to cover peak loads in the system. Technical solutions have been developed for the combustion of Ukrainian coal of various degrees of metamorphism in blends with imported coal, petroleum coke, etc. in existing boiler units of thermal power plants. The work was carried out under extremely tight deadlines and became possible only due to the experience gained at the TETI in the thermal processing of a wide range of solid fuels and their blends [29, 30]. More detailed publications on these works are given in the references to Chapters 7 and 8.

The reader will find a broader coverage of the above developments in the following chapters. I hope that the experience gained by the Institute in deep study of physical and chemical processes accompanying the co-combustion of two solid fuels and the practical implementation of the developed technologies in operating boilers of different capacities will be useful to a wide range of scientists and engineers in the energy sector.

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**RESEARCH
ON THE COMBUSTION RATE
OF BINARY FUEL BLENDS**

This chapter presents experimental and computational research on the specific characteristics of co-firing and the mutual influence of coals with different degrees of metamorphism. The aim is to create conditions for the efficient combustion of coal fuel blends in existing pulverized coal boiler units. To achieve this, research on the kinetic characteristics of the conversion of the carbon residue from energy coal was conducted, and the interaction rates of coal coke residue with oxygen in the air were determined. The results and methods for calculating the specific combustion rate of coal coke residue over a wide temperature range are provided based on the constants obtained. A method for calculating the combustion dynamics of coke residue in a flow, for both individual coal brands and binary blends, is presented.

The specific combustion rate for a wide temperature range can be written as follows:

$$W_m = 1/((1/W_{kin}) + (1/W_{diff})), \quad (1)$$

where W_{kin} is the specific combustion rate per the current mass of carbon in the internal kinetic region (1/s) and W_{diff} is the specific combustion rate in the external diffusion region (1/s).

At relatively low particle temperatures, when the oxygen concentration on the reacting surface does not differ from its value in the flow, the combustion rate increases with temperature by the Arrhenius law, since diffusion limitations can be neglected in the kinetic region. With a further increase in temperature, the rate of transitions to the external diffusion combustion region, where the kinetic component can be omitted.

In the case of solid fuel combustion in a fixed bed at 950–1150 °C, the specific combustion rate is determined by both the kinetic and diffusion components. In the case of pulverized combustion (at combustion temperatures >1600 °C), the combustion rate is mainly determined by external diffusion limitations.

2.1. Research methods

2.1.1. Experimental facilities

RSK-1 installation for studying the kinetic characteristics of coal coke residue combustion with oxygen in the air. The RSK-1 installation was designed to study the kinetic characteristics of the interaction between coal cokes and oxygen in the air at temperatures up to 1000 °C. The core of the installation is a differential pulse reactor, which operates under conditions close to the ideal displacement of the gas phase and allows for the maintenance of temperature gradients in the reaction zone of less than 10 °C along its height. The ideal blending of coke residue particles is achieved by forming a fluidized bed.

The RSK-1 installation is constructed with a vertical tubular furnace equipped with adjustable electric heating. Inside, a straight-flow cylindrical reactor made of heat-resistant steel is placed. The reactor has a height of 1.1 m and an internal diameter of 0.033 m. At its bottom, there is a bed of magnesium oxide that preheats the gases entering from below. Above this bed, there is a gas-distribution grid for the fluidized bed, which prevents the sample particles from falling through [1, 2]. The supply of inert gas and air is arranged using a system of cylinders with air and inert gas. The temperature of the gases in the zone where the coke particles reside is measured with a thermocouple and an analog-to-digital converter.

The principal scheme of the RSK-1 installation is shown in Figure 2.1.

The experiment is conducted as follows. A sample of coke residue weighing about 0.1 g is placed on the grid, and the reactor is heated to the desired temperature. The fluidization of the bed is ensured by the flow of inert gas, whose flow rate is measured with a rotameter.

After stabilizing the temperature, a portion (pulse) of the reactant gas or air with a volume of $3 \cdot 10^{-4} \text{ m}^3$ is introduced into the flow using a dosing valve. The air is preheated as it passes through the bed. The switch from inert gas to reactant gas is made without interrupting the flow using a six-way valve and a loop of the predetermined volume. As the gas passes through

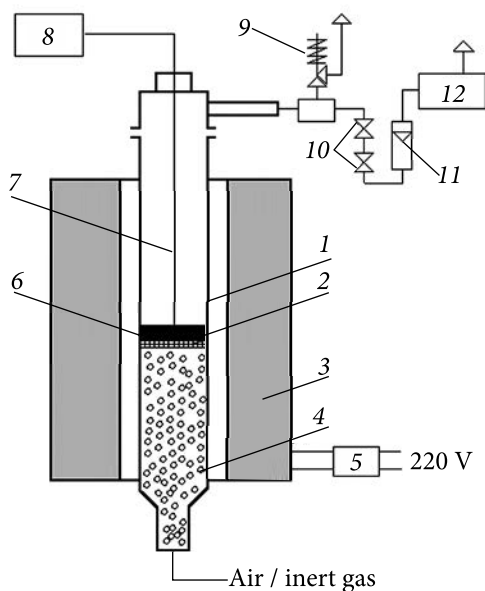


Fig. 2.1. RSK-1 installation for studying the kinetic characteristics of coal coke residue combustion: 1 — reactor, 2 — perforated grid, 3 — electric furnace, 4 — magnesium oxide filling, 5 — autotransformer, 6 — tested coke sample, 7 — thermocouple, 8 — temperature recorder, 9 — valve, 10 — needle valves, 11 — flow meter, 12 — gas analyzer

the fluidized bed, it reacts with the carbon, causing a slight increase in temperature. The combustion products (CO and CO_2) are cooled and filtered before being analyzed by a gas analyzer. After each pulse, the temperature in the inert gas flow stabilizes. Once the carbon conversion products' concentration falls below the sensitivity threshold of the gas analyzer, the maximum degree of carbon conversion for that temperature is recorded. The temperature is then raised above 900°C , and a control air pulse is introduced to complete the combustion of the residual carbon. When no combustion products are detected at the outlet, the experiment is considered completed.

The main advantages of the pulse experiment in the fluidized bed are the close-to-isothermal conditions of the coke reaction and the possibility of using slower but more accurate gas analyzers such as chromatographs or a Siemens Ultramat 23 combined gas analyzer. The latter measures CO and CO_2 in optical cells and oxygen in an electrolytic cell. Its readings are recorded by a computer every second, allowing for the integration of reaction product curves.

Coke samples were prepared in a quartz reactor in a fluidized bed with inert gas at 900°C for 40 min. The experiments were conducted on coke samples with particle sizes of $\delta = 0.09\text{--}0.2$ mm. The gas temperature in the reaction zone ranged from 653 K to 1033 K. The gas flow rate in all experiments was constant and amounted to $1.17 \cdot 10^{-5} \text{ m}^3/\text{s}$ [1, 2].

Pyrolysis-M installation. Experiments to determine the dynamics of volatile matter release and the kinetic characteristics of coke-ash residues from peat, bituminous coal, and their blends containing 5, 10, 15 and 20% peat were carried out using the laboratory "Pyrolysis-M" installation (Fig. 2.2). The fuel particle size ranged from 0.63 to 1 mm, and the size of the bed-forming sand particles was 0.2 to 0.4 mm. The total height of the layer with ash residue additives in the stationary state was 35–40 mm, while the total height of the working zone of the reactor was 210 mm.

The experiment begins when a fuel sample, weighing between 0.15 and 0.3 g, is introduced into the preheated reactor ($550, 650, 750$, and 850°C) through the airlock system. The fuel samples are introduced into the reactor via an airlock chamber mounted on a thermally insulated plug at the top of the reactor. The samples drop into the bed by gravity through a tube with an 18 mm diameter immersed 100 mm into the working zone. The outlet pipe for gaseous products is located just below the thermally insulated plug. Thus, the movement of the fuel sample is not affected by the gas outlet. The fluidizing and reacting agent—air—is supplied to the reactor from below. A metal mesh layer confines the reaction zone, preventing the magnesium oxide particles from falling. The mesh also securely holds the thermocouple junction 30 mm above the magnesium oxide layer. Air is supplied by a compressor, and the excess pressure in the reactor is measured with a manometer, while the air flow is measured with a rotameter. The gaseous products of oxidative pyrolysis and combustion exit through a water-cooled cyclone, where dust and tar are initially trapped. The products are then transported to the mass spectrometer through a poly-

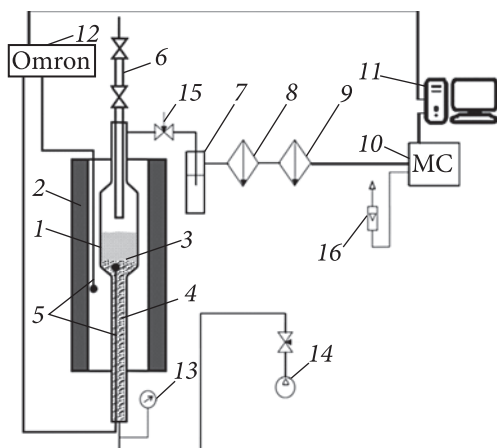


Fig. 2.2. Laboratory Pyrolysis-M installation: 1 — reactor, 2 — furnace, 3 — layer of inert material, 4 — MgO bed, 5 — thermocouples, 6 — airlock chamber, 7 — bubbling device, 8 — condensate collector, 9 — filter, 10 — mass spectrometer, 11 — computer, 12 — temperature controller, 13 — pressure gauge, 14 — compressor, 15 — air flow regulator, 16 — rotameter

ethylene tube with an inner diameter of 7.5 mm. Before entering the mass spectrometer, a three-way valve divides the gas flow into two parts: one part, carried by a constant flow through a fine filter, is supplied to the mass spectrometer, while the other is vented into the atmosphere. A magnetostatic mass spectrometer MX-1215, paired with a computer, is used as a fast-response gas analyzer, with a response time of less than one second. The mass spectrometer registers ion currents through direct current amplifiers over six parallel independent channels. The method for gas analysis is based on a linear dependence of the output voltage from the six channels of the mass spectrometer (tuned to the molecular mass of the main singly charged gas ion) on the partial pressure of the gas in the input gas mixture, with a total inlet pressure of about 0.1 MPa.

The measuring complex, consisting of the mass spectrometer, a multichannel analog-to-digital converter, and a computer, continuously determines and records the partial pressures of H_2 , CO , N_2 , CO_2 , O_2 , and Ar with a time step of 1 s.

The dependence of ion current on the partial pressure of gases in the analyzer chamber is affected by the conditions in the inlet system, which may change due to residual dust and tar contamination. However, this effect is the same for all gases and can be avoided by normalizing the raw data to 100%. The result of the normalization process is the volumetric fractions of H_2 , CO , N_2 , CO_2 , O_2 , and Ar . Water vapor and hydrocarbons starting from CH_4 were not considered in these measurements.

During the experiment, the stages of volatile release, incomplete combustion of volatiles, and combustion of the carbon in the coke residue occur sequentially. The volatile release stage is characterized by a drop in the oxygen concentration to almost background levels with increasing CO_2 , CO , and H_2 concentrations. This stage is considered complete when H_2 concentrations drop to background levels. The combustion of the coke residue is marked by a rapid decrease in CO concentrations, a slower decrease in CO_2 concentrations, and the corresponding increase in O_2 concentration. The maximum temperature of the fluidized bed is reached due to the combustion of the coke residue.

The experiment is considered complete when CO_2 and CO concentrations drop to their background levels and the temperature of the fluidized bed returns

to its initial value. The primary results of the experiment are the volumetric concentrations of H_2 , CO , O_2 , Ar , CO_2 , and N_2 , as well as the bed temperature, recorded with a time step of 1 s.

The air flow rate was selected so that to ensure fluidization of the bed in the gas rate range in the reactor ω :

$$\omega_{on} < \omega < \omega_{cr},$$

where ω_{on} and ω_{cr} are the rates at the onset of fluidization and the particle carry-over limit, respectively.

According to the recommendations in [3, 4], the critical rate ω_{cr} is calculated as:

$$\omega_{cr} = (Re_{cr} \cdot \nu_g) / d_1, \quad (2)$$

where Re_{cr} is the Reynolds number, calculated using the equation:

$$Re_{cr} = Ar / (1400 + 5.22\sqrt{Ar}).$$

Ar is the Archimedes number, ν_g is the kinematic viscosity of the gas (m^2/s), d_1 is the equivalent diameter of the particle (m).

The rate ω_{on} is calculated using an expression similar to equation (2), with the substitution:

$$Re_{on} = Ar / (18 + 0.61\sqrt{Ar}).$$

The optimal gas rate for required heat and mass transfer conditions in the fluidized bed is determined using:

$$Re_{opt} = Ar / (18 + 5.22\sqrt{Ar}). \quad (3)$$

2.1.2. Methods of experimental data processing

Method for processing experimental data obtained using the RSK-1 installation. According to [1, 7—11], the specific combustion rate for the current mass of carbon in the internal kinetic and internal diffusion regions W_m (1/s) is described by the equation:

$$W_m = k_0 \cdot \exp(-E_a / R \cdot T_p), \quad (4)$$

where k_0 is the preexponential factor (1/s), E_a is the effective activation energy (J/mol), R is the universal gas constant (8.314 J/(mol · K)), and T_p is the temperature of the particles.

The preexponential factor is given by:

$$k_0 = k_0' \cdot C_0,$$

where k_0' is the rate constant for the heterogeneous reaction ($m^3/(kg \cdot s)$), C_0 is the oxygen concentration in the flow where the coke particle burns (kg/m^3).

The rate constant for the heterogeneous reaction is:

$$k_0' = \beta \cdot S_{sp} \cdot k_0'',$$

where $\beta = 0.375 \cdot ([CO] + [CO_2]) / (0.5 \cdot [CO] + [CO_2])$ is the stoichiometric coefficient that converts the mass of reacted oxygen into the mass of reacted carbon ($0.375 \leq \beta \leq 0.75$), S_{sp} is the specific surface area of the particle (m^2/kg), k_0'' is the chemical reaction rate constant (m/s).

The specific surface area of a particle is determined as

$$S_{sp} = 6 / (\rho_p \times d_p),$$

where ρ_p is the particle density (kg/m^3) and d_p is the particle diameter (m).

The most illustrative indicator of the transition between reaction regions is the effective activation energy E_a , which is determined by the slope of the logarithmic dependence of the specific combustion rate on the inverse temperature (Arrhenius coordinates). In the internal kinetic region, the value of E_a is highest, reflecting the true activation energy of heterogeneous combustion. In the internal diffusion region, the effective value of E_a decreases by almost half with increasing temperature, due to the shrinking pore-reacting surface (the reaction shifts to the external surface) [7, 11]. In the external diffusion region, the exponential dependence of the reaction rate on the inverse temperature changes to a temperature dependence with an exponent of about 1.75, which is characteristic of the free diffusion rate of oxygen.

The combustion process of coke residue in the external diffusion region is a complex heterogeneous physicochemical process that includes such stages as the delivery of oxygen to the particle surface and the chemical reaction occurring on it. To describe the specific combustion rate in this region, certain assumptions are made: the reaction occurs on the external surface of the particle with the formation of final combustion products, the reaction is first-order, and the oxygen concentration on the entire surface is the same at any given moment, with the volume being constant.

According to [9, 13], the rate of heterogeneous combustion, accounting for the contributions of both heterogeneous (kinetic) and external (diffusion) components, can be expressed in terms of the amount of oxygen consumed per unit surface area per unit time ($kg/(m^2 \cdot s)$):

$$K_s^{O_2} = C_0 / (1/k + 1/\alpha_d), \quad (5)$$

where k is the heterogeneous combustion rate constant (m/s) and α_d is the diffusion mass transfer coefficient (m/s).

Using the specific combustion rate for the current mass of carbon, equation (5) becomes [9]:

$$W_m = \beta \cdot S_{sp} \cdot C_0 / (1/k + 1/\alpha_d). \quad (6)$$

At relatively low particle temperatures, when the oxygen concentration on the reacting surface does not differ from its value in the flow, the combustion rate increases with temperature according to the Arrhenius law. In the kinetic region, $\alpha_d \gg k$, and the value $1/\alpha_d$ in equation (6) can be neglected. Therefore, for the kinetic region, the specific combustion rate (1/s) is:

$$W_k = \beta \cdot S_{sp} \cdot C_0 \cdot k, \quad (7)$$

where k is determined from equation (4).

According to [11], the parameter β at temperatures above 1000 °C approaches 0.375, meaning that almost all the primary CO is homogeneously oxidized to CO₂.

With increasing temperature, the rate of the heterogeneous reaction becomes comparable to the rate of oxygen delivery to the particle surface, causing diffusion limitations to influence the reaction rate. For the transition region, W_m is determined by equation (6).

With a further increase in temperature, combustion shifts to the external diffusion region, where $\alpha_d \ll k$, so in equation (6), the value $1/k$ can be neglected. Hence, the specific combustion rate (1/s) in the external diffusion region is:

$$W_d = \beta \times S_{sp} \times C_0 \times \alpha_d. \quad (8)$$

The diffusion mass transfer coefficient (m/s) is calculated by the equation:

$$\alpha_d = \text{Nu}_d^{\text{O}_2} \times D/d_p,$$

where $\text{Nu}_d^{\text{O}_2}$ is the diffusion Nusselt number and D is the molecular diffusion coefficient (m²/s).

The diffusion Nusselt number expresses the dependence of the reaction rate on the hydrodynamic properties of the surrounding medium and is a function of the Reynolds number (Re). According to [13, 14], at low flow rates (Re < 100), the diffusion Nusselt number can be assumed to be $\text{Nu}_d^{\text{O}_2} = 2$.

The molecular diffusion coefficient [15]

$$D = D_0 \times (T/T_0)^{1.75},$$

where D_0 is the molecular diffusion coefficient under normal conditions (m²/s).

Using equations (7) and (8), the specific combustion rate for a wide temperature range (1/s) can be expressed as in equation (1).

The activation energy and chemical reaction rate constant were calculated using the least squares method from the dependence $W_m = f(T)$. To do this, the expressions above were linearized using the following relationships [1, 16]:

$$\begin{aligned} Y &= A + B \times X, \\ Y &= \ln (W_m \cdot T_p / (\beta \cdot 273)), \\ A &= \ln (C_0 \cdot k_0'' \cdot S_{sp}), \end{aligned}$$

$$B = -E_a/R,$$

$$X = 1/T_p.$$

The values of coefficients A and B were calculated by the equations:

$$A = [(\sum_{i=1}^N x_i^2) \times (\sum_{i=1}^N y_i) - (\sum_{i=1}^N x_i) \times (\sum_{i=1}^N x_i \times y_i)]/\Delta, \quad (9)$$

$$B = [N (\sum_{i=1}^N x_i \times y_i) - (\sum_{i=1}^N x_i) \times (\sum_{i=1}^N y_i)]/\Delta, \quad (10)$$

$$\Delta = N (\sum_{i=1}^N x_i^2) - (\sum_{i=1}^N x_i)^2, \quad (11)$$

where N is the number of experimental points at various temperature levels.

The values of A and B obtained from equations (9)—(11) were used to calculate the activation energy and the chemical reaction rate constant using the following expressions:

$$E_a = B \times R, \quad k_0'' = \exp(A)/(C_0 \times S_p).$$

The aim of processing the experimental results is to determine the specific combustion rate and the degree of conversion of the coking residue. Based on the current composition of the combustion products, their volumetric consumption, and the volume of the dosing loop, the specific combustion rate within the impulse can be determined based on measuring the mass flow rates of CO and CO₂ according to the gross reaction C+O₂ using expressions [1, 7, 8]:

$$W_m = (\Delta m/\Delta t)/m, \quad W_{m0} = (\Delta m/\Delta t)/m_0,$$

$$(\Delta m/\Delta t) = G_n \cdot ([CO] + [CO_2]) \cdot M_c / 22.4,$$

where W_m is the specific combustion rate based on the current mass of carbon, kg/(kg·s); W_{m0} is the specific combustion rate based on the initial mass of carbon, kg/(kg·s); $\Delta m/\Delta t$ is the decrease in the mass of carbon per unit time, kg/s; m_0 is the initial mass of carbon, kg; G_n is the air consumption, nm³/s; [CO] and [CO₂] are the concentrations of CO and CO₂, i.e., volume fractions; M_c is the molar mass of carbon, kg/kmol.

The degree of carbon conversion after the i -th impulse is found using the expression:

$$x_i = 1 - (m_i - \Delta m_i) / m_0,$$

where m_i is the current mass of unreacted carbon, kg; Δm_i is the decrease in the mass of carbon per impulse, kg. The initial mass of carbon m_0 is determined from the data of technical analysis of the coke.

The temperature of burning particles (T_p , K) was calculated considering the unevenness between the particles and the gas and was determined based on the thermal balance of the particles. For low reaction temperatures ($T_p < 950$ K), radiative heat exchange between the gas and the particle can be neglected. For the bubbling bed conditions, the equation for determining the temperature non-uniformity between the gas and the particle (ΔT , K) takes the form [7, 8]:

$$\Delta T = (Q \cdot W_{m0} \cdot d_e^2 \cdot \rho_m^a) / (6Nu \cdot \lambda_g),$$

where Q is the heat effect of the reaction (for the reaction $C + O_2 = CO_2$, $Q = 32.8 \cdot 10^3$ kJ/kg [15]); d_e is the equivalent diameter of the particle, m; ρ_m^a is the apparent density of the particles, kg/m³; Nu is the Nusselt number; λ_g is the thermal conductivity coefficient of the gas, W/(m · K).

The Nusselt number for conditions of convective-conductive heat exchange [17]:

$$Nu = 6 + 0.1 \cdot Ar^{0.39},$$

where Ar is the Archimedes number:

$$Ar = (g \cdot d_e^3 / \nu_g^2) \cdot (\rho_m^a - \rho_g) / \rho_g,$$

where g is the acceleration of gravity, m/s²; ν_g is the kinematic viscosity of the gas, m²/s; ρ_g is the density of the gas, kg/m³.

Typically, during the impulse, the temperature in the reacting layer did not rise more than by 5 K. Even at the highest temperatures of the experiment, the temperature gradient between the particle and the gas did not exceed 10 K.

In the case of constant reactor temperature, the main result of the experiment is carbon conversion curves, i.e., the dependences $W_m = f(x_i)$. According to the known methodology [13, 18–20], in the presence of quasi-stationary sections on the conversion curves, the subsequent sample of the same coal coke is brought to the beginning of the quasi-stationary section in impulses at constant temperature, and then before each subsequent impulse, the temperature is increased. Within the quasi-stationary sections, this allows obtaining the experimental dependence $W_m = f(T_p)$, necessary for determining the kinetic characteristics of combustion. In particular, the activation energy is found from the straight line slope of $\ln W_m = f(1/T_p)$ in the Arrhenius coordinates.

Gas consumption was measured using rheometers calibrated to standard instruments, with a relative error of less than 2.5%. The relative error of the gas analyzer was no more than 1% of the measured range, with the ability to switch the attenuation coefficient from 1 to 1000. Since the concentration of CO in the reaction products in the experiments was no more than 0.02 and no less than 0.002 of the concentration of CO₂, this allowed maintaining approximately constant instrument errors for CO₂ and CO (approximately 2% relative in the mid-range) throughout their concentration ranges. The absolute measurement error of the mass of coal and coke samples was 0.001 g, corresponding to a relative error of 1% at a sample mass of 0.1 g. The volume of the dosing loop was determined by weighing during filling with water with an error of less than 0.25%. Ultimately, the main measure of the accuracy of the obtained results was the convergence of the final degree of conversion, determined in the experiment through gas analysis after the final combustion of the carbon residue and from the technical analysis of the initial coke.

Thus, the provided calculation methodology allows determining the specific combustion rate of the coking residue and the degree of its conversion based on

the experimental data obtained from the RSK-1 setup, calculating the temperature of the coke particles considering their overheating during reaction with air oxygen, and obtaining the kinetic characteristics of the reaction of the coking residue with air oxygen.

Methodology for processing experimental data obtained from the Pyrolysis-M setup. The longest of all combustion stages of solid fuel particles is the burning time of the coke residue. It is this time that is crucial for calculating the burning time of solid fuel in the fuel industry [21]. The combustion characteristics of a coke residue particle depend on the ratio of the diffusion rate of oxygen to the reacting surface of the solid particle and the rate of heterogeneous carbon reaction, which in turn depends on the process temperature.

One of the most common methods for describing the burning of coke residue is the Arrhenius equation based on a first-order reaction model, where the specific combustion rate of carbon, W_m , is described by the expression [22]:

$$W_m = k_0 \cdot \exp^{\frac{-E_a}{R \cdot T_p}},$$

where k_0 is the preexponential factor, 1/s; E_a is the effective activation energy, J/mol; R is the universal gas constant, 8.314 J/(mol · K).

The pre-exponential factor is given by

$$k_0 = k_0' \cdot C_0,$$

where k_0' is the rate constant for the heterogeneous reaction, m³/(kg · s); C_0 is the concentration of oxygen in the flow where the coke residue particle is burned, kg/m³.

The rate constant for the heterogeneous reaction (m³/(kg · s)) is expressed as

$$k_0 = \beta \cdot S_p \cdot k_0'',$$

where β is the stoichiometric coefficient for converting the mass of reacted oxygen into the mass of reacted carbon; S_p is the specific (per unit mass) surface area of the particle, m²/kg; k_0'' is the chemical rate constant for the reaction, m/s.

Obtaining kinetic constants such as activation energy, rate constants for the heterogeneous reaction, and chemical rate constants while considering external diffusion limitations will allow the calculation of the specific combustion rate of coke residue for selected fuel types, enabling the computation of the burning time of a fuel particle of a certain size at a specified temperature.

Based on the composition of combustion products and their volumetric flow rate obtained during the experiment, the specific combustion rate per unit time was determined:

$$W_{m0} = \frac{\frac{\Delta m}{\Delta t}}{m_0},$$

where W_{m0} is the specific combustion rate relative to the initial mass of carbon, kg/(kg · s); $\Delta m/\Delta t$ is the decrease in carbon mass per unit time (determined from

the mass flow rates of CO and CO₂ based on the gross reaction $C + O_2$), kg/s; m_0 is the initial mass of carbon, kg.

The degree of carbon conversion at any moment is determined by the expression:

$$x_i = 1 - \frac{m_i}{m_0},$$

where m_i is the current mass of unreacted carbon, kg.

Considering the significant increase in the temperature of the burning particle relative to the gas and reactor wall temperatures, the overheating of the particle was calculated from the thermal balance, considering the convective and radiative heat exchange using the equation:

$$\Delta T = T_g - T_p = \frac{Q \cdot W_{m0} \cdot \rho_p^k \cdot d_e^2}{6 \cdot Nu \cdot \lambda_g} + \frac{d_e \cdot \delta \cdot \varepsilon_{pw}}{Nu \cdot \lambda_g} \cdot (T_w^4 - T_p^4),$$

where T_g , T_p , and T_w are the temperatures of gas, particle, and wall, respectively, K; Q is the heat effect of the reaction $C + O_2 = CO_2$, kJ/kg; ρ_p^k is the apparent density of the particles, kg/m³; d_e is the equivalent diameter of the particle, m; λ_g is the thermal conductivity of the gas, J/(m · s · K); δ is the Stefan-Boltzmann constant, J/(m² · s · K⁴); ε_{pw} is the integral emissivity.

Given the particle temperature at any moment in both parts of the equation, an iterative method was applied for its solution with a time discretization of one second. The particle overheating ranged from 110 to 270 °C depending on the initial temperature in the reactor.

Each sample of the study was conducted taking into account particle overheating in the temperature range from 667 to 1204 °C.

The dependence of the specific (relative to the initial mass) burning rate on the degree of carbon conversion rate (X) in coke residues from bituminous coal, peat, and their blends at four temperature levels (550, 650, 750, and 850 °C) exhibits a gentle slope, characterized by a deviation of W_{m0} at each point of no more than 10% from the average value. The range of constant specific burning rates is within $X = 0.1$ – 0.7 at a particle temperature of 600 °C and tends to narrow with increasing temperature.

The presence of a region of constant specific combustion rate relative to the initial mass of carbon over a wide conversion range allowed for the use of its average values and temperature values to construct the dependence $W_{m0} = f(T)$.

The specific combustion rate for a wide temperature range includes kinetic W_k and diffusion W_d components and is represented by equation (1).

The specific combustion rate in the external diffusion region was determined by the equation:

$$W_d = \frac{\beta \cdot S_p \cdot C_0 \cdot Nu_d^{O_2} \cdot D}{d_p},$$

where $Nu_d^{O_2}$ is the Nusselt diffusion criterion; D is the molecular diffusion coefficient, m²/s.

The apparent density of the coke residue particles necessary for determining S_p was taken as 1400 kg/m^3 for bituminous coal and 615 kg/m^3 for peat. With the calculated diffusion component of the rate and experimentally obtained total specific combustion rate from equation (1), W_κ was obtained.

2.2. Blends of anthracite with lean coal and anthracite with bituminous coal

The study of the kinetic characteristics of the reaction of the coke residue from energy-grade coals with oxygen in the air [1, 2, 16, 23, 24] was conducted on the RSK-1 installation according to the methodology described in subsection 2.1.2.1 for conducting experiments and processing experimental data. The coal samples, which consisted of standard ground coal dust, were taken from the dust feeders of the power units of thermal power plants in Ukraine: anthracite from the Tripoli deposit, lean coal from the Zmiivska TPP, and bituminous coal from the Ladyzhynska TPP. The technical analysis of the initial coal dust is presented in Table 2.1.

Experiments were conducted on coke samples with particle sizes ranging from 0.09 mm to 0.2 mm. The required fraction was obtained by sieving the coal dust through laboratory sieves. From the sifted coal, cokes were obtained for kinetic studies, with ash content presented in Table 2.2. The difference in ash content between the initial dust and the obtained coke residues is related to the different distributions of mineral inclusions and coal-mineral growths by particle size for various coal grades. The blends were formed by blending equal mass samples of cokes from two grades of coal.

The study of the kinetic characteristics of the reaction of the coke residue from coal with oxygen in the air began with determining the dependence of the reaction rate W_m on the conversion degree X under isothermal conditions ($W_m = f(X)$ at $T = \text{const}$). This dependence allows us to define the boundaries of the quasi-stationary region — the range of carbon conversion degrees in which

Table 2.1. Technical analysis of the initial dust samples

Coal type	R_{90} , %	W^a , %	A^d , %	V^d , %
Anthracite (A)	6—8	0.67	27.19	3.73
Lean coal (L)	9—12	0.65	24.68	7.65
Bituminous coal (B)	20—25	5.5	24.98	40.55

Table 2.2. Ash content in the obtained cokes (fraction 0.09—0.2 mm)

Ash content	Coal type				
	A	L	B	A/L blend	A/B blend
A^d , %	10.6	16.9	33.6	13.7	22.1

the reaction rate changes by no more than 10%. Experimental studies of the temperature dependence of the burnout rate ($W_m = f(T)$) were conducted within the defined quasi-stationary reaction areas, following the methodology described in section 2.1.2.

2.2.1. Dynamics of conversion of dust-like particles of coke residue under isothermal conditions

The dependence of the conversion rate of coke residue on the conversion degree under isothermal conditions at atmospheric pressure for coke samples of each coal grade separately and their blends was determined over a temperature range from T_{min} to T_{max} with a step of 25 °C. T_{min} and T_{max} were determined empirically according to the recommendations in [10]. $T_{min} = 550$ °C was defined as the minimum temperature at which, during the reaction of the least reactive anthracite coke with oxygen in the air, the amount of reaction products (CO, CO₂) exceeds the sensitivity of the gas analyzer. $T_{max} = 600$ °C was defined as the maximum temperature at which the degree of carbon conversion per pulse for the most reactive bituminous coal coke does not exceed 10%. It should be noted that under these conditions, the content of combustion products CO₂ and CO at the reactor outlet did not exceed 5 %, meaning that the reactions in all cases occurred in conditions of excess oxidizer. The dependences of the specific oxidation reaction rates of coke from A and L coals and their blend on the carbon conversion degree at a reactor temperature of $T_p = 550$ °C (823 K) are presented in Figure 2.3.

As follows from Figure 2.3, the dependence of the burn-off rate of the coke residue from coal grades A and L at a constant temperature has a quasi-stationary area and is characterized by a practically constant burn-off rate, the value of which does not deviate from the average by more than 10%. The boundaries of the quasi-stationary region for A coke are $X = 10$ –40% and for lean coal $X = 12$ –30%. For the A/L blend, there is a region of constant reaction rate that does not depend on the carbon conversion degree in the range $X = 0$ –30% (curve 3 in Fig. 2.3), although within this conversion range, the blend components separately (up to $X = 12\%$ for semianthracite coal coke L and up to $X = 10\%$ for anthracite coke) do not exhibit quasi-stationary burn-off rate regions. The gentle area for the blend was formed by overlapping the burn-off rates of the blend components. Combustion under excess oxygen conditions occurs independently of each other. This is also evidenced by the closeness of experimental curve 3 and calculated curve 4, which represents the averaged curve of the blend calculated using the system of equations (12)–(13), based on the experimental data from curves 1 and 2:

$$W_{m,i \text{ blend}} = [(\Delta m / \Delta \tau)_{iA} + (\Delta m / \Delta \tau)_{iB}] / (m_{iA} + m_{iB}), \quad (12)$$

where $W_{m,i \text{ blend}}$ is the specific combustion rate of the blend per current mass of carbon, kg/(kg · s); $(\Delta m / \Delta \tau)_{iA}$ and $(\Delta m / \Delta \tau)_{iB}$ — reduction in the mass of carbon per unit time in the i -th pulse for the blend components A and B, kg/s; m_{iA} and

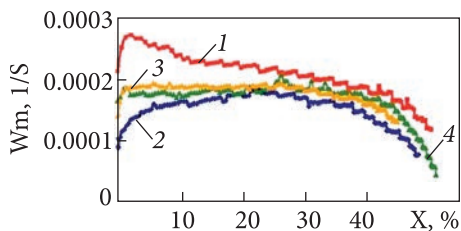


Fig. 2.3. Dependence of the oxidation reaction rate of coke residue from coal grades A and L and their 1:1 blend on the carbon conversion degree: 1 — L; 2 — A; 3 — A/L blend; 4 — calculated averages

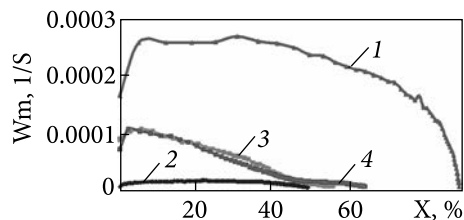


Fig. 2.4. Dependence of the specific combustion rate of the coke residue from coal grades A and B and their 1:1 blend on the carbon conversion degree: 1 — B; 2 — A; 3 — A/B blend; 4 — calculated averages.

m_{iB} are the current mass of carbon that has not reacted after the i -th pulse of the blend components A and B, kg.

$$x_{i\text{blend}} = 1 - (m_{iA} + m_{iB}) / (m_{0A} + m_{0B}), \quad (13)$$

where $x_{i\text{blend}}$ is the degree of conversion of the blend after the i -th pulse; m_{0A} and m_{0B} are the initial mass of carbon for the blend components A and B, kg.

Figure 2.4 shows the dependences of the specific combustion rate of coke residue from coals A, B, and A/B blend reacting with oxygen in the air on the carbon conversion degree at a reactor temperature of $T_p = 550^\circ\text{C}$ (823 K). Such a dependence for bituminous coal coke (curve 1 in Fig. 2.4) exhibits a quasi-stationary region within $X = 10\text{--}50\%$.

Curve 2 (for A) in Figure 2.4 is analogous to curve 2 in Figure 2.3. The combustion rate of the A/B blend (curve 3) does not exhibit a quasi-stationary region. At the beginning of combustion ($X < 20\%$), it is close to the combustion rate of bituminous coal coke (considering its share in the blend), while in the range $X = 20\text{--}40\%$, it decreases and reaches the combustion rate of anthracite coke after $X = 40\%$. This behavior is explained by the fact that at the start of combustion, primarily bituminous coal coke burns off in the blend. After its burn-off, the ratio of the cokes in the blend changes in favor of increasing the share of anthracite coke, which leads to a decrease in the combustion rate. After reaching a conversion degree of $X = 40\%$, only anthracite coke remains, which explains the gentle region at $X = 40\text{--}60\%$. In Figure 2.4, curve 3 is close to curve 4, which was constructed using the system of equations (12)—(13), confirming the absence of interaction in the combustion of coke residue particles of different metamorphism degrees under isothermal conditions and in an excess oxygen environment.

The highest value of temperature non-uniformity (the excess particle temperature over the gas temperature) in the experiments at 550°C reached 0.7°C during the combustion of bituminous coal coke.

Similar experiments were conducted at 575 and 600°C . They confirmed that, in general, the combustion rate dependences for the coke residues from blends

A/L and A/B do not exhibit a quasi-stationary region. The boundaries of the quasi-stationary regions for coke residues from individual coal grades at 550, 575 °C, and 600 °C are summarized in Table 2.3.

2.2.2. Determination of the kinetic characteristics of coal coke residue combustion in the internal kinetic and internal diffusion regions of reaction

The study of the dependence of the combustion rate of blends of coal coke residue with significantly different degrees of metamorphism (A and B) on the carbon conversion degree showed that determining kinetic constants is complicated, in general, by the absence of quasi-stationary reaction regions for blends. On the other hand, the obtained data indicate the absence of interaction between the combustion of coal coke residue particles of different degrees of metamorphism under isothermal conditions and in an excess oxygen environment. Therefore, kinetic constants were determined separately for anthracite coke, lean coal, and bituminous coal residues.

To determine the kinetic characteristics of coal coke residue combustion, the dependence $W_m = f(T)$ was obtained for samples of anthracite, lean coal, and bituminous coal, as well as for blends A/L and A/B. The dependence $W_m = f(T)$ was measured starting from a temperature of $T = 380$ °C, which was increased stepwise by 10 °C. The calculation of the specific combustion rate of carbon, taking into account the temperature non-uniformity between the gas and particles, was performed using the methodology described in subsection 2.1.2.1. The dependence of the specific combustion rate on temperature for coke residue from anthracite, lean coal, and their blend is shown in Figure 2.5 [25, 26].

In Figure 2.5, the specific combustion rate of the blend lies between the specific combustion rates of anthracite and lean coal across almost the entire temperature range. Starting from a temperature of 630 °C, the reaction rate of the blend reaches the combustion rate of anthracite. This indicates that the coke residue of the lean coal in the blend has practically burned out.

Figure 2.6 presents the interaction rate curves for anthracite coke, bituminous coal coke, and their blend [1, 16].

Table 2.3. Boundaries of quasi-stationary regions of carbon conversion for different temperatures and coal grades

Temperature, °C	Boundaries of quasi-stationary regions by X, %		
	A	L	B
550	10—40	12—30	10—50
575	15—55	20—40	30—60
600	20—54	25—50	35—60

Fig. 2.5. Dependence of the specific combustion rate of the coke residue from coal grades A, L, and their 1:1 blend on the inverse temperature: 1 — L; 2 — A; 3 — A/L blend

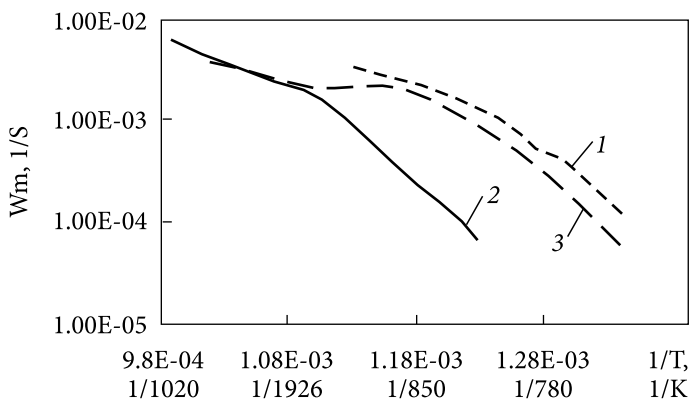
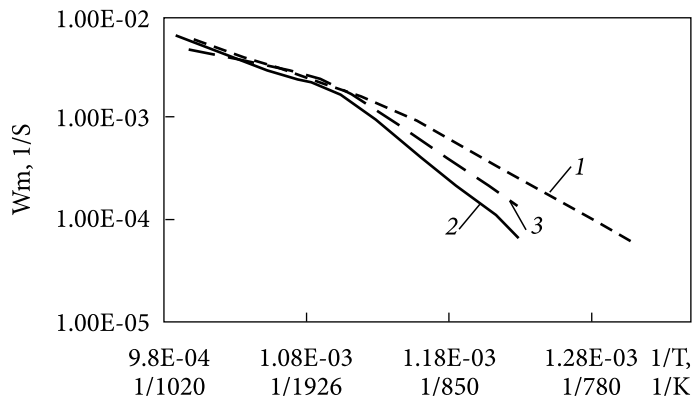


Fig. 2.6. Dependence of the combustion rate of the coke residue from coal grades A, B, and their 1:1 blend on the inverse temperature: 1 — B; 2 — A; 3 — A/B blend

The combustion rate of the A/L blend (curve 3 in Fig. 2.6) in the temperature range of 470 to 560 °C approaches the combustion rate of bituminous coal coke (considering its share in the blend). In the range from 560 to 630 °C, the combustion rate of the blend remains constant and approaches the combustion rate of anthracite. This is due to the increased share of anthracite coke in the blend, as the bituminous coal coke burns out. Starting from 630 °C, the combustion rate of the blend corresponds to the combustion rate of anthracite, indicating that the bituminous coal coke in the blend has practically burned out.

The data obtained from the experiments on the RSK-1 installation allows for the determination of the kinetic characteristics of the interaction process of coke residues from individual coal grades, using the Arrhenius approximation. This also helps identify the temperature ranges for internal kinetic and internal diffusion reaction regimes, which are necessary for calculating the carbon conversion rate. These characteristics were determined using the least squares method by linear approximation of the specific combustion rate in the Arrhenius coordinates.

The analysis of the results revealed two reaction regions for the coke residue from coal grades A, L, and B (with a particle size of $d = 0.09\text{--}0.2$ mm) in the

presence of oxygen from the air. In the particle temperature range up to 627 °C (900 K) for anthracite coke residue, up to 622 °C (895 K) for lean coal coke residue, and up to 520 °C (793 K) for bituminous coal coke, there is an internal kinetic limitation on the reaction rate. Starting from particle temperatures of 637 °C (910 K) for anthracite coke, 632 °C (905 K) for lean coal coke, and 530 °C (803 K) for bituminous coal coke, internal diffusion limitations begin to dominate. The results of the kinetic characteristic calculations for the studied samples in these regions are presented in Table 2.4 [16].

The obtained kinetic characteristics differ from the values previously obtained by Maistrenko [7, 10]. To assess the reliability of the kinetic characteristics obtained and to identify the reasons for the mentioned discrepancy, the kinetic constants were used to calculate the reaction rates in the internal kinetic region ($W_{\text{int.k}}$) and the internal diffusion region ($W_{\text{int.d}}$) for coke particles from A, L, and B coal grades with an average size of $d = 0.145$ mm by the following expressions [7, 9]:

$$W_{\text{int.k}} = C_0 \cdot k_0'' \cdot (273/T_p) \cdot \exp(-E_a/(R \cdot T_p)),$$

$$W_{\text{int.d}} = \beta \cdot (273/T_p) \cdot S_{sp} \cdot C_0 \cdot k_0'' \cdot \exp(-E_a/(R \cdot T_p)).$$

The dependences of the specific combustion rate on temperature in the form $\ln(W_m) = f(1/T_p)$ for the kinetic characteristics listed in Table 2.4 and obtained by Maistrenko are presented in Figure 2.7 for cokes from three energy coal grades studied.

By Figure 2.7, *a*, for the coke residue of anthracite coal, the carbon conversion rate calculated using the kinetic constants from [10] for the internal kinetic and internal diffusion regions with a particle size of $\delta = 0.145$ mm practically coincides with the conversion rate calculated based on the kinetic characteristics obtained in the experiments. For the coke residue of lean coal (Fig. 2.7, *b*, the rate

Table 2.4. Kinetic characteristics of the oxidation reaction rate of coal coke residues from anthracite, lean coal, and bituminous coal in the internal kinetic and internal diffusion regions of the reaction (average particle size $d = 0.145$ mm)

Coke residue	k_0' , m ³ /(kg·s)	k_0'' , m/s	E_a , kJ/mol
<i>Internal kinetic region ($\beta = 0.45$)</i>			
Anthracite	1.2×10^{11}	1.02×10^{10}	221.7
Lean coal	1.62×10^7	1.35×10^6	152.5
Bituminous coal	1.83×10^{11}	1.39×10^{10}	202.4
<i>Internal diffusion region ($\beta = 0.75$)</i>			
Anthracite	6.18×10^4	3188	108.4
Lean coal	1.6×10^4	798.6	96.5
Bituminous coal	7.39×10^4	3333	100.9

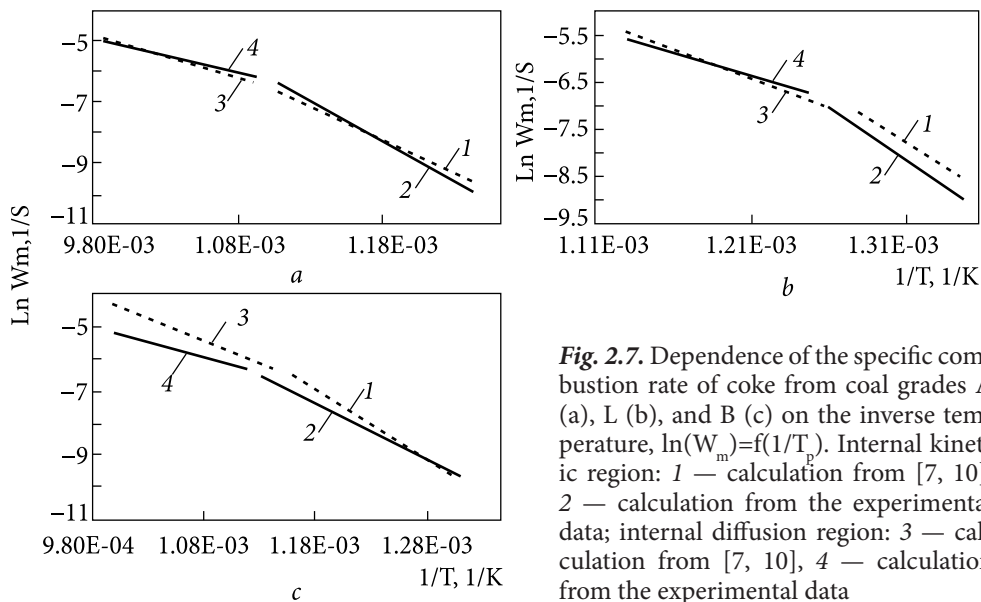


Fig. 2.7. Dependence of the specific combustion rate of coke from coal grades A (a), L (b), and B (c) on the inverse temperature, $\ln(W_m)=f(1/T)$. Internal kinetic region: 1 — calculation from [7, 10], 2 — calculation from the experimental data; internal diffusion region: 3 — calculation from [7, 10], 4 — calculation from the experimental data

calculated using the kinetic constants of Maistrenko is higher than that obtained experimentally. This discrepancy is explained by the differences in the degree of metamorphism between the samples of the same coal grade: in [10], the study involved coal with a volatile matter (VM) content $V^{daf} = 10\text{--}12\%$, while the sample used in the experiments had the lower VM content ($V^{daf} = 8\%$), and thus, the lower reactivity.

By Figure 2.7, c, the combustion reaction rate of the bituminous coal coke residue in the internal kinetic region, obtained from the experiments, is lower than the rate calculated using the kinetic constants from [10]. However, in the internal diffusion region, the experimentally obtained rate practically coincides with the calculated rate. The transition temperature from the internal kinetic to the internal diffusion regime for gas and lean coals is about 10 K higher than the temperature calculated in [10]. These differences can be attributed to variations in the ash content and average particle size of the coke studied compared to [10].

Considering the differences in the values of kinetic constants associated with the variations in ash content, particle size, and coal reactivity within each grade, the established trends in the temperature dependence of the specific combustion rate and the transition point between the internal kinetic and internal diffusion regions generally confirm the conclusions of the study [10].

Thus, the obtained kinetic constants for the reaction rate of anthracite, lean, and bituminous coal coke residues with oxygen in the air can be used to calculate their specific combustion rate over a wide range of temperatures.

2.3. Blends of bituminous coal with peat

The time of the VM release from the studied fuel samples and their blends was determined using gas analysis, following the methodology described in subsection 2.1.2, and is presented in Table 2.5.

As seen from the results, the VM release time for peat is significantly shorter than for bituminous coal at any given temperature, although the VM content in peat is much higher. In the blends, the slower VM release rate from coal is the determining factor, so the peat content has little effect on the overall VM release time.

The dependence of the total, kinetic, and diffusion-specific combustion rates of the coke-ash residue of bituminous coal on the inverse temperature is shown in Figure 2.8.

The values of the activation energy and the chemical rate constant were calculated using the least squares method from the dependence $W_k = f(T)$ and are presented in Table 2.6. The obtained kinetic characteristics make it possible to determine the specific conversion rates of the coke-ash residues of the studied fuels within wide ranges of particle sizes and temperatures.

Comparing the kinetic combustion rates of the cokes of the blends and individual fuels (Fig. 2.9), one can see that pure peat has the highest combustion rate. In the blends, as the peat content increases, the overall combustion rate also increases, but after 10% peat content, this increase becomes insignificant.

Table 2.5. Dependence of volatile matter release time on temperature

Sample	Volatile matter release time, s			
	550 °C	650 °C	750 °C	850 °C
Bituminous coal	22	13	13	13
Peat	9	11	7	9
5% peat blend	25	13	13	10
10% peat blend	22	18	13	10
15% peat blend	22	13	12	13
20% peat blend	22	16	12	13

Table 2.6. Kinetic characteristics of the combustion rate of coke-ash residue ($\beta = 0.45$; average particle size 0.815 mm)

Sample	$k_o', \text{m}^3/(\text{kg} \cdot \text{s})$	$k_o'', \text{m/s}$	$E_a, \text{kJ/mol}$
Bituminous coal	64.1	93.5	57.7
Peat	267.7	171.4	61.9
5% peat blend	43.0	60.9	53.8
10% peat blend	188.4	259.2	66.1
15% peat blend	170.9	228.1	65.3
20% peat blend	131.1	169.6	62.4

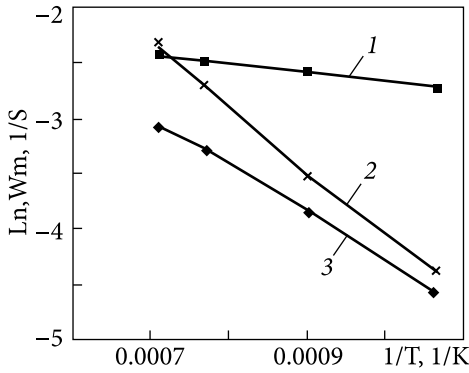


Fig. 2.8. Dependence of the specific combustion rate of bituminous coal coke on the inverse temperature: 1 — diffusion component of the combustion rate; 2 — kinetic component of the combustion rate; 3 — total combustion rate.

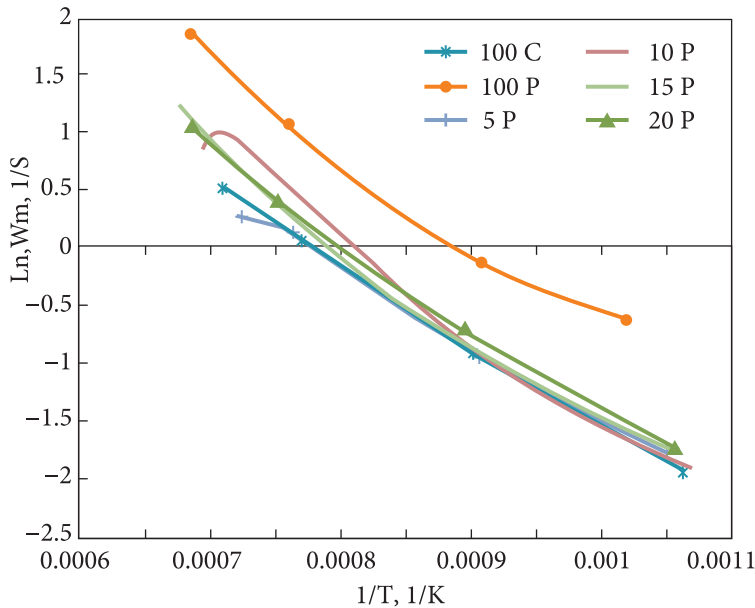


Fig. 2.9. Dependence of the specific kinetic combustion rate of the cokes from bituminous coal, peat, and their blends on the inverse temperature

The same trend can be seen in Table 2.7, which shows the burnout time of the sample at 850 °C after the introduction into the reactor. As the peat content in the blend increases, the burnout time decreases, with the shortest time observed for pure peat. However, after increasing the peat content beyond 10%, the burnout time changes little. This confirms the previous conclusion that the optimal rather than maximum peat content in the blend with bituminous coal is in the range of 10—15%.

The effect of peat content on the combustion of blends at different temperatures was determined. It was shown that peat is a more reactive fuel, and as the

Table 2.7. Burnout time of fuel samples with different peat contents

Peat content in the blend, %	0	5	10	15	20	100
Burnout time of sample, s	90	69	50	52	52	31

peat content increases, the VM release time decreases, and the kinetic combustion rate of the coke residue increases.

It was determined that at 10% peat content, the effect of peat on the combustion rate of the blend becomes maximal. With further increases in peat content, the effect diminishes.

2.4. Engineering method for calculating the combustion of binary solid fuel blends

2.4.1. Main provisions

Using the results of the research on the kinetic characteristics of the interaction between coal coke residues and oxygen in the air, as well as the method for calculating the burnout dynamics of coal coke residues in coal blends in an isothermal flow, it is possible to develop an engineering method for calculating the dynamics of pulverized coal combustion in blends of different coal grades in a non-isothermal flow, based on the following provisions.

It is known that the release of VM plays a key role in determining the ignition and combustion conditions of a pulverized coal flame [13, 14, 19]. During the combustion of a blend, the heat released from the combustion of VM from bituminous coal raises the flow temperature, which in turn intensifies the heating of anthracite particles, thereby reducing the induction time of the pulverized coal flame ignition and increasing its temperature. On the other hand, the combustion of a greater amount of VM than that in the anthracite leads to a decrease in oxygen concentration in the flame core, which reduces the burnout rate of the coke residue particles. The engineering method for calculating the burnout dynamics of blends of coals with different degrees of metamorphism considers the effect of temperature and oxygen concentration changes on the coal combustion rate over time.

The calculation begins with determining the initial parameters such as the characteristics of the coal, the ratio of different coal grades in the blend (both as-received and combustible mass), the excess air coefficient, and the initial flow temperature. Based on these parameters, the specific air consumption for burning 1 kg of the coal blend and the amount of combustion products, considering the excess air coefficient α , can be determined.

At the initial stage of combustion, it is necessary to determine the time of VM release, the heat released during their combustion, and the oxygen concentration after the VM has burned. The engineering method for calculating the burnout dynamics of coal blends is reduced to determining the degree of conversion of

the blend that has reacted over a certain time interval. For this, the total combustion time must be divided into equal intervals. To determine the degree of conversion, the fraction of carbon that has not yet reacted in each time interval is to be calculated. This fraction is determined from the previous iteration based on the specific combustion rate of the coke residue, which depends on the particle temperature and the oxygen concentration in the flow. The oxygen concentration at time i , considering α , is determined based on the specific oxygen consumption for the combustion of volatiles and the fraction of the coke residue in the blend that has already reacted.

The flow temperature is determined from the thermal balance of the coal combustion process. The heat release over a certain time interval is calculated as the product of the fraction of coal that has burned in this interval, the initial mass flow, and the calorific value of the fuel. At the initial stage of combustion, heat release occurs due to the combustion of VM. The flow temperature increase above a given time interval is determined by the heat release, heat losses, and mass flow rates of combustion products, air, ash, and unburned carbon.

For a given temperature and particle size for each coal grade, using the kinetic constants of the interaction rate of the coke residue with oxygen and the calculations, the specific combustion rate of the coke residue at an oxygen concentration of 21% is determined for each component of the coal blend. After that, the specific combustion rate of the coke residue is determined at the current oxygen concentration. The specific combustion rate decreases proportionally to the reduction in oxygen concentration in the flow. Based on the calculated specific combustion rate, the degree of conversion of the coke residue and the coal can be determined.

The combustion of pulverized coal particles in the furnaces of power boilers takes place in a non-isothermal dusty gas flow of high-temperature combustion gases. Therefore, to perform engineering calculations, based on empirical data of the Standard method, numerical coefficients are needed that generalize the nonlinearity of the dependence of the combustion rate on the content of the high-reactivity component in the blend. Obtaining such coefficients empirically requires a large number of boiler tests when burning blends with different component ratios. Such experiments are expensive and labor-intensive. A simplified calculation of the combustion of coal blends in a flow reactor allows for the determination of the dependence of the combustion rate of the blend on the content of the high-reactivity component.

The calculation of the combustion of coal blends with different degrees of metamorphism in a flow reactor for simplification includes several assumptions. It is assumed that the velocity and temperature of the gas phase and solid particles are the same, meaning that there is no heat exchange between them. Heat transfer is described solely by the heat flow to the walls. Heat losses are set as a constant heat flow through the reactor walls.

The combustion of coal in a flow reactor, unlike the combustion of a pulverized coal flame in a boiler furnace, has differences associated with the lack of

preheated air, limited recirculation of combustion gases to the flame root, and the lower radiation heat flux density. Therefore, to ensure ignition conditions for the pulverized coal flame, part of the heat must be compensated for by burning natural gas.

2.4.2. Development of a method for calculating the burnout dynamics of pulverized coal coke residue and coal blends in an isothermal flow

Studies on the kinetic characteristics of the interaction between coal coke residues and oxygen in the air have shown that under isothermal conditions and an excess of oxygen, the coke residues of the blend components burn independently. Thus, the mutual influence between the components of the blend on the burnout rate takes place due to changes in the thermal balance during the volatile release and combustion stage and differences in the specific burnout rate of the coke residues at the same gas temperature in the flow.

The burnout dynamics of the coke residue in the flow are influenced not only by the specific burnout rate but also by the gradual reduction in oxygen concentration in the gas volume, as it is consumed by the combustion process. During the ignition and combustion of the fuel blend, the coke residue of the less reactive coal and the lower VM content will react under conditions of reduced oxygen concentration, as the more reactive component, with the higher volatile content, will consume part of the oxygen in advance.

The specific oxygen consumption for the combustion of the entire coal blend, considering α , is determined by the following expression [14, 15, 27]:

$$v_{c+v\ \alpha}^{O_2} = (v_v^{O_2} + v_c^{O_2}) \times \alpha, \quad (14)$$

where $v_v^{O_2}$ and $v_c^{O_2}$ are the specific oxygen consumptions for the combustion of VM and coke, respectively (m^3/kg).

According to [29, 27], the specific oxygen consumption for the combustion of VM and coke is determined by the elemental composition of the coal:

$$v_v^{O_2} = (0.0889 \times (C_v^{daf} + 0.375 \times S_v^{daf}) + 0.265 \times H^{daf} - 0.0333 \times O^{daf}) \times 0.21, \\ v_c^{O_2} = (0.0889 \times (C_c^{daf} + 0.375 \times S_c^{daf})) \times 0.21,$$

where C_v^{daf} and C_c^{daf} are the carbon contents (%) in the dry ash-free mass that convert to VM and remain in the solid state, respectively (%); S_v^{daf} and S_c^{daf} are the same for sulfur contents.

The specific oxygen consumption for the combustion of the coke residue after volatile release, considering the excess oxidizer coefficient α , is determined by the equation:

$$v_{c\ \alpha}^{O_2} = v_{c+v\ \alpha}^{O_2} - v_v^{O_2}. \quad (15)$$

For the case of blend combustion, equations (14) and (15) take the following form:

$$v_{c+v \text{ a b}}^{O_2} = ((v_{v1}^{O_2} + v_{c1}^{O_2}) \times w_1 + (v_{v2}^{O_2} + v_{c2}^{O_2}) \times w_2) \times \alpha, \quad (16)$$

$$v_{c \text{ a b}}^{O_2} = v_{c+v \text{ a b}}^{O_2} \times (v_{v1}^{O_2} \times w_1 + v_{v2}^{O_2} \times w_2), \quad (17)$$

where w_1 and w_2 are the mass fractions of coal 1 and 2, respectively (in the combustible mass).

Using equations (16) and (17), the oxygen volume fraction for coke residue combustion after VM release, considering α , can be calculated as:

$$\varphi(O_2)_{k \text{ a b}} = 21 \times v_{c \text{ a b}}^{O_2} / v_{c+v \text{ a b}}^{O_2} \times (100 / (21 \times v_{c \text{ a b}}^{O_2} / v_{c+v \text{ a b}}^{O_2} + 79)).$$

The burnout dynamics of the coke residue in the flow are calculated discretely over time, meaning the entire burnout time is divided into equal time intervals Δt . The initial specific combustion rate W_m , which occurs at an oxygen volume fraction of 21 %, is determined according to Subsection 2.3.2. As the coke residue burns out, the specific combustion rate after the i -th interval decreases proportionally to the reduction in oxygen concentration in the flow:

$$W_{mi} = W_m \times \varphi(O_2)_i / 21, \quad (18)$$

where $\varphi(O_2)_i$ is the oxygen volume fraction after the i -th Δt , determined by the expression:

$$\varphi(O_2)_i = \varphi(O_2)_{c \text{ a}} \times [v_{c \text{ a}}^{O_2} - x_i \times (22.4/M_c) \times (C_c^{daf} + S_c^{daf})/100] / v_{c \text{ a}}^{O_2}, \quad (19)$$

where x_i is the degree of conversion of the coke residue after the i -th Δt ; $M_c = 12$ is the molar mass of carbon (g/mol).

The degree of conversion of the coke residue after the i -th Δt is calculated by the equation:

$$x_i = W_{mi-1} \times (1 - x_{i-1}) \times \Delta t. \quad (20)$$

To calculate the burnout dynamics of binary coal blends in an isothermal flow, it is assumed that the release and combustion of volatile matter from both coal grades occur simultaneously, and the combustion of coke residues from both grades occurs at the same temperature and oxygen concentration. In this case, equation (19) for blends takes the form:

$$\begin{aligned} \varphi(O_2)_{i \text{ b}} &= \varphi(O_2)_{c \text{ a b}} \times \{v_{c \text{ a b}}^{O_2} - [1 - ((1 - x_{i1}) \times w_1 + (1 - x_{i2}) \times w_2)] \times (22.4/M_c) \times \\ &\quad \times (C_{c \text{ b}}^{daf} + S_{c \text{ b}}^{daf})/100\} / v_{c \text{ a b}}^{O_2}, \end{aligned} \quad (21)$$

where $C_{c \text{ b}}^{daf}$ and $S_{c \text{ b}}^{daf}$ are the carbon and sulfur contents, respectively, in the dry ash-free mass that remains in the coke residue of the blend (%).

