Evaluation and Comparing of the Carbon Dioxide Emission Coefficients for the Combustion of Gaseous and Liquid Hydrocarbons

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Evaluating and comparing the carbon dioxide emission coefficient during fuel combustion is an important topic given the current interest in air quality and environment pollution. For this goal, we collected liquid and gaseous hydrocarbon samples for which we determined the content and caloric power using specialized and authorized laboratories. The computational model for calculating the carbon dioxide emission coefficient has been derived based on mathematical relations selected from relevant literature, and was applied in a number of case studies, based on data from the analysis documents. These results allowed the comparison of complete combustion of some hydrocarbon fluids from the point of view of carbon dioxide emissions.

Keywords: carbon emission, combustion, gaseous and liquid hydrocarbons, caloric power

Economic development and providing thermal comfort for humans, on one hand, and the emission of carbon dioxide following such activities generating pollution of the environment, on the other hand, are two topics of utmost current interest. As a result, various studies have been performed, including: periodical statistical research regarding electrical and thermal energy production, energy resources and consumption, monitoring of carbon dioxide emissions, and their classification according to various criteria [2, 7-9].

Selected data from reports by the National Statistics Institute on the energy balance and the structure of energy utilities suggests that in 2012, compared to 2011, in Romania, the coal-based electrical energy decreased by 4%, the liquid hydrocarbons-based energy decreased by 14.3%, and the gaseous hydrocarbons-based energy increased by 4% [7].

Meanwhile, the proportion of coal consumption in thermo-electrical energy production decreased in 2012 vs 2011 from 58.6% to 56.1%; on the contrary, gaseous hydrocarbons proportion increased from 13.7 to 14.5% in the same period [7].

Monitoring carbon dioxide emissions allowed the calculation of their prevalence in various areas of activity; figures 1 and 2 illustrate these data for the period 2010-2011, in Romania and in the European Union. Note that the largest fraction, both in Romania and in the European Union, is corresponding to the electrical and thermal energy production (48 and 40.2%, respectively) [8].

Figure 3 shows the annual emission of carbon dioxide in Romania in 2010-2011; note the increase in 2011 vs. 2010 [9].

Heat generation through conventional methods is mainly based on the transformation of chemical energy stored in fuels into thermal energy, by combustion. Fuel combustion is the rapid oxidation of a material in the presence of oxygen, accompanied by heat and light production.

Fuels are burned substance, developing heat and fuel elements containing carbon, hydrogen and sulfur. A fuel

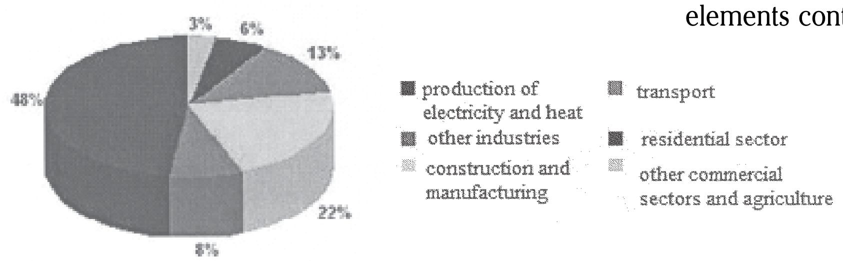

Fig. 1. Proportion of CO_2 emissions by area of activity in Romania (source: International Energy Agency – IEA) [8]

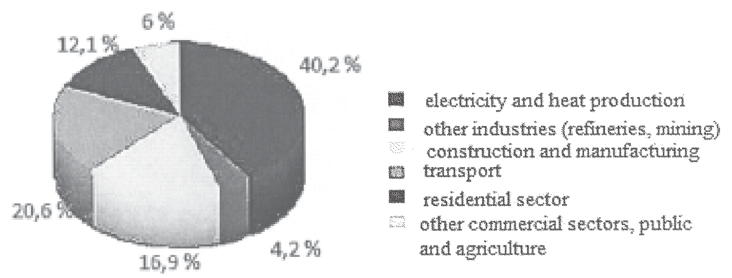

Fig. 2. Proportion of CO_2 emissions by area of activity in EU (source: International Energy Agency –IEA) [8]

