UDC 502.175:620.9 doi: 10.20998/2079-0821.2021.01.13

O. H. LEVYTSKA, Y. V. VOYTENKO, A. O. ORISHECHOK

COMPARATIVE ASSESSMENT OF GASEOUS FUEL EMISSION

The work presents estimated comparative assessment of emissions release in combustion products during work of high–power steam boilers with the use of traditional fuel – natural gas and alternative fuels – blast–furnace and coke–oven gases generated in the process of technological cycle at iron and steel and coke–chemical enterprises. Calculation algorithm is shown and formulas for assessment of carbon content in exhaust gases are defined, conclusions on ecological efficiency of gaseous fuels are given.

The purpose of the work was to evaluate the emissions of harmful substances generated during the combustion of natural, blast furnace and coke oven gases, justification of the calculation of carbon content of a given chemical composition and determine the optimal environmental impact of analogues of natural gas.

The comparative estimation of pollutant emissions into atmospheric air during combustion of natural, coke oven and blast furnace gases revealed:

– high sulfur dioxide emissions from combustion of blast furnace and coke oven gases due to the presence of sulfur compounds in the composition of these gases;

– relatively high emissions of nitrogen compounds for natural and coke oven gases and relatively low emissions for blast furnace gas;

– carbon emissions are high for all types of fuels which have been considered, most carbon dioxide gets into the air when burning natural gas, least – when burning blast furnace gas;

– significantly higher methane emissions are observed during the combustion of natural and coke oven gases, respectively, smaller – for blast–furnace gas combustion;

– coke oven and natural gases are characterized by low mercury emissions.

Comparative assessment of the calculated values of hazardous substances emissions in the combustion products in the process of combustion of natural, coke–oven and blast–furnace gases shows that even at lower working heat of combustion values the coke–oven and blast–furnace gases can compete with natural gas.

For the first time, a comparative characterization of the emissions of harmful substances in the combustion of natural, coke oven and blast furnace gases is presented, and it is shown that the gases used in coke and metallurgical industries, which are used as analogues of natural, are logical to use, but require the installation of treatment systems. The paper defines a formula for calculating the carbon content in natural gas from the Urengoy–Uzhhorod gas pipeline. The provided calculations and the introduction of simplified formulas serve as an example for the calculation of emission factors and emissions in assessing the level of safety of existing equipment and can be used in the development of permit documents of enterprises that carry out emissions of harmful substances to the environment.

Keywords: emissions, greenhouse gases, hazardous substances, emission indexes, combustion

О. Г. ЛЕВИЦЬКА, Ю. В. ВОЙТЕНКО, А. О. ОРІШЕЧОК

ПОРІВНЯЛЬНА ОЦІНКА ВИКИДІВ ПРОДУКТІВ ЗГОРЯННЯ ГАЗОПОДІБНИХ ПАЛИВ В АТМОСФЕРНЕ ПОВІТРЯ

В роботі приведена розрахункова порівняльна оцінка викидів шкідливих речовин у продуктах згоряння при роботі високопотужних парових котлів із використанням традиційного палива – природного газу та альтернативних палив – доменного та коксового газів, що утворюються в ході технологічного циклу на металургійних та коксохімічних підприємствах. Показаний алгоритм розрахунку та визначені формули для оцінки вмісту вуглецю у вихідних газах, наведені висновки щодо екологічної ефективності газоподібних палив.

Метою роботи стала оцінка викидів шкідливих речовин, що утворюються в ході спалювання природного, доменного та коксового газів, обгрунтування розрахунку вмісту вуглецю у паливі заданого хімічного складу та визначення оптимального з точки зору впливу на довкілля аналогів природного газу.

При порівняльній розрахунковій оцінці викидів забруднюючих речовин в атмосферне повітря при спалюванні природного, коксового та доменного газів виявлено:

– високий викид діоксиду сірки при спалюванні доменного та коксового газів із–за наявності сполук сірки у складі цих газів;

– порівняно високі викиди сполук азоту для природного і коксового газів і порівняно низькі – для доменного газу;

– викиди сполук вуглецю є високими для всіх розглянутих видів палив, найбільше сполук вуглецю потрапляє в повітря при спалюванні природного газу, найменше – при спалюванні доменного газу;

– значно більший викид метану спостерігається при спалюванні природного і коксового газів, відповідно менший – при спалюванні доменного;

– коксовий та природний газ характеризуються незначними викидами ртуті.

Порівняльна оцінка розрахункових значень викидів забруднюючих речовин у продуктах згоряння в процесі спалювання природних, коксових та доменних газів показує, що навіть при нижчих робочих теплотах спалювання коксовий та доменний гази можуть конкурувати з природним газом.

В роботі вперше наведена порівняльна характеристика викидів шкідливих речовин при спалюванні природного, коксового та доменного газів та показано, що отримані на коксохімічному та металургійному виробництвах гази, котрі використовуються як аналоги природного, є логічними у використанні, але потребують встановлення очисних систем. В роботі визначена формула для розрахунку вмісту вуглецю у природному газі із газопроводу Уренгой–Ужгород. Наведені розрахунки та введення спрощених формул слугують прикладом для розрахунку коефіцієнтів емісії та викидів при оцінці рівня безпеки діючого устаткування та можуть бути використаними при розробці дозвільних документів підприємств, що здійснюють викиди шкідливих речовин у довкілля.

