EXHAUST GASES FROM INTERNAL COMBUSTION ENGINES AND THEIR IMPACT ON THE ENVIRONMENT

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Abstract

This paper presents the basic characteristics of gaseous combustion products (CO_2, CO, NOx, SOx, NH_3, etc.) in internal combustion engines (ICE) and their harmful impact on the environment, i.e., the ecological context. Special attention is given to the formation of $CO_2$and CO, specifically the reaction kinetics $CO_2=CO+0.5\cdot O_2$ as the dominant gases in the exhaust gases of ICE. At an ambient temperature of 298K, the considered reaction ΔH=282990 kJ is endothermic and the equilibrium constant at normal pressure (1.013·105Pa) is much less than one $Kp'=1.40\cdot 10^{-45}$, which means that the equilibrium of the reaction is shifted to the left, towards the reactant CO_2. This practically means that the formed CO_2 in the exhaust gases remains stable and, as a greenhouse gas, has an impact on the 'greenhouse effect.' Only at significantly high temperatures, above 2000K, does a slight formation of CO and reduction of CO_2 occur.

Keywords*: exhaust gases, carbon-dioxide, thermodynamic functions, equilibrium constant*

JEL classification: Q53, Q42

1. INTRODUCTION

Internal combustion engines represent one of the most widespread sources of energy in transportation, industry, and agriculture. However, the combustion process of fuel in these engines is far from ideal, leading to the formation of various gaseous and solid combustion products. Among the most significant pollutants are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), sulfur dioxide (SO_2), and hydrocarbons (HC).
In addition to gases, engines, particularly diesel engines, also emit soot resulting from incomplete combustion of hydrocarbon fuel.

Carbon monoxide is a colorless and toxic gas. It is produced by the incomplete combustion of fossil fuels such as coal and gasoline or oil. When inhaled, CO blocks the transport of oxygen to the brain and other organs.

Carbon dioxide is a greenhouse gas and contributes to global warming. In direct contact, CO_2 is not harmful.Large amounts of CO_2 are emitted from diesel engines, but due to incomplete combustion of fuel in the engines, CO is formed while CO_2 is reduced according to the formula $CO_2+0.5\cdot O_2=CO$.

Nitrogen oxides (NOx) are formed at high temperatures, which is common in diesel engines, and concentrations are usually high.

Large amounts of CO_2 are emitted from diesel engines, but due to incomplete combustion of fuel in the engines, CO is formed while CO_2 is reduced according to the formula. Nitrogen oxides (NOx) are formed at high temperatures, which is common in diesel engines, and concentrations are usually high. NOx emissions contribute to acid rain and the formation of photochemical smog. Sulfur oxides, particularly SO_2, are produced from sulfur present in diesel fuel. Today's low-sulfur fuels significantly reduce SO_2 emissions, but in lower quality fuels (heavy fuel oil, crude oil) they are still significant [1,2,3] .
Ammonia (NH_3) is not a primary combustion product but mainly appears as a byproduct in exhaust gas after-treatment systems [4,5].

The emission of gaseous pollutants and soot directly depends on the type of fuel, the operating mode of the engine, the design of the combustion system, as well as the applied emission control systems (catalysts, particulate filters, SCR systems). In the context of tightening environmental regulations, especially those defined in EU standards (e.g., Euro 6/VI), reducing gas and soot emissions becomes a key challenge in the development of new engines and the improvement of existing technologies.

2. REGULATIONS AND LEGAL PROVISIONS ON THE EMISSION OF EXHAUST GASES INTO THE ATMOSPHERE

The air we breathe must have certain characteristics, i.e. components that do not negatively affect humans and other living beings; there must not be any other components exceeding the limit that negatively affect living beings, especially humans. Figures 1, 2 and 3 show CO emissions in Bosnia and Herzegovina for the years 2016 and 2022. It can be observed that the highest CO emissions are in the Tuzla Canton (TK). It can also be noted that there is a reduction in CO emissions from internal combustion engines (ICE) in 2022 compared to CO emissions in 2016.

