The background of the cover features a close-up photograph of coal. The top-left portion is a light gray triangle, and the bottom-right portion is a dark gray triangle. The central area shows a pile of dark, irregular coal chunks, with a single, larger, more reflective piece of coal in the lower-left foreground.

**Department of Physical and Technical Problems of Power Engineering
of National Academy of Sciences of Ukraine
Representative office «Polish Academy of Sciences» in Kyiv
Coal Energy Technology Institute of NAS of Ukraine
Private Joint Stock Company «TECHENERGO»**

**THE FIRST
UKRAINIAN-POLISH
WORKSHOP**

**IMPROVING THE EFFICIENCY
AND ENVIRONMENTAL
PERFORMANCE OF THE COMBUSTION,
GASIFICATION AND THERMOCHEMICAL
CONVERSION OF SOLID FUELS**

ABSTRACTS OF THE REPORTS



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INVESTIGATION OF THERMAL CONVERSION MECHANISM OF COALS AND THEIR BLENDS WITH DIFFERENT ORGANIC WASTES

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The aim of our research was to study the influence of plastic wastes, expired pharmaceuticals, and other additives on the mechanism of thermal conversion of coals. We focused on the influence of additives on the modification of: a) the yield and changes in composition of volatile products of coal pyrolysis; b) the macromolecular structure, texture, and properties of residual coals; c) the structural-chemical parameters of “mobile phase” of coals (soluble in different solvents); along with the changes in composition of the material condensed on the surface of swollen coal grains. Such field of research is predetermined by the changes in solid, liquid, and gas phases under the influence of temperature and additives. The explanation of the changes in all phases allows a better understanding of the mechanism of thermal conversion of coals.

In the research we used the following techniques:

1. The pyrolysis of coals and their blends in a thermobalance was conducted according to the method described in works [1, 2]. The coals and their blends were ground up to <0.2 mm, placed into a platinum crucible, and pyrolyzed in a Q50-TA Instruments thermobalance in a flow of high-purity nitrogen. The volatile products of pyrolysis were registered by a Thermo Scientific interface and analyzed by an iS10 Nicolet spectrometer manufactured by Thermo Scientific. However, this procedure did not allow us to analyze the interactions between the volatile products of destruction and pyrolysis residues.
2. The method below was applied to obtain information on the nature of interactions between the gas and solid phases. The pyrolysis process of coals of different rank and their blends with additives was analyzed in a laboratory pyrolysis unit with the use of X-raying [3]. The ground coal samples of 480 g were pyrolyzed in a pyrolysis chamber. The chamber was one-side and vertically heated in an electric furnace. The heated charge was X-rayed and the changes in it were registered on X-ray films. The temperatures were measured by stationary and non-stationary thermoelements. Such laboratory device made it possible to examine the volatile products of destruction and mobile phase [4].

3. The volatile products condensed on the surface on coal grains. The yield of condensed material, which was rinsed away from the surface of swollen grains, was determined using microwave or ultrasonic extraction [4]. The structural-chemical parameters of pyrolyzed coals, extracts, and residues after extraction were analyzed by the FT-IR method using the DRIFT or ATR technique [5]. SeZn or diamond monocrystals were used in the research. The extracts were investigated by UV-spectroscopy.

4. The composition of extracts was examined by GC-MS [6].

5. The co-pyrollysates of coals with additives were studied with the method of X-ray diffraction (XRD) and scanning electron microscopy (SEM) [2, 6, 7].

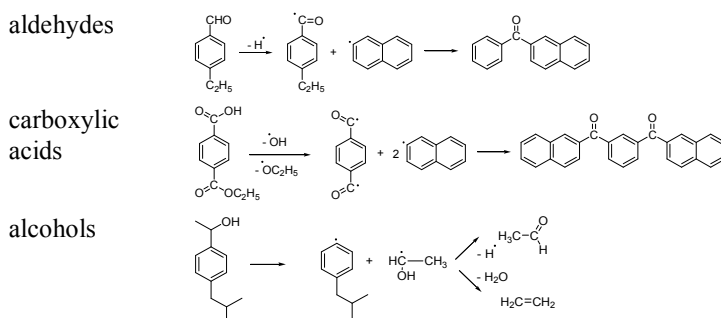
6. The electrical resistivity (ρ) was determined according to the procedure described in [5, 8]. The tangent of dielectric losses and dielectric permeability were determined in a standard measuring cell of a capacity of 14 pF.

Some conclusions made in our research. It was stated that the yield of volatile products tends to increase during co-pyrolysis of different rank coals with expired pharmaceuticals (EP). The addition of 2 wt.% polyethylene terephthalate (PET) wastes to coals leads to a twofold increase in yield of volatile products of blends.

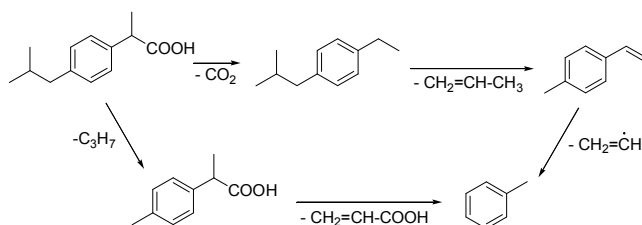
An addition of EP results in higher conversion of compounds from the coal matrix. Additional research on the composition of „mobile phase” as a material extracted from the co-pyrollysates is required for better understanding of the mechanism of influence of studied additive on changes in the material of co-pyrollysates. The amount of PAHs changes in different way under the influence of EP in the composition of organic mass soluble in dichloromethane material (OMSDCM) that was extracted from the zone of maximum plasticity of higher rank coal (HRC) and lower rank coal (LRC). EP increases the contribution of PAHs in HRC by 1.84 times and totally decreases the contribution of PAHs in LRC. It was stated that the additives cause greater changes of structural-chemical parameters in OMSDCM than in the pyrollysates. Compounds of lower ability to form strong hydrogen bonds appear at the plastic stage of co-pyrolysed coals under the influence of additives. In the composition of OMSDCM, an increase in contribution of compounds with a greater number of rings was registered: benzo(b) fluorantene, benzo(k) fluorantene, benzo(e)pyrene, and benzo(a)pyrene. The presence of perylene (not determined in the extract of HRC pyrolyzed without additives) was noticed. This points out to a decreasing trend in contribution of the compounds with a lesser number of rings and the increase in amount of five-ring compounds.

Our investigations show that the addition of 2% PET significantly influences on the changes in structure and texture of pyrolyzed coals and in tangent of dielectric losses, permittivity and resistivity. The nature of changes in the electric and dielectric properties of pyrolysed coals during co-carbonisation with PET shows that PET promotes the formation of cross bonds between these macromolecules and diminishes their mobility.

The addition of EP reduces the content of determined PAHs in the composition of OMSDCM from LRC. Alcohols, aldehydes, acids, and esters are formed during pyrolysis from *(RS)*-2-[4-(2-methylpropyl)phenyl]propionate] acid, and there appear free radicals from them that can react with other aromatic radicals:



This can be attributed to the reactions between hydrocarbons and alkyl radicals being formed from ibuprofen. The pyrolysis products of *(RS)*-2-[4-(2-methylpropyl)phenyl]propionate] acid are formed under anaerobic conditions:



Literature: [1] V. Zubkova et al. Fuel Processing Technology 128(2014)265; [2] V. Zubkova, A. Strojwas, M. Jarzab. Fuel 117A(2014)776 [3] V. Zubkova. Fuel 83(2004)1205; [4] V. Zubkova, M. Czaplicka, A. Puchała. Fuel 170(2016)197; [5] V. Zubkova. Journal of Analytical and Applied Pyrolysis 92(2011)50 E1; [6] V. Zubkova, M. Czaplicka. Fuel 96(2012)298; [7] V. Zubkova, A. Strojwas, M. Walczak. Energy and Sources Part A 38(2016)1318; [8] V. Zubkova. Fuel 86(2006)1652.

THERMOGRAPHIC RESEARCH OF MORPHOLOGICAL MSW COMPOUNDS COMBUSTION PROCESS

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Total amount of implementation of technologies for gasification and syngas production are constantly increasing in the last decade. Interest in gasification of carbon containing materials is renewed for the following main reasons:

- accumulation of carbonaceous materials, such as Municipal Solid Waste (MSW), which is a source of environmental degradation in the world;
- lack of natural gas in several countries, including - economically developed;
- MSW is possible to use as fuel to produce heat.

In order to investigate the combustion process for components of morphological composition in MSW an automatic system for collecting and processing of experimental data was developed. At its base the model of thermo-gravitational test setup is designed with wide range of features in order to conduct experiments.

Strain gauge calibration was performed using set of standard weights from 1 to 500g with 1g step, that corresponds to discrete strain gauges datasheet FSG15N1A. Calibration of heating furnace systems performed by experimental determination of the temperature dependence of heater supply voltage (static characteristics) under stable thermal conditions.

Further studies were carried out with the same heating mode and mass of a sample that equal 15-21g. During the experiment, signals of the primary converters were transferred to measurement and data processing system, which after proper treatment withdrawn at the monitor, which allowed to observe the progress of the process online.

A first set of experiments was performed with all major components of MSW, results are shown in Table 1. Analysis of results shows that the nature of mass change curves of different components does not depend on their chemical composition and is mainly determined by the way how process is staged, and the latter as it is – by the rate of sample heating.

The second set of experiments with a patterned sample of MSW, artificially composed of components studied in the first set was conducted separately. Morphological composition of MSW pattern is equivalent to average compound numbers according to most of publications. Kinetics of MSW pattern mixture

combustion is shown in Fig. 1.

Table 1. Indicators of morphological composition of MSW based on the results of research on pattern thermogravitational installation;
 M^A – mass of ash; M^B – combustible mass; M^C – dry weight;
 M^W – weight of moisture; M^P – working mass.

№	Component	Results					
		Mass, g			Mass, %		
		M^P	M^C	M^A	W	A	$C^P+H^P+O^P$
1	Wood 1	16,00	12,75	-0,75	20,31	(*)	79,69
2	Wood 2	19,79	15,88	-1,17	19,76	(*)	80,24
3	Potato	20,13	19,04	-1,08	5,41	(*)	96,59
4	Meat	15,83	10,42	-1,08	34,18	(*)	65,82
5	Diagram paper	16,63	13,88	-0,21	16,54	(*)	83,46
6	Skin	13,7	11,5	0,1	16,06	(*)	83,94
7	Office paper	16,89	15,46	3,08	8,47	18,2	73,33
8	Garden Waste	17,01	13,42	-0,25	21,11	(*)	78,89
9	Tetra Pak	17,21	15,17	-0,75	11,85	(*)	88,15
10	Plastic (partial combustion)	15,38	14,71	-0,62	4,36	(*)	95,64
11	Plastic (complete combustion)	20,88	20,88	1,25	0,00	6,0	94,00
12	MSW (average)	18,04	16,42	0,29	8,98	(*)	91,02

(*) Within the mass measurement uncertainty.

The entire mass was crushed, thoroughly mixed separated into 5 parts with (18 ± 1) g, which were used to conduct five experiments under the same conditions as with components of morphological structure in the first set. During the processing of results it was defined that uncertainty of indicators does not exceed $\pm 5\%$. Analysis of pattern MSW mass results shows its basic similarity to the nature of mass change in individual components.

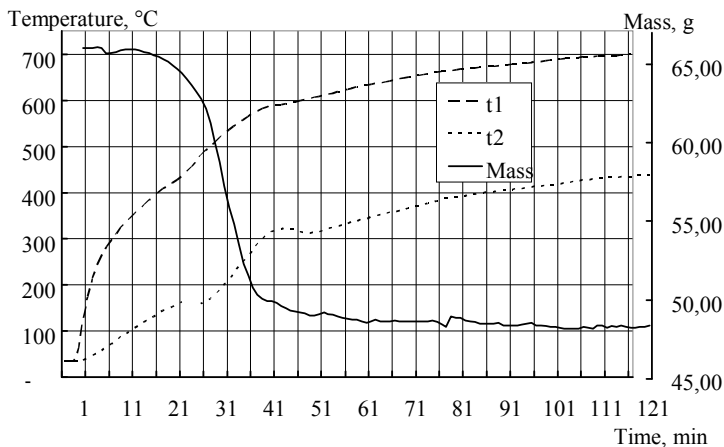


Figure. 1. Kinetics of MSW combustion (pattern mixture).

During conducted experiments all fly ash was taken out through the exhaust vent, hearth ash after burning of sample remained at the bottom of bucket. According to different authors, the composition and properties of ash depend on the composition of raw MSW and technological parameters of burning process. The study of the chemical composition of the ash shows that the main elements of the ash are: Si, Al, Fe, Mg, Ca, K, Na and Cl. Main chemical compounds in ash are: SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , Na_2O , K_2O .

In experiments conducted the ash remained in the form of powder material, in some cases keeping the form of raw materials pieces. The preferred color of ash – light-gray, in some cases – from light to dark gray that is explained via impurities of unburned carbon which appeared in individual pieces due to low flow of oxygen. Brown color is likely to iron oxides.

The composition and thermal properties of ash are important in process of MSW thermochemical disposal, affecting specific calorific value of MSW as fuel and the magnitude of the adiabatic temperature of gases during process. Mentioning this impact should be consecrated thermodynamic calculations of a second iteration and further research.

BIOCOAL AND TORREFIED BIOFUEL PRODUCTION FROM BIOMASS RESIDUES

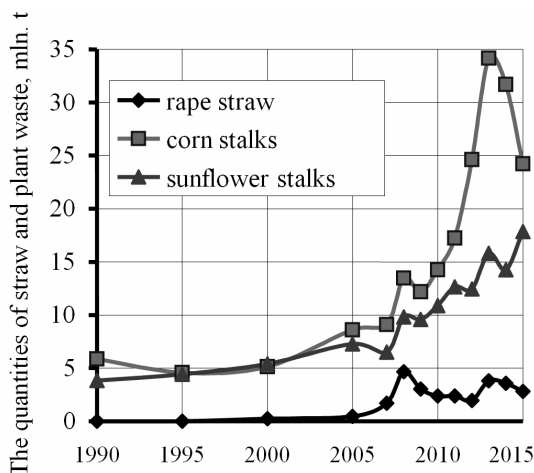
PhD, Reader V. P Klius

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Biocoal and torrefied biofuel is a refined form of biomass residues, applied for energy purpose. The higher energy density cuts transportation and storage costs, allowing to increase transport distances and use of biomass residues. Biocoal also has coal-like properties. This makes it a more suitable fuel for stoves designed for coal.

Biocoal is produced during a process called partial pyrolysis, in which biomass is treated at the temperature of 500–800 °C. Heating degrades chemical substances of biomass, breaking the long-chain polymer compounds into organic molecules. The pyrolysis process produces charcoal the highest temperature and torrefied biofuels at lower temperatures.

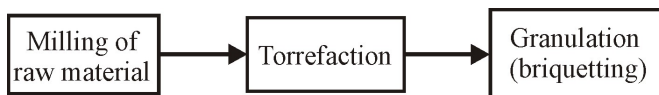
Resources of biomass residues in Ukraine



Advantages of torrefied fuel

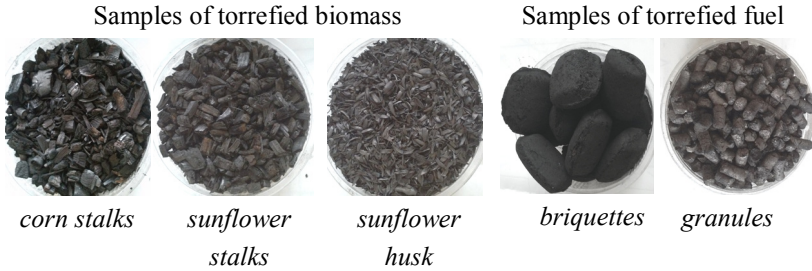
1. The heat of combustion is nearly 20–25 MJ/kg
2. Low hygroscopicity
3. Better logistics
4. The use on combined heat and power plants with coal
5. Use as a domestic smokeless fuel

Scheme of torrefied fuel production



Milling of raw material and granulation (briquetting) of torrefied biomass carried out on the standard equipment. The special mild pyrolysis reactor (know-how) has been developed for torrefaction of raw material. The torrefaction temperature is 160–340 °C. The torrefaction takes 0.5–2.5 hours. Torrefied biomass

output is 50–65 %. Liquid waste (condensate, resin) are absent. The process of partial gasification is autothermal, controlled by blast air supply. The stage of the project is creation of pilot plant.



Biocoal production equipment



Feedstock: wood chips, pellets, crushed plants stalks. Possible humidity of raw material is up to 50%

Products	dry mass output	calorific value
Biocoal	20...30%	25–27 MJ/kg
Pyrolysis gas	1.0...1.6 m ³ /kg	5.4...7.6 MJ/m ³



Biocoal samples from wood chips, cropped willow, sunflower stalks and straw pellets

Areas of use

1. Production of high-calorific briquettes from biocoal.
2. Pyrolysis gas for heat and electricity production.

The technology of torrefaction and biocoal production from biomass residues was verified and ready for industrial use.

THERMODYNAMIC ESTIMATION OF COMBINED SOLID FUEL GASIFICATION PROCESS WITH AN UNKNOWN SET OF INDIVIDUAL SUBSTANCES

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In published work [1], convenient, but overly simplified model of the system with the elemental composition C-H-O, which gasification products consist of CO₂, CO, H₂, CH₄, H₂O, is considered ; the systems comprising the elements S and N in combustible mass composition as well as SiO₂ and metal oxides Fe, Al, Ca, K, Mg et al. in dry weight, are not examined. However, some of these elements at high temperatures may form gaseous components or present in form of dust, exerting adverse effects on the environment, even in trace amounts.

The aim of this work is to create a mathematical model based on fundamental physic laws and suitable for multicomponent solid fuel gasification processes analysis with an uncertain set of individual substances. Seeking model assumes achievement the state of adiabatic equilibrium by complex two-phase system, to which the original is approximated due to high speeds of the gasification reactions at high process temperatures.

In our model construction the following assumptions are used:

- 1) The gasification products are a biphasic mixture of substances (gas and condensed phases) in the adiabatic equilibrium state;
- 2) Each element masses in the initial and final states are equal; the number of material balance equations is equal to number of elements in system;
- 3) equilibrium conditions are fulfilled by addition of independent equations according to mass action law (MAL) to system; the number of equations is equal to number of individual substances in final state minus number of elements in system;
- 4) adiabatic equilibrium state is determined by the equation of thermal balance, which express equality of initial mixture total enthalpy at $T = T_{исх}$ and products at adiabatic reaction temperature;
- 5) initial mixture non-combustible oxides are involved in formation reaction of condensed and gas phases.

The model structure.

Material balance for i-th element: $\Sigma i(исх, T_{исх}) = \Sigma i(пр, T_{ад})$ (1)

MAL for homogeneous reaction: $aA + bB = cC + dD$: $Kp = p_C^c \times p_D^d / p_A^a \times p_B^b$ (2a)

MAL for heterogeneous reaction: $aA(c) + bB = cC + dD$: $Kp = p_C^c \times p_D^d / p_b^b$ (2б)

$$\text{System heat balance: } \Sigma I_{\text{исх}}(T_{\text{исх}}) = \Sigma I_{\text{пр}}(T_{\text{ад}}) \quad (3)$$

For solid fuels and their mixtures, determining the total enthalpy by most accurate data [2] is not possible, unless a full set of individual substances is not specified. In this case, lower or higher calorific value is used, determined either experimentally (calorimetric bomb), or by one of empirical formulas (Mendeleev, Dulong and others.).

To perform the calculation, you can determine the fuel total enthalpy through the complete combustion process (provided that $Q_{\text{н}}^{\text{p}}$ is known):

- for $\alpha = 1$, the amounts of feed air and the product are calculated from the material balances, as the amounts of CO_2 , H_2O , N_2 are constant regardless of the products temperature;

- total enthalpy of products $I_{\text{пр}}$ at $T = 298.15 \text{ K}$ is calculated according to [2]; it is $I_{\text{исх}}$ by heat balance equation;

- fuel total enthalpy: $I_{\text{гор.м.}} = I_{\text{исх}} - I_{\text{воздуха}}$;

- air mass: $M_{\text{возд}}(\alpha) = M_{\text{возд}}(1) \times \alpha$

Feed mixture total enthalpy, referred to 1 kg, is equal to:

$$I_{\text{гор.м.}} / (1 + M_{\text{возд}}(\alpha));$$

Further, based on the values $M_{\text{возд}}(\alpha)$ и $I_{\text{гор.м.}}$, referred to 1 kg, it is possible to calculate all parameters adiabatic equilibrium state according to a model (1) – (3).

Since the accounting system consists of equations in an amount far exceeds the possibility of hand computation, at the present level for calculations of process indicators, computer programs are used. Our calculations are made using TERRA program [3].

To improve the technical and economic parameters of the gasification process, combination of solid waste with fossil coals are used. Analysis of combined fuels parameters allows you to find the optimal solution of technological problems, and search for the optimum is possible in two ways:

- addition of 10–20% of solid waste to coal in power plants in order to save the fossil fuels, and for waste management;

- addition of 10–20% of coal to MSW for improvement generating gas calorific value in production processes for power generation or synthesis gas for chemical technology.

The following example shows the calculation of adiabatic equilibrium state of coal gasification products and municipal solid waste mixture.

Table 1. Starting components characteristics (dry weight): 1 – coal mine Belorechenskaya, Ukraine; 2 – municipal solid waste, Ukraine (physical model); Combined fuel: 3 – coal – 80%, solid waste – 20%; 4 – coal – 20%, solid waste – 80%.