Ключові слова: викиди, парникові гази, шкідливі речовини, показники емісії, спалювання.

Е. Г. ЛЕВИЦКАЯ, Ю. В. ВОЙТЕНКО, А. О. ОРИШЕЧОК

СРАВНИТЕЛЬНАЯ ОЦЕНКА ВЫБРОСОВ ПРОДУКТОВ ЗГОРАНИЯ ГАЗООБРАЗНЫХ ТОПЛИВ В АТМОСФЕРНЫЙ ВОЗДУХ

В работе приведена расчетная сравнительная оценка выбросов вредных веществ в продуктах сгорания при работе высокомощных паровых котлов с использованием традиционного топлива – природного газа и альтернативных топлив – доменного и коксового газов, образующихся в ходе технологического цикла на металлургических и коксохимических предприятиях. Показан алгоритм расчета и определены формулы для оценки содержания углерода в отходящих газах, приведены выводы по экологической эффективности газообразных топлив.

Целью работы стала оценка выбросов вредных веществ, образующихся в ходе сжигания природного, доменного и коксового газов, обоснование расчета содержания углерода в топливе заданного химического состава и определения оптимального с точки зрения влияния на окружающую среду аналога природного газа.

При сравнительной расчетной оценке выбросов загрязняющих веществ в атмосферный воздух при сжигании природного, коксового и доменного газов выявлено:

– высокий выброс диоксида серы при сжигании доменного и коксового газов из–за наличия соединений серы в составе этих газов;

– сравнительно высокие выбросы соединений азота для природного и коксового газов и сравнительно низкие – для доменного газа;

– выбросы соединений углерода высоки для всех рассмотренных видов топлив, больше соединений углерода попадает в воздух при сжигании природного газа, меньше всего – при сжигании доменного газа;

– значительно больший выброс метана наблюдается при сжигании природного и коксового газов, соответственно меньший – при сжигании доменного;

– коксовый и природный газ характеризуются незначительными выбросами ртути.

Сравнительная оценка расчетных значений выбросов загрязняющих веществ в продуктах сгорания в процессе сжигания природных, коксовых и доменных газов показывает, что даже при более низких рабочих теплотах сжигания коксовый и доменный газы могут конкурировать с природным газом.

В работе впервые представлена сравнительная характеристика выбросов вредных веществ при сжигании природного, коксового и доменного газов и показано, что полученные на коксохимическом и металлургическом производствах газы, которые используются как аналоги природного, логичны в использовании, но нуждаются в установке очистных систем. В работе определена формула для расчета содержания углерода в природном газе из газопровода Уренгой–Ужгород. Приведенные расчеты и введение упрощенных формул служат примером для расчета коэффициентов эмиссии и выбросов при оценке уровня безопасности действующего оборудования и могут быть использованы при разработке разрешительных документов предприятий, осуществляющих выбросы вредных веществ в окружающую среду.

Ключевые слова: выбросы, парниковые газы, вредные вещества, показатели емиссии, сжигание.

Introduction. Modern society with the development of innovation technologies and implementation of effective monitoring researches puts forward new requirements for the safety and environmental friendliness of engineering processes. Therewith, one of the key issues is the impact of industrial enterprises on atmospheric air and ways of pollution abatement under such an impact. This work considers the issues of atmospheric air pollution in the process of fuel combustion to ensure the operation of high–power steam boilers. There are assessed emissions during operation of the stated boilers on fossil gaseous fuel – natural gas and on blast–furnace and coke–oven gases.

Analysis of major achievements and literature. An economic resource is involved in natural gas extraction unlike with blast–furnace and coke–oven gases, negative influence on natural ecological systems occurs. The main driving force on the way of searching for alternative energy sources is the fullness of fossil fuels. Blast–furnace and coke–oven gases are obtained as co–product in metallurgical and cake and by–product processes. Synthesis of these gases is not accompanied by waste generation and exploitation of soil ecosystems.

Thuswise, interdisciplinary international consortium of research centre (ArcelorMittal Global R&D Asturias and Maizières, Centro Sviluppo Materiali, Swerea MEFOS, VDEh–Betriegsits) has successfully implemented project aimed at expanding the use of blast–furnace gas in steel–making furnaces [1].

It has been established that the process for high–pressure hydrogen recovery from coke oven gas is known [2] and blast–furnace and coke–oven gases are used in heat–treating furnaces and annealing lines in the metal melting industry [3, 4], a low emission coke oven system using oxy–fuel combustion of coke oven gas was adopted to limit nitrogen oxides (NOx) emission and realize carbon dioxide (CO_2) enrichment [5]. But comparative assessment of emissions in the process of combustion of these types of fuels and fossil minerals remains a pressing issue. Primarily, this is because the stated emissions provoke a greenhouse effect.

This phenomenon is constantly evolving and over the last years has significantly increased its negative impact on the planet. So, for instance, recent researches predict climate warming during the course of the 21st century between 1.0 and 3.7°C [6], and in 1993 author of the article [7] pointed out that greenhouse effect could cause further warming by 0.3°C over the course of decade, unless appropriate measures are taken, that can cause global changes in the structure of agriculture, precipitation, water resources, rising sea level and coastal flooding, occurrence of such phenomena as droughts and hurricanes [7].