$C_{c \text{ b}}^{daf}$ and $S_{c \text{ b}}^{daf}$ are calculated as weighted averages based on the mass fraction ratios of coal w_1 and w_2 :

$$C_{c \text{ b}}^{daf} = C_{c1}^{daf} \times w_1 + C_{c2}^{daf} \times w_2,$$

$$S_{c \text{ b}}^{daf} = S_{c1}^{daf} \times w_1 + S_{c2}^{daf} \times w_2.$$

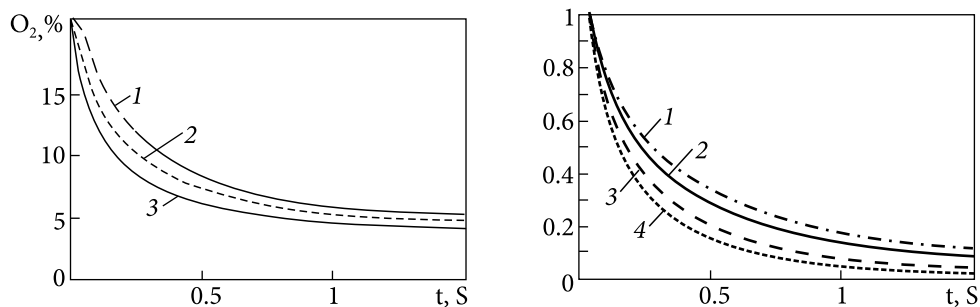


Fig. 2.10. Change in the oxygen volume concentration in the flow over time: 1 — anthracite, 2 — A/B blend, 3 — bituminous coal

Fig. 2.11. Change in the fraction of unreacted carbon ($1 - X_c$) over time: 1 — anthracite in A/B blend, 2 — anthracite, 3 — bituminous coal, 4 — bituminous coal in A/B blend

Using this methodology, the burnout dynamics of anthracite, bituminous coal, and their 1:1 blend were calculated separately in a flow at a constant temperature of 1700 °C and an initial air excess coefficient $\alpha = 1.2$. Fig. 2.10 shows the change in the oxygen volume concentration in the flow over time, from 0 to 1.5 seconds. During the combustion of bituminous coal, the oxygen volume concentration decreases the fastest (curve 3), which is associated with the higher VM release compared to anthracite, requiring oxygen for combustion, as well as the higher specific combustion rate of the coke residue.

The curve of the decrease in the oxygen volume concentration during the combustion of the blend (curve 2) lies between the dynamic curves for anthracite and bituminous coal.

Figure 2.11 shows the change in the fraction of unreacted carbon over time from 0 to 1.5 s. As seen, the anthracite component in the blend burns slower than in the case of burning separately, while the bituminous coal component in the blend burns faster than when burned alone. This can be explained by the change in oxygen concentration at the beginning of coke residue combustion. After the release and combustion of VM, the oxygen concentration in the flow during blend combustion is lower than during the combustion of anthracite alone but higher than in the separate combustion of bituminous coal.

The presented calculation demonstrates the influence of oxygen concentration changes on the combustion dynamics of coke residue during the combustion of coal blends under isothermal conditions. It does not account for changes in specific combustion rates due to variations in flow temperature caused by heat release from the combustion of VM and coke residue. Even such a simplified approach provides burnout times that are close to the actual residence times of pulverized particles in the fuel volume of pulverized coal boilers (1—1.5 s in the zone of maximum heat release; 5—6 s in the entire furnace) [13, 19]. This confirms that calculating the specific combustion rate of coke residue from individual fuels and blends over a wide range of temperatures, using the obtained kinetic characteris-

tics and methods that account for diffusion limitations allows for a reliable representation of the pulverized combustion process of coal blends from components with different degrees of metamorphism .

2.5. Calculation of the burnout dynamics of coal and coal blends in a flow reactor

The calculation of the burnout dynamics of coke residue in the flow is performed discretely over time. At each iteration, based on the flow temperature, the specific combustion rate is determined for an oxygen volume fraction of 21%. The specific combustion rate for the current oxygen concentration is determined based on the oxygen volume concentration. The fractions of carbon and oxygen that have reacted over a given time interval are then calculated based on the current specific combustion rate. The heat release is determined from the fraction of carbon that has reacted, which allows the temperature for the next iteration to be calculated. The comparative calculation for different fuels and blends is performed under the condition of the same reactor thermal capacity, with an air excess coefficient of $\alpha = 1.2$.

For igniting coal dust, the air and coal flow were heated to 900—950 °C using heat from the combustion of natural gas under stoichiometric conditions, after mixing the combustion products of the gas with the air and coal dust flow. The thermal power required to heat the flow Q_g (kW) is determined by the equation [27]:

$$Q_g = \Delta T^{i-1} \times (G_a \times c_a + G_{pr.g} \times c_{pr.g} + G_c \times c_c + G_{ash} \times c_{ash}),$$

where ΔT^{i-1} is the temperature step to the required value, °C; G_a , $G_{pr.g}$, G_c , and G_{ash} are the flow rates of air, gas combustion products, carbon, and ash, respectively, kg/s; c_a , $c_{pr.g}$, c_c , and c_{ash} are the specific heat capacities of air, gas combustion products, carbon, and ash, respectively, kJ/(kg · °C).

The air flow rate, considering the excess coefficient α , is determined by the elemental composition of the coal [28—29]:

$$G_a = G_{coal} \times (0.0889 (C^r + 0.375 \times S_{org+inorg}^r) + 0.265 \times H^r - 0.0333 \times O^r) \times \alpha \times \rho_a,$$

where G_{coal} is the coal consumption based on dry ash-free mass, kg/s, and ρ_a is the air density, kg/m³.

The gas combustion products flow, when mixed with air, reduces the oxygen volume fraction. The oxygen volume fraction, expressed as a percentage, after the complete combustion of the gas, is determined by the equation:

$$\varphi(O_2)_a = 21 \times V_{a\alpha} / (V_{a\alpha} + V_{pr.g}),$$

where $V_{a\alpha}$ and $V_{pr.g}$ are the air and gas combustion product flow rates, respectively, considering excess air, m³/s.

After the release and combustion of VM, the oxygen volume fraction is determined by the equation:

$$\varphi(\text{O}_2)_{k\alpha} = 21 \times (V_a - v_v^{\text{O}_2}/0.21) / (V_a - v_v^{\text{O}_2}/0.21 + V_{\text{pr.g}} + v_v^{\text{O}_2} \times 0.79/0.21/0.709),$$

where 0.709 is the nitrogen volume fraction in the combustion products.

The oxygen volume fraction after the i -th time interval for the case of single-grade coal combustion is determined by equation (19), and for the case of binary blend combustion, by equation (21).

The flow temperature at a given time T_f^i (°C) is determined by the equation:

$$T_f^i = T_f^{i-1} + \Delta T_f^i.$$

The temperature difference to which the flow is heated in the zone corresponding to the i -th time interval for the blend is determined by the thermal balance of the combustion process:

$$\begin{aligned} \Delta T_f^i = [& G_{\text{coal1}} \times (x_1^i - x_1^{i-1}) \times Q_{\text{coal1}}^{\text{daf}} \times w_1 + G_{\text{coal2}} \times (x_2^i - x_2^{i-1}) \times Q_{\text{coal2}}^{\text{daf}} \times w_2 - Q_{\text{loss}}] / \\ & [G_a \times c_a \times (1 - x_1^i) \times w_1 + G_a \times c_a \times (1 - x_2^i) \times w_2 + G_{\text{pr.coal1}} \times c_{\text{pr.coal}} \times x_1^i \times w_1 + \\ & + G_{\text{pr.coal2}} \times c_{\text{pr.coal}} \times x_2^i \times w_2 + G_{\text{pr.g}} \times c_{\text{pr.g}} + G_{\text{coal1}} \times c_{\text{coal}} \times (1 - x_1^i) \times w_1 + \\ & + G_{\text{coal2}} \times c_{\text{coal}} \times (1 - x_2^i) \times w_2 + G_{\text{ash}} \times c_{\text{ash}}], \end{aligned}$$

where G_a , $G_{\text{pr.coal}}$ and G_{ash} are the flow rates of air, coal combustion products, and ash, respectively, kg/s; Q_{loss} is the heat loss through the reactor walls, kW; c_a , $c_{\text{pr.coal}}$, $c_{\text{pr.g}}$, c_{coal} and c_{ash} are the average heat capacities of air, coal combustion products, natural gas, coal, and ash, respectively, at T_a , kJ/(kg · °C).

The duration of VM release and ignition, according to [13, 19], for standard station-milled dust is taken as 0.04 s.

The degree of coke residue conversion for the i -th time interval is determined by equation (20). The specific combustion rate after the i -th time interval W_m^i , considering the oxygen concentration in the flow, is determined by equation (18), while the initial specific combustion rate at an oxygen volume fraction of 21% for temperature T_a^i is determined by the method described above.

Using this methodology, the burnout dynamics in the VGP-100V flow reactor was calculated separately for anthracite and bituminous coal, as well as their 1:1 blend [30]. The coal characteristics used in the calculations are presented in Table 2.7.

Table 2.7. Characteristics of coals used in the calculations

Coal type	A ^r , %	W ^r , %	S ^r , %	V ^{daf} , %	C ^r , %	H ^r , %	O ^r , %	N ^r , %	Q _i ^r kcal/kg
Anthracite	20.93	8.43	1.75	3.50	65.70	1.24	1.34	0.62	5550
Bituminous coal	21.03	9.26	3.47	38.85	55.05	3.80	6.27	1.12	5292

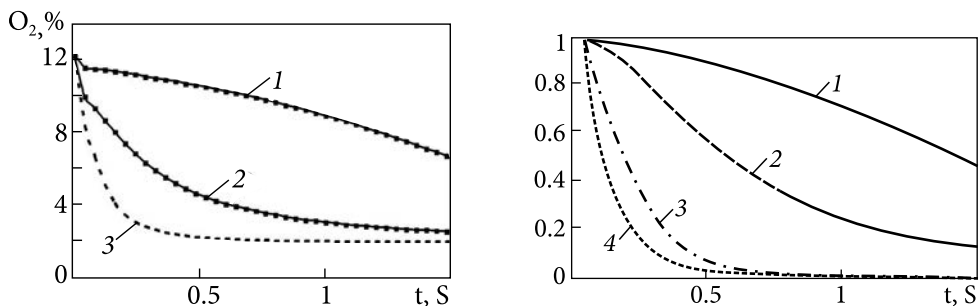


Fig. 2.12. Change in oxygen volume concentration in the flow over time (calculated): 1 — anthracite; 2 — 1:1 A/B blend; 3 — bituminous coal

Fig. 2.13. Change in the fraction of unreacted carbon over time: 1 — anthracite alone; 2 — anthracite in 1:1 A/B blend; 3 — bituminous coal in 1:1 A/B blend; 4 — bituminous coal alone

The change in oxygen volume concentration in the flow over time during the combustion of A, B, and their 1:1 (based on heat) blend is shown in Fig. 2.12.

By the figure, the oxygen volume concentration corresponding to the combustion of the blend (curve 2) is closer to the curve for bituminous coal combustion (curve 3) than curve 1, meaning that the anthracite component of the coal blend burns over all the time under reduced oxygen concentration conditions. Figure 2.13 shows the change in the fraction of unreacted carbon over time from 0 to 1.5 s for the combustion of A and B coal separately and in a blend.

As seen in Figure 2.13, despite the reduced oxidizer concentration, the anthracite component in the blend burns faster than anthracite alone, and the overall burnout rate of the blend (Fig. 2.14) is close to that of bituminous coal. These results can be explained by the increased combustion temperature of the blend compared to the separate combustion of anthracite. The temperature increase occurs due to the heat from the combustion of the volatiles in bituminous coal at the initial combustion stage, as well as the faster burnout of its coke residue due to the higher specific combustion rate at the same flow temperature as that for anthracite.

Figure 2.15 shows the flow temperature during the combustion of anthracite and bituminous coal separately and their 1:1 blend over time from 0 to 1.5 seconds. The calculation indicates that due to the heat released from the volatile matter combustion at the beginning of combustion, the flow is heated by 73 °C when burning anthracite, by 472 °C when burning bituminous coal, and by 235 °C when burning the blend. For the anthracite component in the blend, this temperature increase leads to a significant rise in the specific combustion rate of the coke residue. This is due to the fact that for 0.05 mm anthracite particles in the temperature range of 1100 to 1900 °C (corresponding to the combustion temperature in a boiler furnace), the external diffusion limitation is weak, meaning combustion occurrence in a transitional region where the dependence of the specific combustion rate on temperature remains significant.

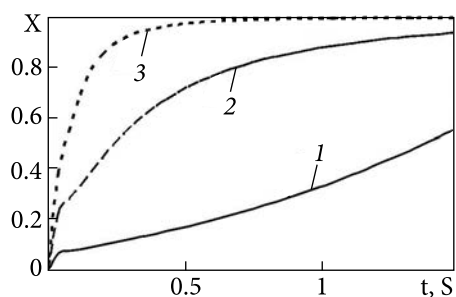


Fig. 2.14. Degree of coal conversion (calculated): 1 — anthracite; 2 — 1:1 A/B blend; 3 — bituminous coal

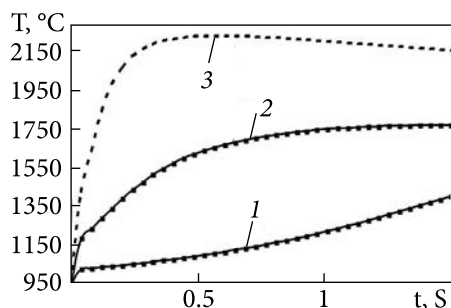


Fig. 2.15. Flow temperature over time (calculated): 1 — anthracite; 2 — 1:1 A/B blend; 3 — bituminous coal

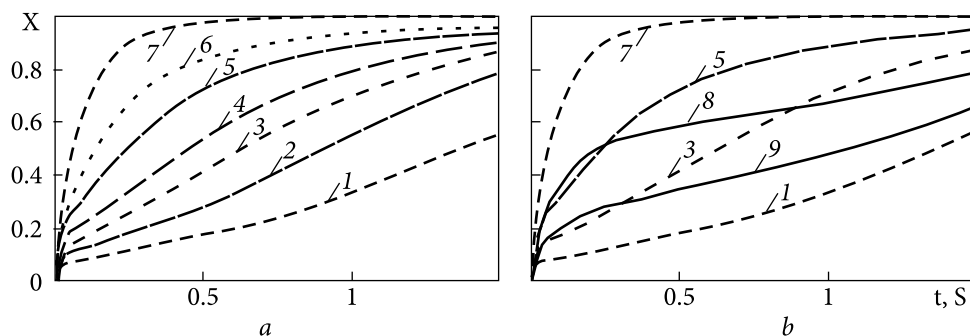


Fig. 2.16. Change in the degree of conversion of A/B blends over time: (a) calculated using the above described methodology: 1 — 0% B, 2 — 10% B, 3 — 20% B, 4 — 30% B, 5 — 50% B, 6 — 70% B, 7 — 100% B; (b) calculated based on the independent burnout dynamics of A and B coals: 8 — 50% B and 9 — 20% B

Along with the increase in the combustion temperature of the anthracite component, there is a decrease in the combustion temperature of the bituminous coal component compared to its separate combustion. However, this temperature reduction does not lead to a significant decrease in the combustion rate (Fig. 2.14, curve 3), since for bituminous coal particles with an average size of 0.05 mm in this temperature range, combustion occurs in the external diffusion reaction region, where the specific combustion rate is only slightly dependent on temperature.

The reduction in oxygen concentration in the flow after the release and combustion of volatile matter also influences the burnout rate of the anthracite component in the blend. The oxygen volume concentration decreases by 0.7% for anthracite, by 5.9% for bituminous coal, and by 2.3% for the blend.

The calculation showed that the increase in the combustion temperature of the anthracite component in the blend has a dominant effect on its burnout rate, outweighing the inhibiting effect of the reduced oxidizer concentration in the

flow after the release and combustion of volatile matter, provided that there is enough oxygen in the flow for the complete combustion of the coal.

To determine the dependence of the blend's combustion rate on time and the ratio of the two coal types, the burnout dynamics of anthracite blends with 5, 10, 20, 30, 40, 50 and 70% bituminous coal were calculated using the above described methodology. The results of these calculations are presented in Figure 2.16, *a*.

Figure 2.16, *b* shows the dependence of the blend conversion degree, calculated linearly based on the ratio of the two coal types, using the dependences obtained for the separate combustion of the parent coal types (curves 8 and 9).

The discrepancy between the dependences calculated with and without considering the mutual influence of the blend components indicates that the time dependence of the blend conversion degree for different ratios of the two coal types is nonlinear. This means that the degree of burnout of a blend with a given ratio cannot be calculated linearly based on the separate burnout dynamics of the specific blend component coal types.

2.6. Conclusions

It has been found that there is no quasi-stationary region in the carbon conversion over time, which can be explained by the accelerated depletion of the more reactive component. This makes it impossible to obtain kinetic characteristics for the interaction of the blends with oxygen. However, it was shown that the conversion curves of the blends are weighted averages of the conversion curves of the independently reacting components. The specific combustion rate of the blend in excess oxygen conditions at each temperature corresponds to the weighted average specific combustion rates of the components. This proves the possibility of calculating the combustion rate and degree of burnout of a fuel blend based on the specific combustion rates and burnout degrees of the components.

For coke residues of anthracite, lean coal, and bituminous coal dust with typical pulverization and ash content for TPPs, and for blends of anthracite and lean coal dust under isothermal conditions in the temperature range of 380–630°C, the boundaries of quasi-stationary conversion sections have been determined, and the kinetic characteristics of carbon's interaction with oxygen in the internal kinetic and internal diffusion reaction regions have been identified, confirming and refining the results of previous researchers.

It was proven that at temperatures typical for pulverized combustion with liquid slag removal, the combustion of bituminous coal coke residue particles occurs in the external diffusion reaction region, where the specific combustion rate depends on temperature by a power law. In contrast, anthracite combustion occurs in the transitional region, where the temperature dependence of the specific combustion rate is much stronger and approaches an exponential dependency.

The effect of peat content on the combustion of blends at different temperatures has been determined. It was shown that peat is a more reactive fuel, and

with peat content increasing, the time for volatile matter release decreases, while the kinetic combustion rate of the coke residue increases.

The optimal peat share (10%) at which the effect on the blend combustion rate is maximal was determined. With further increase in peat content, the effect diminishes.

Based on the results of kinetic studies, a method for calculating the burnout dynamics of pulverized blends of coals with different degrees of metamorphism in a flow was developed. The method is based on step-by-step calculating the burnout degrees of the components and the thermal balance of the flow, determining the oxygen depletion and temperature increase, and using them as initial conditions for the next step.

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THERMOGRAVIMETRIC STUDIES OF CO-FIRING OF TWO SOLID FUELS

3.1. Thermogravimetric analysis methods

Thermogravimetry is a method for research and analysis based on recording the change in mass of a sample depending on its temperature. An installation for thermogravimetry consists of continuous weighing scales, an oven, thermocouples, and a software temperature controller.

There are two methods of conducting a thermogravimetric experiment: quasi-isothermal one, i.e., at a constant temperature of the furnace, and the most common — dynamic one, i.e., when the temperature of the furnace changes over time (usually at a constant heating rate). As a result, the dependence curves of the sample mass change (thermogravimetric curve, TG) or the rate of mass change (differential thermogravimetric curve, DTG) on time or temperature are obtained.

The principal schematics of the thermogravimetric analyzer used in the studies described below is shown in Figure 3.1.

Primary experimental data are obtained in the form of numerical data, as well as in a graphical form, as shown in Figure 3.2. The data include curves of mass change, temperature, mass change rate, and temperature change rate during the experiment.

Also, Figure 3.2 shows schematically the stages of thermal transformation of the studied samples, such as the release of moisture (dehydration), the formation and release of volatile matter (devolatilization), and the burnout of coke ash fuel residue. This division is conditional and used to simplify calculations. Real dehydration at a certain point in time occurs simultaneously with the beginning of the release of volatiles, and it is also impossible to distinctly separate the stage of coke combustion. Nevertheless, the practice of calculations and their verification show the advisability of such simplifications [1]. To determine individual stages of thermal decomposition of fuel samples, three temperatures must be identified for each stage:

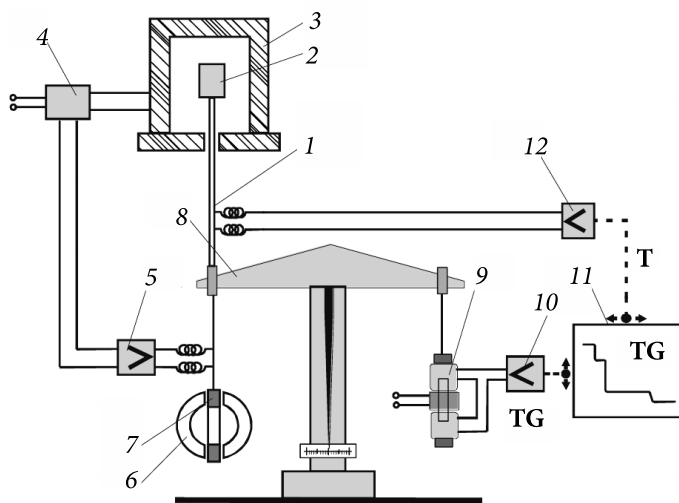


Fig. 3.1. Principal schematics of a derivatograph Q-1000: 1 — ceramic pipe; 2 — sample holder; 3 — furnace; 4 — switch of the heating regulator; 5 — amplifier; 6 — magnet; 7 — winding; 8 — scales; 9 — differential transformer for converting the TG signal; 10 — amplifier; 11 — recording device; 12 — amplifier

- Initial temperature T_o , at which the sample mass is 0.975 of that at the initial temperature;
- Maximum temperature T_{max} , at which the second derivative of the mass change over time is zero;
- Final temperature, at which the first derivative of the mass change over time has a minimum and the second one equals zero.

3.1.1. Description of data processing and generalization methods

Modern TGA and DTG methods combined with infrared spectroscopy and differential calorimetry are widely used in almost all engineering branches of science.

Accordingly, substances from food products, polymers and solid household waste, biofuels, and even fossil fuels were analyzed. Such diversity led to the development of advanced methods of processing and generalization of experimental data [2—7]. Based on [2, 8], it seems possible to provide the following classification of the analysis methods (Table 3.1). The advantages of the non-isothermal method [9] include the possibility of avoiding the need to obtain and process isothermal curves for calculating the kinetic constants of the process.

We applied non-isothermal methods of TG analysis to study the kinetic characteristics of the fuel thermal destruction processes, including the stages of dehydration and devolatilization. The actual coke residue combustion kinetics was studied by the quasi-isothermal method. Non-isothermal TG analysis is used according to one of three methods [7, 8]: differential, integral, and isoconversion method.

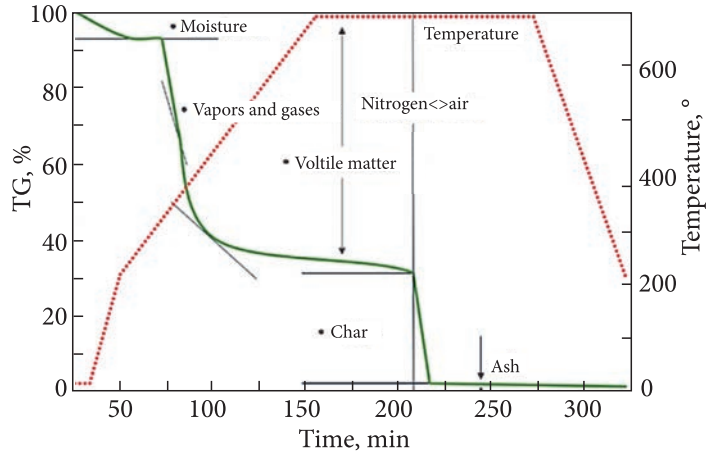


Fig. 3.2. Example of a thermogravimetric curve

Table 3.1. Methods for determination of kinetic characteristics [2, 8, 10, 11, 12, 13]

Model methods		Isoconversion methods	
Isothermal curves	Non-isothermal curves	Isothermal curves	Non-isothermal curves
Standard	Differential, Freeman—Carol, Coats—Redfern, Senum—Yang, Starink	Normative Friedman AIS method	Kissinger Flynn—Wall—Ozawa

The change in the mass of a solid particle in a certain process can be mathematically described by one equation including physical constants and corresponding model functions:

$$\frac{dm(\tau)}{d\tau} = -k \cdot f(m(\tau)), \quad (3.1)$$

where $m(\tau)$ is the current mass of a certain test sample component at time τ ; k is the reaction rate constant; $f(m(\tau))$ is a function that describes a certain reaction model. The conversion degree is determined taking into account the change in the test sample mass from the beginning to the end of the process.

$$\alpha = (m_0 - m_\tau) / (m_0 - m_\infty), \quad (3.2)$$

where m_0 is the initial mass of the sample; m_∞ is the sample mass at the end of the process under consideration; m_τ is the sample mass at time τ .

The term “conversion” in this case refers exclusively to the constituent process under consideration. That is, in the case of consideration of the process of moisture release during heating of the particle, it will be about the conversion of moisture, whereas when considering the process of release of volatiles, it will

mean the conversion of the volatiles in the composition of the combustible mass of the sample, i.e., the corresponding values in (3.2) relate exclusively to a specific process. At the same time, the denominator of formula (3.2) is determined by the value of this fuel component, which participates in this transformation. Critical for generalizing the data is the determination of the time (parameters) of both the beginning of the dehydration process and its end and the beginning of the next process (devolatilization or coke residue post-burning) and, accordingly, the determination of the mass of the reacting component. For example, for dehydration, this is the point where the second time derivative of the mass change function passes through zero in the range of 170–200 °C, changing the sign from “+” to “–”, that is, where the local reaction rate becomes minimum.

The reaction rate constant is given in the form of the Arrhenius equation:

$$k = A \cdot \exp(-E / RT),$$

where A is a pre-exponential factor, $1/s$; E is the activation energy, J/mol ; R is the universal gas constant, $8.314 J/(mol \cdot K)$; and T is the temperature, K .

Taking into account the Arrhenius equation and (3.2), equation (3.1) acquires the form:

$$\frac{d\alpha}{d\tau} = A \cdot \exp(-E / RT) f(\alpha). \quad (3.3)$$

A detailed analysis of applying equation (3.2) methods for processing experimental data of TGA and reaction model analysis is given in [2–5].

When the sample is heated at a constant rate, the time dependence of temperature looks like

$$T = \beta\tau + C, \quad (3.4)$$

where β is the heating rate.

Combining (3) and (4), we get

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha). \quad (3.5)$$

As a rule, heterogeneous volatile yield reactions are broadly described by power or special functions $f(\alpha)$. Common in the processing of TGA data is the assumption about the first order of the reaction [14–18]. By grouping the variables and logarithmizing (3.5) within the framework of the assumption, we get:

$$\ln\left(\frac{\beta}{1-\alpha} \frac{d\alpha}{dT}\right) = -\frac{E}{RT} + \ln A. \quad (3.6)$$

Equation (3.6) forms the methodological basis of the differential approach to the determination of kinetic constants based on TG studies and is the basis of the well-known Friedman method [2, 4, 8]. A detailed analysis of data processing features and interpretation by methods based on equation (3.6) is given in [8, 9].

Despite its simplicity, Friedman's method has significant drawbacks associated with the need to define (3.6) by indicators of conversion degree and the derivative of the mass change function over time. A critical point of this methodology is also the need to scale the value of the da/dT derivative based on the real m_r curve and to precisely determine the initial content of this component, which is an extremely difficult task [8, 13, 16, 17].

According to the integral approach, which has become widely used [2–7, 9, 11, 17], equation (3.6) is integrated as

$$\beta \int_0^{\alpha} \frac{d\alpha}{1-\alpha} = \beta \cdot \ln(1-\alpha) = -A \int_0^T \exp\left(-\frac{E}{RT}\right) dT. \quad (3.7)$$

Since the expression on the right-hand side of (3.7) is not analytically integrated, a significant number of expressions, usually in the form of series or rational fractions, have been proposed to obtain acceptable approximations [2, 7–8, 18–20]. In [9], it is proposed to apply the method of integration by parts. By using the variable $x = \frac{E}{RT}$, we will get $g(\alpha) = -\frac{AE}{\beta R} \int_{\infty}^x \frac{\exp(-x)}{x^2} dx$, and the

function $p(x) = \int_{\infty}^x \frac{\exp(-x)}{x^2} dx$ is integrated by parts:

$$\int_{\infty}^x \frac{\exp(-x)}{x^2} dx = \frac{e^{-x}}{x^2} - \int_{\infty}^x \frac{2e^{-x}}{x^2} dx.$$

Applying integration by parts to the integral on the right-hand side of this expression, we have

$$\begin{aligned} \int_{\infty}^x \frac{2e^{-x}}{x^3} dx &= \frac{-2e^{-x}}{x^3} + \int_{\infty}^x \frac{6e^{-x}}{x^4} dx, \\ \int_{\infty}^x \frac{6e^{-x}}{x^4} dx &= \frac{6e^{-x}}{x^4} - \int_{\infty}^x \frac{6 \cdot 4e^{-x}}{x^5} dx, \\ p(x) &= \frac{e^{-x}}{x^2} \left(1 - \frac{2}{x} + \frac{6}{x^2} - \frac{24}{x^3} + \dots + (-1)^{n-1} \frac{n!}{x^{n-1}} \right). \end{aligned} \quad (3.8)$$

Limiting to two terms of the series, we will obtain the well-known Coats–Redfern approximation [7]:

$$\ln \left[\frac{-\ln(1-\alpha) \cdot \beta}{T^2 \left(1 - \frac{2RT}{E} \right)} \right] = \ln \left(\frac{AR}{E} \right) - \frac{E}{R} \frac{1}{T}. \quad (3.9)$$

In the general case, the equation approximated by series looks like:

$$\ln \left[\frac{-\ln(1-\alpha) \cdot \beta}{T^2 \left(1 - \sum_2^n (-1)^{n-1} \frac{n!}{x^{n-1}} \right)} \right] = \ln \left(\frac{AR}{E} \right) - \frac{E}{R} \frac{1}{T}. \quad (3.10)$$

Equations of the form (3.9) and (3.10) make it possible to determine the kinetic characteristics based on the results of TG experiments, using only current data from thermogravimetric curves and not referring to the complicated determination of the derivatives of the mass change over time. Senum and Yang proposed the following approximation of the temperature integral [8, 17]:

$$p(x) = \frac{e^{-x}}{x^2} \left(\frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \right). \quad (3.11)$$

It should be noted that the Coats—Redfern and Senum—Yang methods are iterative.

The definition of the temperature integral was proposed by Starink [21] based on the linear approximation of the $p(x)$ logarithm:

$$p(x) \cong \frac{e^{(-1.0008x-0.312)}}{x^{1.92}}. \quad (3.12)$$

Table 3.2. Approximate analysis of the studied fuels

Fuel	V ^{daf} , %	A ^d , %	W ^r , %	Q _p ^r kcal/kg
Crashed pine pellets	84.20	0.64	4.20	4033
Crashed wheat straw pellets	74.52	8.90	9.20	3596
Pulverized anthracite	6.67	29.68	1.15	5415

Table 3.3. Temperature ranges and distribution of fuel sample mass by thermal decompo

Fuel samples	Thermal decomposition			
	Dehydration			
	Range, °C	Max temp., °C	Mass fraction, %	
Anthracite	92—289	99	2.0	
Pine pellets	39—173	101	6.7	
Wheat straw pellets	37—167	99	6.6	
Anthracite/pine pellets 1:1 blend	78—179	98	2.9	
Anthracite/pine pellets 9:1 blend	47—228	100	3.4	
Anthracite/wheat straw pellets 9:1 blend	42—187	85	3.1	

Substituting (3.12) into (3.7), we get:

$$\beta \cdot \ln(1-\alpha) = -\frac{AE}{R} \cdot \frac{e^{(-1.0008x-0.312)}}{x^{1.92}}. \quad (3.13)$$

After substituting $x = E/RT$ in (3.13) and performing a series of transformations, we obtain:

$$\ln \left[\frac{-\ln(1-\alpha) \cdot \beta}{T^{1.92} \cdot e^{-0.312}} \right] = \ln \left(A \left(\frac{R}{E} \right)^{0.92} \right) - 1.0008 \frac{E}{R} \frac{1}{T}. \quad (3.14)$$

Thus, in general, the considered methods of determining kinetic constants con-

sist in the analysis of dependence graphs $\ln \left(\frac{1}{1-\alpha} \frac{d\alpha}{dT} \right)$, $\ln \left[\frac{-\ln(1-\alpha) \cdot \beta}{T^2 \left(1 - \frac{2RT}{E} \right)} \right]$,

$\ln \left[\frac{-\ln(1-\alpha) \cdot \beta}{T^{1.92} \cdot e^{-0.312}} \right]$ or other approximate dependences on $\frac{1}{T}$, which are

a straight line with an angle of inclination $\frac{E}{R}$ and the addition of the preexponential factor A .

Therefore, the analysis of available and recommended in literature methods for processing and generalizing experimental data and the preliminary analysis of the initial data of the TG analysis allow us to formulate the following conclusions:

- Differential data processing methods should be used when it is possible to distinguish the beginning and end of the process and accurately determine the target component of the analyzed reaction.

sition stages

stages of fuel samples						
Devolatilization			Coke burnout			
Range, °C	Max temp., °C	Mass fraction, %	Range, °C	Max temp., °C	Mass fraction, %	
n/d	n/d	n/d	289—966	n/d	33.5	
173—413	350	57.6	413—942	n/d	35.7	
167—410	339	54.2	410—913	n/d	31.7	
179—408	n/d	26.0	408—965	n/d	27.1	
228—404	258	8.7	404—966	n/d	32.2	
187—380	n/d	8.9	380—955	n/d	35.3	

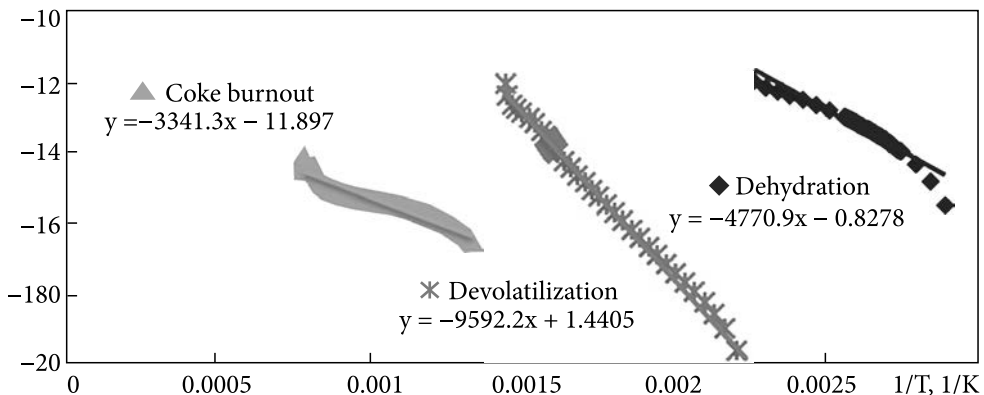


Fig. 3.3. $\ln \left[-\ln(1-a)b / T^2 \left(1 - 2 \frac{RT}{E} \right) \right] = f(1/T)$ correlation for pine pellets. Heating rate — 20 °C/min

- Based on the characteristic derivative plots for individual types of biomasses with well-defined derivative minima, we should use the differential data processing method, which, for simplicity and clarity, allows us to obtain kinetic characteristics.

- For blends of biomass with low-reactivity anthracite from the Ukrainian deposits, it seems better to apply the Coats-Redfern integral method, which does not require a preliminary determination of the dependence of the derivative on temperature.

3.1.2. Results of experimental data processing

Next, the results of the calculation of the kinetic characteristics of blends of anthracite with pine or wheat straw pellets are presented. The characteristics of the studied fuels are given in Table 3.2 and Table 3.3 presents the data on the distribution of test samples by stages of thermal decomposition.

In view of its higher efficiency in comparison with the differential approach to the generalization of TG curves, the integral method of calculation was chosen for further analysis.

The experimental data on the thermal decomposition of biomass/coal blends, as well as on individual fuels that were obtained by the Coats-Redfern integral method, are shown in Figure 3.3. As seen, the selection of stages by the described above integral method allows, approximating the series in the all temperature interval with linear dependences. They make it possible to determine the kinetic constants that describe the successive processes of thermal destruction. As mentioned earlier, during the non-isothermal TGA study of the thermal destruction of biomass and coal samples in an oxidizing environment (air) at the beginning of heating, a slight increase in the mass of the sample was observed, which was

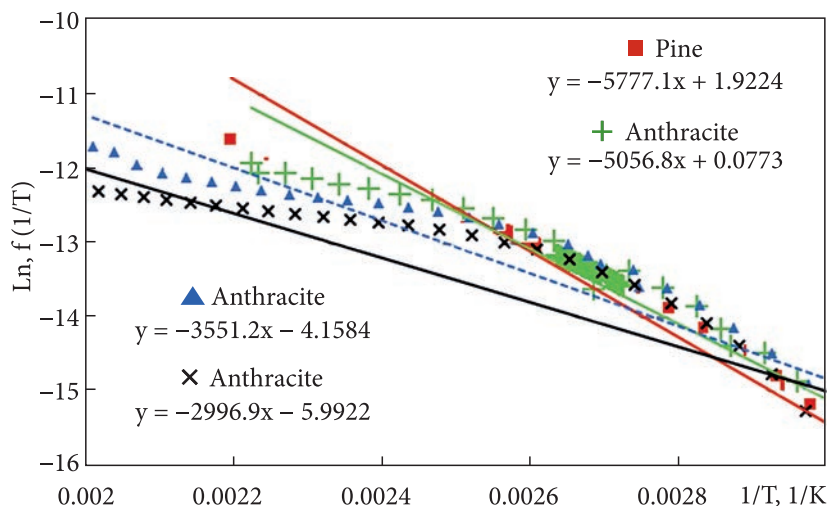


Fig. 3.4. $\text{Ln} \left[-\text{Ln}(1 - \alpha) \beta / T^2 \left(1 - 2 \frac{RT}{E} \right) \right] = f(1/T)$ correlation for anthracite, pine pellets, and their blends at the dehydration stage. Heating rate — 20 °C/min

associated with the adsorption of water vapor from the air. Taking into account the range of the dehydration process affects both the determination of the current degree of conversion and the moisture content in the sample. The dehydration process starts, when the largest sample mass is reached.

The data shown in Figure 3.4 were obtained in the temperature zone of moisture release for coal, pine pellets, and their blends, considering the mentioned above.

As follows, in a sufficiently wide range of temperature changes, all series of experimental results are close enough when approximated by straight lines, which allows for determining the kinetic constants by the methods described above. Comparing the data for the crushed pine pellets shown in Figs. 3.3 and 3.4, we can note that the expansion of the temperature range of the devolatilization process into the region of lower temperatures as a result of taking into account the initial heating of the sample and, accordingly, slightly changing the calculation of the current degree of conversion, we obtain proper kinetic parameters. Thus, in the first case, the multiplier at the inverse temperature is -4770.9 against -5777.1 when we take into account the initial warm-up. There are also differences in the parameter $\text{Ln}(E/RT)$ values, which reflects the free item of the generalizing linear equation.

The increase in the coal share leads to the experimental data deviation from the approximating lines, which is seen from the given data. This is explained by the fact that the first-order reaction model is adopted according to data processing methods. Being corresponding fairly closely to the real picture in the case of biomass alone or with a significant share of biomass in the blend, the first-order model ceases to correspond to the realities in the case of the coal dehydration process or blends with its predominant share. The change in the mechanism of the

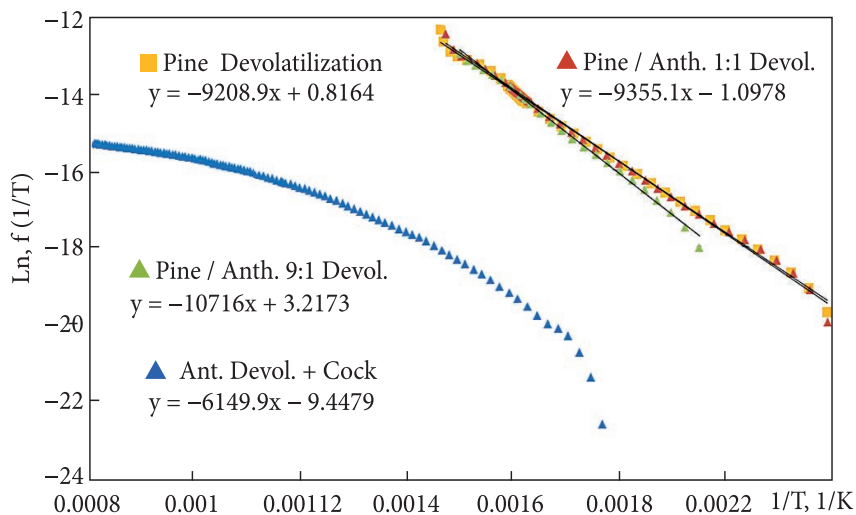


Fig. 3.5. $\text{Ln} \left[-\text{Ln}(1-\alpha) \beta / T^2 \left(1 - 2 \frac{RT}{E} \right) \right] = f(1/T)$ correlation for coal, pine pellets, and their blends at the devolatilization stage. Heating rate — 20 °C/min, oxidizing environment

process can be applied by introducing the generalization of data for two regions of the temperature range, but this will lead to significant complications in data processing methods with little improvement in the accuracy of generalization.

The results of the calculation for coal/pine blends in the temperature ranges of devolatilization are shown in Figure 3.5 and for the ir cock burnout — in Figure 3.7.

As seen from the Figures, the presence of even a small fraction of biomass in the blend leads to significant differences in the devolatilization process. Thus, all series of experimental results for pine pellets and blends at any biomass share are grouped almost near a single approximating line. A slight difference in the angular coefficients does not lead to a noticeable difference in the rates of release of volatiles or the temperature range of the process. Figure 3.6 shows the results of the numerical integration of the Arrhenius equation based on the found kinetic constants.

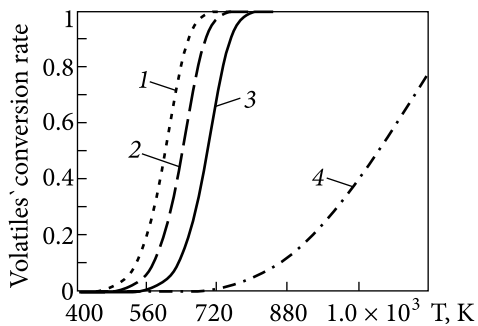


Fig. 3.6. Dependence of the degree of conversion of VM of pine pellets, anthracite, and their blends on the temperature during devolatilization according to the found kinetic parameters (Figure 3.5): 1 — pine pellets; 2 — 1:1 anthracite/pine blend; 3 — 9:1 anthracite/pine blend; 4 — anthracite

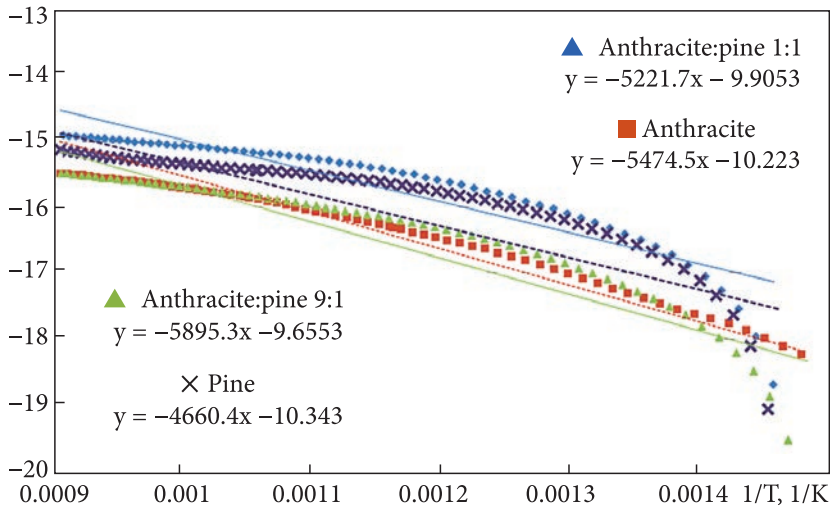


Fig. 3.7. The $\ln\left[-\ln(1-\alpha)\beta/T^2\left(1-2\frac{RT}{E}\right)\right] = f(1/T)$ correlation for pine pellets and coal in the cock burnout zone. Heating rate 20 °C/min

Table 3.4. Dehydration kinetics of anthracite, biomass, and their blends

Fuel	Preexponential factor, 1/s	Activation energy, J/(mol · K)	Temperature range, °C
Anthracite	7.432	24 917.06	41.6—288.0
Pine pellets	39 499.36	48 029.98	46.1—172.9
Wheat straw pellets	2 848.674	40 735.27	46.6—166.2
1:1 Anthracite/pine pellet blend	5 462.33	42 046.24	46.8—176.1
9:1 Anthracite/pine pellet blend	55.53	29 524.68	50.9—225.5
9:1 Anthracite /wheat straw pellet blend	7 652.619	45 699.56	52.4—185.7

Table 3.5. Devolatilization kinetics of anthracite, biomass, and their blends

	Preexponential factor, 1/s	Activation energy, J/(mol · K)	Temperature range, °C
Anthracite	—	—	—
Pine pellet	20 833.67	76 562.79	172.9—411.2
Wheat straw pellet	5.861945	36 527.56	166.2—407.6
1:1 Anthracite/pine pellet blend	27 603.07	76 559.47	176.1—407.1
9:1 Anthracite/pine pellet blend	26 7478.2	89 092.82	225.5—400.6
9:1 Anthracite /wheat straw pellet blend	34 136.62	75 422.95	185.7—379.9

Table 3.6. Coke burnout kinetics of anthracite, biomass, and their blends

Fuel	Preexponential factor, 1/s	Activation energy, J/(mol · K)	Temperature range, °C
Anthracite	0.484	51105.31	288.0—1005.5
Pine pellet	0.262	43413.52	411.2—989.4
Wheat straw pellet	0.110	35146.61	407.6—981.6
1:1 Anthracite/pine pellet blend	0.151	38743.12	407.1—1002.1
9:1 Anthracite/pine pellet blend	0.198	45519.21	400.6—1004.3
9:1 Anthracite/wheat straw pellet blend	0.0852	38810.23	379.9—983.0

As shown, the coal in the proportion of 1:1 and even 9:1 only slightly shifts the curve toward the higher temperatures, which reflects the conversion rate of biomass only. Moreover, even with the presence of only 10% of the biomass in the blend, the rate of devolatilization far exceeds the rate found by the laws of additivity. This indicates the presence of a certain synergistic effect, at least in the devolatilization zone. Indeed, the joint participation of coal and the smallest fraction of biomass does not lead to averaging the release rates of volatile components (for example, averaging curves 1 and 4 in certain proportions), but, in fact, acquires kinetic parameters of biomass with a characteristic rate of devolatilization.

The data shown in Figure 3.7 demonstrate the main regularities revealed above in the analysis of thermogravigrams and derivative grams of the corresponding processes. The data on blends of pine pellets and coal were obtained in the coke burnout zone. On the other hand, the data on coal cover both the region of devolatilization and the burnout zone itself, since it does not seem possible to single out the devolatilization zone for coal. Despite the extremely different reactivity of biomass and coal cokes, the experimental points are grouped very close, and the angles of the slope of the approximating lines are quite close. That the data on the pine pellet and the 1:1 blend are almost identical, whereas the data for the 9:1 blend are almost identical to the coal data.

The obtained data for all three characteristic areas, which are associated with the stages of combustion, were processed by methods described above and are presented in Tables 3.4—3.6.

3.1.3. Calculation of thermal destruction stages based on the found kinetic characteristics

The accuracy and reliability of the obtained kinetic constants were confirmed by comparing experimental data and the results of calculations of the stages of thermal degradation of solid fuel in the Mathcad environment. The differential equation

$$\frac{d\alpha}{dT} = \frac{A_i}{\beta} \exp\left(-\frac{E_i}{RT}\right) \cdot (1 - \alpha), \quad (3.15)$$

Fig. 3.8. Comparison of the experimental and calculated data for the dehydration stage of ground straw pellets

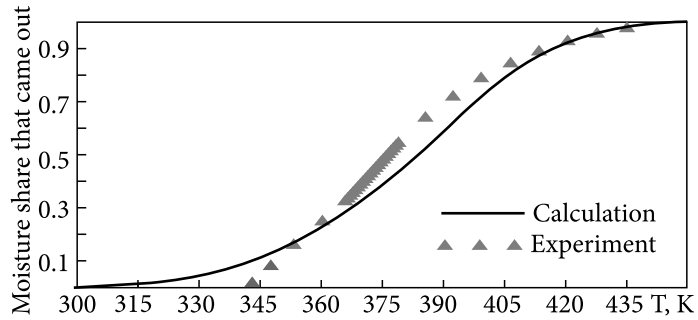


Fig. 3.9. Comparison of the experimental and calculated data for the dehydration stage of ground pine pellets

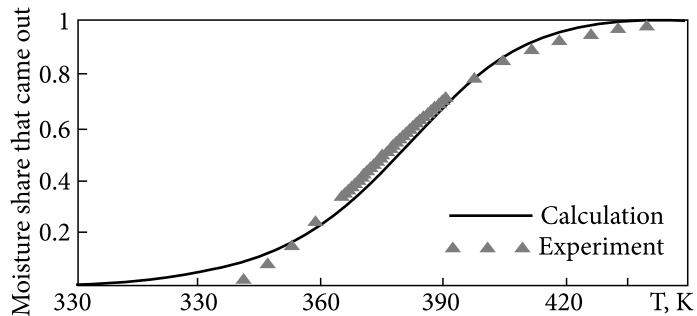
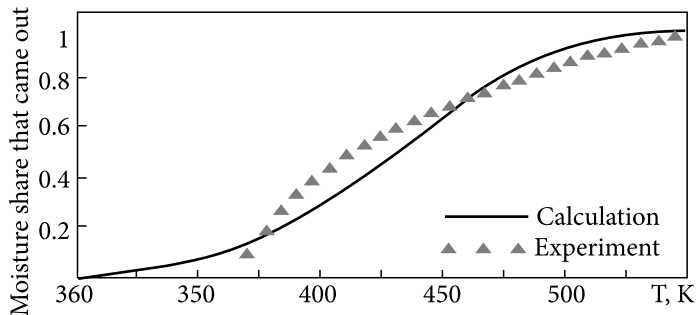


Fig. 3.10. Comparison of the calculated and experimental data for the moisture release during coal heating at a constant rate



where A_i and E_i are the preexponential factor and the activation energy, respectively, was solved. The results of the calculations are shown in Figs. 3.8—3.12.

As seen from the given data, the obtained kinetic constants allow us to accurately calculate the stage duration and the amount of moisture released at any moment of the process. Figure 3.10 shows the calculated and experimental data for the dehydration stage of domestic anthracite. Some discrepancy in the calculated degree of moisture release in the area $\alpha = 0.4 \div 0.6$ is explained by the two factors mentioned above in the analysis of the original thermogravimetric curves.

Firstly, the discrepancies are related to the impossibility of accurately determining the beginning and end of the moisture release due to the peculiarities

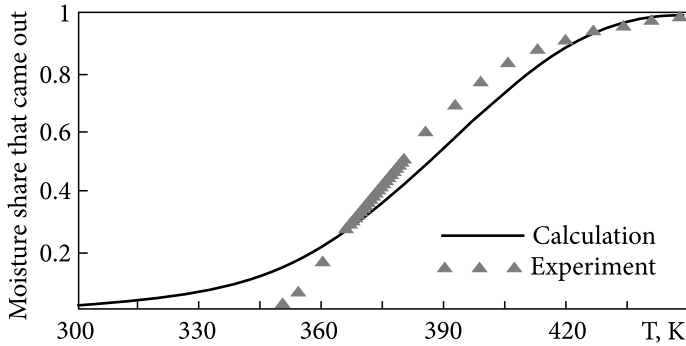


Fig. 3.11. Comparison of the calculated and experimental data for the dehydration stage of the 1:1 anthracite/pine blend

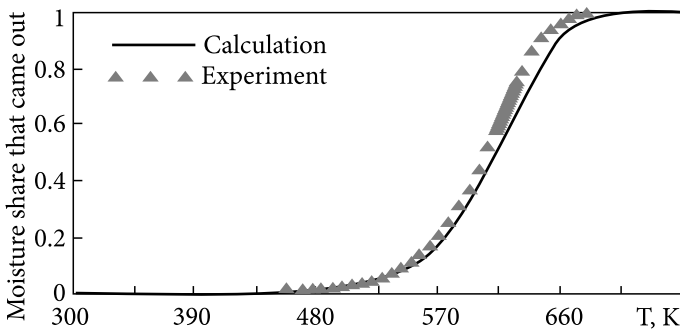


Fig. 3.12. Comparison of the calculated and experimental data on the degree of conversion for the devolatilization stage of straw pellets

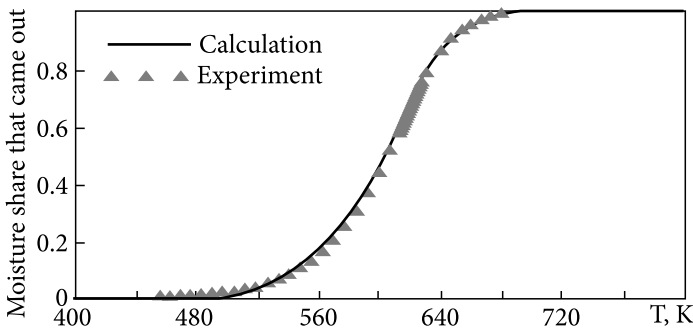


Fig. 3.13. Comparison of the calculated and experimental data on the degree of conversion for the devolatilization stage of 1:1 anthracite/pine blend.

inherent in the forms of the connection between moisture and anthracite. Secondly, due to the low initial moisture of the coal, the share of absorbed moisture at the beginning of sample heating (about 1 mg) reaches 35–50% of the sample's moisture content according to the technical analysis. The specified circumstances, leading to certain deviations in the dynamics of the process, however, allow for accurately enough determining the temperature range of the moisture release process, and, accordingly, the duration of the process at known sample heating parameters. In addition, the moisture balance determined in this way completely coincides with the results of the technical analysis.

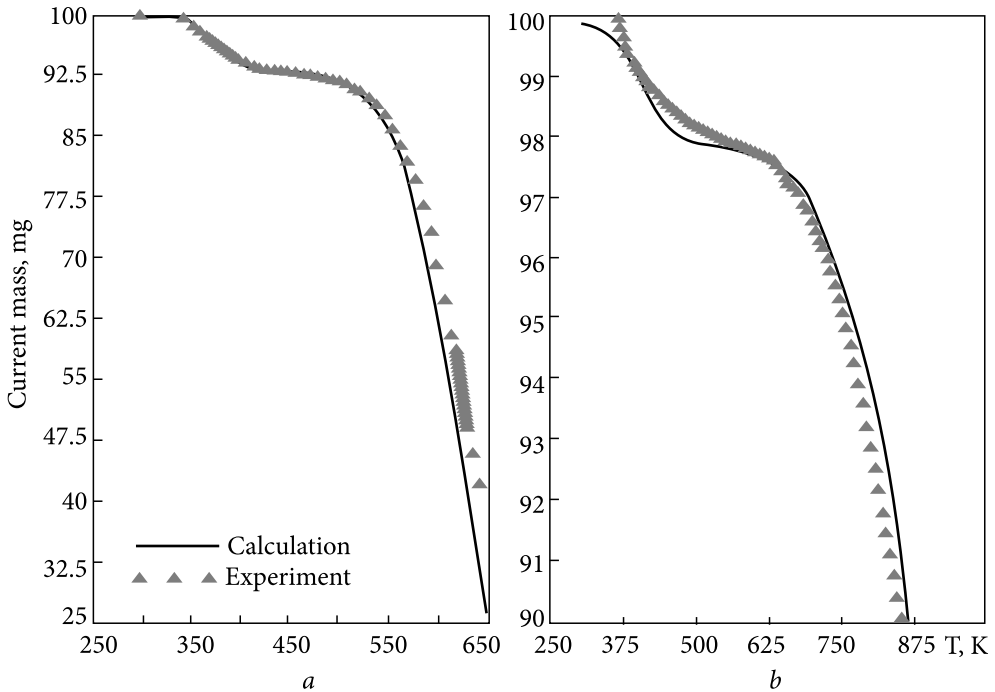


Fig. 3.14. Change in the current mass of pine pellets (a) and anthracite (b) as a function of the heating temperature at the stages of dehydration and devolatilization

It should be noted that the presence of biomass in the blend significantly affects the kinetics of thermal destruction. Shown in Figure 3.11 data testify to this.

As seen, there is a fairly close coincidence of the calculated and experimentally determined moisture shares, which is primarily due to the ability to determine the beginning and the end of the process much more accurately by the zero and minimum values of the derived thermogravimetric curve. This makes it possible to determine both the content of the component in the blend and the degree of conversion. Analogous data for the devolatilization are shown in Figures 3.12 and 3.13.

As seen from the figures, there is an almost complete coincidence of the data calcu-

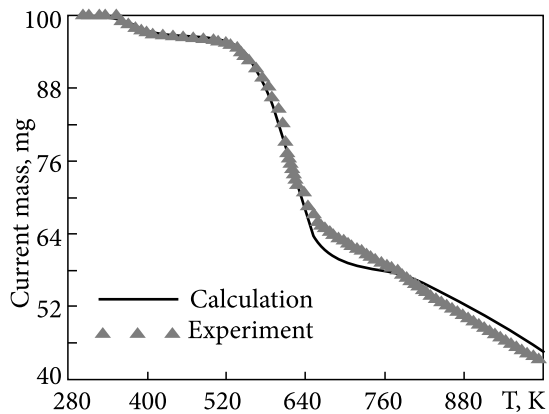


Fig. 3.15. Change in the mass of 1:1 anthracite/pine blend as a function of the heating temperature at all combustion stages: dehydration, devolatilization, and cock burnout

lated from the obtained kinetic constants and the data determined experimentally. A close match is observed both for individual fuels and for blends (Figs. 3.12 and 3.13).

The obtained kinetic constants made it possible to calculate the gradual thermal destruction by sequentially solving three (or two) differential equations, based on which, the current mass of the fuel weight during heating was determined. The results are shown in Figs. 3.14 and 3.15.

As seen, the obtained kinetic constants for the stages of thermal destruction of solid pulverized fuels adequately reflect the described processes and allow one to sufficiently accurately predict both the balance ratios of the components and the dynamics of the process itself.

3.2. Improvement of thermogravimetric methods for calculating fuel combustion kinetics using the example of pine pellets

To improve the accuracy of determining the kinetic characteristics of the fuel combustion process, a comparison of the methods described in Section 3.1 for summarizing individual stages of thermogravimetric research, namely the Freeman differential method with the Coats—Redfern, Senum—Yang, and Starink integral methods, was performed on a pine pellet sample using a graphic construction technique for the stage of devolatilization. The results are shown in Figure 3.16.

When analyzing the results of the calculations, the first thing to draw attention to is the significant difference in the shape of the conversion curve $d\alpha/dT$ according to the differential and three integral methods, which is smoother for the latter. In addition, the integral methods showed a higher accuracy of the thermogravimetric curve approximation. The Senum—Yang and Starink methods turned out to be the most accurate, however, the Starink approximation was chosen for the calculations, as it requires significantly less complicated calculations.

Basing on the researchers' recommendations, we assumed in our previous studies the presence of a first-order reaction $n=1$. In this case, the kinetic analysis of thermogravimetric curves is performed by plotting a straight line in semi-logarithmic coordinates (Fig. 3.17). This approach showed good results for the fuel devolatilization stage but significantly worse for the dehydration stage and cock combustion. Therefore, calculations were carried out to determine the optimal order of the reaction and to vary the number of experimental points that are taken into calculation for the smallest possible deviation of the graph from the linear dependence (Note the value of the approximation for the dehydration stage).

For the general case (when the reaction order is $n \neq 1$), the numerical solution of $p(y)$ in the Starink and Senum-Yang approximations have the following form:

$$\text{Ln} \left[\frac{-\text{Ln}(1-\alpha)^{1-n} \cdot \beta}{T^{1.92} \cdot e^{-0.312} \cdot (1-n)} \right] = \text{Ln} \left(k_0 \left(\frac{R}{E} \right)^{0.92} \right) - 1.0008 \frac{E}{R} \frac{1}{T}, \quad (3.16)$$

$$\text{Ln} \left[\frac{-\text{Ln}(1-\alpha)^{1-n} \cdot \beta}{T^2 \left(\frac{y^4 + 18y^3 + 86y^2 + 96x}{y^4 + 20y^3 + 120y^2 + 240y + 120} \right) \cdot (1-n)} \right] = \text{Ln} \left(\frac{AR}{E} \right) - \frac{E}{R} \frac{1}{T} \quad (3.17)$$

The optimality criterion for varying the number of experimental points was the minimum deviation of the calculated and actual masses of the sample fractions such as the mass of moisture, volatile matter, or cock residue.

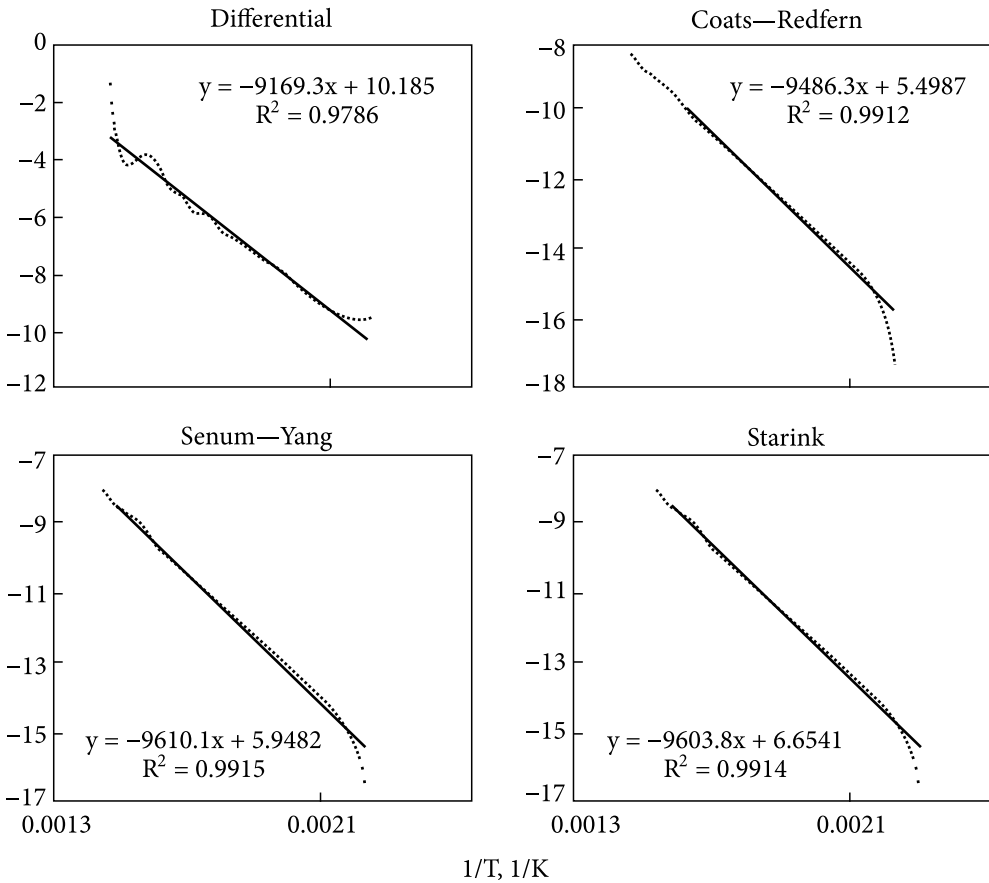


Fig. 3.16. Comparison of the generalized accuracy of the TG curves of pine pellets' volatile matter yield by different methods

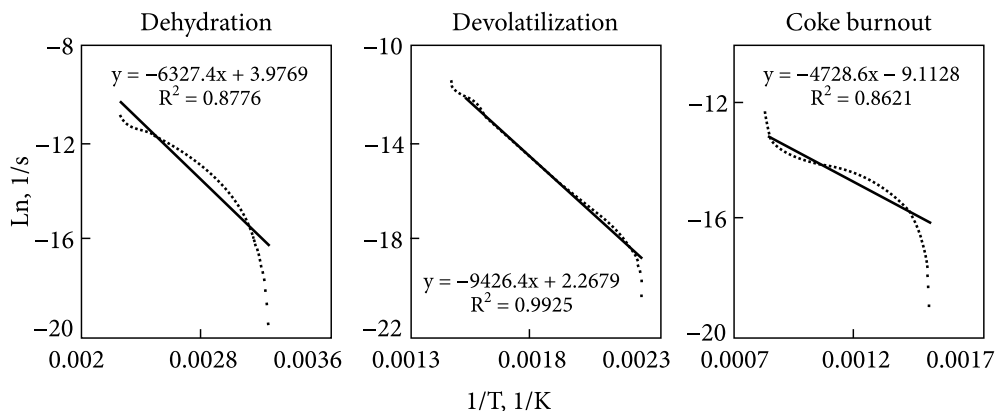


Fig. 3.17. Generalization of TG studies of pine pellets by the integral method into Starink approximation for the first order reaction

Calculations were carried out using the Mathcad software package. The dependence of the approximation reliability on the reaction order shows an extremum, which was taken as the optimal value. For the stage of pine dehydration, the value of the approximation reliability increased from 0.87 to 0.96. Varying the number of experimental points allows us to improve this value up to 0.99.