Fuel	Elemental composition						Q_l^d , MJ/kg
	C^d	H^d	N^d	S_t^d	O_d^d	A^d	
1	69.3	4.6	1.5	4.0	5.2	15.4	28.1
2	51.6	7.4	0.1	0.2	27.5	13.2	22.1
3	65.8	5.2	1.2	3.2	9.7	14.9	27.0
4	55.1	6.84	0.38	0.96	23.04	13.64	23.3

Table 2. Gasification products composition (gas phase) of combined fuels 3 and 4:

Gas	$T_{ад}$, K	H_2	H_2O	H_2S	N_2	$C(c)$	CO	CO_2	CH_4
fuel: 3 – coal – 80%, solid waste – 20%									
3	1365	12.7	1.0	0.50	54.2	0	29.1	1.1	0
fuel: 4 – coal – 20%, solid waste – 80%									
4	1353	15.8	4.5	0.2	50.4	0	24.2	3.5	0

Conventions

T – temperature, K;

I – total enthalpy;

Q_H^p – lower heating value.

ад – adiabatic, исх – starting, пр – product, гор.м. – combustible mass; возд – air

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THE DETERMINATION OF THE DEGREE OF COAL OXIDATION

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State Enterprise „Ukrainian State research coal-chemistry institute (UKHIN)”

The introduction of Ukrainian State Standard DSTU 7611:2014 „Coal. Method for the determination of oxidation and degree of oxidation” in the quality control of coal deliveries at coke plants permits characterization of the coal in terms of its ignition temperature.

The principle of the method is to compare the temperatures of ignition of initial tested coal, reduced and oxidized coal.

The installation for determination of coal oxidation is a laboratory complex (Fig.1) comprising electric furnace 1, copper block 2, thermocouples 3 and 4, furnace temperature regulator 5, four sets of test tubes 6, burettes 7, glasses 8, two laboratory supports 9.

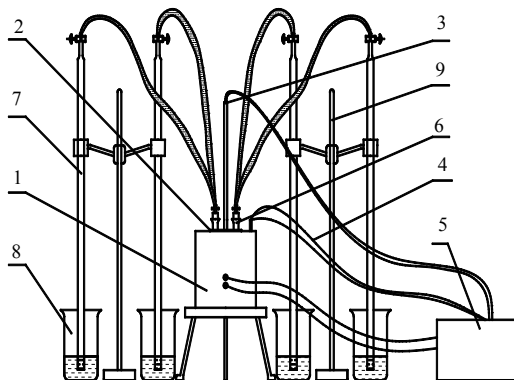


Fig. 1 Installation for determine of coal's inflammation temperature: 1 – electric furnace; 2 – copper block; 3, 4 – thermocouples; 5 – furnace temperature regulator; 6 – test tubes; 7 – burettes; 8 – glasses; 9 – laboratory supports

The main component of the installation is an electric furnace with copper block where the coal sample is heated in order to determine its ignition temperature.

During the experiment a sample of coal with a particle size of less than 0.2 mm

is used. To determine the ignition temperature $t_{ig,un}$ of unoxidized coal, we mix 0.5 g of coal with 0.25 g of sodium nitrite and 0.0125 g of benzidine. To determine the ignition temperature t_{ig} of any coal sample, we mix 0.5 g of coal with 0.25 g of sodium nitrite. To determine the ignition temperature $t_{ig,o}$ of oxidized coal, we mix 2.0 g of coal with 1.0 cm³ of hydrogen peroxide and then hold the mixture for 24 h in a dark place until drying is complete. A weighed sample (0.5 g) of the mixture is taken and 0.25 g of sodium nitrite is added.

The resulting mixture is transferred into a dry test-tube. The test-tubes are closed up with rubber stoppers with glass tubes inserted into, which are connected to burettes with rubber (silicone) tubes; burettes are filled with water and then the open end is immersed into a glass of water to a depth of 20–30 mm. The system is checked for leaks. The burette is connected to a test-tube turning the tap.

The test-tubes are dropped into a block of a device which enables simultaneous heating of the four test-tubes. In the center of the block a recording unit of thermocouple is set which generate heating at a rate of 5 °C/min. At the moment of explosion (ignition of the coal tested), which is accompanied by a sharp decrease of the water level in the burette as a result of the pressure of gases evolved, the registration of temperature is taken.

According to the above-mentioned standard, the assessment of coal oxidation is based on the following parameters:

Coal oxidation (Δt , °C) is a difference in ignition temperatures between unoxidized and initial tested coal, as it is calculated according to (1):

$$\Delta t = t_{ig,un} - t_{ig}, \quad (1)$$

where $t_{ig,un}$ is the ignition temperature of unoxidized coal, °C; and t_{ig} is the ignition temperature of the given coal sample, °C.

The degree of oxidation (d_0 , %) of coal is calculated from the formula:

$$d_0 = ((t_{ig,un} - t_{ig}) / (t_{ig,un} - t_{ig,o})) \cdot 100, \quad (2)$$

where $t_{ig,o}$ is the ignition temperature of oxidized coal, °C.

**THE EXPERIENCE OF COAL ENERGY TECHNOLOGY INSTITUTE
IN FUNDAMENTAL AND APPLIED STUDIES AIMED AT
IMPLEMENTATION OF ADVANCED ENERGY TECHNOLOGIES
AND POSSIBLE JOINT RESEARCH PROJECTS
TO PROVIDE SUSTAINABLE DEVELOPMENT IN ENERGY SECTORS**

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The realization of R&D projects in Ukraine is strongly affected and determined by the state priorities. Of great importance for the Ukraine now is the stabilization of the situation in energy sector and further development and implementation of advanced proven energy technologies.

It is clear that during the 2014–2015 the situation in Ukraine was drastically changed. For the last decade, and specially 3–5 years, the new priorities and challenges were also arrived and are to be addressed in all fields such as social, political, economic ones and R&D.

The special features of the current situation in Ukraine (and in the world) that affect the R&D studies, in particular conducted by Coal Combustion and Gasification Division (CCGD) of CETI in energy field, are as follows.

First, the trends and policy of development of energy sectors have been significantly changed. We can see permanent movement to substitute fossil fuel, in particular coal that important to us, by renewable energy source while producing heat and power energy at power plants/CHP.

Second, the introduction of alternative fuels (such as biomass, secondary derived fuel (SRF)/refuse derived fuel (RDF), not widely used peat etc.) are taking place.

Third, the implementation of new energy technologies and power units should meet strong ecological standards on emissions such as, for example, Directive 2010/75/EU accepted also in Ukraine. So, the energy technology to be implemented should be both advanced and environmentally friendly ones.

Fifth, according to Energy Strategy of Ukraine by the year of 2035 and other current legislation the implementation of technologies and measures to improve energy efficiency (EE) and energy savings are of great importance. During the 2015/2016 the implementation of EE measures in Ukraine became “painful questions” because of very high tariffs on district heating service and high price for natural gas for dwellings resulting in almost 8–10 mln. citizens to be as vulnerable

ones (requiring subsidies).

At least but not last, the increase of energy security of Ukraine (decrease of the use of imported natural gas, its substitution by alternative solid fuels, diversification of energy source by involvement from friendly countries, etc.) is the state priority according to updated Energy Strategy of Ukraine by the year of 2035.

All the above measures should provide stabilization of energy sector of Ukraine and its further sustainable development.

Accounting for the above mentioned, the recently updated core activities of the CETI are as follows.

1. The development/extending of scientific basis for combustion, gasification and other processes of physical and chemical treatment of solid fuels (including coal, biomass, RDF, other alternative fuels).
2. The development/adaptation of advanced clean energy technologies and improvement of existing technologies of heat treatment of solid fuel with the aim of their implementation in energy sector and industry.
3. Applied and fundamental studies on energy efficiency and energy savings.
4. The development/improvement of methods for flue gas cleaning and techniques to diagnose/analyze the emissions.
5. The development of methods to upgrade coals and its logistics, obtain new fuels.

Among these activities Coal Combustion and Gasification Division (CCGD) focuses particular attention to both fundamental and applied aspects of the development of energy technologies. Usually, we try to cover all questions related to whole chain of the project within the span of responsibility: starting from deep studies of combustion / gasification kinetics etc. (as part of R&D activities); technology screening and scoring (as part of concept study preparation); evaluation of energy reserves (coal, biomass, etc.) and quality parameters (reactivity, proximate/ultimate analysis etc.), assessment of heat and material balance of energy processes of interest (as part of pre-feasibility study); development and improvement of technological scheme, e.g. process flow diagram etc., (as part of feasibility study preparation); recommendations on key design elements of energy equipment (furnace, seal pot, etc.) (as part of FEED stage); taking part in economic evaluation and commissioning of the equipment.

The examples of R&D studies and projects, carried out by CCGD's experts or where they participated, are presented below along with possible proposal to establish/extend R&D activities within the joint project open-for-cooperation.

Project on solid fuel combustion/gasification kinetics. The CCGD-division

has bench-scale facility to study combustion kinetics and dynamics (fig.1). The special feature of the facility is the possibility to inject pulse of gas-reactant into the reactor where sample (single batch) of char of interest is placed initially flowing by inert gas. The temperature of the process can be varied up to 1100 °C (and elevated pressure can be also set). Permanent CO, CO₂, O₂, NO, SO₂ concentration can be registered using Siemens Ultramat 23. The result of investigation: reaction rate as function of temperature, the dependence of reaction rate as function of conversion at given temperature, kinetic constants (fig.2). There is also similar high temperature drop-tube reactor to study combustion dynamics for coal batch.

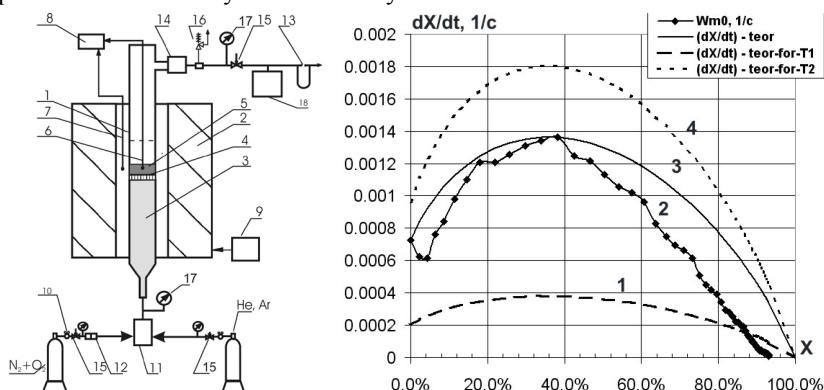


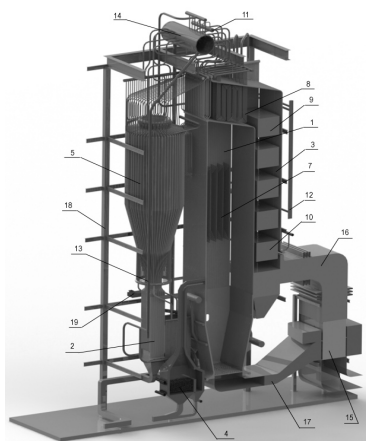
Fig 1 (left) – Bench-scale facility to study combustion kinetics in a pulse-reactor

Fig 2 (right) – The results of investigation (example): reaction rate as a function of conversion (X) at specified temperature along with predicted trendlines based on Random Pore Model (combustion kinetics of bituminous coal).

Possible joint project can be prepared to study new type of solid fuel and its characteristics in a wide range of regime parameters. The comparison of results from TGA and pulse-reactor is needed as well as reactor upgrade.

Project on the development of concept of CFB-reactor and technological scheme to burn solid fuel in circulating fluidized bed (CFB).

Recently the project to develop outline of small scale CFB-steam generator (75 ton of steam/h) and whole technological scheme has been completed having the objective to involve high ash bituminous coal washing wastes and/or its blend in electricity / heat production.



The project was prepared along with domestic boiler design bureau “Energomashproject”.

Similar joint project can be established to consider optimum design and concept of CFB boiler at Ukrainian CHP bearing in mind special features (kinetic characteristics, etc.) of bituminous coal from Poland as export fuel as well as measures to prevent SO_x emissions.

Project on pre-feasibility study preparation for substitution of the use of natural gas by blend of coal and RDF/biomass at combined heat and power plant (CHP). Currently in Ukraine there are ongoing projects aimed at implementation of CHP plants based on co-combustion of RDF/SRF and bituminous coal in CFB. The projects could be potentially financed within the loan (3.656 bln. USD) from China Development Bank Corporation.

Possible joint project can cover R&D questions related to peculiarities of characteristics of municipal solid waste (MSW) and obtained RDF, study of combustion of blend made from RDF/biomass and coal, EU legislation on wastes and experience of Poland in these fields.

Project on combustion tests and further commissioning of new CFB boiler unit. In 2011–2012 the commissioning of first 210 MWe CFB boiler unit, firing high ash anthracite schlemm, at Starobeshevo Power Plant (now at occupied by Russia area) was completed and commercial operation was started. During almost three years, the experts of CCGD were involved in commissioning process giving recommendations on optimization of combustion process and equipment (mainly, cyclones, seal-pot, FBHE tube bundle, etc.). The unique experience has been accumulated.

Possible joint project can cover R&D activity on evaluation of CFB-boiler performance and analysis within the large scale combustion tests (e.g., at CFB boiler in Poland), including assessment of emissions, optimum limestone parameters (Ca/S, particle distribution etc.), bottom ash/fly ash characteristics and its way of utilization. The bituminous coal to be investigated can be from Poland (potentially exportable one) and could have similar parameters as those of Lviv-Volyn coal basin. The project is connected to previous one aimed at advanced solid-fuel fired CHP implementation.

The list of the above projects and proposals is not complete and can be added/modified. The specialists of Coal Combustion and Gasification Division have more than 25 years of the experience in participation in international projects and are ready for joint mutual cooperation.

THE REGULARITIES FOR BURNING OF HYDROGEN-WATER-COAL FUEL

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In recent years, widespread abroad has received the process of burning coal-water fuel (CWF) in heating plants and thermal power plants. This trend is due mainly to the environmental benefits of the process, as it allows to drastically reduce the emissions of dust and toxin substances into the environment.

On the other hand, currently some progress are reached in developing of a process for producing the hydrogen by electrochemical oxidation of the coal.

We can assume that combining these two processes will be able to create a more advanced power plants.

The aim of this study is to develop a process of burning hydrogen-water-coal fuel (HWCF).

The studies will develop the technology as much as possible adapted to changing properties of coals from field to field while preserving the environmental benefits of combustion processes of the high-moisture fuels.

The novelty of the study lies in the fact that for the first time, hydrogen is used to activate the process of burning of coal-water fuel. Moreover, hydrogen is produced directly on the thermal power plant (TPP).

High erosive wear of equipment leads to the need for using the multiple combustion chambers, allowing periodically pull them out of service for replacement of worn parts and assemblies without affecting the TPP. With this solution, it is advisable to send the coal flow sequentially from chamber to chamber for complete combustion.

It follows that the fuel fed into the initial chamber with a large excess of the oxygen followed by reduction of the ratio in the final chamber to a value close to stoichiometric.

For comparison, the combustion mode is selected close to the testing regimes of boilers at the mine Lutuginsky-North (Donetsk coalmine) [1]. The difference lies in the using the hydrogen for ignition and for lighting the flame in the furnace.

The moisture of fuel - 53 %, the surface of coal particles (DB brand coal) - $317 \text{ m}^2/\text{kg}$, equivalent to particle diameter of 80 μm , content of 24 % inorganic part. The burning in the combustion chamber fed $1.35 \cdot 10^{-3} \text{ kg/carbon}$ and $5.11 \cdot 10^{-3} \text{ m}^3/\text{s}$ air.

When launching stand for hydrogen ignition of water-coal fuel (WCF) fed the hydrogen in an amount of $2,15 \cdot 10^{-3} \text{ m}^3/\text{s}$ and the air is additionally supplied in an amount of $0,66 \cdot 10^{-3} \text{ m}^3/\text{s}$. After ignition the hydrogen consumption is reduced to $0,27 \cdot 10^{-3} \text{ m}^3/\text{s}$. Ignition temperature – 480–500 °C, the combustion temperature – 650 °C.

Air for spraying and combustion of WCF supplied by air blower, hydrogen fed to the combustion by compressor.

The nozzles are mounted at the underside of the chamber. Tilting of nozzles relative to vertical 15°. This arrangement of the injectors ensures intersection the mixtures of water-coal fuel stream with air and a hydrogen-air flow at an angle of 30 °.

Provided pre-heating of the combustion chamber and the WCF to 50–60 °C.

Air is supplied with deficiency to the stoichiometric value, so that to fired only 37% of the carbon. Unburned carbon particles are trapped by a water seal, and sent for further post-combustion.

Hydrogen was produced in a balloon reactor by reaction of ferrosilicon or ferrosilicoaluminum alloys with water (In the future will use the hydrogen produced by the electrochemical oxidation of coal [2]).

The composition of the combustion products produced in the laboratory bench, vol. %: N_2 – 78,2; CO_2 – 13,7; CO – 2,1; O_2 – traces. Analyses were performed on laboratory gas chromatograph type LHM-8MD.

When comparing the theoretical and experimental data, it is assumed that decreasing of activation energy is carried out by the combustion of hydrogen, seeing that the system is in a diffusion field where reactions rate is determined by the intensity of heat and mass transfer [3].

The amount of burned carbon estimated by the heat exchange rate and compared with that obtained in the experiment. The discrepancy between the data does not exceed 15%.

Economic calculations show that the cost of hydrogen produced by the electrochemical method is in the range of \$ 1646 per ton. By reducing the cost of electricity at night is twice low the cost is reduced to \$ 958 per ton, which allows to use of hydrogen for lighting the flame instead of natural gas.

The greatest decrease in the cost of hydrogen is achieved by a radiation-electrochemical method of its production, as well as generation of electricity by high-temperature binary cycle [4, 5].

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MERCURY EMISSIONS BY UKRAINIAN COAL-FIRED THERMAL POWER STATIONS

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Mercury is one of the most dangerous toxic substances. It represents a global contaminant of the environment. Beginning from 1850, due to human activity, about 200 thousand tons of mercury has come to the environment [1]. At present, the mankind throws out to the environment about 2 thousand tons of mercury per year, including 299 tons of mercury coming to water. However, the existing estimate of annual mercury emissions is quite uncertain: it gives a range from 1010 to 4070 tons.

The main sources of mercury emission to the atmosphere are gold mining, fuel burning, nonferrous metallurgy, and cement production. Due to fuel burning (all kinds of the use), up to 500 tons of mercury is thrown out every year, which is equal to 24% of the total anthropogenic emissions [1]. The decrease in mercury emission by energy plants, first of all, by thermal power stations, represents a topical ecological problem that is actively discussed in the world.

In 2013, the Minamata Convention on mercury was open for signing by different countries. This document represents an obligatory juridical agreement whose aim is to protect the human health and environment against the harmful influence of mercury. The Convention was prepared under the aegis of the United Nations Environmental Program (UNEP). The countries that have signed and ratified the Convention will have to perform a series of measures for the prevention of mercury emission to the atmosphere and to develop a plan of specific acts for its realization on their territory. At present, the Convention was signed by 128 and ratified by 38 countries. Ukraine has not signed this Convention. In Ukraine, mercury and its compounds (in terms of mercury) is referred to the first class of danger (abnormally dangerous) [2].

In the United States, the standard MATS (Mercury and Air Toxics Standards), introduced in 2011, and standards NESHAP (National Emission Standards for Hazardous Air Pollutant) serve as a legislative base of the control of mercury emission by coal-fired thermal power stations and cement-producing enterprises.

Mercury is present in coals of all types and comes to the environment at their burning. The total world mercury emission to the atmosphere from coal-fired thermal power stations constitutes 316 (204 – 452) tons/year, or 16% of all anthropogenic mercury emission [1]. The specific mercury emission at coal-fired thermal power stations and industrial power plants in the world are from 0.07 to 0.3 ppm. The main factors determining the volumes of mercury emission from thermal power engineering are the volumes of fuel consumption, mercury content in it, and the presence of cleaning installations at thermal power stations.

In 2016, the total volume of coal mining in Ukraine constituted 40.9 million tons, including 32.5 million tons of power-generating coal and 8.4 million tons of coking coal. At present, about 30 million tons of coal is consumed at Ukrainian thermal power stations and heat stations per year.

The mercury content in coal beds depends on their genesis, and, therefore, the mercury concentration for different deposits changes from 0.01 ppm to 300 ppm. For example, it is equal to 0.01–3.3 ppm for bituminous coal of the USA, 0.01 – 0.85

ppm for Russia, and 0.01–1.0 ppm for South African Republic [1, 3]. The mercury content in coals of the south-west basins of China is 0.55 ppm.

Mercury mineralization has been studied quite thoroughly for Ukrainian coal of the Donetsk basin, where the average mercury content is much higher than the background values and constitutes 0.70 (0.08 – 8.55) ppm [4]. The Donbass is a mercury province with a series of mercury deposits in its central part. Experimental data show that, in all zones or regions of the Donbass, which are notable either for the mercury content in coal-bearing series, or for the geographic sign (Central, East, South, or North Donbass), one can see polymodal distributions: along with the background Hg concentration, there are abnormal and sharply abnormal ones [4–6]. The first are connected with “diffused mercury mineralization”, while the second with “enriched mercury mineralization”. The coal of central region of the Donbass is most enriched with mercury: its average content here constitutes 1.21 ppm. In the coal of mines of Central coal-mining region, the maximal values of mercury content exceed the concentration 2.10 ppm. Furthermore, the mercury content in some coal beds of the Mykytivka ore field reaches 30 ppm.