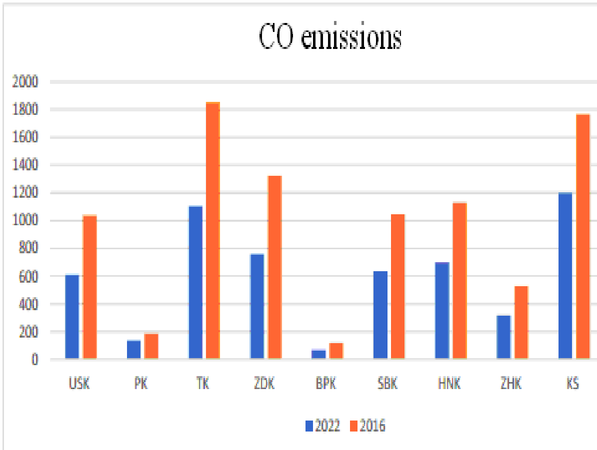

Figure 1. *CO emissions in tons by canton in theof Bosnia and Herzegovinafor the years 2016 and 2022 [6]*

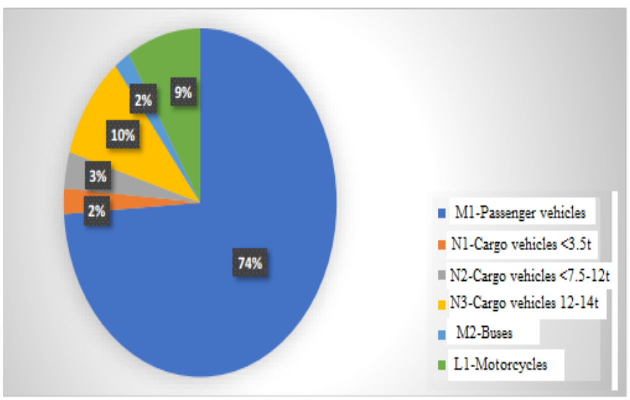

Figure 2. *Percentage share of individual categories of vehicles in carbon monoxide (CO) emissions in the of Bosniaand Herzegovina in 2022. [6]*

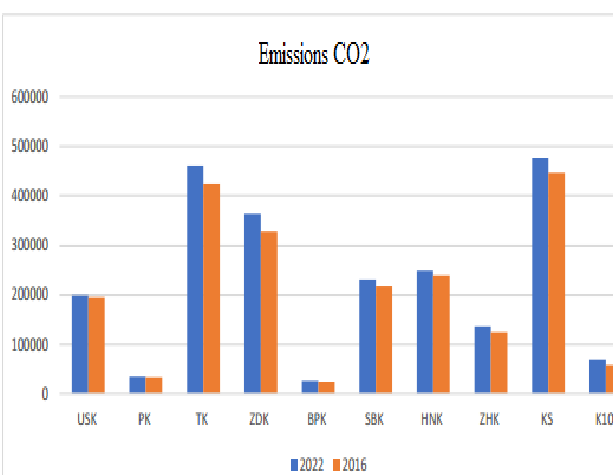

Figure 3*. CO_2 emissions in tons by cantons in the of Bosnia and Hezegovina for the years 2026 and 2022 [6]*

The participation of individual vehicle categories in carbon dioxide (CO_2) emissions in Bosnia and Herzegovina in 2022 refers to passenger vehicles, which account for 74% (Figure 4).