To check the accuracy of the calculations, the found kinetic characteristics were used to construct the thermogravimetric curve of the experiment. In Figure 3.18, the black solid line is for the experiment, the two dash-dotted lines are calculations with the first-order reaction, the dashed line is the optimal value of the reaction order, and the solid curve is the variation in the number of experimental points included in the calculation. As seen, the best result for the stage of pine dehydration was shown by the integral method with the Starink approximation at the order of reaction equaled to 2.14 and variation of experimental points. The divergence in determining the mass of the fraction is 0.005—774% (Figure 3.18). For the stage of devolatilization, the calculation accuracy increased insignificantly. The best result was also shown by Starink's method, and the reaction order was 0.8 (Fig. 3.19).

For the cock residue combustion stage, the integral method in the Senum — Yang approximation showed the greatest accuracy, which increased the approximation accuracy from 0.87 to 0.88 (Fig. 3.20). Such a low accuracy of generalization for the stage of cock residue burning, even with the use of improved calculations, can be explained by the fact that the division of the thermogravimetric curve into stages is conditional and the last stage describes simultaneously the end of the devolatilization and the start of cock burnout.

Figure 3.21 compares the complete thermogravimetric curve of the experiment with calculations using the first-order reaction in the Starink and Senum—Yang approximations, as well as the green curve consisting of the best results for each stage of thermal decomposition of the pine pellet sample.

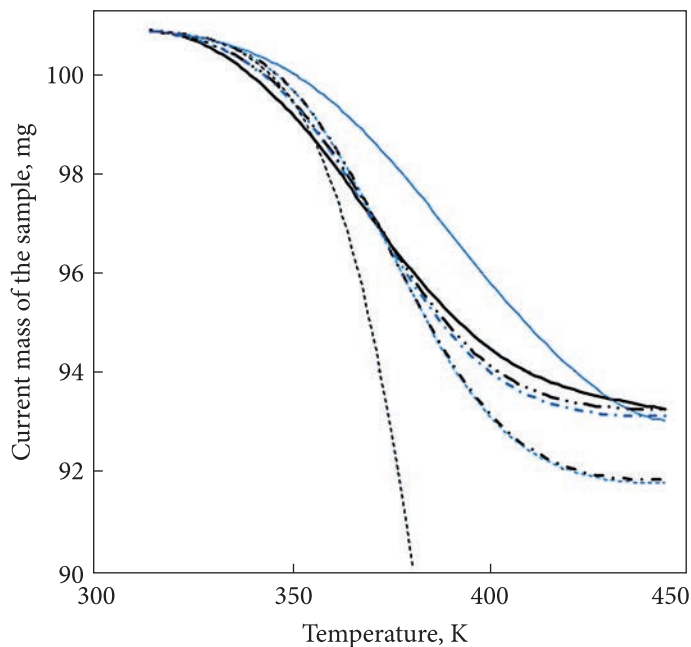


Fig. 3.18. Calculation results for the dehydration stage of pine pellets

— Experiment
 - - - Starink $n = 1$ cut = 0
 - · - Starink $n = 2.26$ cut = 0
 - · · Starink $n = 2.14$ cut = 8.3%
 — Senum $n = 1$ cut = 0
 - - - Senum $n = 2.27$ cut = 0
 - · - Senum $n = 2.14$ cut = 8.3%

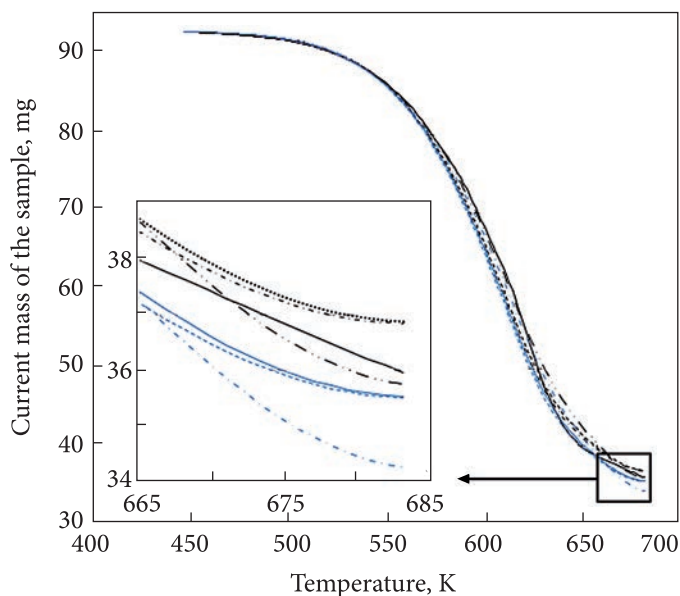


Fig. 3.19. Calculation results for the devolatilization stage of pine pellets

— Experiment
 - - - Starink $n = 1$ cut = 0
 - · - Starink $n = 1.04$ cut = 0
 - · · Starink $n = 0.8$ cut = 7.6%
 — Senum $n = 1$ cut = 0
 - - - Senum $n = 1.4$ cut = 0
 - · - Senum $n = 0.8$ cut = 7.6%

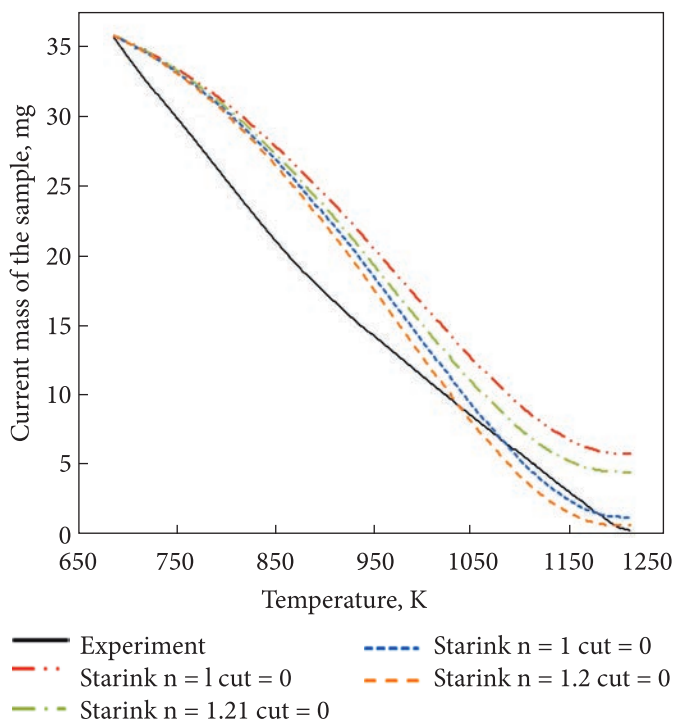


Fig. 3.20. Calculations results for the cock burn-out stage for pine pellets

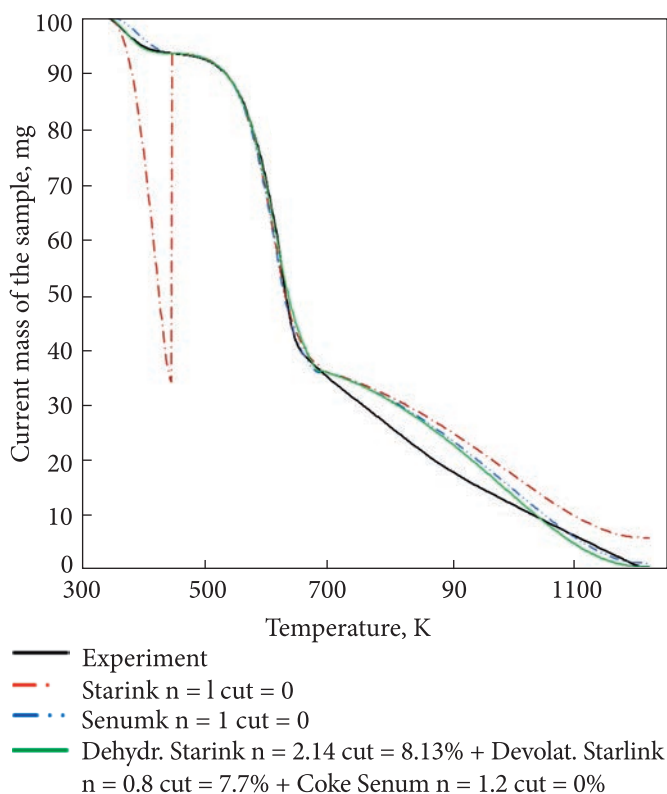


Fig. 3.21. The resulting comparison of the complete experimental TG curves for burning pine pellets with the TG curves obtained by other approximations considered

Summarizing, the kinetic constants of the thermal destruction stages of anthracite, pine, and their mixtures obtained from TG studies adequately reflect the described processes and allow predicting the balance ratios of components and the dynamics of the processes. Improvement of the methodology for calculating a fuel combustion kinetics has shown that for determine the kinetic characteristics with maximum accuracy, it is necessary to choose the optimal method of a TG experiment generalization, the reaction order, and vary the number of experimental points taken into account for each individual stage of a fuel thermal destruction.

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THERMOCHEMICAL CO-CONVERSION OF HIGHLY METAMORPHOSED COAL AND BIOMASS

4.1. Characteristics of samples and research methods

It is known that the joint conversion of two types of solid, solid and liquid carbon-containing resources of different origins almost always leads to non-additivity effects — increasing the yield of a certain type of products and changing their properties and intensification of the combustion process [1—3]. That is why the authors chose several blocks of research as a goal.

One of the sections is dedicated to the joint thermolysis of highly metamorphosed coal with biomass waste; another — to the co-firing of coal of different metamorphism (genesis) and quality; another — to the effects of non-additivity during the thermal conversion of various coal-based composite fuels, and so on.

This section is devoted to the study of the thermochemical conversion of two types of biomass and their co-pyrolysis

Table 4.1. Characteristics of highly metamorphosed coal A

Coal sample	W ^a , %	A ^d , %	V ^{daf} , %	C ^{daf} , %	H ^{daf} , %	N ^{daf} , %	S ^{daf} , %
Dust for flaring	4.49	21.8	7.3	89.3	1.4	0.75	0.52

Table 4.2. Composition and decomposition temperatures of biomass components according to [6, 7]

Biomass	Component content, %		
	Cellulose	Hemicellulose	Lignin
Wheat straw	30—40	40—50	12—17
Pine pellets	45—50	17—25	25—30
Interval of thermal decomposition, °C	300—380	200—320	280—430

Table 4.3. Characteristics of the used biomasses and their ash residues
(according to Source: https://digitalfare.com/4sight/...pine_wood_ash_1119)

Parameter	Wheat	Pine	Parameter	Wheat	Pine
W^a , %	7.63	8.43	<i>Chemical composition of ash, %</i>		
A^d , %	8.90	0.40	SiO_2	54.00	2.00
S^d , %	0.17	0.03	Al_2O_3	2.18	—
V^{daf} , %	81.80	85.90	Fe_2O_3	2.00	0.07
W^r , %	9.20	8.70	MgO	2.52	8.21
Cl^d , %	0.07	0.04	CaO	12.95	41.10
<i>Elemental composition, %</i>			Mn_3O_4	0.09	2.54
C^{daf}	50.29	51.87	TiO_2	0.16	—
H^{daf}	6.24	6.33	SO_3	5.30	6.69
$(N + O)^{daf}$	43.30	41.63	P_2O_5	2.12	4.67
S^{daf}	0.17	0.03	K_2O	11.75	10.96
<i>Melting point of ash (oxidizing medium), °C</i>			Na_2O	1.45	—
t_A	1000	1300			
t_B	1120	1310			
t_C	1140	1325			

with highly metamorphosed coal (A). For the experiments, a sample of coal dust used at Ukrainian TPPs for the production of heat and power energy and two types of biomass — wheat straw (B1) and pine wood (B2) pellets — were chosen. They also constitute a solid domestic raw fuel resource (Tables 4.1—4.3) [4, 5].

To substantiate possible differences in the impact of biomass, data on the typical component composition of the types of bio-raw material selected for research and their thermal characteristics are required (Tables 4.2 and 4.3).

The results of technical and elemental analyses and the chemical composition of the ash from the investigated biomass samples are given in Table. 4.3.

4.2. Thermographic and spectroscopic studies of the conversion of waste wood (pine pellets) and agrotechnical (wheat straw pellets) biomasses

The pyrolysis process of separate bio-raw materials — wheat straw (B1) and pine wood (B2), as well as their blends with coal in a ratio of 1:1, was studied in the Q50 thermobalance of TA Instruments (Fig. 4.1). The volatile products (VP) of pyrolysis using the TGA/FT-IR interface (Fig. 4.1, middle) were transferred to the Thermo Scientific Nicoletis10 spectrometer

(Fig. 4.1, left) to record their FT-IR spectra. The spectra were processed using the OMNIC9 software [8].

Sample portions were heated to 750 °C in an atmosphere of pure nitrogen at a heating rate of 4 °C/min. Curves of mass loss and mass loss rate of both types of biomass and their blends depending on temperature are presented in Figure 4.2.

The data show that during pyrolysis, the emission of volatile products from samples of different biomasses differs significantly, as does the rate of mass loss.

The maximum rate of release of VPs from pine pellets (B2) is shifted toward higher temperatures, however, at the final temperature of thermolysis (750 °C), the total yield of volatiles from B2 is 85.8%, while the yield of volatiles from the sample of wheat straw (B1) is significantly lower, 80.7%. The yield of volatiles under these conditions from the coal sample is close to zero (Fig. 4.2).

This is in good agreement with the data of Table 4.3, in accordance with the standard indicator V^{daf} . The obtained results also show that the volatile straws have the lower molecular mass, but the potential (sum of volatiles) is greater in pine pellets (about 5%). This means that the set of possible cross-reactions with the organic matter of coal is wider in the presence of pine pellets.

This is due to the peculiarities of the chemical structure of the raw materials, which is also reflected in the FT-IR spectra of VPs (Fig. 4.3).

The spectra show that the VPs of pine differ from those of straw by the increased content of oxygen groups and substituted and unsubstituted CH groups. The VPs of B2 contain not only a higher content of ethers, phenols, alcohols,

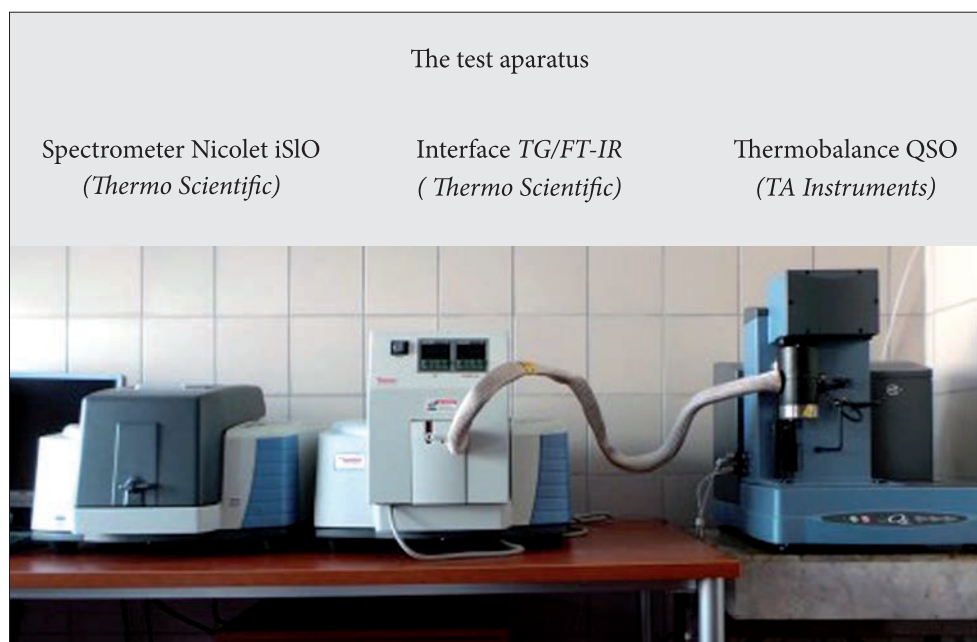


Fig. 4.1. Analytical devices for studying the thermolysis of blends and their components

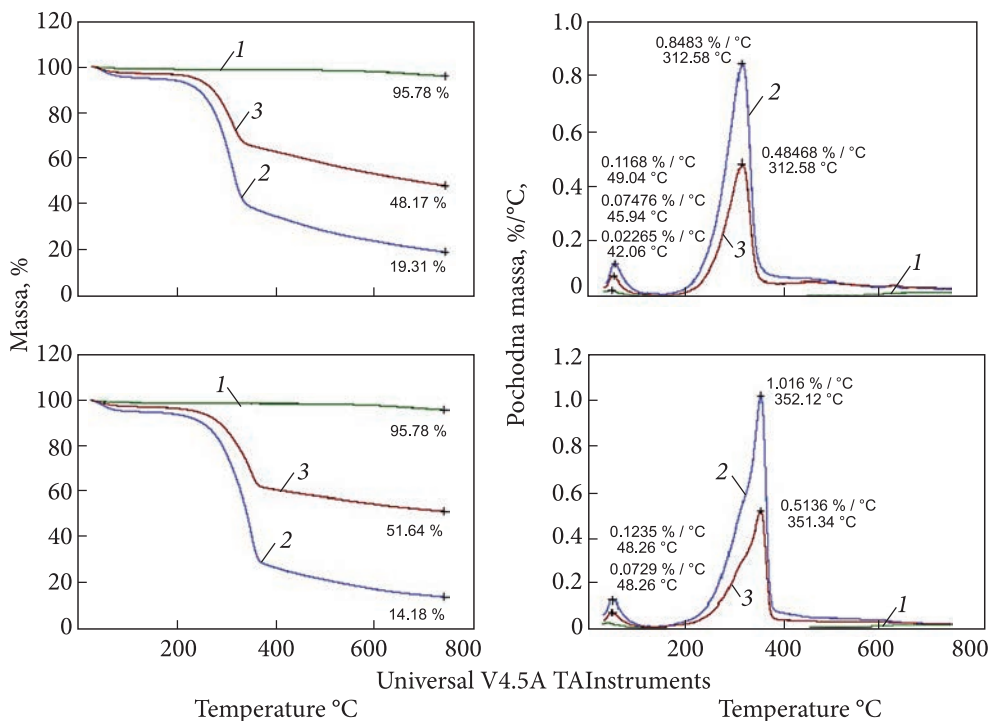


Fig. 4.2. The results of the derivatographic analysis of studied blends (curve 3, above — A/B1, below — A/B2) and their components (curve 1 — coal, curve 2 — biomass)

and compounds containing carbonyl fragments (in the composition of carboxyl, aldehyde, and ketone groups) but also a wider range of them. This is signaled by small additional bands in the region of $1000\text{--}1400\text{ cm}^{-1}$, as well as the appearance (or increase) of absorption at $\nu = 2700\text{--}2750\text{ cm}^{-1}$. The final result of thermolysis ($750\text{ }^{\circ}\text{C}$, 180 min) according to the DTA data (Fig. 4.2) shows that the experimental yield of solid residue for sample A/B1 is more than 48% while calculated by the rule of additivity, it is significantly larger — 57.5%, i.e.; the deviation from additivity is more than 9%. The mass of the solid coal residue under these conditions is almost 96%, which indicates an extremely small conversion of the organic mass of coal. For the A/B2 blend, the experimental yield of the solid residue is 51.6%, while the one calculated by the rule of additivity is about 55%, that is, the deviation from the sum of the yields exceeds 3% [9]. Thus, under the effect of volatile biomass matter in the reaction zone, already at $300\text{ }^{\circ}\text{C}$, the degree of thermal conversion of coal increases, while the volatile components of B1 affect the process more actively.

The course of pyrolysis of coal and biomass blends is also illustrated by the Gram—Schmidt curves (G—Sch) (Fig. 4.4), which allow us to compare the development of the thermal destruction process over time. As seen, the release of volatile products of the blend ends after 80—90 min, that is, in the range of

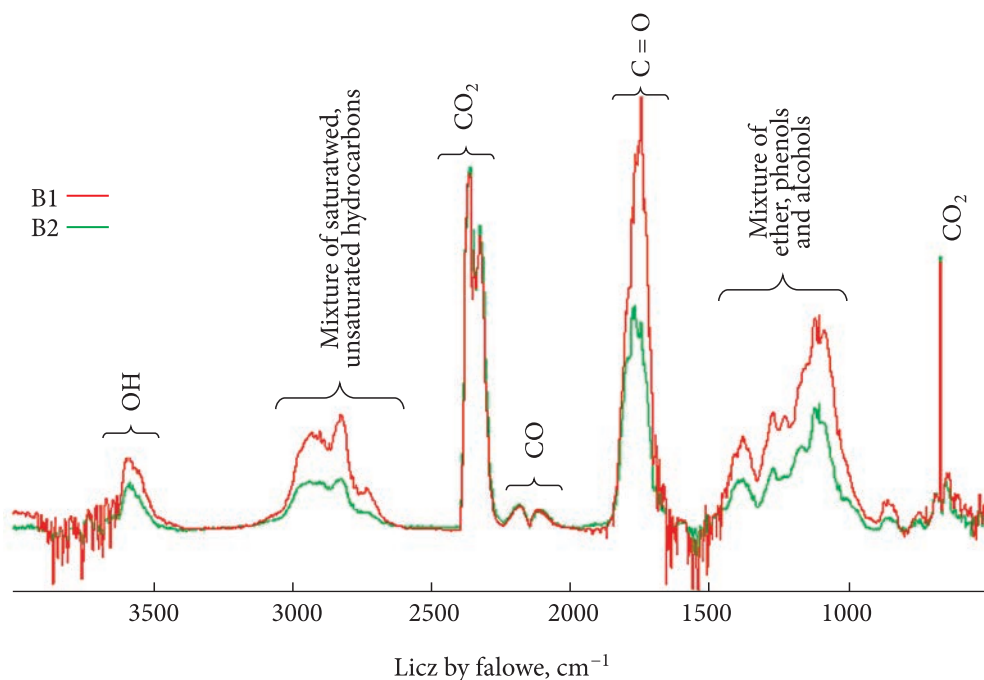


Fig. 4.3. FT-IR spectra of volatile pyrolysis products from biomasses studied

350 ± 50 °C, the increase in temperature already leads to the process of carbonization (partial combustion and condensation reactions) of the studied raw materials.

The G—Sch curves show a significant deviation of the shape and area of the blend curves from the same indicators for the individual starting components, which is most evident from 110 to 180 min of thermolysis. Note that the maximum rate of thermolysis of coal (determined by a separate experiment), which coincides with the data of TGA, Figure 4.2, is reached only at 170 min of the process (temperature about 680 °C), while the maximum rate of mass loss of wheat straw occurs at 110 min and pine straw — at 132 min.

For the investigated blends, the carbonation maxima shift, remaining significantly closer to the biomass indicators of B1 and B2 (118 and 145 min, respectively). At the same time, the intensities of the maxima increase by 2—3 times, and the area under the normalized curves deviates from the additive value by 1.7 times for the A/B2 blend and by 2.6 times for A/B1. This indicates a significant intensification of the process of thermal decomposition of mixed fuel raw materials in comparison with coal alone.

4.3. Differences in volatile products of joint thermolysis. Assessment of interaction of components of mixed raw materials

To determine the causes of the distinctly expressed synergistic effect, FT-IR spectra of VP of biomass (Fig. 4.3) and similar spectra of mixed VPs (Fig. 4.5) were obtained. For ease of comparison, the intensities are normalized relative to that of CO_2 at 2350 cm^{-1} .

The mentioned interactions result in both the increase in the yield of volatile components of the mixture in comparison with that of either mixture component alone and the change in their composition when mixed with coal (the appearance of absorption bands at $\nu = 3700\text{--}3750\text{ cm}^{-1}$ and 1500 cm^{-1}) (compare Figs. 4.3 and 4.5).

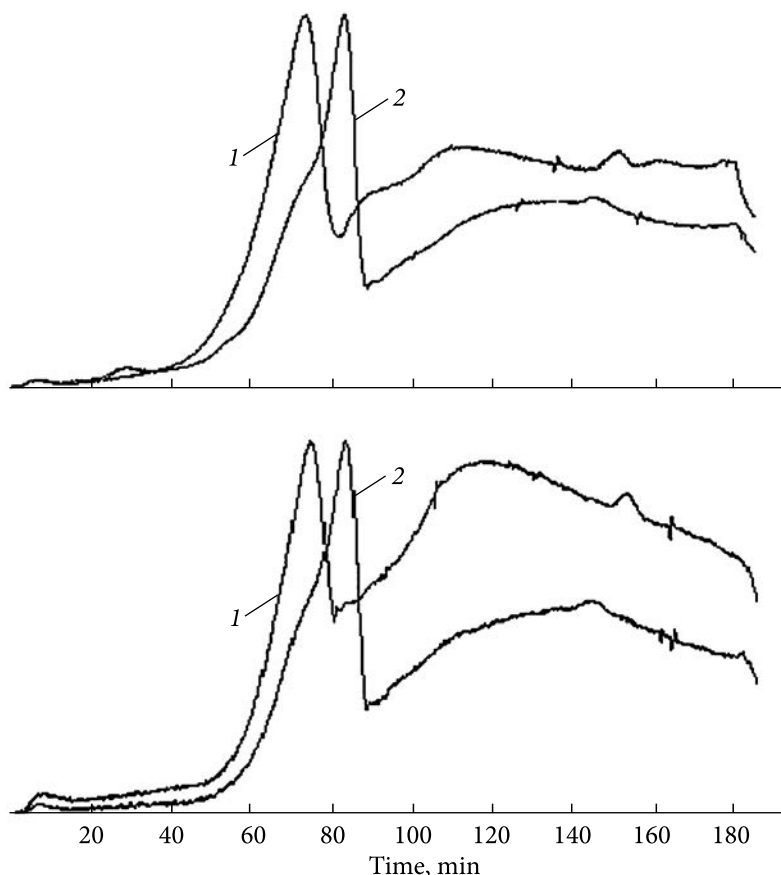


Fig. 4.4. Comparison of G—Sch curves of the thermolysis of biomasses (upper graph: 1 — B1; 2 — B2) and their blends with coal (lower graph: 1 — A + B1; 2 — A + B2)

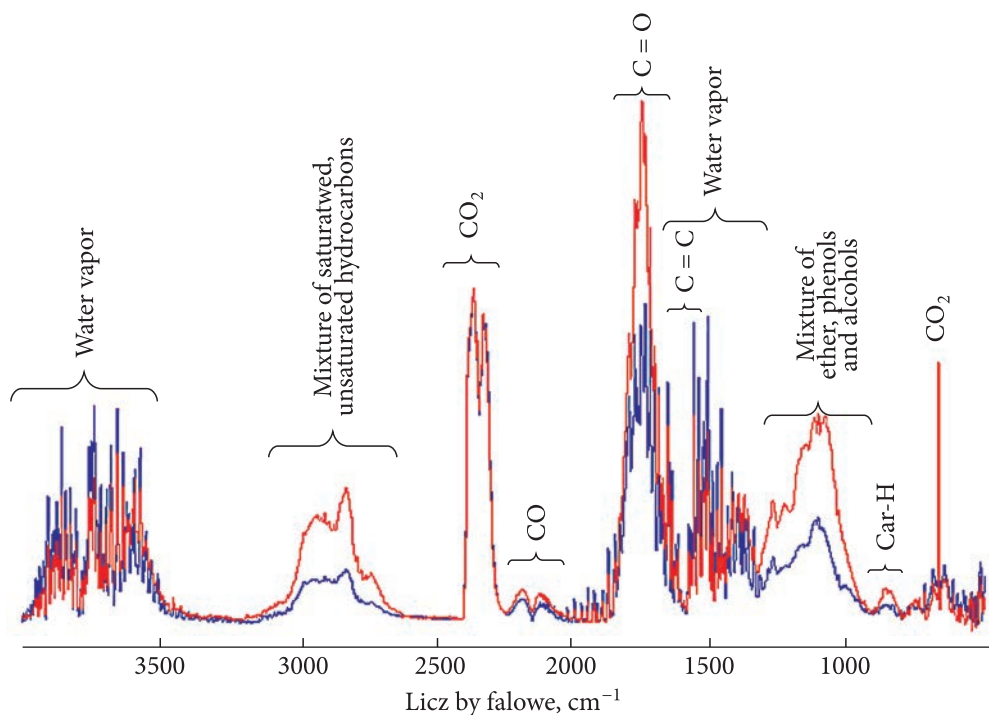


Fig. 4.5. FT-IR spectra for VPs from the thermolysis of A/B1 (blue line) and A/B2 (red line) blends

Table 4.4. Relative intensities (I_x/I_{2350}) of absorption bands (cm^{-1}) of IR spectra of volatile products of thermolysis of biomasses B1 and B2 and their blends with anthracite A

Sample	3750	3700	3600	2800	1750	1500	1380	1100	650
B1	—	—	0.13	0.14	0.63	—	0.17	0.38	0.11
A/B1	0.58	0.64	0.64	0.16	0.94	0.90	0.22	0.30	0.16
B2	—	—	0.42	0.33	1.04	—	0.29	0.62	0.77
A/B2	0.26	0.40	0.30	0.40	1.56	0.62	0.40	0.60	0.80

Comparative analysis of the spectra using the calculation of the relative intensity of the characteristic bands to the intensity of the band with $\nu = 2350 \text{ cm}^{-1}$, made it possible to establish (Table 4.4) that the number and intensity of the considered peaks in the case of mixtures significantly exceed the additive value of the intensities.

Taking into account the Bouguer-Lambert-Beer law, which postulates a proportional dependence of the intensity of absorption on the concentration of the substance, we can state that, under the condition of independent decomposition of the components, the values of the peak intensities at $\nu = 3600 \text{ cm}^{-1}$ (hydroxyl

absorption) should be 0.07 for A/B1 and 0.21 for A/B2 (1:1). Similarly, all the characteristic bands of the IR spectra of the mixture were considered. We see that in the spectra of the volatile VPs of the blends, new peaks appear, inherent purely to coal — aromatic C=C oscillations (bands at $\nu = 1500\text{ cm}^{-1}$) and bands of hydroxyl groups, intermolecular hydrogen bonds, and water vapor (within $3700\text{--}3750\text{ cm}^{-1}$).

Also shows that there is an increase in absorption associated with the release of CO_2 during the interaction of the mixture components (thin band at $\nu = 650\text{ cm}^{-1}$), where a noticeable deviation from additivity can also be determined, which is more significant for the A/B1 mixture.

That is, the VPs of the blends are enriched with aromatic molecules, water vapor and ether, carbonyl- and carboxyl-containing compounds. In other words, during the thermolysis of blends, the emission of steam and aromatic compounds with oxygen-containing groups of different functionalities is facilitated. There are polycondensation reactions and, most likely, decarboxylation due to cross-reactions, as well as enhanced formation of aromatic ethers. It is these interactions that are the cause of the synergistic effect, which is manifested in the non-additivity of the outputs of solid products, acceleration of the beginning, and intensification of the destruction of the organic matter of coal.

4.4. Properties of solid products of joint thermolysis

Solid products (SP) of co-conversion of coal and various types of biomasses require detailed study, as they can be a further new energy-chemical resource and provide even more detailed insight into the course of co-conversion processes of selected components. This applies, in particular, to the development of the surface and porosity during the joint combustion of such raw materials as coal and plant biomass that differ in initial characteristics. So, this is one of the key issues for predicting the reactivity of the system and the course of combustion [10], which, accordingly, becomes necessary for adequate modeling of the co-firing process. For example, it was found that during the combined thermolysis of the 1:1 mixture of coal, (76.3% C^d , 5.3% H^d) and corn stalks (46.6% C^d , 5.7% H^d) (here and later on, mass%), a significant increase in the specific surface area (determined by the BET method) of SPs — from 5 (in the initial blend) to $50\text{--}60\text{ m}^2/\text{g}$ in the solid residue at $750\text{ }^\circ\text{C}$ and holding for 30 min. This fact requires making adjustments to the CFD modeling system [11].

Accordingly, part of our work is devoted to studying the characteristics of solid products of the combined thermolysis of domestic coal of the anthracite group with agricultural waste (wheat straw pellets (B1)) and wood biomass (pine wood pellets (B2)) in terms of their morphology and energy value. In addition, the content and distribution of trace elements (both toxic and catalytically active) in the products of joint thermolysis of selected compositions is practically significant. The morphological features of the obtained SP were studied with a scanning electron microscope (SEM) (Fig. 4.6).

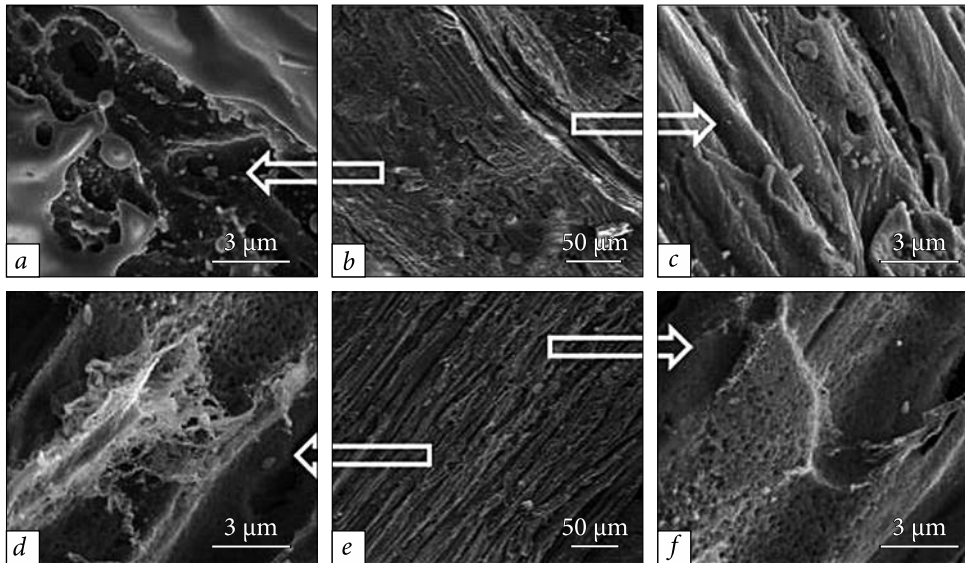


Fig. 4.6. SEM micrographs of SP of biomass pyrolysis: *a, c, d, f* — B1 and B2 at M25k; *b, e* — B1 and B2 at M1k (1k — magnification by 1000)

It is noticeable that the surface relief of pyrolysis products of B1 and B2 differs since they have different genes and component compositions (Table 4.2). The morphology and texture of their surfaces are significantly different. Solid products from pine pellets look more structured and denser, while ones from wheat straw are much more destroyed and broken and exhibit more developed porosity. The elemental composition of SP from B1 and B2 also differs, as evidenced by the results of microanalysis (EDX chromatography spectra (Figs 4.7 and 4.8)). Differences in the composition of biomass are also associated with the presence of organic-mineral inclusions in plants, which can be one of the reasons for differences in the course of the pyrolysis process.

A detailed study of micrographs of SP of blends at M25k showed that a higher degree of interaction (gasification) of anthracite in the presence of both types of biomass is manifested in the appearance of small depressions (holes) on the surface of anthracite grains (Fig. 4.7), which may be due to the active interaction of volatile substances of straw with anthracite. The solid remains of the thermolysis of coal alone (A) reveal signs of surface development only when the picture is magnified at 25k (3—4 caverns in the field of view), while the SP of blends have numerous surface irregularities, which are especially noticeable on the products of the blend of coal with wheat straw. At the maximum magnification, it becomes obvious the presence of numerous (on samples A/B2 and A/B1) depressions of different diameters on the surfaces of mixed SP and the surface of the SP from the A/B1 blend; a wide and deep pore is fixed, selected from the few ones fixed at a magnification of 25k.

Practical interest in the further fate of SP of thermolysis of blends is associated with the low content of trace elements in them. Microanalysis of grains of

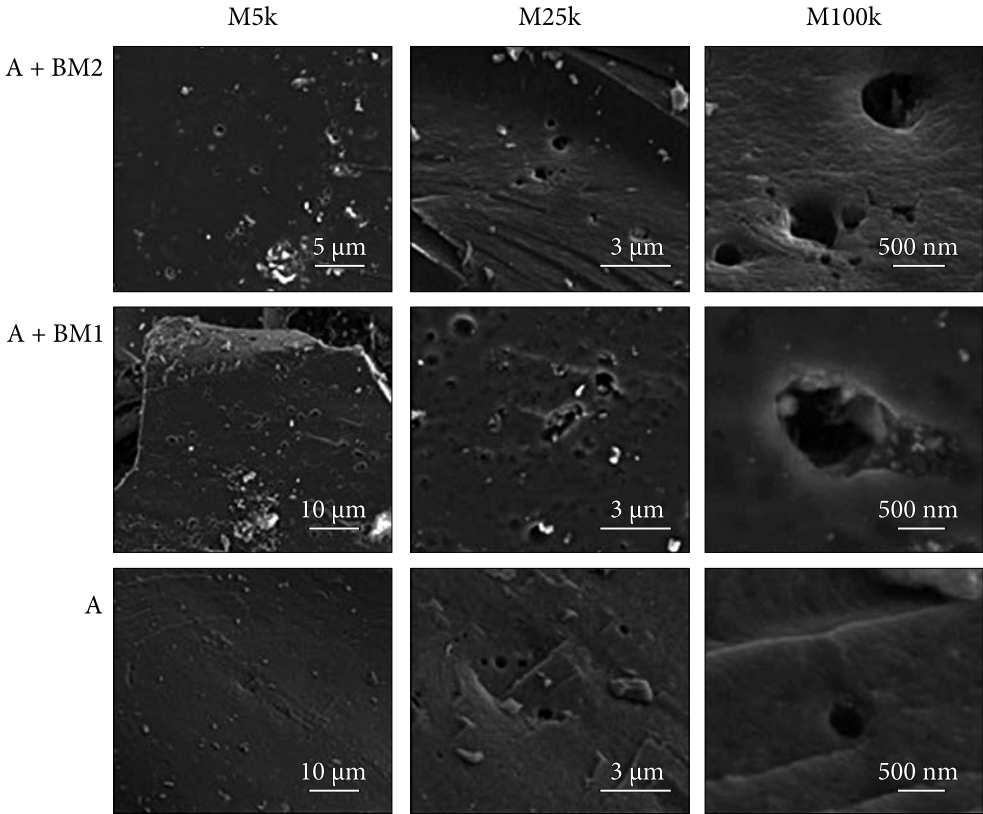
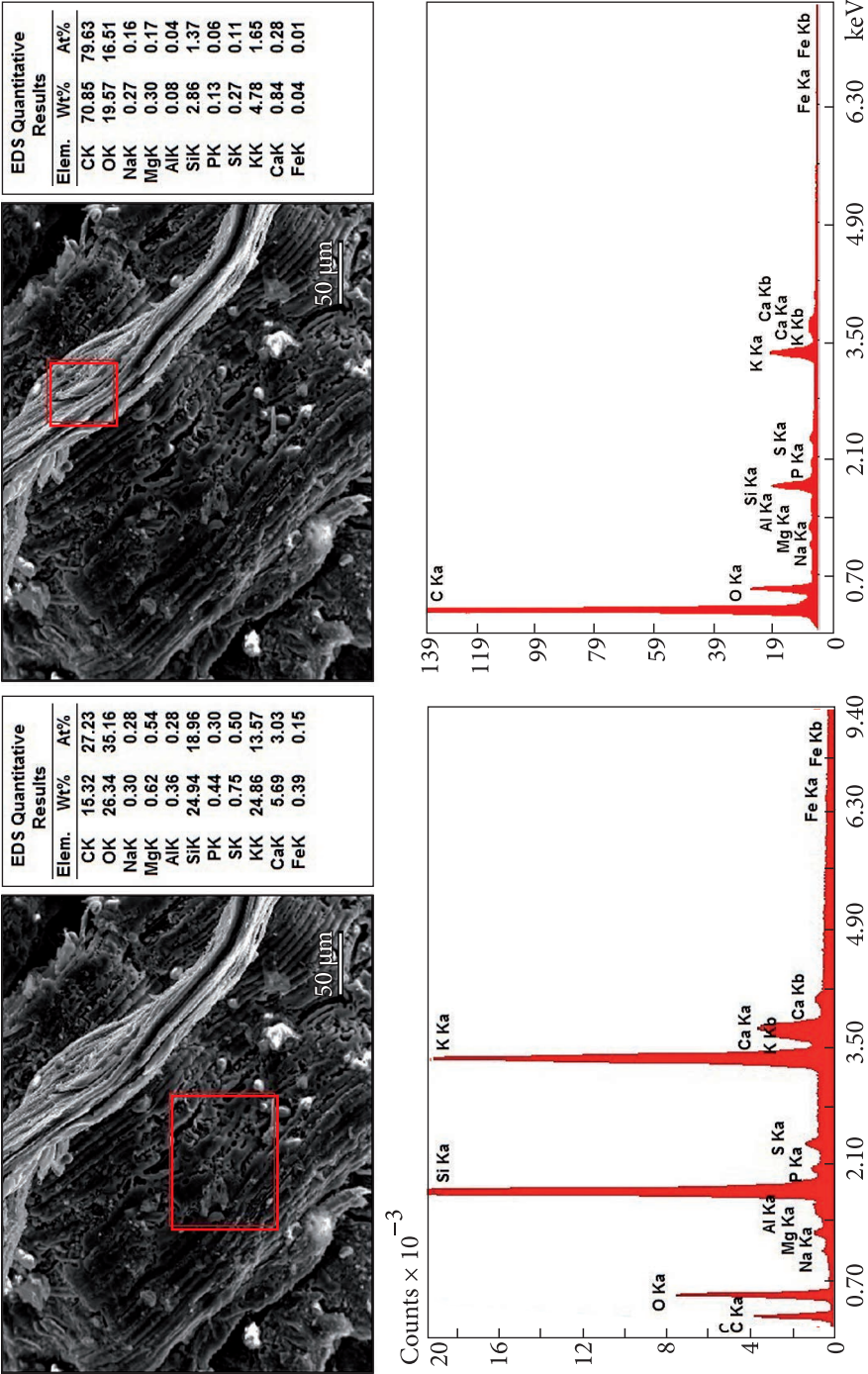


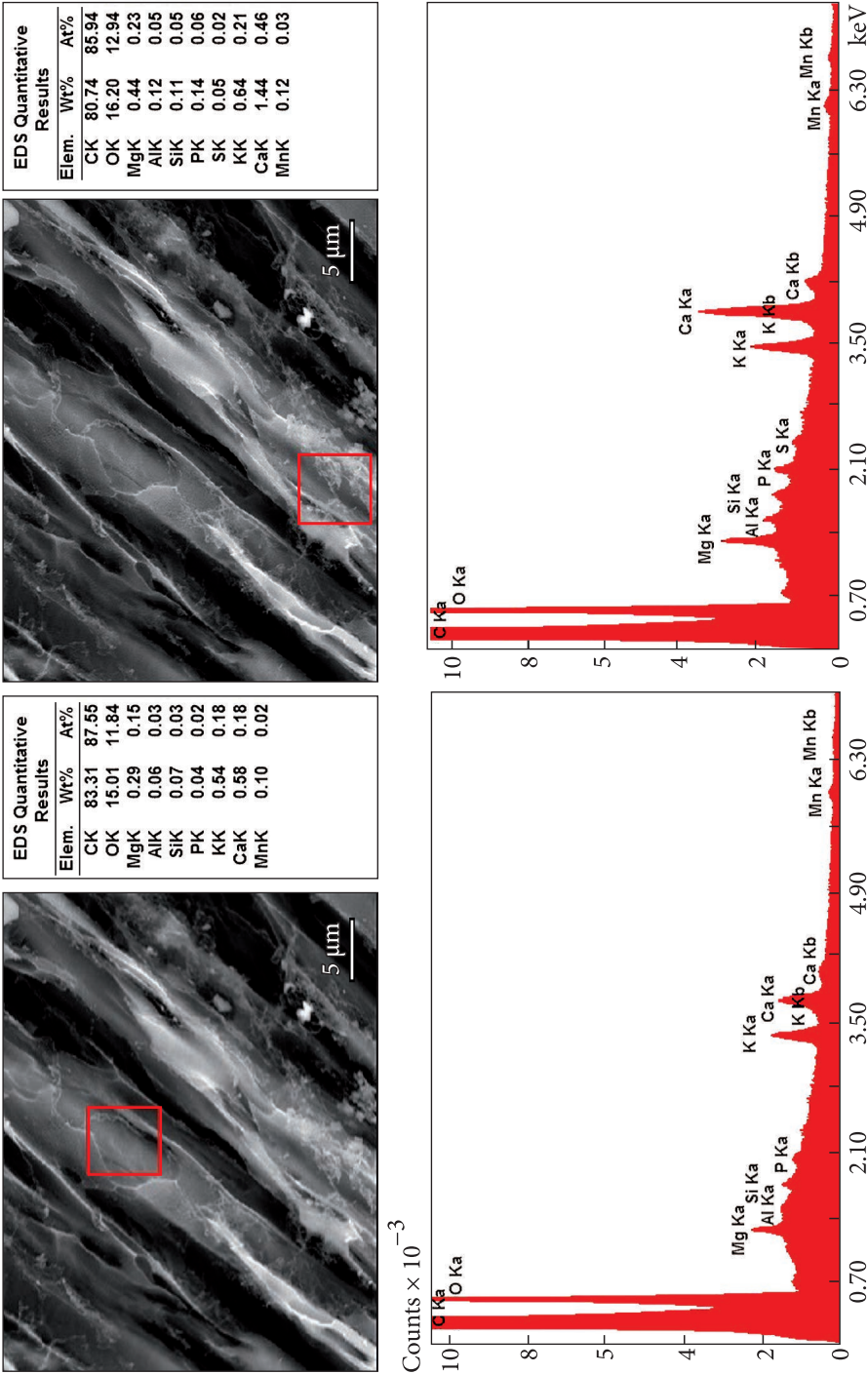
Fig. 4.7. SEM micrographs of the surface of grains of coal alone (A) and pyrolyzed with B1 and B2 at different magnifications

pyrolyzed samples of coal, biomass, and SP mixtures was carried out by the method of energy-dispersive X-ray spectroscopy (EDX). The EDX spectra of different areas of SP from biomass B1 at M5k indicate their heterogeneity where the looser dark area is characterized by a low carbon content ($\sim 15\%$) in contrast to the light area (photo on the right), which reflects a much more carbonized material with a carbon content of over 70% (Fig. 4.8).

Instead, the dark area is characterized by a high content of silicon and potassium ($\sim 25\%$ either) and an increased content of Ca (6%), which makes it possible to assert the high mineralization of the dark area of the studied sample.

It can be seen that we are talking about the composition of the heavily ashed inner part of the straw stem. At the same time, the light area can most likely characterize a more carbonized shell of the stem, where the concentration of mineral components is significantly lower. The content of sodium, magnesium, and aluminum does not exceed 0.5% . The content of silicon is an order of magnitude lower than in the dark region of the image (i.e., in the composition of the sheath of the straw stem). It can be argued that the ash-forming minerals of straw are





contained mainly in the middle of the stem, reflecting the thermolysis results for this type of biomass.

On the other hand, the EDX spectra of SP of pine pellets indicate the homogeneity of the obtained material. The morphology of the samples in the field of view is characterized by a close uniform folded structure, which also has lighter and darker shades that alternate evenly (Fig. 4.9).

The analysis showed that in these two areas, the concentrations of carbon (81–83%), oxygen (15–16%), magnesium (0.3–0.4%), and calcium (0.6–1.4%) lie in close limits, the potassium content is very low (0.06–0.6%), as is the aluminum content (0.06–0.12%). The obtained results are in good agreement with the data of the technical analysis and on the chemical composition of the ash (Tables 4.2 and 4.4). There was determined a small amount (0.1–0.12%) of manganese, which was not found in other research objects and whose content in the original pine pellets is quite noticeable (2.54%).

As for SP of thermolysis of coal alone (Fig. 4.10), the photos and EDX spectra record the homogeneity of the structure, a smooth surface with even chipping and two analysis zones — on the frontal (left) and chipped (right) surfaces.

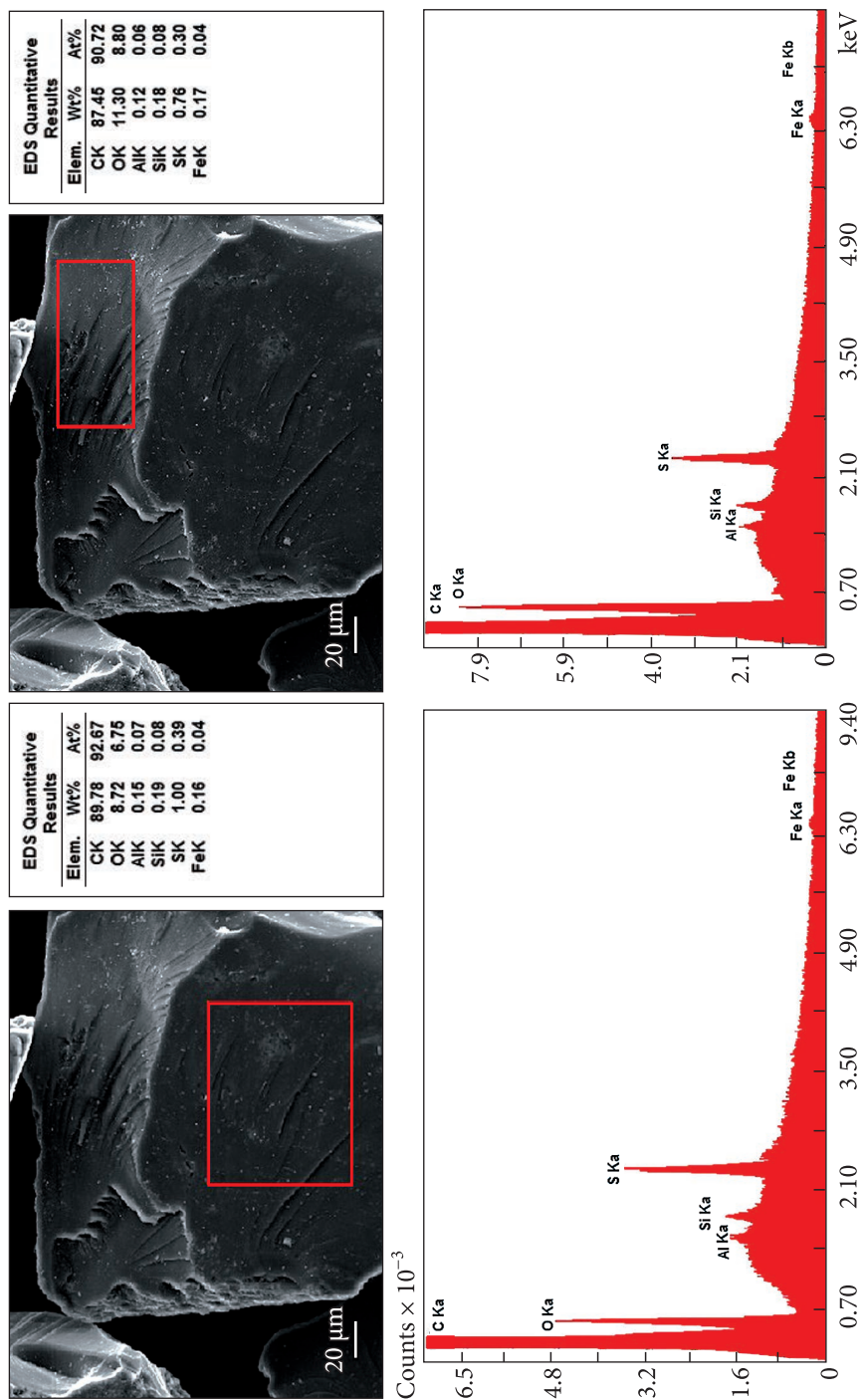
For both zones of the SP of coal, the carbon content is high (89.8–87.5%), the oxygen content is in the range of 8.7–11.2%, and the aluminum and silicon contents do not exceed 0.20%. Significant concentrations of iron and sulfur indicate the presence of pyrite or iron sulfate in coal pyrolysate. Iron, obviously, is also contained in other compounds here, most likely, these are mineral phases of oxides. From the EDX spectra (Fig. 4.10), it becomes obvious that there are no reflexes characteristic of potassium (K) in the samples of solid coal products.

Of special scientific and practical interest are the results of the EDX study of mixed solid products and the influence of the type of biomass on the content of the main elements that make up the solid products of the blends (Figs. 4.11 and 4.12).

In this case, a peak of potassium is recorded on the grain surface from a blend of coal/wheat straw B1 and, in some cases, an increased content of silicon (Fig. 4.11). No potassium reflexes were found on the surface of solid products for coal grains with B2 (Fig. 4.12). Potassium compounds are a genetic property of both types of biomass (K_2O content in straw ash is 11.75%, and in pine ash, it is slightly lower — 10.1% along with a very low ash content — 0.4%).

Under the conditions of joint thermolysis of coal and wheat raw material with higher ash content (~9%), these compounds are concentrated in the SP from blends in the form, probably, of silicates.

During the thermolysis of a blend of coal with low-ash pine pellets, the potassium content is reduced to the limit of the device's sensitivity. The absence of sodium and iron in the SPs also indicates that they were present in the raw materials in the composition of less refractory compounds (perhaps, as carbonates and chlorides) and became VPs during the thermochemical destruction of the original compounds of the blend.



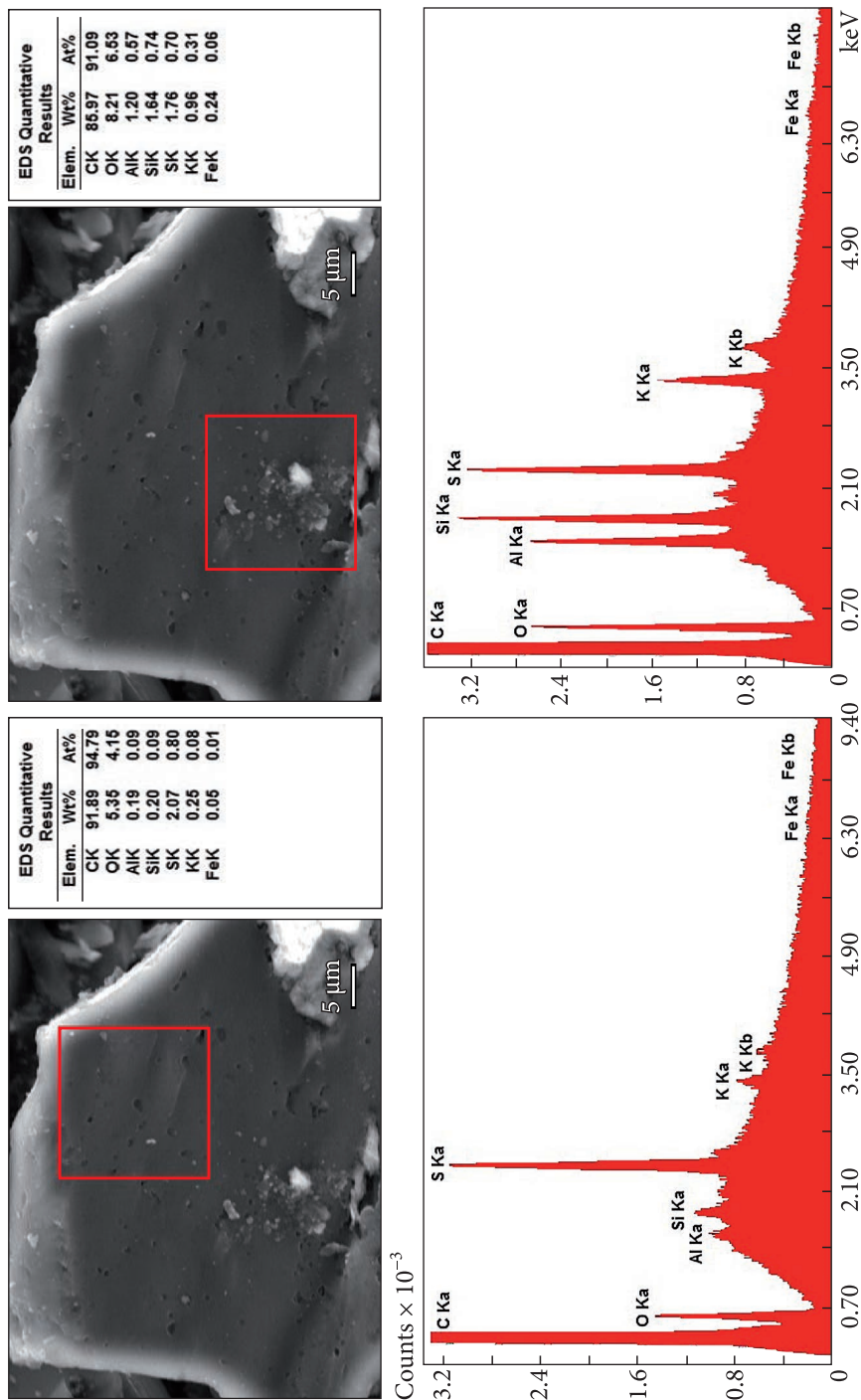


Fig. 4.11. Micrographs and EDX spectra of SPs of pyrolysis of the A/B1 blend

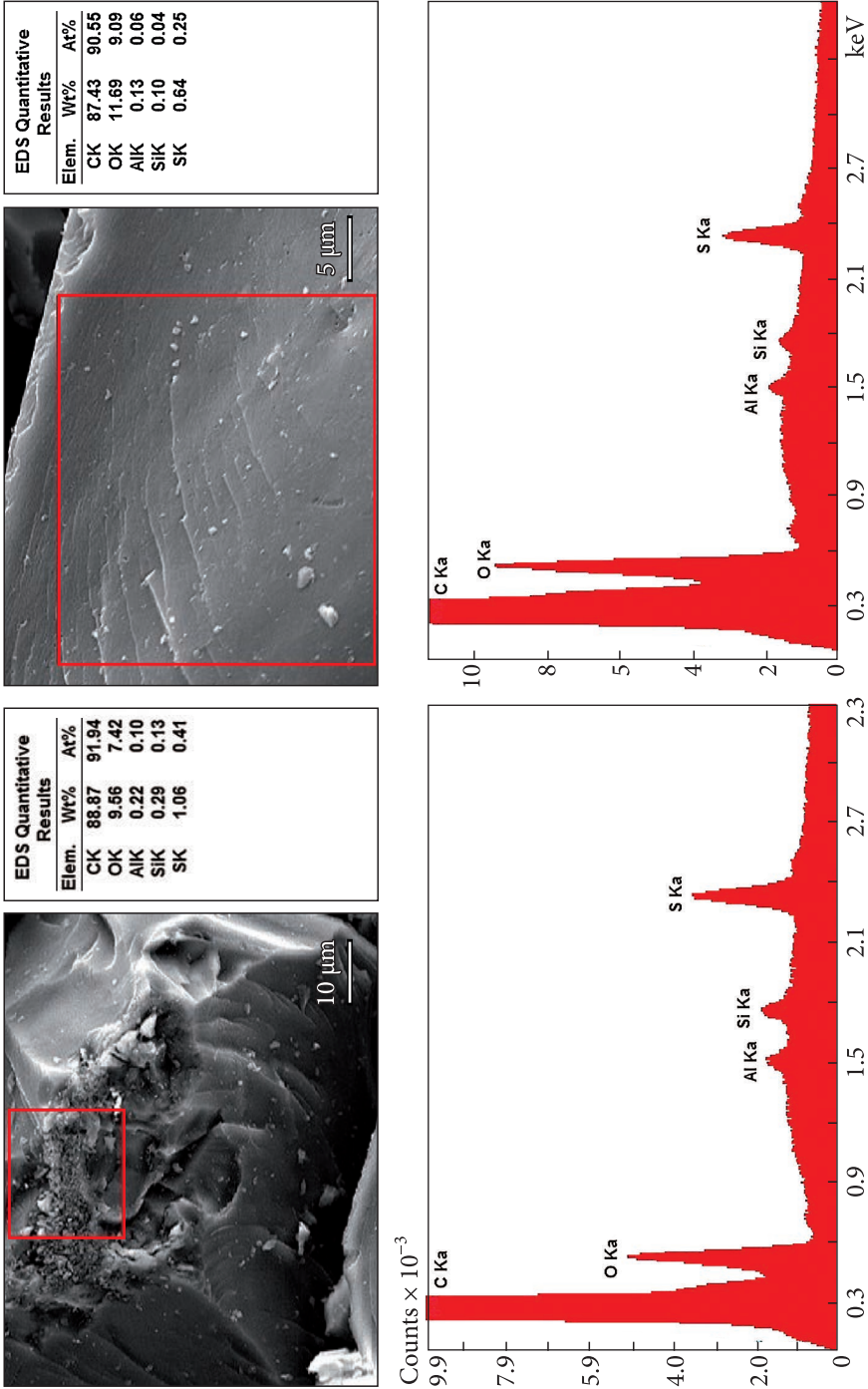


Fig. 4.12. Photos and EDX spectra of SPs of pyrolysis of the A/B2 blend

The high heat of combustion of blends of coal and both types of biomass was determined with the help of the Trypilska TPP. The results are placed in Table 4.5. A visual inspection of the collected ash residues after the calorimetry of the initial blends allowed us to establish that the ash residue of the A/B1 blend is composed of well-sintered black balls of high mechanical strength.

Instead, the ash residue of the A/B2 SPs is a black powder that is easily crushed. This confirms the previous conclusion about the influence of the content of mineral phases of the initial blends on the reactivity of raw materials and the properties of SPs. It was not possible to examine the residues for the chemical composition of the ash mixtures due to the insufficient mass of the samples.

4.5. Technological characteristics of the initial composite raw materials and prospects of using them

It is known that the heat of combustion of mixed fuels is an additive value, i.e., a simple sum of certain indicators of the components [1]. To evaluate the deviations of the experiment from the calculation, we compared the experimental and calculated values of the heat of combustion of blends and the initial components (Table 4.5).