Generally, three forms of mercury can exist in the environment, i.e., gaseous mercury Hg^0 , inorganic mercury in the form of Hg^{2+}_2 or Hg^{2+} , and organic mercury that is associated with organic compounds (e.g., CH_3Hg^+ , CH_3HgCH_3 , etc.). In coal with the background mercury content, two forms predominate: mercury bound with mineral components (Hg^{sulf}) (pyrite mainly in the form of a fine-dispersed fraction, FeS_2 and other sulfides) and mercury connected with organic substances (Hg^{org}) [5]. In coal with abnormally high mercury content, one can meet also metallic mercury (Hg^0) and cinnabar (HgS).

Mercury distribution is usually controlled by two properties of coal: its ash and sulfur content. High-ash coal is richer with mercury than low-ash [5–7]. One can observe the following dependence: the higher ash content in coal, the greater is mercury content in it, other conditions being equal. Just Hg^{sulf} gives the maximal contribution to the total mercury content. In the course of coal enrichment, 30–70% of mercury passes to concentrates that are burned afterwards, and the remaining mercury is dispersed in tailing, slime, and intermediate material [5, 7]. In the concentrates, one can find organic and micromineral pyrite mercury (Hg^{pyr}).

The mercury content in flue gases is determined by its quantity in the initial fuel and the specific features of burning conditions. As coal is burned in the furnace of a boiler, mercury passes to flue gases in the form of vapor of elemental mercury Hg^0 , oxides and salts Hg^{2+} , and free or chemisorbed mercury at ash or coke-like underburning

particles.

As follows from experimental data, mercury inflow to the gaseous and aerosol phases from the high-temperature zone of the furnace is equal to 98–99% for coal-fired furnaces with dry slag removal [3, 5]. Elemental mercury (Hg^0) possesses unique physical properties: low melting point (-38.89°C) and high vapor tension (boils at a temperature of 357.25°C). Therefore, at temperatures characteristic of the furnaces of power boilers ($1300\text{--}1700^\circ\text{C}$), mercury passes to the gaseous state. Elemental mercury Hg^0 in flue gases goes to the chimneys of thermal power stations and thrown out to the atmosphere. The only way to decrease the atmospheric emission of mercury is its oxidation by the scheme $\text{Hg}^0 \rightarrow \text{Hg}^{2+}$. Only Hg^{2+} can be sorbed at ash carryover (at the surface of carbon, silicate, and sulfate phases) and also in scrubber gypsum. However, oxidized mercury is water-soluble and, coming to the natural environment, can be subjected to a series of chemical transformations and pass to the high-toxic form, namely, methylmercury $[\text{CH}_3\text{Hg}]^+$.

We have analyzed 20 samples of coal from anthracite to gas coal of the Donetsk and Lviv-Volyn deposits with an ash content A^d from 30.3 to 48.7% and sulfur content S_t^d from 0.9 to 3.5% [5]. For analysis, we used a PA-915+ Zeeman mercury spectrometer and its new modification PA-915M (group of companies «Lumex»). The statistical processing of results gives the average mercury content and root-mean-square deviation in the samples of the Donetsk deposit 0.39 ± 0.23 ppm and Lviv-Volyn 0.41 ± 0.17 ppm. The level of mercury content for coal of the Lviv-Volyn basin was determined first.

We have also analyzed 6 samples of cannel coal of the Novomoskovsk deposit (West Donbass) with ash content A^d from 7 to 15% and sulfur content S_t^d to 2%, which are characterized by a heightened level of the concentration of salts of alkali metals. We used for analysis a spectral semi-quantitative method. The statistical processing of results gives the average mercury content and root-mean-square deviation in these samples 0.33 ± 0.19 ppm.

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CATALYTIC APPROACH FOR IMPROVING THE SOLID FUELS GASIFICATION AND HYDROGEN OR HYDROCARBONS PRODUCTION FROM THE ORGANIC WASTES

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The current state of the Ukraine's economy demands a self-sufficiency of the raw materials, energy, and chemical commodities. Particularly, a promising way concerns a use of renewables for biofuels, syngas, and hydrogen production. Efficient and environmentally friendly renewable raw materials in Ukraine could be used by their conversion to solid fuels with subsequent conversion of the resulting solid biofuels to the synthesis gas for highly advanced fuel cell power plants. One

approach is based on the production of bio-coal that does not contain tar and sulfur with ash content up to 10% and show that the activation of the biomass chemical compounds and their further carbonation increases the yield of charcoal. The highest yield of charcoal and the highest content of fixed carbon were obtained for a sample that was treated with H_3PO_4 .

The efficiency of the gasification processes is substantially improved by the use of the appropriate catalysts. It allows to increase the rate of the low-temperature processes of gasification, to reduce temperature and pressure, maintaining a high gasification rate, and adjusting the composition of the products. The results of our studies indicate that additional treatment waste biomass by nickel and iron ions increases the yields of charcoal in the carbonization reaction and increase the concentration of hydrogen in the steam coal gasification. In the process of the steam gasification of solid renewables, the syngas is produced, which is regulated by the catalytic reaction water-gas-shift reaction.

The high-temperature catalyst of the process of the conversion of carbon monoxide that contains the oxides of copper and cerium applied on silica gel has been created. Synthesis of modified catalysts for high-temperature conversion of carbon monoxide was based on the use of the metal oxides as components of the catalytic systems that are characterized by high chemical resistance to sulfur compounds. Tests of the synthesized catalyst have been carried out using the laboratory installation of the coal conversion in the Institute of Coal Energy Technology.

Liquid products formed during the carbonization of the solid renewable raw materials significantly decrease the gas yield and, respectively, the yield of the synthesis gas. Depending on the conditions of the carbonization process of organic compounds and initial raw materials, approximately 32% of coal, 29% of gas, and 39% of liquid products are obtained. Liquid products form aqueous emulsion of various oxygen-containing compounds e.g. carboxylic acids, phenols, esters, ketones, aldehydes, and hydrocarbons. Some peculiarities concerning the main physical, chemical, and structural characteristics of heterogeneous catalysts with respect to their activity in the processes of low-temperature steam transformation of pitches of pyrolysis and their separate components have been revealed. A study of steam conversion of volatile compounds directly during carbonization of renewable raw materials and subsequent steam gasification, in order to develop technological modes of catalytic gasification of solid renewable raw materials has been conducted.

Catalytic systems have been proposed for conversion of tar obtained by

pyrolysis of solid renewable raw materials. Catalysts contain transition metals and their oxides. It was determined that in the process of the steam catalytic reforming supported metal exchange with Pt on Ni increases the conversion and hydrogen yield and reduces carbon deposition on the catalyst.

The obtained results allow purposeful regulating the functional properties of multi-functional catalysts for conversion of biomass and "volatile" in order to optimize the conditions of the process of catalytic carbonization of biomass and its further steam conversion, and, thus, improve the basic parameters of the process of the synthesis gas, hydrogen, and biofuels production.

We have developed the fuel pellets for hydrogen production by catalytic pyrolysis of the solid organic waste, e.g. biomass and plastics, containing nanostructured iron or nickel catalyst. The developed fuel pellets provide a high yield of product up to 95%. The use of a catalyst based on Ni nanoparticles increases the hydrogen yield comparing to Fe nanoparticles. Moreover, using wood-polypropylene pellets leads to higher hydrogen yield and lower hydrocarbons yield comparing to wood-polystyrene pellets.

Using the process of carbonization and steam gasification it is possible to obtain both synthetic liquid or gaseous fuel and the desired synthesis gas composition for further chemical syntheses. In turn, synthetic gasoline for petrol engines, methane or other valuable substances, e.g. methanol, higher alcohols, dimethyl ether, propane-butane mixtures, etc. are prepared using the synthesis gas as a feedstock. Methanol can be converted to gasoline (processes Mobile, Synthol), or used as an additive for motor fuel. A promising substitute for diesel fuel is dimethyl ether. We have developed a highly selective new catalysts which gives an opportunity to obtain different types of fuels from synthesis gas.

Catalysts for derivation of light hydrocarbons, petrol fraction, diesel fraction, and also solid paraffin are developed. Multifunctional catalysts of the new generation for synthesis of the highest aliphatic alcohols from synthesis gas, which can be used both as motor fuels and high-octane additives and compositions to motor fuel of poor quality, have been created. We have developed the original two-cascade method using the same catalysts, which allows to increase productivity at the feed conversion of 83,5% and products selectivity of 85%.

The highly efficient multifunctional catalyst of dimethyl ether synthesis from synthesis gas is developed. We have developed a single-stage method of dimethyl ether synthesis directly from synthesis gas with a higher yield, comparing to the existing industrial two-phasic method.

Thus, the new catalysts for Fischer-Tropsch synthesis providing hydrocarbons synthesis with the primary maintenance of certain fractions from synthesis gas, derived from the raw materials other than oil, e.g. natural gas, different classes of coals, peat and biomass has been developed. The proposed methods demonstrate higher productivity and efficiency comparing to existing analogues.

CONDITIONS OF VOLATILES BURNING AT BIOMASS COMBUSTION

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Conditions of volatile and air mixtures burning with regard to flammable components and oxygen content, adiabatic temperatures, their ability to forced ignition or to the thermal self ignition in volume were analyzed. Design and operational mode measures for proper ignition and burning of volatile substances depending on biomass moisture content were substantiated and unwanted burning modes identified.

Key words: biomass, volatiles, ignition, burning.

Thermochemical transformations of biomass are associated with harmful substances origin and at improper equipment operation with their emission into atmosphere. Particulate matter and submicron particles emissions at biomass combustion are associated with improper burning processes, especially those of volatile substances. Improvement of volatiles burning out and preventing their carrying out from furnace is a priority approach to environmentally safe biomass combustion [1, 2].

In small boiler, which are the most wide spread, biomass is combusted in bed on fixed or moving grate. As it was shown in [3], actually, owing to biomass thermolysis, there is separate burning of two fuels derived from it – the volatile substances and the coke residue, and thermal conditions at their combustion differ. Concentrations of combustible components and oxygen, which are formed in volatiles and air mixtures, were analyzed [4]. The relative (dimensionless) lower explosive concentrations of combustible gases $r_n^{r,lel}$ depending on moisture content of wood fuel W_r and air to fuel ratio in volatile and air mixtures α_v are presented at figure below.

Early it was shown [4], that at $r_n^{r,lel} < 1$ and/or oxygen content $r_{O_2} < 12\%$ vol. forced ignition of mixtures from open fire or spark is impossible. Volatile and air

mixtures can be divided into regions of reach $\alpha_v < 1$ and lean $\alpha_v > 1$ mixtures; with high $r_{O_2} > 12\% \text{vol.}$ and low $r_{O_2} < 12\% \text{vol.}$ oxygen concentration, able $r_n^{r,lel} > 1$ and not able $r_n^{r,lel} < 1$ for forced ignition. Mutual overlaps of these regions allow separate seven zones (marked with numbers in circle at figure) in which named parameters are uniform.

Based on data [3], adiabatic burning temperatures t_{ad} were calculated for volatiles and air mixtures corresponding for these zones. Adiabatic burning temperatures determine possibility and rates of gas mixtures burning out [5].

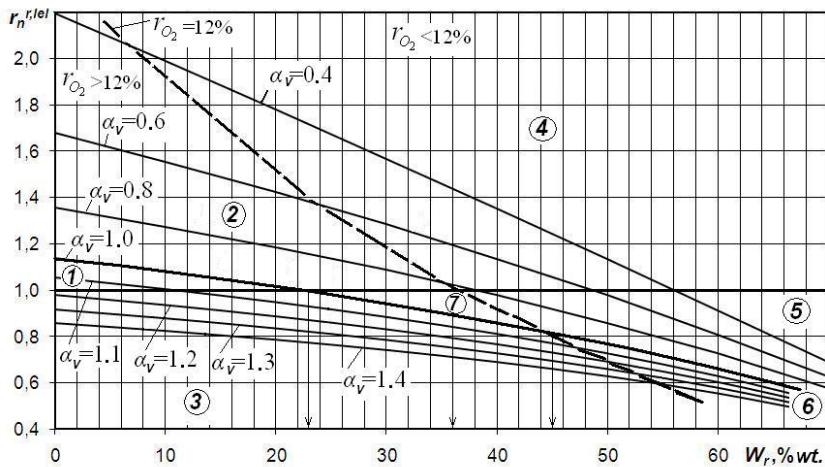


Figure. Volatiles and air mixtures $r_n^{r,lel}$ depending on W_r and α_v

In zone 1 at biomass moisture content $W_r < 23\%$ volatiles and air mixtures are able to forced ignition, burning occurs at $\alpha_v = 1.0 - 1.2$ with high temperatures $t_{ad} = 1372 \dots 1550 \dots 1666^\circ\text{C}$, such conditions are favorable for complete combustion.

In zone 2 at biomass moisture content $W_r < 36\%$ volatiles and air mixtures are able to forced ignition at $\alpha_v = 1.0 - 0.4$, with high temperatures $t_{ad} = 1161 \dots 1372 \dots 1666^\circ\text{C}$, but because of insufficient oxygen content $\alpha_v < 1.0$ burning will be incomplete. For such mixtures after ignition the secondary air should be added to ensure operational total air excess $\alpha_v > 1$ with mixture properties transition to zone 3.

In zone 3 all mixtures are lean and not able for forced ignition, but they can react according to mechanism of thermal self-ignition in volume [5]. At $W_r = 0 \dots 45\%$ and $\alpha_v = 1.0 - 1.4$ adiabatic temperatures are in range from $t_{ad} = 1350 \dots 1550^\circ\text{C}$ to $t_{ad} = 988 \dots 857^\circ\text{C}$ facilitating gas phase reactions. Provided sufficient residence time, complete combustion is possible and furnace with refractory lining is essential. At W_r

= 45...55% adiabatic temperatures are below 800°C with reactions delay. Reaction rate can be raised due to furnace refractory lining and air preheating.

In zone 7 mixtures have high combustible components content but are not able for forced ignition. Such mixtures can occur at combustion of biomass $W_r=23 \dots 45\%$ with insufficient air supply ($\alpha_v < 1$), but they can react according to mechanism of thermal self-ignition in volume. Because of high adiabatic temperature $t_{ad}=988\dots1372^\circ\text{C}$ and lack of oxygen combustion will be incomplete. At biomass combustion such mixtures of volatiles with air are not desirable.

In zones 4 and 5 reach volatiles and air mixtures $\alpha_v < 1.0$ are diluted with water vapor, which is formed at moisture evaporation and biomass thermolysis, and are not able to forced ignition mainly because of low oxygen concentration $r_{O_2} < 12\%\text{vol.}$

In zone 6 at $W_r > 45\dots55\%$ mixtures are diluted with water vapor, contain sufficiently of oxygen $\alpha_v > 1.0$ but its concentration $r_{O_2} < 12\%\text{vol.}$ insufficient for forced ignition. At $\alpha_v=1.0 - 1.4$ adiabatic temperatures are from $t_{ad} = 988\dots644^\circ\text{C}$ lowering to $t_{ad} = 620\dots557^\circ\text{C}$ with increase of biomass moisture content. At low temperatures volatiles ignition is retarded or even impossible.

Mixtures of **zones 4, 5, 6** can be carried out from furnace as unreacted or heated due to chemical reactions, mixing with hot gases and contact with red-hot refractory resulting incomplete burning and cracking of volatiles with particulate matter emission.

Additionally kinetics of solid biofuels thermolysis and formed coke-ash residue burning out are studied. Based on these data environmentally friendly technologies of biomass combustion can be created. We are looking for scientific and industrial partners for further researches and development of new equipment for baled straw, straw pellet, wet wood chips combustion.

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PREPARATION AND PULVERIZED COMBUSTION OF ANTHRACITE WITH BITUMINOUS COAL BLENDS AT ZMIYIVSKA TPP

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7 of the 14 TPPs in Ukraine are designed to burn bituminous coal, 7 – anthracite and semi-anthracite. After the outbreak of hostilities increase, bituminous coal production in western Donbas and in Lviv-Volyn Basin compensated the stop of coal supply from temporarily uncontrolled territories. But semi-anthracite and anthracite are mined only on temporarily uncontrolled territories of Donbas, and even thence mines remain Ukrainian, supplies are complicated by logistical and political factors. Offers in the world market and the capacity of Ukrainian ports for supplying the low-reactive steam coal are not enough. Also, there is lack of money and time for total anthracite boilers reconstruction with their transfer to bituminous coal.

At the end of 2015 at Zmiyivska TPP under the direction of CETI for the first time it was implemented the burning of anthracite blend with 27–32% bituminous coal in TP-100 and TPP-210 boilers which have anthracite and semi-anthracite as basic fuels. The blend's volatile yield ($V^{\text{daf}} = 14\text{--}16\%$) corresponded to semi-anthracite and did not need any reconstruction of pulverizing system and boilers. Burning of the fuel blend allowed to expand TPP fuel base by 40%. Increased blend's volatile yield compared with anthracite facilitated pulverized ignition and allowed boilers with liquid slag removal to operate in the range of 65–100% load without gas and oil addition.

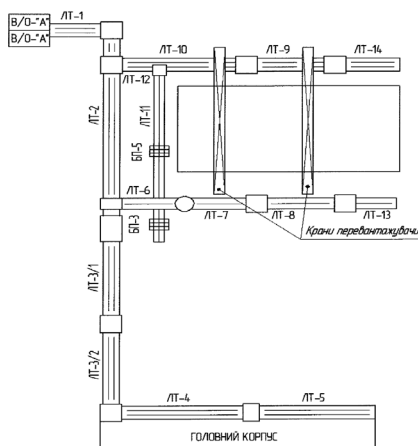
In order to turn a fuel blend burning from experiment into the main mode of Zmiyivska TPP boiler operation, which lasts more than 15 months, certain scientific and practical problems had to be solved with homogeneous mixing at the TPP' stock and with in-furnace regime optimizing of fuel blend pulverized combustion.

Features of coal stock at Zmiyivska TPP (Fig. 1) is the presence of two grab cranes and two conveyor belts galleries along. This allows to realize mixing technology "one line - two feeders" when anthracite and bituminous coal supply from individual piles or from car dumpers, and to return the blend into the stock to control

homogeneity.

Homogeneity of the mixture is controlled by the sampling a representative number of increments (the lot of the blend to 1,000 tons – 16 increments, of 1000–2000 tons – 24 increments, of 2000–3000 tons – 36 increments), calculating the mean value and standard deviation values of V^{daf} in increments. The blend is homogenous if the standard deviation of V^{daf} is $\leq 2\%$. In order to 95% increments not exceed V^{daf} upper limit of semi-anthracite 18%, the average V^{daf} must not exceed 14%. Such results were obtained when testing in late 2015 on a fresh blend. However, when the ongoing operation it should consider the impact of segregation of particles during blend storage and processes while transporting the blend to coal mills.

Fig. 1. Scheme of coal stock of Zmiyivska TPP



To determine the influence of these factors, in June 2016 the tests were carried out which showed that standard deviation slightly increased during the storage (Fig. 2a), but with additional mixing when siltings and in coal bunker the standard deviation is reduced to less than 1% (Fig. 2b). This allows to increase the average value V^{daf} mix up to 15–16%.

Organization of the fuel blend combustion has the following features. As the volatiles and high reactive coke residue of bituminous coal burn faster than anthracite, oxygen concentration decreases, which may slow the anthracite ignition and burn. However, the evaluation calculated using the kinetic constants obtained earlier in CETI showed that at temperatures typical for pulverized combustion the bituminous coal particles burn in external diffusion mode, and anthracite particles - in transition mode, where the dependence of the combustion temperature is stronger. Therefore, reducing the rate of anthracite burning due to lowering the oxygen concentration can

be compensated by increasing jet temperature due to additional heat generation from the combustion of volatile matter and coke residue of bituminous coal. But this is true only in the presence of excess air in the main burners.

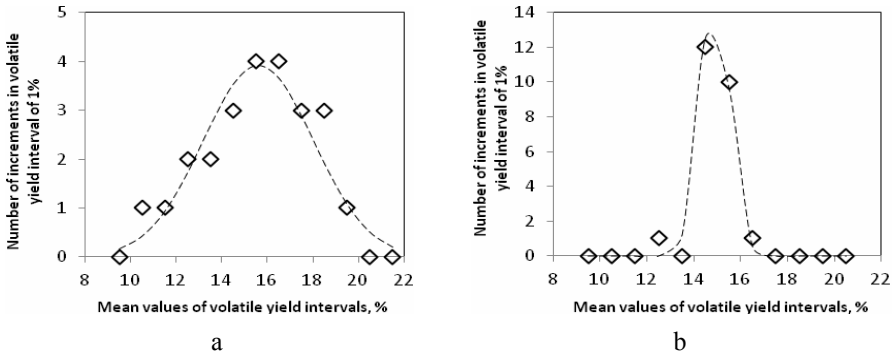


Fig. 2. The density distribution of values of V^{daf} in blend increments compared to normal distribution:

- a – from the pile of blend, average $V^{daf} = 15.5\%$, standard deviation of 2.4%;
- b – from raw coal feeder, average $V^{daf} = 14.9\%$, standard deviation of 0.6%.