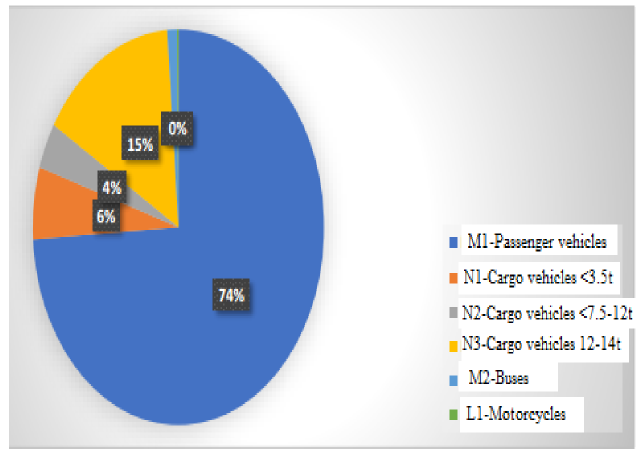

Figure 4. *Percentage share of individual categories of vehicles in carbon dioxide (CO2) emissions in the of Bosnia and Herzegovina in 2022 [6].*

The limit that determines the maximum allowable amount of a harmful substance in a unit of observed volume is called the Emission Limit Value (ELV). It is evident that the ELV is a Quality Standard, a tolerance limit. Table 1 shows the ELVs of individual harmful substances emitted by a gasoline engine. From Table 1, it can be observed that the goal of Euro 5 and 6 requirements is a further reduction in NOx emissions.

Table 1. *Limit values (maximum allowed quantities (g/km)) of certain harmful substances from internal combustion engines [7]*

	Year	CO	HC	HC+NOx	NOx	PM
Diesel engines		(g/km)				
Euro 1	1992/07	3.16	-	1.13	-	0.18
Euro 2	1996/01	1.00	-	0.70	-	0.08
Euro 3	2000/01	0.64	-	0.56	0.50	0.05
Euro 4	2005/01	0.50	-	0.30	0.25	0.025
Euro 5	2009/09	0.50	-	0.23	0.18	0.005
Euro 6	2014/09	0.50	-	0.17	0.08	0.005
Otto engines		(g/km)				
Euro 1	1992/07	3.16	-	1.13	-	-
Euro 2	1996/01	2.20	-	0.50	-	-
Euro 3	2000/01	2.30	0.20	-	0.15	-
Euro 4	2005/01	1.00	0.10	-	0.08	-
Euro 5	2009/09	1.00	0.10	-	0.06	0.005
Euro 6	2014/09	1.00	0.10	-	0.06	0.005

3. MATHEMATICAL MODEL

3.1 Thermodynamic functions

For the chemical reaction [3]:

$$a_1 A_1 + a_2 A_2 + a_3 A_3 + \cdots = b_1 B_1 b_2 B_2 + b_3 B_3 + \cdots \quad (1)$$

where:

A_i , B_j - symbols for chemical substance

a_i - stoichiometric coefficients for reactants

b_j - stoichiometric coefficients for products.

Thermodynamic functions $\Delta H, \Delta S, \Delta G$ at 298K and $1.013 \cdot 10^5$Pathey are defined using the expression [8]:

$$\Delta H = \sum_j b_j \cdot \Delta h_j - \sum_i a_i \cdot \Delta h_i \quad (2)$$

$$\Delta S = \sum_j b_j \cdot s_j - \sum_i a_i \cdot s_i \quad (3)$$

$$\Delta G = \sum_j b_j \cdot \Delta g_j - \sum_i a_i \cdot \Delta g_i \quad (4)$$

where:

a_i - the number of kilomolesof the i-th reactant components

b_j - the number of kilomoles of the j-th component for products

Δh_i - bond enthalpy of the i-th component

Δh_j - bond enthalpy of the j-th component

s_i - specificentropies and connections of the i-th component

s_j -specific entropies and connections of the j-th component

Δg_i -specific free enthalpies of the i-th component

Δg_j -specific free enthalpies of the j-th component.