According to the data of United States Environmental Protection Agency the fossil fuel combustion produces about 65 % of global emissions of greenhouse gases [8, 9]. In comparison with other hydrocarbon fuels, such as natural gas, coke–oven gas has high hydrogen sulphide content [10], for that reason industrial enterprises implement state–of–the–art desulphurisation technologies [11, 12].

In Ukraine, vacuum–carbonate, arsenic–soda and mono–ethanolamine purification methods, integrated purification of coke–oven gas from hydrogen sulphide and ammonia with ammonia decompounding using high–efficient catalysts have been developed [13, 14].

In addition, the problem of the shortage of energy resources is well known and pressing for specialists. For that reason, search for alternative energy sources is one of the priority tasks in the economy of countries all over the world. Resource–saving and reuse of waste and by–product recovery are ways to solve these problems.

The practice of coke–chemical and iron and steel enterprises proves that the use of blast–furnace and coke–oven gases in the production will allow not to spend money on natural gas and to utilize by–products.

Formulation of the problem. This is precisely why there is a need to compare the qualitative composition of emissions in the process of combustion of natural gas and alternative blast–furnace and coke–oven gases and to formulate environmental conclusions on the feasibility of using gaseous fuels synthesized at industrial enterprises at industrial enterprises and in heating civic buildings, and their advantages or disadvantages compared to natural gas, which is the objective of this work.

Research results. When determining the gross emission of hazardous substances for combustion units, there is used the method of continuous measurements with the application of in–process control devices or as per calculation of the index of hazardous emission – the specific value of emissions that is determined for a particular unit and takes into consideration the fuel characteristics, in particular its chemical composition, combustion processes and methods of emission reduction, assessment of the purification systems performance [15].

Despite the purification of coke oven gas from sulfur compounds, ammonia, benzene [16], emissions of polluting substances into the atmosphere are made.

The gross emission of a hazardous substance entering into the atmospheric air in the process of combustion of gaseous fuels for the relevant period is calculated as the product of the index of hazardous emission k_i, fuel consumption for this period B and lower wet heating value of this fuel Q_i^r.

Indexes of hazardous emission are calculated according to procedure [15]. Taking into consideration the chemical composition of the natural, blast–furnace and coke–oven gases under study and the operation of gas cleaning plants, the following calculations are used in the work.

To determine the indexes of emissions of NO_x and sulphurous anhydride, it is necessary to take into consideration the effectiveness of primary measures to reduce emissions η_{I}, efficiency of flue gases purification from pollutant η_{II}, purification plant performance coefficient β. When determining NO_x emission indexes, it is also necessary to take into consideration degree of pollutant emission reduction when operating at low load f_n. Emission indexes of NO_x and sulphurous anhydride are calculated according to formulas [15]:

$$k_{NO_x} = k_{NO_{x0}} \quad f_n \; 1-\eta_I \quad 1-\eta_{II}\beta \;\; ;$$

$$k_{so_2} = \frac{10^6}{Q_i^r} \cdot \frac{2S^r}{100} \; 1-\eta_{I} \quad 1-\eta_{II}\beta \;\; .$$

When ignoring the mass content of moisture and ash, the sulfur content in the fuel per working mass [15]:

$$S^{daf} = S^r = \frac{100}{\rho_n} \; 0{,}941 \cdot m_{H2S} \quad .$$

Emission indexes and emissions of carbon oxides and dioxides are separately identified in the work.

Emission indexes of carbon oxides with consideration for fuel heat loss due to combustible losses q_4 are calculated according to [15]:

$$k_{CO} = k_{CO_o}\left(1 - \frac{q_4}{100}\right).$$

Considering the fact that the value of combustible losses is $q_4 = 0$ for coke–oven, blast–furnace and natural gases, we obtain the equation:

$$k_{CO} = k_{CO_o}$$

Emission indexes of carbon dioxides with consideration for oxidation rate of fuel carbon ε_C are calculated according to formula [15]:

$$k_{CO_2} = \frac{44}{12} \cdot \frac{C^r}{100} \cdot \frac{10^6}{Q_i^r} \cdot \varepsilon_c$$

Carbon content in fuel per working mass will be [15]:

$$C^{daf} = C^r = \frac{100}{\rho_n}\left(\sum \frac{12p}{12p+q} m_{C_pH_q} + 0{,}429 m_{CO} + 0{,}273 m_{CO_2}\right)$$

Index of mercury emission with consideration for mercury capture efficiency in dust–extraction plant η_{gzu} [15]:

$$k_{Hg} = k_{Hg_o}(1 - \eta_{gzu})$$

Since when changing the parameters of technological processes of fuel combustion it is possible to vary the consumption of the same fuel, the best option would be to set the same fuel consumption values for all considered types of fuels. In the calculations, we set the fuel consumption equal to 1 t.

Hazardous substances emissions in the process of combustion of coke–oven, blast–furnace and natural gases were calculated for the units with heating capacity from 50 to 300 MW. In the processes of combustion there is used coke–oven gas purified at coke–chemical plants, therefore, the numerical values used in the calculations are relevant specifically for the purified coke–oven gas. To determine the magnitude of the hazardous substances emissions in the process of combustion of combustible gases, the lower wet heating value of the fuels, listed and presented in table 1.