CETI experts analyzed the distribution of air in Zmiyivska TPP boilers considering air blowing, pulverizing system, suction in the furnace and convective pass, and show that the excess air in the main burners of TP-100 boilers is implemented within loads of up to 85%; in the main burners of TPP-210 boilers air is a shortage in the whole range of loads (Fig. 3).

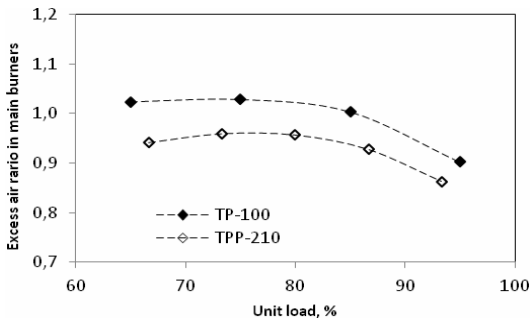


Fig. 3. Dependence of the excess air in the main burners on the load at the units of 200 MW (boilers TP-100) and 300 MW (boilers TPP-210).

The complex of organizational and technical measures was proposed to reduce unburned carbon loss when burning blend of anthracite with bituminous coal in TP-100 and TPP-210 boilers, in particular, by the alternation of full mills load with work on fewer mills number with reduced air flow to waste burners, by use recycling of spent drying agent from mill fans to mills with the aim to reduce waste drying agent

flow, and others. Their implementation only for TP-100 boilers of units №№ 1-6 has reduced the loss with unburned carbon from 4.4–6.9% down to 3.3–4.1% (Fig. 4).

Overall, under the scientific and practical assistance of CETI in 2016 at Zmiyivska TPP was used almost 300 ths. tons of domestic bituminous coal in the mixture with anthracite, while blend volatile yield corresponded to semi-anthracite. When fuel blend combustion, pulverizing systems and TP-100 and TPP-210 boilers were not reconstructed, oil and gas additional fuel was not used, average heat loss with unburned carbon in the boilers of 200 MW units was less than 4.8%. This increased fuel base of TPP by 40%, thus avoiding the summer stops, increased range of load control units and improved their technical and economic parameters compared with anthracite combustion.

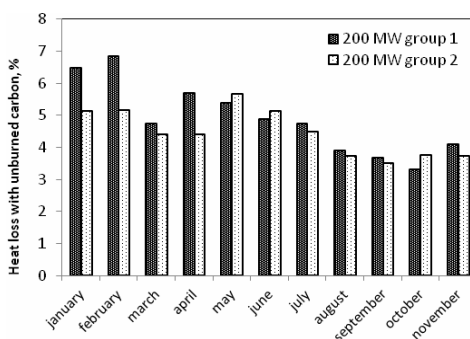


Fig. 4. Dynamics of heat loss with unburned carbon in TP-100 boilers of Zmiyivska TPP in 2016.

The burning blend of anthracite with bituminous coal can be recommended for other thermal power plants. This annual consumption of bituminous coal to Zmiyivska and Krivorizka TPPs could reach 1 mln. tons each other, to Tripilska and Pridniprovsk TPPs - up to 0.7 mln. tons each other. Prior to transfer anthracite TPPs to bituminous coal burning, it will reduce the deficit of anthracite and semi-anthracite, improve combustion modes and create additional markets for state-owned mines.

COMPARISON OF WASTE CONVERSION TECHNOLOGIES: WHY WESTERN EQUIPMENT IS UNACCEPTABLE IN UKRAINE

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The last few decades, the interconnected problems of the production of alternative synthetic gaseous fuels via conversion of carbon-containing materials as

well as utilization of hazardous wastes by means of plasma technologies were widely discussed. The synthesis gaseous fuel, mixture CO and H₂, is obtained in these processes. It can be used to make the facility energetically self-sufficient or as a separate fuel to commercialization of the project.

Industrial equipment of the Western countries for solid waste processing based on the using of air torch is well known, for example Integrated Multifuel Gasification technology (IMG) [1] and Westinghouse Plasma Corporation (WPC) [2]. We develop technology of solid waste processing contrastingly based on the steam torch [3].

Waste as renewable source of energy. There's a problem of environment pollution when using municipal solid waste as energy source. Earlier, they have been used for the heat production by means of direct combustion processes. Now this technology is presented by the next generation of the well-known in Kyiv waste processing plant "Energy" [4].

Modern technology does not assume the use of the combustion process generally, because of risk of dioxins and furans formation in case of chlorinated raw material processing. These compounds are among the most toxic ones – their maximum permissible emission to the atmosphere in the refinement products can't exceed 10^{-10} g/m³. Currently, this problem is adjusted by the Directive 2000/76/EC [5]. Accordingly, the temperature should be maintained at 1100 °C in case of incineration of waste containing more than 1% wt. of halogenous organic substances under conditions of chloride. Each local volume of gas produced in the processing has to be kept at this temperature over time ≥ 2 s. In many countries, as former countries of the USSR, where the level of chlorine in the waste is unknown beforehand, other technologies can't be applied at all, apart from those satisfying the above requirements of the Directive 2000/76/EC. It is directly related also to the technologies of medical waste processing, at least in those countries where medical materials still contain chlorinated components.

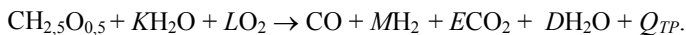
Another problem is if the waste contains in its composition heavy metals; incineration leads to the formation of ash, which is itself a hazardous waste. The latter environmental hazard is particularly dangerous in the case of recycling the sewage sludge of urban wastewater treatment plants.

Plasma gasification of sewage sludge. During sewage treatment, the main pollutants are separated as sewage sludge. Its characteristics depend on the original pollution load of the water being treated, as well as the sludge treatment being carried out. The Kyiv wastewater treatment plant (known as Bortnychi station of aeration),

which processes municipal and industrial sewage and run-off rain water, obtain 9000 m³ wastewater over a twenty-four period. 9 million tones of sewage sludge are stored near this station currently.

The special problem of this waste is heavy metal in its compound [3]. The fact is that using of plasma technology, after the processing results in the minimum amount of solid residue, at the level of several percentages of its initial mass. Moreover, being fused to glass-like mass (vitrified), it is in fact a neutral substrate, safe for the environment. The temperature of the process vitrification is above 1400-1700 K.

In order to optimize the plasma-steam gasification process of sewage sludge, there where analyzed the next reaction [3]:



Here $Q_{TP} = Q_R + \Delta Q$ is the total thermal energy, where component Q_R is a result of chemical reactions in a mixture and ΔQ is introduced into the reactor of gasifier by plasma torch jet such a way that reacting mixture has reached the desired temperature T_p to obtain quality products of gasification.

The data of analysis where used to compare the economic efficiency of the technologies [1–4]. They are presented lower in the table, where the symbols are introduced: C – annual capacity of equipment (t/a), P – power generation of electricity to consumers per year (MW·h/a), I – investments.

Conclusion. As can be seen, the traditional waste processing plant [4] ("Energy-2") requires specific investments I/C, close to the plasma technologies [1,2]. On the contrary, it has the worst indicators P/C concerning the possibility of investment return due to production of additional electric energy for external consumers. All three samples of Western technologies [1, 2, 4] have a very high cost; it cannot be compensated by production of additional electric energy.

Indicator	Technology			
	"Energy-2" [4]	IMG [1]	WPC [2]	GI NASU [3]
C, t/a	224.000	100.000	534.000	4.000
P, MW·h/a	63.000	68.000	427.000	4.200
I	130 mln. €	65 mln. €	307,5 mln. USD	1,2 mln. USD
I/C, USD(€)/t	580	650	575	300
P/C, kW·h /t	240	680	800	1050

Acknowledgments. This study was supported by Ministry of Education and Science of Ukraine; project "The development of steam-plasma technology of

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AN ALTERNATIVE SOLUTION TO ESP RECONSTRUCTION FOR THE COAL FIRING THERMAL POWER PLANTS IN UKRAINE

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Ukraine, when became a Contracting Party to the Energy Community, has committed itself to implement after 31 December 2017 the requirements of Directive 2001/80/EC. This implies that it should be provided that the exit concentration of the dust collectors installed downstream coal firing boilers shall not exceed 50 mg per normal cubic meter [1]. Directive 2010/75/EU on industrial emissions requires that existing combustion plants should secure 20 mg/Nm³ emission limit value [2]. However, this requirement must be met at chimney for all gas cleaning plants. The required dust concentration in the flue gas (FG) after dust collectors is driven by the requirements for the quality of the end product of desulphurization plant installed

downstream. Therefore, the required emission value after fly ash collector may range from 50 to 500 mg/Nm³. The fleet of fly ash collectors at Ukrainian thermal power plants (TPP) includes:

- Venturi wet scrubbers, installed in 1960s, with efficiency ranging from 85 to 92 %;
- dry-type electrostatic precipitators (ESP) of PHDS and UH2 type, installed in 1960s, with 7.5 m high collecting electrodes and actual efficiency 90–96 %;
- dry-type electrostatic precipitators of types EHA, EHB, EH3, UH3, installed in the period 1970–1980, with 12 m collecting electrodes and actual efficiency 95–98.5 %.

After 2009, only at 15 of 90 Ukrainian TPP power units new electrostatic precipitators were installed, with 14–15 m high collecting electrodes, having efficiency above 99.5% and outlet fly ash concentrations below 50 mg/Nm³.

Replacement of existing dust collectors with new electrostatic precipitators is a cardinal, but costly solution. For 200 MW power unit, such a measure costs about UAH100 million, and for 300 MW power unit – about UAH150 million. An alternative to complete replacement of the existing electrostatic precipitator with a new one could be the reconstruction of core assemblies and installation of dusted flow cleaning system using the louver cyclone separator, as shown in the diagram (Fig. 1).

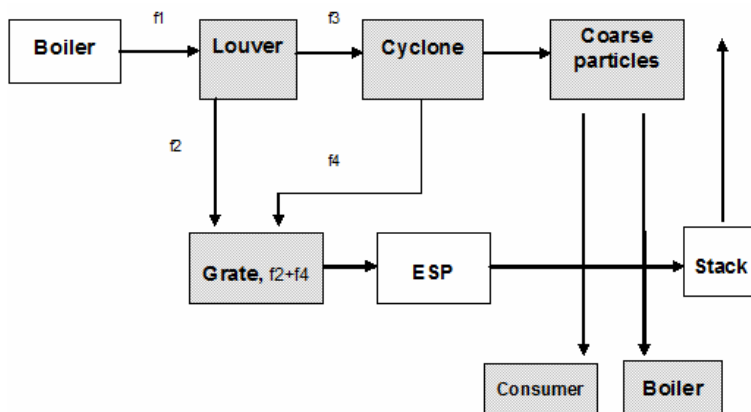


Fig. 1. Flow diagram for the flue gas cleaning system with louver separator and cyclone, and flue gas recirculation to the inlet of ESP.

The louver separator, placed upstream the ESP gas distribution grate, can separate up to 50% of the dust flow mass with 10% of gas flow [3]. This highly dusted stream

with a high concentration of large particles is then directed to and cleaned in the cyclone. From the outlet of the cyclone the flow with un-captured dust is returned to prechamber of the electrostatic precipitator. This is mixed with the rest 90 % of the gas flow containing particles that were not bended by louver, and the resulting mix enters ESP prechamber.

Installation of the louver concentrator leads to modification of mass distribution function f_1 of the dusted flue gas flow of coal-fired TPP boilers. The resulting distribution f_3 at the outlet of louver dust separator is characterized by elevated concentration of heavier solid fly ash particles, which shifts the original particles distribution function f_1 toward "heavier phase" (virtual diffusion of particles in the space of sizes), which makes their capturing more effective in inertial deposition devices, prior to their entering the finer cleaning installation (ESP or FF).

Curves of the efficiency of dust particles separation in the dust separator louver and in cyclone are well approximated by a function of the type $F = 1 - \text{Exp} [-KD_p]$, where D_p is the diameter of dust particle; K is the value which depends on the design parameters of the inertial cleaning apparatus.

The calculation of the louver efficiency was conducted by interpolation of the available experimental data [3]; and the calculation of the cyclone efficiency was done using the empirical formula [4], which also is obtained from generalization of experimental data. The calculation results of modeling the changes in original size distribution of the dust particles, after preliminary FG cleaning using the louver dust separator and in the cyclone, are shown in Fig. 2.

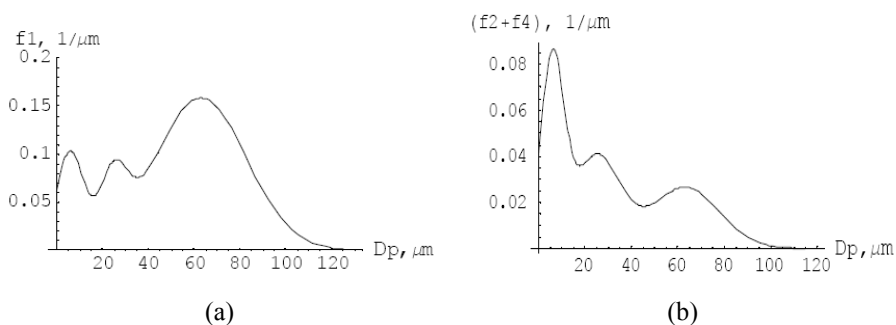


Fig. 2. Fly ash particles size distributions behind the pulverized coal boiler (a) and at the inlet to ESP (b), after FG being cleaned at louver and cyclone and returned to ESP.

Calculations showed that at initial 40 g/Nm^3 fly ash particles concentration in flue gas

behind the coal firing boilers installation of preliminary cleaning system with louver separator and cyclones allows achieving dust particles concentration of about 15 g/Nm^3 at the inlet to ESP, for further flue gas finer cleaning.

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COKE CHEMICAL WASTE USAGE AT JOINT CONVERSION WITH COAL INTO DURABLE CARBON SORBENTS

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It was investigated the lows and solid products for thermolysis ($450\text{--}700^\circ\text{C}$) of blends of long flame coal (D) with coal tar (CT), polymers (P) of benzene separation and coke chemical wastes: fuse (F), sour tar (ST), distillation residue (DR) too.

For performance it was chosen surplus coal I (D) (sizes $d - 0,5\text{--}2,0 \text{ mm}$) with characteristics : W^a 11,1%; A^d 1,8%; V^{daf} 43,8%; elemental composition of organic mass (% daf): C 80,0; H 5,3; S 1,0; N 1,9; O 11,8.

Using infrared spectroscopy shows, that yet at combining the stage chemical interaction between components takes place. So, the relative intensity of the absorption bands in the region of hydroxyl intermolecular connections ($\nu = 3400 \text{ cm}^{-1}$) and functional O-containing fragments ($\nu = 1100\text{--}1040 \text{ cm}^{-1}$) in 1,3 – 2,5 time higher than in initial coal spectra.

Table 1. Characteristics of coke chemical wastes (CCW) and semi-products (P, CT)

Indexes	Fuse	Sour tar	Polymers	Coal tar	Distillation residue
Density (ρ , g/sm ²)	1.25	1.27	1.12	1.15	0.96
W ^a , %	10.0	23.7	1.6	2.2	—
A ^d , %	6.4	0.2	0.1	0.1	5.2
C ^{daf} , %	88.6	75.9	86.6	91.4	—
H ^{daf} , %	5.5	4.9	5.3	5.5	—
S ^{daf} , %	1.5	4.7	4.1	0.9	4.9
O ^{daf} +N ^{daf} , %	4.4	14.5	4.0	2.2	—

Its values exceed considerably 15%, as can be at additive behavior of the blends.

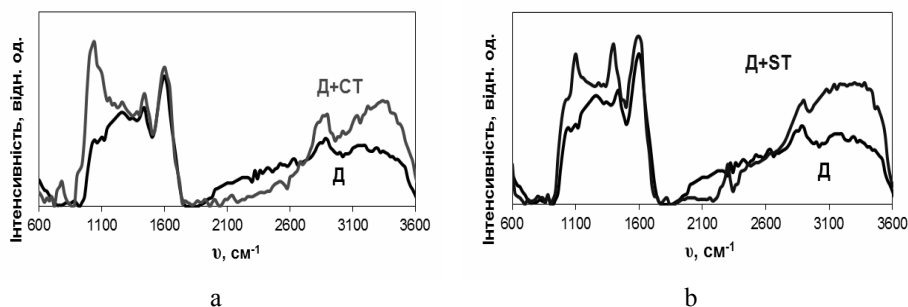


Fig. 1 data show IR-spectra of D-coal and it blends with (CT) (a) and (ST) (b).

The criterion for waste-coal combinations first was chosen the indentation resistance (IR) of blends, determined by modified Brinell method. IR value for blends is maximal when 15% is the waste concentration and it depends on density of waste.

At the blends thermolysis (450 and 700°C) one of products are carbonizates, their yield (52–64%) arcwise diminishes with the height of identation resistance (IR). At the same time yield of carbonizates proportionally related to the density of the applied waste.

The influence of CCW on increase of mechanical durability of carbonizates was established (table 2). Maximal effect was educed at coal tar (CT) usage for all carbonization temperature (450–7000C), when durability index changed from 67% (for initial coal carbonizate) to 91–95% for blending carbonizates.

Obtained on first stage carbonizates have were activated by water steam at 800⁰ C. Activated carbon (AC) yield depends on blend composition, and varies in interval 79 – 90 %. Specific surface S_{BET} (m²/r) and total volume V_{Σ} (sm³/g) of pores determines on N₂ or CO₂, adsorbed at $(p/p_0) \sim 1$. By method of BJH mezopore volume was determined (V_{me} (cm³/r) on N₂- isotherm desorption. Volume of

micropores (V_{mi} (cm³/g)) was determined by DR –method.

Table 2. Generalized indexes of waste density (ρ), IR blends and durability (mechanical strength (MS) of carbonized and activated materials

Sample	MS (%) ($t_{carb} - 450^0C$)	IR initial blends	Waste density ρ , g/sm ³
Carbonizate D	64.5	12.7	–
“ – “ – “ – “ D-F	88.1	24.0	1.25
“ – “ – “ – “ D-P	84.9	41.0	1.12
“ – “ – “ – “ D-DR	89.0	48.0	0.96
“ – “ – “ – “ D-CT	90.8	24.1	1.15
“ – “ – “ – “ D-ST	88.3	16.3	1.27
MS for sorbents ($t_{activation} - 800^0C$, $\tau = 1$ h)			
Sorbent from D - CT	90.1	–	–
Sorbent from D - P	88.3	–	–
Sorbent from D	58.4	–	–

Results of table 3 demonstrated that waste influence on porosity development is not positive (at 30 min activation). Optimal time of activation is 1–2 hours. Indexes of activation, porous structure expected from CO₂-isotherms, as a rule have more higher value (specific surface – 390–450 m²/g), then the same from N₂ – isotherms. For more long time activation these values are drawn together.

Table 3. Some indexes for porous structure of AC from blends (at N₂ and CO₂ adsorptives)

Sample	Activation time, min.	CO ₂ S _{BET} , m ² /g	N ₂ S _{BET} , m ² /g	CO ₂ V _{micro} , sm ³ /g	N ₂ V _{micro} , sm ³ /g
D	30	350-	170	0,162-	0,051
D-P	30	370	163	0,158	0,062
	60	380	229	0,166	0,089
	120	394	242	0,174	0,102
D-CT	30	350	100	0,153	–
	60	356	100	0,160	0,035
	120	396	250	0,177	0,108
D-DR	30	342-	130	0,152	0,053
	60	350-	148	0,153-	0,064
	120	453	486	0,203	0,208

Activated by steam samples with coke chemical waste using have S_{DFT} more 500–600 m²/g, part of micropores consist of 76–90%. At the same time these ACs differ in higher mechanical durability in comparison with AC from alone coal (table 2).

MODERN FUEL CELL POWER SYSTEMS. COAL AND SOLID ORGANIC WASTE GASIFICATION FOR HYDROGEN-RICH SYNTHESIS GAS PRODUCTION

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The use of fuel cell (FC) power units at coal-fired power plants will enable an increase in the efficiency of coal energy conversion into electricity by 50–60% and a decrease in CO₂ emissions into the environment by 30–50% without application of CO₂ underground disposal units. In this case, the CO₂ emissions into the environment will be 611 to 733 g/kWh of generated electricity when using anthracite, and 548 to 658 g/kWh of generated electricity when using brown coal.

In 2015, the world market sales of fuel cell power plants (FCPP) were 1.1 bln. USD [1]. The total electric capacity of FCPPs, sold in 2015, was 340 MW: 82% for stationary use and 18% for transport. 64% of FCPPs use proton exchange membrane (PEM) fuel cells (FCs), 21% – solid oxide fuel cells (SOFCs), and 15% – other (molten carbonate electrolyte FCs, phosphoric acid FCs, and alkaline FCs). The total electric capacity of FCPPs, implemented from 2013 to 2015, is 700 MW. More than 100 companies and enterprises are engaged in development and implementation of FCPPs in the world. Leaders in the production and sale of FCPPs in 2015 were: Fuel Cell Energy (USA), Intelligent Energy (UK), Ballard (USA), Hydrogenics (Canada), and Plug Power (USA). FCPPs in comparison with conventional power plants have the following advantages: high energy efficiency (due to the direct conversion of chemical energy of fuels into electricity), the best performance on harmful emissions into the environment (the preliminary treatment of gas is required for FC operation), the possibility of independent high-efficiency decentralized use (low capacity and high electrical efficiency), reliability, and low noise (FCPP is completely closed power plant that do not use sophisticated equipment, has a small number of moving parts, and has not electrical surge in case of changing the electric load). When coal and solid organic waste are used in FCPP, than preliminary gasification of solid fuel into the cleaned hydrogen-rich synthesis gas or pure hydrogen is required at thermal power plants. The electrical efficiency up to 60% can be achieved by using high temperature fuel cell as a component of integrated combined cycle coal power plant.