A comparison of the calculated and experimental data on the heat of combustion of the blends shows that the differences in the values Q^r for the coal-biomass systems are insignificant. For the coal-wheat straw system, it lies within $\pm 1\%$ and for the coal-pine system, it does not exceed $\pm 2\%$.

From the viewpoint of caloric value, the studied blends fully meet the European requirements for the quality of fuels (Table 4.6). Analyzing the initial characteristics of the selected raw materials (Tables 4.1 and 4.3) and the data of Table 4.6, we can see that the European requirements apply and are fulfilled regarding the content of moisture, sulfur, and chlorine (which is on the limit in one of the components of the blend) [12].

There remains a question of the content of nitrogen and toxic trace elements (cadmium, mercury, arsenic, chromium, etc.) in the initial blends studied. Both additional efforts and the appropriate equipment park are required for this.

Table 4.5. Heat of combustion of initial components and their blends (1:1)

The lower heat of combustion per working mass	Coal	Pellets of wheat straw (B1)	Pellets of pine (B2)	Caloric value of 1:1 blends			
				Experiment		Calculation	
				Coal/B1	Coal/B2	Coal/B1	Coal/B2
Q^r , MJ/kg	23.31	15.05	17.62	18.94	19.79	19.16	20.45
Q^r , kcal/kg	5563	3596	4211	4527	4729	4580	4887

Table 4.6. The main European quality standards for fuel pellets

Parameter	DIN 51731 Germany	O-Norm M — 7135 Austria	DIN plus Germany	SS 187120 Sweden
Diameter, mm	4—10	4—10	—	—
Length, mm	<50	<5 + D	<5 × D	<5 × D
Density, kg/dm ³	>1.0—1.4	>1.12	>1.12	—
Humidity, %	<12	<10	<10	<10
Bulk mass, kg/m ³	650	≥650	650	650
Briquette dust, %	—	<2.3	<2.3	—
Ashiness, %	<1.5	<0.5	<0.5	<1.5
Q ^r , MJ/kg	17.5—19.5	>18	>18	>18
S ^t , %	<0.08	<0.04	<0.04	<0.08
N ₂ , %	<0.3	<0.3	<0.3	—
Cl ₂ , %	<0.03	<0.02	<0.02	<0.03
As, mg/kg	<0.8	—	<0.08	—
Pb, mg/kg	<10	—	<10	—
Cd, mg/kg	<0.5	—	<0.5	—
Cr, mg/kg	<8	—	<8	—
Cu, mg/kg	<5	—	<5	—
Hg, mg/kg	<1.5	—	<1.5	—
Zn, mg/kg	<100	—	<100	—
Fastener, binding materials, %	—	<2	<2	—

“—” means that there is no data or the exact value is not determined.

Not only the structural group (based on IR spectra) composition of volatile substances [9] but also the molecular composition and assessment of their environmental safety require further research.

The development of the specific surface area and porosity of the experimental raw materials in the process of co-conversion of coal and biowaste also requires a more detailed study with the involvement of special sorption methods, since SEM does not make it possible to assess the porosity formed in the solid residue granules during the co-conversion of raw materials.

After all, the specific surface of solid products of pyrolysis, which develops under the influence of volatile biomass matter, is of essential importance for technological calculations of the combustion process.

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SIMULATION OF CO-FIRING OF TWO SOLID FUELS

5.1. Introduction

One of the methods for studying the effect of adding biomass to coal on the parameters of their co-firing process is numerical simulation. The relevance of numerical simulation of processes in the furnace of pulverized-coal boilers results from the need for pre-experimental determination of the qualitative and quantitative impact of certain design and technological changes on the efficiency of the furnace and the environmental characteristics of the boiler unit. Although the ANSYS Fluent package does not directly provide for the calculation of the combustion of two different solid fuels, this limitation can be circumvented. It is necessary to briefly dwell on some of the features of setting such a task in this program.

5.2. Mathematical model of co-firing of two solid fuels in ANSYS Fluent

It is well known that when modeling processes such as heterogeneous combustion of solid biomass, the mathematical apparatus should include, in addition to equations describing hydrodynamics and heat transfer, equations describing chemical reactions between fuel components and oxidants, as well as processes representing certain stages of heterogeneous combustion, namely dehydration (moisture loss), devolatilization (evolution of combustible gases from coal particles), and burnout of coke residue of biomass. Also, the modeling of combustion processes should take into account the contribution of radiation heat transfer, which can be significantly complicated by the presence of a “grey” environment of flue gases that absorb and radiate in certain frequency ranges, and radiating particles of hot coke.

5.2.1. Calculation equations. Turbulence

In general, there is no doubt about the adequacy of the representation of hydrodynamics and heat transfer processes in single-phase fluids, since the correctness of the model in these cases is determined only by the adequacy of the boundary conditions,

which, even in relatively simple cases, can be difficult, as well as by the setting of semi- and empirical closures of systems of differential equations.

In the above cases, these will be turbulence models and determination of physical constants of modeled working fluids.

The nature of the relations for closures of systems of differential equations of hydrodynamics is demonstrated by the example of the continuity equation and the equations of conservation of momentum in the form of Reynolds time averaging of turbulent variables of the Navier-Stokes equations (by the accepted international terminology for RANS equations):

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0, \quad (1)$$

where ρ is the particle density and u — the particle velocity

$$\begin{aligned} & \frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = \\ & = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right) \right] + \frac{\partial}{\partial x_j}(-\rho \overline{u'_i u'_j}). \end{aligned} \quad (2)$$

As seen, equations (1) and (2) have the form of Navier-Stokes equations, in which the velocity components are averaged over time. Instead, the last term in parentheses, $-\rho \overline{u'_i u'_j}$, represents the Reynolds stress and must be modeled to close the system of equations (2).

The FLUENT and CFX ANSYS packages include 7 turbulence models that can be used in the programmed form as well as in User Defined Mode (UDF).

The most widely used is the k- ϵ model, according to which the Reynolds stress is defined as

$$-\rho \overline{u'_i u'_j} = \mu_t \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \left(\rho k + \mu_t \frac{\partial u_k}{\partial x_k} \right) \delta_{ij} \quad (3)$$

and the turbulent viscosity

$$\mu_t = \rho C_\mu \frac{k^2}{\epsilon}.$$

For the turbulent kinetic energy k and dissipation ϵ , the following equations were obtained [1]:

$$\begin{aligned} & \frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_i}(\rho k u_i) = \\ & = \frac{\partial}{\partial x_i} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_i} \right] + P_k + P_b - \rho \epsilon - Y_M + S_k, \end{aligned} \quad (4)$$

$$\frac{\partial}{\partial t}(\rho \varepsilon) + \frac{\partial}{\partial x_i}(\rho \varepsilon u_i) = \frac{\partial}{\partial x_i} \left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_i} \right] + C_{1\varepsilon} \frac{\varepsilon}{k} (P_k + C_{3\varepsilon} P_b) - C_{2\varepsilon} \rho \frac{\varepsilon^2}{k} + S_\varepsilon, \quad (5)$$

where $P_k = -\rho \overline{u'_i u'_j} \frac{\partial u_j}{\partial x_i}$, $P_k = \mu_t S^2$, $S \equiv \sqrt{2 S_{ij} S_{ij}}$ is the average strain rate tensor,

$P_b = \beta g_i \frac{\mu_t}{Pr_t} \frac{\partial T}{\partial x_i}$ takes into account the ejection force, Pr_t is the turbulent Prandtl

number, $C_{1\varepsilon}$, $C_{2\varepsilon}$, C_μ , σ_k and σ_ε are empirical constants, which are introduced into the turbulence model menu by default with the following values: $C_{1\varepsilon} = 1.44$, $C_{2\varepsilon} = 1.92$, $C_\mu = 0.09$, $\sigma_k = 1.0$ and $\sigma_\varepsilon = 1.3$.

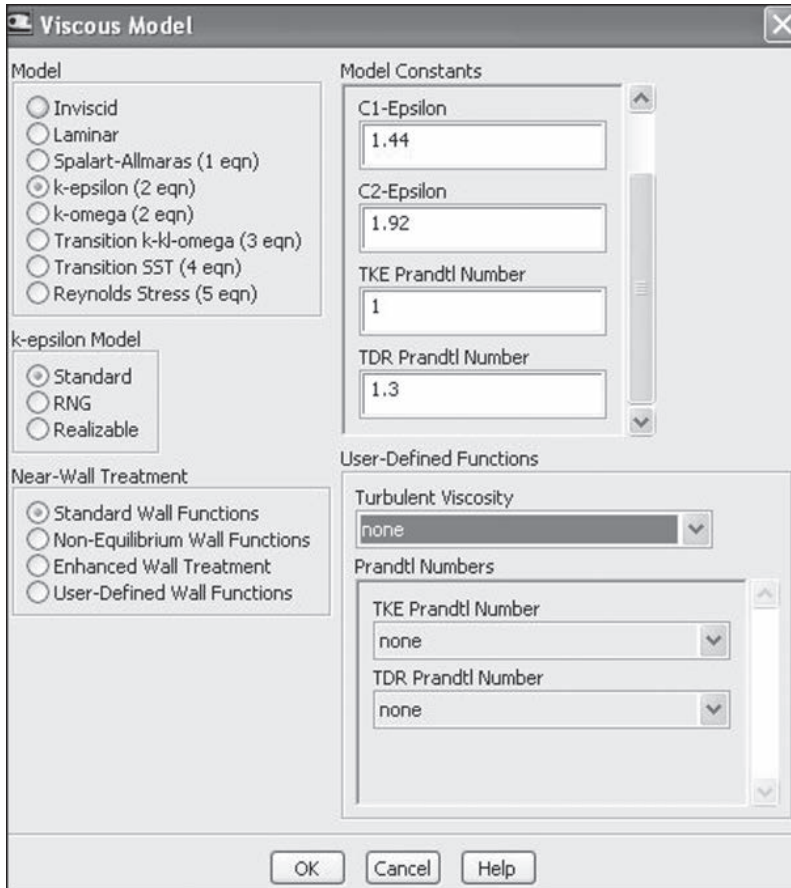


Fig. 5.1. Menu bar for selecting and defining the turbulence model and parameters

Figure 5.1 shows the menu bar for defining a turbulence model in the FLUENT package.

As seen, the FLUENT software package provides the widest possibilities for specifying turbulence models based on both experimental data available in the literature and the user's data, if the CFD models of certain specific processes are validated in a wide range of changes in the regime and flow parameters, with the possibility of simultaneous direct experimental measurement of certain integral parameters in a certain specific regime and determination of the values of model constants inherent in this process on this basis.

5.2.2. Boundary conditions

The definition of heat transfer boundary conditions at the boundaries of the computational array can cause significant complications. Indeed, the thermal boundary conditions can be set by one of three methods when modeling processes in a fluid (gas) field.

On the other hand, in real conditions, it is practically impossible to find cases when the heat exchange at the boundaries of the fluid field (Fluid) could be described either by the well-known function $t = t(x, y, z, \tau)$ for a non-stationary problem, or in the form of a heat flow distribution at the boundaries' calculation array $q = q(x, y, z, \tau)$.

In real conditions, the temperature or heat flux distribution is formed taking into account both the transfer processes within the array and the processes in the bounding walls and at the wall-environment boundaries. When modeling combustion processes, where the expected thermal stress of the volume is significant, the adiabatic temperature of the array itself, as well as the boundary temperature (and, as a result, the distribution of the boundary heat flux), will be formed both by the intensity of local heat generation (heat sources in the conservation equations) and by the processes of heat removal from the boundaries and flue gases leaving the computational array. Of course, it is theoretically possible to model the volume of the reacting flow together with the array walls and the flow leaving the computational array, but even in this case, it seems impossible to adequately reflect the thermal boundary conditions, since it is unrealistic to take into account the variable heat transfer conditions, including variations in the parameters of convective and radiative heat transfer. In addition, the attempt to include walls, which have a relatively simple heat conduction mechanism, in the design volume is significantly complicated by the need to take into account the contact thermal resistance between individual layers of insulating structures. Also, it should be kept in mind that the peculiarities of the wall geometry — small thickness compared to the lateral thickness, as well as the presence of layers — necessitate the generation of small meshes, which ultimately leads to a very significant complication of the design meshes when the number of design nodes is multiplied. As already noted, this complication does not guarantee the automatic achievement of the adequacy of boundary conditions to real ones, and at the same time, due to

the increase in computational time, it makes it impossible to implement models without special computing equipment. Thus, attempts to achieve the adequacy of boundary conditions by mechanically complicating computational grids seem unjustified in the sense of comparing machine time consumption — model adequacy also when taking into account the need to use semi- and empirical closures not only in turbulence models, as discussed above but also when programming numerous homogeneous and heterogeneous reactions, as well as drying and volatile and pyrolytic reaction stages, which is especially important in modeling biomass combustion. The issue is further complicated by the need to include in the system of design equations the array of the equations for radiation heat transfer, which include both the geometric characteristics of the array and the variable optical characteristics of the medium, the composition of which changes within the array along with the optical characteristics of the walls inside.

Given the above, it seems reasonable :

- to develop calculation models exclusively for the array in which combustion and related processes take place along the flue gas flow until they leave the boundaries of a particular technological device (reactor, preheater, burner, etc.);
- not to take into account insulating walls but instead to take into account the heat transfer in the walls and the heat transfer from the wall to the environment by determining the equivalent heat transfer coefficient from the outer surface of the array, the value of which would include all thermal resistances on the way of the calculated array to the environment (the actual heat transfer from the array to the inner wall, thermal resistance in the multilayer insulating wall, and heat transfer resistance of the outer wall);
- to take into account the effective temperature difference between the mass and the environment so that the value of equivalent heat transfer coefficients would be insignificant, and the accuracy of their determination would have a slight effect on the heat flow from the wall outward .

The values of equivalent heat transfer coefficients can be determined in validation modeling of combustion processes of model fuels (methane, for example), for which the kinetic constants of the combustion process and stoichiometry are known with sufficient accuracy, in experimental reactors and calculations of certain integral process parameters that could be compared with measured experimental data when implementing the model ed process in an experimental reactor.

5.2.3. Kinetics

Modeling of kinetic characteristics is the most difficult task since the data available in the literature differ by several orders of magnitude [1—12]. In addition to the quite understandable difficulties in conducting high-temperature high-precision experiments related to the measurement of micro changes in the sample mass during the reaction and the accuracy and adequacy of the results obtained are affected by both the methodology conditions of the experiment (drop tube, flash pyrolyzer, TGA, etc.) and the type of model used (single or

multi-stage, taking into account co-reactions or not, etc.). That is why it is even difficult to compare the data available in the literature, as they are often presented in different dimensions without explaining the model used for the calculation.

Given that a detailed study of this issue is extremely difficult, we will present the main provisions for the application and modification of submodels for volatile yields from biomass, heterogeneous combustion of coke residue, and homogeneous combustion of volatiles. One of the options for recalculating the kinetic constants of coke residue combustion will be presented in the next subsection.

5.2.4. Devolatilization model

A one-stage model was adopted, according to which:



The reaction rate is described by the one-step Arrhenius equation $k = A \times \exp(-E/RT)$, thus

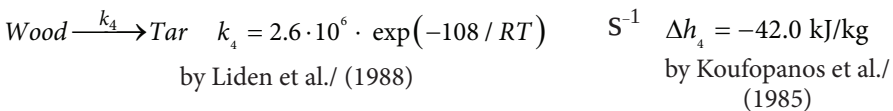
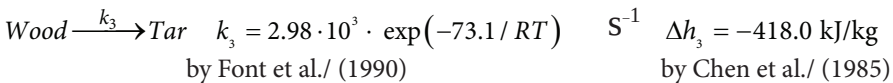
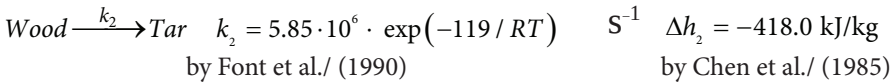
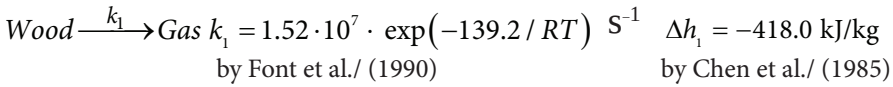
$$-\frac{dm_p}{dt} = k \left[m_p - (1 - f_{v,0}) m_{p,0} \right],$$

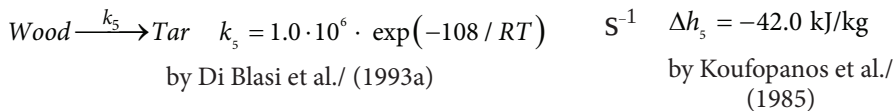
where m_p is the variable mass of the biomass fraction, $m_{p,0}$ is the initial mass of the particle, and $f_{v,0}$ is the initial volatile matter (VM) content.

This well-known approach was adopted in [1,2], where several models of volatile yield were analyzed in detail and the values of the pre-exponential factor A and the activation energy E found in accordance with the type of model were presented.

For the single-stage model, the data are given in the range for E from 180×10^6 to 250×10^6 J/kg $\times$ mol and 2×10^{13} and 6×10^{15} s⁻¹ for A .

The following constants were proposed in [12]:





Obviously, with such differences in data, it is not possible to justify the use of certain constants.

In modeling the devolatilization process, we used the data available and quite close to the yield of VM from tars (Tar-Gas).

5.2.5. Coke residue burnout model

For such a model, the data available in the literature are even more divergent than discussed above. Obviously, more factors play a role, including, first of all, a wide variety of biomass types — sources of coke residue, pyrolysis conditions, and models used. For the model of coke residue burnout, the data obtained by the TETI [13] were adapted to the model, and the activation energy value was taken from [14], $E = 89000 \text{ J/mol}$.

5.2.6. Model of homogeneous combustion of volatiles

According to the FLUENT Tutorial Guide, constants specific to methane combustion were used, since the activation energy for most gases differs slightly.

5.2.7. Modeling the fuel characteristics of biomass

According to the proximate and ultimate analyzes of the woody biomass to be utilized, the following parameters were introduced into the CFX sub-model of the HC Fuel materials (Fig. 5.2).

5.2.8. Development of geometric models of calculation arrays

The first step in creating a mathematical model is to create a geometric model that represents the structure. The geometric model can be created in the Gambit software package as the best-suited one to work with the software package used for calculations — ANSYS — and also has a built-in function to create a calculation mesh with the necessary parameters based on the created geometric model, and also provides for the division of surfaces into zones, describing these zones with various boundary conditions.

The geometric model is built in four stages (for example, for a vertical reactor, Fig. 5.3):

1. Building a three-dimensional model from simple three-dimensional elements, including cylindrical elements and cut cones; with the added such elements, mutual transfer, conjugation, and addition and subtraction operations are performed to create the volume under study.

Details of HC Fuel

Basic Settings | Proximate/Ultimate Analysis | Mixture Materials

Proximate Analysis

Option: As Received

Ash Fraction: 0.01

Moisture Fraction: 0.3

Fixed Carbon Frac.: 0.2

Volatiles Fraction: 0.49

Ultimate Analysis

Option: Dry Ash Free

Carbon Fraction: 0.5

Hydrogen Fraction: 0.08

Oxygen Fraction: 0.4

Nitrogen Fraction: 0.02

Chlorine Fraction: 0.0000

Sulphur Fraction: 0.000

Volatiles Release

Yield Enhancement: 1.23

Volatiles Molar Mass

Option: Automatic

Heating Value

Option: Higher Heating Value

Heating Value: 15.19 [MJ/kg]

Ref. Temperature: 25 [C]

Reference Pressure: 1 [atm]

Details of bio air 2 in Default Domain in Flow Analysis 1

Basic Settings | Boundary Details | Fluid Values

Boundary Conditions

HC Fuel

HC Fuel

Particle Behaviour

☒ Define Particle Behaviour

Mass And Momentum

Option: Normal Speed

Normal Speed: 8 [m s⁻¹]

Particle Position

Option: Uniform Injection

☒ Particle Locations

Particle Locations: Equally Spac

Number Of Positions

Option: Direct Specifi

Number: 100

Particle Mass Flow

Mass Flow Rate: 0.2 [kg s⁻¹]

☒ Particle Diameter Distribution

Option: Discrete Diamet

Diameter List: 2, 0.003, 0.005 [m]

Mass Fraction List: 4*0.25

Number Fraction List: 4*0.25

Heat Transfer

Option: Static Temperat

Static Temperature: 300 [K]

Fig. 5.2. Input data for the model of biomass fuel characteristics

2. Performing surface stitching operations, combining unbonded volumes into one.

3. Specifying boundary conditions on the surfaces of conditionally adiabatic walls, walls with heat transfer, fuel entry zones, and combustion product exit zones.

4. Dividing the surface into a mesh with the subsequent division of the volume into a computational mesh, which makes it possible to set different types of division, different mesh parameters, and parameters for conjugating surface and volume meshes.

Thus, when creating the first few geometric models, there was a problem of balance between the mesh cell size and the smallest geometric dimensions of the model, i.e., the size of the subdivision cell was larger than the geometric dimension to be subdivided.

This was especially true for such elements as supply pipes and burner inlets. To obtain a sufficiently accurate result on the small surfaces of the experimental unit model, it was necessary to set geometric dimensions with a small mesh step, but such a small step was not satisfactory, since it led to the grinding of the mesh of the main volume of the model, which created difficulties with the processing of the model mesh and significantly complicated the calculation, increasing the time required to solve the problem.

After creating several grids with different parameters, to compare their performance and efficiency of calculations, a mesh with a variable cell spacing was chosen. In this mesh, the technique of increasing the step from the minimum on the smallest geometric surface to the step specified for the division of the main volume was used (Fig. 5.4). This solution made it possible to significantly increase the accuracy of calculations for small geometric surfaces, without undesirable complication of the model by unnecessary increase in the number of calculation nodes.

Taking into account the flow characteristics at the transition from the main burner area to the diagnostic section with the expansion, an uneven mesh spacing was also used in the longitudinal part of the reactor. Thus, a mesh spacing of 5 mm was adopted at the expansion point, followed by a transition to 30 mm. Accordingly, the mesh with a variable spacing was displayed

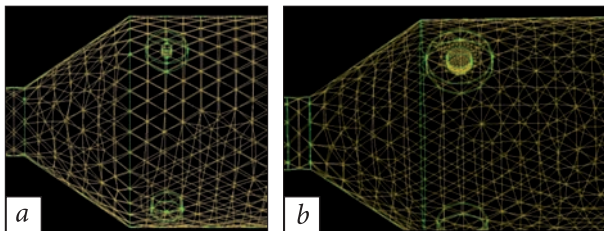
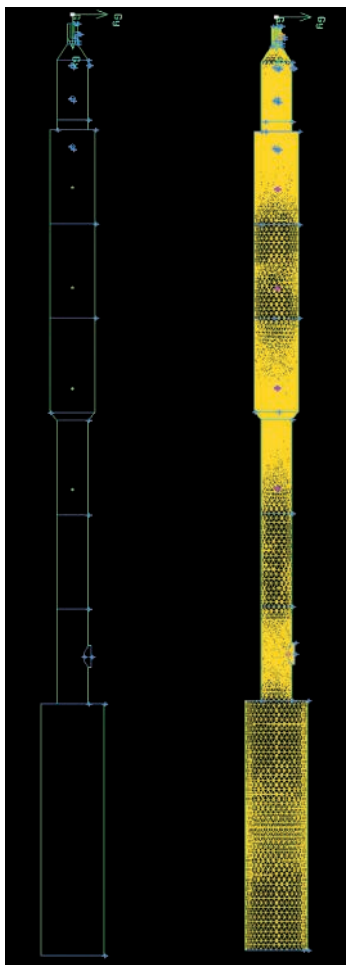


Fig. 5.3. The sequence of building a geometric volume and mesh generation according to stages 1–4

Fig. 5.4. Comparison of a constant spacing mesh (a) and a variable spacing mesh (b) at the point of connection of the auxiliary burner

in the middle of the volume to more accurately calculate the flow parameters in the wall region and other places where the flow characteristics change.

5.3. Recalculation of kinetic coefficients

While developing approaches to detailed quantitative description and analysis of the process under study, an attempt at its numerical simulation by the ANSYS Fluent program was made. This well-known program for the calculation of fluid dynamics and heat and mass transfer, including combustion processes, unfortunately, is not directly designed to describe the combustion of a mixture of different pulverized solid fuels. Therefore, approaches to approximate modeling need preliminary comments and explanation of the program features.

The *Discrete Phase model* used in ANSYS Fluent allows one to specify the input of several coals with different flow rates, particle size distributions, Proximate and Ultimate analysis parameters, the heat of combustion, as well as such parameters as *Volatile Component Fraction* and *Combustible Fraction* — volatile and solid carbon contents per dry mass, respectively. However, the *Non-Premixed Combustion model* necessary for the calculation of the combustion process assumes the possibility of describing thermochemical processes by the parameter mixture fraction in one of two possible modifications — *single mixture fraction* or *two mixture fractions*. When modeling the combustion of solid particles, it is possible to use either of these modifications.

The latter operates with two different compositions — primary (for coal, it is coke) and secondary (volatiles), whereas in the single mixture fraction modification, a single composition describes both coke and volatiles. The single mixture fraction model is considered less accurate, but it has an advantage in that the second mixture fraction (secondary) remains unused and can be used (as stated in the program documentation) to specify the composition of the secondary gaseous or liquid fuels. The ANSYS Fluent documentation is silent as to its applicability for specifying the composition of the second solid fuel. Since the dependence of the mixture fraction parameter on the coal characteristics is calculated and tabulated in a separate PDF file before the main modeling starts based on the specified composition and characteristics of a particular solid phase, this file usually cannot correspond to the parameters of the mixture of two different coals.

A rather obvious but far approximate approach to resolve this difficulty is to use weighted averages of the composition and properties of the coal mixture. In this case, when using the PDF file corresponding to a mixture of two coals in the required mass ratio, the proximate analysis data, ultimate analysis, and heat of combustion of volatiles are set as weighted averages taking into account the ratio of their quantities in the coal mixture. Thus, the mixture of different coals is replaced by one fictitious coal with intermediate characteristics. This approach can be called a “fictitious mixture” modeling.

Another approach is based on the assumption that the secondary mixture fraction can be used to specify the composition of not only liquid or gaseous but

also the second solid fuel (technically, the program allows for such a specification). In this case, a more correct description of the process can be expected. This approach will be further referred to as a “real mixture” modeling.

When calculating the processes in the furnace of a boiler unit, the burnout rate of solid particles is taken into account. This parameter is described in the literature by different models even with the same diffusion-kinetic approach and for the same reaction of oxidation of particle carbon by air oxygen. Accordingly, the criteria characterizing the combustion rate differ as well. Therefore, to use the values of combustion rate constants known from domestic studies, it is necessary to find their relationship with the constants used in CFD modeling programs. Unfortunately, in the known works [15–17] on modeling solid fuel combustion in ANSYS Fluent software, the issue of finding the combustion rate constants is not touched upon. This study aims to fill this gap.

The ANSYS Fluent program uses the Baum—Street kinetic-diffusion model, which defines the combustion rate of a coal particle as in [18]

$$\frac{dm_p}{dt} = -A_p \frac{\rho R T_0 Y_{ox}}{\mu_{O_2}} \frac{1}{\frac{1}{D_0} + \frac{1}{\Re}}, \quad (6)$$

where m_p is the particle mass, A_p [m²] — its surface area, μ_{O_2} [kg/kmol] — molecular mass of oxygen, R [J/ kmol *K] — universal gas constant, T_0 [K] and ρ [kg/m³] are the temperature and density of the gas phase, Y_{ox} — mass fraction of oxygen in the flow, D_0 [s/m] — diffusion rate coefficient

$$D_0 = C_1 \frac{[(T_p + T_0)/2]^{0.75}}{d_p}, \quad (7)$$

T_p and d_p — temperature and size of a particle $\Re$ [s/ m] — kinetic rate coefficient

$$\Re = C_2 e^{-(E/RT_0)}, \quad (8)$$

C_1 , C_2 and E are parameters set for calculation.

The values of the activation energy E and the pre-exponential factor C_2 of the Arrhenius equation characterize a particular brand of coal or other solid fuel.

From the calculations concerning the preheater of a pulverized coal boiler, it follows that the particle temperature usually exceeds the local temperature of the gas phase by the value ΔT , which is several hundred degrees. Taking this into account, let us present expression (2) as follows

$$D_0 = C_1 \frac{(T_0 + \Delta T / 2)^{0.75}}{d_p}.$$

Also, using the expressed in (1) density of the gas phase based on the equation of state of a perfect gas, we have instead of (6):

$$\frac{dm_p}{dt} = -A_p p Y_{ox} \frac{\mu}{\mu_{O_2}} \frac{1}{\frac{1}{D_0} + \frac{1}{\Re}}, \quad (9)$$

where p is the static pressure in the flow and μ is the molecular mass of the gas phase.

By the domestic literature (e.g., [19]), in the kinetic-diffusion regime, the particle burning rate is expressed by a dependence similar to (9) but operating with other parameters:

$$\frac{dm_p}{dt} = -\frac{\beta A_p C_0}{\frac{1}{\alpha_K} + \frac{1}{\alpha_d}}, \quad (10)$$

where β is the stoichiometric coefficient (changing from 0.375 when only CO_2 is formed in the reaction to 0.75 when reacting to CO), C_0 [kg/m^3] is the volume concentration of oxygen, and α_d [m/s] is the diffusion transfer coefficient

$$\alpha_d = \frac{Nu_d D}{d_p}.$$

Here

$$D = 0.18 * 10^{-4} * \left(\frac{T_0}{273} \right)^n, \quad [\text{m}^2/\text{s}]$$

is the oxygen diffusion (to the particle surface) coefficient. The parameter $n = 1.5 \dots 2$ (1.75 is usually accepted), the criterion Nu_d is close to 2, and the kinetic coefficient α_K [m/s] can be found as

$$\alpha_K = k_0 e^{-E/RT_0},$$

where k_0 is a pre-exponential factor.

Expressing in (5) C_0 through the mass fraction of oxygen as $C_0 = \rho Y_{ox}$, where the density ρ is found from the equation of state of a perfect gas, instead of (10), we have:

$$\frac{dm_p}{dt} = -\frac{\beta A_p p \mu Y_{ox}}{RT_0 \left(\frac{1}{\alpha_K} + \frac{1}{\alpha_d} \right)}. \quad (11)$$

The combustion kinetics of domestic fuels is characterized by a pair of k_0 and E values. To find the parameters C_1 and C_2 of the model [18], it is reasonable to

adopt the approach in which the kinetic and diffusion components of both models are mutually equated, and the values of E are considered the same.

Thus, we find:

$$C_1 = \frac{0.18 \cdot 10^{-4} \mu \beta Nu_d}{R \cdot 273^{1.75}} \left(\frac{1}{1 + \frac{\Delta T}{2T_0}} \right)^{0.75}, \quad (12)$$

$$C_2 = \frac{\mu \beta}{RT_0} k_0. \quad (13)$$

The dimensions of these parameters are: C_1 [s/K^{0.75}], C_2 [s/m], which coincides with the dimensions found directly from expressions (7) and (8).

To estimate the influence of various factors on the degree of difference in the burning rates of coal coke according to models [18] and [19], calculations were performed according to relations (9) and (11) using (12) and (13) when varying the initial parameters: $T_0 = 750 \dots 2500$ K, $d_p = 10 \dots 300$ μ m, $\beta = 0.375$ and 0.75 , $Y_{ox} = 0.05$ and 0.01 , $E = 140$ MJ/kmol, $k_0 = 6.3 \cdot 10^4$ m/s, and $E = 80$ MJ/kmol, $k_0 = 4 \cdot 10^3$ m/s. It was assumed that $\Delta T/T_0 = 0.1$ or 0.0 . It follows from the comparison of particle burning rates by the considered models (Fig. 5.5) that without taking into account the difference in temperature of the particles and gas phase, the models give the same results, whereas with taking into account the difference T_p from T_0 , the burning rate by the ANSYS Fluent model decreases for the accepted value of $\Delta T/T_0 = 0.1$ the scatter relative to the linear approximating dependence is small. As follows from the expressions (7) and (6), if the difference between T_p and T_0 is neglected, a decrease in the burning rate dm_p/dt is caused by a decrease in the calculated coefficient of the diffusion rate D_0 .

When using expressions (12) and (13) to calculate C_1 and C_2 by the values of the kinetic constants of the model [16], the difficulty arises that (12) and (13), along with the parameters that can be considered constant in the computational domain, include variables, namely the temperatures of the gas phase T_0 and particles T_p (or the temperature difference ΔT). The preservation of these parameters

in the transformation process is due to the incomplete identity of temperature dependences of combustion rates in the models [18] and [19]. To overcome this difficulty, we introduce a constant temperature, which can be called a 'determining' temperature, to be used instead of T_0 in the calculation.

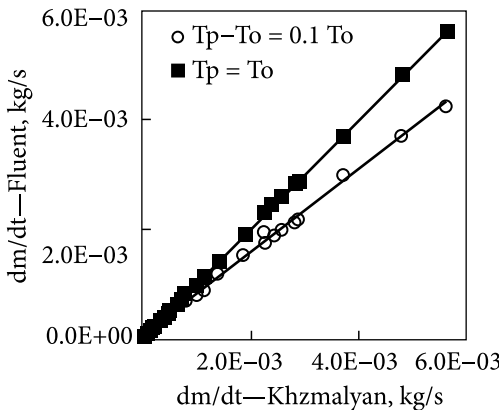


Fig. 5.5. Comparison of coal particle combustion rates by models [18] and [19] at particle temperature exceeding the gas phase temperature by 10% and at their equality.

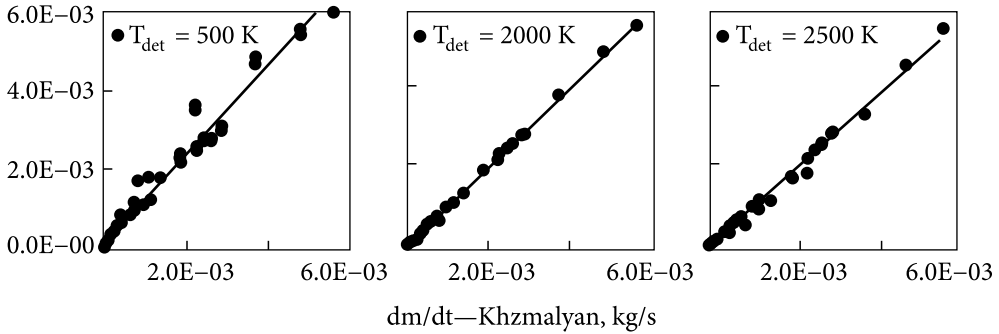


Fig. 5.6. Correlation of particle combustion rates by Khzmalyan and ANSYS Fluent models at three determining temperature and $\Delta T/T_0 = 0.1$

tion of C_1 and C_2 , and we also consider the ratio $\Delta T/T_0$ unchanged. It should be noted that when calculating the combustion rate shown in Figure 5.5 by varying T_0 , the same temperature was used in (7) and (8) to calculate C_1 and C_2 . This is possible in manual calculations but unacceptable in computer-aided ones, since the latter must be set as numerical constants.

The correlation of the combustion rates by the models [18] and [19] at several values of T_{det} is shown in Figure 5.6. As seen, satisfactory agreement takes place at T_{det} close to 2000 K. The variation of the mean square value of the ratio of the

combustion rates for the considered models $K = \left(\frac{(dm_p/dt) - \text{Fluent}}{dm_p/dt - \text{Khzmalyan}} \right)_{avr.}$

depending on the used determining temperature is shown in Figure 5.7.

As follows from (12) and (13), the increase in T_{det} compared to T_0 causes an increase in the parameter C_1 and a decrease in C_2 , which corresponds, as follows from (7) and (8), to an increase in D_0 and decrease in $\mathfrak{R}$. This means a shift of the particle combustion regime to the diffusion region.

Since the value of $\Delta T/T_0 = 0.1$ was used effectively at will, it is of interest the influence of the adopted deviation of T_p from T_0 on the difference in the calculation results for the models under consideration. Such a check at $T_{det} = 2000$ K for $\Delta T/T_0 = 0.05$ and 0.15 did not give a noticeable difference from the data shown in Figure 5.7. This suggests that the values of $T_{det} = 2000$ K and $\Delta T/T_0 = 0.1$ can be used as quite universal. Of course, in cases where the calculation conditions differ much from those given above, such an assumption needs additional verification and possible correction.

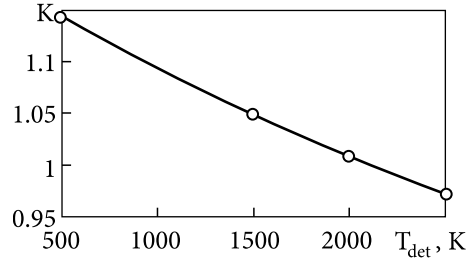


Fig. 5.7. Effect of the adopted value of the determining temperature on the average ratio of combustion rates by the models [18] and [19]

Thus, based on the assumptions made, a methodology was developed to convert the reaction rate constants of carbon of coke residue from coal with oxygen, widely presented in the domestic literature, into the parameters necessary for calculating the combustion of solid fuel particles in the ANSYS Fluent package. The results of calculations showed that the chosen approach gives a small error in the combustion rate ($\sim 1\%$), which can be considered acceptable.

5.4. Co-firing calculations for real boilers as an example

5.4.1. Co-firing of coal and biomass in the TPP-210A boiler

To verify the possibility to change boiler parameters during co-firing biomass and coal, we will simulate the operation of boiler units using fuel mixtures. The relevance of numerical modeling of processes in the furnace of pulverized coal boilers stems from the need for preliminary pre-experimental determination of the qualitative and quantitative impact of certain design and technological changes on the efficiency of the furnace and the environmental characteristics of the boiler unit. For this purpose, the processes in the two-chamber furnace of the TPP-210A boiler, designed to operate on anthracite, were calculated in the ANSYS Fluent software.

Model adequacy verification. *Initial data.* The initial data for the calculation are based on the data sheet of the TPP-210A boiler at the Trypilska TPP and the standard calculation method [20]. The geometry of the computational domain — the furnace of a two-chamber boiler with wet bottom ash removal (one shell) — is shown in Figure 5.8.

Gambit software was used to build the geometry of the computational domain and to divide this domain into cells of a mesh. The computational domain is bounded by the walls and surfaces of the fuel component inlets and gaseous product outlets and consists of 5 zones. Zone 1 (pre-furnace) with pitched walls has six burners that supply the air mixture and secondary air, and zone 5 ends

Table 5.1. Air mixture and secondary air inlet parameters

Parameter	Consumption of air		Consumption of coal		Temperature, K	Swirl, degrees
	to the burner, kg/s	to the furnace, kg/s	to the burner, kg/s	to the furnace, kg/s		
Aeromix	6.642	39.852	2.82	16.917	387	45
Secondary air	21.466	128.68	0	0	663	60
Air inclusions	0	7.022	0	0	303	0
Total	28.088	175.55	2.82	16.917		

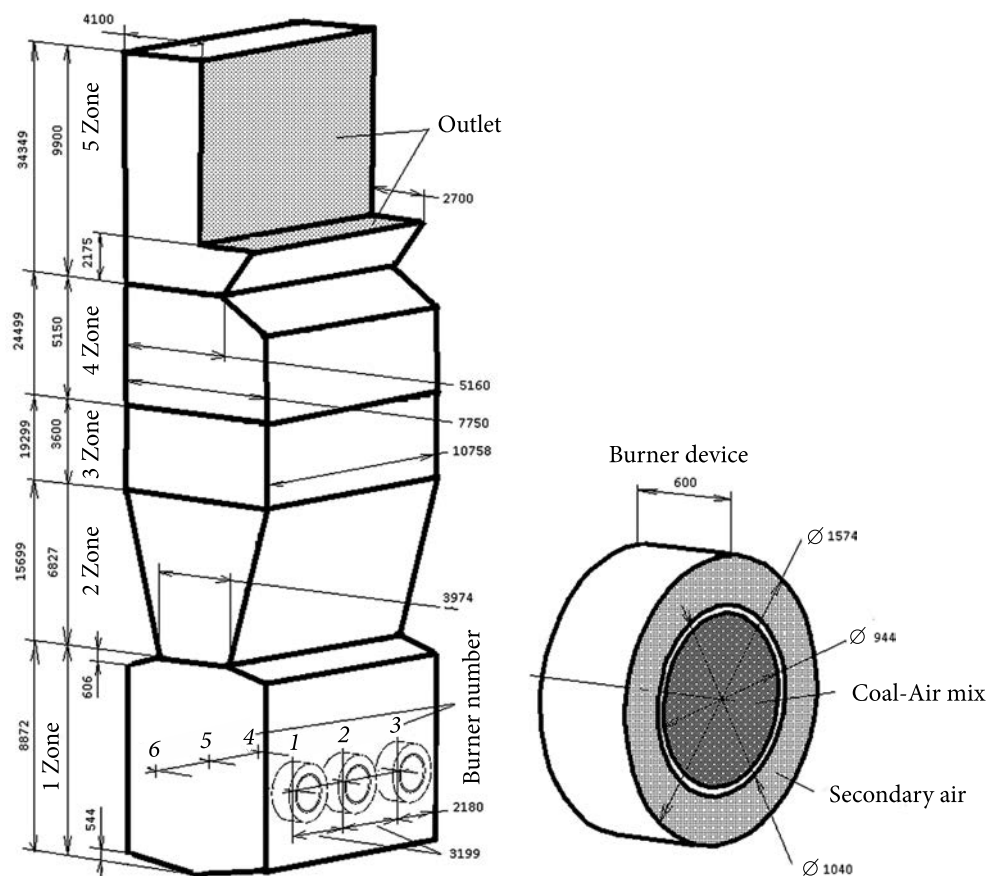


Fig. 5.8. Scheme of the design area — the furnace of the TPP-210A boiler

with an outlet that coincides with the surfaces of the screens, in accordance with the recommendations [20]. The slag outlet holes are also included in the wall surface of zone 1. The parts of the burners included in the model are made short to reduce the number of calculations. To take into account the inflow of external air into the furnace, the geometry of the computational domain should also include the entry points for this air. In zone 1, they are designed as circular slots with a width of 0.1 m around the burners, at the beginning of zones 2 and 3 — as slots with a height of 0.15 m in the front and rear walls, and at the beginning of zone 5 — in the rear wall.

The parameters of air and coal dust specified in Table 5.1 were set as boundary conditions at the inlets, and atmospheric pressure was set at the outlets.

The swirl angles are indicated relative to the axial direction of the burners. The swirl direction is to the left for burners 1 and 4 and to the right for the others. The coal consumption is taken from the boiler data sheet at the nominal load, and the

secondary air temperature is taken from the same data. The total air consumption, by the recommendations of [20], corresponds to the value of the excess air coefficient at the furnace outlet = 1.2, including suction of 0.05. When distributing the costs between the air mixture and secondary air, recommendations [21] for the considered boiler were used. Air inclusions are distributed equally across the zones.

The determination of the boundary conditions on the furnace walls was a particular problem. The zone-by-zone calculation of the furnace using the standard method yielded, in particular, the values of the degrees of wall blackness (0.68 and 0.75, respectively, for the insulated and non-insulated zones), the temperatures of wall surfaces averaged over the zone surfaces (more precisely, the surfaces of fouling on the walls) $T_{w,avr}$, and the density of heat flux $q_{w,avr}$ into the walls. However, the calculation of the furnace using the boundary conditions on the walls in the form of surface temperatures did not give satisfactory results. This is due to the large unevenness of the actual distribution of the heat flux density on the zone wall surfaces and the corresponding unevenness of the wall surface temperature (confirmed by the calculation results). A more adequate boundary condition may be the thermal resistance of the wall surfaces. ANSYS Fluent provides for the opportunity to use such a boundary condition and does not even require model adjustment (i.e., via selecting walls of a certain thickness and creating a computational grid in them). This feature is implemented by determining the wall thickness and thermal conductivity of its material, as well as the temperature on the outside of the wall, which is taken into account by the software with an additional analytical solution of the one-dimensional (normal to the wall) equation.

The temperature of the heat transfer medium (steam or water) $T_{stm,avr}$ flowing in the screens is used as the temperature of the outer wall surface. Thus, the value of the effective thermal resistance of the walls includes the resistance of the boundary layer of the coolant. At the same time, we used the average temperature

Table 5.2. Parameters of thermal boundary conditions on the zone walls

Zone	$T_{stm,avr}$, °C	RT, m ² · K/W	Zone	$T_{stm,avr}$, °C	RT, m ² · K/W
1	342	0.00635	4	429	0.00310
2	383	0.00250	5	441	0.00354
3	406	0.00278			

Table 5.3. Composition and properties of coal

As received coal, %				Elemental composition, DAF, %					Q_p^r , MJ/kg
V ^r	A ^r	W ^r	C(solid)	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf}	
4	19	7.5	69.5	92.52	1.97	0.58	1.57	2.58	24.76

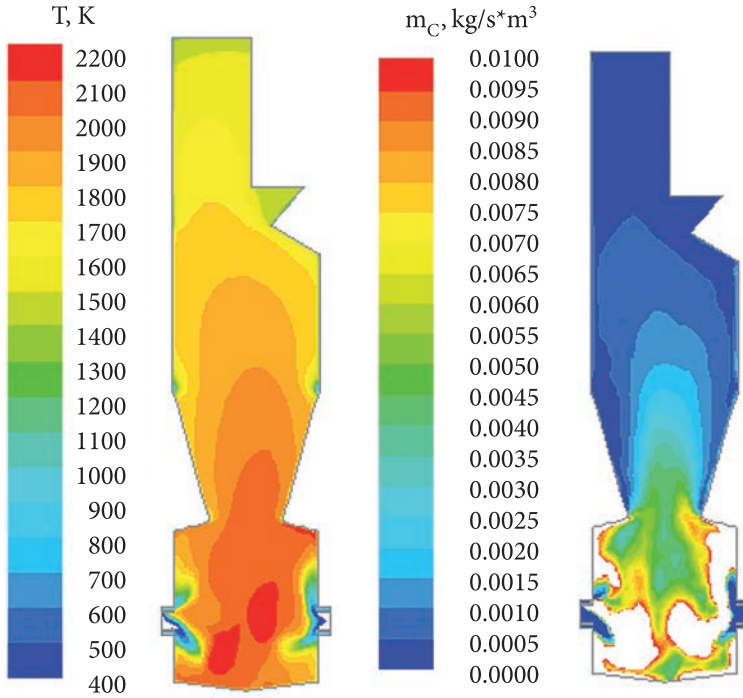


Fig. 5.9. Temperature (left) and coal burning intensity (right) fields in the vertical section of the furnace along the axes of burners 2 and 5. The white field in the right figure is the area where the upper limit of the scale is exceeded.

of the heat carrier in different parts of the walls (screens), which was estimated by the data from the boiler's passport and its hydraulic scheme. The effective thermal resistance $R_T = (T_{W,avr} - T_{stm,avr}) / q_{W,avr}$ for different zone walls ranged from 0.0031 to 0.0064 m² · K/W. The best correspondence to the experimental data was obtained with a 20% reduction in the thermal resistance of the walls for non-insulated zones. The parameters of the boundary conditions are given in Table 5.2.

The process of combustion of coal particles in the ANSYS Fluent software is modeled taking into account the composition of the working mass of coal, elemental composition, heat of combustion, and the distribution of coal particles by size. In our calculations, based on the data from [21], for the TPP-210A boiler, the values of the polydispersity index in the Rosin-Rammler distribution equal to 1.09 and the residue on the sieves R_9 and R_{200} — to 8 and 0.2%, respectively, were taken. The average particle size d_{avr} (for which $R_{d_{avr}} = 100 \cdot e^{-1}\%$) is 40 μm. The composition of the coal, taken in accordance with [20], is given in Table 5.3.

The software provides the possibility to take into account the difference between the total amount of volatiles in coal, including the high-temperature volatile

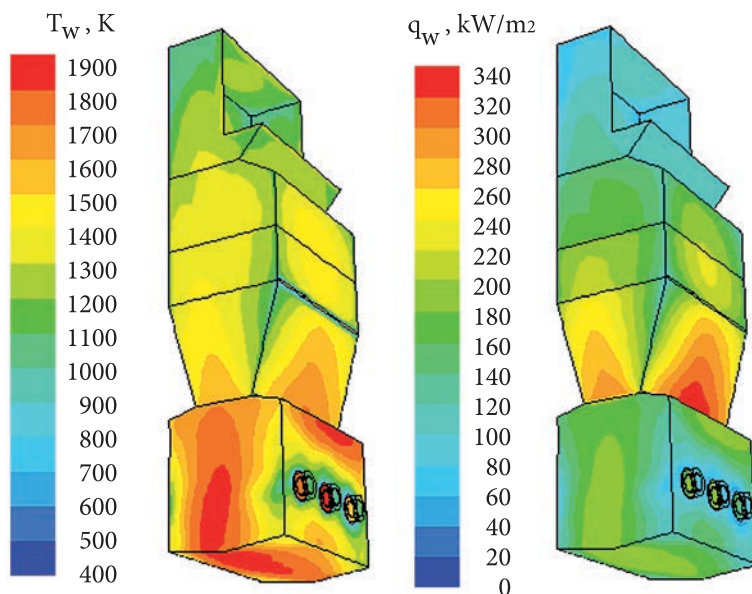


Fig. 5.10. Wall surface temperature (left) and wall heat flux density (right)

yield, and the value determined by standard analysis. The ratio of these volatile amounts equal to 2.4 was assumed in the calculations for coal [22].

Moreover, the turbulence model in the realizable modification, the non-premixed combustion model of particle combustion in the 1-mixture fraction formulation, the discrete phase model of coal particle motion, the P-1 radiation model, the two-competing-rates devolatilization model, and the kinetics/diffusion-limited model of coal combustion were used in the calculation.

Modeling results. The main results of the calculation of processes in the furnace of the TPP-210A boiler in the nominal regime are shown in the following Figures. 5.9—5.10.

The modeling results revealed large irregularities in the distribution of parameters not only along the height of the furnace but also in horizontal sections, as well as along the wall surfaces, even within the same zone.

Comparison of the calculation results with other data. The modeling results were compared with the results of the standard calculation and the data of the experimental study by Shagalova and Schnitzer [21] of the processes in the furnace of the TPP-210A boiler when it operates on anthracite with a 90% load. It should be noted that the experimental results given in [21] at 77 and 65% loads do not differ significantly from the parameters at 90% load. This suggests that changing the load from 90 to 100% will not greatly affect the result either. Therefore, we may ignore the difference in load for the modeling conditions and the experiment under consideration. Evaluating the comparison presented in Figures 5.11—5.13, we can note a satisfactory correspondence.

Fig. 5.11. Comparison of the change in the average temperature of the gas phase along the furnace height by the results of modeling and experimental data from [21]

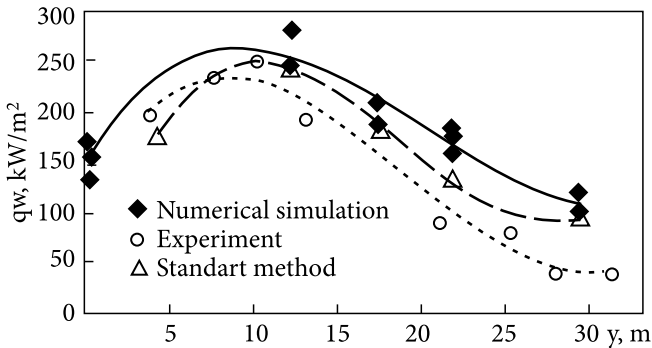
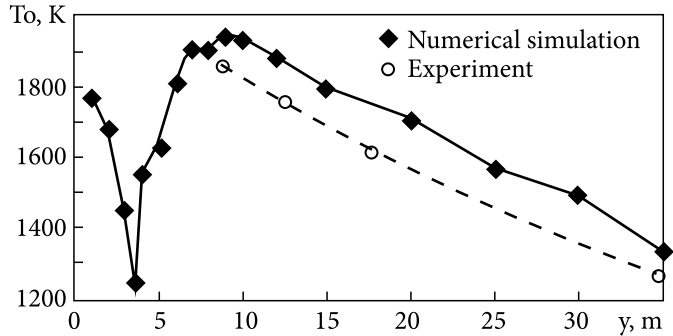
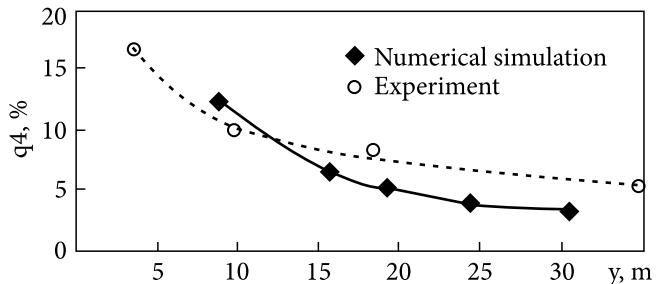


Fig. 5.12. Comparison of the change in the averaged (over the wall surfaces) heat flux density along the furnace height by the results of modeling, experimental data from [21], and calculation by the standard method

Fig. 5.13. Comparison of the change of underburned fuel along the furnace height by the results of modeling and experimental data from [21]



To sum up, we have assessed the results of the modeling of processes in the furnace of the TPP-210A boiler using ANSYS Fluent as satisfactory. Therefore, both the selected models and their settings can be used in replacing part of the main fuel with biomass.

Modeling the combustion of a coal / biomass mixture in the pre-firing chamber. Due to the large volume and duration of calculations of the processes in a full boiler furnace, the main part of variant calculations was performed for the pre-furnace, and only verification calculations were performed for the entire furnace.

The geometry of the calculation area of the pre-furnace concerning the variant of pellets feeding to the pellet splitters installed in the central air flow is shown in Figure 5.14.

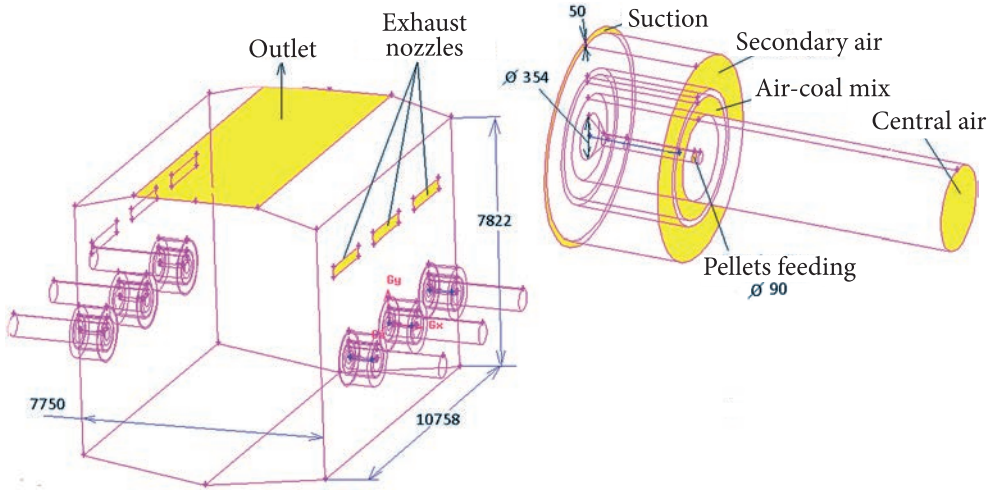


Fig. 5.14. Geometry of the calculation area of the pre-furnace for the variant of pellets feeding to the splitter in the central air flow.

Table 5.4. Characteristics of anthracite and pellets studied

Characteristic	Fuel	
	Anthracite	Pellets
<i>Proximate analysis</i>		
A ^r , %	19	0.365
W ^r , %	7.5	8.7
V ^r , %	4	78.43
Cs, %	69.5	12.51
<i>Ultimate analysis</i>		
C ^r , %	68.00	47.17
H ^r , %	1.45	5.756
O ^r , %	1.90	37.86
N ^r , %	0.58	0.127
S ^r , %	1.57	0.027
<i>Calorific value</i>		
Q _p ^r , MJ/kg	24.23	17.63

The calculations took into account the cold air suction, which was modeled by making radial slots 50 mm wide around the burners and supplying the exhaust air with fine coal dust through the exhaust nozzles. The pulverized coal consumption was set for the nominal load, the oxidant excess factor $\alpha_F = 1.25$, and including suction, $\alpha_{suc} = 0.05$. The coal particle size was assumed to correspond to the Rosin-Rammler distribution in the range from 5 to 200 μm with an average particle size of 40 μm . The effective particle size of pellets was assumed to be 200 μm , which corresponds to particles with a maximum size of 400–500 μm . In the calculations, such a small size can be justified by the assumption that due to the high percentage of volatiles (and moisture), large particles of the injected pellets can break into smaller ones when heated in the flow. The technical and elemental analyses data, as well as the lower calorific values of the anthracite and pine pellets used in the calculations, are shown in Table 5.4.

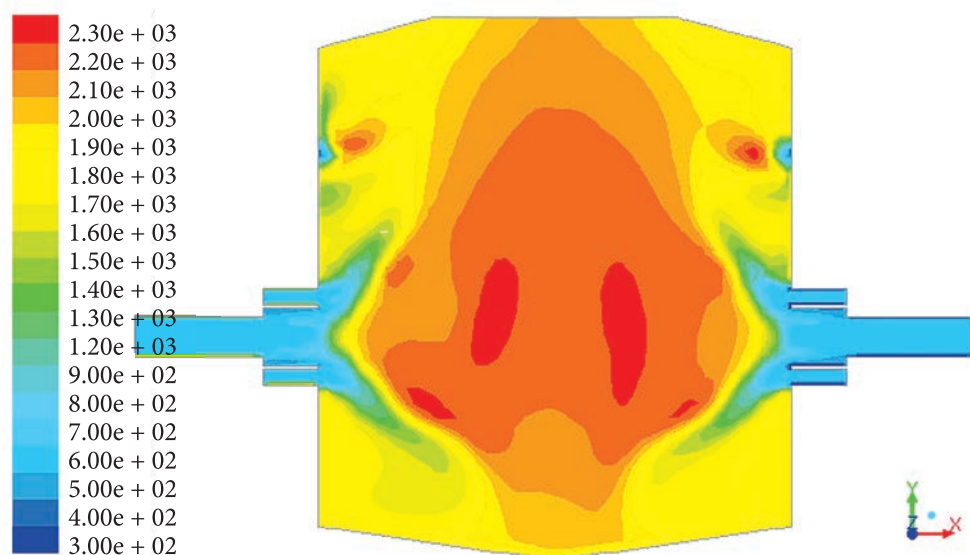


Fig. 5.15. Temperature field in the vertical plane along the axes of the central burners (hereinafter referred to as the $z = 0$ plane) when pellets are not fed

In the modes with pellets, their consumption was selected based on the conservation of thermal energy of the fuel relative to the mode without pellets, with the ratio of heat contributed by coal and pellets as 9:1. The oxidizer consumption was determined using the above oxidizer excess coefficient, taking into account the difference in the amount of oxidizer required for the combustion of coal and pellets.

It is worthwhile to dwell on the setting of the flow swirl in the burners since its value significantly affects the calculation results. The direction of the swirl was set for burners 1 and 4 (see Fig. 5.8) to the left (i.e., counterclockwise, looking along the flow) and for the rest of them — to the right. The swirl rate was set by the angle between the velocity vector at the respective burner inlets and the axial direction. This angle was 20 degrees for the central air and 25 and 50 degrees for the air mixture and secondary air, respectively.

In the calculations, several options for pellet feeding locations were tested, namely: along the axis of the central air of the burners on the splitter (together with the air mixture into the exhaust nozzles below the burners).

Let's first focus on the results of calculations and for the initial variant, that is, without pellet feeding. Below are some illustrations of the calculation results (Figs. 5.15 and 5.16).

The results obtained show that the maximum gas phase temperatures (up to 2000 °C) are in the central area of the preheater in the cross-section of the burners along the height. The most intensive combustion of fuel takes place near the sites

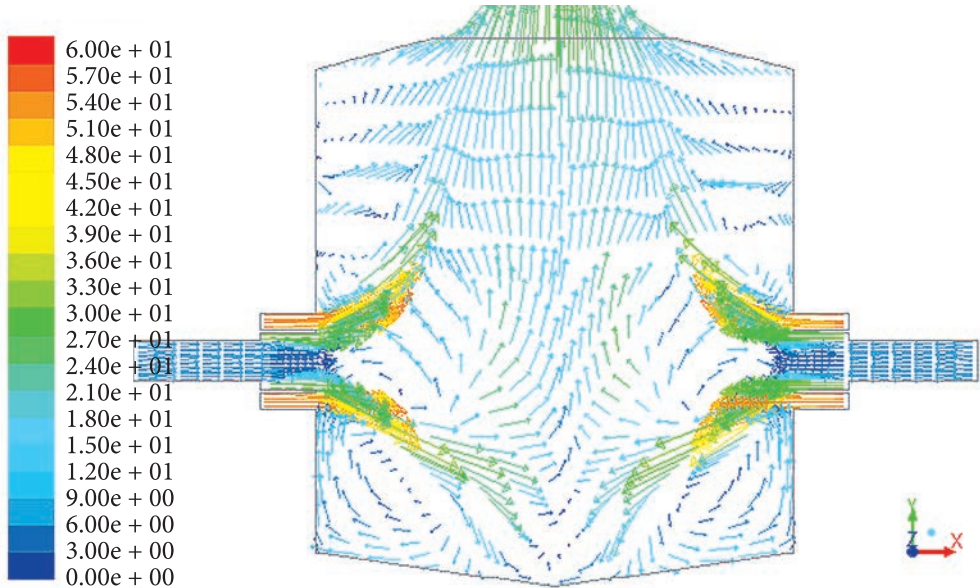


Fig. 5.16. The field of velocity vectors in the $z = 0$ plane without pellet feeding

Table 5.5. Comparison of calculation results at different pellet injection sites

Pellet injection site	Output parameters		Burnout of coke residue from	
	T, °C	O ₂ concentration, %	coal, %	pellets, %
No biomass	1647	4.4	92.6	—
Into the air mixture	1678	4.6	93.5	94.2
Into the splitters	1673	4.7	93.6	96.6
Under the burners	1676	4.6	94.3	88.5
Into the discharge nozzles	1673	4.5	95.4	65.2

of its injection into the pre-furnace and leads to intensive oxidant consumption. The velocity vectors demonstrate the suction of combustion products to the root of the torches from the burners. A brief comparative summary of the calculation results for different pellet injection sites is given in Table 5.5.

These data show that the increase in the average mass flow temperature at the outlet of the computational area by 35—40 °C when pellets are fed practically does not depend on the site of their introduction into the preheater. The outlet oxygen concentration also changes slightly. The most significant effect of the pellet inlet is on the completeness of anthracite burnout in the preheater.