Table 1 – Lower wet heating values of coke–oven, blast–furnace and natural gases

Type of fuel	Combus–tion process	Q^r (per volume) mJ/m^3 [15]	ρ, kg/m^3 [15]	Q^r (per mass), mJ/kg
Coke–oven gas	in–chamber combustion	16.61	0.483	34.39
Blast–furnace gas	in–chamber combustion	3.94	1.296	3.04
Natural gas*	in–chamber combustion	33.08	0.723	45.75

* – Urengoy–Uzhhorod gas pipeline

When ignoring the value of moisture content, we set $Q^d = Q^r$, where Q^d, Q^r – lower dry and wet according to fuel calorific value. When ignoring the value of moisture content, we set $Q^d = Q^r$, where Q^d, Q^r – lower dry and wet according to fuel calorific value.

Emissions after gaseous fuels combustion contain sulphurous anhydrides, NOx, carbon oxides and dioxides, mercury. It is worth noting that, unlike coal of various grades, there are no heavy metals in the combustion products of the gaseous fuels under study, unlike high– and low–sulfur residual oils – vanadium compounds and unlike biomass, pellets, briquettes and the above coals and residual fuel oils, the combustion products of the natural, blast–furnace and coke–oven gases contain no suspended particulate matter.

Results and discussion. Industrial facilities and the main purification equipment of the majority of coke–chemical enterprises in our state were built in the age of industrialization, when the main objective was ramp–up of industrial products output. Together with the main products – coke, there was increased the volumes of coke–oven gas, which was generated during the high–temperature heating of the coal charge in coke blast furnaces.

Coke–oven gas consists of pyrogenic water vapours, coal–tar pitch, methane, hydrogen, carbon oxides and dioxides, nitrogen compounds, ammonia, hydrogen sulphide, ammonocarbonous acid, a large amount of unsaturated aromatic hydrocarbons, naphthaline and other substances [13]. For industrial use, gas with such chemical composition is unacceptable, therefore it is purified in by–product–recovery departments of coke–chemical enterprises.

Within the influence of coke–chemical enterprises, there may be residential buildings and summer cottages, therefore the goal of specialists is emission reduction generated in the process of coke–oven gas combustion. Considering high hydrogen sulfide content in coke–oven gases, which leads to significant sulfur–dioxide emissions, the enterprises of the industry are working with capacities that implement reagent vacuum–carbonate, arsenic–alkaline and monoethanolamine methods of gas purification from hydrogen sulphide.

When comparing these three methods, the authors [15] acknowledge the fact that in the process of coke–oven gas purification using arsenic–alkaline method, sulfur–dioxide emission and correspondingly the enterprise payments for environmental pollution and damage to the environment will be high. When comparing the monoethanolamine and vacuum–carbonate method, the first one is more efficient, two–stage purification with the vacuum–carbonate method corresponds to the monoethanolamine method. Considering high toxicity of the monoethanolamine reagent, the use of two–stage vacuum–carbonate purification will be appropriate from the perspective of the impact on personnel and environment.

Today, coke–chemical enterprises use coke–oven gas for heating–up coke furnace batteries, steam generating units at their in–house combined electric–power and heat–generating plants [15].

Practice of by–product coke plants proves that coke–oven gas used for work of in–house combined electric–power and heat–generating plants, is high–grade alternative to natural gas. Such combined electric–power and heat–generating plants heat the buildings of enterprises. Unfortunately, a substantial amount of coke–oven gas is still disposed of using gas escape equipment at the by–product coke plants, while this resource can be used to heat neighboring residential buildings.

Blast–furnace gas is co–product of metallurgical production, which is generated in blast furnaces in the process of iron smelting. Its main components are nitrogen compounds, hydrogen compounds, carbon oxides and dioxides, methane.

Prior to be used at metallurgical plants, blast–furnace gas is cleared of suspended particulate matter. Purification takes place in several stages with the use of dry–type collectors and methods of wet purification – scrubber filters, Venturi pipe.

Today, blast–furnace gas is used for heating–up steam generating units of combined electric–power and heat–generating plants and for production needs [17]. Considering the experience of Dnieper Metallurgical Combine, blast–furnace gas is low–calorie product, generating a substantial amount of combustion products [17]. However, such cases are not frequent. A substantial amount of gas is disposed of by flare.

According to procedure [15], it is demonstrated that natural gas from Urengoy–Uzhhorod and Central Asia–Central gas pipelines contains no hydrogen sulphide, therefore, sulfur–dioxide emissions in the process of combustion of this gas will be absent.

Unlike natural gas, coke–oven and blast–furnace gases contain hydrogen sulphide (table 2).

Enterprises of Ukraine, which use blast–furnace and coke–oven gases, usually do not use desulfurization equipment and sorbent agents for sulfur retention. In the absence of such equipment, the coefficient value of the operation of the desulfurization unit, the efficiency of flue gases purification from sulfur oxides and the efficiency of sulfur retention by ash or sorbent agent in the electric power plant will be equal to zero. Table 2 presents sulfur content, calculated emission indexes and values of sulfur–dioxide emission in the process of combustion of coke–oven and natural gases.