Practical application of fuel cells in industrial scale requires appropriate normative documents. As of September 1, 2016, 17 international standards developed by

IEC/TC 105 on fuel cell technologies are in force. In Ukraine, harmonized with the international standard DSTU EN 62282-3-100:2014 (EN 62282-3-100:2012, IDT) “Fuel cell technologies – Part 3-100: Stationary fuel cell power systems – Safety” was approved in 2014. In 2016, another two standards are in the works: DSTU EN 62282-3-300 (EN 62282-3-300: 2012, IDT) “Fuel cell technologies – Part 3-300: Stationary fuel cell power systems – Installation” and DSTU EN 62282-5-1 (EN 62282-5-1: 2012, IDT) “Fuel cell technologies – Part 5-1: Portable fuel cell power systems – Safety”.

Assembly units of a new dual-purpose installation DualEks for production of energy (electricity and heat) and chemicals (hydrogen and liquid products) were created in the Coal Energy Technology Institute of National Academy of Sciences of Ukraine [2]. To determine the key parameters of the assembly units, there was tested the possibility of the production of process gas during the gasification of wood coal, wood waste, sewage sludge from Bortnychi aeration station (Kyiv), and polyurethane foam waste in the downdraft moving bed gasifier. The gasification unit with fuel cell generator is planned to be used in 2018.

Two-stage process of solid organic waste gasification is realized. Steam plasma flow was fed into the gasifier’s zone of carbonization. The obtained products were fed into the zone of partial air oxidation. Gasification of conversion product residues occurred at the bottom of the gasifier. Experimental studies were performed both with and without the use of steam plasma torch.

The decrease in carbon dioxide yield in the process gas was 52.8%, and equivalent ratio of air flow for wood coal gasification was reduced from 0.63-0.84 to 0.38-0.53 mol/mol at the average specific yield of gas of $250 \text{ Nm}^3/(\text{m}^2 \cdot \text{h})$ due to the lining of the gasifier and the cyclone, and feeding of air and steam into the middle part of the gasifier during wood coal gasification. Cold gas efficiency of wood coal gasification was 61.6%. The low heat value of the process gas was up to 4.5 MJ/Nm^3 . Addition of steam to the air led to an increase in the ratio of H_2/CO in the obtained gas from 0.22 to 0.6–1.29 mol/mol, and the hydrogen yield (in the gas produced during air/air-steam gasification) on dry ash-free basis of wood coal from 0.16–0.34 to 0.58–0.89 Nm^3/kg .

During air/air-steam gasification of sewage sludge from Bortnychi aeration station (Kyiv), the yield of process gas was $1.37\text{--}2.63 \text{ Nm}^3/\text{h}$. The low heat value of the produced gas was $2.1\text{--}3.7 \text{ MJ/Nm}^3$. The equivalent ratio of the air flow for gasification was 0.36–0.53 mol/mol at the specific yield of gas of $280\text{--}536 \text{ Nm}^3/(\text{m}^2 \cdot \text{h})$. Cold gas efficiency of gasification was 59.4%. Addition of steam to

the air led to an increase in the molar ratio of H_2/CO in the obtained gas from 0.77–0.85 to 2.1–2.7 mol/mol, and the hydrogen yield in the produced gas on dry ash-free basis of sewage sludge from 0.41–0.47 to 0.61–0.76 Nm^3/kg .

From sewage sludge from Bortnychi aeration station (Kyiv), there was produced gas, which after cleaning can be used to produce liquid motor fuels without the use of shift reactor and to generate electricity in high-temperature fuel cells.

As a result of air gasification of wood waste, there was produced dry process gas with low heat value of 4,1–6,5 MJ/Nm^3 at the equivalent ratio of air flow for gasification of 0.24–0.37 mol/mol, specific yield of gas of 234–461 $Nm^3/(m^2 \cdot h)$, and cold gas efficiency of 81.5%. The ratio of H_2/CO in the obtained gas 0.45–0.52 mol/mol, and the yield of hydrogen in the produced gas on dry ash-free basis of wood waste was 0.28–0.44 Nm^3/kg .

Calcium hydroxide inside polyurethane foam particles was used to provide an additional source of steam and conversion of macromolecular compounds during air gasification of wood waste.

During the air gasification of wood waste (50 wt.%) with the addition of calcium hydroxide (50 wt.%), which was inside the polyurethane foam particles, at the solid waste consumption of 386 g/h, air flow rate of 1.03 Nm^3/h , velocity of solid waste bed movement in the gasifier of 26.2 cm/h, yield of 1.38 Nm^3/h of dry gas with low heat value of 3.4 MJ/Nm^3 , equivalent ratio of the air flow of 0.524 mol/mol, and specific gas flow rate of 281 $Nm^3/(m^2 \cdot h)$, the cold gas efficiency was 59.22%. The ratio of H_2/CO in the produced gas rose from 0.37 to 0.78 mol/mol due to evaporation of moisture from the wood and decomposition of the calcium hydroxide. During the release of steam in the time of calcium hydroxide decomposition, the yield of hydrogen in the produced gas on dry ash-free basis of wood waste was 0.32–0.49 Nm^3/kg .

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CO-COMBUSTION OF SOLID BIOMASS IN PULVERIZED ANTHRACITE-COAL FIRING BOILERS

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The combustion of the solid biomass in Ukrainian boilers can not only reduce harmful emissions, but also diversify the generations' fuel base and to substitute the lighting natural gas in case of high-ash anthracite combustion.

The pine and pulverized anthracite co-combustion studied at the experimental unit with fuel rate of 30 kg/h. The co-combustion of pulverized domestic anthracite and wood in the experimental unit has proven its technical realizability and a noticeable potential to significantly improve the quality of low-reactive anthracite combustion. On the basis of the co-combustion regimes' the optimal thermal share of the biomass was determined that is about 10% and provides torch stabilization without gas lighting and highest degree of the coal carbon conversion.

Table 1 – The experimental regime characteristics

Regime	Coal ash content, % sawdust coal			Conversion degree, %		Excess air	Total power, kW	Residence time, s	Gas temperature in sections, °C				Fuel share under heat, %			
									1	2	3	4	gas	gas/sawdust*	coal	sawdust
Natural gas and coal combustion																
1	24,8	0	63,4	0,74	146,6	0,9	1340	1340	1330	1200	11,3	6,9	88,7	0		
2	27,9	0	60,8	0,76	141,4	0,9	1300	1350	1355	1250	11,7	7,2	88,3	0		
3	24,8	0	59,2	0,8	147,8	0,9	1002	1275	1320	1202	12,0	6,5	88	0		
4	27,9	0	52,3	0,82	146	0,8	940	1260	1380	1320	25,7	20,8	74,3	0		
5	27,9	0	73,3	0,86	148,1	0,9	940	1090	1100	1010	26,8	20,2	73,2	0		
Biomass and coal co-combustion																
6	24,8	80	56,5	0,47	172,9	0,8	1380	1445	1405	1290	0	2,9	92,9	7,1		
7	27,9	80	70,4	0,78	154,4	0,7	1445	1445	1415	1305	0	13,9	80,9	19,1		
8	27,9	80	75,9	0,85	145,7	0,7	1445	1445	1405	1330	0	8,4	85,7	14,3		

Notes: * – the natural gas/sawdust heat share taking into account its consumption for air heating up to 320°C at TPP that is operated.

The kinetics of pine sawdust cokes burn out been studied by the fluidized bed unit RSK-1D. The samples of the pine wood, pellets of wheat straw, rape, corn and soy studied by TG method.

The internal kinetic mode of pine cokes' samples' combustion size 0,1–1,6 mm in temperatures' range of 390–560°C was set at the RSK-1D unit as indicated by lack of cokes' particles' size impact, as well as reactant gas rate changes in reactor for interaction rate with air oxygen.

Using the TG method, the kinetic characteristics of individual stages of the biomass thermal conversion obtained. Comparison of pine sawdust and wheat straw pellets' devolatilization kinetics with those available in the literature indicates the difference in the rate of devolatilization that may be explained by the difference in sample heating rate, size of sample particles, variation in organic and mineral composition of samples, methods of reaction constants calculation and interpretation. At the same time, the devolatilization proximity of the wheat straw pellets of different crops under the present study obtained in similar conditions, is observed.

Table 2 – The pre-exponential factor (k_0) and activation energy (E) calculation results for stages of dehydration and devolatilization of fuel samples studied and its literature analogues

Fuel sample	Heating rate, °C/min.	Fuel thermal decomposition stage			
		dehydration		devolatilization	
		k_0 , 1/s	E, kJ/mol	k_0 , 1/s	E, kJ/mol
Pine sawdust 1	5	4373,85	39,19	80,02	54,76
Pine sawdust 2	5	1018,31	35,02	2627,79	71,34
Wheat straw pellets	20	1,51	16,35	177,03	52,15
Rape pellets	20	8,90	22,82	472,72	55,58
Corn pellets	20	13,18	23,32	2145,44	63,11
Soy beans pellets	20	443,86	33,78	740,19	56,57
Pine sawdust [12]	15	–	–	$6,60 \cdot 10^8$	102,30
Pine [13]	10	–	–	$7,32 \cdot 10^7$	122,56
Pine sawdust [14]	20	13,60	24,52	164400	87,37
Wheat straw [15]	30	–	–	$1,57 \cdot 10^7$	115,59
Wheat straw [14]	20	13,70	25,85	92470	82,00
Soy beans [16]	5–20	–	–	–	182,00

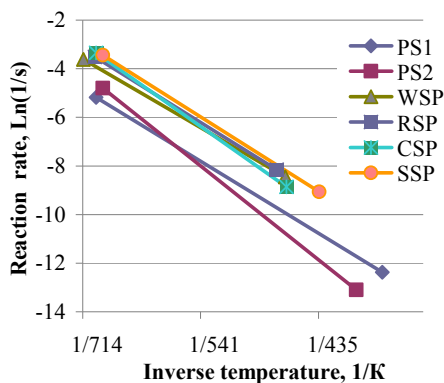


Figure – The comparison of the volatile yield rate dependencies from pine sawdust and pellets' sample reciprocal temperature studied, where:
 PS1 and PS2 – pine sawdust as per 1 and 2;
 WSP – wheat straw pellets;
 RSP – rape straw

The studies' results presented can be used in calculations of the separate co-combustion processes to implement at TPP's of Ukraine.

CARBONIZATION AND GASIFICATION OF UKRAINIAN SOLID ORGANIC WASTES AND COALS WITHOUT AND WITH THE USE OF CATALYSTS

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The complex of research on the conversion of solid organic waste, whose ultimate goal was to obtain char coal, hydrogen-rich gas, and clean hydrogen, was carried out. New experimental installations for solid organic waste carbonization were created and the Fuel Cell Test Installation was used in Coal Energy Technology Institute of National Academy of Sciences of Ukraine (CETI NASU) to solve this problem. New nanostructured catalysts for the conversion of volatile matters were created in the L.V. Pysarzhevsky Institute of Physical Chemistry of National Academy of Sciences of Ukraine (IPC NASU). The research of the conversion of Indian solid waste of the sugar production from sugar cane (bagasse) was carried out and the new Indian nickel catalyst for conversion of volatile matters was tested within the framework of international cooperation with Indian Institute of Petroleum (IIP).

To increase the yield of wood coal, the solid wastes were preliminary impregnated with 5% water solutions of H_3PO_4 and NaOH, and 0.2% water solution of CaO. Preliminary impregnation of the samples with 5% water solutions of H_3PO_4 enabled an increase in the dry coal yield from cotton 1.55 times, and from the paper 1.50

times. An increase in wood coal yield was: 1.1 times after the impregnation of husk with 0.2% water solution of CaO, 1.3 times with 5% water solution of NaOH, and 1.8 times with 5% water solution of H₃PO₄ in comparison with the yield of coal from a pure sample. The samples of coal obtained from waste cotton, sunflower husks, and lignin (after preliminary impregnation with 5% water solution of H₃PO₄) were used to produce hydrogen-rich synthesis gas at the Fuel Cell Test Installation using lime (CaO/C = 4–6 g/g) at temperatures of 650–720 °C, 700–780 °C, and 800–900 °C, respectively. During the steam gasification of coal obtained from waste cotton, sunflower husks, and lignin, there was produced dry synthesis gas with hydrogen content up to 81.4, 74.3, and 69.7 vol. %, respectively.

The gas with low content of hydrogen (to 13 vol. %) and high content of CO₂ (above 49 vol. %) was obtained as a result of sunflower husk carbonization without the use of catalysts. Dry gas with content of hydrogen up to 52 vol. % (with the low heat value (LHV) of 8.4–12.8 MJ/Nm³) and wood coal (with the LHV of 20.3 MJ/kg) were produced using a nickel catalyst for the conversion of volatile matters obtained after sunflower husk carbonization. After the steam gasification of coal (obtained from sunflower husks) at 745–770 °C using fluidized bed with Ni-catalyst and lime, there was obtained dry hydrogen-rich synthesis gas, containing, wt. %: H₂ = 72.5, CO = 13.6, CH₄ = 2.5, CO₂ = 11.4. The degree of CO₂ capture by lime was 64.5%, and LHV of the obtained synthesis gas was 10.4 MJ/Nm³.

Stage carbonization process of natural (C₆H₁₀O₅)_n and synthetic (C₁₀H₈O₄)_n polymers was determined at the time of the research of the carbonization of waste cloth of polyester (65 wt. %) and cotton (35 wt. %) without the use of catalysts. The coal with LHV up to 30.2 MJ/kg was obtained as a result of polyester and cotton cloth carbonization. Nanostructured Ni-catalyst of IIP and Fe-catalyst of IPC NASU were used for the research of the carbonization of waste cloth of polyester and cotton. An increase in the yield of dry gas after carbonization was 11.0 wt. % using Fe-catalyst and 19.7 wt. % using Ni-catalyst in comparison with the carbonization without the use of catalysts. Without the addition of steam and using only catalysts, the molar ratio H₂/CO in the produced gas was increased from 0.25 to 1.02 using Ni-catalyst and up to 1.25 using Fe-catalyst. An increase in the content of hydrogen in the produced dry gas was 3.6 and 2.8 times due to the use of Fe- and Ni- catalysts, respectively, in comparison with the carbonization without the use of catalysts.

New types of solid fuel to produce hydrogen were created and tested. Calcium hydroxide was used in the carbonization reactor as a source of steam for solid fuel

and lime conversion, carbon dioxide capture, and as a catalyst for volatile conversion. Prepared fuel was mixed with calcium hydroxide, which was prepared by mixing lime CaO with distilled water.

New catalysts of IPC NASU for volatile matter conversion were used in the time of research at the installation for solid waste carbonization. An increase in the hydrogen content in the produced gas was provided both due to an increase in the hydrogen content in the initial mixture and catalytic steam reforming. Gas with a hydrogen content of more than 80 vol. % (82.1 vol.%) was obtained as a result of the conversion of a mixture of wood, polypropylene, nickel oxide, and calcium hydroxide. The yield of dry gas from a mixture of wood, polypropylene, and calcium hydroxide (10.1/10.1/79.8 wt.%) was 130.3 ml/g of fuel (the yield of hydrogen was 62 ml/g of fuel). The yield of dry gas from a mixture of wood, polypropylene, calcium hydroxide, and Fe-catalyst (10.5/10.5/76.7/2.3 wt.%) was 139 ml/g of fuel (the yield of hydrogen was 62 ml/g of fuel). The yield of dry gas from a mixture of wood, polypropylene, calcium hydroxide, and Ni-catalyst was 267 ml/g of fuel (the yield of hydrogen was 219 ml/g of fuel).

An analysis of the experimental data showed that the process of solid organic waste gasification should be carried out in two stages: at the first stage, to remove volatile matters from solid organic waste by their steam/steam-oxygen conversion; at the second stage, to gasify the obtained char coal by air (oxygen) or steam (steam-oxygen) blast depending on the composition of the wastes.

Due to the shortage of low-volatile coal at the thermal power plants of Ukraine, there were conducted a series of studies on the carbonization of coal with low (brown coal) and medium (bituminous coal) degree of metamorphism to produce low-volatile coal. The gaseous products of carbonization were used to produce hydrogen-rich gas. Gas with LHV of 9.9 to 12.5 MJ/Nm³ was obtained during carbonization of brown coal from Zhitomir region (ZR).

An increase in hydrogen content in the produced dry gas was 3.4 and 9.3 times due to the use of Fe-Cr and Ni- catalysts, respectively, for the conversion of volatile products of the carbonization of brown coal from Kirovohrad region (KR) of Ukraine.

Dry gas with hydrogen content of 18 to 67 vol. % was obtained as a result of steam conversion of volatile matters of Lviv-Volyn (LV) bituminous coal at temperatures of 450 to 690 °C. Dry gas with hydrogen content of 31 to 62 vol. % was obtained as a

result of steam conversion of volatile matters of ZR brown coal at temperatures of 350 to 550 °C. There are determined the effect of the reduction of the ash content on an increase in the reactivity of char coals obtained from LV bituminous coal and KR brown coal during their reaction with steam. According to the analysis of experimental data, it was found that there is no need in coal cleaning from the ash before its steam gasification if the ash content of bituminous or brown coal is less than 35%. An increase in the gasification temperature by 30–60°C is sufficient to mitigate the effect of an increase in the ash content on a decrease in gasification process reaction rate.

It is found that steam gasification (with CO₂ capture) of KR brown coal with ash content of 9 to 31% needs temperature of 650 to 800 °C and the use of sorbent based on calcined dolomite to capture CO₂. Steam gasification (with CO₂ capture) of LV bituminous coal with ash content of 5 to 33% needs temperature of 750 to 850 °C and the use lime to remove CO₂.

AERODYNAMIC CALCULATIONS OF AIR-GAS FLOW PASS OF ELECTROSTATIC PRECIPITATOR AT THE DOBROTIVIR TPP

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One of the most important aspects which have effect on electrostatic precipitator's efficient are even distribution of waste gases flow in active cross-section of working chamber. Therefore in all cases of irregular distribution of waste gases flow performance parameters of device are worse than what we can deliver in case if flow crossing equally all the working elements.

Lot of books and scientific papers are discussing about efficiency increasing of different technological equipment because of aerodynamic characteristic improvement. After many years of experiments were development a theoretical basis for designing of important air-gases pass elements.

Due to improving of computers and specialized software systems, decided to use CFD software package for designing of electrostatic precipitator's air-gases flow. Combination of theoretical information, operational experience and computing equipment afford us to decrease time for development, capability to adjust structure on the design phase and achieve the maximum efficiency of device. Besides that, it

afford to decrease dimensions and amount of materials for devices.

Aimed to decrease amount of ash wasting in atmosphere, at the 160 MW power unit no. 8 of Dobrotvir TPP scrubbers with Venturi coagulators were retrofitted by electrostatic precipitators. Necessity to place all new equipment in slots of old scrubbers was the main problem of this retrofitting. At the time of designing of waste gases purification equipment for power unit no.8 of Dobrotvir TPP for avoiding waste gases, flow differences in active cross-section after commissioning decided to calculate aerodynamics of electrostatic precipitator's flow section by CFD software package.

Due to limited space at the construction site, the main requirements for optimal equipment configuration did not fulfill:

- no enough space in plan view between air preheaters of boiler and electrostatic precipitator for placing gas ducts and distribution devices;
- no ability for placing inlet gas ducts of electrostatic precipitator and outlet gas ducts of air preheater on the same axle in plan view, for avoiding waste gases flow imbalance by device width because of asymmetric inlet gases duct;
- due to long length of electrodes (12 meters) organization of even gases flow throughout the height of working chamber was difficult.

For solving this issues, next technical solution were through:

- gases duct from each air preheater gone directly to own diffusor of electrostatic precipitator (4 pcs.);
- aiming of even gases flow distribution through the height by installing of 3D triangular fence in each diffusor of electrostatic precipitator, which divide inlet chamber on few horizontal channels;
- inclination of front wall of diffusor also assists for even gasses flow distribution;
- after 3D triangular fence installed one flat fence from holed metal plate with free section equal 0.45.

Aerodynamic simulations shows, that installed gas distribution devices can't even distribute gases flow in active cross-section of electrostatic precipitator, especially on outer gasses duct. Therefore installed two stage of guide plates in diffusors of inlet gas ducts. After numerous simulations, an optimal angle of guide plate was founded, which provide necessary distribution of waste gasses.

After power unit has been commissioned, were performed investigations for check and improve waste gasses distribution in active cross-section of electrostatic precipitator. Comparing of results of tests and aerodynamic simulation shows that inaccuracy were no more, than 10%.

Results of tests shows that CFD software package are effective solution for simulation of aerodynamic flow and aerodynamic design calculations of air-gas flow passes waste gasses purification equipment.

THE PERSPECTIVES OF THE COAL TO COAL REBURNING TECHNOLOGY APPLICATION TO TPP 312 BOILER FOR NO_x CONTROL

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At the solid fuel combustion one of the methods of NO_x emissions reducing is referred to as reburning or fuel staging. This technique provides destroying of NO_x after it has been formed. Fuel staging involves introducing the fuel into the furnace in step mode. Typically, the bulk of the fuel is burned in the furnace at near stoichiometric conditions. The balance of fuel with a limited amount of air, is then injected to create a reducing zone part way through the combustion process. The reducing conditions form hydrocarbon radicals, which strip the oxygen from previously formed NO_x, thereby reducing overall NO_x emissions. The balance of the air required to complete the combustion process is then added. The efficiency of the reburning method is 50–60% [1, 2].