In all cases, it increases compared to the mode without pellets but most significantly, by 2.8%, when pellets are fed into the discharge nozzles. However, this

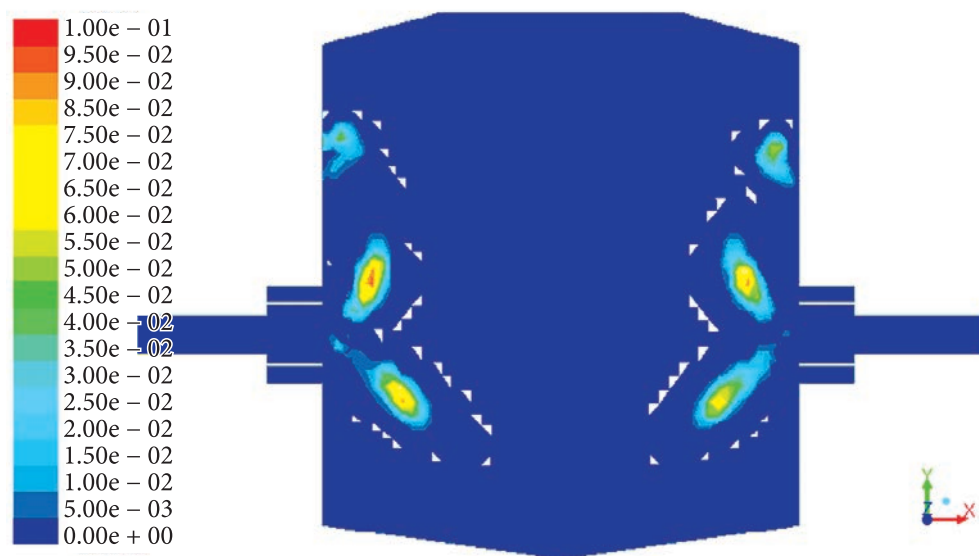


Fig. 5.17. Anthracite coke combustion intensity field (kg/m^3) in the $z = 0$ plane when pellets are fed into the air mixture

variant also has the lowest pellet coke burnout. However, this probably should not be decisive when choosing a pellet injection point, since, firstly, as seen from Table 5.5, there is little coke in the pellets (and their volatiles in all variants burn completely), and secondly, in this case, we are talking about burnout in the pre-furnace, whereas in the furnace, the pellets, as obtained in the calculations of the entire furnace, burn out.

In general, the calculations performed, in our opinion, do not demonstrate an evident advantage of any particular site of pellet injection.

Below are illustrated the main results of calculations of anthracite combustion together with pellets relative to the option of their introduction with an aerosol mixture (Figs. 5.17 and 5.18).

From the above results, it follows that pellet feeding does not significantly affect the temperature and combustion intensity fields of anthracite in the pre-heater. As for the combustion of pellets, this process takes place in almost the entire pre-furnace, although the volumetric intensity of pellet combustion is much lower than that of anthracite, mainly due to the low amount of coke in the pellets. Despite the relatively low consumption of pellets, the intensity of their volatile yield is higher than that of anthracite. This explains the intensified ignition and burnout of anthracite when pellets are fed.

Combustion of coal/biomass blends in the entire furnace volume. The calculations of the parameters in the furnace were performed for the variants without and with the injection of biomass into the air mixture. The corresponding temperature fields shown in Figure 5.19 do not differ significantly. The distributions

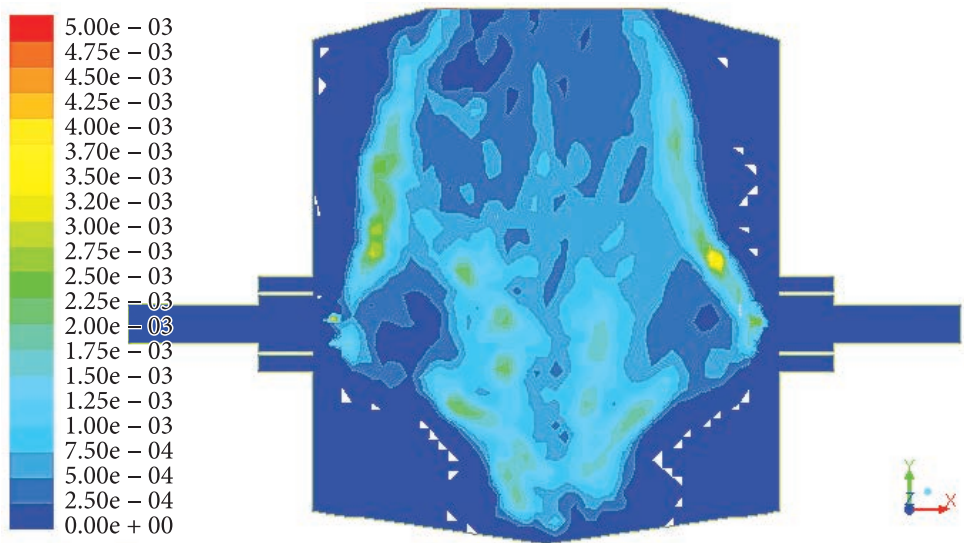


Fig. 5.18. The field of coke pellet combustion intensity in the plane $z = 0$ when pellets are fed into the air mixture

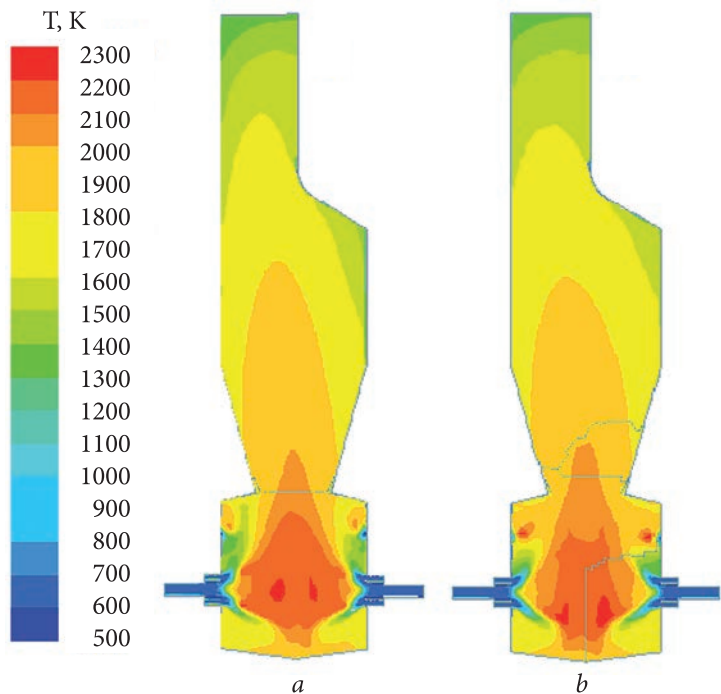


Fig. 5.19. Temperature fields in the $z = 0$ plane for the variants of calculation of the furnace without biomass (a) and with biomass injection into the air mixture (b)

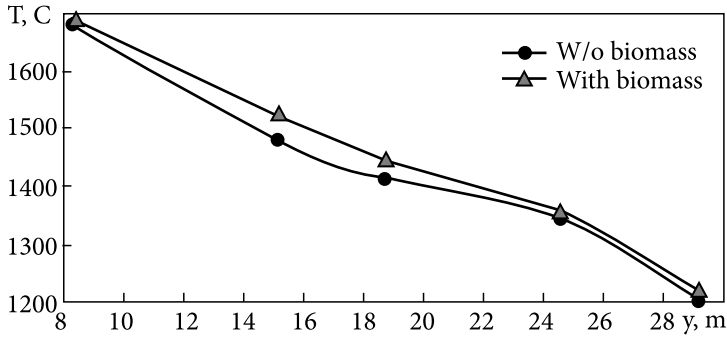


Fig. 5.20. Change in the averaged cross-sectional gas phase temperature along the furnace height

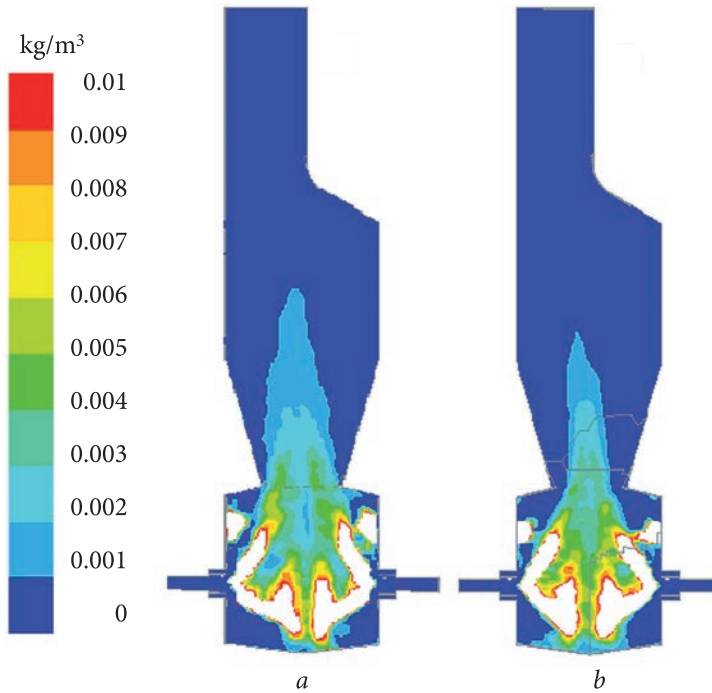


Fig. 5.21. Burnout intensities of coke residue in the $z = 0$ plane for the variants of calculation of the furnace without biomass (a) and with biomass injection into the air mixture (b)

of flow temperatures along the furnace height (Fig. 5.20) are also quite close, although they increase slightly when the biomass is fed. On the contrary, the intensity of coke residue burnout with biomass feeding (Fig. 5.21) slightly decreases, but this is due to the decrease in the amount of coke residue in the fuel (from 12.61 to 11.35 kg/s) because of the replacement of 10% of coal with an equivalent

amount of biomass, which has a much lower share in the coke residue. Indeed, if we relate the amount of burnt coke residue to its initial amount, the share of burnt coke residue for the considered options is 98.69 and 98.76%, respectively, that is, practically unchanged.

5.4.2. Co-firing of bituminous coal and peat in the TPP-210A boiler

The following options are possible for peat and coal co-firing:

- Direct combustion, where peat and coal are fed simultaneously into the steam generator furnace. In this case, it is possible to mix peat with coal directly at the fuel storage facility, grind them together, and feed simultaneously into combined burners. Modifications of this technology are available, where peat is preliminarily prepared in separate grinding devices and fed into combined burners or special burners.

- Combustion of peat gasification products obtained in a separate gasifier together with coal in a boiler.

Further, based on the ANSYS Fluent program [18], the effect of adding peat or its gasification products to the main fuel (bituminous coal) on the processes in the furnace of the TPP-210A boiler was considered. For comparison, the parameters in the furnace without peat addition were calculated as a baseline.

Baseline mode — with bituminous coal. Modeling the flow, heat transfer, and combustion processes in the boiler's fuel bed was carried out using the ANSYS Fluent software. For this, a computation mesh was created based on the geometry of computation area shown in Figure 5.8.

The characteristics of the main fuels are given in Table 5.6.

The calculations were performed for the thermal power mode equivalent to 100% load when the boiler is fired with coal, which corresponds to a bituminous coal consumption of 17.02 kg/s. The size distribution of coal particles is assumed to be in the range of 5 to 200 μm with an average size of 40 μm according to the Rosin-Rommler distribution and a distribution parameter of 1.15. The oxidant excess factor at the furnace outlet is 1.2, including 0.05 for suction [21]. Air suction is assumed to be evenly distributed through annular slots around the periphery of the burners, along the perimeter of the bottom baffle section, in the front and rear walls at the entrance to zone 4, and in the rear wall at the entrance to zone 5.

Impact of adding peat to bituminous coal. Calculations were also performed for the co-firing of Volyn's peat with bituminous coal in the furnace with

Table 5.6. Fuel characteristics

Fuel	W^a , %	W_t^r , %	A^d , %	S_t^d , %	V^{daf} , %	t_A , °C	t_B , °C	t_C , °C	Q_i^r , MJ/kg
Bituminous coal	1.99	1.8	21.9	2.3	38.9	1260	1360	1390	24.092
Peat	18.3	18.9	24.5	0.87	69.8	1360	>1400	—	12.573

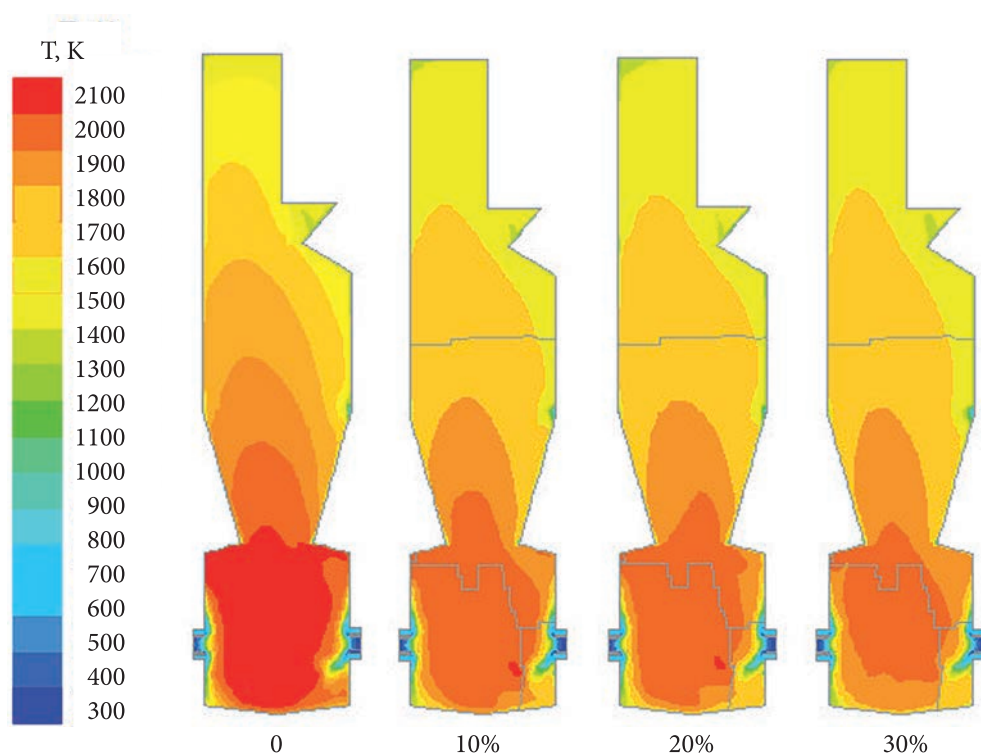


Fig. 5.22. Flow temperature distributions in the vertical cross-section of the furnace for different peat shares in the fuel

a variation of the share of peat heat contribution and the constant total thermal energy of the fuel. The peat particle size was taken according to the Rosin-Ramler distribution in the range from 20 to 300 μm with an average size of 72 μm and a distribution parameter of 1.15. Peat particles are fed into the burners together with coal at the inlets for the air mixture.

The share of peat (by heat) in the binary blends varied in the calculations from 0 to 30%. The obtained temperature fields in the vertical section of the furnace are shown in Figure 5.22. The tendency to decrease the temperature in the pre-furnace with an increase in the share of peat is obviously due to the lower calorific value of peat compared to coal. This indicates that with an increase in the share of peat, the steam output of the boiler will decrease, which is not acceptable. Therefore, according to the temperature fields, the maximum share of peat in direct combustion should be limited to $10 \pm 5\%$.

The analysis of fuel combustion shows that the solid carbon of bituminous coal is reduced (Fig. 5.23), while peat carbon, as well as that of volatile coal and peat, burns out completely.

It should be noted that the results obtained relate to the accepted peat particle size according to the Rosin-Ramler distribution with an average size of 72 μm .

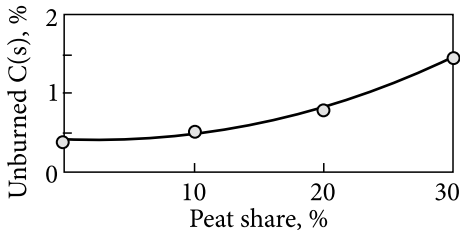


Fig. 5.23. Unburned solid carbon in the furnace versus the peat share in the fuel

The authors of the publications, for example, usually report larger particle sizes for biomass as a fuel close to peat by its characteristics [23], due to the complexity of its grinding. Therefore, it is of interest to assess the impact of increasing the size of peat particles on their burning.

For this purpose, in the calculations, with other parameters unchanged in the regime with a 30% share of peat, the size of peat particles was varied, which had been assumed to be monodispersed. The effect of this factor on the burnout of solid carbon of peat and binary mixture is shown in Figure 5.24.

As shown, when the size of peat particles is larger than 1 mm, their burnout, as well as the burnout of all fuel in the boiler furnace, is significantly reduced. The permissible particle size can be increased by taking into account two factors. Firstly, a reduction in the peat share in the fuel, which will reduce the impact of peat underburning on the overall fuel underburning, and, secondly, the difference in the shape of biomass particles from the sphericity assumed in the calculations: they are elongated, which is more favorable for burning than the spherical shape. That is, the maximum peat particle size can be considered 1 mm, and the average particle size after milling should be 0.3—0.5 mm.

With a peat share of up to 30%, the surface temperature of the preheater walls (Fig. 5.25) remains significantly higher than the temperature of normal wet bottom ash removal for bituminous coal at 1490 °C, so no deterioration in ash removal conditions is expected, although it should be kept in mind that peat ash is more refractory than coal ash.

Co-firing of coal with peat gasification products. Preliminary calculations of peat gasification were carried out. The composition of the gas obtained as a result of peat gasification is shown in Table 5.7.

The gas output from the gasifier is 1.269 kg of gas per 1 kg of peat input, and the calorific value of peat gas was calculated as the sum of the calorific values of combustible components, taking into account their shares.

The site of generator gas injection into the furnace was varied in the calculations, and the optimal one was chosen on the front and rear walls of the pre-furnace, as shown in Figure 5.26.

Table 5.7. Composition of generator gas at the gas burner inlet

Mass fraction							Calorific value, Q^r_p , MJ/kg
C	N ₂	H ₂ O	CO ₂	CH ₄	H ₂	H ₂ S	
0.4051	0.2286	0.2266	0.0674	0.0604	0.0072	0.0047	8.059

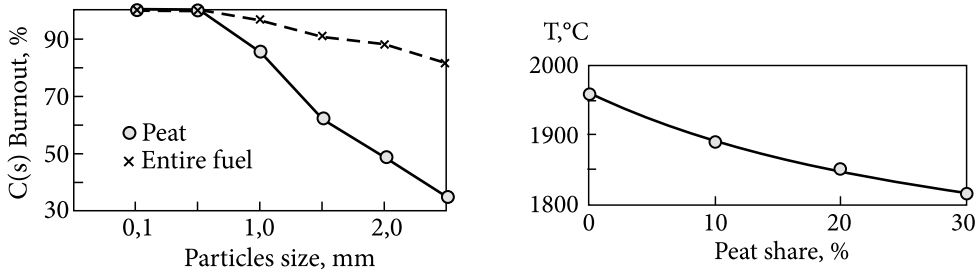


Fig. 5.24. Influence of the size of monodisperse peat particles on the burning of their solid carbon and the solid carbon of the entire fuel when the peat share is 30%

Fig. 5.25. Surface temperature of the central part of the bed versus the peat share in the fuel

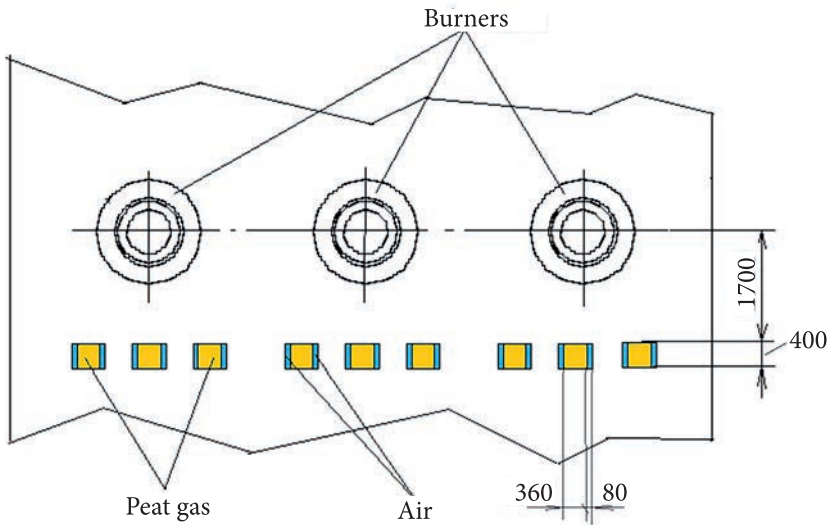


Fig. 5.26. View of the front wall of the pre-furnace with nozzles for peat gas and oxidizer injection in the variant with their location on the front and rear walls below the main burners

The temperature fields in the furnace are shown in Figure 5.27. As seen, the furnace temperature changes insignificantly with the increase in the gas share in the binary mixture. Accordingly, the advantage of using preliminary gasification is that the share of peat by heat value can be increased up to 30% without significantly reducing the steam output of the boiler unit. With the share of peat gas increasing to up to 30%, the amount of unburned coal is small.

Figure 5.28 shows the surface temperatures of the pre-furnace walls with 30% peat gas share by heat. As seen, the slag flowing down the front and rear walls is prevented by the low surface temperature in the area of the main burners. Therefore, the process of wet bottom ash removal is possible only along the side walls of the

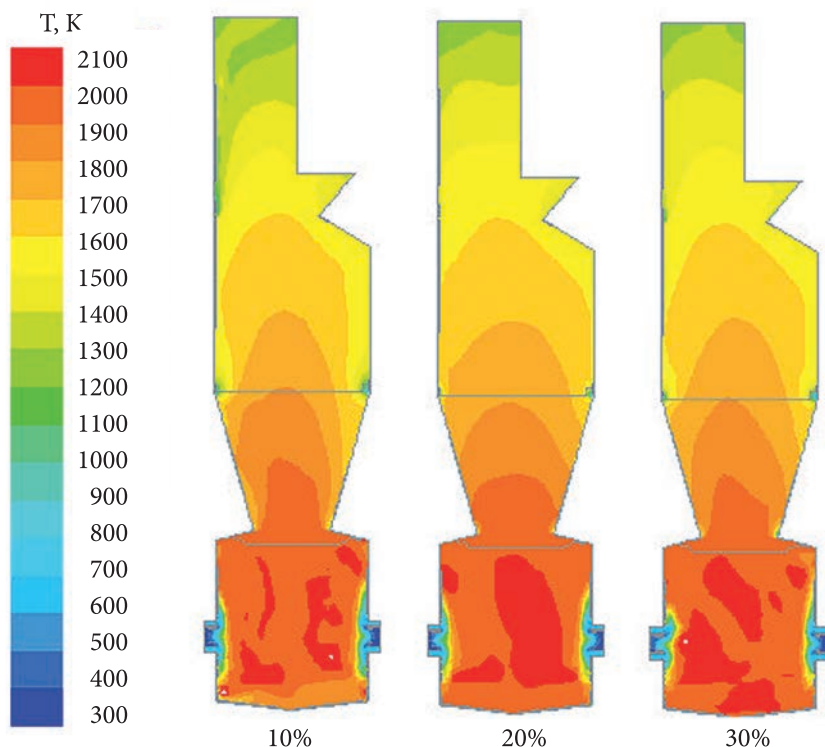


Fig. 5.27. Temperature fields in the vertical cross-section of the furnace at different shares of peat gas in the fuel

pre-furnace. Their minimum temperature is close to that of normal wet bottom ash removal for the coal used (1763 K). Hence, to ensure reliable wet ash removal, it is advisable to slightly increase the surface temperature of the pre-furnace walls. For this purpose, it is recommended to increase the thickness of the furnace lining by 10–20% or to use a material with a lower thermal conductivity coefficient.

To avoid the disadvantages associated with the supply of wet peat gas (obtained by mixing gasification products with the waste drying agent) to the boiler furnace, an approach without such mixing but with condensation of pyrolysis moisture in the treatment chamber is possible. The results of modeling this approach when 20% dry peat gas is fed into the boiler furnace are shown in Figure 5.29. The modeling results for wet gas are compared with the changes in the side wall surface temperature and gas phase temperature along the vertical axis of the preheater.

Figure 5.29, *b* shows that the nature of the temperature distribution of combustion products during the combustion of a binary mixture containing dry generator gas (curve 1) differs significantly from the temperature profile formed during the co-combustion of wet synthetic peat gas and bituminous coal (curve 2). Whereas dependence 2 reflects a monotonous distribution of flue gas tempera-

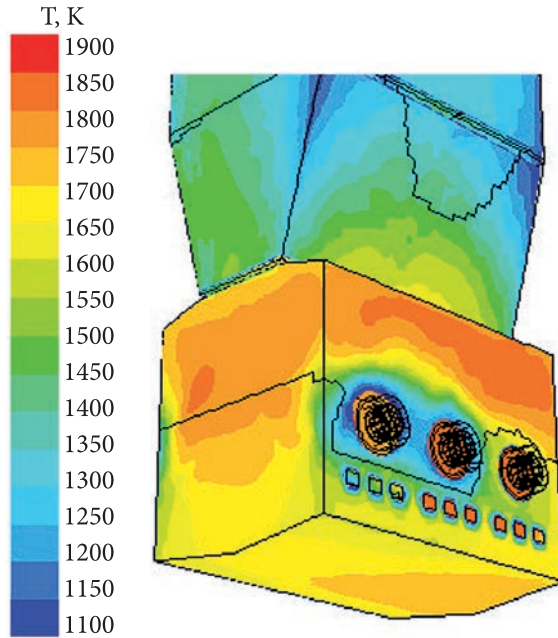


Fig. 5.28. Pre-furnace surface temperatures at 30% peat gas share

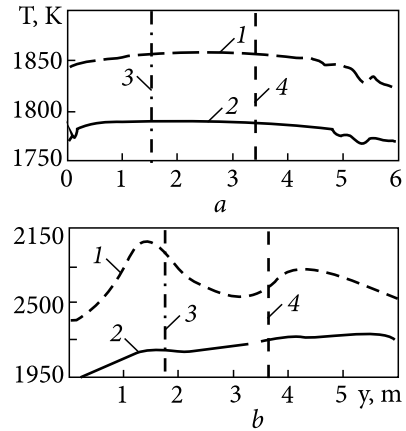


Fig. 5.29. Variation of the side wall temperature along the line 4.17 m from the back wall (*a*) and the gas phase temperature along the flow axis 3.78 m from the side wall and 5.445 m from the back wall (*b*) for dry (1) and wet (2) peat gas operation conditions; 3 — main burners level; 4 — peat gas nozzels level

tures with a weakly detected maximum, curve 1 contains two well-defined temperature peaks at $T_{\max 1}(y = 1.5 \text{ m}) = 2130 \text{ K}$ and $T_{\max 2}(y = 4.2 \text{ m}) = 2100 \text{ K}$. The former ($h = 1.5 \text{ m}$) is related to the influence of dry generator gas combustion, and the latter ($h = 4.2 \text{ m}$) is mainly due to the combustion of bituminous coal. In the lower part of the pre-furnace at the point $y = 1.5 \text{ m}$, the maximum temperature of combustion products (curve 1) $T_{\max 1}$ is 150 K higher than the flue gas temperature (curve 2). Such an increase in the temperature of combustion products in the range $0 < y < 1.8 \text{ m}$ is due to an increase in its calorific value and oxygen concentration (due to the absence of the volume fraction of H_2O), which increases the rate of homogeneous reactions. The increase in flue gas temperature leads to an increase in the intensity of radiation to the side wall of the preheater. Therefore, the temperature level of liquid slag in this zone when burning a binary mixture with dry generator gas is higher than when burning a binary mixture with wet synthetic peat gas (Fig. 29, *a*), which significantly increases the stability of liquid slag flow.

The comparison shows that the supply of dry peat gas to the furnace is preferable because, in addition to the advantages mentioned above, it allows for an increase in the reliability of liquid slag removal.

Brief conclusions:

- The ANSYS Fluent simulation of the processes in the furnace of the TPP-210A boiler when it operates on bituminous coal with the addition of peat

allowed us to assess the effect of the amount of Volyn's peat in the fuel on the fuel combustion process.

- The addition of peat to the main fuel of solid particles and gas obtained as a result of preliminary gasification of Volyn's peat was considered. The gas was introduced into the furnace through a system of holes in the front and rear walls of the pre-furnace below the main burners.

- In all the considered modes with the share of additional fuel by heat up to 30%, the fuel conversion efficiency was close to 100%. The calculations confirm the possibility of using peat or its gasification products as an additive to the main fuel of a TPP boiler.

- Based on the average temperature level in the boiler furnace, it is possible to recommend the use of a maximum peat share of 10% for direct co-firing of peat with bituminous coal and a maximum peat share of 30% for combustion of bituminous coal with peat gasification products.

5.4.3. Using renewable fuels to reduce nitrogen oxides

The numerical modeling of processes in the furnace of pulverized-coal boilers is relevant for a number of reasons, in particular, because of the need to have a tool for determining in advance the qualitative and quantitative impact of certain design and technological changes on the parameters of furnace efficiency and environmental characteristics of emissions. In particular, this will allow analyzing the impact of burners on the formation of nitrogen oxides in the boiler furnace.

The formation of nitrogen oxides depends significantly on the combustion process of the fuel itself. In the existing boiler furnaces, creating conditions to reduce the formation of nitrogen oxides leads to an increase in coal underburning and instability of the boiler operation in general, and vice versa, better conditions for the combustion of pulverized coal mean better conditions for the formation of nitrogen oxides.

Therefore, there is a need to create technical solutions that could reduce nitrogen oxide emissions without significantly worsening the combustion conditions. At the same time, the implementation of such solutions will depend on the type of fuel that is burned due to different temperature conditions in the fuel and the reactivity of coal.

ANSYS Fluent [24, 25] includes all three known mechanisms of nitrogen oxides formation during fuel combustion yielding the so-called thermal, prompt, and fuel nitrogen oxides.

The NO_x concentration produced in combustion systems is usually low. As a result, the chemical composition of NO_x has little effect on the predicted flow field, temperature, and concentrations of the main combustion products. It follows that the most effective way to use the NO_x model is as a post-processing step to the main combustion calculation. The following sequence of steps is used for the calculation:

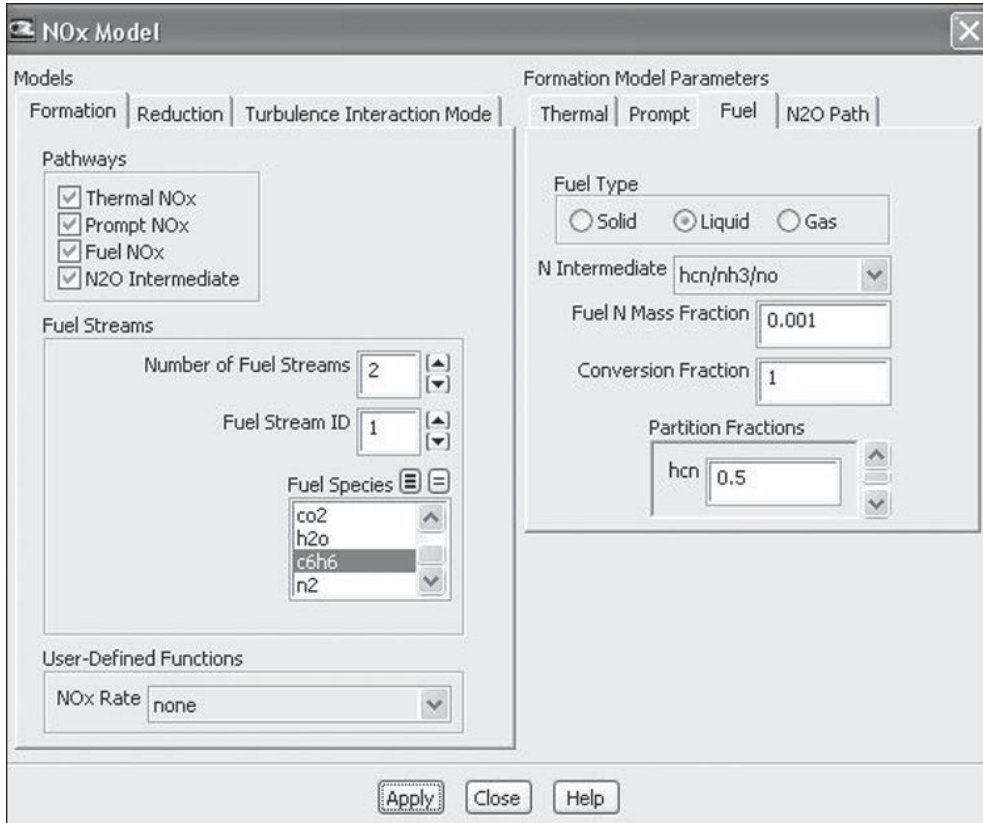


Fig. 5.30. NO_x model dialogue box selects the NO_x models that will be used to calculate NO, HCN, NH₃, and N₂O concentrations

1. The combustion process is calculated using ANSYS Fluent as usual.
2. The required NO_x models (thermal, prompt, fuel, and/or intermediate N₂O) are included.
3. Boundary conditions for NO (and HCN, NH₃, and N₂O if required) at the flow inlets are defined.

Enabling NO_x models. To enable NO_x models and set the appropriate parameters, the NO_x Model dialogue box (for example, Fig. 5.30) is used.

The average NO formation rates will be calculated directly from the average concentrations and temperatures in the flow field.

Defining fuel flows. ANSYS Fluent allows one to define multiple fuel flows when modeling the formation of prompt or fuel NO_x. For multiple solid-coal fuel flows, they must have the same values for the coal-related parameters in the Fuel tab, i.e., the mass fraction of N in the carbon and the surface area.

Setting the thermal NO_x parameters. The program uses three methods for calculating thermal NO_x. The method to be used is specified using the Thermal tab in the Formation Model Parameters section of the NO_x Model dialogue box.

Setting the Prompt NO_x parameters. Prompt NO_x formation is predicted using the following equation. For each fuel stream specified in the Fuel Stream ID text box on the Formation tab, the parameters in the Prompt tab in the Formation Model Parameters section of the NO_x Model dialogue box are set as follows:

- The Fuel Carbon Number parameter specifies the number of carbon atoms per fuel molecule.
- The equivalence factor is set as

$$\text{Equivalence Ratio} = \frac{\text{actual fuel - to - air ratio}}{\text{stoichiometric fuel - to - air ratio}}.$$

For any carbon number, the limits of the equivalence factor are as follows: if it is greater than 1.57, the equivalence factor is limited to 1.57. If it is less than or equal to 4, an additional limit applies. If the equivalence factor is between 0.365 and 0.685, an average value of 0.525 is taken.

Calculation of nitrogen oxides formation. Fuel. The main design fuel for the TPP-210A boilers at TPP is Donetsk anthracite coal; the boiler unit is also designed to burn natural gas from the Shebelinsk field. However, it should be noted that today, most TP-100 boilers in Ukraine operate either on lean or bituminous coals. In this regard, the burners are designed as PCB burners, and the dust system is equipped with safety explosion valves.

The main technical characteristics of the solid fuels used in the calculations are given in Table 5.8. Lean and bituminous coals were chosen as the main fuels for the boiler due to the current problems with the supply of the design fuel to the power plants and the gradual conversion of some TPP-210A boilers to bituminous coal.

The furnace of the TPP-210A boiler was calculated in a three-dimensional formulation, the scheme of which is shown in Figure 5.8. The suction ports around the burners at the beginning of zones 3 and 5 are taken into account. The solid phase flow rate is selected based on the thermal capacity of 408 MW, and the air flow rate corresponds to the oxidant excess ratio for the entire furnace of 1.25. In the design variants, the share of biomass (by heat) varied from 0 to 30%.

As we have noted in [53], due to contradictory information in the literature on the values of the conversion factors of volatile nitrogen and coke to nitrogen

Table 5.8. Fuel characteristics

Fuel	Ultimate analysis, DAF					Proximate analysis			
	C, %	H, %	O, %	N, %	S, %	A ^r , %	W ^r , %	V ^r , %	Q _p ^r , MJ/ kg
Lean coal	88.06	4.35	2.40	1.26	3.93	24.8	1.0	11.1	25.2
Bituminous coal	80.00	5.51	8.40	1.45	4.64	24.8	1.0	29.7	23.7
Pine pellets	51.87	6.33	41.63	0.14	0.03	0.4	1.0	85.0	19.3

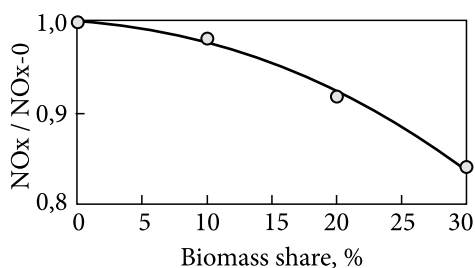


Fig. 5.31. Effect of biomass addition to bituminous coal on the concentration of nitrogen oxides at the furnace outlet of the TPP-210A boiler

oxides [49—51], on which the results of calculations using the ANSYS Fluent program for the concentration of nitrogen oxides at the furnace outlet depend, we assumed a conversion factor of 0.2. Therefore, it is desirable to operate with rather relative than absolute NOx concentrations, as they are less sensitive to the coefficients used.

The calculations have shown that when operating on bituminous coal, the concentration of nitrogen oxides at the furnace outlet of the TPP-210A boiler gradually decreases with increasing biomass content, and at 30% of biomass, it is almost 17% of the initial value (Fig. 5.31). This, however, is accompanied by increased unburned fuel (Fig. 5.32), although this increase can be considered insignificant. At the same time, the amount of heat transferred to the furnace walls slightly decreases (Fig. 5.33) with an increase in the share of biomass (by 7% at a biomass share of 10% and by 23% at a biomass share of 30%), which indicates a decrease in the overall power of the boiler unit. This should be taken into account when developing systems for co-firing of coal and biomass.

It should also be noted that the temperature and combustion intensity fields (Fig. 5.34) for boiler operation without biomass and with 10% biomass feed have the following differences: the temperature in the bottom of the combustion chamber decreases with the addition of biomass due to its lower calorific value; the temperature at the height of the furnace is also slightly lower, which leads to a slight decrease in the degree of fuel burnout but at the same time reduces the formation of thermal nitrogen oxides. The combustion zones show the presence of a short flame, especially when biomass is added.

Note that the share of coke residue that is not burned out with added biomass is consistently lower than that in the case of burning bituminous coal alone (Fig. 5.35).

When operating on lean coal, the effect of biomass feeding on the concentration of nitrogen oxides at the furnace outlet of the TPP-210A boiler (Fig. 5.36) is slightly less. With an increase in the share of biomass, the concentration of nitrogen oxides decreases by 14 at 30% biomass compared to the baseline. This is also accompanied by a tendency to increase unburned fuel (Fig. 5.37), up to 2.6% in total. In this variant of the boiler operation, it is more significant compared to the operation on bituminous coal. However, when feeding 5 and 10% of biomass, the unburned fuel in the furnace of the TPP-210A boiler drops from 2.0 to 1.6%. This is due to improved ignition conditions for less reactive fuels. The change in

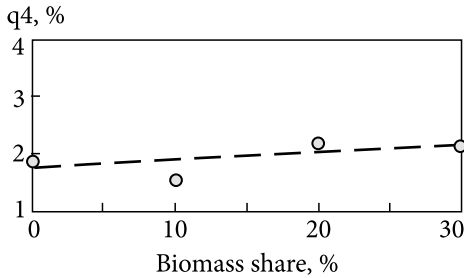


Fig. 5.32. Effect of biomass addition to bituminous coal on the unburned fuel amount in the TPP-210A boiler furnace

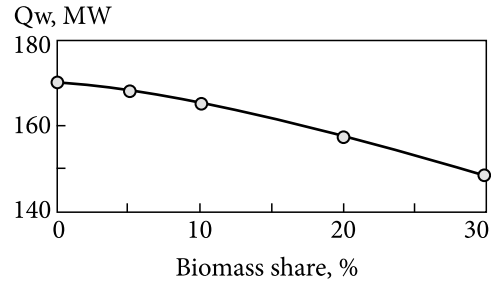


Fig. 5.33. Effect of biomass addition to bituminous coal on the amount of heat transferred to the TPP-210A boiler furnace walls

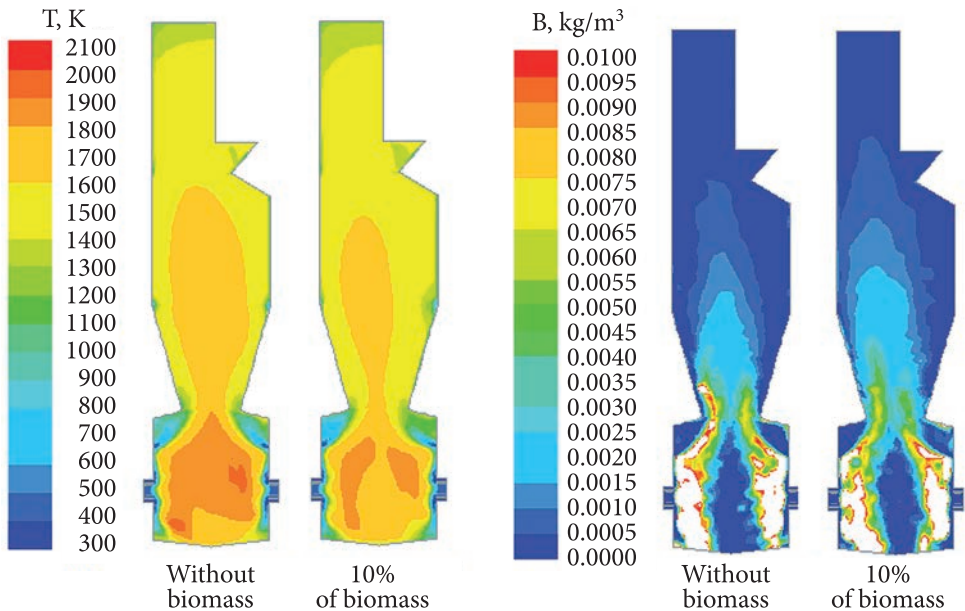


Fig. 5.34. Fields of temperature and intensity of combustion in the initial mode and after biomass addition to the fuel in the bituminous coal-fired mode of TPP-210A boiler

heat fluxes during the operation of lean coal with biomass is almost the same as with bituminous (Fig. 5.38).

The temperature fields (Fig. 5.39) for the operation of a lean coal boiler without biomass and with 30% biomass have the following differences: the temperature in the bottom zone is significantly reduced with the addition of biomass, which is caused by its lower calorific value; the temperature along the

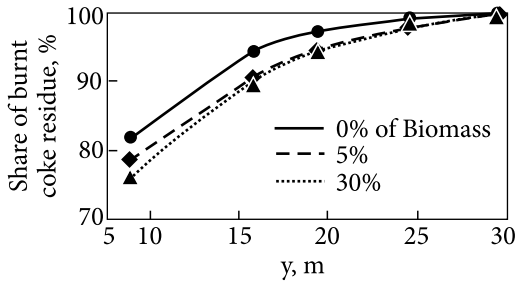


Fig. 5.35. Effect of the biomass addition to the main fuel on the distribution of coke burning intensity along the height the TPP-210A boiler furnace operating on bituminous coal

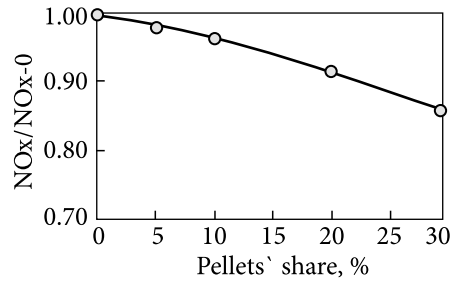


Fig. 5.36. Effect of biomass addition to lean coal on the concentration of nitrogen oxides at the furnace outlet of the TPP-210A boiler

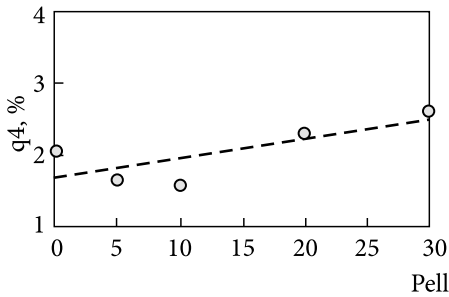


Fig. 5.37. Effect of biomass addition to lean coal on the unburned fuel amount in the TPP-210A boiler furnace

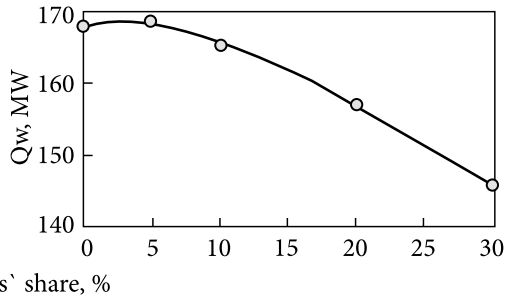


Fig. 5.38. Effect of biomass addition to lean coal on the amount of heat transferred to the TPP-210A boiler furnace walls

height of the furnace is also slightly lower, which leads to a slight decrease in the degree of fuel burnout (Fig. 5.40) but simultaneously reduces the formation of thermal nitrogen oxides; the temperature of the combustion products at the furnace outlet is also lower, which ensures the safety of the boiler unit. This should be taken into account due to the lower melting point of ash in most types of biomass, which, at high temperatures in front of screen superheaters, can lead to their slagging.

When the boiler operates on lean coal, the share of coke residue that is not burned out along the height of the furnace at low biomass shares (5—10%) first decreases and then begins to increase (Fig. 5.40). This indicates that the unburned biomass improves the ignition of lean coal compared to bituminous coal due to its lower reactivity.

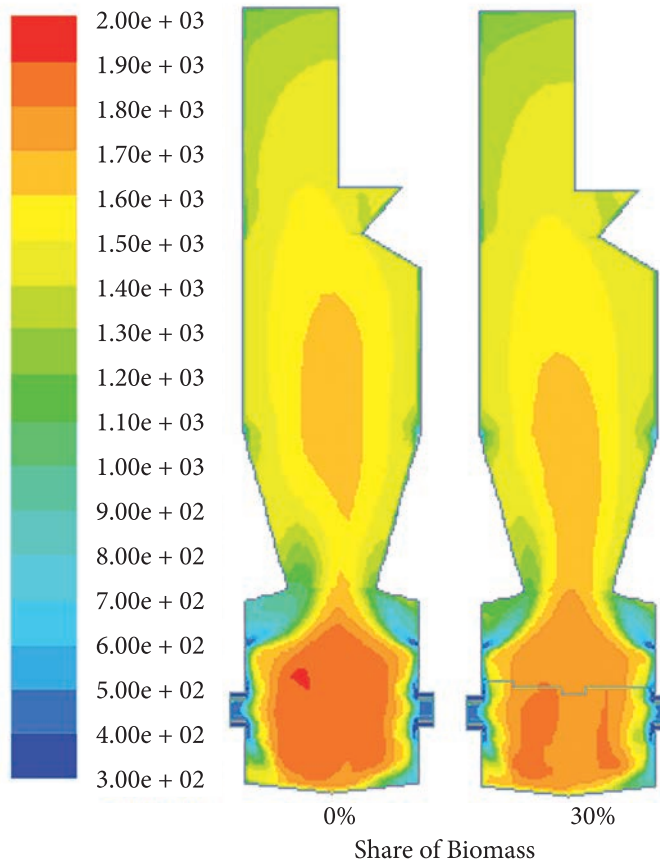


Fig. 5.39. Temperature fields in the baseline mode and after biomass addition to the fuel when the TPP-210A boiler operates on lean coal

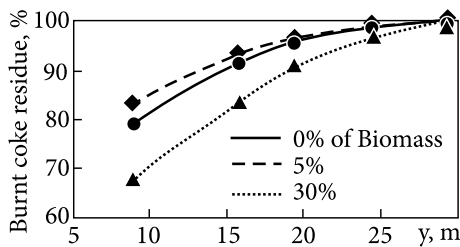


Fig. 5.40. Effect of the biomass addition to the main fuel on the distribution of coke burning intensity along the height of the TPP-210A boiler furnace operating on lean coal

To sum up, the presented studies have shown the possibility of reducing the formation of nitrogen oxides when coal and solid renewable energy sources (such as biomass) are co-combusted. This effect is partly due to the lower nitrogen content in the organic matter of biomass compared to coal and partly due to the lower temperature in the furnace.

In the course of the study, we modeled the operation of boilers of the main types of 300 MW TPP units in the Ukrainian power system. The main and typical representatives of boilers of such units are the TPP-210A boiler units.

Taking into account the current fuel balance of Ukraine, the main modeling was performed for gas coal with an ash content of 24.8% and a calorific value of 23.7 MJ/kg and pine pellets with an ash content of 0.4% and a calorific value of 19.3 MJ/kg. Co-firing of biomass and lean coal with an ash content of 24.7% and a calorific value of 25.2 MJ/kg was also modeled for the TPP-210A boiler.

The modeling was carried out with a biomass heat share of 0, 10, 20, and 30% for the nominal boiler operation. For the calculations, three-dimensional models of boiler units with a mesh of up to 1 million cells were created using the Gambit software.

5.5. Conclusions

The relevance of numerical modeling of processes in the furnaces of pulverized coal boilers derives from the need for pre-experimental determination of the qualitative and quantitative effect of certain design and technological changes on the efficiency of the furnace and the environmental characteristics of the boiler unit.

Modeling is a convenient but sophisticated tool for testing different fuel combustion options or replacing one fuel with another.

The basics of using ANSYS Fluent to calculate the co-firing of two solid fuels were shown.

Calculations of the co-firing showed that:

1) Increase in the average mass flow temperature at the outlet of the computational area by 35—40 °C when pellets are fed practically does not depend on the site of their introduction into the preheater.

2) Based on the average temperature level in the boiler furnace, it is possible to recommend the use of a maximum peat heat share of 10% for direct co-firing of peat with bituminous coal and 30% for combustion of bituminous coal with peat gasification products.

3) For the TPP-210A boiler, when co-firing gas coal and biomass, an increase in the share of biomass from 0 to 30% leads to an increase in the total unburned fuel from 1.9 to 2.2%, while the concentration of nitrogen oxides decreases by 17%.

4) For the TPP-210A boiler, when co-firing lean coal and biomass, an increase in the share of biomass from 0 to 30% leads to an increase in the total unburned fuel from 2.0 to 2.7%, while the concentration of nitrogen oxides decreases by 15%.

5) The results show that co-firing coal and biomass can be used to reduce nitrogen oxide emissions with a slight increase in unburned fuel at a biomass share of up to 15%.

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REDUCING THE EFFECTS OF SLAGGING AND CORROSION DURING CO-FIRING COALS WITH DIFFERENT DEGREES OF METAMORPHISM AND SALINITY

Fossil fuels as a component of global fuel resources will play a significant role in the energy sector of many countries for many years to come. However, suitable coal basins with powerful and accessible seams are almost exhausted. That is why many countries are forced to use their off-balance energy resources, such as carbon-containing waste, peat, low-quality low-calorie coal, carbon mixtures of various origins, etc.

One of these energy resources may be the so-called salty coal (SC), which occupies a significant place among the reserve energy sources of many countries (China, the USA, Poland, Kazakhstan, Ukraine, Australia, etc.) [1]. Such coal is characterized by a high content of alkaline and alkaline earth metals, but at the same time retains attractive thermal characteristics [1]. Domestic SC deposits are located in Western and Northern Donbas, with explored reserves of about 10–12 billion tons (according to forecasts, they can be as high as 25 billion tons). There are five main SC deposits in Ukraine: Novomoskovske, Petrykivske (Western Donbas) and Bohdanivske, Starobilske, and Petrivske (Northern Donbas) (Fig. 6.1) [1, 2, 3]. Their characteristics are listed in Table 6.1.

The involvement of SC in the country's fuel balance as a blended fuel for electricity and heat production will reduce the possible deficit of bituminous coal, which is currently used by TPPs [4]. The use of domestic coal reserves at TPPs and CHPPs is also justified for reasons of energy security.

The main obstacles to the use of salty coals are undesirable technological and environmental consequences of their processing due to the presence of aggressive mineral compounds in coal [5]. Such impurities are all fusible sodium and chlorine compounds that play a major role in the formation of slag on the heating surfaces during coal combustion. Chlorine, along with sulfur, is the main corrosive agent and one that actively pollutes the environment [2, 3].

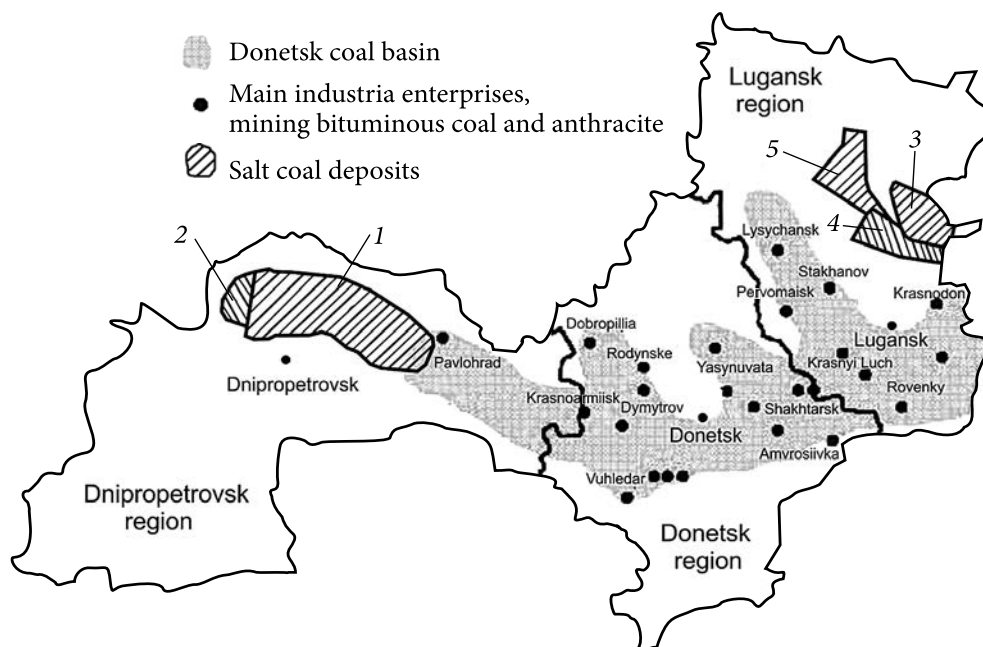


Fig. 6.1. Map of the location of forecasted mines of salty coal deposits in Ukraine: 1 — Novomoskovske deposit; 2 — Petrykivske deposit; 3 — Bohdanivske deposit; 4 — Petrivske deposit; 5 — Starobilske deposit

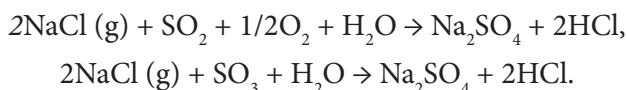
Table 6.1. Characteristics of salty coal deposits in Ukraine

Deposit	Brand	LHV Q_{daf}^r , MJ/kg	Ash A^r , %	Moisture W^r , %	V_{daf}^r , %	Na_2O in ash, %	Cl, %	S, %
Novomoskovske	B	30.1—31.5	10.0—15.0	7—12	44.0—47.0	1.9—10.9	0.6—0.9	2.1—4.2
Petryakivske	L	20.9	16.2	45	41.0—43.0	1.6—8.9	0.3—0.6	0.2—1.8
Bohdanivske	B	29.4—31.7	12.6—14.6	7—11	41.2—42.6	1.2—8.4	0.3—0.6	1.6—2.1
Petrivske	B	29.7—31.5	5.6—17.0	6—11	40.5—44.5	1.3—8.7	0.3—0.6	1.7—2.5
Starobilske	B	29.3—31.0	7.0—16.1	9—18	41.1—47.4	1.3—8.7	0.3—0.6	1.6—2.2

The Starobilske coal area (Petrivske and Starobilske deposits) has not been fully explored; B — Bituminous coal, L — Lignite coal.

All inorganic components of coal can produce ash deposits on the working surfaces of boiler units, but their behavior depends on the operating temperature in the furnace, surface temperature, fly ash melting point, gas flow rate, fuel particle size, properties, and combustion method. It is known that one of the most fusible components in the composition of salty coal is halite (sodium chloride ($NaCl$) — 39.34% Na, 60.66% Cl, $t_{melt} = 801$ °C). Halite is highly soluble in water

(35.85 g of NaCl dissolves in 100 g of water at 20 °C). Being in the vapor state, sodium chloride condenses on the heating surfaces and on fly ash particles, which increases their stickiness, creating conditions for the formation of the primary slag layer. Further adhesion of ash components leads to the formation of a thicker and stronger primary slag layer. At furnace temperatures, fuel sodium chloride is almost completely sublimated and reacts with sulfur oxides to form sodium sulfate (strong tenardite) [6]:



As a result, heat transfer deteriorates sharply, and the temperature of the gases at the furnace outlet increases, which reduces the efficiency of the unit and can completely disable it [7, 8].

Other minerals also exhibit a similar tendency to slag and form solid deposits on convective heating surfaces, among which potassium and calcium compounds deserve special attention. They interact with sulfur oxides and water vapor to form gypsum and cement-like deposits [2].

Along with the intensive formation of ash deposits and slagging, salty coal can lead to high-temperature corrosion of heating surfaces, which grows with increasing temperature and higher chlorine and sulfur content in coal [6, 8–10]. The basic mechanisms of corrosion under the influence of chlorine-containing compounds are well described in [11] by Krause from the Battelle Institute (USA), who showed that hydrogen chloride plays a leading role in high-temperature corrosion during the combustion of salty coal.

Despite all the negative technological and environmental aspects of salty coal, one of the most perspective areas may be its use as a blended fuel. Given the high energy (fuel) characteristics and the presence of a natural catalytic complex in salty coal (high content of salts of alkaline and alkaline earth metals and various trace elements), it can play the role of a catalytic component to increase the total reactivity of the blend.

However, it is known that when combusting blends, the rules of additivity are not always followed, which can lead to either a decrease or an increase in the slagging ability of the fuel. This partly depends on the chemical composition of minerals that are native components of the blend and form new compounds at specific combustion temperatures. Hence, it is important to conduct original research to determine the effect of the mineral composition of the source fuels and blends on their slagging and corrosion properties, as well as on the composition of the mineral phases of the ash formed as a result of combustion, to determine the optimal fuel systems.

6.1. Assessment of slagging and corrosion properties of coal with a high content of low-melting salts

This section addresses the issues related to the use of raw materials with a significant content of low-melting salts, with an emphasis on the mechanisms of slagging and corrosion that occur during their combustion and so-combustion with other fuels. A review of the original studies [5, 12–15] considers the complex processes of slag formation, which impede efficient heat transfer and can lead to accidents.

Paper [15] describes in detail the phenomenon of slag formation, which is defined as the accumulation of molten ash on the walls of fuel plants, gasifiers, or boilers. This phenomenon is negative, as it reduces thermal efficiency and can cause damage to metal surfaces and thermal insulation materials due to the corrosive activity of volatile components [16]. An example of the slagging mechanism is shown in Figure 6.2.

The main results of the study highlight the importance of understanding the slagging mechanisms to optimize the combustion process and prevent the negative consequences associated with corrosion and reduced boiler performance.

In world practice, various factors are used to predict the behavior of coal in a boiler unit during its combustion. Based on the chemical composition of the ash (Table 6.2), they make it possible to calculate the slagging and fouling of furnace surfaces.

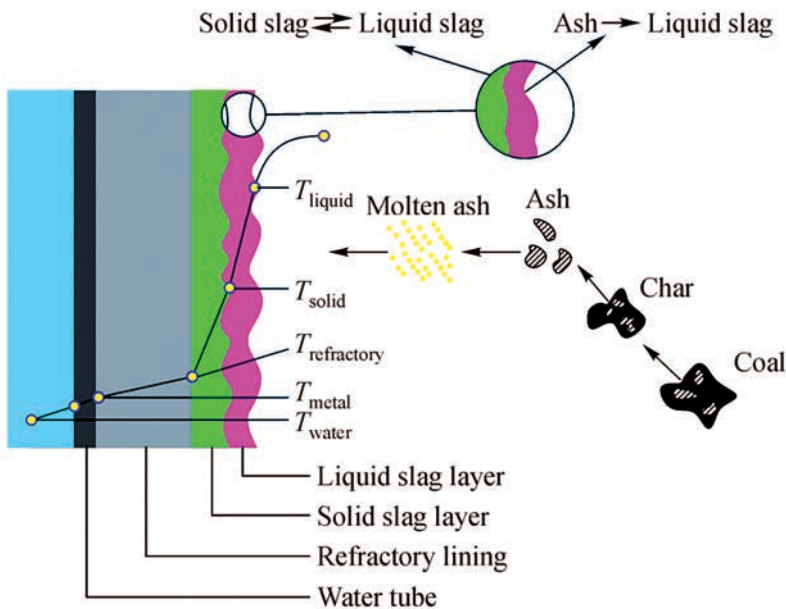


Fig. 6.2. Mechanism of slag and deposit formation inside the gasifier [16]

This method is also widely used by various researchers to determine the predictive characteristics of the processes of fouling (R_f) and slagging (R_s) when using various alternative fuels [17, 18].

$$R_s = (B / A) \cdot S^d, \quad R_f = (B / A) \cdot \text{Na}_2\text{O},$$

where B is the sum of basic oxides, %: $B = \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$; A is the sum of acid oxides, %: $A = \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{TiO}_2$; S^d is the sulfur content in coal, %; Na_2O is the content of sodium oxide in ash, %.

The values of R_s and R_f vary widely and determine the degree of propensity of fuel slagging and fouling (SP and FP, respectively) as follows:

$$\begin{array}{ll} R_s < 0.6 \text{ — low SP} & R_f < 0.2 \text{ — low FP} \\ R_s = 0.6 \div 2.0 \text{ — medium SP} & R_f = 0.2 \div 0.5 \text{ — medium FP} \\ R_s = 2.0 \div 2.6 \text{ — high SP} & R_f = 0.5 \div 1.0 \text{ — high FP} \\ R_s > 2.6 \text{ — severe SP} & R_f > 1.0 \text{ — severe FP} \end{array}$$

The calculated values of R_s and R_f for individual samples and their blends are shown in Table 6.3. As we can see, for the samples of ordinary steam coal (lean and gas), these indicators of slagging and surface fouling are at a low level. At the

Table 6.2. The chemical composition of the ash of the studied fuels

Sample	Na ₂ O	MgO	K ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	SO ₃	P ₂ O ₅
Salty coal 1	6.8	2.8	0.8	15.6	13.2	7.9	37.3	0.3	13.8	1.2
Salty coal 2	3.4	1.7	1.1	10.7	27.5	14.0	21.8	0.3	13.0	0.2
Bituminous coal	0.5	1.6	1.8	2.1	14.9	20.2	51.1	0.8	2.5	1.1
Lean coal	0.7	1.9	1.9	3.8	7.5	26.7	54.0	1.1	1.2	0.5

Table 6.3. Estimated slagging and fouling parameters for the studied samples of original and mixed fuels

Sample	Salty coal 1 (Na ₂ O = 6.8%)		Salty coal 2 (Na ₂ O = 3.4%)	
	R_s	R_f	R_s	R_f
Salty coal (S)	2.59	5.86	0.90	1.41
Bituminous coal (B)	0.67	0.15	0.67	0.15
Lean coal (L)	0.21	0.14	0.21	0.14
50:50 S/B blend	0.89	0.63	0.73	0.45
40:60 S/B blend	0.82	0.47	0.72	0.37
20:80 S/B blend	0.72	0.26	0.69	0.24
50:50 S/L blend	0.46	0.64	0.39	0.45
40:60 S/L blend	0.38	0.47	0.34	0.36
20:80 S/L blend	0.27	0.25	0.27	0.23

same time, for salty coal 2 with an average impurity content, we have medium indicators of slagging tendency and high indicators of fouling, and for salty coal 1 with high impurity content, we have very high indicators for both characteristics. This indicates a high probability of surface fouling when using salty coal.