Table 2 – Calculation parameters of sulfur–dioxide emission indexes for coke–oven and blast–furnace gases

Fuel	H_2S, % [15]	S^r , %	k_{SO} , g/GJ	E, kg
Coke–oven gas	0,4	0,12	69,79	2,4
Blast–furnace gas	0,3	0,03	197,37	0,6

With a slight difference of the hydrogen sulfide content in the compared types of gaseous fuels, the value of sulfur–dioxide emission index for blast–furnace gas is higher.

Calculation of sulfur content in the fuel takes into account the value of the fuel density – the lower density (table 1), the higher values of the calculated emission index. Despite the significantly higher value of sulfur–dioxide emission index, the emission of this pollutant in the process of combustion of blast–furnace gas will be four times lower than the similar emission in the process of combustion of coke–oven gas as a result of much lesser lower wet heating values.

The combustion processes of combustible gases in a significant number of industrial enterprises of Ukraine is carried out in the absence of special equipment, therefore, for a comparative analysis of the emission values of NOx and nitrogen dioxides, the emission factors of NOx and nitrogen dioxides for the gases in question will be considered according to procedure [15].

Emission indexes of NOx and nitrogen dioxides with disregard for measures to emissions reduction for coke–oven, blast–furnace and natural gases are presented in table 3. Emission indexes are significantly higher for NOx, among them the highest values are obtained in the process of combustion of coke–oven gas, the lowest values – for blast–furnace gas. Emission indexes of nitrogen dioxides have the highest values in the process of combustion of gases generated at production. When combusting natural gas, almost all nitrogen is oxidized to NO_x.

Emission values of NOx and nitrogen dioxides for the considered types of fuels, calculated on the basis of emission indexes, are presented in Fig. 1.

NOx are indicative of the emission value among nitrogen compounds emitted into the atmospheric air in the process of combustion of combustible gases. Higher emission values were obtained for natural and coke–oven gases, the lowest value – for blast–furnace gas.

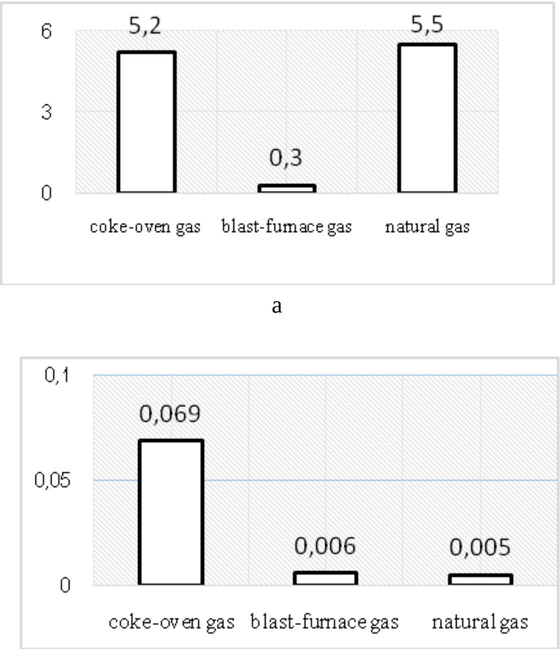
Table 3 – Emission indexes of NOx and nitrogen dioxides in the process of in–chamber combustion of combustible gases with disregard for measures to emissions reduction, g/GJ [15].

Emission index	Coke–oven gas	Blast–furnace gas	Natural gas
NO_x	150	100	120
Nitrogen dioxide	2	2	0.1

At the same time, nitrogen dioxide emissions in the process of combustion of natural and blast–furnace gases will be lower. The highest emission value for this pollutant was obtained for coke–oven gas.

However, contribution of the nitrogen dioxides to the nitrogen compounds emission is negligible. When estimating emissions of these compounds, the lowest total emissions are characteristic of blast–furnace gas. Total emissions of NOx and nitrogen dioxides will be the highest for natural gas.

Interestingly, at high values of NOx emission indexes for coke–oven gas compared to natural gas, the emission value of this pollutant will be higher for natural gas. And at similar values of the emission indexes of nitrogen dioxides for coke–oven and blast–furnace gases, the first one, in the process of combustion, will provide a high emission. Thus, density and lower wet heating value play an essential role in the formation of pollutant emissions.



a

b

Fig. 1 – NOx emissions (a) and nitrogen dioxides emissions (b) in the process of combustion of 1 t fuel, kg

Composite index of carbon oxides emissions in accordance with [15] for natural gas is 15 g/GJ, let us assume for blast–furnace and natural gases the emission index of carbon oxides at the level of the corresponding index during operation of stationary engines with the use of gaseous fuel, which also makes 15 g/GJ.

To determine the index of carbon dioxide emissions in the process of combustion of gaseous fuels, it is necessary to calculate the carbon content. Since in the process of gases combustion, which are considered in the work, the ash mass content in the fuel per working mass (%) is $A^r = 0$, and the value of the moisture mass content in these gases per working mass (%) is low, and it can be neglected in the calculations, we get equation $C^{daf} = C^{\,r}$.