The test runs of the reburning system installed in the TPP 312 boiler (unit №4) of the Ladyzhyn Power Plant, which uses natural gas as a reburn fuel, has confirmed efficiency of this method to reduce NO_x emission [3]. Currently due to the high natural gas price and limitations on the natural gas consumption in Ukraine it's application as the reburn fuel is limited. At the same time the coal can be used as a reburn fuel.

Compared with the natural gas, the coal as a reburn fuel requires relatively longer residence time throughout the reburn zone and a larger upper furnace space to achieve the complete carbon burnout. Because the carbon burnout can be a constraint limiting the amount of reburn fuel that can be injected, the reburning coal particle size distribution is a key parameter. In some applications, pulverizer improvements (e.g., addition of dynamic classifiers) or replacement with micronized coal (i.e., coal pulverized to a very high fineness) pulverizers may be necessary to achieve acceptable NO_x reduction and carbon burnout performance.

To reduce NO_x amount the reburning system using a pulverized coal as a reburn fuel was mounted in the unit №6 of the Ladyzhyn Power Plant. As planned, the reburn burners will use the coal dust of the same fraction, as the primary burners use

without additional grinding. The reburning system was installed in the standard TPP 312 boiler during its reconstruction. Detail description of this reburning system is given in [4]. The TPP 312 runs on the bituminous coal with volatile content about 40%.

To transport the coal dust toward the reburn burners it is planned to use flue gases. The standard TPP 312 boiler was equipped with two flue gas fans having $2 \cdot 10^5 \text{ m}^3/\text{h}$ of the mass flow rate at the gas temperature of 400°C . The fuel preparation system consumes 50% of the flue gas amount, while the other $2 \cdot 10^5 \text{ m}^3/\text{h}$ of the flue gases is sent to the flue gas recirculation nozzles in the upper part of the boiler close to the superheater pipes. For the reburning system the transport of coal dust to additional burners is planned to be organized by the flue gas using two flue gas fans with productivity from $30 \cdot 10^3$ to $60 \cdot 10^3 \text{ m}^3/\text{h}$ each. Depending on the productivity of these flue gas fans $60 \cdot 10^3$ or $120 \cdot 10^3 \text{ m}^3/\text{h}$ will be used to transport the aero-mixture to additional burners, while the rest portion of the flue gas ($140 \cdot 10^3$ or $80 \cdot 10^3 \text{ m}^3/\text{h}$) will be sent to the flue gas recirculation nozzles.

The commercial CFD code was used to predict turbulence, combustion, and heat transfer in the full-scale fired utility boiler TPP 312 furnace. The non-premix combustion model was employed to describe the chemical reaction and heat transfer process accrued in furnace. The turbulence was described by RNG $k - \varepsilon$ turbulence model. The Lagrange model was applied to predict the gas-solid flow field. The energy equation was solved directly, where the radiation is depicted by DO model. The volatilization process is simulated by one-step reaction model. The char combustion is simulated by the diffusion- kinetics model. The simulation without the reburning system was considered as the baseline conditions.

The results of numerical simulation have allowed determine the efficiency of NOx reduction by the reburning system at the design conditions. It was concluded that the coal flow to the additional burners in amount of 10% provides better value in terms of unburned carbon in fly ash and temperature level near super-heater pipes. In this case, for the thermal boiler load of 210–280 MW_e around 20–26% of the nitrogen oxide reduction is expected. The growth in the reburning system efficiency is possible by ensuring of the optimal air excess in the reburning zone beginning, which must be $\text{SR}_{\text{adb}} = 0.9$.

The results of optimization calculations have shown that without the reburning system the reliable operation of combustion system occurs in the range of turbine load from 210 to 275 MW_e at the following technological parameters: fuel consumption by the additional burners is 10%; $\text{SR}_{\text{main burner}}$ is 1.2; SR_{adb} is 0.9; the coal

dust transport to the additional burners is provided by the clean flue gas. In this case, depending on the boiler thermal load, the expected NO_x reduction can be 25–30%. The level of nitrogen oxide emission to the ambient ranges from 400 to 595 mg/m³.

In the case of modernization of the existing reburning system, the reliable boiler unit operation is occurred in the range of turbine thermal load from 210 to 280 MWe at the following technological parameters: fuel consumption by additional burners is 10%; $SR_{\text{main burner}}$ is 1.15; SR_{adb} is 0.9; the coal dust transport to the additional burner is provided by the blend of flue gas and air. The expected nitrogen oxide reduction by the reburning system is 50–60%. The level of nitrogen oxide emission to the atmosphere ranges from 250 to 340 mg/m³, which is closely to the EU requirements. The modernization of the existing coal-to-coal reburning system requires installation of the third flue gas fan for the feeding of the flue gas to recirculation nozzles and the unit to prepare the blend of the flue gas and air to transport the coal dust to additional burners.

The further NO_x reduction can be reached by application of the advance three-stage reburning system. This reburning method is a combination of the reburning method and the selective non-catalytic reduction method.

Conclusions

The reliable operation of TPP 312 thermal boiler with coal-to-coal reburning system is possible at 10% of the fuel supply to additional burners. To ensure conditions of the liquid slag removal from boiler it is not recommended the boiler thermal load not less than 210 MWe, while to prevent slagging of the superheater pipes the maximum thermal load must not exceed 280 MWe.

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THE TECHNOLOGICAL BASES OF REMOVING HARMFUL IMPURITIES FROM SALTY COAL AND PERSPECTIVES OF THEIR USE IN ENERGY

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Currently, the problem of ensuring the country's domestic energy supply is one of the most pressing. Of all the fossil fuels (oil, gas, coal), Ukraine can fully satisfy itself demand only with coal. Annual coal production in Ukraine, according to data for year 2013, is about 80 million tons [1], of which: 40.1 million tons is assigned for power generation; 30.0 million tons – for steel industry; 6.9 million tons for export; 3.0 million tons for other applications (including the own needs of coal mines). Total reserves forecasted resources amount to about 42.5 billion tons. Under these conditions, coal is the only energy commodity, stock of which potentially would be enough to ensure energy security of the country and contribute to the development of energy, metallurgy and chemical industry.

It should be noted that the most powerful and affordable coal seams have been already depleted, and those remained are of low capacity (0.8–1.2 m) and found at depths greater than 1000 m. At the same time, Ukraine has significant off-balance reserves (about 10–12 billion tons) of so-called salty coal, which is not currently excavated. Deposits of this coal are characterized by shallow depth of occurrence (300–600 m), big seams thickness (in some cases, up to 3–5 m), suitable calorific value (7,000 kcal/kg) and low ash content (10–15%) [2–4]. Involvement of salty reserves of coal in the fuel mix for electricity and heat production will expand the fuel base of thermal power plants of Ukraine, and also reduce the shortage of gaseous coal group.

Today 5 salty deposits of coal are known in Ukraine (Table 1): Novomoskovske, Petryakovske in Western Donbass (Dnepropetrovsk region), as well as Bogdanovske, Starobilske, Petrovske in North Donbas (Luhansk region) [2–4]. At the moment, Petrovske and Starobilske deposits are not fully investigated, today exploration is suspended, but in the long term, will be regained.

Distinctive feature of salty coal is the presence of impurities in the form of various compounds of sodium (Na) and chlorine (Cl), at concentrations above their normal content in coals. In Ukraine salty refers to coal, in the ash of which content of Na₂O equals 2%, or above 0.4% per dry mass of coal, wherein the chlorine content is

limited to not more than 0.5% per dry mass of coal [2–4]. The main difficulties related to the development and use of the deposits of salty coal are associated with some technological features. In case of direct combustion of these coals, environmental performance of the power units is worsening, in some cases slagging can occur, as well as damage of the metal parts and insulating carborundum boiler materials due to metal corrosion. Most slagging considered the coal, which is composed of halite (NaCl), which, being heated to 800°C, settles and accumulates in the form of a solid slag layer, which deteriorates the heat transfer capacity of working surfaces and could not be removed by conventional methods.

Table 1 – Characteristics of the salty coal deposits in Ukraine

Depsit	Brand	Reserves bln t	LHV Q_{daf}^r , kcal/kg	Ash A^r , %	Moisture W^r , %	Volatiles V_{daf}^r , %	Na ₂ O in coal, %	Chlorine, %
Novo- moskovske	B	7.6	7200– 7500	10–15	7–12	44–47	0.6–1.0	0.6–0.9
Petryakovske	L	0.3	5000	16.2	45	41–43	0.44–1.0	0.34–0.65
Bogdanovske	B	1.6	7020– 7580	12.6– 14.6	7–11	41.2–42.6	0.5–0.7	0.3–0.6
Petrovske	B	1.2	7100– 7500	5.6– 17.0	6–11	40.5–44.5	0.5–0.9	0.34–0.6
Starobilske	B	0.8	7000– 7400	7.0– 16.1	9–18	41.1–47.4	0.5–0.9	0.3–0.6

The possibility of using salty coal for decades attracted attention of scientists around the world. This is due to the fact that coal deposits with a high content of Na and Cl are explored in many countries – Germany, Poland, the USA, Kazakhstan, Russia, the Czech Republic, the UK, Australia and others (Fig. 1).

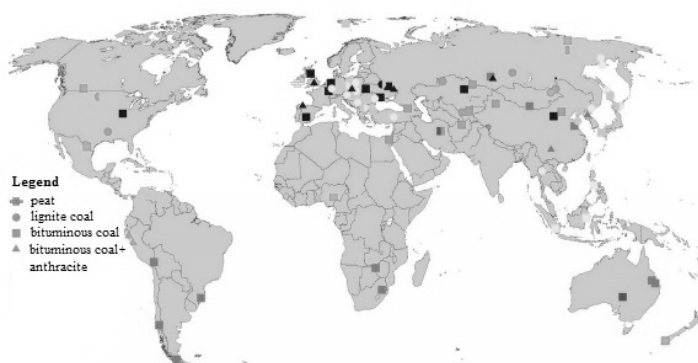


Fig. 1 – Coal deposits with a high content of Na and Cl [5]

Today in the world there are two directions of the energy use of salty coal: without desalting and with desalting [2–7]. The first direction includes as conventional way of low-metamorphised power generating coal using (that include salty coal) – their combustion at TPPs, boiler houses, as search of new ways of raw salty coal using – pyrolysis, gasification, liquefaction, semi-coking, complex processing with humates extraction. Wherein, to use the power generating salty coal following the conventional scheme as fuel, usually offers the solutions, such as: previous coal dilution, measures to transfer sodium in high-melting compounds, changing of furnace and boiler designs.

The second direction provides the previous coal preparation in salt (desalination). Wherein, the most part of the proposed solutions is based on different variants of the salty coal washing. Also, the methods that are based on ion exchange, desalted by means of coal treatment with chlorhydrid and fluorohydrogen acids, consistently with NaOH and HCl solutions, ammonia water treatment.

Taking into account the salty coal peculiarity of the Ukrainian deposits in comparison with the salty coal of deposits in other countries, in particular the presence of the Na and Cl in water-soluble compounds, the experiments on coal cleaning by means of water washing have been made by us. Coal desalting process by water washing is characterized with several factors, such as the duration of contact of coal with water, the mass ratio of water and coal, as well as the conditions under which the contact of coal with water occurs (nature and intensity of mixing, temperature of the medium, particle size).

As the result of the experiments conducted, the number of input boundary conditions was defined, as well as necessary operational processes which allow to reach positive effect of salt coal desalination (Table 2).

Table 2 – Separate parameters and input boundary conditions of coal desalination

No.	Parameters, process	Boundary conditions	Notes
1	2	3	4
1	Coal size	Raw coal of grade D size not less than 0 ÷ 13 mm	The mean size of coal particle $D_{av} \leq 3$ mm
2	Coal concentration (C) in coal-water mixture	$C \leq 50\%$	The most appropriate ratio of solid and liquid phases ($T \div \mathcal{K}=1 \div 3$) ($C \leq 0,33$)
3	Output salinity	$< 10 \div 12$ g/l on NaCl	–
4	Coal-water mixture temperature	Stipulated by standard for enterprise shops	Admissible, if it is possible to use the exhaust heat of an enterprise

1	2	3	4
5	Mixing activation	The rate of water flow (Vw.f.) is greater than the rate of coal particle in it (V c.p.) $Vw.f. > Vc.p.$	The presence of turbulent flows
6	Mechanical coal dewatering	Coal operating humidity after dewatering $W_v^p < 25\%$	–
7	Specific contents of coal particles size – 0,074 mm in coal-water mixture	No more than $32 \div 35\%$ at concentration of solid phase in coal-water mixture $C \geq 50\%$	The possible start of reverse adsorption

Obtaining these curves allowed to create a salt coal cleaning technology. Salt coal firstly is subjected to grinding to produce a – 3 mm class. After this, the coal was purified in a washing machine at ratio S:L = 1:3 during the time of 5–15 min. Then demineralized coal, in one or two stages, is dewatered and dried to a moisture content 8%, or simply dried for the preparation of a coal-water slurry. Washing water, with which the process of desalination was arranged, is further demineralized. After that, the resulting distillate is recycled. Thus, a closed loop for the aqueous phase solves the problem of the use of scarce water resource. It is proposed to arrange the desalting process at the washing factories, where the necessary water management is available, as likewise the needed equipment – crushers, dewatering, drying equipment, by which coal is enriched by the ash indicators and which at the same time can be used in the process of desalting.

Based on technical characteristics of the machines and devices (Table 3) performing manufacturing operations on coal preparation and set in present paper the desalination characteristics (Table 2), the most appropriate and practically manufactured device to use the method of the salty coal washing are jigging machines.

Table 3 – The residence time of coal with water in devices and machines of coal preparation plants

No	Type of equipment, devices	t (time)	No	Type of equipment, devices	t (time)
1	Concentrating tables	< 85 s	5	Dehydrating bins	8–12 hours
2	Screw classifiers	< 28 s	6	Washing machines	< 20 s
3	Jigging machines	< 300 s	7	Elevators	< 40 s
4	Spiral separators	< 60 s	8	Screening machines	< 8 s

* For conditions: raw coal, coal size 0–13 mm, $d_{av} = 3$ mm

The wide range of the above-mentioned parameters monitoring in jiggling machines, the building of their interaction chain, the automatization of the coal desalination process on the basis of the existing devices – salt meters gives all grounds to state that the coal preparation on salt definitely could be implemented in jiggling machines without large additional capital expenditures.

Conclusions

1. As a result of the studies performed, the effect of a number of technological factors on the process of desalting of the Ukrainian salt coals was identified.
2. The technical solution which is based on the possibility of the salt coal cleaning at preparation plants where the necessary equipment – crushing, desiccant, drying – are available, whereby the enrichment on ash is occurred and which simultaneously could be used during the desalination process, is proposed.
3. The most suitable device to implement the method of the salt coal washing at preparation plants are jiggling machines. Their construction, regimes and operation parameters are completely meet the particular conditions of the salts' removing from coal.

The following step of our studies shall be the possibility determination of the salt coal using without its previous desalination.

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THE DEVELOPMENT OF TYPICAL (REFERENCE) TECHNOLOGICAL SCHEME ON THE BASIS OF MEDIUM-SCALE 75 T/H CFBC BOILER TO INVOLVE HIGH-ASH COAL WASHERING WASTES FOR HEAT AND ELECTRICITY PRODUCTION

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Now it is important for the Ukraine to involve additional energy sources for electricity and heat production while meeting high ecological standards on emissions according to the Directive 2010/75/EU.

The current shortage in coal, resulted from the situation in Donbass region, requires to pay attention to: significant reserves of coal preparation wastes (Fig.1), accumulated in the territory of Ukraine; its quality; selection of proper fuel handling and pre-treatment technology to be further effectively used; choice of relevant combustion technology and so on.

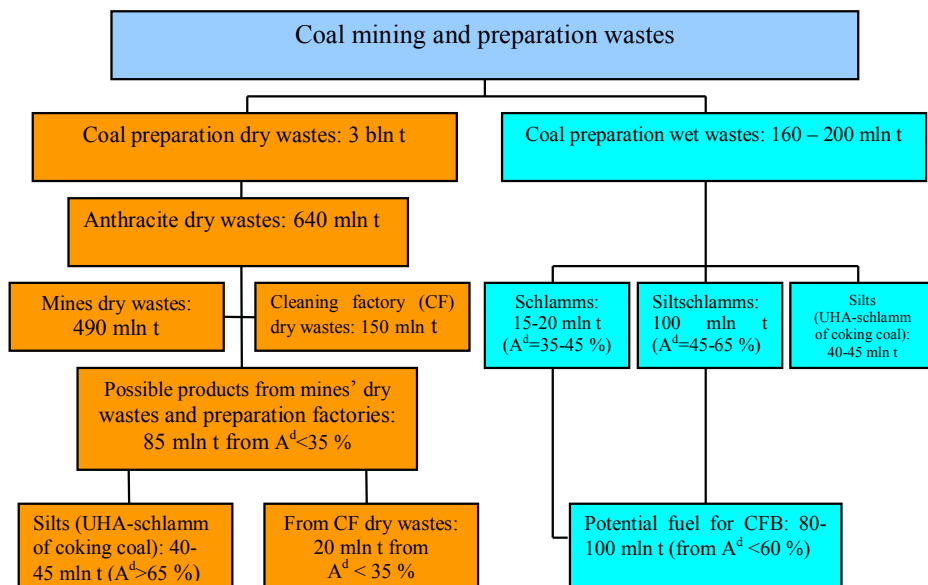


Figure 1 – Coal mining and preparation/cleaning wastes

Among the technologies having high potential to effectively burn high ash coal it is necessary to highlight the combustion in circulating fluidized bed (CFBC).

The technological scheme of utilization of high ash coal washering waste has been developed for typical coal cleaning factory (CCF). Its annual output is about 8

mln t, there is a possibility to clean coal for 5 different coal classes (coal particle sizes). The CCF's wastes to be utilized are of two types: 1) ultra high ash (UHA) coal waste and so called "promproduct" – intermediate coal waste having moderate ash content ($A^d \approx 36\text{--}39\%$).

UHA coal waste is resulted from coal particle floatation – the process of cleaning of coking coal based on its washering in heavy liquids. UHA coal waste has extreme ash content and moisture, the latter is because of the problem to effectively dry clay-containing and very fine particles. As typical example it was selected the CCF that produces: 1 mln t of UHA coal waste annually (having ash content $A^d \approx 64\%$; moisture $W^r \approx 37\%$); and up to 160 ths. t of "promproduct" annually (moderate ash content coal cleaning waste).

Within the framework of work aimed at site selection for the implementation of a new clean coal CFB technology it was evaluated a number of parameters and CFB-boiler performance, including electrical capacity of the CFB Power Plant (PP) capable of firing dried UHA coal waste.

It is found that the maximum electrical capacity of the CFB-Boiler Unit fueled by UHA coal waste of such amount can be about 88 MWe with annual UHA waste consumption at about 684 ths. t (annual operation period of PP – 7000 hours). Originally it was planned to demonstrate the viability of the technology at power unit having 20 MWe capacity based on a CFB-boiler with steam output of 75 t/hour. The technological scheme and preliminary drawings (concept of boiler design) for the boiler were prepared by CETI along with partner (SPKTB Energomashproekt) are shown on Fig. 2 and Fig. 3 correspondingly.

During the development of CFB-boiler design it was determined and evaluated its technical and economical performance as a part of 20 MWe power unit being fueled by two types of coal wastes: UHA coal waste and "promproduct" which characteristics are given in Table 1.

Table 1 – Design parameters of ultra high ash coal waste and "promproduct"

Fuel	W^r_t , %	A^r , %	Ultimate analysis, %					Low heating value Q_i^r , kcal/kg
			C^r	H^r	O^r	N^r	S^r	
UHA coal waste	8	58,88	25,85	1,85	4,65	0,50	0,27	2200
Promproduct	6	39,48	44,49	2,95	5,74	0,82	0,52	4000

Notes: UHA parameters are given for wastes-after-drying

The variants of complete complex treatment for UHA coal waste and "promproduct" (including fuel handling, preparation, drying, combustion and

electricity production) were considered on the basis of their combustion in a CFB-boiler.

The main systems of the treatment complex include:

1. UHA coal waste handling and preparation system designed to decrease the moisture content of initial UHA waste from $W^T = 35\text{--}37\%$ to $W^T = 7\text{--}8\%$ and facilitate its particle agglomeration. Promproduct is not to be dried because it has initial moisture content applicable for CFB combustion.

2. The concept design of CFB-Boiler (E-75-6,3-500 F type) with natural circulation having steam capacity of 75 t/h, steam temperature of 500°C and pressure 6.3 MPa, capable of regulating load within the range of 60–100% of nominal output was prepared.