The calculations for the blends with 50% salty coal content show a significant reduction in slagging and fouling propensity to medium values. In the blends with gas coal, both salty coal samples show medium values of R_s and R_f , while in the case of the blend with lean coal, low R_s values and medium R_f are observed. The significant influence of ordinary steam coal on the R_s and R_f values for the blends is obviously due to the higher ash content of the samples, in particular, due to the high content of acid oxides in the ash (the sum of aluminum and silicon oxides exceeds 70%).

Table 6.2 also shows that the most sensitive indicator to the blending of different types of coal is the R_f index (which decreases from 1.41 to 0.23 for less salty coal and from 5.86 to 0.25 for more salty coal). Less sensitive is the R_s index, which decreases from 0.90 to 0.27 for coal with medium impurities and from 2.59 to 0.27 for coal with high levels of undesirable impurities due to the blending of salty coal with ordinary energy fuels.

The obtained values of R_s and R_f for the blends indicate the prospects of using salty coal as a blended fuel, as well as the possibility of predicting the reduction of slagging and fouling since they take into account the characteristics of both components of the blend.

6.2. Composition of water-soluble compounds of salty coal from Ukraine's deposits

To determine the substances that can affect slagging and corrosion processes, a study was conducted to determine the native mineral composition of water-soluble compounds present in salty coal from different Ukrainian deposits. Table 6.4 shows the characteristics of the salty coal samples studied.

To obtain a concentrate of dry water-soluble minerals that determine the behavior of salty coal in thermochemical processes, the water washing method was used at the optimized parameters such as time, temperature, and the ratio of solid to water phases [19]. The resulting solutions were evaporated to obtain air-dry mixtures, the phase composition of which was analyzed using a DRON-4M diffractometer. Semi-quantitative phase analysis of the diffractograms was performed using the MATCH* software.

Figure 6.3 shows a general view of the diffractogram of substances in the water extract of salty coal from the Novomoskovske deposit 1 (Western Donbas), and Table 6.5 lists the results of the analysis of diffractograms of all samples. The main minerals washed out of salty coal are various compounds that include sodium, calcium, magnesium, iron, chlorine, and sulfur.

Analyzing Table 6.5, it can be noted that the predominant substances in water extracts found in all samples are halite and gypsum. Thus, in the samples

Table 6.4. Characteristics of the samples of salty coals

Sample	Ash A ^d , %	Volatiles V ^{daf} , %	Moisture W, %	Na ₂ O in ash, %	Sulfur S, %
Novomoskovske 1	11.5	44.1	8.1	9.40	2.1
Starobilske 1	7.3	43.7	20.3	6.57	2.8
Starobilske 2	11.8	47.4	14.3	3.39	5.4
Bohdanivske 1	5.3	42.8	12.7	6.92	1.2
Bohdanivske 2	11.2	41.1	9.6	3.60	2.7

Table 6.5. Composition of minerals in water extracts of salty coal samples

Minerals	Values d of XRD reflexes	Content, %
<i>Novomoskovske deposit, sample 1</i>		
Halite (NaCl)	d = 3.26; 2.81; 1.99 A°	66
Gypsum (CaSO ₄ · H ₂ O)	d = 4.30; 3.76; 3.18; 3.05; 2.60 A°	25
Melanterite (FeSO ₄ · 7H ₂ O)	d = 5.14; 4.51; 3.76; 3.20 A°	8
<i>Starobilske deposit, sample 1</i>		
Halite (NaCl)	d = 3.26; 2.81; 1.99 A°	85
Gypsum (CaSO ₄ · H ₂ O)	d = 3.79; 3.07; 2.79 A°	15
<i>Starobilske deposit, sample 2</i>		
Halite (NaCl)	d = 3.27; 2.80; 1.99 A°	9
Magnesium Chloride (MgCl ₂)	d = 5.99; 2.99; 2.80 (78) A°	20
Melanterite (FeSO ₄ · 7H ₂ O)	d = 5.14; 4.54; 3.77; 3.23; 3.20 A°	25
Calcium Sulfate (CaSO ₄)	d = 3.45; 2.88; 2.22; 2.19 A°	11
Gypsum (CaSO ₄ · H ₂ O)	d = 4.26; 3.05; 2.60; 2.22 A°	33
Calcium Chloride (CaCl ₂)	d = 3.05; 3.45 (48); 2.10 A°	2
<i>Bohdanivske deposit, sample 1</i>		
Halite (NaCl)	d = 3.26; 2.81; 1.99 A°	17
Magnesium Chloride (MgCl ₂)	d = 5.98; 2.99; 2.78 A°	35
Calcium carbonate (CaCO ₃)	d = 4.25; 3.04; 2.49; 2.28; 2.09 A°	29
Calcium Sulfate (CaSO ₄)	d = 3.47; 2.88; 2.40; 2.19 A°	19
<i>Bohdanivske deposit, sample 2</i>		
Halite (NaCl)	d = 2.82(81); 1.99 A°	9
Gypsum (CaSO ₄ · H ₂ O)	d = 4.30; 3.81; 3.07; 2.88; 2.68 (67); 2.60; 2.22; 2.08 A°	91

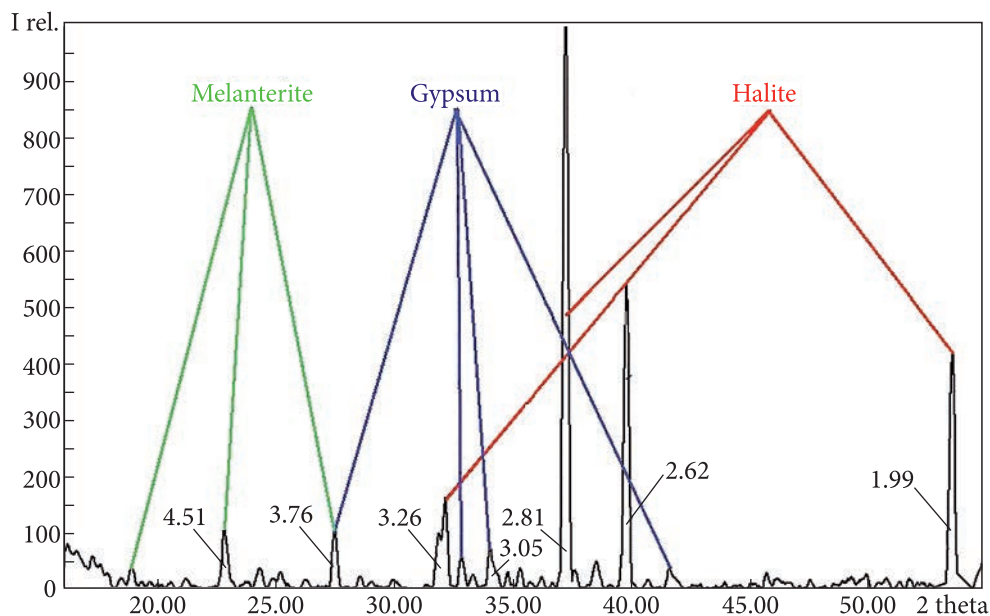


Fig. 6.3. Diffractogram of the water extract of salty coal from the Novomoskovske deposit

of Novomoskovske 1 and Starobilske 1, their contents are 66 and 85% of sodium chloride and 25 and 15% gypsum, respectively. A greater variety of minerals was found in the dry substances of sample Starobilske 2: halite (~8%), magnesium chloride (~20%), melanterite (~25%), gypsum (~33%), calcium sulfate (~11%), and calcium chloride (~2–3%). This is due to the significant content of not only chlorine compounds but also sulfur compounds (5.4%) in the ori-

Table 6.6. Characteristics of minerals found in water extracts of salty coals

Mineral	Formula	MM, a.m.u	Density, g/cm ³	T _{melt} , °C	Solubility in 100 g H ₂ O at 20 °C
Halite	NaCl	58.4	2.17	801	35.85 g
Magnesium chloride	MgCl ₂	95.2	2.32	707	35.3 g
Calcium chloride	CaCl ₂	110.9	2.51	772	74 g, 159 g at 100 °C
Calcium sulfate (Anhydrite)	CaSO ₄	136.1	2.96	1420	0.2036 g, 0.067 g at 100 °C (precipitates)
Semi-dry gypsum	CaSO ₄ × × 0.5H ₂ O	145.1	2.67—2.73	Decomposed at 163 °C	Slightly soluble (as gypsum)
Gypsum	CaSO ₄ × × 2H ₂ O	172.2	2.32	Decomposed at 128 °C	0.206 g at 20 °C 0.212 g at 30 °C

ginal salty coal. Sample Bohdanivske 1 turned out to be even more interesting as such that contains at least four minerals, namely halite (~17%), magnesium chloride (~35%), and calcium sulfate (~19%) along with an unexpected mineral calcium carbonate (~29%).

The study of sulfate content in dry matter revealed unexpected results, especially in the context of the salt solubility data presented in Table 6.6. However, these results confirm the information from the 1990s studies. In particular, it was found that, in addition to halite ($\geq 75\%$), the solids of Novomoskovsk salty coals also contain sulfates such as gypsum and glauberite, which can also affect the technological processes of burning such coal.

These data indicate that despite similar salinity levels ($\geq 2\%$ Na_2O in ash), SC samples differ significantly in their natural mineral composition, even within the same deposit. This is an important factor for their combustion, as low-melting eutectics of minerals require a special approach to the organization of the process. In addition, a detailed study of the native minerals of salty coal can be useful for selecting fuel blends that could be adapted to combustion in existing boiler units.

6.3. Effects of synergism when using coal blends

To ensure the complete ashing of the samples, an experiment was conducted to determine the mass loss under the influence of temperature using the thermogravimetric method. It was determined that the final ashing temperature of salty coal samples was 500—550 °C, at which the sample was almost completely burnt out. Figure 6.4 shows the temperature dependence of the mass change and the rate of mass change of salty coal when heated at a rate of 5 °C/min. As seen, the curves are quite close on the graphs, with a slight difference observed only in the initial phase — the formation and yield of volatile substances, which may reflect the

Table 6.7. Comparison of the masses of ash residues from samples of single coals and their binary blends

Sample	Ratio, %	Mass of ash, g (experiment)	Mass of ash, g (theory)	Deviation, %
Salty coal 1	100	0.180	—	—
Salty coal 2	100	0.290	—	—
Lean coal	100	0.520	—	—
Salty coal 1 / Lean coal	50:50	0.356	0.350	1.686
Salty coal 1 / Lean coal	60:40	0.331	0.316	4.532
Salty coal 1 / Lean coal	40:60	0.424	0.384	9.434
Salty coal 2 / Lean coal	50:50	0.440	0.405	7.955
Salty coal 2 / Lean coal	60:40	0.408	0.382	6.372
Salty coal 2 / Lean coal	40:60	0.456	0.428	6.141

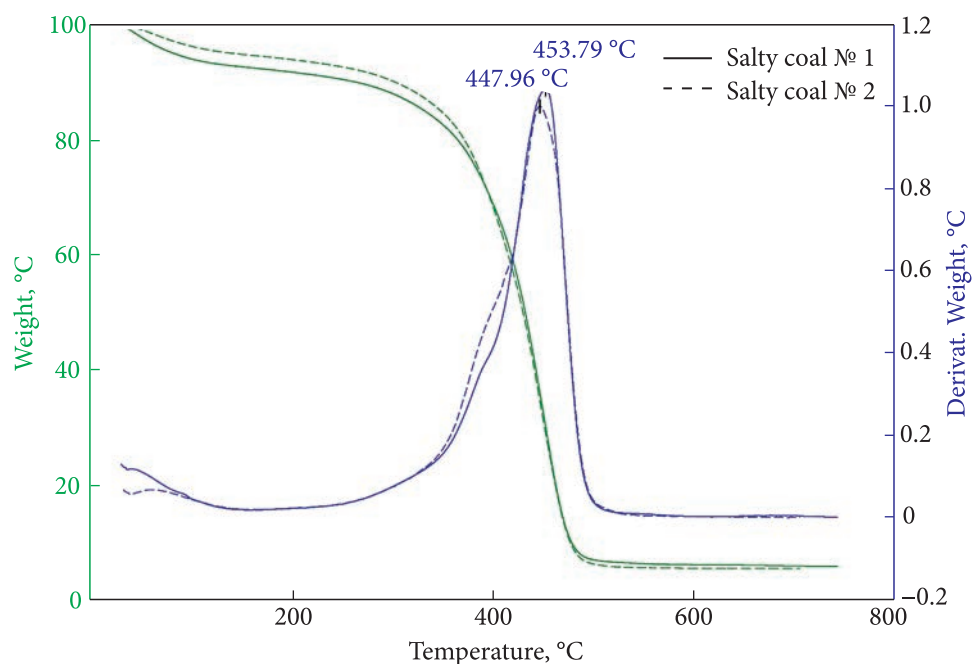


Fig. 6.4. Curves of weight change during the combustion of salty coal

different amounts of minerals present in salty coal that have a catalytic effect. The temperature $T_{\max}$ corresponding to the maximum mass loss rate was determined for both samples. Thus, for coal with a high content of alkali and alkaline earth metals, this temperature is 453.79 °C, while for coal with average content of impurities, the temperature is 447.95 °C.

To determine the mutual influence of the mineral part of two fuels of different salinity during co-firing, the following studies were performed. The coal samples were crushed to a fraction of 0–0.2 mm. After that, the samples of salty and lean coal (separately), as well as their blends weighing 3 g, were subjected to heat treatment in vessels for 3 h (1 h of heating to 850 °C, 2 h of holding



Fig. 6.5. Samples of ash from salty, lean coal, and their blends: 1 — salty coal 1, 2 — lean coal, 3 — salty coal 2, 4–7 — blends

at 850 °C). As seen in Figure 6.5, SC samples, which have a dark brown color, are distinguished, indicating a significant concentration of iron.

Table 6.7 shows the composition of the studied blends of salty and lean coal, which were used to establish the phenomenon of additivity during the combustion of composite fuels.

Experimental data on the ash mass of the blends indicate that the ash residue is formed in an amount that exceeds the theoretically calculated one by the additivity rule. This indicates the presence of a synergistic effect during co-firing, which suggests possible chemical interactions during ashing the blends and the formation of new compounds.

The deviation from additivity varies within 1.5—9.0% for different blends, which emphasizes the importance of studying these processes. The results of weight analysis of ash blends also provide additional opportunities of studying mineral phases and understanding their properties.

6.4. Formation of new refractory compounds during combustion of coal blends. Determination of ash melting characteristics

The chemical analysis of ash does not reflect the actual composition of the native fuel, as it only determines the oxides of the main elements that are formed during the ashing of any natural raw material. The calculated slagging (R_s) and fouling (R_f) parameters (see Section 6.1) provide only a general idea of the processes that could occur during the combustion of individual coal samples and their blends.

To study in more detail the specific mineral compounds and ways of their interaction under conditions of co-firing of different fuels with different metamorphism and salinity, special studies of ash residues were conducted. Information on the chemical composition of the ash of the studied fuels is given in Table 6.2. The samples were subjected to heat treatment in a muffle furnace (SNOL brand) at 850 °C (to remove volatile substances and fusible salts) for 3 h until the complete ashing.

Minerals in the ash residues after combustion were diagnosed using a DRON-4M diffractometer. Semi-quantitative phase analysis of the diffractograms was performed using the MATCH* software. X-ray diffraction is one of the most effective non-destructive methods for studying the structure of materials and the composition of a wide variety of mineral compounds. Its importance can hardly be overestimated in the study of the newly formed mineral phases and their transformation in the processes of high-temperature fuel conversion or chemical modification. The obtained diffractograms of ash residues of salty coal, ordinary steam gas, and lean coal, which were burned separately, and their blends are shown in Figures 6.6 and 6.7.

The analysis of diffractograms of ash from ordinary steam gas (Fig. 6.6, *a*) and lean coal (Fig. 6.7, *a*) showed a fairly simple ash structure of both samp-

les, which mainly consists of traditional simple oxides and a small amount of more complex silicates and aluminosilicates. Although gas and lean coals differ in grade and technical characteristics, their diffractograms have a significant number of similar intense reflexes. For both samples, the main mineral is silicon oxide (main reflexes: 4.28; 3.35; 2.70; 2.12; 1.82; 1.54; 1.38; 1.25 Å°), the content of which exceeds 60 % of the total number of compounds. At the level of 5—10% in the ash of the samples, we determined aluminum oxides (main reflexes: 2.88; 2.21; 1.98; 1.87; 1.42 Å°) and iron oxides (main reflexes: 3.68; 2.86; 2.52; 2.42; 1.69; 1.49; 1.45 Å°) and aluminum silicate (Al_2SiO_5). Also, small amounts of calcium oxide, calcium and magnesium silicates, as well as more complicated aluminosilicates were found.

The ash structure of salty coal samples is much more complex (Fig. 6.6 and 6.7, b). The obtained diffractograms have a larger number of intensive reflexes representing different mineral groups. Table 6.8 shows the main mineral phases in the composition of salty coal ash 1 and 2. They contain significantly less silicon oxide and more iron oxide compared to the samples of ordinary steam coal. Aluminum and calcium oxides have low levels or are not detected at all. Also, which is very important, more complex compounds are detected in significant quantities — various sulfates, silicates, and aluminosilicates. Not all the identified minerals are

Table 6.8. Main minerals in salty coal ash

Mineral	Formula	$T_{\text{melt}}, ^\circ\text{C}$	Content, %	
			Salty coal 1 6.8 % Na_2O in ash	Salty coal 2 3.4 % Na_2O in ash
Silicon oxide (Quartz)	SiO_2	1370	~8	~27
Iron oxides	$\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$	1565	~25	~19
Calcium sulfate (Anhydrite)	CaSO_4	1420	~25	~18
Calcium silicate	CaSiO_3	1544	~10	—
Calcium orthosilicate	Ca_2SiO_4	2130	~4	~14
Calcium aluminosilicate (Anorthite)	$\text{CaAl}_2\text{Si}_2\text{O}_8$	1553	~10	~4
Hercynite	FeAl_2O_4	1440	—	~3
Iron silicate (Fayalite)	Fe_2SiO_4	1173	—	~4
Sodium sulfate (Thenardite)	Na_2SO_4	883	~5	~2
Sodium silicates	$\text{Na}_2\text{SiO}_3, \text{Na}_2\text{SiO}_4$	1088—1120	~7	—
Nepheline	NaAlSiO_4	1526	—	~3

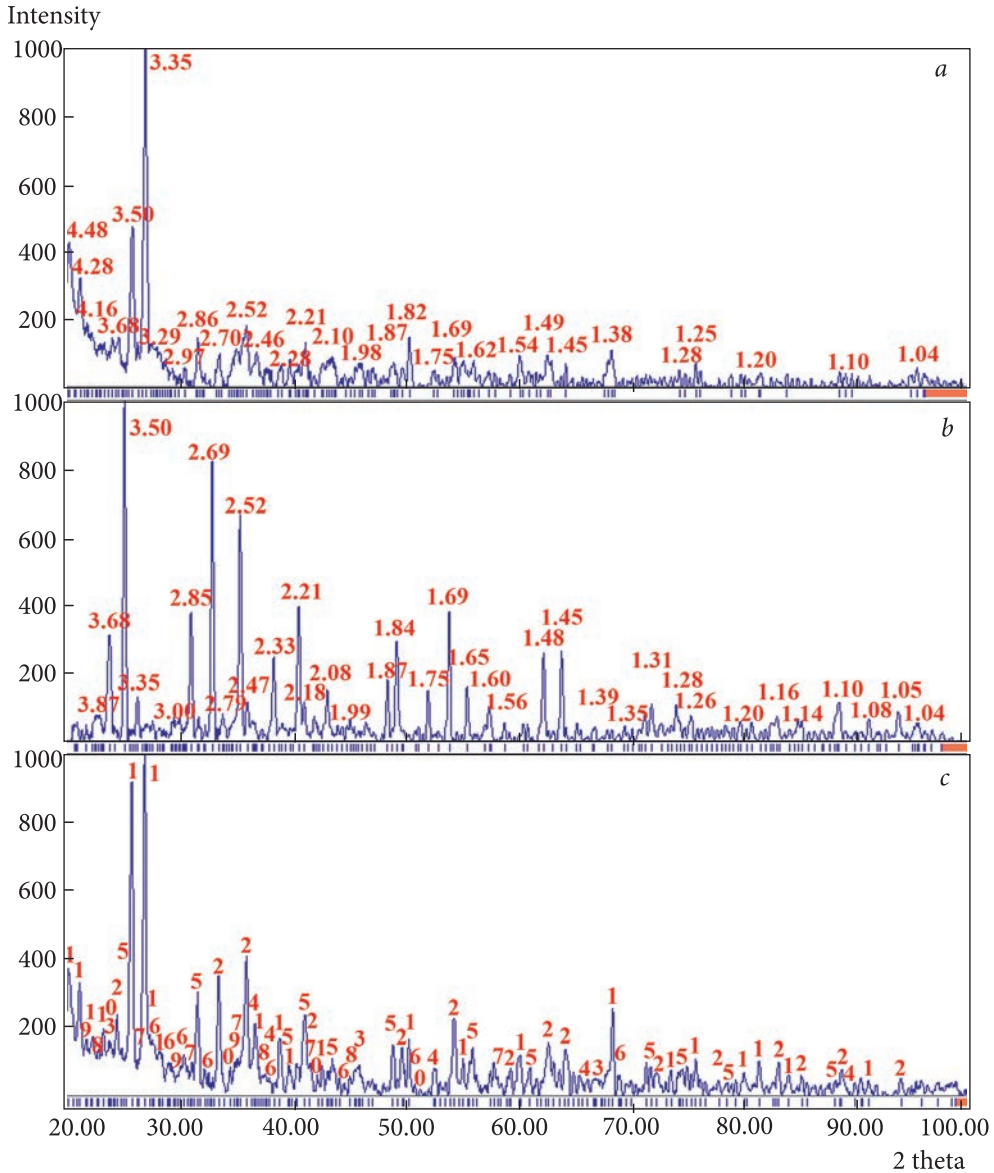


Fig. 6.7. Diffractograms of ash from lean coal (a), salty coal 1 (b), and their 50:50 blend (c): 1 — SiO_2 ; 2 — Fe_2O_3 , Fe_3O_4 ; 3 — Al_2O_3 ; 4 — CaO ; 5 — CaSO_4 ; 6 — Ca_2SiO_4 , CaSiO_3 , Ca_3SiO_5 ; 7 — Al_2SiO_5 ; 8 — Na_2SiO_4 ; 9 — NaAlSiO_4 , $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$; 0 — $\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_2$, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$

the combustion of salty coal (slagging and under-deposit corrosion). The obtained XRF results do not contradict the data on the chemical composition of salty coal ash (Table 6.2) and correlate with the literature data of domestic and foreign works [3, 20, 21] on the mineral composition of salty coal ash residue.

As determined in Section 6.3 and from the review [22], when combusting fuel blends, additive dependences of reactivity on their composition are only occasionally observed, but synergistic or antagonistic effects occur much more often. This necessitates an experimental study of the mutual influence of coals on each other. The key factors affecting these processes are the ratio of components, the reactivity of each fuel (organic mass structure, metamorphism), and the composition of the mineral fraction.

The analysis of ash diffractograms of blends of salty coal with steam gas coal or lean coal (Figs. 6.6 and 6.7, *c* respectively) in a ratio of 50:50 allowed us to establish that co-firing of two fuels with different characteristics produces ash with a wider assortment of minerals. It consists of mineral phases of both individual original fuels and more complex newly formed compounds. The most intense reflexes correspond to silicon and iron oxides (about 55%), which is similar to the results obtained for individual fuels of steam gas and lean coals. The other simple oxides (Al_2O_3 and CaO) and aluminum silicate (Al_2SiO_5) were detected in small amounts (up to 5 %). Calcium sulfate (CaSO_4) and calcium silicates (Ca_2SiO_4 , CaSiO_3 , and Ca_3SiO_5) were detected at the level of 10%. Sodium sulfates and silicates («unwanted» for us) are present in small amounts. The minerals of the nepheline group manifest themselves by distinct reflexes. Also, at the level of sensitivity (about 2%), a variety of more complex compositions are determined,

Table 6.9. Content of main substances in ash samples of blended fuels

Mineral composition (main phases)	Content of the main mineral phases, %					
	Salty coal/Gas coal			Salty coal/Lean coal		
	20:80	40:60	50:50	20:80	40:60	50:50
SiO_2	~52	~49	~50	~46	~52	~48
Fe_2O_3 , Fe_3O_4	~7	~5	~5	~6	~5	~6
CaSO_4	~8	~8	~7	~11	~10	~11
Ca_2SiO_4 , CaSiO_3 , Ca_3SiO_5	~6	~10	~12	~8	~12	~12
$\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{Ca}_2\text{Al}_2\text{SiO}_7$	~3	~5	~5	~2	~4	~4
Al_2SiO_5	~10	~5	~6	~12	~5	~4
Na_2SiO_4	—	~2	~2	—	~2	~2
Na_2SO_4	—	—	~2	—	~2	~2
NaAlSiO_4 , $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$	~6	~9	~12	~7	~8	~9
$\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_2$, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$	—	—	—	—	—	~2

which include Ca, Al, Fe, Si, Mg, and K. One of these compounds in a blend with lean coal is ultramarine $\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_2$. Among the others, the following minerals can be identified — KAlSi_3O_8 , Fe_2SiO_4 , $\text{Ca}_3\text{Fe}_2(\text{SiO})_4$, Fe_2SiO_4 , CaFeSiO_4 , MgSO_4 , and MgSiO_3 .

Table 6.9 shows the distribution of the main mineral phases depending on the percentage (20 to 50%) of salty coal 1 in blends with gas coal or lean coal.

The analysis of ash diffractograms from blends of salty coal 1 with gas or lean coals in different ratios (from 20 to 50%) allowed us to establish a wide variety of mineral phases that were re-formed. The composition of the ash from gas and lean coals has a rather strong influence on the newly formed minerals, due to the significant content of aluminosilicate (Al and Si oxides, Table 6.2) in the ash. According to the literature reviews [23, 24], aluminum and silicon oxides exhibit absorption/ capture mechanisms and, when burned with fuels that have a significant content of alkali and alkaline earth metals (Na, K, Ca, Mg) in the ash, can create more complex new crystalline phases. Such formations are called bertolides, which are non-stoichiometric compounds whose form of existence is not a molecule but a phase (i.e., a chemically bound huge aggregate of atoms), the composition of which, as our experiment showed, depends on the mineral composition of the initial components and their ratio.

In this context, the reactions that occur with Na compounds are quite important. The analysis showed a significantly lower number and intensity of sodium silicate (Na_2SiO_4) reflexes and the complete absence of sodium sulfate (Na_2SO_4) reflexes in blends where ordinary gas coal dominates. Instead, more complex and refractory minerals were identified: a group of nepheline minerals — Nepheline (NaAlSiO_4), Jadeite ($\text{NaAlSi}_2\text{O}_6$), and Albite ($\text{NaAlSi}_3\text{O}_8$) and a group of ultramarines — Hauyne ($\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_2$) and Nosean ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$). Possible reactions for the formation of minerals of the nepheline and ultramarine groups are as follows:

- 1) $\text{Na}_2\text{SO}_4 + 2\text{Al}_2\text{SiO}_5 \rightarrow 2\text{NaAlSiO}_4 + \text{Al}_2\text{O}_3 + \text{SO}_3(\text{g})$,
- 2) $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{NaAlSiO}_4 + \text{SO}_3(\text{g})$,
- 3) $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{NaAlSi}_2\text{O}_6 + \text{SO}_3(\text{g})$,
- 4) $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 6\text{SiO}_2 \rightarrow 2\text{NaAlSi}_3\text{O}_8 + \text{SO}_3(\text{g})$,
- 5) $\text{Na}_2\text{SO}_4 + 6\text{NaAlSiO}_4 \rightarrow \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$.

A similar mechanism of absorption/ capture can be imagined in the case of calcium compounds, namely calcium sulfate (CaSO_4), which also has a significant content in salty coal. These related elements in mixtures also form simple and complex silicates (CaFeSiO_4 , CaSiO_3 , $\text{CaAl}_2\text{Si}_2\text{O}_8$) during ashing:

- 1) $2\text{CaSO}_4 + \text{Fe}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{CaFeSiO}_4$,
- 2) $\text{CaSO}_4 + 2\text{SiO}_2 \rightarrow \text{CaSi}_2\text{O}_3 + \text{SO}_3(\text{g})$,
- 3) $\text{CaSO}_4 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SO}_3(\text{g})$,
- 4) $\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8$,



To estimate the slagging properties of coal, the initial slagging temperature can be calculated with acceptable accuracy for practice from the average chemical composition of the mineral part of coal [25]. The value of T_{slag} depends on the ratio of components of acid ($A = \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$) and basic ($B = \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$) oxides.

$$T_{\text{slag}} = 945 + 7.77 \cdot k_o \text{ for } k_o \geq k_o^\kappa, k_o^\kappa = 2.25,$$

$$T_{\text{slag}} = 940 + 52.23 / k_o \text{ for } k_o < k_o^\kappa,$$

where $k_o = A / B = (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2) / (\text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$

For fuels with a high content of alkali and alkaline earth metals, the T_{slag} temperature is lower and can be calculated taking into account the correction $T_{\text{alk}} = 12 \cdot (\text{Na}_2\text{O} + \text{K}_2\text{O} - 1.8)$.

Our calculations based on empirical formulas for salty coal and samples of gas and lean coals allowed us to establish a significant difference in the initial slagging temperature of these fuels. For the salty coal sample, the calculated T_{slag} is 900 °C (Table 6.10), while for the steam gas and lean coal samples, it is 1020—1040 °C. Such a low initial slagging temperature can be explained by the presence of a significant content of low-melting components in salty coal, the main of which is halite (sodium chloride (NaCl), $T_{\text{melt}} = 801$ °C). At the same time, for the mixtures of salty coal with gas or lean coals in a ratio of 50:50, the calculated T_{slag} is ~970 °C. With a further increase in the share of ordinary gas coal in the blend, the initial slagging temperature will increase accordingly, which is a condition for the trouble-free use of salty coal.

It should be noted here that the actual (determined by standard methods) ash melting temperatures differ from those calculated above. For example, for salty coal, the temperature of ash deformation (DT) is 1060 °C (Table 6.10), while for gas coal samples it exceeds 1200 °C. As known, one of the main problems in the energy use of coal with a high content of alkali and alkaline earth metals at TPPs is the rapid formation of fouling, hard deposits, and under-deposit high-temperature corrosion of the metal of the heating surfaces at the

outlet of the boiler unit furnace. This is due to the low melting point of the ash (~1150 °C), which is lower than the temperature of gases in this area. The analysis of the ash DT for samples of the 1:1 blend of salty coal with gas coal showed an increase in this temperature by 70—90 °C compared to the original salty coal sample. This almost corresponds to the required temperature in the specified area (at the furnace outlet),

Table 6.10. Slagging and ash deformation temperatures of coal samples

Sample	$T_{\text{slag}}, ^\circ\text{C}$ (calculated in [26])	$t_a, ^\circ\text{C}$ (defined by standard methods)
Salty coal 1	900	1060
Gas coal	1022	1260
Lean coal	1038	1350

which in turn indicates a reduction in slagging and corrosion processes when using such a blend.

The formation of new refractory substances, as well as an increase in the initial slagging temperature when co-firing salty coal with ordinary gas coal (in a certain ratio), may be one of the arguments in favor of using mixed raw materials (including salty coal) in the Ukraine's energy sector.

6.5. Determination of metal corrosion processes during combustion of coal with high salt content

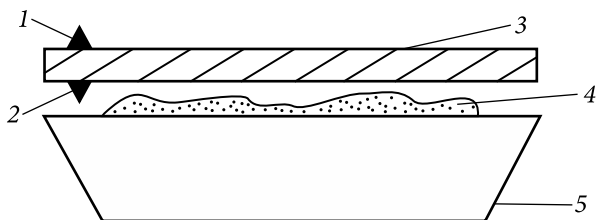
The XRD characteristics of the identified mineral phases (Section 6.2) and their semi-quantitative analysis showed that sodium chloride is not the predominant mineral in all samples. Sulfate phases, primarily calcium sulfate, also play an important role in the formation of ash deposits. Another reason for the slagging of heating surfaces is considered iron-containing coal minerals [21, 27–28].

An experiment was conducted to investigate the morphology of corrosion during the combustion of salty coal. A ceramic vessel was loaded with a thin layer of 5 g of fuel sample, which was covered with a metal plate of ordinary steel (grade 1kp) by the scheme in Figure 6.8. The samples were burned in a muffle by heating from room temperature to 800–950 °C and kept at this temperature for 2 h until the complete ashing. For the experiment, samples of the main salty coal deposits of Ukraine with different content of harmful impurities were selected, the characteristics of which are given in Table 6.4.

As a result of the experiment, some photos were taken (Fig. 6.9). Metal plates exposed to salty coal volatiles have a different appearance from both the outer and inner surfaces. Visual analysis of the surface of metal samples after exposure to volatile products of native salty coal (Fig. 6.9) revealed that intensive descaling and exfoliation of scale layers occurred. The loose volumetric layers on the outer surface (*a, c, e, g*) of a complex pattern are bordered by small surface formations localized in the middle of the plate. At the same time, the morphology of the inner plate surface (*b, d, f, h*) is quite different — the areas affected by high-temperature gases are distinctly visible, and that is not accompanied by significant effects of swelling but is characterized by a slight separation of the surface layer.

The outer surface of the metal under the influence of hot gases of salty coal samples Bohdanivske 1 (Fig. 6.9, *a, c*) and Starobilske 1 is significantly covered

Fig. 6.8. Schematic of the experiment on metal surface corrosion: 1 — outer surface; 2 — inner surface; 3 — metal surface; 4 — coal sample; 5 — ceramic vessel



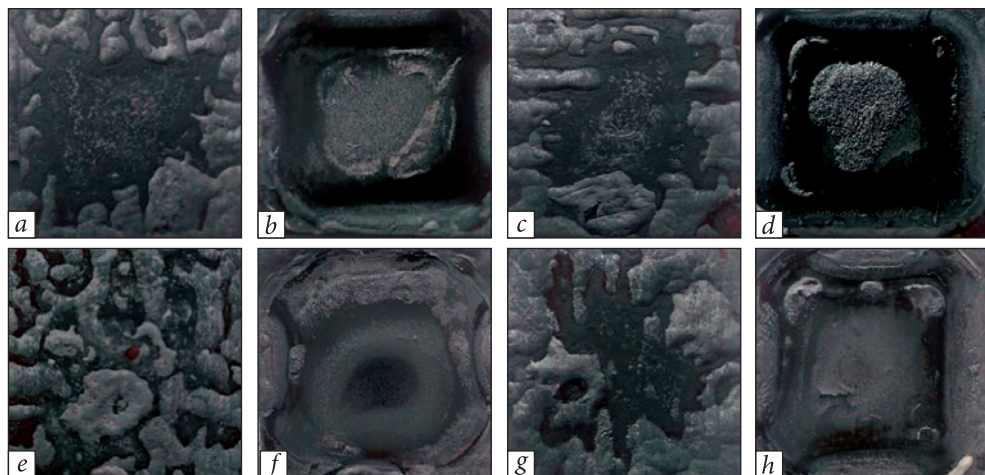


Fig. 6.9. Photos of metal surfaces after exposure to volatile products of salty coal samples Bohdanivske 1 (*a, b, c, d*) and Starobilske 1 (*e, f, g, h*)

(up to 60—70%) with swollen scaly formations that can be easily separated by mechanical intervention. A similar picture is observed for other salty coal samples, although in some cases of lower intensity. A high brittleness of the metal plates was also noted, indicating a possible manifestation of more active corrosion of the metal surface and destruction of the plate body.

The loose volumetric layers of metal were carefully separated from the plate surface and subjected to X-ray diffraction analysis to determine the phase composition of the formations that appeared on the metal plates during the combustion of salty coal. Diffractograms of exfoliation (from the inner surface) of the salty coal samples with the highest content of alkali and alkaline earth metals are shown in Figure 6.10.

As seen, the obtained diffractograms have a rather large number of peaks of different intensities, and most of the intensity reflexes are similar for all samples. The analysis of them revealed that these peaks correspond to simple iron oxides of different valences. Additionally, compounds responsible for corrosion processes were identified. The general mineral composition of the collected exfoliations obtained at different temperatures is shown in Table 6.11.

The analysis of the data in Table 6.11 and the results obtained in Section 6.2 allowed us to determine the tendency (directly proportional) of the dependence of the content of iron sulfide and iron chloride in the scales on the content of sulfates and chlorides in salty coal. The higher-temperature combustion of salty coal at 900 °C causes, on the one hand, a sharp drop in the FeO content and, on the other hand, a more active formation of iron chlorides, which indicates the development of corrosion processes by the scheme proposed by Krause [11].

Figure 6.11 shows photos of a metal surface exposed to the combustible gases of gas (steam) coal, which is widely used in the energy sector. Under these

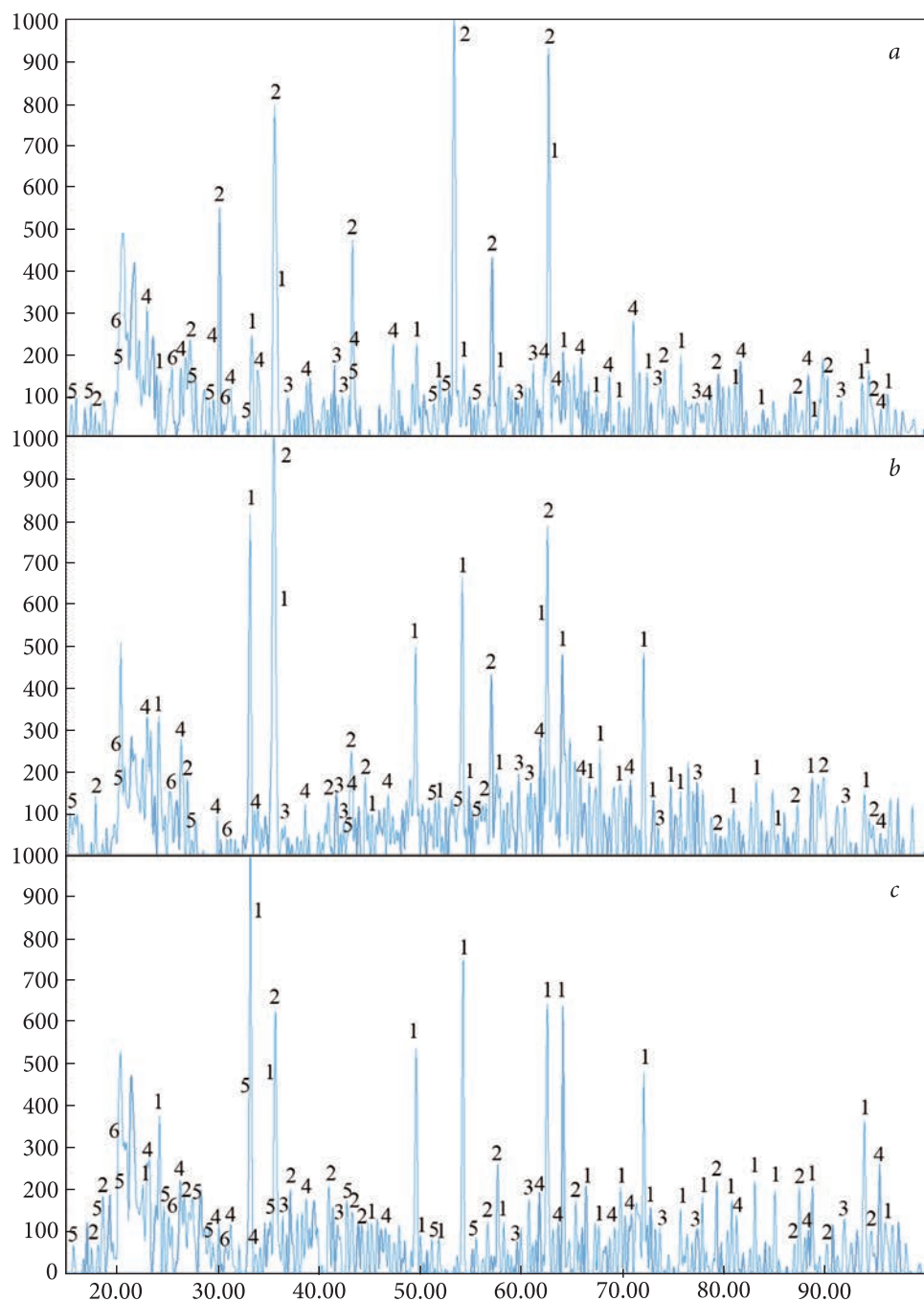


Fig. 6.10. Diffractograms of scale formed due to interaction of metal with volatile substances of salty coal at 800 °C: *a* — Bohdanivske 1; *b* — Starobilske 1; *c* — Novomoskovske 1. 1 — Fe_2O_3 ; 2 — Fe_3O_4 ; 3 — FeO ; 4 — FeS_x ; 5 — FeCl_x

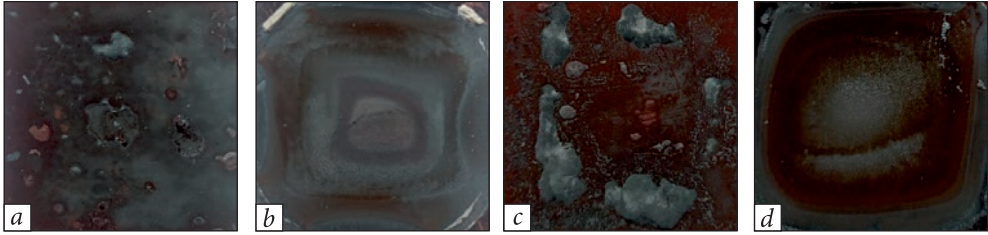


Fig. 6.11. Photos of metal surfaces after exposure to gas coal combustion products: *a, c* — outer surface; *b, d* — inner surface

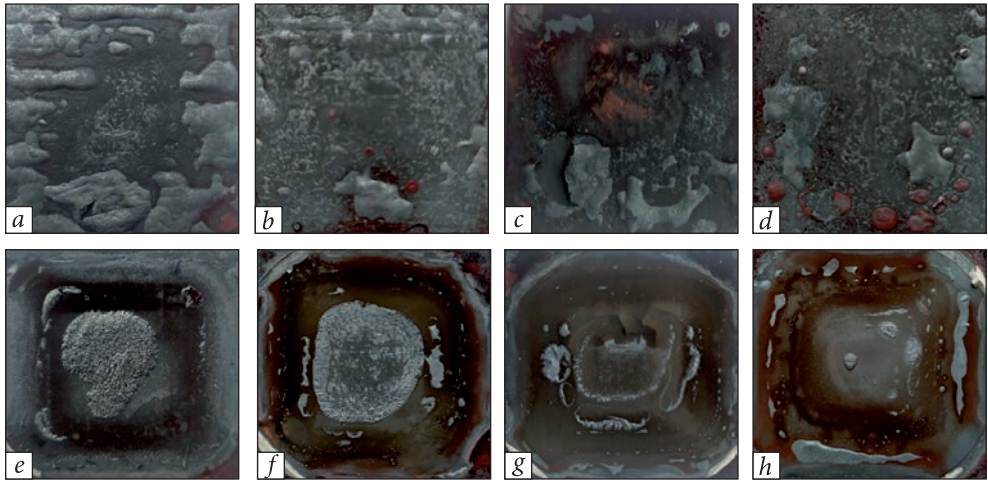


Fig. 6.12. Influence of fuel blending on corrosion processes: (*a, e*) gases of the original SC; (*b, f*) 80:20 SC/GC blend; (*c, g*) 50:50 SC/GC blend ; (*d, h*) 30:70 SC/GC blend

Table 6.11. Phase composition of metal plate exfoliation, %

Sample	Fe_2O_3	Fe_3O_4	FeO	FeS_x	FeCl_x
800 °C					
Starobilske 1	~44	~25	~15	~13	~3
Bohdanivske 1	~35	~17	~28	~16	~4
Bohdanivske 2	~18	~34	~23	~25	~0
Novomoskovske 1	~30	~23	~15	~15	~12
900 °C					
Starobilske 1	~46	~20	~4	~24	~6
Bohdanivske 1	~24	~44	~6	~16	~10
Novomoskovske 1	~48	~15	~8	~13	~16

combustion conditions, the metal surface looks almost undamaged, with no visible signs of corrosion. It is noticeable that there is no active exfoliation on the surface; only there are small red lesions in some areas. The inner side of the plate shows clear contours of temperature effects with no sign of corrosion.

To assess the effect on corrosion processes of blending salty coal with ordinary gas coal, similar experiments were conducted (according to the scheme in Fig. 6.8), but instead of individual fuels, pre-prepared blends were loaded into ceramic shuttles. Figure 6.12 shows photos of the plate surfaces after exposure to blends of salty coal and gas coal in different ratios.

The photos show that the addition of gas coal to salty coal significantly reduces corrosion, even in the case of a relatively small percentage of gas coal. At a ratio of 50:50 or lower, the effect of aggressive compounds on the metal surface becomes almost imperceptible. The results suggest that the processes of iron oxidation and sulphation are less intense in blended fuels. The presence of other natural mineral compounds in gas coal affects both the amount of scale formed and its qualitative composition.

6.6. Conclusions

One of the attractive and rational ways of possible use of salty coal is its co-firing with other fuels that have different ash and reactivity characteristics. When creating a binary composite raw material, not only the content of low-melting salts is «diluted» (reduced) by adding another fuel (coal with high content of Al and Si in the ash) to salty coal but also the prerequisites for the formation of refractory mineral phases are created that do not complicate the combustion process.

The results obtained from the determination of mineral substances in the ash residues from composite fuels indicate the formation of more complex (3—4-component) mineral phases with new melting characteristics in the ashing process. This significantly differentiates them from the mineral ash phases from the individual components of mixtures. The simultaneous decrease in the content of low-melting sulfates and silicates (determined by a drop in the intensity of the corresponding reflexes on the diffractograms of ash residues) indicates the formation of ash with a higher melting point (for 50:50 blends, an increase in the temperature by 70—90 °C is achieved).

It was found that composite fuel with the involvement of salty coal at its content of 20 to 50% in the blend significantly reduces the effects of slagging and corrosion activity of fuel to the acceptable level for the energy use of this domestic resource with the so-called “deferred demand”.

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PREPARING FUEL MIXTURES AND THEIR COMBUSTION AT TPPs AND CHPPs

It has been shown in the previous chapters that the co-firing of two fuels with significantly different properties aims at improving the technological, safety, and environmental characteristics of combustion using existing equipment the expanding and/or universalizing fuel base. Among the co-combustion options, the following can be distinguished:

- Combustion of different fuels as a mixture.
- Joint combustion of different fuels in one furnace but with independent feeding and preparing.
- Alternating combustion.

Existing in Ukraine TPP and CHPP boiler units with steam-generating capacity from 90 to 2650 t/h are designed for pulverized coal combustion. This means the need to mill the coal to a dust-like state and dry to a state of coal dust flowability, which is usually performed simultaneously with the use of a drying agent, such as hot air or exhaust gases. Apart from two boiler units of the Dobrotvirska TPP, which have pulverizing systems with direct pulverized coal injection into the burners, the rest boilers have pulverizing systems including an intermediate pulverized coal hopper equipped with dust feeders, individual for each burner, and a system for pneumatic pulverized coal transportation to the burners. It follows that only solid fuels of similar grinding properties are suitable for combustion at TPPs and CHPPs in the form of a mixture, such as anthracite, hard coal, petroleum coke, carbon-containing ash dump material, and sludge and dry coal manufacturing wastes. As for an alternating combustion, it is the presence of an intermediate pulverized coal hopper that creates a risk of fire and explosion hazard when switching to fuels with different spontaneous combustion properties and explosive ability.

This chapter examines the specifics and practical experience of the production, pulverization, and combustion of coal mixtures at TPPs and CHPPs.

7.1. Objectives and potential components for the production of fuel mixtures

The practice of burning coal mixtures is quite widespread in the world. Mixtures are used to reduce the cost of electricity generation, to ensure optimal heat of combustion and fuel ignition conditions, and to control the level of nitrogen and sulfur oxide emissions [1]. However, as a rule, coal of similar grades with comparable volatile yield for a dry ash-free basis — bituminous coal (gas coal by the Ukrainian standard nomenclature), subbituminous coal (long-flame coal), and lignite — is used to prepare mixtures. Worldwide, there is no experience in preparing and burning mixtures of solid fuels with significantly different properties.

The purposes of producing fuel mixtures in Ukraine are closely related to the structure of boiler equipment at thermal power plants and the history of their fuel base development. Deposits of Ukraine include coal of all grades, from anthracite to lignite coal, and our country is among the top three countries in the world in terms of anthracite reserves. Therefore, the boiler units of half of Ukrainian TPPs and most coal-fired CHPPs were designed to burn anthracite, while the rest — gas coal.

In the 2000s, the task of complete refusal of “backlighting” (oil or gas addition for temperature stabilization) when combustion of low-reactive anthracite was actual, which to a certain extent was completed by organizing combustion of anthracite and lean coal blends. This was first implemented under the guidance of Academician O. Maistrenko in the TPP-210 boiler of the Zmiivska TPP unit No. 8 [2], after which the addition of lean coal to anthracite at TPPs became a common practice. It should be noted that anthracite and lean coal belong to the same group of low-reactive fuels; combustion of low-reactive coal and gas-coal mixtures was previously not allowed by industry standards due to both different fire and explosion safety conditions of pulverizing systems and different combustion characteristics of these fuels. However, as early as in the late 2000s, in the face of a temporary shortage of lean coal, the issue of creating anthracite mixtures with the addition of gas coal arose. With the start of hostilities in eastern Ukraine (from 2014 to 2021), supplies of Donetsk anthracite and lean coal ceased, but the import of these coal grades (from South Africa, the USA, and the Russian Federation) was still possible, although its cost was higher than that of domestic coal. In these conditions, the task of partial replacement of anthracite in existing boiler units of anthracite power units using the maximum possible gas coal share has become relevant.

Since 2017, some anthracite-fired boiler units at TPPs and CHPPs that have been reconstructed to use gas coal have partially solved the problem of replacing anthracite at TPPs and CHPPs. However, the temporary occupation of part of Donbas resulted in a fuel shortage, which can be overcome by both importing coal and using carbon-containing solid fuel waste, such as waste from manufacturing petroleum coke, sludge and dry coal manufacturing waste, as well as ma-

terial from ash dumps of power plants. The listed fuels differed in their properties from the operational requirements for existing boilers: coal manufacturing waste with high ash content, petroleum coke with low ash and high sulfur content, imported bituminous and subbituminous coal from some suppliers with high moisture content, low ash content, high calorific value, and explosive ability. Their use in existing boilers was possible only as part of mixtures with given characteristics.

Table 7.1 shows the characteristics of fuels used to prepare mixtures for anthracite-fired TPPs after 2013 [3, 4]. The characteristics of imported coal from different suppliers are specified as well.

Anthracite and gas coal are fuels with fundamentally different reactivity. For a long time, it was believed that since volatile substances and high-reactive coke residue of gas coal burn faster than anthracite, this causes a decrease in oxygen concentration in the combustion zone and, as a result, slows down the ignition and burning of anthracite. In addition to various fire and explosion safety conditions of the pulverizing systems, this was the second reason for not using mixtures of anthracite with gas coal. However, studies of the TETI NASU have established (see Chapter 2) that since under pulverized coal flame conditions, gas coal burns closer to the external diffusion zone with a relatively weak power-law dependence on temperature, whereas anthracite burns closer to the internal diffusion zone

Table 7.1. Average characteristics of fuels for the production of mixtures

Fuel	Source	Characteristics				
		W_t^r , %	A^d , %	Q_i^r , kcal/kg	V^{daf} , %	S_t^d , %
Anthracite	Donbas	8.0	23.0	5500	5.0	1.3
	Imports (Russian Federation)	8.0	15.0	6100	2.5	0.6
Lean coal	Imports (South Africa)	10.0	26.0	5200	14.0	1.8
	Imports (USA)	10.0	25.0	5400	15.0	1.3
	Imports (Russian Federation)	10.0	13.0	6300	14.5	0.6
Gas coal	Ukraine (Western Donbas, Pavlohrad)	8.0	23.0	5400	40.0	1.8
	Ukraine (Lviv-Volyn basin)	11.0	22.0	5200	42.0	2.8
	Imports (Kazakhstan)	13.0	7.0	5900	44.5	0.8
Petroleum coke	Ukraine; imports	4.0	6.0	7600	11.0	6.0
Dry coal manufacturing waste	Ukraine	6.0	64.0	2100	32.5	1.7
Material of TPP and CHPP ash dumps	Ukraine	21.0	69.0	1360	46.0	0.8
	Ukraine	8.0	84.0	700	4.0	0.2

with a strong exponential dependence on temperature, then, when burning an A/G mixture, the decrease in the combustion rate of anthracite due to a decrease in the concentration of oxygen consumed for the combustion of gas coal VM is largely compensated by an increase in the flame temperature due to the intense heat generation when combustion of gas coal VM and a more reactive gas coal coke residue. The condition for this is an excess of oxidizer on the main burners, and the result is stabilization of the ignition of the mixture anthracite component without gas-oil “backlighting” and an increase in its burnout rate.

Boilers of anthracite power units of 200, 300, and 800 electrical MW with pulverized combustion are designed to use anthracite with a volatile yield on dry ash-free basis $V^{\text{daf}} < 8\%$ and lean coal with $V^{\text{daf}} = 8\text{—}18\%$. To maintain the conditions for molten slag removal, the temperature in the lower part of the furnace should be over 1550°C . Boilers of the 200 and 300 MW units have pulverizing systems with ball-drum mills and intermediate pulverized coal hoppers, while drying and transportation of pulverized coal to burners is performed using hot air. Boilers of 800 MW power units of the Slovianska TPP are fed with pulverized coal from the central pulverizing factory, where coal is dried in rotary dryers with steam-heating panels; milling is conducted in non-ventilated ball-drum mills, and pulverized coal is transported to the boilers by air through high-concentration dust pipelines. For all pulverizing systems, exceeding the volatile yield by more than 18% causes cases of pulverized coal spontaneous combustion and/or explosion. Thus, a requirement for the mixture composition is the correspondence of the volatile yield to lean coal, i.e., $V^{\text{daf}} \leq 18\%$ [5, 6].

The current technological standard for sulfur dioxide emissions from anthracite-fired boilers is no more than 3400 mg/nm^3 at 6% O_2 in exhaust gases and for boilers operating based on gas coal — no more than 5100 mg/nm^3 . With a basic fuel calorific content of 5200 kcal/kg , this corresponds to a maximum dry sulfur content of $S_t^{\text{d}} = 1.4$ and 2.1% , respectively [7]. This limitation should be taken into account when preparing mixtures with petroleum coke and Lviv-Volyn's coal. Since the fuel is additionally mixed during pulverization, this requirement applies to the average sulfur content value in the mixture.

The permissible gas coal share in mixtures for anthracite-fired boilers is determined by the volatile yield (Fig. 7.1) and sulfur content in the components (Fig. 7.2) [4]. By the criterion of the permissible VM yield of mixtures with anthracite, the permissible gas coal share is 30—35%. By the criterion of permissible sulfur content, the Western Donbas' gas coal share in the mixture can exceed 35%, while the Lviv-Volyn's coal share is limited to 30%. In anthracite/petroleum coke mixtures, the permissible share of the latter is limited to 10%. Increasing the petroleum coke share to 15% without violating environmental standards is possible only when using low-sulfur lean coal, the import of which has ceased in wartime conditions.

The pulverized coal fineness is determined by the residue on the sieve of $90\text{ }\mu\text{m}$ R_{90} . The choice of the optimal pulverized coal fineness depends on many factors [8]. The general requirement is to increase the reacting surface for less

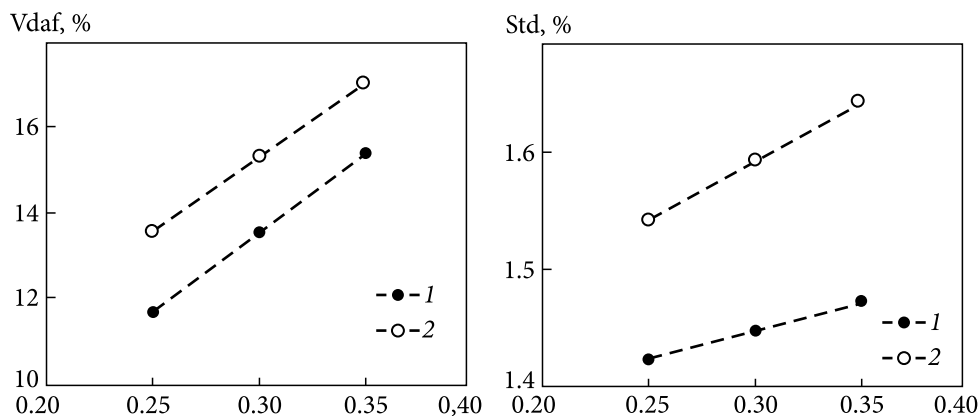


Fig. 7.1. Dependence of the mixture VM yield on the gas coal share at an anthracite VM yield V_{daf} of (1) 5.0% and (2) 2.5%

Fig. 7.2. Dependence of the sulfur content in mixtures with Donetsk anthracite on the gas coal share: 1 — from Western Donbas, 2 — from Lviv—Volyn basin

reactive coal; other requirements take into account the fire and explosion safety of pulverizing systems, the presence of discharge burners for dusty drying agents in pulverizing systems of anthracite boilers, and electricity spent for milling. The current standards set for anthracite $R_{90} = 4\text{--}8\%$, for lean coal $R_{90} = 8\text{--}12\%$, and for gas coal $R_{90} = 20\text{--}25\%$. Calculation estimates by the TETI NASU show that, depending on the volatile yield of the mixture, the optimal pulverized coal fineness should increase linearly from $R_{90} = 8\text{--}10\%$ at $V_{daf} = 8\text{--}12\%$ to $R_{90} = 12\text{--}14\%$ at $V_{daf} = 14\text{--}18\%$ [4].

Boilers designed or reconstructed for pulverized gas coal combustion (in Ukraine usually with molten slag removal), according to the National standard DSTU 4083:2012 [6], use coal of the 1st quality category (the lower heat value on an “as received” basis (LHV) — not less than 5000 kcal/kg). This does not mean that there is no restriction for LHV “from behind” and/or on ash content “from below”. The fact is that the temperature level in the lower part of the furnace for stable ignition of pulverized burning, and molten slag removal, on the one hand, and the protection of the wall screen tubes of the lower part of the furnace from thermal overloads, on the other hand, are provided by the so-called “garnissage” coating — a layer of solidified slag on the shotcrete coating of the screen tubes or on the studded screen tubes of the furnace “ignition belt”. This determines the minimum permissible ash content of the fuel — at least 16—18%. Fuels with a lower ash content can be used in such boilers only in a mixture with a higherash component.

As for anthracite and lean coal, the pulverization safety requirements are set only for the maximum permissible volatile yield on the dry ash-free basis V_{daf} , therefore this criterion for gas coal is insufficient. In recent years, the world-wide

criterion of explosive ability K_T has been used to quantitatively assess the tendency of coal dust to spontaneous combustion and explosion [8, 9]. The methodology for calculating K_T for each specific coal uses the carbon, hydrogen, and oxygen contents, fuel volatile yield, and lower heat values on the dry ash-free basis as well as the coal ash content on the dry basis as input parameters. They are used to calculate the volatile substance heat value and the lower concentration limit of flame propagation of volatile substance combustible components mixed with air. The same is calculated with some correction for non-volatile coke and ash. Finally, the K_T value is calculated as follows.

Sum of C, H, and O on a dry ash-free fuel basis, %:

$$\Sigma = C^{\text{daf}} + H^{\text{daf}} + O^{\text{daf}}.$$

Recalculation of C, H, O, and V^{daf} on the oxygen basis of the fuel, %:

$$C_0^{\text{daf}} = 100 \times C^{\text{daf}}/\Sigma, H_0^{\text{daf}} = 100 \times H^{\text{daf}}/\Sigma, O_0^{\text{daf}} = 100 \times O^{\text{daf}}/\Sigma,$$

$$\text{and } V_0^{\text{daf}} = 100 \times V^{\text{daf}}/\Sigma.$$

Recalculation of the lower heat value on the oxygen basis of the fuel, kJ/kg:

$$Q_0^{\text{daf}} = 100 \times Q_i^{\text{daf}}/\Sigma.$$

Carbon content in coke (non-volatile residue), %:

$$C_0^{\text{coke}} = C_0^{\text{daf}} + H_0^{\text{daf}} + O_0^{\text{daf}} - V_0^{\text{daf}}.$$

Heat of volatile substances, kJ/kg:

$$Q_{\text{vol}} = 100 \times (Q_0^{\text{daf}} - 329 \times C_0^{\text{coke}})/V_0^{\text{daf}}.$$

Lower concentration limit for flame propagation of volatile substances mixed with air, %:

$$m_{\text{vol}}^{\text{low}} = 126000/Q_{\text{volat}}.$$

The same, including the impact of ballast (coke and ash), %:

$$m_{\text{vol(bal)}}^{\text{low}} = 100 \times m_{\text{vol}}^{\text{low}} \times (1 + (100 - V^{\text{d}})/V^{\text{d}})/(100 + m_{\text{vol}}^{\text{low}} \times (100 - V^{\text{d}})/V^{\text{d}}).$$

Criterion of explosive ability:

$$K_T = V^{\text{d}}/m_{\text{vol(bal)}}^{\text{low}}.$$

The requirements for pulverizing systems for hazard group III ($1.5 \leq K_T \leq 3.5$) correspond to those specified in [10, 11] for hard coal with a volatile yield of more than 30%. In the research of the TETI NASU, using the certificates of quality and technological properties for the products of Ukrainian producers of coal of the gas (G) and long-flame (DG) grades, which were issued by UKRNDIVUHLEZBAHACHENNIA institute from 2012 to 2016, K_T values were

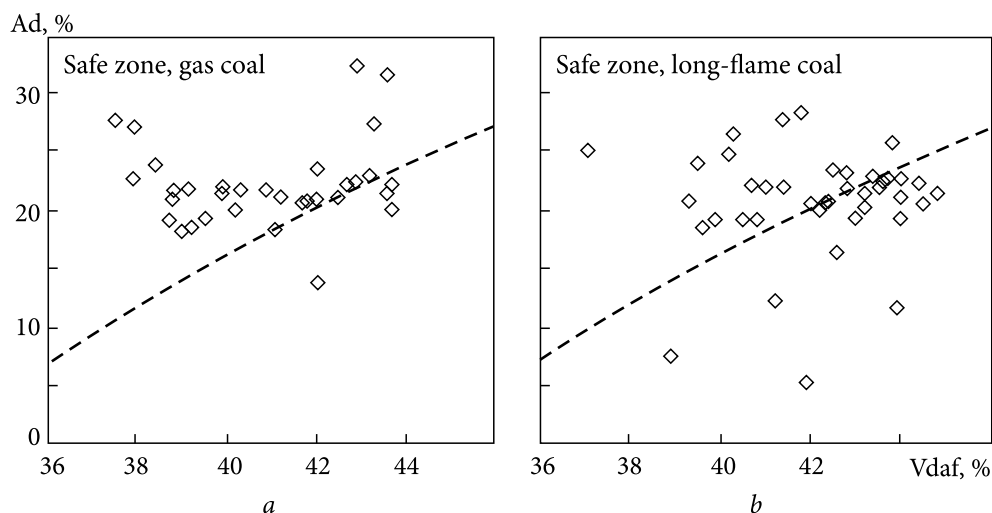


Fig. 7.3. Assessment of the pulverization safety of domestic coal products of the gas (a) and long-flame (b) grades by the criterion $A^d \geq 100 \times (1 - 33.5/V^{daf})$

calculated, and it was substantiated that K_T exhibits a linear dependence not on V^{daf} but on V^d , while safe conditions for $K_T < 3.5$ are implemented according to the criterion (Fig. 7.3) [12—14]:

$$A^d \geq 100 \times (1 - 33.5/V^{daf}).$$

This means that while composing a mixture, for each coal with an actual V^{daf} value, it is possible to find an ash content level in the mixture that guarantees safe pulverization without changing the pulverizing system equipment.