To determine the carbon mass content in the fuel per working mass it is necessary to know the amount of carbon–containing compounds in the fuels under study and their density. Tables 4, 5 present chemical composition as per carbon–containing compounds of natural, coke–oven and blast–furnace gases with consideration for these procedures [15] and study results as to compounds content C_nH_m in coke–oven gas at coking plant.

Table 4 – Volume ratio of carbon–containing compounds, %, in natural gas from Urengoy–Uzhhorod gas pipeline [15]

CH_4, %	C_2H_6, %	C_3H_8, %	C_4H_{10}, %	CO_2, %	ρ_n, kg/nm^3
98.90	0.12	0.011	0.01	0.06	0.723

Table 5 – Volume ratio of carbon–containing compounds, %, in coke–oven and blast–furnace gases [15]

Gas	CH_4, %	C_2H_4, %	C_3H_6, %	C_6H_6, %	CO, %	CO_2, %	ρ_n, kg/nm^3
Processed coke–oven	22.5	1.3	0.4	0.2	6.8	2.3	0.483
Blast–furnace	0.3	–	–	–	28.0	10.5	1.296

Taking the above mentioned into consideration, the formula for calculation of the carbon mass content in natural gas per working mass will look like:

$$C^{daf} = C^r = \frac{100}{\rho_n}\left(\frac{12}{12+4}m_{CH_4} + \frac{12\cdot 2}{12\cdot 2+6}m_{C_2H_6} + \right.$$

$$\left. + \frac{12\cdot 3}{12\cdot 3+8}m_{C_3H_8} + \frac{12\cdot 4}{12\cdot 4+10}m_{C_4H_{10}} + 0,273 m_{CO_2}\right)$$

For coke–oven gas, the formula will look like:

$$C^{daf} = C^r = \frac{100}{\rho_n}\left(\frac{12}{12+4}m_{CH_4} + \frac{12\cdot 2}{12\cdot 2+4}m_{C_2H_4} + \frac{12\cdot 3}{12\cdot 3+6}m_{C_3H_6} + \right.$$

$$\left. + \frac{12\cdot 6}{12\cdot 6+6}m_{C_6H_6} + 0,429 m_{CO} \quad + 0,273 m_{CO_2}\right).$$

For blast–furnace gas, the formula will look like:

$$C^{daf} = C^r = \frac{100}{\rho_n}\left(\frac{12}{12+4} m_{CH_4} + 0,429 m_{CO} + 0,273 m_{CO_2}\right).$$

When calculating the carbon mass content in natural gas per working mass, the mass values of carbon–containing compounds are calculated according to formulas of procedure [15] or recalculated to mass with consideration for values of volume ratio of carbon–containing compounds.

According to procedure [15], recommended value ε_c for natural gas makes 0.995. Let us assume ε_c = 0.995 for blast–furnace and coke–oven gases.

Necessary data and calculation results of emission indexes of carbon dioxides for the fuels under study are presented in table 6.

Calculated values of emissions of carbon oxides (a) and carbon dioxides (a) in the process of combustion of 1 t fuel are presented in Fig. 2.

Table 6 – Calculation parameters of emission indexes of carbon dioxides for gaseous fuels

Fuel	Q_i^r [15] *	C^r [15]	ε_C [15]	k_{CO_2}
Natural gas	45.75	73.73	0.995	58849.43
Coke–oven gas	34.39	40.68	0.995	43195.44
Blast–furnace gas	3.04	16.05	0.995	192792.71

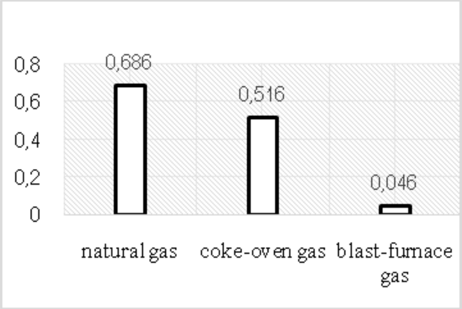
* while neglecting the value W^r – moisture content, it is accepted $Q^d = Q^r$ and lower volumetric wet heating value is recalculated into mass one

At the same emission indexes of carbon oxides, emissions of these compounds in the process of combustion of different fuels are significantly different. A tonne of burnt natural or coke–oven gas will provide more than ten times more carbon oxide emissions than a tonne of burnt blast–furnace gas.

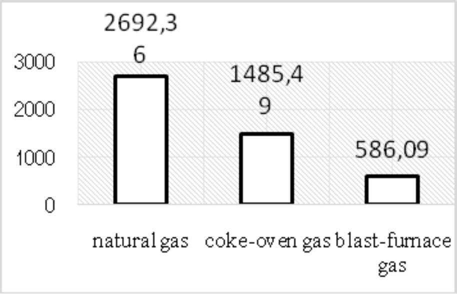
When analyzing emissions of carbon–containing compounds, a significant proportion is accounted for by carbon dioxides emissions. Emission index of carbon dioxide is the highest for blast–furnace gas, but the highest emission values will be in the process of combustion of a tonne of natural gas, and the lowest – specifically in the process of combustion of blast–furnace gas.

In this case, the total emission in the process of combustion of carbon oxides and dioxides will be the highest for natural gas and the lowest for blast–furnace gas.