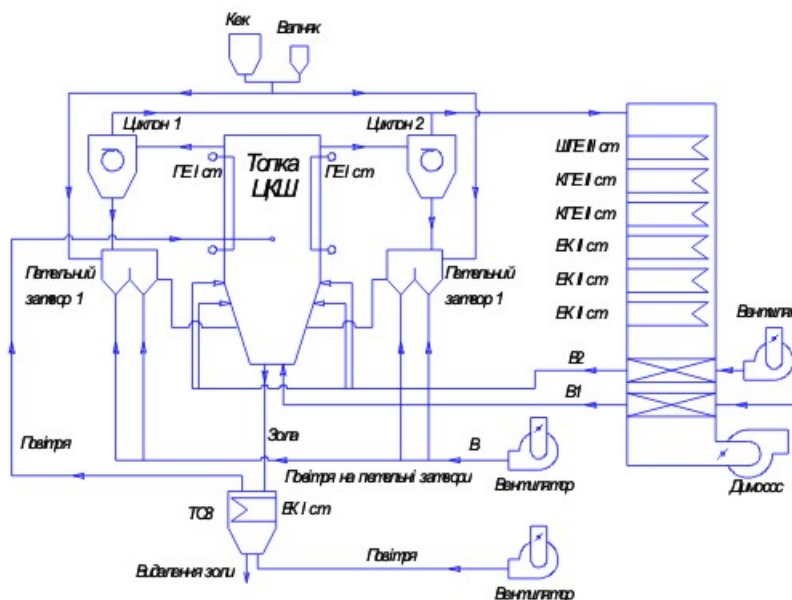


Figure 2 – General process flow sheet for ultra high ash and “promproduct” CFB combustion at E-75-6,3-500 F CFB boiler unit

It is assumed that the CFB Power Unit has 20 MWe capacity and work in condensed mode of operation (with load regulation within 60–100% of MCR – maximum continuous rating). The generation of electricity can be based on steam turbine of SST-150 type of Siemens company. Boiler island is also accompanied with the following systems: limestone preparation and feeding system aimed in-furnace removal of SO_x emissions; sieve for agglomerated and dried UHA waste (included in

fuel drying system); electrostatic precipitator (ESP) and other auxiliary equipment. The operation of this CFB-boiler while burning high ash wastes will allow to achieve low NO_x and SO_x emissions (less than 200 mg/m^3 at 6% O_2 at STP conditions (standard temperature and pressure)) and meet the requirements of European Directive 2010/75/EU. Summarized performance of the developed by CETI and partners variants for high ash wastes utilization in environmentally acceptable manner with electricity production is given in Table 2.

Table 2 – Main characteristics of variants of electricity production with the use of clean combustion of coal cleaning waste in CFB based on 20 MWe CFB Boiler Unit

Parameters	Value	
Power unit capacity (electrical)	20 MWe	20 MWe
Fuel	UHA coal wastes	Moderate ash content coal waste “promproduct”
Low heating value, Q_i^r , kcal/kg	2200	4000
Ash content (dry basis), A^d , %	64	41,7
Moisture, W_t^r , %	8	6
Steam turbine	SST-150	SST-150
Mode of operation of steam turbine	condensed	condensed
CFB-boiler performance		
Steam capacity, t/h	75	75
Live steam pressure n_{apy} , MPa	6,3	6,3
Live steam temperature, °C	500	500
Combustion process and fuel consumption		
Flow rate of dried fuel at the inlet of boiler, t/h (ths. t/year)	26,6 (186,2)	14,63 (102,5)
Flow rate of air for combustion, ths. normal m^3/h	87,2	82,8
Flow rate of flue gas, ths. normal m^3/h	95	88,2
Flow rate of ash, t/h (ths. t/year)	15,7 (109,9)	5,8 (40,6)
Fuel handling and preparation		
Flow rate of raw UHA waste for power unit ($A^d=64\%$, $W_{t_{\text{BU}}}^r = 37\%$), t/h (ths. t/year)	38,85 (272)	—
Flow rate of moisture removed while drying raw UHA waste from $W_t^r=37\%$ to 8% , t/h	12,25	—
Flow rate of raw UHA waste at the inlet of 2-nd stage of drying system ($A^d=64\%$, $W_{t_{\text{II}}}^r=25\%$), t/h	32,63	—
Fuel consumption (natural gas) on heat generator of UHA waste drum-type driers, ths. m^3/h (ths. m^3/year)	1,86 (13)	—
Fuel consumption on heat generator of UHA waste drum-type driers (promproduct usage), t/h. (ths. t/year)	3,72 (26)	—

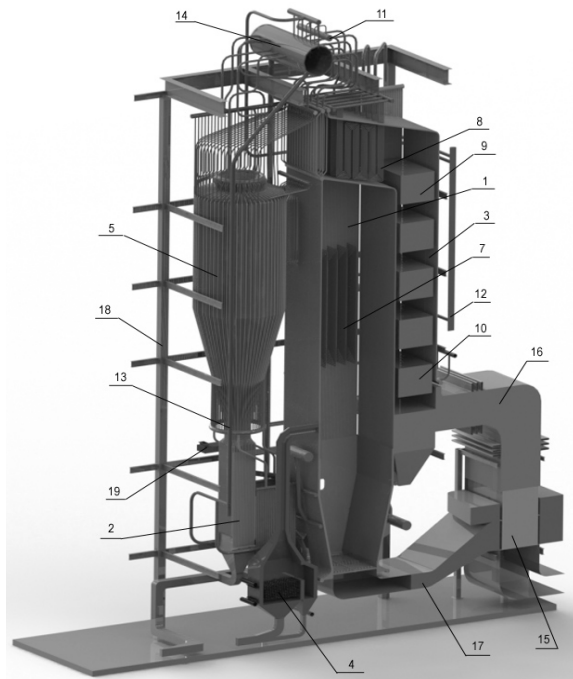


Figure 3 – Schematic view of E-75-6,3-500 CFB-boiler designed for UHA combustion: 1 – furnace screens panels; 2 – seal-pot; 3 – convective shaft screens' panels; 4 – bed ash cooler; 5 – cyclones; 6 – fly-ash-handling system; 7 – wing-panel superheater; 8 – convective superheating surfaces; 9 – convective superheater; 10 – economizer; 11 – condenser; 12 – steam cooler; 13 – pipelines within the boiler; 14 – boiler drum; 15 – air heater; 16 – boiler passes; 17 – primary air ducts; 18 – boiler supporting structure; 19 – fuel-handling system

Total capital investment on 20 MWe CFB Power Plant is estimated to be about 26,5 mln USD including: boiler (along with construction) – 6,75 mln USD, steam turbine with generator and auxiliary – 6,88 mln USD, fuel handling and preparation system – 1,5 mln USD. Evaluation of capital cost needed for E-75-6,3-500F boiler manufacturing was made according to its specification and weight characteristics which were obtained during the development of preliminary (outline) design, the local Ukrainian price was used for evaluating expenses on the heating surfaces and metal construction, isolation and lining materials, additional equipment and boiler information and control system.

DEVELOPMENT OF NON-WASTE PRODUCTION TECHNOLOGIES TO CLEAN THE FLUE GAS FROM POLLUTANTS

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The power industry is a key sector of the economy of any country. In the Integrated Energy System of Ukraine the thermal power industry has an important role manoeuvrable and rescue capacity. The main fuel for thermal power plants in Ukraine is the domestic coal from Donetsk and Lviv-Volyn basins. The annual consumption in thermal power industry of Ukraine tens of millions of tons of coal and tens of billions of cubic meters of natural gas results the emissions in the air over a million tons of sulphur dioxide, more than 250 thousand tons of nitrogen oxides, more than 300 thousand tons of dust [1]. The large part of the equipment at Ukrainian thermal power plants operates more than 250 thousand hours. They are doing have the DeSOx and DeNOx plants, and existing dust collectors are outdated and have the actual efficiency from 88 to 98%. This prevents comply with environmental requirements, as defined in the Directive 2010/75/EU on industrial emissions [2]. Table 1 shows the typical concentration of pollutants in flue gas at coal power plants in Ukraine compared with the emission limit values under Directive 2010/75/EU on industrial emissions [2] for existing boilers. The coal boilers should reduce the concentration of dust in the 15-65 times, sulphur dioxide – in 12–36 times, nitrogen oxides – 3–9 times.

Table 1 – Emission at Ukrainian TPP and Requirements of Directive 2010/75/EU

Pollutant	Actual concentration, mg/Nm ³	Requirements of Directive 2010/75/EU, mg/Nm ³
Dust (fly ash)	300–1300	20
SO ₂	2500–7200	200
NO _x	600–1800	200

The cardinal decision of the technical, economic and environmental problems in the power system is the implementation of new power units with high fuel efficiency and low emissions of pollutants, as is done in Poland. But it needs the tens of billions of Euros and considerable time In Ukraine to 2025 is selected the way of rehabilitation of existing power units increasing their capacity by 8-10%, a decreasing in specific fuel consumption and a constructing the new installations of flue gas cleaning. In

Ukraine has developed the National emission reduction plan (NERP) from large combustion plants, which implies compliance with Directive 2010/75/EU on emissions of dust and sulphur dioxide to 31.12.2028 and nitrogen oxides – to 31.12.2033 by reducing the line gross emissions of pollutants since 01.01.2018. Table 2 shows the value of the annual reductions in pollutants gross emissions of large combustion plants that are included to the NERP for the country and the major operators.

Table 2 – Annual reductions of pollutants gross emissions

Operator	Number of plants	Thermal rated input, MW	SO ₂ , tpa	NO _x , tpa	Dust, tpa
Ukraine	91	64813.6	96603.0	9163.7	20070.6
DTEK Energo	18	26976.4	55863.3	5673.1	10049.3
Centrenergo	5	10296.0	26722.2	1605.9	5323.7
Donbassenergo	5	5898.0	9309.3	882.0	3119.1
Ukreteploenergo	7	3384.5	3957.6	676.7	1378.5

This task can be performed only by using the best available techniques [3]. The obligatory condition of use of flue gas cleaning technology for thermal power plants is complete utilisation of formed by-products. It is corresponded the modern principle of operation for coal power unit – HELE (High Efficiency Low Emission).

The use of the precipitators with height of electrostatic collecting electrode at least 14 meters ensures the dust content less than 50 mg/Nm³ [1]. Additional dust removal for the comply with the limit concentration of 20 mg/Nm³ carry out in the desulphurisation plant, which is placed after the electrostatic precipitators. the fly ash must be sent to customers in a dry form.

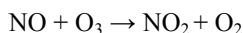
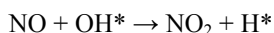
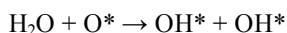
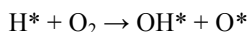
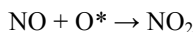
The main desulphurisation technology in the world power industry is the wet limestone scrubber with forced oxidation of which provides efficiency up to 98%. It uses natural mineral (limestone) and form the gypsum CaSO₄×2H₂O as by-product. Its disadvantages are high capital and operating costs, large production area, large own needs, the availability of waste water. This technology is feasible for the power units with total capacity more than 500 MW (the steam capacity is more than 1600 tph).

An alternative is semidry ammonium desulphurisation, the specific capital costs by almost three times lower than the previous technology (~ 80 \$US/kW). The sorbent is a water solution of ammonia NH₃, and the product is the dry powder of ammonium

sulphate $(\text{NH}_4)_2\text{SO}_4$, which is a fertiliser [4]. The results of laboratory and modelling investigations have shown the possibility to achieve an efficiency of about 95%.

To achieve the output NO_x concentrations in flue gas of 200 mg/Nm^3 at coal thermal power plants is use the technology of selective catalytic reduction (SCR). The products of this technology are molecular nitrogen and water vapour.

It is proposed to carry out the oxidation of nitric oxide NO to the soluble nitrogen dioxide NO_2 by reaction with radicals:



The radicals O^* , OH^* , H^* can be formed in the process of ozone generation and electrical, catalytic and plasma-chemical conversion of water vapour. The conversion of nitrogen dioxide to nitric acid HNO_3 and nitrous acid HNO_2 will occur in water. The final product is to be ammonium nitrate NH_4NO_3 .

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THE USE OF BIOMASS FOR ENSURING OF INDUSTRY POWER NEEDS

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Biofuel Energy Potential in Ukraine.

The climatic features and properties of the soil determine the place of Ukraine as a producer of agricultural goods in the international division of labour. The production and processing of agricultural products generate huge amounts of waste. Energy potential of this waste give a chance to significantly reduce the needs of industry in traditional fuels. Biomass is considered to be one of the most significant alternative energy sources. The evaluations of Ukraine's bioresource potential vary widely. Research [1] determine the energy straw potential as a 2.5M tons of oil equivalent. Under an optimistic scenario, an opportunity to grow the biomass on empty areas is taken into account, and its yield is expected to be over 21M tons of oil equivalent [2]. So, Ukraine's biopotential could enable the substitution of the natural gas volume ranging from 4.3 up to 25.6 billion m³.

The problems and prospects of biofuel use.

Cost efficiency of the project is the key criterion for the decision on biofuel usage. In Ukraine cost of natural gas is two or three times higher than cost of biofuel in a volume equivalent to the natural gas in terms of its energy potential. Availability of proven technologies and equipment is another important driver, which determines use of biofuel in technological processes. Therefore, the task of creating reliable and cost-efficient industrial objects, which use biomass for substitution of natural gas, with minimum payoff periods, was instrumental in defining the work program of biofuel use. As a prospective investor is primarily interested in the reference site where proposed solution is already used so that the investor can find out about it on site, it was decided to start the development of demo projects as the first step.

Two types of technologies of biofuel use in thermal technological processes exist, which are based on two different principles – direct combustion and gasification. The highest effect is reached in case of direct combustion of pre-treated biomass in boiler furnaces or kilns. Biomass pre-gasification technology competes with direct combustion in a number of applications. Any energy transformation causes irreversible thermodynamic losses, which makes the fuel's primary energy utilization somewhat less efficient than direct combustion. However, gasification has an indisputable advantage over direct combustion when the project is specifically intended to generate electric energy, process steam, in cogeneration technologies and

combined processes of producer gas combustion simultaneously with natural gas and in the same burner. Study of technological chains using natural gas as a fuel enabled to develop the criteria to assess applicability of the specific technology for natural gas substitution [3].

Direct biomass combustion. Task setting, process specifics and implementation.

As the first step in project implementation, technical requirements were defined, which fuel had to meet to ensure complete combustion of particles in the combustion space. At the same time, the type of fuel was to be taken into account. Parameters that determine combustion speed are fraction composition and moisture of solid particles. The time of the particles' combustion was experimentally determined on the installation of fluidized bed with inert heat carrier during combustion in the air at 900°C temperature. It follows from this experiment that wood waste burns out about two times quicker than the particles of sunflower husk. The deviation in the level of particles' moisture from the natural moisture (10–12%) results in the increase of their burnout time.

The results of the research are shown in Figure 1. Experimental data regarding wood sawdust have coincided with the results of mathematical process modelling completely. Another difference between the processes of biomass and gaseous fuel combustion is varying theoretical combustion temperatures and amount of air needed for complete burnout of the fuel. In the process of shifting to biomass' usage, specific features of its burning process are crucial. The research has enabled to formulate requirements to biofuel for efficient burning in the rotary kilns (Table 1).

Based upon the evaluation of local biomass resources by factory experts, sunflower husk was selected as the principal biofuel, with possibility to use waste wood (sawdust) as well. The task of shifting to usage of biomass presupposed the development of both technical requirements to the fuel, and technology of its co-combustion with natural gas.

The results of biofuel properties investigation and the specifics of its burning were used as fundamentals for creating automated complex of biomass usage as a fuel – natural gas substitute – in the rotary kiln. The complex includes a fuel depot, biomass pneumatic conveying line, a burner device, as well as a control and automation system (Figure 2).

Table 1 – Requirements to biofuel

Type of fuel	Fractional composition, mm	Moisture, operating condition, W^r , %	Ash content, dry condition. A^d , %	Volatile yield, dry condition, V^{daf} , %
Sunflower husk	0–1,5	9–11	2,3...3,5	73,5...75,6
Wood sawdust	0–3,0	10–14	0,6...1,5	78,9...82,4

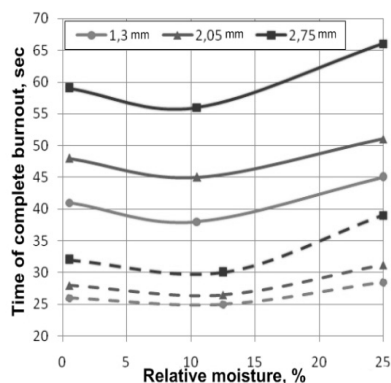


Fig 1. Dependence of the biofuel burnout time on the moisture and particle size; husk is shown with solid line and wood sawdust – dashed line.

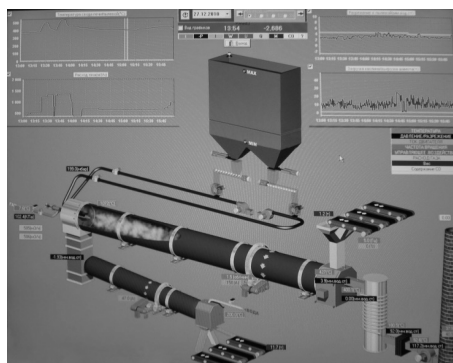


Fig. 2. The outline of complex for biomass burning in the rotary kiln.

The direct combustion technology was implemented on the rotary kilns of producing refractory clay and lime burning of several large industrial companies operating in Ukraine. Our first experience with the technology of biofuel direct combustion has been received in 2010 year during technical re-equipment and operation of the rotary furnace of Vatutinsky refractories plant (Cherkasy region, Ukraine). The furnace specifications: 75 m length, 3.5 m diameter, 15 ton/hour output of final product. Average gas consumption before the project was 2200 m³/hour.

The results of partial natural gas substitution with biofuel on the rotary furnace of Vatutinsky refractories plant are shown in table 2. Adjustment and alignment work held for optimization of the kiln operating modes at joint combustion of natural gas and biofuel have demonstrated little dependence between kiln temperature mode on one hand, and the ratio between gas and biofuel on other. During burning of mid-temperature fire-proof compounds the degree of natural gas

substitution reached 70%, while in process of burning of high-temperature fire-proof compounds – it was up to 50%. The complex has been successfully operated since 2010. Annual volume of natural gas substitution with biofuel is over 10 million m³.

Table 2 – Indicators of the kiln operation using natural gas and sunflower husk

No.	Value	Unit of measurment	Mode No.			
			1	2	3	4
1	Gas consumption	m ³ /hour	1410	920	730	570
2	Sunflower husk consumption подсолнечника	kg/hour	1740	2710	3070	3400
3	Kiln thermal power	MW	18,5	18,54	18,45	18,6
4	Total volume of air supplied to the kiln	m ³ /hour	22000	22420	22520	23420
5	Temperature in the kiln burning zone	°C	1175	1160	1157	1154
6	Exit temperature	°C	370	365	360	353
7	Kiln efficiency factor	%	73.2	71,9	70,7	69,7

The technical solution set out above can be successfully used in a number of companies in metallurgy and construction materials sectors. Today in Ukraine have been made re-equipment of seven furnaces on base of developed technology. All systems are in operation, providing the total reduction of natural gas consumption by 70 million m³ per year. As an extra effect of the project implementation, new jobs have been created to provide factories with biofuel.

Biomass gasification. Natural gas substitution with producer gas.

Setting up of a complex with 2.0 MW installed capacity for wood pellets gasification is an example of the development and implementation of biomass gasification technology and equipment. The complex is designed for partial substitution of natural gas in the steam boiler heating system. It includes gas generator (Figure 3a); gas purification and transportation system; dual fuel burner for simultaneous combustion of natural and producer gas (Figure 3b); system of boiler operation automatic support and steam boiler. Complex was developed by the Institute of Gas of the National Academy of Science of Ukraine and has been operated at JSC "Malyn Paper Mill - Weidmann" (Malyn, Zhytomir region, Ukraine) since February 2013. Significant thermal load fluctuations are specific to the company's technological process.

Average producer gas output, taking into account the power change, was 120 m³/hour in natural gas equivalent. On average, 2.7 kg of wood pellets was used for

the substitution of 1 m³ of natural gas. Substitution of natural gas with producer gas did not result in the boiler productivity reduction. Development of an effective system for producer gas purification from resins and resin-containing items was an important result of this effort. Usage of wood pellets for natural gas substitution enabled reduction of costs for natural gas purchase by over 30%.

The fundamentals used for generator development were based upon technology by Sibtermo Company (Krasnoyarsk) applied for Kansk-Achinsk brown coal gasification for semi-coke production purposes [4]. Testing results are presented in Table 3.

Table 3 – Gasification of solid fuels. Gas composition, substitution rates

№	Parameter	Solid fuels for gasification					
		Wood chips (humidity 15%)	Rise husk	Pellets		Lignite	Brown coal
				Sunflower husk	Wood		
	The composition of the producer gas,% vol						
1	H ₂	13.35	11.36	16.86	11.3	12.24	20.01
2	N ₂	48.83	54.8	44.92	49.45	55.24	49.27
3	CO	16.03	15.69	19.51	12.59	11.88	14.10
4	CH ₄	5.57	4.72	5.81	6.71	4.24	3.32
5	CO2	12.49	10.55	9.15	15.84	12.87	11.14
6	C ₂ H ₄	0.77	0.55	0.71	0.95	0.98	0.13
7	C ₂ H ₂	0.16	0.02	0.0	0.34	0.0	0.0
8	C ₂ H ₆	0.11	0.07	0.18	0.21	0.0	0.11
9	C ₃ H ₈	0.07	0.03	0.1	0.13	0.0	0.04
10	H ₂ O	2.62	2.21	2.69	2.49	2.34	1.88
	Σ	100	100	100	100	100	100
	Indicators of substitution and energy data						
1	Low calorific value, MJ/m ³ (kcal/m ³)	6,13 (1464)	5,24 (1251)	6,97 (1664)	6,77 (1617)	4,92 (1175)	5,32 (1270)
2	Solid fuels to replace 1 m ³ of natural gas. kg	3.7	3.3	2.6	2.7	3.2	2.8

About 10% of energy is spent on the cooling of the gas generator body. This energy can be used for heating of the boiler feed water or for technical needs.