The dependence of enthalpy, entropy and free enthalpy of reaction (1) on temperature are defined by the expression:

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta c_{mp}(T) dT \quad (5)$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^{T} \frac{\Delta c_{mp}(T)}{T} dT \quad (6)$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad (7)$$

where are:

$\Delta c_{mp} = \sum_j b_j \cdot c_{mp_j} - \sum_i b_i \cdot c_{mp_i}$ - specific molar heat capacities (8)

If it is $\Delta G > 0$ the reaction proceeds from right to left, i.e. In the direction of formation of reaction reactants. If it is $\Delta G < 0$ the reaction proceeds from left to right, i.e. Towards the formation of reaction products. Values of enthalpy, entropy and free enthalpy of reaction components $CO_2 = CO + 0.5 \cdot O_2$ at $298K$ and $1.013 \cdot 10^5$Pa are shown in Table 2.

Table 2. Thermodynamic data of the reaction components $CO_2 = CO + 0.5 \cdot O_2$ at $298K$ and $1.013 \cdot 10^5$Pa [9]

	Δh **J/mol**	Δg **J/mol**	s **J/(molK)**
CO	-110520	-137150	197.56
O_2	0	0	205.03
CO_2	-393510	-394360	213.64

Heat capacities of individual components of the reaction $CO_2 = CO + 0.5 \cdot O_2$depending on the temperature, they are determined using the expression [10]:

$$C_{mpCO} = 29.556 - 6.5807 \cdot 10^{-3} \cdot T + 2.0130 \cdot 10^{-5} \cdot T^2, \text{kJ/(kmol} \cdot K) \quad (9)$$

$$C_{mpO_2} = 29.526 - 8.8999 \cdot 10^{-3} \cdot T + 3.8083 \cdot 10^{-5} \cdot T^2, \text{kJ/(kmol} \cdot K) \quad (10)$$

$C_{mpCO_2} = 27.437 + 4.2315 \cdot 10^{-2} \cdot T - 1.9555 \cdot 10^{-5} \cdot T^2$,kJ/(kmol $\cdot K$)   (11)

For a chemical reaction:

$$\sum_i a_i \cdot A_i = \sum_j b_j \cdot B_j \quad (12)$$

the chemical equilibrium constant expressed in terms of partial pressures is: $K_p = \frac{\prod_j (p_{B_j})^{b_j}}{\prod_i (p_{A_i})^{a_i}}$

(13)

The value of the chemical equilibrium constant K'_p reduced to pressure $p_0 = 1.013 \cdot 10^5$ Pa is determined by the expression:

$$K_p{}' = e^{-\frac{\Delta G}{R_u \cdot T}} = K_p \cdot p_0{}^{-(\sum_j b_j - \sum_i a_i)} \quad (14)$$

where is:

$R_u = 8.314 kJ/(kmol \cdot K)$ – universal gas constant.

3.2 Results of calculation of thermodynamic reaction functions $CO_2 = CO + 0.5 \cdot O_2$

Using numerical thermodynamic data for the pure components involved in the reaction $CO_2 = CO + 0.5 \cdot O_2$ at 298K and $1.013 \cdot 10^5$ Pa (Table 2) and using expressions (2) to (4) and expressions (13) and (14) the values of the thermodynamic functions can be calculated $\Delta H, \Delta S, \Delta G, Kp'$ considered reactions depending on the reaction temperature (Table 3).

In the temperature interval 298K to 2000K thermodynamic functions ΔH and ΔS are positive, so the sign is ΔG determined by the relative ratio of the enthalpy and entropy terms (equation (7)) (Figure 5). It can be seen that in the considered temperature interval (Table 3, Figure 5). This means that the reaction temperature is a crucial factor for the thermodynamic equilibrium of the considered reaction. In the temperature interval 298K to 2000K the free enthalpy of the reaction is greater than zero $\Delta G > 0$ and the equilibrium constant of the reaction under consideration is very small $K_p{}' << 1$, which means that the reaction is shifted towards the reactants of the reaction.