Emissions of power–generating equipment for combustible gases burning are usually not cleared of methane and nonmethane volatile organic compounds. Therefore, when determining the emission indexes of these compounds, no amendments and additional factors that take into consideration the parameters and effectiveness of the purification equipment are made. Emission indexes of methane and nonmethane volatile organic compounds in the process of combustion of coke–oven, blast–furnace, natural gases are presented in table 7.



a



b

Fig. 2 – Emissions of carbon oxides (*a*) and carbon dioxides (*b*) in the process of combustion of 1 t fuel, kg

Table 7 – Emission indexes of methane and nonmethane volatile organic compounds, g/GJ [15]

Emission indexes	Coke–oven gas	Blast–furnace gas	Natural gas
Methane	1	1	1
Nonmethane volatile organic compounds	—	—	5

Methane emission indexes are the same for all cases considered. The presence of these compounds in emissions in the process of combustion of combustible gases indicates incomplete combustion [15]. Values of methane emissions for combustible gases calculated on the basis of emission indexes are presented in Fig. 3.

Notwithstanding the fact that emission indexes in the process of combustion of the considered combustible gases are the same, emissions due to different values of lower wet heating value and density of each considered fuel are different – the highest for natural gas and the lowest for blast–furnace gas. Nevertheless, the emission values for all considered fuels are quite low.

According to procedure [15], in the process of combustion of coke–oven and blast–furnace gases, emission of nonmethane volatile organic compounds is not provided. This is explained by the initial chemical composition of the gases generated at the iron and steel enterprises. Coke–oven gas prior to be used as an energy resource or prior to recovery is cleared of aromatic carbon–containing compounds in the capture workshops.

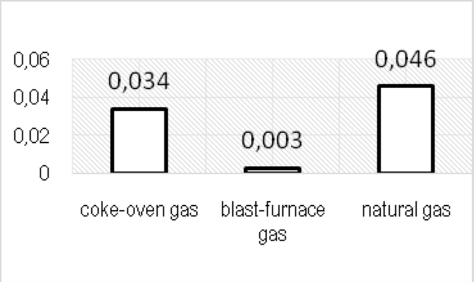


Fig. 3 – Methane emissions in the process of combustion of 1 t fuel, kg

Emission of nonmethane volatile organic compounds for natural gas calculated on the basis of emission index is 0.229 kg per tonne of burnt fuel.

Mercury evolution in small quantities is possible in the process of combustion of coke–oven and natural gases. Calculation parameters of mercury emission indexes for coke–oven and natural gases in the absence of dust–extraction plant are presented in table 8.

Table 8 – Calculation parameters of mercury emission indexes for coke–oven and natural gases

Fuel	k_{Hg} , g/GJ	E, kg
Coke–oven gas	0.035	$1.2 \bullet 10^{-3}$
Natural gas	0.0001	$4.6 \bullet 10^{-6}$

Mercury emission indexes are low. The highest values are shown for coke–oven gas, the lowest – for natural gas. Mercury emission values in the process of combustion of coke–oven and natural gases are insignificant. Experts of coke–chemical enterprises according to facts of the conducted laboratory studies, refute the presence of mercury in industrial gases. When comparing emissions in the process of combustion of the above stated gases, mercury emissions are substantially lower in the process of combustion of natural gas.

Conclusions. A tonne of burnt coke–oven or blast–furnace gas produces a significantly lower emission of carbon oxides and dioxides and lower total emission of NOx and nitrogen dioxides. In the process of combustion of these gaseous fuels there are no emissions of nonmethane volatile organic compounds and methane emissions are the lowest. Advantages of natural gas are the absence of sulfur–dioxide emissions and mercury emissions.

Mercury in fossil gases and by–products of the industry is present in small quantities, therefore its emission in the process of combustion of gases will not exceed the regulatory requirements.

It was also determined in the work that the great amount of atomic carbon in the gaseous fuels under study is converted into carbon dioxide emissions, and atomic nitrogen – into NOx emissions.

When comparing coke–oven and blast–furnace gases, emissions in the process of combustion of the first one by most indicators are higher, but blast–furnace gas is low calorific gas, therefore, in order to meet the same needs it is necessary to spend more blast–furnace gas than coke–oven gas. Compared to natural gas, emissions in the process of combustion of coke–oven gas by the majority of polluting substances are lower.

Comparative assessment of the calculated values of hazardous substances emissions in the combustion products in the process of combustion of natural, coke–oven and blast–furnace gases shows that even at lower working heat of combustion values the coke–oven and blast–furnace gases can compete with natural gas. These gases are co–products at industrial plants, turning the cost of extracting an energy source into a profit due to its recovery. Total values of gross emissions of polluting substances at the enterprise during the use of alternative fuels will also be lower, because emissions after combustion of coke–oven gas or blast–furnace gases when they are recovered in flares are added to the total emissions that occur during technological processes and increase the environmental tax of the industrial enterprise.