7.2. Methods for preparation and criteria for homogeneity of fuel mixtures

Two main methods for preparing mixtures are described in [1]: discrete one, in which dosing is performed by sequentially feeding portions of components with a bulldozer bucket or crane-reloader to the fuel stack or to the receiving hopper of the main conveyor, and continuous one, in which dosing is performed by feeding one conveyor belt with two feeders with a set component consumption ratio. The first method is simpler but does not provide sufficient mixture homogeneity. It can be used at a power plant with a central pulverizing factory, where the requirements for mixture homogeneity are the lowest, since the fuel is additionally mixed during pulverization. In other cases, a continuous method should be used; where it is not technically feasible, a stack of the mixture should be formed by a discrete method with additional mixing with a bulldozer.

Since previously the mixtures consisted only of fuels of similar ranks, the homogeneity of the mixtures was not critical, so it was considered only qualitatively. When producing A/G coal mixtures, the mixture homogeneity becomes the main factor in ensuring the safe operation of the pulverizing system. In this case, it is imperative to quantify the criterion of the required homogeneity and develop a method for its control [4, 12, 20].

The main national standard for coal testing [15] did not include the concept of fuel heterogeneity. For the first time in domestic use, it was introduced during the implementation of the national DSTU ISO 13909 standard “Bituminous Coal, Anthracite and Coke. Mechanized Sampling” (in 8 parts) developed with the participation of the TETI NASU of Ukraine. In particular, in Part 7 [16], as a degree of heterogeneity for the target fuel indicators, their dispersion in point samples (increments) is indicated, or the standard deviation, which is the square root of the dispersion. A necessary condition for representativeness of sample collection of increments in terms of lot heterogeneity for any indicator is their number n_1 related to the fuel mass in the lot M , tons, set by the expression:

$$n_1 = n \times (M/1000)^{0.5},$$

where n is the minimum number of point samples for a mixture lot weighing up to 1000 tons according to [15]. The increments are taken from the mixture flow or the stack, fulfilling the condition of their uniform distribution over the tested fuel lot.

The criteria for the mixture homogeneity in terms of ash content and volatile yield differ. According to DSTU 4096-2002 “Lignite Coal, Hard Coal, Anthracite, Oil Shale and Coal Briquettes. Methods of Sampling and Preparation of Samples for Laboratory Testing” [15], fuel is considered homogeneous by ash content and such, the quality of which is characterized by one combined sample, if the error in testing a fuel lot by ash content does not exceed 10 % relative at an average ash content of fuel up to 20% (for example, at an average ash content of 16%, the absolute error should not exceed $16 \times 0.1 = 1.6\%$) and 2% at an average ash content of fuel over 20%.

According to DSTU ISO 13909-2:2005 “Hard Coal, Anthracite and Coke. Mechanized Sampling. Part 2. Coal. Sampling From Moving Flows” [17], the value of maximum sampling error for ash content depends on the variation of ash content in increments and the number of increments that constitute the combined sample and is equal to

$$P_L = 2 \times (V_i/n + V_{PT})^{0.5},$$

where V_i is the ash content dispersion in increments, n is the number of increments and V_{PT} is the dispersion of preparation and analysis of the combined sample (usually taken as $V_{PT} = 0.2$). With the value of the maximum test error $P_L \leq 2\%$, specified in DSTU 4096, this expression leads to the condition $V_i/n \leq 0.8$.

Table 7.2 shows the maximum permissible value of dispersion and standard deviation (SD) — the square root of dispersion — to meet this requirement for

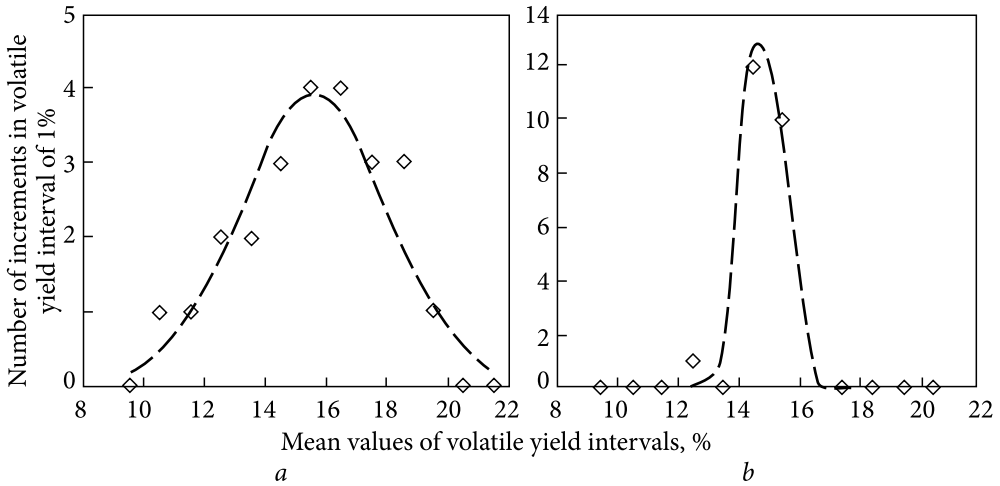


Fig. 7.4. An example of the distribution density of the number of increments by mean V^{daf} values for a lot of anthracite/gas coal blend produced at the Zmiivska TPP coal storage site: (a) in the mixture stack (mean $V^{\text{daf}} = 15.4\%$, $\text{SD} = 2.4\%$), (b) in the feeder of the raw coal hopper of the boiler (mean $V^{\text{daf}} = 14.9\%$, $\text{SD} = 0.6\%$)

different numbers of increments (the recommended minimum number of increments per lot according to DSTU ISO 13909-2 is 10, and 16 is the recommended minimum number of increments per lot of up to 1000 tons for manufactured coal, whereas 32 is that for raw coal according to DSTU 4096).

Unlike the ash content, which forms a “garnissage” coating on average, the volatile yield is an indicator that determines the spontaneous ignition tendency of each portion of coal fed to the mill and is not to exceed the limit in each part of the lot. By the general theory of errors, any part of the mixture lot is within the range of $(V^{\text{daf}}_{\text{(aver.)}} \pm \text{SD})$ with a 67% confidence probability. If the upper limit of this range does not exceed $V^{\text{daf}} = 18\%$, it means that the mixture corresponds to lean coal with the same confidence probability in terms of volatile yield. For reasons of ensuring fire and explosion safety of pulverizing systems, the maximum average value of V^{daf} for anthracite-fired power plants and without a central pulverizing factory should not be 18% but 18% — SD. Tests have

Table 7.2. Maximum permissible value of dispersion and SD to meet the fuel homogeneity demand

Number of increments	Maximum dispersion	Maximum SD
10	8.0	2.83
16	12.8	3.58
32	25.6	5.06

shown that in the mixture produced at the TPP coal storage site, the SD ranges from 2% for a continuous mixing method to 2.5% for a discrete method with additional mixing (Fig. 7.4, a), i.e., the maximum permissible average value is $V^{\text{daf}} = 15.5\text{--}16.0\%$. When feeding the mixture for combustion, due to additional mixing in the transportation system in the coal hopper, SD decreases

to <1%. Thus, the difference between the maximum average for the mixture and the limit for lean coal V^{daf} values increases to 2.0—2.5 SD value, and the confidence probability of the mixture compliance with lean coal increases to more than 95% (Fig. 7.4, *b*).

7.3. Experience in producing and burning mixtures with partial replacement of anthracite with gas coal

In 2009, in the conditions of temporary shortage of lean coal for anthracite-fired TPPs, which was necessary to improve the flame ignition conditions, the SE “Vuhillia Ukrainy”, based on the technology for the “G/A Thermal Coal” mixture production [18—20] developed by the Technical Standardization Committee of Ukraine TK 92 “Coal and its Processing Products” with the participation of the TETI NASU, organized at SE “Slovianoserbska coal preparation plant (CPP)” an experimental production of a mixture of 10–12% gas coal and 90—88% anthracite with a volatile yield of mixture corresponding to lean coal ($V^{\text{daf}} = 8—9\%$). Scientific support at all stages of testing for pulverization and combustion of G/A coal at the Trypilska and Zmiivska TPPs was provided by the TETI NASU of Ukraine [21—25].

The results of statistical processing of the increment parameters taken from railcars at the entrance to the Trypilska TPP (Fig. 7.5) indicate the uniformity of blending by grades when producing G/A coal: SD for volatile yield is 1.2%. The ash content variation in the samples is larger but not critical for the pulverizing system. The G/A coal storage was organized on a separate site, and no spontaneous stack heating was observed over all the time.

The tests have proven that the G/A fuel behavior during pulverization and combustion does not differ from that of lean coal. It has been found that there is no segregation of different particle size fractions (coarse particles from separator return, pulverized coal in the hopper, fine particles of discharge from the cyclone to the discharge nozzles) by volatile yield. By comparing the results of various tests, it was proven that part of unburned carbon decreases monotonically with an increase in the fuel mixture volatile yield, regardless of the grade of its components — anthracite/lean coal or anthracite/gas coal (Fig. 7.6).

After the successful completion of tests in the winter of 2009—2010, G/A coal was burned without oil or gas addition at the Trypilska and Zmiivska TPPs. In total, more than 1 million tons of G/A coal were burned. As a result of the implementation, a patent of Ukraine “Coal Fuel for Pulverized Combustion” was obtained [18], and proposals for the preparation of gas and lignite coal mixtures at beneficiation plants were issued as a patent of Ukraine “Method for Increasing the Heat of Combustion of Lignite” [25]. Thus, the fundamental possibility of burning a homogeneous mixture of anthracite with 10—12% of gas coal in anthracite-firing boiler units has been shown to improve the flame ignition conditions and increase the efficiency of anthracite combustion. Based on this

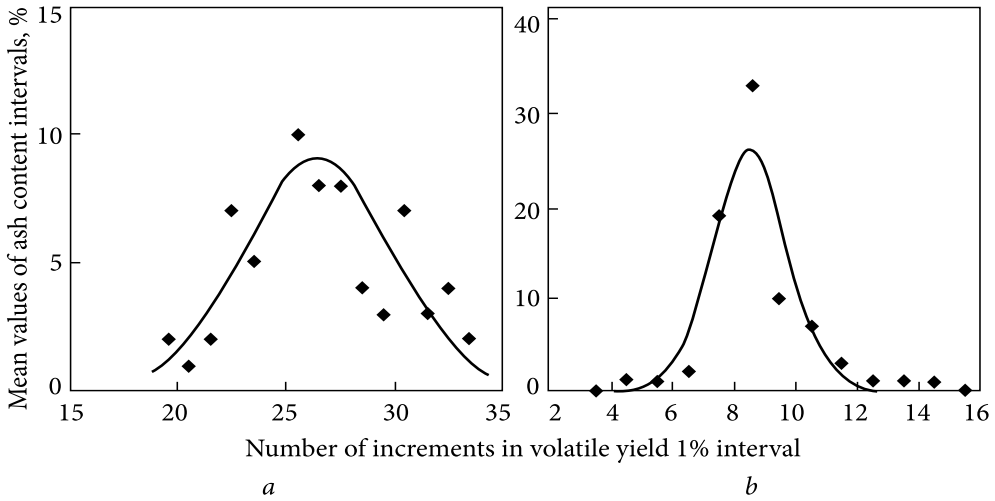


Fig. 7.5. Distribution density of the number of increments by (a) ash content A^d (average $A^d = 26.7\%$, $SD = 3.4\%$) and (b) volatile yield V^{daf} (average $V^{daf} = 8.9\%$, $SD = 1.2\%$) at the Trypilska TPP entrance: dots — fact, line — normal distribution

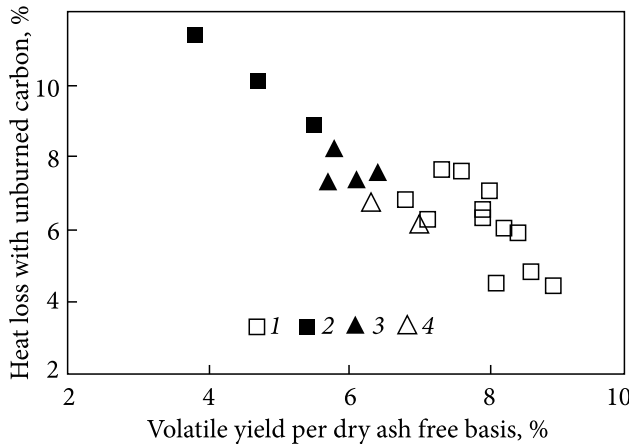


Fig. 7.6. Dependence of part of unburned carbon on the volatile yield during various tests on the combustion of coal mixtures in TPP-210A boiler units of the Trypilska TPP: 1 — experiments in 2013 (anthracite/lean coal); 2 — experiments in 2009 (anthracite/gas coal); 3 — long-term test data within 11.2009—02.2010 (anthracite/gas coal); 4 — long-term test data within 03—04.2013 (anthracite/gas coal)

experience, the provisions were included to the DSTU 4083:2012 “Hard Coal and Anthracite for Pulverized Coal Combustion at Thermal Power Plants. Technical Conditions” [6] and the “Rules for Technical Operation of Electric Power Stations and Networks” [10], provisions were included in the supply of properly prepared fuel mixtures to TPPs proving the possibility of their safe pulverization and combustion through testing.

In 2015, under the conditions of limited supplies of Donetsk anthracite and the complete cessation of lean coal supplies, the task arose to produce anthracite/gas coal blends at Zmiivska TPP but with increasing the gas coal share to 30—32% to replace anthracite as much as possible without reconstructing boiler units.

In view of the positive experience in burning G/A coal at Trypilska and Zmiivska TPPs by PJSC Centrenergo and the presence in DSTU 4083:2012 of the provision on the possibility of supplying fuel mixtures to TPPs, the “Program of Priority Measures to Expand the Fuel Base of TPPs of PJSC Centrenergo with the Involvement of Domestic Coal of the Gas Group” has been developed by the TETI NASU and approved by the Ministry of Energy and Coal Industry of Ukraine. This program aims to expand the fuel base of the Zmiivska TPP through the use of a fuel mixture with the addition of domestic gas group coal, which corresponds to lean coal in terms of technological characteristics, by the beginning of the autumn-winter period of 2015—2016. The program included the following main stages:

- Production of the fuel mixture test lot with the addition of domestic gas group coal at the coal storage site of the Zmiivska TPP, testing the mixture to prove its proper homogeneity and compliance with lean grade in terms of ash content, moisture content, and volatile yield.
- Test combustion of the fuel mixture test lot in the selected boiler unit of Zmiivska TPP.
- Organization of long-term test combustion of fuel mixture in one or two boiler units of Zmiivska TPP.

At the Zmiivska TPP coal storage site, which had two grab cranes and two galleries of belt conveyors (Fig. 7.7), mixing was implemented using the “one conveyor — two feeders” technology with the supply of anthracite and gas coal from different stacks or railcar dumpers, as well as the return of the mixture to the coal storage site to control homogeneity. The production and testing of homogeneity of the fuel mixture test lot was performed at the Zmiivska TPP coal storage site in the period of November 12—20, 2015. The following materials were used for mixing: Donetsk anthracite of the 0—6 mm class ($W_t^r = 8.2\%$, $A^d = 21.0\%$, $V^{daf} = 4.5\%$, $Q_i^r = 5500$ kcal/kg) and gas coal of the 0—13 mm class ($W_t^r = 8.5\%$, $A^d = 23\%$, $V^{daf} = 39\%$, $Q_i^r = 5450$ kcal/kg).

The tests have proven that the mixture produced at the TPP coal storage site is sufficiently homogeneous to ensure fire and explosion safety conditions of pulverizing systems (see Fig. 7.4). Based on the test results, the enterprise standard STP 05.1-30641927-001:2015 “Hard Coal and Anthracite. Methodology for Blending and Control of Quality and Technological Parameters of Coal Mixture Homogeneity” and TU U 05.1-30641927-112:2015 “Hard Coal for Pulverized-Coal Combustion. Technical Specifications” have been developed.

The test mixture combustion was planned taking into account the above conclusions, according to which, in the presence of excess air, the decrease in the anthracite combustion rate due to a decrease in oxygen concentration is compensated by an increase in the flame temperature due to additional heat release during combustion of VM and gas coal coke residue and preliminary zone-by-zone thermal calculations of the furnace based on the data calculated in [26—28] on the burning fuel share distribution over the height of the furnace. The test combustion was conducted using the 200 MW No.6 unit of TP-100 boiler at the

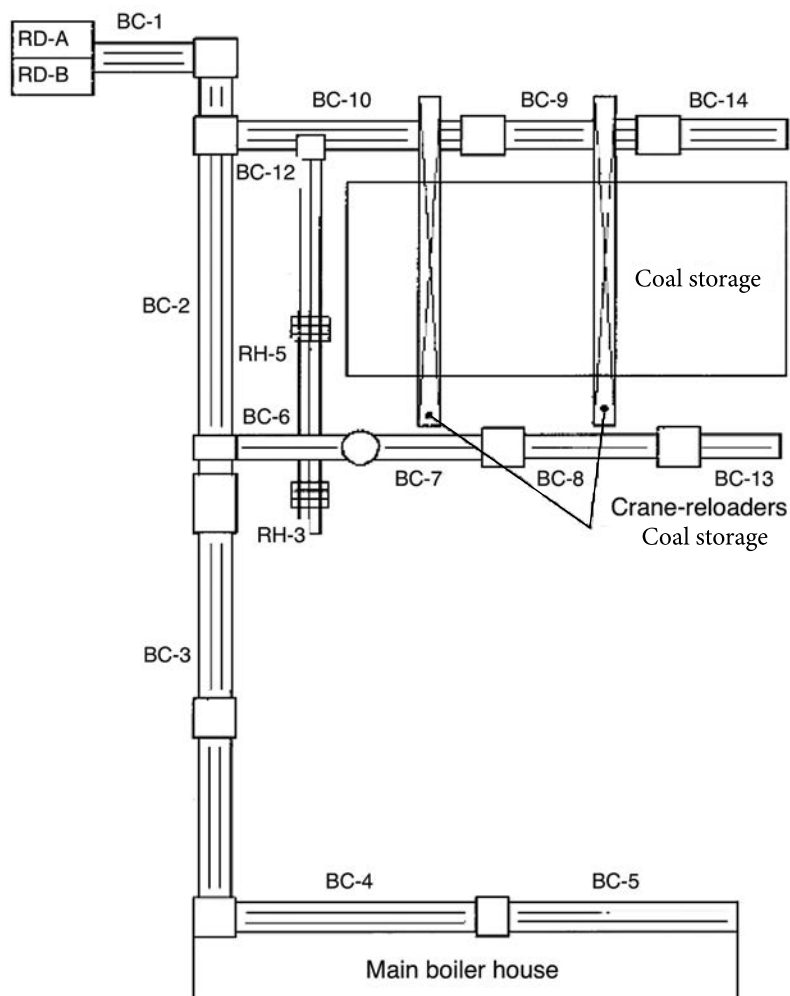


Fig. 7.7. Diagram of the coal storage site at the Zmiivska TPP: RD — railcar dumper; BC — belt conveyor; RH — receiving hopper

Zmiivska TPP from 20.11.2015 to 22.11.2015. The boiler operated in the unit load range of 130—165 MW with a pulverized coal particle size of $R_{90} = 7\text{—}8\%$. The tests have revealed that the performance of pulverizing systems does not differ from that characteristic of lean coal: there is no dust segregation by volatile yield; the boiler unit performance does not differ from that characteristic of lean coal; molten slag removal at minimal loads improves compared to anthracite, and heat losses with unburned carbon are 4.2—5.2%, which is less than when burning anthracite and is typical for a mixture of anthracite and Donetsk lean coal [29—31]. It has also been proved that, provided that the volatile yield and ash content are homogeneous, the mixture behaves and should be considered a uniform homo-

geneous fuel that corresponds to lean coal in terms of technological characteristics. Based on the test results, regime cards for boilers of 200 and 300 MW units have been developed.

In the course of further operation, anthracite and gas coal were fed to 200 and 300 MW units exclusively in the mixture. The gas coal proportion in the mixture ranged from 26.7 to 32%, and the volatile yield of the mixture was from 13.6 to 15.8%. The level of unburned carbon in the boilers of 200 MW units compared to the burning of anthracite decreased from 4.2–5.2% to 3.3–4.1%, in the boilers of 300 MW units — from 6–10% to 5–6%, and the load range without violating of molten slag removal conditions was expanded from 70–100% to 62.5–100%.

Thus, contrary to the traditional idea that anthracite burnout conditions deteriorate in joint combustion with more reactive fuel, the test results and long-term operation fully confirmed the prediction of improved combustion performance of anthracite — gas coal mixture. During 2016, almost 1 million of such a mixture was burned in Zmiivska TPP's 200 MW and 300 MW units, including more than 300 thousand tons of domestic gas coal, which means that the TPP fuel base was increased by one and a half times [3, 4, 24, 29–32].

Double-furnace 300 MW boiler units P-50 and TPP-210A at the Krivoriz'ka TPP of DTEK DNIPROENERGY JSC have Donetsk lean coal as a project fuel. Due to its high grindability, they are not equipped with three, like anthracite, but only with two pulverizing systems, one per boiler body. Other differences from anthracite-fired boilers are the reduced hot air temperature and the increased level of location of the main burners. The attempts to burn anthracite in the boilers of the Krivorizka TPP since 2004 have led to a decrease in the capacity of the units due to the limitation of the milling capacity of the mills and deterioration in the stability of ignition and molten slag removal, which required gas-oil “backlighting”.

At the end of 2017, due to the complete cessation of coal supplies from Donbas and restricted imports from South Africa, Siberian anthracite remained the only available resource of low-reactive fuel for the Krivoriz'ka TPP (0–6 mm class, $W_t^r = 12.0\text{--}13.5\%$, $A^d = 9.0\%$, $V^{daf} = 3.1\%$, $Q_i^r = 6400\text{ kcal/kg}$). Its properties are related to the peculiarities of mining (hydraulic method from thick seams): low ash content but high moisture content. In addition, its volatile yield does not exceed 3.5%, which determines its extremely low ignition and reaction ability, while making it impossible to burn it without “backlighting”. On the other hand, DTEK had a significant production of its own gas coal, which determined the task to arrange the production at the coal storage site and combustion in TPP boilers of a mixture of Siberian anthracite with 30–35% of gas coal from DTEK's production.

Despite the outward similarity, the coal storage site and fuel supply scheme of the Krivoriz'ka TPP differ significantly from the Zmiivska TPP. The conveyor scheme makes it possible to mix fuel using the “one conveyor — two feeders” technology with a return to the coal storage site to control homogeneity using only two railcar dumpers operating in parallel, which requires a simultaneous

supply of components and is rare in practice. For the anthracite already available in the coal storage site, a technological scheme was developed with the mixture formation in 3 stages: primary stack in the form of an anthracite/gas coal/anthracite “sandwich” with a layer thickness of no more than 1 m, bulldozing the fuel to the point of grabbing by the grab crane, which grabs the material along the entire “sandwich” height, and the formation of the finished mixture stack with a crane-reloader, spreading the grabs along the length of the stack.

Test mixture lots were produced using both technologies. According to the “one conveyor — two feeders” technology, railcar dumpers 1 and 2 were used, configured for 600 and 300 t/h for anthracite and gas coal, respectively. The first test lot of anthracite and Pavlohrad gas coal concentrate mixture (0—100 mm,

Table 7.3. Results of producing mixture lots and testing their homogeneity at the coal storage site of the Krivoriz’ka TPP

Date	Number of increments	Mass, tons	Parameter	W _r ^r , %	A ^d , %	V ^{daf} , %	Q _i ^r , kcal/kg
First lot — coal storage site							
07.12.17	54	11500	Average	13.6	14.74	12.13	Average 5980
			SD	0.86	1.26	1.75	
09.12.17	55	12300	Average	13.4	11.94	12.15	
			SD	0.78	1.92	2.19	
First lot — raw coal feeders							
08.12.17	10	600	Average	13.4	13.46	11.92	Average 6040
			SD	0.65	1.14	0.97	
10.12.17	6	380	Average	12.9	11.93	11.08	
			SD	0.71	0.26	0.64	
Second lot — coal storage site							
05.03.18	72	20250	Average	12.70	16.26	12.44	5729
			SD	0.81	2.73	2.50	
09.03.18	20	1560	Average	11.34	15.06	11.97	5858
			SD	0.59	2.06	1.98	
12.03.18	34	4515	Average	11.70	16.04	12.31	5839
			SD	0.60	1.61	1.50	
16.03.18	30	3515	Average	11.67	16.86	12.72	5770
			SD	0.49	1.97	2.31	
21.03.18	32	4000	Average	13.89	17.41	13.35	5610
			SD	0.64	1.49	1.09	
27.03.18	37	5350	Average	11.05	17.75	14.50	5745
			SD	0.39	2.38	1.48	

$W_t^r = 11.1\text{--}12.2\%$, $A^d = 23.0\%$, $V^{daf} = 37.5\%$, $Q_i^r = 5000\text{--}5100$ kcal/kg) was produced of a total volume of about 24 thousand tons. For the production of the second test lot using the “sandwich” technology with a total volume of 39 thousand tons, raw Pavlohrad gas coal was used, $W_t^r \leq 10\%$, $A^d \leq 36\%$. The results of producing and testing the homogeneity of the mixture lots (Table 7.3) showed sufficient mixture homogeneity for its feeding to the test combustion and a significant increase in homogeneity (reduction of SD by the ash content and volatile yield) in a sample collection of increments from the raw coal feeder.

The test combustion of test mixture lots was performed using P-50 (st. No. 2) and TPP-210 (st. No. 5 and 8) boilers. The combination of high coal moisture content, low hot air temperature, and excessive cold air suction led to a decrease in the temperature of the air mixture behind the mills to $77\text{--}89$ °C in boiler st. No. 5 and to $64\text{--}72$ °C in boiler st. No. 2. Nevertheless, combustion reliability and molten slag removal without “backlighting” were ensured in the load range of $65\text{--}85\%$ of the nominal one. During the test combustion of the first mixture lot, part of unburned carbon was $5.5\text{--}7.0\%$ in boiler st. No. 5 and $2.8\text{--}3.8\%$ in boiler st. No. 2, and of the second lot — $3.5\text{--}5.5\%$ in boiler st. No. 8. This is $1.5\text{--}2.5\%$ more than is typical for these boilers when burning lean coal but significantly less compared to burning anthracite ($10\text{--}12\%$).

Based on the test results at the Krivoriz’ka TPP, the enterprise standard for the production and quality control of the mixture at the coal storage site, a certificate and technical conditions for the fuel mixture, as well as regime cards for burning the mixture in TPP-210 and P-50 boilers with molten slag removal and without “backlighting” have been developed. The test program and intermediate test results were approved by the Electricity Section of the Scientific and Technical Council of the Ministry of Energy and Coal Industry of Ukraine (Protocol of 19.02.2018). In 2017-2018, a mixture of low-reactive high-moisture Siberian anthracite with $30\text{--}35\%$ of Pavlohrad gas coal with a mixture volatile yield of $14.5\text{--}15.5\%$ was used as the main fuel at Krivoriz’ka TPP; in this case, the use of the mixture proved to be the only alternative to natural gas “backlighting”, without which it was impossible to provide stable ignition and combustion of low-reactive anthracite with an extremely low volatile yield [3, 4, 24, 32].

Among the anthracite TPPs, the Slovianska TPP (PJSC Donbasenergo) stands out, having an 800 MW power unit with a TPP-200-1 boiler on pulverized coal fed through high-concentration pipelines from the central pulverizing plant, equipped with three non-ventilated drying and milling systems* including steam panel dryers, drum mills, and centrifugal mechanical separators (Fig. 7.8). Drying and milling systems are designed for anthracite with a volatile yield of $V^{daf} < 8\%$. When using mixtures with gas coal, it is impossible to fill the non-gas-tight drying and milling systems of a pulverizing coal plant with exhaust gases

*This means the absence of a gaseous drying agent flow. Aspiration systems (removing evaporated moisture and fine dust) of steam panel dryers and mills with appropriate aspiration fans are in operation.

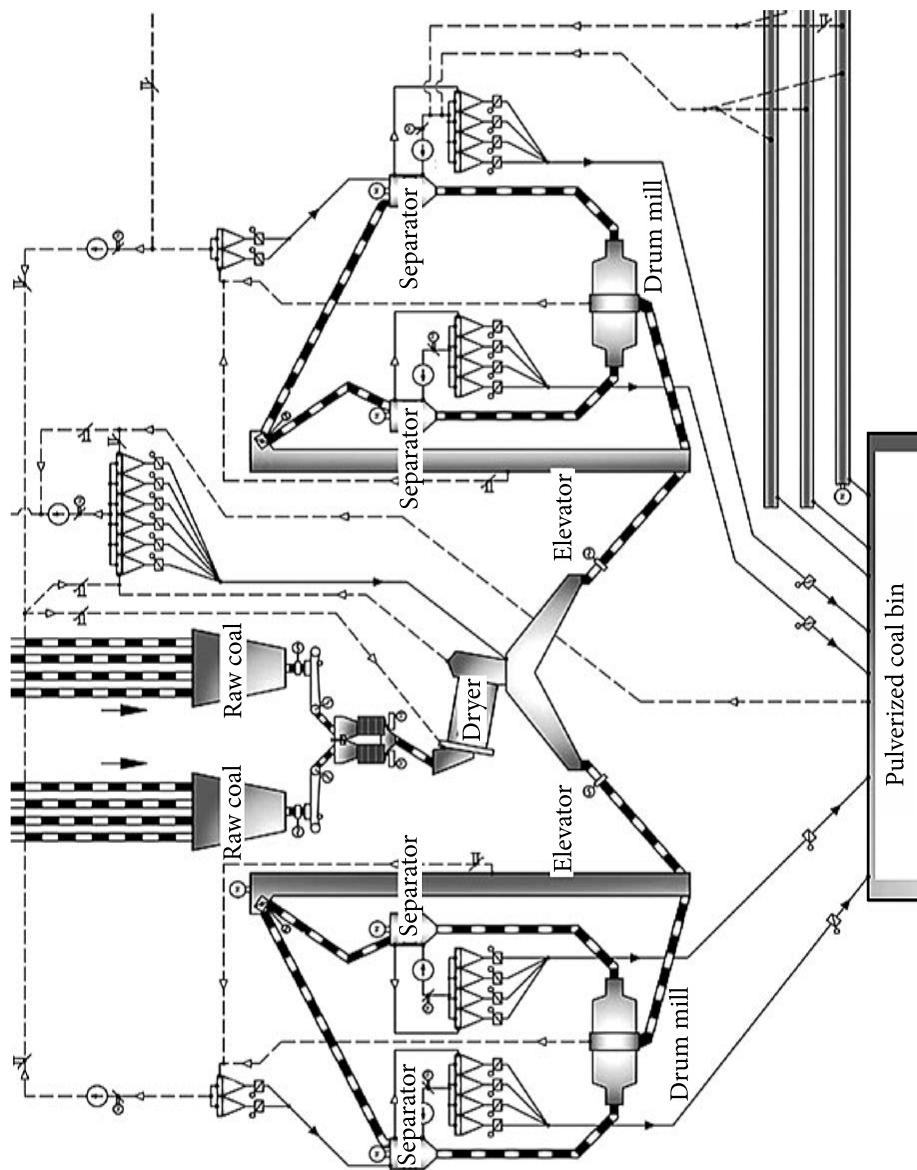


Fig. 7.8. Diagram of the drying and milling system of the central pulverizing plant at the Slovianska TPP

containing less than 16% of oxygen due to the long distance of their transportation from the boiler and is unreasonable due to a significant decrease in boiler efficiency when sampling large volumes of exhaust gases. At the same time, the existing norms [10, 11] permit gas coal drying in the air, provided that the temperature of the fuel in any element of the pulverizing system does not exceed 70 °C.

The analysis of the drying process at the central pulverizing plant revealed that the assumption adopted in the known methods for calculating non-ventilated pulverizing systems (Lebedev, 1962; Kiselgof, 1971) about the equality of temperatures of dried coal and moist air sucked from the dryer [33, 34] is valid only for the case of drying and milling anthracite with residual moisture of pre-dried and pulverized coal less than 1%. In fact, moisture from capillary-porous materials is removed sequentially: surface moisture, capillary moisture in macropores, so-called interface moisture, capillary moisture in micropores, and moisture from poly- and monomolecular adsorption. The first three types of moisture correspond to the wet state, whereas the last three — to the hygroscopic state of the material [35, 36]. It is known from studies of the drying process of porous materials (Rebinder, Kazansky, 1960) that their surface temperature approaches the ambient temperature only in the last stages, which corresponds to the loss of molecularly adsorbed (hygroscopic) moisture.

Although the temperature of the panels, where saturated steam condenses, is 120—150 °C, the coal temperature remains constant and close to the so-called “wet bulb temperature” during most of the drying period in the wet state. This is the temperature that a wet material takes in an unsaturated medium during the evaporation process of physically and chemically unbound moisture: it is the lower than the medium temperature, the lower the degree of its saturation [36—38]. The performed calculations [5, 39] have shown that the main mechanism of gas coal drying in the steam panel dryers should be based on the principle of under-drying coal to the hygroscopic moisture (by regulating the heat release from steam panels by changing the steam pressure). Under these conditions, the temperature of the pre-dried coal will be equal to the “wet bulb” temperature, which can be kept at a safe level for gas coal of no more than 70 °C by adjusting the ratio between coal and aspiration air consumption. In a balanced process, when the moisture content of the pre-dried coal is greater than the hygroscopic moisture content, the heat of the milling bodies is consumed to evaporate the residual moisture and to heat the air ventilating the mill, so that the pulverized coal temperature does not change compared to the pre-dried coal temperature.

Given these patterns, the TETI NASU has developed safe drying modes for mixtures of anthracite and lean coal with gas and for pure gas coal, taking into account the places of increased risk of dust heating and smoldering – the pulverized coal outlet from the mills, additionally heated by the heat released by milling bodies, fine dust captured by electrostatic precipitators, as well as high-concentration pulverized coal pipelines from the pulverizing plant to the boiler-pulverized coal hoppers. The essence of the recommendations was to reduce the temperature of the heating panels from 180—190 to 120—130 °C by reducing the steam pressure

from 3.6 to 0.9—1.5 bars, to increase the flow rate of aspiration fans to reduce the “wet bulb” temperature, to increase the residual moisture level of the pre-dried coal before milling from 3 to 5—6%, to coarsen pulverized coal particle size to the level recommended for lean or gas coal, to organize cold air suction before electrostatic precipitators to cool the captured dust of discharge, and to cool the compressed air used for high-concentration pneumatic transport, to 70 °C.

Tests performed in 2019—2020 showed the safety of the conditions for pulverizing lean coal and anthracite — gas coal mixtures with a proportion of gas coal in the mixture from 30 to 70%. However, taking into account the fact that the depth of anthracite component burnout decreases with the coarsening of milling, it was considered optimal to organize separate milling of low-reactive anthracite and gas coals in different drying and milling systems of the pulverizing plant with the following different pulverized types of coal mixing already in the pulverized coal hoppers of the TPP-200-1 boiler. As of March 2020, one of the three drying and milling systems of the pulverizing factory was operating on pure gas coal, with the boiler improving its molten slag removal, reducing part of unburned carbon from 3.3—3.6% to 1.2—2.3% and increasing the boiler load control range from 70—100% to 65—100%. After testing the combustion modes in 2021, the entire TPP was switched to gas coal [4, 5].

7.4. Experience in producing and burning mixtures of coal with solid fuel waste

In 2018, even before the introduction of measures for safe gas coal combustion, in the conditions of a general coal shortage at the Slovianska TPP, specialists from the TETI NASU performed tests on the making up and subsequent combustion of fuel mixtures in the TPP-200-1 boiler [4, 5, 40—43]:

- low-ash imported lean coal ($W_t^r = 10.8\%$, $A^d = 15.2\%$, $V^{daf} = 16.1\%$) and about 13% of carbon-containing ash dump material ($W_t^r = 6.7\%$, $A^d = 83.5\%$, $V^{daf} = 7.5\%$); mixture parameters are $W_t^r = 10.2\%$, $A^d = 25.8\%$, $V^{daf} = 15.7\%$;
- medium-ash imported lean coal ($W^r = 7.5\text{—}10.0\%$, $A^d = 15.0\text{—}18.0\%$, $V^{daf} = 15.0\text{—}16.0\%$, $Q_i^r = 6000$ kcal/kg) and about 16% of dry waste from bituminous coal manufacturing ($W^r = 7.0\text{—}7.8\%$, $A^d = 63.0\text{—}67.0\%$, $V^{daf} = 30.0\text{—}35.0\%$, $Q_i^r = 2124\text{—}2277$ kcal/kg); mixture parameters are $W^r = 8.0\text{—}10.0\%$, $A^d = 24.0\text{—}26.0\%$, $V^{daf} = 17.0\text{—}18.0\%$, $Q_i^r = 5300\text{—}5500$ kcal/kg;
- imported anthracite ($W^r = 6.7\%$, $A^d = 31.4\%$, $V^{daf} = 3.5\%$, $S_t^d = 1.4\%$, $Q_i^r = 4950$ kcal/kg), lean coal ($W^r = 8.2\%$, $A^d = 16.4\%$, $V^{daf} = 16.0\%$, $S_t^d = 0.3\%$, $Q_i^r = 6450$ kcal/kg), and about 8.5% of domestic petroleum coke ($W^r = 5.2\%$, $A^d = 1.4\%$, $V^{daf} = 9.7\%$, $S_t^d = 5.8\%$, $Q_i^r = 7670$ kcal/kg); mixture parameters are $W^r = 7.3\%$, $A^d = 27.9\%$, $V^{daf} = 64.0\%$, $S_t^d = 1.55\%$, $Q_i^r = 5360$ kcal/kg.

The first two mixtures were produced by alternately feeding (7:1 and 6:1, respectively) with bulldozer buckets to the receiving hopper and the third one — by forming a mixture stack weighing 4130 tons mixed with a bulldozer at the storage site. To control the mixture homogeneity, 66- point samples were taken from the

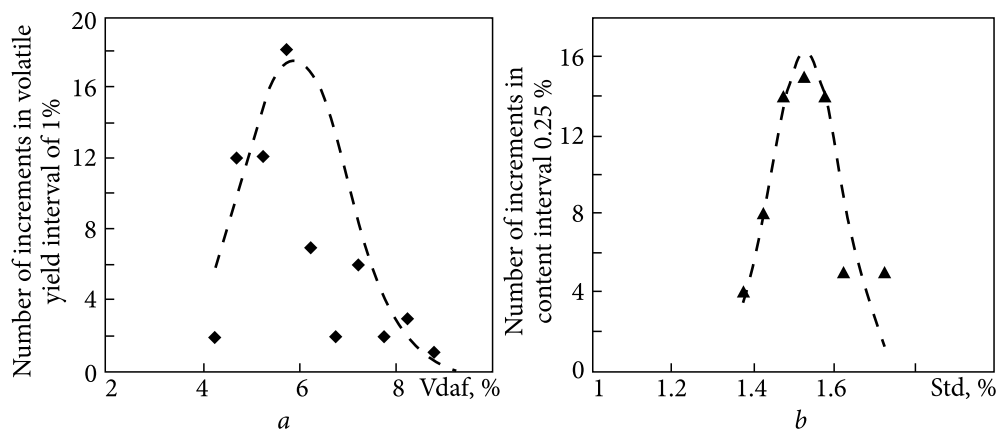


Fig. 7.9. Distribution density of the number of increments in a mixture of anthracite with petroleum coke at the Slovianska TPP storage site by volatile yield V_{daf} , average 6.4%, SD = 1.12% (a) and total sulfur content S_t^d , average 1.55, SD = 0.085% (b): dots — fact, dashed line — normal distribution

stack. The distribution density of the number of point samples by volatile yield and sulfur content is shown in Figure 7.9. The SD indicators give grounds to consider the mixture as a homogeneous fuel.

The test results show the following:

- When adding ash dump material, the milling capacity, fire, and explosion safety conditions during the pulverization process did not change, and the combustion parameters, in particular, the conditions of molten slag removal and the range of load control without “backlighting”, deteriorated compared to lean coal. The additional contribution of carbon heat release from the ash dump material (about 5% of the heat) can be considered positive.

- When adding dry waste from bituminous coal manufacturing, the milling capacity of the pulverizing systems has increased significantly, but at the same time, smoldering of fine dust deposits in the electrostatic precipitator was noted. As the temperature in the flame core has increased significantly compared to lean coal, so molten slag removal conditions, and the range of load control without “backlighting” have improved. The carbon content in fly ash has decreased from 11–15 to 3–7%, which indicates an overall part of unburned carbon decrease from 3.3–3.6 to 2.2–3.3% and an additional contribution of carbon heat release from the ash dump material (about 9% of the heat).

- When adding petroleum coke, the fire and explosion safety conditions for the pulverization process have not changed compared to anthracite and lean coal. The temperature in the flame core has increased significantly, molten slag removal conditions and the range of load control without “backlighting” have improved, and the carbon content in the fly ash has decreased from 11–17 to 7–10%, which indicates an overall part of unburned carbon decrease from 5–6 to 2.5–3.5% due primarily to the complete petroleum coke burnout. Data from

the environmental measurements indicate that the sulfur dioxide content in exhaust gases recalculated for 6% O_2 , 4440 mg/nm³, does not exceed the upper limit of the standardized level (4482 mg/nm³ according to the emission permit dated 18.01.2018) and approximately corresponds to the technological emission standard for lean coal.

In general, the test results have proven the fundamental possibility of using petroleum coke as a 10–15% admixture to the low-reactive fuel at Slov'yanska TPP without changing the composition and operating modes of the equipment, without violating current environmental permits, with an improvement in the molten slag removal mode and the completeness of pulverized coal burnout.

At the end of 2017, the problem of anthracite shortage at the Zmiivska TPP was solved by switching TP-100 boiler units st. No. 2 and No. 5 to gas coal according to the project of KOTLOTURBOPROM LTD. Soon, a shortage of domestic gas coal emerged, to compensate for which, it was necessary to supply coal of the appropriate grade from the USA. However, the LHV of American coal, more than 6500 kcal/kg, was too high for combustion in the reconstructed TP-100 boilers designed for 5000–5400 kcal/kg. The problem was solved by burning a mixture of US coal and carbon-containing material from the TPP ash dump, which ensured the fire and explosion safety of the pulverization process.

To produce the test fuel mixture lot, high-calorific gas coal from the USA was used ($W_t^r = 9.7\%$, $A^d = 7.7\%$, $V^{daf} = 43\%$, $Q_i^r = 6583$ kcal/kg, supplied from railcars), as well as material from the TPP ash dump ($W_t^r = 6.3\%$, $A^d = 84.4\%$, $V^{daf} < 1\%$, $Q_i^r = 700$ kcal/kg, supplied from a separate stack at the storage site). The test fuel mixture lot was produced by the blending method using the “one conveyor — two feeders” technology (see Fig. 7.7). Railcars with US gas coal were delivered to one of the railcar dumpers; fuel was fed to belt 1, then to belt 2 at a consumption of about 700 t/h. The material from the TPP ash dump was fed to belt 14 by grab crane 2 at a consumption of 160–180 t/h.

Then, through belts 9 and 10, it was mixed with gas coal at belt 2. The finished mixture was fed through belt 6 to the active storage site for stockpiling. In total, about 4 270 tons of fuel mixture was produced using 3 336 tons of gas coal (about 78% of the mixture).

A fuel mixture lot was tested while forming a stack of the finished mixture. Point samples were taken from the mixture stack after leveling with a bulldozer at a depth of at least 0.4 m at 32 points located on the surface (16 points) and slopes of the stack (16 points). The results of statistical processing of the results of

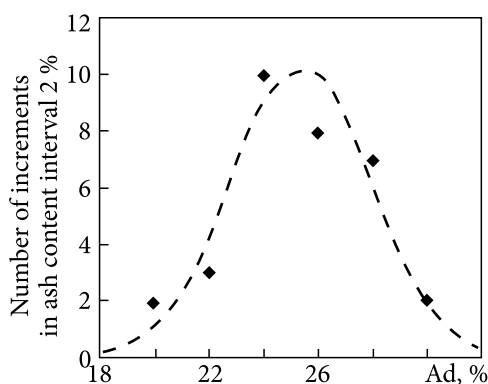


Fig. 7.10. Distribution density of the number of increments in ash content by ash content A^d (average value $A^d = 25.3\%$, $SD = 2.5\%$) compared to the normal distribution

producing and testing the fuel mixture lot are shown in Figure 7.10. They indicate that the average mixture quality meets the requirements for gas coal of the 1st category by DSTU 4083:2012, the ash content distribution in the increments is close to normal (Gaussian), which indicates the absence of a systematic mixing error, and the mixture homogeneity is satisfactory.

In total, more than 15 thousand tons of the mixture were produced and tested for the test combustion, with 28—33 point samples from each lot taken and analyzed. The average LHV in the lots ranged within 5100—5700 kcal/kg, moisture content — 9.6—10.6%, and the ash content on a dry basis — 20—27%. The variation of moisture content, ash content, and volatile yield in the increments within lots did not exceed the characteristic values for manufactured coal and concentrate.

Since the reconstructed boilers used the spent dusty drying agent to transport and fed pulverized coal to the main burners, effective combustion of the mixture was also achieved along with improving technical and economic indicators due to the additional carbon heat contribution of the ash dump material, which was burned out by over 80%, while the carbon content in fly ash did not exceed 2—3%. This fully confirmed the prediction of the possibility of effective post-burning of carbon of the ash dump material when it is fed to the main burners and ensured the successful TPP operation in the winter season of 2017—2018 [3].

The boilers of the Cherkaska CHPP of the BKZ-220-100 GC type are the only ones in Ukraine with cyclone pre-furnaces with molten slag removal. The boilers were designed to burn gas coal concentrate from the Donetsk basin with the following characteristics: LHV $Q_i^r = 4850$ kcal/kg; ash content on the as-received basis $A^r = 19.6\%$ ($A^d = 22.5\%$); moisture content on as-received basis $W^r = 13.0\%$; sulfur content on as-received basis $S^r = 4.0\%$; volatile yield $V^{daf} = 43\%$; ash flow temperature $t_c = 1300—1360$ °C. In recent years, these boilers have successfully burned domestic gas coal with the following parameters: $W_t^r \leq 14\%$, $A^d = 18—25\%$, $V^{daf} \leq 44\%$, $S_t^d = 2.0—3.0\%$, $Q_i^r = 4800—5400$ kcal/kg, and ash flow temperature $t_c < 1400$ °C. Of the above parameters, the most critical in terms of the organization of conditions for stable molten slag removal in horizontal cyclone pre-furnaces are ash content and ash flow temperature.

The long-flame coal (0—50 mm) supplied from Kazakhstan for Cherkasy CHPP in the context of a general fuel shortage in 2021 had the following characteristics: $W_t^r = 11.6\%$, $A^d = 13.0\%$, $V^{daf} = 45.3\%$, $S_t^d \leq 0.6\%$, $Q_i^r = 5507$ kcal/kg, and ash flow temperature $t_c > 1450—1500$ °C. Such coal can be burned in BKZ-220-100 GC boilers only in a mixture with fuel with the higher ash content (to provide a protective coating of the cyclone pre-furnace walls) and with the lower ash flow temperature (to ensure free molten slag removal from the pre-furnaces). It is also important that due to the high volatile yield and low ash content, the explosive ability coefficient K_t exceeds 4.5 (with a maximum permissible value of 3.5), and it can only be reduced by increasing the ash content.

The most affordable of the high-ash fuels for mixturing is the carbon-containing material from Cherkaska CHPP ash dump with the following pa-

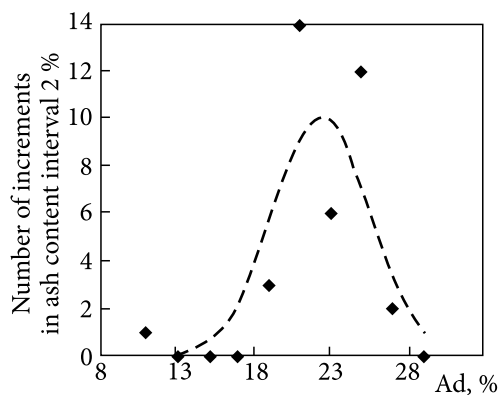


Fig. 7.11. Comparison of the distribution density of the number of increments by ash content by ash content A^d with the normal Gaussian distribution for a lot as a whole (average $A^d = 22.4\%$, $SD = 3.09\%$)

rameters: $W_t^r = 22\text{--}24\%$, $A^d = 70\%$, $V^{daf} = 40\text{--}42\%$, $S_t^d \leq 0.4\%$, $Q_i^r = 1100\text{--}1300$ kcal/kg, and ash flow temperature $t_c \leq 1330$ °C. The high VM yield on the dry ash-free basis at the actual ash content in this material is only partially related to the discharge

of dusty drying agent into the convective pass, the main contribution to the sample mass loss during the analysis of VM yield is made by inert products of thermal decomposition of moistened ash into CO_2 carbonates and hydrated moisture. At the same time, it should be noted that, unlike the carbon-containing ash from the Zmiivska TPP, the carbon in the ash dump material of the Cherkaska TPP is represented mainly by coal dust not captured by the battery cyclones of the open pulverizing system, which, together with the spent drying agent, is discharged before the ash traps and has enough volatile substances for a stable ignition. Therefore, the use of ash dump material to create a mixture allows for at least partial utilization of this carbon, improving the technical and economic characteristics of the boiler. The calculated ratio of the components in the mixture of 85:15 was previously determined as the closest to the quality of the project fuel in terms of ash and LHV, as well as the possibility of ensuring a high-quality molten slag removal mode.

An important condition for producing a mixture of the above components is its thorough mixing to obtain maximum homogeneity. While the fuel storage facilities have been used to average fuel of similar quality grades with mechanical mixing using a bulldozer on the storage site, the homogeneity of a mixture of fundamentally different components with a significant difference in ash content could only be obtained by using a scheme of feeding components from tared swing feeders to one conveyor with subsequent additional mixing on three overflows on the way to the raw coal hoppers, which was realized by the TETI specialists [43].

During the three cycles of loading the mixture into the boiler raw coal hoppers (about 400 tons), a total of 41 increments were taken with equal time intervals using a sampling machine and the sample preparation machine located in the crushing building. The results of the statistical analysis of increments are shown in Figure 7.11. The SD value of ash content for all analyzed increments (3.09%) is significantly lower than the permissible SD value for this number of increments (5.51%), which indicates sufficient mixture homogeneity. As much as 87% of increments have an ash content in the range of 19.3–25.5%. Only one increment has revealed a pure long-flame coal movement due to the short-term suspension

of the ash material component in the receiving hopper, due to which the SD for the ash content of one of the three sub-lots slightly exceeded the permissible value, but this cannot have an impact on the quality of fuel in the pulverizing system due to its additional mixing on the bulk and in the raw coal hoppers.

The average ash content of the test mixture lot (22.4%) is the same as that of the project coal (22.5%). The average LHV of the mixture is 100–150 kcal/kg lower than that of the project coal (due to higher moisture content and lower level of higher heat value on a dry ash-free basis), but, like the project coal, it belongs to the 2nd quality category according to DSTU 4083:2012, whereas the LHV of pulverized coal dried to 2% moisture content (5330–5400 kcal/kg) belongs to the 1st quality category. A slightly higher value of volatile yield compared to the project coal is not critical for hammer mills which are included in the pulverizing systems of boilers at the Cherkaska CHPP and is within the permissible range of 35–45% according to DSTU 4083. In terms of sulfur content (0.6%), the mixture looks much better than the project coal and provides a decrease in sulfur dioxide emissions by several times compared to domestic coal. According to the totality of parameters, the mixture is a full-fledged substitute for the project fuel, which was confirmed by its test combustion in BKZ-220-100 HZ boilers.

7.5. Results and prospects for using coal mixtures at TPPs in Ukraine

The examples provided in this chapter on the production and combustion of mixtures of significantly different types of coal at TPPs and CHPPs to improve the combustion conditions of anthracite and its partial replacement with domestic gas coal, to bring the characteristics of imported coal to the operational requirements of existing pulverized coal boilers, and to involve residual carbon from coal waste and petroleum coke in the fuel base of power plants should be supplemented by the use of mixtures of imported coal with refractory ash and domestic coal for ensuring the conditions of reliable molten slag removal [3, 29, 44, 45]. Given this, in general, by the beginning of 2022, the mixtures had been burned at 4 TPPs and 6 CHPPs, with a total volume of over 9 million tons, and the volume of anthracite replacement with imported non-project fuels and domestically mined gas coal had been over 6 million tons. Based on the experience gained, DSTU 4083:2012 “Hard Coal and Anthracite for Pulverized Coal Combustion at Thermal Power Plants. Technical Conditions” [6] and the “Rules for Technical Operation of Electric Power Stations and Networks” [10] included the provisions on the supply to TPPs of properly produced fuel mixtures proving the possibility of their safe pulverization and combustion through testing. Research and developments in the direction of manufacturing and burning homogeneous fuel mixtures along with the results of their implementation at TPPs and CHPPs have become one of the most important parts of the work of TETI NAS of Ukraine “Scientific bases of innovative technologies of anthracite replacement at thermal power

plants and their implementation”, marked by the State Prize of Ukraine in the field of science and technology for 2019.

In addition to ensuring the uninterrupted operation of TPPs and CHPPs in the face of the cessation of Donetsk anthracite supplies, this section also addresses an important strategic task. After the reintegration of Donbas, its anthracite mines will also return, which will be expensive and environmentally dangerous to close immediately. At the same time, low reaction ability makes Donetsk anthracite uncompetitive compared to imported lean coal. Combustion of Donetsk anthracite as part of fuel mixtures with mixture properties close to those of lean coal makes it possible to restore its demand for existing TPP boiler units designed for low-reactive coal and to burn it with acceptable technical and economic performance without “backlighting” in an extended load control range.

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CO-FIRING OF BIOMASS AND COAL AT TPPs AND CHPPs

This chapter is devoted to the peculiarities and practical experience of co-firing coal with biomass or peat in one furnace device with independent feeding and preparing in pulverized coal boilers and boilers with a dense bed, as well as alternating combustion of coal with biomass and/or peat.

8.1. Goals and peculiarities of co-firing of biomass and coal

Within the framework of the policy declared by developed countries to reduce greenhouse gas emissions, taking into account the “carbon neutrality” of biomass [1], the lack of sulfur in it, low generation of nitrogen oxides during its combustion [2] and significant resources in Ukraine [3, 4], the use of biomass as an environmentally friendly substitute for fossil fuels is becoming increasingly relevant. In particular, the envisions of the new Energy Strategy of Ukraine until 2050 expanding bioenergy capacity, including CHPPs, to 18 GW [5]. In more specific but no less ambitious plans of NPC “Ukrenergo” for the coming years, the construction of 1.1 GW of new thermal power plants operating based on biomass is planned, which will require \$1.2 billion of investment, or nearly \$1,100 per set kW of capacity [6].

However, the feasibility of these plans raises doubts. The elimination of investment surcharges on the energy tariff with the introduction of the “new energy market” in 2019 [7] left two main sources for the return on investment in the energy sector: through the increased “green tariff” for electricity sales or the lower fuel costs used in new or reconstructed power plants. Technical problems associated with the cost of fuel pellets or granules manufacturing with unifying characteristics from raw fibrous biomass with a wide range of properties, as well as the underdeveloped supply logistics, etc. make the price of biomass in energy equivalent at least as high as that of steam coal (about 5,450 UAH/ton

of CE* as of the beginning of 2024), while the cost of electricity generated from biomass is no lower than the cost of electricity from coal, which approximately corresponds to the market average price [7]; that is, the source of return on investment in the construction of large biomass power plants through lower fuel costs is no longer viable.

On the other hand, the seasonal nature of agrobiomass supply makes year-round fuel provision for large energy facilities impossible, making biomass be considered as a supplementary fuel only. Co-firing biomass with coal in existing pulverized coal boiler units at TPPs is considered worldwide as a short-term, low-cost, and sustainable option for utilizing renewable energy that carries low risk and requires minimal investment while promising reductions in emissions of CO₂, sulfur dioxide, and nitrogen oxides [8–10]. When conducting developments in this direction, it is important to consider the conclusions of the studies [11–13] regarding the criterion of the stated specific combustion products' consumption (the ratio of the specific stoichiometric consumption of combustion products to the LHV of the fuel). This value is significantly higher for biomass than for coal, which ensures a decrease in the adiabatic combustion temperature and an increase in the heat removal from the furnace to the convective heating surfaces. Based on this criterion, the conversion to biomass combustion without loss of power while maintaining the dimensions of the furnaces of small and medium-sized coal boilers is limited by a decrease in the heat absorption by the furnace to a level below the required shear of heat for evaporation. For subcritical and supercritical pulverized coal boilers of high power, such conversion could disrupt conditions for molten slag removal. This explains the widespread adoption of technologies for coal/biomass co-firing (CBCF) in flame, as they do not require a major reconstruction of existing pulverized coal furnaces. The analysis of international experience [8, 10, 14–17] shows that the most common types of CBCF technologies are as follows:

1. Direct CBCF, where biomass and coal are simultaneously fed into the furnace of the steam generator. At the same time, the options when biomass is mixed with coal directly at the fuel storage site, milled together, and simultaneously fed into combined burner systems are not acceptable for Ukraine's existing pulverized coal boilers with ball-drum mills and intermediate pulverized coal hoppers. This is due to the different mechanisms of milling biomass and coal, as well as the varying propensity to spontaneous combustion and explosive ability of milled biomass and pulverized coal. Modifications of this technology which involve pre-processing biomass using separate milling devices and feeding it into combined burners or specially designated burners are more suitable for domestic conditions.

2. Parallel CBCF, which involves connecting the existing pulverized steam coal generator to a separate steam generator burning milled biomass in a flame within the same power unit;

*CE (coal equivalent) — conventional fuel with LHV of 7000 kcal/kg (29.309 MJ/kg).

3. Indirect CBCF, which involves processing the biomass in primary furnaces or gasifiers, with the resulting pyrolysis gas or gasification products' co-firing with coal in the furnaces of steam generators.

In Ukraine, a project for CBCF in the existing pulverized TPP-210A coal boiler of 300 MW unit has also been developed [18, 19], which is discussed in detail in Section 8.2. However, the implementation of this and other similar projects is hindered by the Ukrainian legislation, which does not provide for a “green tariff” for the share of clean energy generated by biomass when co-fired with coal. As a result, such projects lack a mechanism for return on investment. Another factor that complicates the use of biomass in large-scale energy production is the supply of gas to the energy sector under the mechanism of “Imposing Special Obligations”, that is, at a preferential price. For TPPs, this price is 10,950 UAH, while for CHP plants, it is 16,500 UAH per 1,000 m³, including VAT (9,460 and 14,260 UAH/ton of CE, respectively) [20]. Given the lower efficiency of boilers when burning biomass, the additional costs of storage, fuel preparation, and arrangement of efficient combustion and ash capture, the difference between the price of biomass and the preferential prices for gas of TPPs and CHPPs is not large enough to ensure a return on investment for converting gas and oil boilers at power plants to biomass combustion within an acceptable timeframe. Nevertheless, developing such projects in the long term seems necessary.

Industrial heat power engineering is hardly covered by state regulation of energy prices. In particular, a significant part of industrial CHPPs have boilers that are either gas-oil or anthracite-fired with a dense bed, converted to natural gas long ago [21]. The relevance of replacing gas with biomass has increased due to the rise in gas prices, which are significantly higher for the industrial sector than the preferential prices for TPPs [4]. According to the Ukrainian Energy Exchange, the market price of imported gas (including VAT but excluding domestic transportation costs) ranged from 20,000 to 27,000 UAH per 1 000 m³ (17,300 to 23,300 UAH/tons of CE) in the second half of 2023. This difference in gas and biomass prices allows expecting a reasonable return on investment, if not in new construction, then at least in the reconstruction of existing boilers. Additional arguments in favor of reconstruction rather than new construction include the possibility of carrying it out within a short period between production seasons. It should be noted that opting for reconstruction over new construction is not specifically a Ukrainian choice caused by the difficult economic conditions of enterprises. Thus, in the 2010s, in 10 eastern US states, about a third of the 31 776 boilers at boiler plants and industrial CHPPs operated on coal, gas, and oil were considered more feasible to convert to biomass through reconstruction rather than replacement [22]; Denmark and Germany prioritize the reconstruction of medium-capacity industrial and municipal boilers to switch them to biomass [23]. Certainly, this requires to take into account differences in biomasses related to combustion processes, slag formation, and the heat irradiation of combustion products.

The main physical characteristics of solid plant biomass as a fuel include low bulk density (40—300 kg/m³), high moisture content (15—40%), diversity, and

fibrous nature of its original structure (husks, wood waste, wood chips, straw, stems, cobs, etc.), which significantly complicates fuel preparation. To reduce transportation costs and increase the convenience of storage and combustion, biomass is chopped and pressed, which results in reducing the moisture content to below 10% and increasing the bulk density to over 500–600 kg/m³; the particle size is unified, calorific value increases, and the specific volume of combustion products per unit of energy produced decreases. The most commonly used form of biomass fuel is pellets — compressed cylinders with a diameter of 6–10 mm and a length of 60–100 mm that have gained sufficient mechanical strength [2, 3, 18]. Pellets made from agrobiomass waste, such as sunflower husks, are considered cheaper than wood-based ones [3, 4]. The kinetic characteristics of biomass pyrolysis and combustion compared to coal are described in detail in Chapters 2–4.

Although the ash content of solid biomass fuel does not usually exceed 3–8%, it is the properties of its mineral component that play a crucial role when choosing a method for combusting it at power plants. The fact is that the high content of alkali metal oxides in the ash of agrobiomass waste (up to 25–40%, depending on the volume and degree of absorption of mineral fertilizers applied [3, 24–27]) determines low slagging temperatures of the convective heating surfaces of boilers, which results in frequent forced shutdowns for cleaning. Typically, the temperature at which slagging of solid fuels with high content of alkali and alkaline earth metal oxides in the ash begins is considered 945 °C [28]. However, this does not mean that the furnace outlet temperature of 900 °C is safe for slagging. The presence of unburned carbon in the fly ash determines the possibility of smoldering of its deposits on heating surfaces, which can cause the temperature to rise before the ash begins to melt. For this reason, the deposits on the heating surfaces of boilers, where the agrobiomass combustion occurs in flame or combined flame-bed furnaces and the mass loss due to fly ash incineration reaches 40–70%, have a molten, dense, and strong structure, which is poorly amenable to mechanical cleaning. These deposits significantly reduce heat absorption and increase heat loss with exhaust gases [29]. The only exception is the combustion of a small agrobiomass share in pulverized coal boilers, where the accumulation of deposits from the biomass fly ash is hampered by the abrasive properties of the coal fly ash. However, in general, wood biomass and peat are preferred for combustion in flame furnaces, as their ash contains significantly lower levels of alkali metals.