This practically means that the CO2 emitted in the exhaust gases of SUS engines is very stable and affects the greenhouse effect, i.e. in larger quantities it affects the warming of the earth or the earth's atmosphere. Only above 2000K does a slight reduction of CO2 occur and the formation of CO.

Table 3. Thermodynamic reaction functions as a function of temperature.

T (K)	ΔH (kJ)	ΔS (kJ/K)	$T \cdot \Delta S$ (kJ)	ΔG (kJ)	Kp' $(-)$	Kp $(Pa^{1/2})$
298	282990	86.44	25759	257232	$1.40 \cdot 10^{-45}$	$4.46 \cdot 10^{-43}$
400	283546	88.05	35220	248324	$3.72 \cdot 10^{-33}$	$1.18 \cdot 10^{-30}$
600	284558	90.09	54054	230503	$8.55 \cdot 10^{-21}$	$2.72 \cdot 10^{-18}$
800	286254	92.49	73992	212260	$1.38 \cdot 10^{-14}$	$4.40 \cdot 10^{-12}$
1000	289572	96.15	96150	193421	$7.88 \cdot 10^{-11}$	$2.51 \cdot 10^{-8}$
1200	295492	101.47	121740	173689	$2.75 \cdot 10^{-8}$	$8.75 \cdot 10^{-6}$
1400	304835	108.66	152124	152708	$2.00 \cdot 10^{-6}$	$6.38 \cdot 10^{-4}$
1600	318658	117.85	188560	130090	$5.66 \cdot 10^{-5}$	$1.80 \cdot 10^{-2}$
1800	337864	129.13	232434	105428	$8.72 \cdot 10^{-4}$	0.28
2000	363390	142.55	285100	78296	$9.02 \cdot 10^{-3}$	2.87
2273	410136	164.38	373636	36493	0.14	46.15

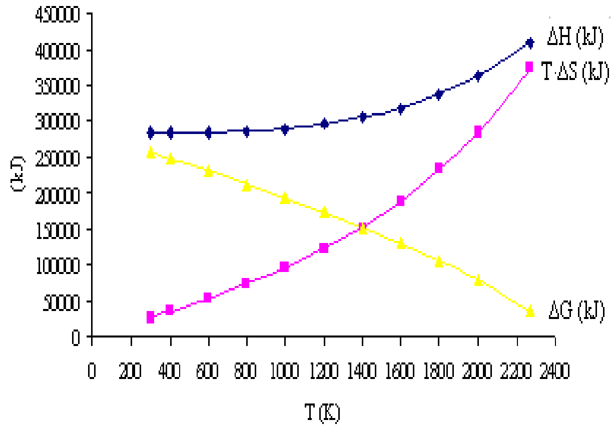

Figure 5. *Thermodynamic reaction functions* $CO_2 = CO + 0.5 \cdot O_2$ *from the temperature*

4. CONCLISION

The paper presents the basic properties of gaseous combustion products (CO_2, CO, NOx, SOx, NH_3, etc.) in internal combustion engines (SUS engines) and their harmful impact on the environment.
The ELVs of individual harmful substances emitted by each SUS engine are presented.
It was noted that additional reduction of NOx emissions requires the introduction of Euro 5 and Euro 6 fuels. Introducing this fuel as a quality standard also has a positive effect on the reduction of CO emissions in the exhaust gases of SUS engines.

Special attention is paid to the formation of CO_2 and CO, i.e. the kinetics of the reaction as dominant gases in the exhaust gases of SUS engines.
At an ambient temperature of 298K, the considered reaction is endothermic and the equilibrium constant at normal pressure (1.013·105Pa) is much less than one, which means that the reaction equilibrium is shifted to the left, i.e. in the direction of the reactant CO2.
This practically means that the CO_2 formed in the exhaust gases remains stable and as a greenhouse gas has an impact on the "greenhouse" effect. Only at significantly high temperatures, higher than 2000K, does a slow formation of CO and reduction of CO_2 occur.

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