References

1. Víctor Cuervo–Piñera, Diego Cifrián–Riesgo, Phuc–Danh Nguyen, Valerio Battaglia, Massimiliano Fantuzzi, Alessandro Della Rocca, Marco Ageno, Anders Rensgard, Chuan Wang, John Niska, Tomas Ekman, Carsten Rein, Wolfgang Adler. Blast Furnace Gas Based Combustion Systems in Steel Reheating Furnaces: Energy Procedia, 2017, 120. https://doi.org/10.1016/j.egypro.2017.07.215
2. S.C.J. Van Acht, C. Laycock, S.J.W. Carr, J. Maddy, A.J.Guwy, G. Lloyd, L.F.J.M. Raymakers. Simulation of integrated novel PSA/EHP/C process for high–pressure hydrogen recovery from Coke Oven Gas: International Journal of Hydrogen Energy, 2020, 45(30), pp. 15196–15212
3. Sébastien Caillat. Burners in the steel industry: utilization of by–product combustion gases in reheating furnaces and annealing lines: Energy Procedia, 2017, 120. https://doi.org/10.1016/j.egypro.2017.07.152
4. Sunghoon Kim, Minsoo Kim, Yong Tae Kim, Geunjae Kwak Jiyong Kim. Techno–economic evaluation of the integrated polygeneration system of methanol, power and heat production from coke oven gas: Energy Conversion and Management, 2019, 182, pp. 240–250.
5. Zhenxing Li, Qun Yi, Yuke Zhang, Huan Zhou, Yingjie Zhao, Yi Huang, Dan Gao, Yanhong Hao. Numerical study and design

strategy for a low emission coke oven system using oxy–fuel combustion of coke oven gas: Journal of Cleaner Production, 2020, 252, https://doi.org/10.1016/j.jclepro.2019.119656

6. Thomas R. Anderson, Ed. Hawkins, Philip D. Jones. CO2, the greenhouse effect and global warming: from the pioneering work of Arrhenius and Callendar to today's Earth System Models: Endeavour, 2016, 40(3). https://doi.org/10.1016/j.endeavour.2016.07.002
7. P.C.Jain. Greenhouse effect and climate change: scientific basis and overview: Renewable energy, 1993, 3 (4–5). https://doi.org/10.1016/0960–1481(93)90108–S
8. European Environment Agency, EMEP/EEA air pollutant emission inventory guidebook / Publications Office of the European Union, 2016, 28 с. doi:10.2800/247535. URL: https://www.eea.europa.eu// publications/emep–eea–guidebook–2016
9. An official website of the United States Environmental Protection Agency [online] URI: https://www.epa.gov/ghgemissions/global–greenhouse–gas–emissions–data
10. K. Sridhar, J. Abbas Mohaideen. Environmental Impact and Forecast of pollutants from coke oven gas and natural gas combustion: International Journal of Engineering Research and Development, 2012, 1(1), pp. 42–45.
11. Nigam Mohit , Singh Randhir, Kumar Naveen, Upadhyaya Sushant. Desulphurization of Coke Oven Gas: International Journal of Scientific Research and Reviews, 2013, 2(1), pp. 13–22.
12. O. I. Platonov. Experience in sulfur–extraction from coke–oven gas: Coke and Chemistry, 2007, 50(8), pp. 226–231.
13. Levytska O., Avramenko S., Kramarova N. Ekologo–ekonomichne obg'runtuvannya vy'boru metodu ochy'stky' koksovogo gazu vid sirkovodnyu: Zbirnyk naukovykh prats DDTU, 2010, 3, pp. 177–182. (in Ukrainian)
14. An official website of the Giprokoks company [online] URI: https://giprokoks.com/ua/chemical–production
15. Collection of emission indicators (specific emissions) of pollutants into the air by different productions. First redaction. Vol. I. Donetsk, Ukrayinskij naukovij centr tehnichnoyi ekologiyi [Ukrainian Scientific Center of Technical Ecology], 2004. 184 p. (in Ukrainian)
16. Jingying Li, Suisui Zhang, Yan Nie, Xiaoxun Ma, Long Xu, LeWu. A holistic life cycle evaluation of coking production covering coke oven gas purification process based on the subdivision method: Journal of Cleaner Production, 2020, 248, https://doi.org/10.1016/j.jclepro.2019.119183
17. An official website of the PJSC «Dneprovsky Iron&Steel Integrated Works» [online] URI: http://www.dmkd.dp.ua/3204

Надійшла (received) 05.03.2021

Відомості про авторів / Сведения об авторах / About the Authors

Левицька Олена Григоріївна (Левицкая Елена Григорьевна, Levytska Olena Hryhoriivna) – кандидат технічних наук, Дніпровський національний університет ім. О. Гончара, доцент кафедри Безпеки життєдіяльності; м. Дніпро, Україна; ORCID: https://orcid.org/0000–0002–8690–6457; e–mail: LLevi@ukr.net.

Войтенко Юлія Володимирівна (Войтенко Юлия Владимировна, Voytenko Yulia Vladimirovna) – Дніпровський національний університет ім. О.Гончара, старший викладач кафедри Безпеки життєдіяльності, м. Дніпро, Україна; e–mail: Juliya.voytenko/1983@gmail.com.

Орішечок Анастасія Олексіївна (Оришечок Анастасия Алексеевна, Orishechok Anastasiia Oleksiivna) – студентка 4–го курсу, спеціальність «Кібербезпека», фізико–технічний факультет, Дніпровський національний університет ім. О. Гончара, м. Дніпро, Україна; e–mail: orishechok.n@gmail.com.