Summary

Substitution of natural gas with biofuel is commercially viable and attractive for many countries. Two technologies of biomass usage are considered in this article: direct combustion and gasification. Each of them has its advantages and areas of application. Technical solutions piloted in industrial scale could be efficiently applied in manufacturing sectors and energy sector.



Fig. 3. Producer gas generation complex: a) – gas generator (3 items), b) – burner device.

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DEVELOPMENT OF 3-D MODELS OF CO-COMBUSTION PROCESSES

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The technology of biomass and coal co-firing (SSBV) at utility thermal power plants become the most promising way of the domestic energy sector modernization. Progress in SSBV technologies allows not only to diversify energy sources and promote energy independence, but it also provides market development biomass energy crops, promotes the development of appropriate logistics and infrastructure, and creates jobs. A wide introduction of this technology apart of the mentioned above will eventually lead to the revitalization of environment.

It was noted that there is a number of factors that determine the optimal conditions of the combustion process but still remain unstudied, thus requiring further study.

Modern packages for 3-D modeling of thermal and hydrodynamic processes provide powerful tools for deep research local characteristics of reacting flows. These methods are particularly efficient in the application to the complex systems such as combustion processes since they provide an opportunity to simultaneously solve a system of equations of mass, momentum, mass components conservation, chemical reactions, diffusion, turbulent and radiation heat transfer. It should be noted that direct experimental study of combustion processes is extremely costly.

Notwithstanding the highest efficiency of 3-d modeling and simulation of the above processes, it should be noted that a number of critical empirical data are still needed in order to lock the system of governing equations together with the adequate boundary conditions.

Among those are the kinetics of some sub stages of biomass combustion such as: demoisturization and devolatilization and optical characteristics (namely absorption and emission) of combustion gases.

A detailed studies have been carried out at CETI and NUFT dedicated to the in-depths investigations of thermal degradation kinetics of the domestic kinds of biomass which looks a promising energy source when being co-fired together with solid as well as gaseous fossil fuels. The results of such study into the combustion kinetic characteristics of various types of biomass as an individual fuel and their mixtures have been presented in generalized form, including the list of frequency

factors and activation energy for the number of biomass types and their mixtures. The said results allowed formulating sub models of individual stages of a complex combustion process and thus to be included as a constituent part into the FLUENT or CFX 3-d process model.

A sub model allowing determining optical characteristics of combustion gases based upon taking into account a spectral portion of absorbed energy as a function of Plank black body emission integral has been further developed. This submodel takes into consideration a mean value of combustion gases absorptivity along with the spectral fraction of black body irradiation. A model of the methane combustion in the cylindrical burner has been developed. The model incorporates the mentioned above spectral absorptivity submodel. The results of the calculations carried out within the 3-D model were compared with the available in the literature experimental results that had been obtained within the same working parameters and operative condition. The comparison shows a close conformity of the results which proves the validity of the proposed optical sub model for the determination of mean linear absorption coefficients of combustion gases and its applicability for the practical 3-D modeling of the combustion processes which then was incorporated into the CFX 3-d model of co-combustion of natural gas with solid biomass.

When dealing with the problems of a model validation one should be aware of the problems associated with the thermocouple errors at temperature measurements in the flames and combustion product flows. A model has been derived aimed at the evaluation of correction factors that are to be applied, when processing data from the direct thermocouples' readings. The model takes into account the convective heat transfer, irradiation on a part of the thermocouple bead, which falls from the combustion products. It also takes into consideration that a part of the thermocouple bead irradiates in the direction of the cooled surrounding. As a result, a transcendent fourth order equation has been obtained and solved numerically by MathCad. A set of correction coefficient was obtained which, when added to the direct readings of thermocouples, have shown a close conformity to the results obtained from the 3-d modeling of the natural gas combustion in the cylindrical down flow reactor. Thus developed correction methodology may be recommended to be used in practice, when experimental temperature measurements may be performed by means of bare thermocouples, when sheathed thermocouple or suction pyrometer can not be used. A number of geometric models of the experimental stand VGP-100 B (pilot stand for experimental studies of combustion Coal Energy Institute of the Academy of Sciences of Ukraine) has been developed and meshed. Data obtained experimentally

and listed above were incorporated into the 3-D model of natural gas combustion and co-combustion of woody sawdust with natural gas.

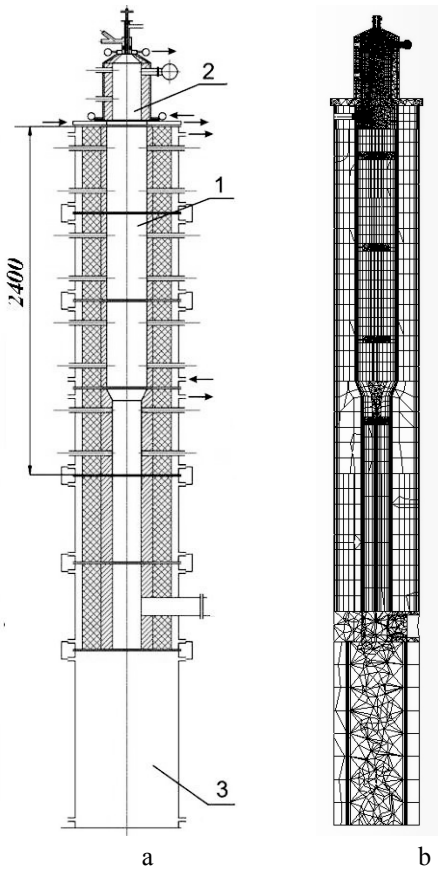


Fig. 1. VGP-100B stand cross section (a) and mesh (b)

1 – burner head, 2 – test sections, 3 – ash bin

The schematics the stand and its mesh are given on Fig.1.

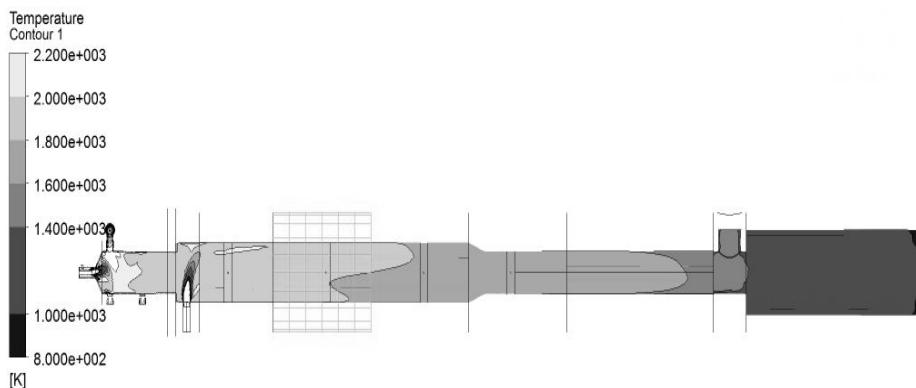
Model validation was performed on the basis of comparison of model simulated data and those measured in physical experiments. Close enough correlation of results confirms the adequacy and accuracy of the model.

The comparison of the calculated heat losses by the stand sections and total are shown in Tabl.1

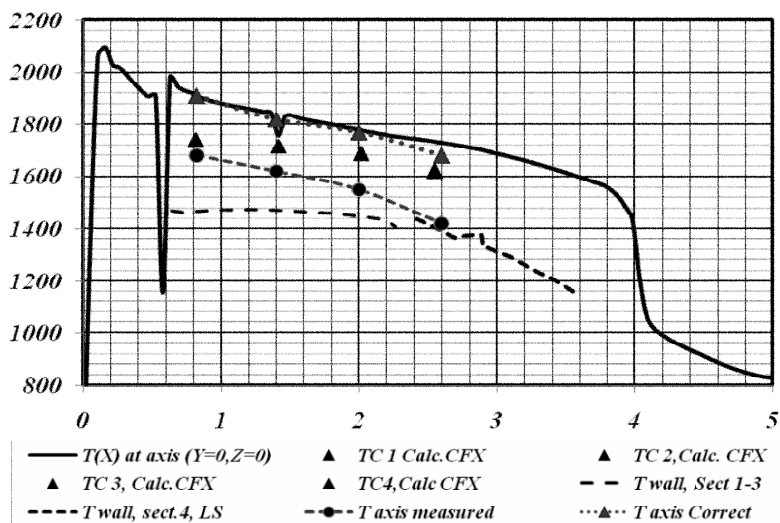
Temperature field inside the VGP-100B stand simulated by CFX model of natural gas combustion and comparison of the direct thermocouple measurements with those simulated are presented in Fig. 2.

Table 1 – Heat losses by sections on the experimental stand VGP-100 B

Part of the experimental set	Heat loss measured on the stand, W	Heat loss of a model, W	Δ , %
Burner	8600	9113	5.9
Flange of a burner	2500	2320	7.2
Diagnostic section	4300	4641	7.3
Total	15400	15738	2.2



a



b

Fig. 2. Simulated temperature field (a) and comparison of direct thermocouple measurements (b) with those simulated. Dots-thermocouple direct measurements, lines-simulated data

As the given results prove, the developed 3-d models adequately reflect real processed and thus can be utilized for simulation of co-combustion processes.

THE TECHNOLOGY OF THE ANTHRACITE COMBUSTION IN TORCH WITH PRELIMINARY THERMOCHEMICAL PREPARATION (TCP)

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At 6 from 14 Ukrainian TPP's the design fuel is Donetsk anthracite with ash content up to 20 % and heating value $Q_i^f = 24\text{--}25$ MJ/kg and have wet bottom removal (WBR). The anthracite is low-reactive coal with small content of volatile matters and therefore requires special events for increasing of torch stability and completeness of combustion.

One of the peculiarities of the anthracite pulverized combustion with wet bottom removal is also increased emissions of NO_x due to high temperature in the furnace. The NO_x emissions' reduction at TPP's of Ukraine with using of De NO_x process systems' requires substantial investments which are too heavy for current state of the industry.

In such conditions, the coal dust thermochemical preparation technology (TCP technology) is one of the problems' solving by means of low cost reconstruction of existing swirl burners which allows to work without gas support at more reactive coal or at usage of coal blends (Anthracite + Lean Coal or Anthracite + Bituminous Coal) and at deterioration of coal quality or decrease of boiler load – with small gas consumption at TCP without using of supporting fuel in the boiler.

The TCP technology consists in heating of the coal dust part (~30%) in burner itself to ignition temperature. Within the short time of coal dust residence in the burner ($\leq 0,1$ s), rapid pyrolysis and thermal grinding of coal particles are occurred. This promotes devolatilization of combustible gases, increase of coke residue's porosity and formation of two-phase mixture of combustible gases' flow at burner outlet (mainly, CO and H_2) with coal dust particles heated to ignition temperature. Under the influence of such flow and radiation flux from furnace, the whole dust ignites in the lower radiant section of the furnace.

The construction of the 70 MW standard swirl burner for TPP-210A boiler of Trypilska TPP was taken as a base during the process of TCP industrial burner's development.

The burner's construction scheme is shown in Figure 1.

The burner has been in industrial operation since November, 27, 2010 to April, 17, 2012 that was 10500 hours of accident-free operation at different load regimes. At the time of investigation operation, the burner was in operation in different regimes

depending on coal quality – both with TCP using and without it. At all regimes the burner provided steady torch in the furnace, absence of the slag adhesion under the burner and slagging of the muffle chamber.

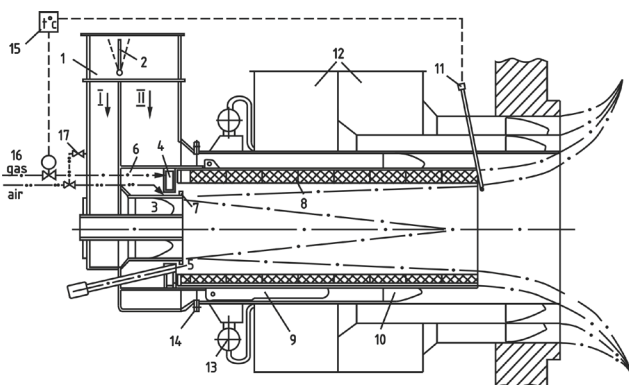


Fig. 1. Burner construction scheme

In the range of coal consumption rates for burner 9–11 t/h, changes of gas flow rates for TCP (from 50 to 200 Nm³/h) at constant coal consumption rate are not significantly influenced on temperature of the two-phase flow. With increase of V^{daf} to 12% (anthracite and lean coal blend) the required natural gas flow rate is reduced to ~30–50 Nm³/h.

In total, the studies shown the burner's performance capacity and the operation efficiency at coal of different grades and different quality (anthracite, anthracite and lean coal blends, lean coal, with volatile matter content: V^{daf} from 6,0 до 13,3% and ash content: A^{r} from 26,2 to 29,0%) and at different power unit's loads.

The average monthly indices of the combustibles' content in fly ash on the side of the TCP burner's operation were for 0,5–0,8% lower.

After shutdown of the boiler and ultrasonic examination of erosion wear of burner's details was conducted. The most heat-stressed details – the muffle, the peripheral swirler, the gas burner and practically did not have erosive wear: local abrasions 0,2–0,4 mm at thickness of 10 mm. The highest erosion (4–5 mm) was marked on side walls of coal box in places of flow sharp turn (at 90°).

The tests carried out in a wide range of coal consumption per burner (6–14 tons of coal per hour). In all specific range of the loads the burner had shown the reliable operation as with application of the thermochemical preparation of the coal as without it.

To determine the effect of TCP method on the furnace performance, the comparative numerical analysis has been made using ANSYS FLUENT software for the operation of TPP-210A boiler equipped with standard burners for combustion of pulverized coal and TCP burners. The simulation program provides computations for the processes of gas and pulverized anthracite combustion, two-phase flow and combined convection and radiation heat transfer in the object in question. Additionally, in the post-processing mode, the formation of nitrogen oxides has been computed.

When computing the nitrogen oxide formation all three mechanisms were taken into account: the thermal, the fuel, and the rapid ones. The computed NO concentration fields confirm the assumption that the main difference in nitrogen oxide formation resulting from the use of TCP method is in the lower part of furnace where active combustion of coal takes place. In the case of TCP burners that have lower temperature of flame core and lower concentration of oxygen in this region of furnace, lower yield of thermal nitrogen oxides is reported. The combustion conditions become even along the furnace vertical, with the diagrams of average NO concentrations being almost equidistant (Fig. 2). Nitrogen oxide concentration is lower by 10—15% in the case of TCP burners.

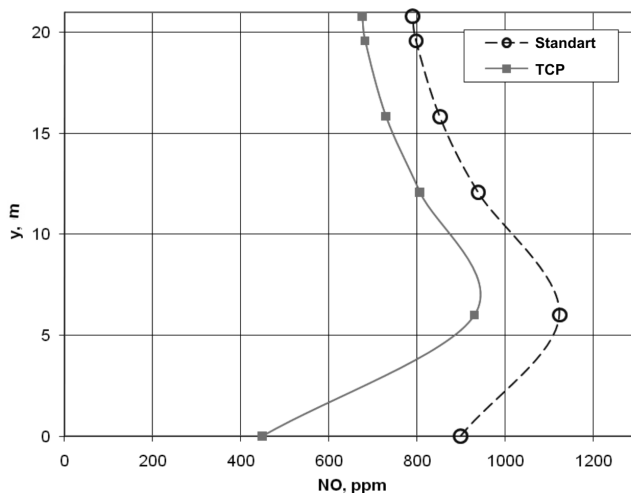


Fig. 2. Average nitrogen oxide concentration along the furnace vertical

Combustion of coke residue lasts as long as coal particles stay in the furnace. In the case of TCP burner, the combustion starts inside the burner and is more intensive near the burner. Further, the solid particle combustion rate becomes even

along the furnace vertical. The share of incompletely burnt coal particles at the exit is 2.09 and 2.87% for the TCP and the standard burners, respectively, which means that early ignition has a more important effect on complete combustion than reduced oxygen concentration.

Clean Coal Technology Centre: Research Potential and Projects Developed to Date

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Coal is the most abundant fossil fuel in the world. Its current share in global electricity production is dominant, and according to forecasts, global coal consumption is expected to considerably increase in the future, mainly due to the steadily growing energy demands in developing countries, such as China and India [1]. In Europe, coal is less important than in the rest of the world; however, for some countries, e.g., Poland, where approximately 85% of electricity generation is based on coal, its significance for the energy security is evident [2].

The steadily increasing demand for primary energy and electricity in the world, accompanied by increasingly stringent environmental requirements associated with the use of fossil fuels, is forcing new directions in the research on alternative and more efficient technologies for coal utilization. **Clean Coal Technologies** are defined as technologies being developed to mitigate the environmental impact of coal energy generation. The term includes any technology which reduces emissions of sulphur, nitrogen oxides, mercury, particulates or other pollutants arising from the use of coal. It also includes efficiency measures which will reduce emissions of CO₂ and carbon capture and sequestration technologies.

The Clean Coal Technologies Centre is the largest European investment project in the domain of coal research infrastructure in recent years. These innovative R&D infrastructures and laboratories created by Główny Instytut Górnictwa in Katowice and Mikołów were realised from the funds of European Regional Development Fund (ERDF) within the Polish Innovative Economy Operational Programme. The R&D of the CCTC comprises laboratories as well as demo installations thanks to which the Centre can realise basic research as well as conduct R&D and demo works concerning the prospective technologies for utilisation of coal. CCT unit in **Katowice** comprises innovative research laboratories equipped with research equipment and

appliances, which support interdisciplinary research on coal utilisation, and in particular:

- properties of solid bodies, liquids and gases,
- minimising the environmental impact,
- process engineering and nanotechnology,
- environment research and monitoring,
- identifying the coal deposits and associated minerals,
- analysing the CO₂ storage potential.

Technological unit in **Mikolów** is focused on conducting large scale R&D works, including in particular:

- process of underground, pressure or non-pressure, coal gasification aimed at production of syngas with a high content of hydrogen and of gases for power use,
- fluidized gasification of solid fuels in surface conditions,
- direct coal liquefaction process aimed at the production of engine fuels and chemical raw materials, processes of hydrogenation and refinement of coal-derived substances,
- separation and purification of process gases using membrane techniques and methods of absorption and adsorption, including the pressure swing adsorption - PSA,
- separation of CO₂ from process gases

The most flagship research projects of the Centre to date have been mainly related to the development of **underground coal gasification technology (UCG)**. The UCG has recently gained considerable attention worldwide as an alternative option of coal recovery, especially from unmineable coal deposits, abandoned for operational or economic reasons [3,4]. It is the process of direct in-situ conversion of coal deposits to gaseous energy carriers or to synthesis gas. This coal extraction technology is believed to increase the amount of coal in the energy balance, while providing the sufficient level of economic, safety and environmental protection [5]. Therefore it is of special interest to Poland with the energy sector based predominantly on coal. The GIG started its research in the field of UCG in 2007 in the frames of the project entitled: *Hydrogen Oriented Underground Coal Gasification for Europe* (HUGE). Within the HUGE project supported by EU RFCS, and completed in July 2010, a wide range of gasification tests were undertaken, from experiments in blocks of coal, both underground and in surface rigs, to high pressure

simulations in surface tests [6-8]. The experiments were supported by small-scale laboratory work, environmental studies and modeling. The HUGE project has demonstrated theoretically, and experimentally in seam, that syngas with high hydrogen content can be produced. However, safety and environmental aspect of the UCG are of the utmost importance when planning research and industrial-scale UCG applications. These issues were subsequently the subject of the further research in the framework of HUGE2 project, which was oriented mostly on environmental and safety aspects of the UCG technology. An underground trial has been performed in mine testing two boreholes system and reactive barriers have been used [9]. Within another, national funded research project entitled *Elaboration of coal gasification technology for a high efficiency production of fuels and electricity* a field-scale underground coal gasification experiment was conducted in a middle of 2014 in the Upper Silesian Coal Basin in Poland. This 60-day air-blown UCG test, carried out in a 5m thick seam of bituminous coal at a depth of about 400 m below the ground level, demonstrated feasibility of UCG in the active mine areas [10].

Currently, UCG research in the Centre is being done within two ongoing EU funded projects: TOPS and Coal2Gas. The main objective of TOPS projects (*Options for coupled underground coal gasification and CO₂ capture and storage*) realized under 7 Framework programme is to develop a generic UCG-CCS site characterisation workflow, and the accompanying technologies, which would address the dilemma faced by the proponents of reactor zone CO₂ storage, and offer technological solutions to source sink mismatch issues that are likely to be faced in many coalfields [11]. This objective will be achieved through integrated research into the field based technology knowledge gaps, such as cavity progression and geomechanics, potential groundwater contamination and subsidence impacts.

Project Coal2Gas (*Enhanced Coal Exploitation through UCG Implementation in European Lignite Mines*) started in 2014 and co-funded by the European Commission under the Research Fund for Coal and Steel (RFCS) is aiming to address underground gasification of lignite seams in order to increase the level of utilization of abandoned lignite resources in previously active conventional mining areas using a UCG technology under special conditions. The project aim will be to prepare a well-monitored field trial and low cost pilot project in Romania's lignite seam. The results of the project will be used to draw the conclusions regarding the applicability of such method as well as the geological, technical and environmental feasibility of UCG in other similar deposits which are known to exist in EU countries and world-wide.

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