In contrast, the experience in burning sunflower husk pellets in a dense bed on a direct-drive grate suggests [11] that if optimal furnace conditions are maintained when the furnace outlet temperature does not exceed 900 °C and the excess air coefficient in the furnace is 1.4, the fly ash incineration mass loss does not exceed 15–20%, while the deposits on heating surfaces have a loose structure and can be cleaned even with steam blowing. The fact should also be considered that when burning pellets in a dense bed, the removal of solid residue from the furnace is significantly lower compared to burning milled biomass in flame furnaces.

Taking into account the mentioned characteristics of biomass fuel, we can conclude that regarding wood waste, other types of biomass with low content of alkali metal oxides in the ash, and peat, the main combustion technologies described in [3, 11] and used in industrial CHPP boilers are suitable for application. These technologies include flame (pulverized) ones, dense and fluidized bed combustion, and combined flame and bed combustion [29]. This is confirmed by years of positive global experience in burning wood waste on its own or co-fired with coal using these technologies. For agrobiomass waste with high content of alkali metal oxide and slagging ash properties, it is more appropriate to burn it in a dense bed in the form of pellets. This method ensures a temperature at the furnace outlet of no more than 900 °C, low removal of solid residue from the furnace in the form of fly ash, and a low content of unburned carbon in it.

This chapter presents the results of developments in co-firing biomass with coal in pulverized coal boilers at TPPs, as well as the experience of converting gas-oil boilers at industrial CHPPs to biomass and gas coal combustion and their subsequent operation. It also addresses the issue of reducing the slagging propensity of heating surfaces when co-firing or alternately firing these fuels.

8.2. Development of technical solutions for co-firing of biomass with coal in pulverized coal boilers at TPPs

As a result of experimental studies conducted with laboratory facilities, using the VGP-100V pulverized combustion unit with a coal capacity of up to 50 kg/hour and mathematical modeling methods, a synergistic effect has been confirmed when co-firing 8—12% biomass with anthracite. That is, this effect improves the ignition and combustion conditions of pulverized anthracite due to the heat release during the combustion of biomass volatile substances [14, 15, 30—34]. It has been revealed that it is expedient to separately prepare and feed pulverized coal and milled biomass to the boiler, considering the different milling properties and safety requirements for pulverizing systems, as well as the optimal particle size for biomass after milling (2—2.5 mm).

According to the Protocol of the Scientific and Technical Council of the Ministry of Energy and Coal Industry dated November 10, 2016, the TETI of NAS of Ukraine was designated as the leading institution for the scientific support for the project on co-firing anthracite and solid biofuel in TPP-210A boilers at the Trypilska TPP. The technical specifications for the project, based on the technical solutions developed by TETI, were approved by the Protocol of the Scientific and Technical Council of the Ministry of Energy and Coal Industry of Ukraine dated April 25, 2017.

The calculated characteristics of the fuels are given in Table 8.1. The value of the stated specific combustion products consumption for anthracite is 0.33 nm³/MJ, for wood pellets 0.35 nm³/MJ, and for the biomass-coal mixture 0.333 nm³/MJ. The similarity of this criterion for anthracite and the mixture indicates that this

biomass share in terms of heat yield does not require structural changes to the furnace, boiler heating surfaces, or significant modifications in the burner system. At the same time, even this share of biomass results in a noticeable reduction in sulfur dioxide emissions (by 9% — from 3523 to 3205 mg/nm³ at 6% O₂) and carbon dioxide greenhouse gas emissions and, most importantly, improves the ignition and combustion conditions of low-reactive anthracite.

The last statement requires further explanation. The fact is that although the adiabatic temperature of anthracite combustion is higher than that of biomass, the calculation of adiabatic temperature uses the total value of LHV of the fuel. However, in practice, the temperature in the active combustion zone is determined by the portion of the fuel that has burned in that zone. This portion depends on the fuel reactivity and the temperature within the combustion zone. For low-reactive anthracite, the calculated burnout rate in the active combustion zone does not exceed 85–88% [35, 36], and in the case of poor-quality anthracite, it may be even lower. This reduces the temperature in the active combustion zone to such an extent that maintaining conditions for molten slag removal requires gas-oil “backlighting” in the furnace. For highly reactive biomass, with a volatile yield exceeding 78%, the burnout rate in the active combustion zone approaches 100%. Therefore, adding biomass to an anthracite flame acts as a kind of “backlighting” which increases the temperature in the anthracite ignition zone. By facilitating ignition, the burnout rate of anthracite in the active combustion zone increases, which, in turn, raises the flame core temperature.

These considerations are confirmed by the results of zone-by-zone thermal calculations, for which the furnace was divided into five zones, as shown in Figure 8.1.

Figure 8.2 shows the calculated outlet temperature of each zone when anthracite is burned separately or together with biomass. It can be seen that in co-combustion, the temperatures in the lower and especially the middle part of the furnace increase, which is also accompanied by an increase in the burnout rate of anthracite. Indeed, the increase in biomass stated specific combustion products consumption slightly increases the heat transfer from the active combustion zone and the furnace outlet temperature. However, due to the use of wood pellets and a limited share of biomass in the fuel, this increase is insignificant and does not affect the slagging conditions of the heat-exchange shields or heat losses with exhaust gases.

Table 8.1. Characteristics of the calculated-fuels for co-firing in TPP-210A boiler

Fuel	Residue on the sieve, μm	Composition on the “as received” fuel basis, %								Q_i^r , MJ/kg	SO_2 , mg/nm ³
		A ^r	W ^r	V ^r	C ^r	H ^r	O ^r	N ^r	S ^r		
Anthracite Shredded pellets	$R_{90} = 7\%$	19.0	7.5	4.0	68.0	1.45	1.90	0.58	1.57	24.23	3523
	$R_{200} = 30\%$	0.37	8.7	78.43	47.17	5.76	37.86	0.13	0.027	17.63	371

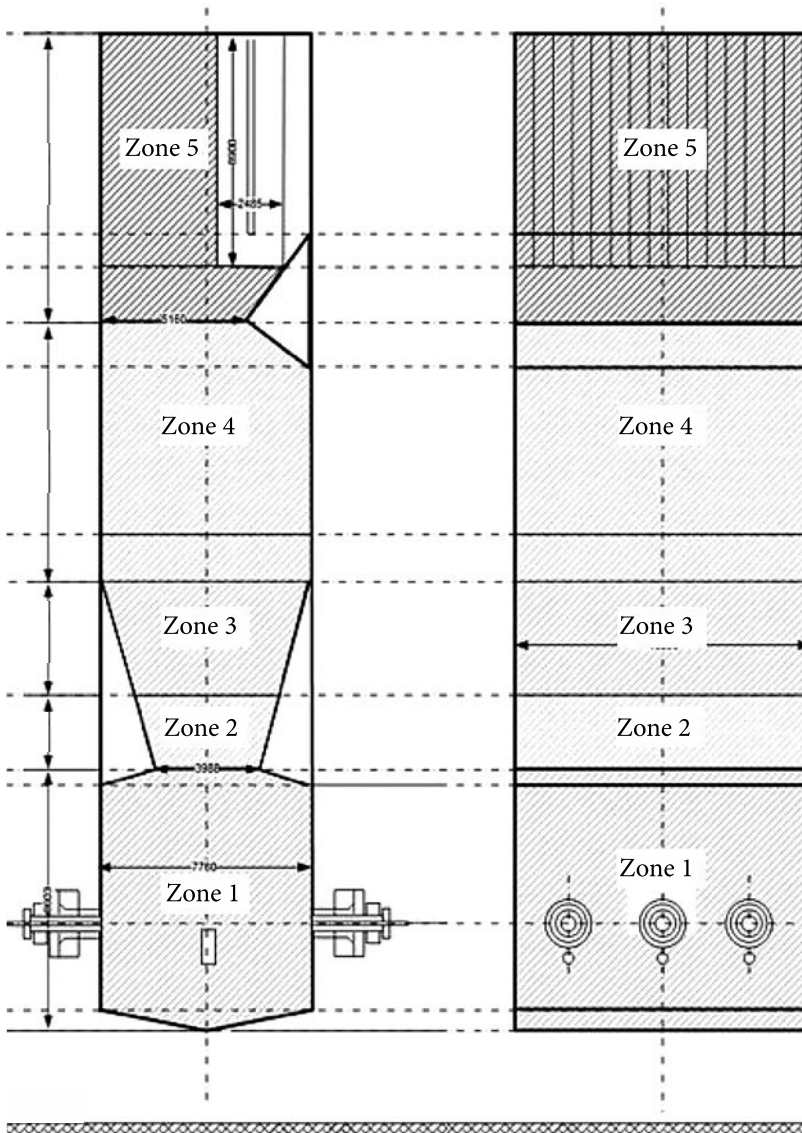
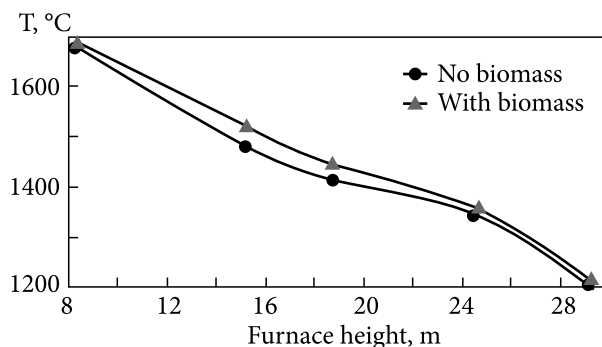


Fig. 8.1. Scheme of the furnace chamber of the TPP-210A boiler with indication of zones for zone-by-zone thermal calculations

Fig. 8.2. Temperature distribution for pulverized fuel and gas flow along the furnace height (at the outlets of zones in the zone-by-zone thermal calculation)



The technical solutions developed by the TETI NASU included the design of a unit for unloading, storage, drying, and shredding wood pellets (Fig. 8.3), as well as a scheme for transportation and the design of a unit for feeding the shredded biomass to the burners. It was taken into account that biomass loses most of its external moisture at the stage of pellet production, so its drying, which is necessary only to ensure flowability, can be arranged in a non-ventilated drum dryer with heated steam panels. Shredding to a particle size of 200 μm can be done in a separate hammer mill, and the temperature of the shredded biomass should be maintained at no more than 45 $^{\circ}\text{C}$ to ensure fire safety, according to the recommendations in [14].

Different bulk densities and particle sizes of pulverized coal and shredded biomass require their separate transportation. In TPP-210A boilers at the Trypil'ska TPP, pulverized coal is transported to the burners through high-concentration supply pipelines under pressure (HCSP_p), which are inserted into the primary air pipelines 2–3 m before the burner inlet [37]. The temperature of the transported air, due to its compression to 4 atm, reaches 100–140 $^{\circ}\text{C}$, while the temperature of the primary air at the HCSP_p pipeline inlet reaches 350 $^{\circ}\text{C}$, which is unacceptable for biomass and may cause it to smolder at the burner inlet. Therefore, for shredded biomass, a high-concentration biomass transport system at underpressure, created by a steam ejector, was chosen [38] (Fig. 8.4) with its introduction directly into the central channel of the burner (Fig. 8.5).

With a biomass consumption rate of up to 1.5 t/h per burner, the capacity of the shredded biomass bunker to ensure the 4-hour operation of 12 boiler burners should be 72 t, the diameter of the HCSP_{UP} pipeline — 50–70 mm, and the steam consumption per ejector — about 70 t/h.

The preliminary design by the TETI based on the developed technical solutions, was approved at the Trypil'ska TPP [17]. Unfortunately, due to the cessation of supply of Donetsk anthracite to the “new energy market”, which has made electricity supply from TPPs unprofitable and investment in the reconstruction of generating equipment impossible, and to the lack of extension of the “green tariff” for electricity generation from a biomass-coal mixture, which made the return on investment in coal-biomass co-combustion unfeasible, the developed

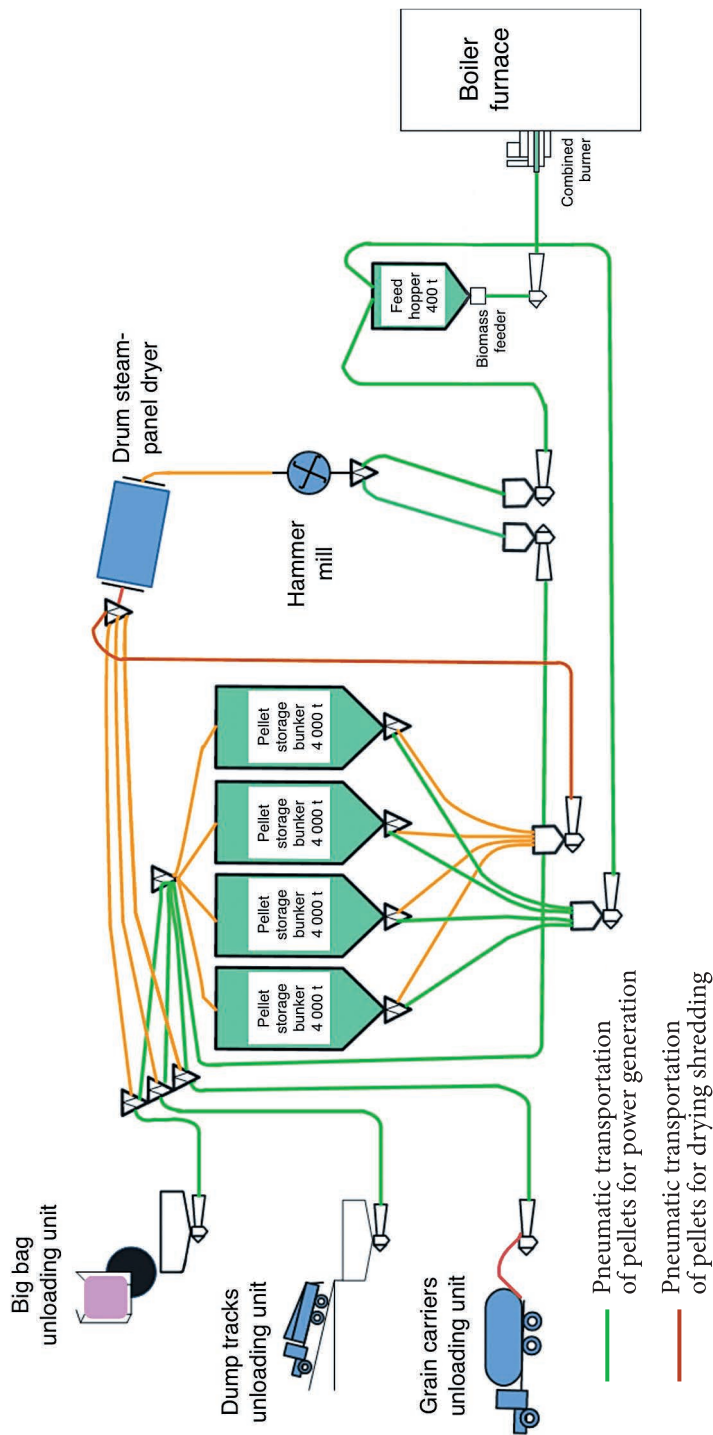


Fig. 8.3. Structural diagram of the units for unloading, storage, drying, and shredding wood pellets for the Trypilska TPP

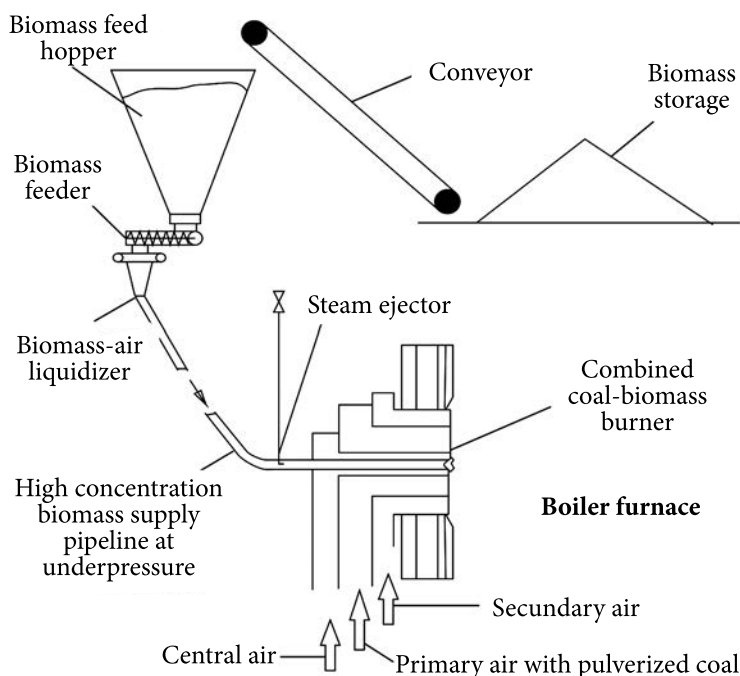


Fig. 8.4. Diagram of shredded biomass transportation to the TPP-210A boiler burner

technical solutions remain unimplemented. However, hopefully, with the improvement of the legislative framework regarding co-combustion, they will find successful practical implementation.

8.3. Experience in converting gas-oil boilers of industrial CHPPs to biomass and gas coal combustion

The basis of the Ukraine's thermal energy sector is formed by steam and hot water boilers of small (up to 11.7 MW, or steam-generating capacity up to 25 t/h) and medium capacity (23.4—35.0 MW, or 35—75 t/h) thermal capacities [21]. Most of them are either gas-oil boilers or anthracite ones with a dense bed, including previously converted to natural gas. With the cessation of delivery of Donetsk anthracite, on the one hand, and the rapid increase in natural gas prices for municipal and industrial needs, on the other hand, the practically and economically viable fuel base for this part of thermal generation has decreased drastically.

The structure of the process of combustion of agrobiomass pellets in a dense bed, including co-combustion or alternating combustion with peat or gas coal as a backup fuel, has some specific features [11, 24, 25, 29, 39—41]. Firstly, set-

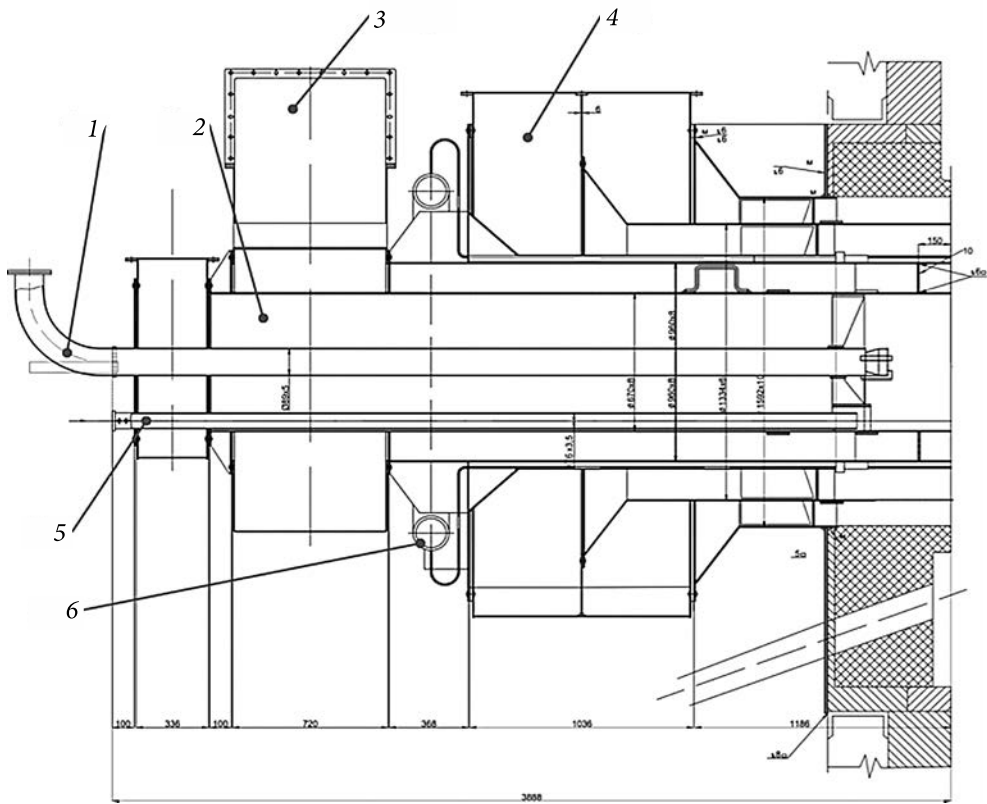


Fig. 8.5. TPP-210A boiler burner, modernized for co-firing anthracite/biomass: 1 — biomass feed channel; 2 — central air channel; 3 — pulverized coal-air mixture channel; 4 — secondary air channel; 5 — fuel oil nozzle channel; 6 — gas collector

ting stable ignition in the bed requires the presence of a refractory-lined arch for radiative heat transfer back into the bed. Secondly, the low ash content of biomass means there is no well-developed protective slag layer to shield the grate from overheating. Therefore, it is expedient to reduce the level of preheating of the blowing air, transferring part of the function of protecting the grate from overheating to the air itself. Thirdly, the significantly different volatile yield and reactivity of the non-volatile residues of biomass and gas coal require sectioning of the under-grate airbox and an advanced secondary blowing system along with an ability to allow for wide-range adjustment of the ratio between primary and secondary air, as well as the distribution of primary air across the grate plane.

The greatest challenge in converting gas-oil boilers to biomass combustion in a dense bed is the change in the heat transfer distribution from the combustion products. Each type of boiler is designed with a specific heat absorption distribution for the working fluid flow, including heating water in the economizer, boiling in the furnace radiant surfaces, superheating steam in the convective surfaces, etc.

In particular, in steam dense-bed boilers, water is heated in the water economizer, boiling is carried out in the furnace- shielding walls, festoon, and convective (boiling) tube bundle, while steam superheating occurs in the convective superheaters. The furnace volume and surface area of the shielded walls, superheater, economizer, and air preheater were originally designed in gas-oil boilers to match the heat absorption distribution required for the working fluid flow with the heat transfer distribution from the products of natural gas or fuel oil combustion.

In the studies [11–13, 42], it was substantiated that the adiabatic combustion temperature, which influences the heat transfer to the furnace-shielding walls, decreases, while the heat transition from the furnace to the convective heating surfaces increases with increasing consumption of the stated specific combustion products. As the share of heat absorbed by the convective surfaces increases with unchanged furnace geometry, the share of heat for boiling decreases. However, by definition, the latter cannot be smaller than the share of vaporization heat in the total enthalpy of the superheated steam at the given temperature and pressure. Therefore, with an increase in the stated specific combustion products, the consumption within the range of 5–8%, converting the boiler to another type of fuel without capacity limitation, is possible only through operational adjustments; an increase in the stated specific combustion products consumption within the range of 8–12% requires an increase in the share of heat absorbed in the economizer, while a further increase requires either enlarging the furnace dimensions or limiting the steam-generating capacity.

The stated specific combustion products consumption for natural gas at the standard value of the excess air coefficient at the furnace outlet ($\alpha = 1.1$) is 0.32. The same for sunflower husk pellets, with a composition on an “as received” basis of $W_t^r = 9.0\%$, $A^r = 8.8\%$, $C = 46.0\%$, $H = 5.0\%$, $O = 30.1\%$, $N = 1.0\%$, $S = 0.1\%$, $Q_r^r = 4272$ kcal/kg in a dense bed at the standard value of $\alpha = 1.4$ exceeds 0.4, which is 25% higher. This requires both an increase in the economizer and furnace dimensions and/or the limitation of the boiler steam-generating capacity.

A significant part of steam generators at CHPPs and boiler plants in the steam-generating capacity range of 10–35 t/h is represented by boilers, originally designed for burning anthracite in a dense bed, with steam parameters of 4 MPa and 440 °C (Fig. 8.6).

In these boilers, fuel from hopper 1 is poured onto direct-drive chain grate 2, under which hot air is supplied from the sectioned blowing box 3. Since anthracite is a low-reactive fuel with a volatile yield of less than 8%, its stable ignition and combustion require high temperatures, which are achieved, among other things, by heating the blowing air supplied under the grate to 250–350 °C. At the front and rear of the furnace, the shielding tubes form protrusions 4 with arches covered by heat-resistant lining underneath. The temperature regime of the fuel ignition is maintained by the radiation from the heated refractory lining of the front arch, while the combustion of the coke-ash residue is maintained by the radiation from the heated refractory lining of the rear arch. The coke residue combustion occurs on the grate, while in the over-bed space of the furnace 5,

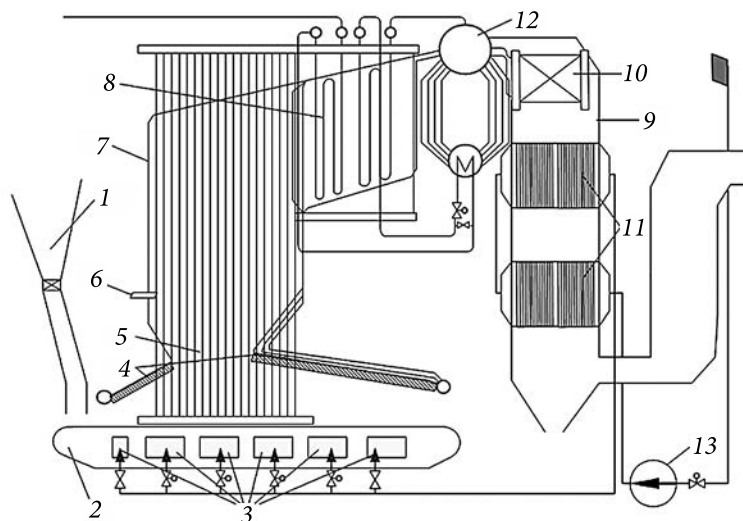


Fig. 8.6. Schematic diagram of a dense-bed boiler for anthracite combustion on a direct-drive grate before reconstruction

the volatile substances and products of incomplete combustion burn out in the secondary air supplied through nozzles 6.

Since the protrusions of the shielding tubes and the refractory arches provide intense re-radiation in the lower part of the furnace, the surface temperature of the bed in the active combustion zone reaches 1600 °C or higher. Due to the high furnace temperature, most of the heat released during combustion is absorbed by the shielding surfaces of the furnace 7, which lowers the gas temperature at the outlet from the furnace chamber down to 900—950 °C. For anthracite, this is a safe level in terms of slagging conditions for shielding steam superheaters 8. In the convective pass 9, combustion products pass sequentially through the water economizer 10 and the tubular air preheater 11, which has two or more stages, and are then discharged through a battery cyclone to the exhaust gas fan and released into the chimney. The slag falls from the end of 3 the grate opposite the fuel feed into the slag bath, from where it is periodically removed. Water and steam are separated in the drums 12, which are equipped with extensive boiling tube bundles located in the turning section of the convective shaft. The blowing air is supplied to the boiler by blast fan 13. Combustion of highly reactive solid biofuel in such boilers is accompanied by overheating the grate and reducing the heat absorption by the furnace shields. This, in turn, results in decreasing the boiler steam-generating capacity and increasing the temperature of the gases at the furnace chamber outlet, potentially causing slagging of the steam superheaters.

To convert boilers of this type to burn solid biofuel (pellets, granules), peat and/or gas coal with maximum use of the existing equipment without increasing the boiler dimensions or reducing its steam-generating capacity, a method has been developed and patented in Ukraine: “Method for Retrofitting an Anthracite

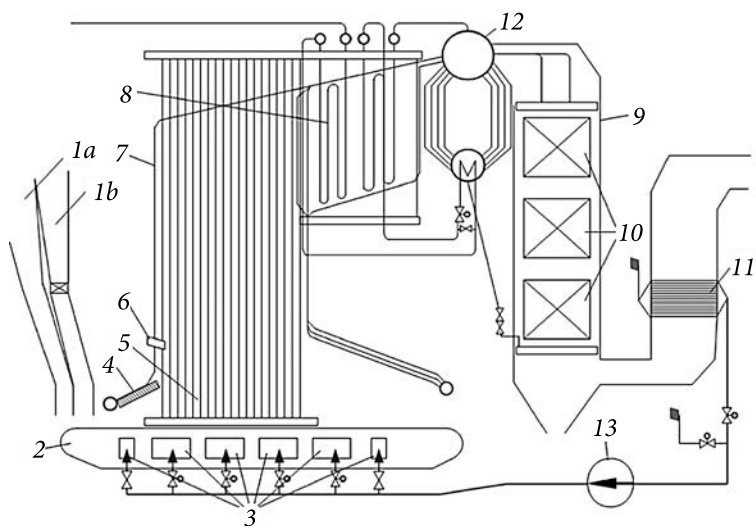


Fig. 8.7. Schematic diagram of the boiler after reconstruction with conversion to solid biofuels and/or gas coal combustion

Steam Boiler to Burn Solid Biofuel and/or Gas Coal” [43]. This method involves equipping the existing furnace with two sequentially arranged fuel hoppers with adjustable feeders that distribute the fuel across the entire grate width. The front and rear protrusions of the shielding tubes are straightened, the refractory lining is removed from the rear arch tubes, the heat-absorbing surface of the water economizer is increased by 2—3 times, and that of the air preheater is reduced by 4—7 times. The air preheater is relocated from the descending section of the convective pass to the ascending section of the gas duct from the convective pass to the battery cyclones and is performed in a reverse flow pattern, where the exhaust gases pass through the inter-tube space, and air flows through tubes placed perpendicular to the gas flow. The blast fan is positioned between the air preheater and the blast box and equipped with a regulated cold air damper, while the existing exhaust fan is replaced with one of 1.5—1.8 times higher capacity (Fig. 8.7).

The reconstructed boiler operates as follows. The fuel is fed from one or both hoppers (1a, 1b) to the initial section of the direct-drive grate. When co-combusting two types of solid biofuel, solid biofuel or peat and gas coal, either type of fuel is fed separately so that the less reactive fuel could form the lower layer on the grate. The ignition of the more reactive fuel, compared to anthracite, is ensured by the heated refractory lining of the front arch, which has a smaller surface area. Volatile substances released from the fuel and products of incomplete combustion continue to burn in the space above the bed due to the supply of secondary air, while the coke residue burns on the grate in the primary air. The low air heating temperature protects the grate elements from overheating. The surface temperature of the layer in the active combustion zone reduced by 250—350 °C

compared to anthracite is sufficient for the complete burnout of more reactive fuel, and in terms of radiation, it is partially compensated by an increase in the active combustion surface along the grate length, the visible fuel-burning area, and the heat-absorbing surface of the shields. The increased stated specific combustion products consumption ensures a lower gas temperature at the furnace outlet compared to anthracite, which reduces the risk of slagging in the shield-type superheaters and increases heat transfer to the convective pass. The heat carried additionally to the convective pass by the furnace gases is utilized in the convective (boiling) tube bundles and the water economizer with an increased heat-absorbing surface, so that the overall heat absorption and steam-generating capacity of the boiler remain unchanged compared to burning anthracite, despite having the same dimensions. The increase in steam temperature due to the enhanced heat absorption in the superheaters is compensated by a standard surface steam cooler placed between the stages.

The reverse design of the air heater increases the heat transfer coefficient on the side of the exhaust gases and significantly reduces their resistance, which is crucial for solid biofuels with increased stated specific combustion products consumption. The relatively low air heating temperature (up to 70 °C) allows the blowing fan to be positioned between the air preheater and the air duct, with air temperature being regulated by a damper for cold air intake at the fan inlet. When burning fuels with increased moisture content or gas coal, the cold air inlet to the induced draft fan is reduced or completely closed.

Boilers of the “Radiant” type at the CHPP of the Khorostkiv branch of LLC “*Radekhiivskiyi Sugar*”, manufactured by Babcock & Wilcox, were previously converted to burn natural gas, with a steam capacity of 20 t/h using anthracite (24 t/h for natural gas). When retrofitting them to burn sunflower husk pellets and/or gas coal in 2019, the developed method was implemented in combination with the following technical solutions [11, 12, 44—46]:

- Reduction in the air heater surface area from 660 down to 100 m² and the air heating temperature from 310 °C down to 50—60 °C.
- Increase in the water economizer surface area from 260 up to 610 m².
- Increase in the number of sections in the under-grate air duct with air distribution, allowing the combustion zone of the pellets to be “extended” to 4—5 m along the grate’s active length, and increase in the radiating surface of the bed.
- Use of direct-drive mechanical grates manufactured by the FPM plant (Mikulov, Poland) instead of those dismantled during the previous conversion to gas.
- Provision of the boiler with two raw fuel hoppers — one for pellets, the other for gas coal, with the possibility of independently regulating fuel consumption (joint or alternating combustion of pellets and coal is provided, with abrasive cleaning of ash deposits from pellet combustion using coal ash).
- Provision of the boiler with a pulse air blowing system for the superheaters and water economizer, which is switched on when the exhaust gas temperature increases to 200 °C.

- Installing a high-efficiency battery cyclone with the possibility of periodically returning captured ash to the furnace for afterburning and bag filters for purifying exhaust gas.

The feasibility of the proposed technical solutions was verified by performing a thermal calculation of the boiler and its components according to the Standard Method [35]. In this case, the calculation of the furnace, festoon, two stages of the superheater, and the convective (boiling) bundle was done for verification purposes, while the calculation for the water economizer and air heater was a design calculation aimed at determining the required heat absorption areas. In the calculation, the value of heat loss with unburned fuel was assumed to be 5%. The results of the calculation for the boiler nominal load are presented in Table 8.2. They confirm that the temperature of the furnace gases is lower than that of slagging, and the share of heat absorbed by the furnace, festoon, and boiling tube bundle is sufficient to ensure the boiling of water pre-heated in the economizer to 220 °C. This determined the choice of the economizer design — a boiling type made of 32×3 mm steel tubes, arranged in a staggered pattern.

To maintain the boiler steam-generating capacity, it was not necessary to increase the volume of the furnace chamber and/or equip it with pre-furnaces. To create enhanced temperature fields for fuel ignition, a 1-meter-long ignition zone was arranged with a ‘tooth’ of pipes of the front shield of the furnace chamber, with a tube-and-brick wall located above the grate. To ensure the complete combustion of the fuel, the cooling zone was restored by relocating the back header of the furnace chamber and arranging a rear arch with tubes of the rear shield. The secondary air nozzles were located above the ‘tooth’ of the front shield. A combination of battery cyclones with bag filters was installed for gas purification. NO_x emissions were reduced through lowering combustion temperatures, and SO_2 emissions were minimized due to the low sulfur content in the biofuel.

Out of 5 boilers at the plant, 4 have been retrofitted (Fig. 8.8), with full automation. The characteristics of the boiler before and after retrofitting are presented

Table 8.2. The results of the thermal calculation of the boiler elements when operating on sunflower husk pellets

Temperature along the exhaust gas flow	°C	Useful heat absorption share	%
Adiabatic combustion temperature	1382	Furnace	34.8
At the furnace outlet	913	Festoon	4.2
After the festoon	860	2nd stage of superheater	8.8
After the 2nd stage of the superheater	723	1st stage of superheater	10.0
After the 1st stage of the superheater	565	Boiling tube bundle	10.7
After the boiling tube bundle	412	Water economizer	15.1
After the water economizer	170	Air heater	1.1
After the air heater	155	Total	84.7



Fig. 8.8. “Radiant” boilers at the Khorostkiv Sugar Plant, retrofitted for burning biomass pellets and/or gas coal

in Table 8.3. After the reconstruction, the boilers can operate using pellets made of wood waste and sunflower husks, peat, gas coal, or a joint supply of these fuels. Co-firing of biofuel pellets with coal has been implemented within the range of their shares from 0 to 100%.

During the autumn seasons of 2019 and 2020, the boilers operated without incidents, running steadily on sunflower husk pellets and gas coal with LHV of 4400—4500 kcal/kg, either separately or in combination (coal — at the bottom, pellets — in the top layer on the grate). When burning pellets, there was practically no unburned carbon in the fly ash, which resulted in loose ash deposits on the convective surfaces, which were easily self-cleaned when switching to gas coal. The most commonly used mode was alternating combustion, in which after a few days of operating on pellets, the temperature of the exhaust gases gradually increased from 150 to 220 °C due to the gradual fouling of the surfaces. After a few hours of gas coal operation, the temperature could drop back to 150 °C due to the abrasive cleaning of the surfaces. The average gross boiler efficiency in this mode was 84—85%, which is significantly higher for this type of boiler compared to operating on the project anthracite and almost equivalent to operating on gas.

BKZ-75GMA boilers of the Radekhiv and Chortkiv Sugar Plants, designed to burn natural gas with a calorific value of 8200 kcal/kg, are vertical water-tube single-drum boilers with natural circulation, with a balanced draft (Fig. 8.9). The prismatic furnace chamber has a horizontal cross-section of $5.14 \times 5.9 \text{ m}^2$ and

a volume of 284 m³, fully shielded by non-covered pipes. Six combined gas-oil burners are installed in two tiers of three in a row on the front wall of the chamber. The superheater is a vertical, coil-type, convective, and two-stage one. The surface steam cooler is installed between the superheater stages. The economizer is steel-made, smooth-tube, coil-type, boilingtype, and two-stage. The air pre-heater is steel, tubular, two-stage, and three-pass. The second stage of the air pre-heater is installed between the stages of the economizer.

The geometric characteristics of the boiler heating surfaces are given in Table 8.4. It should be noted that the specific surface area (relative to the boiler's steam-generating capacity) of the exposed furnace shields of the BKZ-75GMA gas-oil boiler, considering the high flame temperature, is significantly smaller than that of the original anthracite-fired "Radiant" type boiler with a dense bed and the lower average furnace temperature.

The objective of the reconstruction was to convert the boiler to burn sunflower husk pellets while maximizing the use of the existing equipment, without altering the overall scheme and dimensions of the boiler. Considering the potential irregularity in pellet supply, Polish gas coal was selected as the back-up fuel, with the following characteristics in operation condition: $W_t^r = 9\text{--}10\%$, $A^r = 5\text{--}18\%$, and $Q_i^r = 5100\text{--}6200$ kcal/kg.

Table 8.3. Characteristics of the "Radiant" type boiler before and after retrofitting

Characteristics	Before retrofitting	After retrofitting
Fuel	Anthracite	Pellets, gas coal
LHV, kcal/kg	5500	3670
Volume of the furnace chamber, m ³	130	150
Surface of open shields, m ²	120	147
Economizer surface, m ²	260	607
Air heater surface, m ²	660	100
Exhaust gas fan output, thousands of m ³ /h	55	85
Air heating temperature, °C	300—350	50—70
Temperature of the bed in the active combustion zone, °C	1600—1650	1300—1400
Gas temperature at the furnace outlet, °C	900—950	850—900
Economizer outlet temperature, °C	160—180	220—240
Gas temperature at the boiler outlet, °C	180—220	150—220
Steam-generating capacity, t/h	20	20—24
Superheated steam pressure, kg/cm ²	39	39
Superheated steam temperature, °C	440	440
Heat loss with unburned fuel, %	10—15	<5
Gross boiler efficiency, %	74—79	81—86

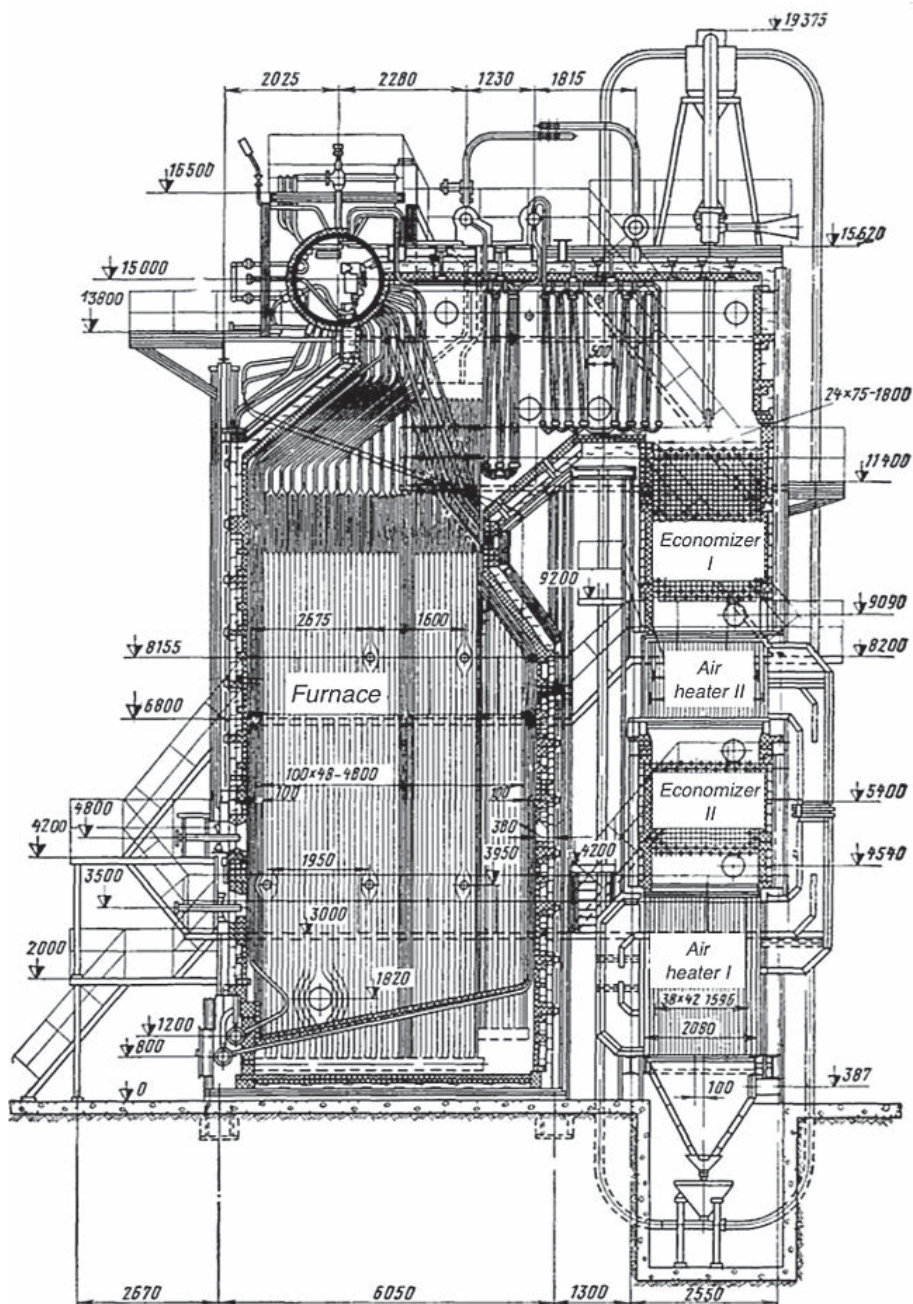


Fig. 8.9. BKZ-75GMA boiler before retrofitting

The main technical solution in the reconstruction [13, 42] was the installation of a mechanical direct-drive grate of the RTP 2x2.85x7.0 type, manufactured by FPM S.A., Poland, in the bottom part of the boiler, due to which, the heat-absorbing surface of the furnace was reduced by 30 m². On the other hand, the grate length chosen to be longer than the furnace depth allowed for the arrangement of an ignition arch lined with carborundum mass in the front part and an unlined arch in the rear part in the cooling and slag removal section. Along with extending the furnace downward by 0.8 m via inserting straight sections in the middle part of the shield panels, which compensated for the loss of the furnace floor surface and even increased the radiant heat-absorbing surface of the furnace.

The technical solution that took into account the above features of biomass combustion in a dense bed was to remove the air heater from the convective shaft and replace it with a water-heated calorifer installed in the primary air duct. This made it possible to add extra stages of the boiling economizer in the given space to compensate for the reduction in heat absorption of the furnace shields. It is important to note that the overall boiler height and the boiler cell plane remained unchanged. The changes in the heat-absorbing areas of the boiler heating surfaces after reconstruction are presented in Table 8.4, and the boiler view after reconstruction is shown in Figure 8.10.

- The other necessary measures implemented during the reconstruction include:
- A fuel hopper was installed with a feeding device equipped with a reversible trolley for the even distribution of fuel over the grate.
 - The subgrate section of the primary air duct was divided to allow for the regulation of air flow rate along the movement of the grate when changing the load or type of fuel (based on non-volatile residue yield).
 - Nozzles for distributed secondary air supply were installed at various depths and heights within the furnace to enable the regulation of the flow rate when changing the load or type of fuel (based on volatile matter yield).

Table 8.4. Geometric characteristics of the BKZ-75GMA boiler heating surfaces before and after retrofitting

Surface, m ²	Before retrofitting	After retrofitting
<i>Radiant heat-absorbing surfaces of the furnace</i>		
Unlined shields	211	230
Lined shields	—	7
<i>Convective surfaces</i>		
Festoon	31	31
Superheater	560	560
Economizer	1070	1594
Air superheater	2150	140*

* Replaced with a water-heated calorifer located in the primary air duct.

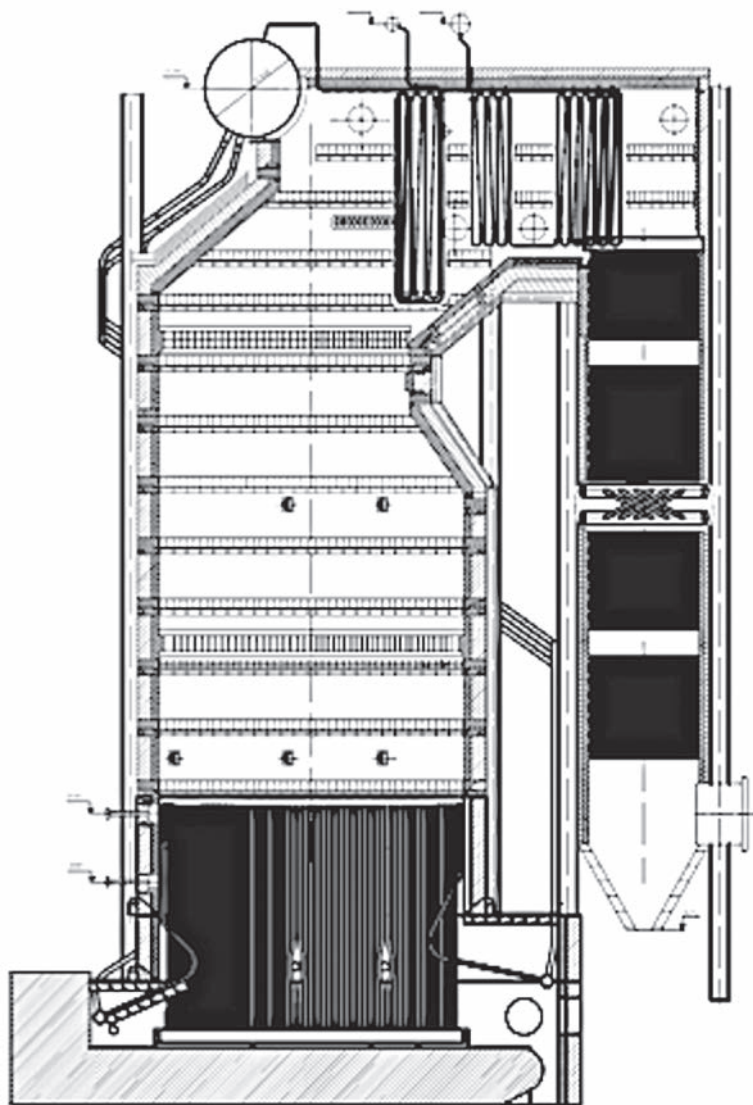


Fig. 8.10. BKZ-75GMA boiler after retrofitting

- A steam-blowing system for heating surfaces was implemented.
- A two-stage gas purifying system based on a battery cyclone and bag filter was introduced.
- A dry ash and slag removal system was implemented, and the exhaust gas fan output was increased.

The technical solutions mentioned were verified through thermal calculations of the furnace and the boiler as a whole. These calculations showed, in particular, that when burning pellets, due to the discussed increase in the stat-

ed specific combustion products consumption compared to gas, maintaining the furnace outlet temperature at 870 °C is guaranteed with a boiler steam-generating capacity of no more than 60 t/h or 80% of the nominal one. However, such steam capacity corresponds to the nominal steam consumption, for example, for the steam turbine P 6-35/5M-1, which is commonly used at sugar plant CHPPs, thus primarily meeting the production requirements.

The boilers were reconstructed during the spring-summer period between the production seasons of the sugar plants. At 2023 prices, the cost of this reconstruction, which included not only the mentioned measures but also a ma-

Table 8.5. Key indicators of the BKZ-75 GMA boiler before and after retrofitting

Indicator	Before retrofitting	After retrofitting
	Fuel	
	Natural gas	Sunflower husk pellet
	Furnace type	
	Chamber	Dense bed on the direct-drive grate
Steam-generating capacity, t/h	75	60
Steam pressure, MPa	4	4
Steam temperature, °C	440	440
Feed water temperature, °C	105	90
Hot air temperature, °C	190	65—80
Gas temperature at the furnace outlet, °C	1250	870
Exhaust gas temperature, °C	145	155—160
Gross boiler efficiency, %	92	86—88

Table 8.6. Comparison of fuel costs before and after retrofitting the BKZ-75 GMA boiler

Indicator	Before retrofitting	After retrofitting
	Fuel	
	Natural gas	Sunflower husk pellet
Commercial price of fuel, UAH/tons of CE	19 634	10 770
Fuel consumption at steam-generating capacity of 57 t/h, tons of CE/h	6.01	6.43
Fuel costs at steam-generating capacity of 57 tons/h, thousand UAH/h	118.0	69.3
Fuel costs for the production season (120 days), million UAH	339.84	199.48

jor overhaul of the boilers with the replacement of drum end caps, most of the convective heating surfaces, draft fan equipment, and more, amounted to about 140 million UAH per boiler.

Table 8.5 presents a comparison of the boiler characteristics before and after reconstruction based on test results when operating on sunflower husk pellets. These results show that the gross boiler efficiency decreased slightly, mainly due to heat loss with unburned carbon in the slag.

At the same time, the significantly lower cost of waste pellets compared to natural gas, when converted to CE, results in substantial cost savings, ensuring the payback of the reconstruction within one production season (Table 8.6) [42, 47]. It should be noted that data of sugar plants on the commercial prices for natural gas and pellets presented in Table 8.6 correlate with the 2023 data from the LCC Ukrainian Energy Exchange on gas and steam coal.

When burning the backup gas coal, the boiler temperature characteristics were the same as when burning pellets. The gross boiler efficiency decreased to 84–85% due to the higher fine content in the coal, a larger share of fines removal from the bed, and, accordingly, a larger contribution of heat loss with unburned carbon in fly ash. However, the cost savings on fuel remained as significant as when operating on pellets.

8.4. Harmful emissions and slagging intensity of heating surfaces during co-firing of agrobiomass with coal

According to the current Technological Standards for Permissible Emissions of Pollutants into the Atmosphere from Boiler Plants Operating on Sunflower Husk, approved by Order No. 540 of the Ministry of Environmental Protection dated 13.10.2009, the technological standard is defined as the maximum mass concentration of a pollutant in dry exhaust gases under normal conditions in the equivalent of 11% for O_2 . Table 8.7 shows the averaged results of measuring the concentration of harmful emissions when burning sunflower husk pellets in the reconstructed BKZ-75 GMA boilers in comparison with the current technological standards for existing plants and with the prospective ones for new and modernized plants for burning husks in a dense layer [42].

The data in Table 8.7 show that the actual level of emissions is lower than the prospective technological standards. This was achieved:

- for dust — due to the low (less than 12%) fly ash removal fraction from the bed, low combustible content in fly ash, effective combination of the battery cyclone and bag filter;
- for SO_2 — due to the low sulfur content in the husk and increased content of alkaline and alkaline earth metal oxides in its ash, which bind sulfurous anhydride;
- for NO_x — due to the relatively low biomass combustion temperature, given the increased stated specific combustion products consumption and decreased temperature of blowing air;

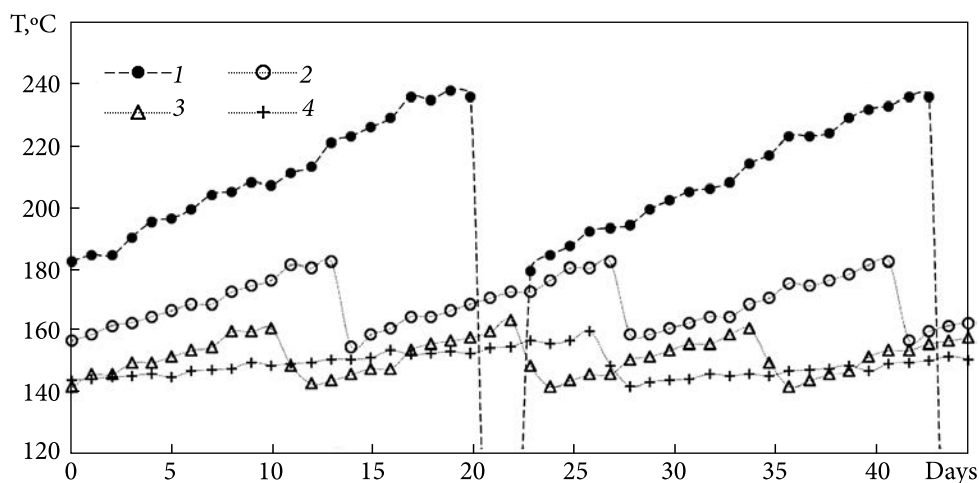


Fig. 8.11. Dynamics of changes in boiler exhaust gas temperature during the production season: 1 — BGM-35 boiler, shutdowns for mechanical cleaning; 2 — BKZ-75 GMA boiler, biomass combustion with periodic steam blowing of surfaces; 3 — “Radiant” type boiler, alternate combustion of biomass and gas coal; 4 — “Radiant” type boiler, joint combustion of biomass (top layer) and coal (bottom layer)

Table 8.7. Normative and actual values of harmful emissions when burning sunflower husk pellets in reconstructed BKZ-75 GMA boilers, mg/nm³ at 11% O₂

Substance	Current standard	Standard for new and modernized plants	Actual
Solid particles (dust)	100	50	18—20
SO ₂	250	250	220—240
NO _x (equivalent to NO ₂)	300	300	250—300
CO	750	250	80—120

• for CO — due to the optimal distribution of the secondary air supply over the furnace.

In parallel with the startup and commissioning of the reconstructed BKZ-75 GMA boilers, industrial tests of heating surfaces slagging were carried out on dense-bed boilers previously converted for burning biomass using our technical solutions (boilers of the “Radiant” type with a steam-generating capacity of 20—25 t/h at the Khorostkiv Sugar Plant) and the gas-oil BGM-35 boiler with a steam-generating capacity of 30 t/h after reconstruction, which was converted to flame-and-bed combustion of biomass, peat, and/or coal according to the technical solutions of JSC “Kotloenergoproekt” at the Gaisyn Sugar Factory [13, 29, 42]. In all cases, the used fuel was sunflower husk pellets (milled in the BGM-35 boiler). Since the “Radiant” type boilers were equipped with two fuel hoppers

with independent feeders during the reconstruction, this made it possible to implement modes of joint layer-by-layer co-combustion (with the bottom layer of coal on the grate) and alternate combustion of pellets with coal.

Figure 8.11 shows the dynamics of boiler exhaust gas temperature changes during 45 days of the production season, which reflects the dynamics of fly ash deposit accumulation on convective heating surfaces. For ease of comparison, the initial days are synchronized for all boilers. It can be seen that in the BGM-35 boiler with flame-and-bed combustion, the accumulation rate of deposits is the highest, and their density and mechanical strength require a shutdown for mechanical cleaning every 3 weeks. In the “Radiant” type boiler, 10 days of biomass combustion or 26 days of layered co-combustion alternated with 2 days of gas coal combustion with complete abrasive cleaning of the heating surfaces with coal fly ash. During the research period, only biomass was burned in the reconstructed BKZ-75 GMA boiler, and the looseness of the deposits allowed them to be cleaned with steam blowing about once every 2 weeks. In some experiments

Table 8.8. Profit from reconstructed CHPP boilers of sugar plants due to the difference in commercial prices for gas and solid fuel

Year	Number of converted boilers steam capacity, t/h	Gas spent, tons of CE (in potential)	Solid fuel spent, tons of CE (in fact)	Commercial price, UAH/tons CE	
				gas	solid fuel
2019	4 × 25	31 680	33 347	5 037	2 221
2020	4 × 25 + 4 × 35	76 032	80 034	6 232	2 221
2021	4 × 25 + 4 × 35 + 3 × 55	128 304	135 057	16 732	3 635
2022	7 × 25 + 4 × 35 + 4 × 55	169 488	178 408	38 415	13 462
2023	11 × 25 + 4 × 35 + 5 × 55	218 592	230 097	19 634	10 769
Total		624 096			

Year	Cost, UAH mln		Difference in the cost of gas and solid fuel, UAH mln	Inflation index relative to 2023	Difference in the cost of gas and solid fuel at the exchange rate of 2023, UAH mln
	gas	solid fuel			
2019	159.56	74.07	85.49	1.52	130.13
2020	473.81	177.77	296.04	1.46	432.88
2021	2146.74	490.88	1.655.87	1.39	2.305.96
2022	6510.82	2401.65	4.109.17	1.27	5.202.21
2023	4291.87	2477.97	1.813.90	1.00	1.813.90
Total			7.960.47		9.885.08

with the reserve gas coal combustion in the BKZ-75 GMA boiler, abrasive cleaning of heating surfaces was achieved, approximately the same as in the “Radiant” type boilers.

Thus, the tests have revealed the lower rate of accumulation of fly ash deposits on heating surfaces when burning sunflower husk pellets in a dense bed on a direct-drive grate, looseness, fragility of deposits, and their ability to be effectively cleaned by steam blowing, compared to flame-and-bed combustion. The effect of abrasive cleaning of the heating surfaces of dense bed boilers from ash deposits during alternate or co-combustion of agrobiomass with coal has been established as well.

8.5. Results and prospects for the implementation of co-firing biomass and coal

In total, from 2018 to 2023, 20 former gas-oil and anthracite boilers of CHPPs of sugar plants with a steam-generating capacity of 20 to 60 t/h were converted to biomass and gas coal with the participation of specialists from the TETI NASU. These boilers have replaced more than half a billion cubic meters of gas with biomass and coal. The profit due to the difference in commercial prices of gas and solid fuel reached UAH 8 billion and almost UAH 10 billion when adjusted for inflation (Table 8.8) [47]. This economic effect should also be distributed to the equipment suppliers and design and assembly organizations, but the participation of scientists from the TETI of NAS of Ukraine, who developed and calculated substantiated technical solutions and accompanied the commissioning of boilers, was very significant.

In addition to the economic effect, there is also the effect of reducing sulfur dioxide emissions due to the low sulfur content in biomass, nitrogen oxides — due to the reduced furnace temperature, and greenhouse carbon dioxide – due to the “carbon neutrality” of biomass.

Efficient technical solutions have been developed for the reconstruction of the former anthracite “Radiant” type boilers at the CHPPs of the Khorostkiv Sugar Plant and gas-oil boilers BKZ-75GMA at the CHPPs of the Radekhiv and Chortkiv Sugar Plants. Their conversion to the combustion of agrobiomass pellets together or alternately with gas coal and/or peat and their successful implementation helped achieve acceptable technical, economic, and environmental indicators and establish the effect of abrasive cleaning of heating surfaces of dense-bed boilers from ash deposits during alternate or joint combustion of agrobiomass with coal, which opens the way to the technical re-equipment of CHPPs and boiler plants of food and processing enterprises, replacing natural gas with cheaper local carbon-neutral fuel and ensuring the payback of the reconstruction.

In fact, the possible scope of the research results is much wider. The idea of using biomass-firing CHPPs for decentralized balancing of the country’s energy system, put forward several years ago [48], has become highly relevant after the

destruction of most of the regulatory generation of TPPs and CHPPs due to the enemy shelling, but until now specific technical solutions for boiler equipment have not been developed. In our opinion, the acquired positive experience should be replicated when creating decentralized thermal generation capacities on carbon-neutral biomass with reserve fuel — peat or gas coal.

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CONCLUSIONS

Blending of two solid fuels, especially of local origin, allows for optimizing the fuel base and combustion processes in the furnaces of boiler units of a wide range of capacities.

Fuel blending contributes to achieving many goals including increasing the reactivity of such blended fuels and solving problems with slagging and corrosion. However, blending without sufficient analysis of the processes that occur during combustion can lead to negative results. The joint behavior of inorganic constituents and some organic constituents is not necessarily linear for mixtures. Methods for blending can also affect the results.

Many economic and environmental benefits can be achieved through proper management of the co-combustion process, such as reduced emissions of sulfur and nitrogen oxides, carbon dioxide, and oxidation of mercury with subsequent mercury capture, and removal of harmful impurities from municipal, industrial, and agricultural wastes.

For Ukraine, restoration of TPP and CHPP capacities and construction of decentralized generating capacities requires the creation of a reliable fuel base, which, given the coal shortage, the need to use biomass waste, RDF/SFR, peat, etc., is possible through the creation of blended fuels and the development of technologies and equipment to use them.

The use of blended fuels should take into account the energy triad — availability of fuel supply, economy, and environmental friendliness, including reduction of harmful and greenhouse gas emissions.

While for existing and renewable boiler units, the task is to bring the properties of blended fuels closer to their design requirements, for boilers under reconstruction and new power plants, on the contrary, design solutions should take into account the properties of available fuels, including agrobiomass, to achieve maximum efficiency and reliability.

The results of research, experience in the development and implementation of the TETI projects, including in wartime conditions, confirm the prospect of using composite fuels in pulverized coal boilers of TPPs and CHPPs and organizing joint or alternate combustion of biomass and coal in dense bed boilers, including those reconstructed from former anthracite and gas oil boilers, to decentralize the generation of electricity and heat.

SUMMARY

The collective monograph summarizes almost twenty years of experience of the Thermal Energy Technology Institute (formerly the Coal Energy Technology Institute) of the National Academy of Sciences of Ukraine in theoretical and practical research on the joint thermal processing of two solid fuels. The research has been applied in boiler furnaces of various capacities, using various technologies, from pulverized coal combustion to bed combustion. The research is unique due to the wide range of fuels involved — coal of all degrees of metamorphism and different countries of origin, pellets from domestic biomass, petroleum coke, coal preparation waste, etc. Such research has contributed to expanding the energy sector's fuel base with local fuels and industrial and agricultural waste, reducing harmful emissions into the environment, creating distributed generation, and thus, to Ukraine's energy independence.

The role and place of solid fuel blend combustion in the energy sector of the world and Ukraine, the study of combustion rates of binary fuel blends, thermogravimetric studies of solid fuel blends and methods for their analysis, and the joint thermochemical conversion of highly metamorphosed coal and biomass are considered along with modeling of co-combustion of two solid fuels, reduction of slagging and corrosion effects during co-firing of coal of different metamorphism and salinity, and preparation of fuel blends for their combustion at TPPs and CHPP in Ukraine.

Монографія узагальнює майже двадцятирічний досвід Інституту теплоенергетичних технологій НАН України в теоретичних і практичних дослідженнях спільної термічної переробки двох твердих палив. Дослідження були застосовані в топках котлів різної потужності, з використанням різних технологій, від спалювання пиловугільного палива до спалювання в шарі. Унікальність дослідження полягає в широкому спектрі залучених видів палива: вугілля всіх марок, біомаса, нафтовий кокс, відходи вуглезбагачення тощо. Такі дослідження сприяють розширенню паливної бази енергетики за рахунок місцевих палив, відходів промисловості та сільського господарства, зменшенню шкідливих викидів, створенню розподіленої генерації, а отже, енергетичній незалежності України.

Дослідження буде корисне для фахівців у галузі теплоенергетичних технологій, управлінців, здобувачів освіти за спеціальністю «Теплоенергетика».

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