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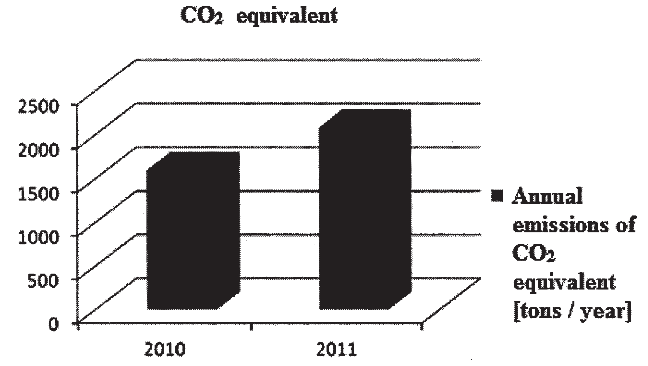

Fig. 3. Change in CO_2 emissions 2010- 2011 [9]

must meet a number of conditions; namely, it needs to be easily accessible from nature, not toxic, cheap and plenty enough so that the cost of heat produced is competitive in the energy market at that time [3].

For solid and liquid fuels, but also for gas, the mass composition is expressed by the equation:

$$g_C + g_H + g_{Sf} + g_O + g_N + g_W + g_M = 1 \quad (1)$$

Gas fuels are frequently characterized by the volumetric composition:

$$\sum_i \left(r_{C_mH_n}\right)_i + r_{CO} + r_{CO_2} + r_{H_2} + r_{H_2S} + r_{O_2} + r_{N_2} + r_W = 1 \quad (2)$$

For liquid petroleum fuels, where the relative density - ρ_{15}^{15} is known, the carbon fraction and the hydrogen fraction can be calculated as [1]:

$$g_C = 0.15\rho_{15}^{15} + 0.74 \ ; \quad g_H = 1 - g_C \quad (3)$$

Another property of fuels is the caloric power: the heat developed by complete combustion of the unit amount of fuel with minimum amount of air. Depending on the state of water aggregation resulting from the combustion we distinguish between:

- superior caloric power H_s, when the water vapour contained in the fuel gases is discharged as a liquid, thus releasing condensation latent heat in the combustion space;
- inferior caloric power H_i, when the fuel gas is removed with the water vapour in the gaseous state.

Although $H_s > H_i$, because liquid water can be combined with some components of the combustion gases resulting in corrosive fluids, it is recommended that the combustion gas containing water vapour be discharged; thus from practical point of view H_i is of particular interest. The mathematical relationship between the superior and inferior caloric power is obtained taking into account the heat necessary for vaporization of water in the fuel gases:

$$H_i = H_s - 2510\left(9g_H + g_W\right) \quad (4)$$

For fuel mixtures, the heat output is calculated as:

$$H_{am} = \sum_{i=1}^{n} g_i H_i \quad (5)$$

$$H_{am} = \sum_{i=1}^{n} r_i H_i \quad (6)$$

For liquid petroleum fuels, the caloric power can be calculated using an empirical relationship [1]:

$$H_i = 46\ 434 + 3169\rho_{15}^{15} - 8793\left(\rho_{15}^{15}\right)^2 \quad (7)$$

The application of relations (4), (5) and (7) gives the result expressed in kJ / kg. For gaseous fuels equation (6) should be used, and the caloric power in that case is expressed in kJ/m_N^3 [1, 3, 6].

Combustion calculation is aimed to determine the amount of air needed to carry out the chemical reactions of burning and the mass and volume of flue gas. Apart from some special cases, the oxygen needed for combustion is taken from the atmosphere. Complete combustion results in carbon dioxide, sulfur dioxide, water vapour, nitrogen and oxygen (in the case where more air was introduced than theoretically necessary). No oxygen is present in fuel gases if the theoretically required amount $\alpha = 1$ of air is used. Hydrocarbons contain carbon and their combustion results in carbon dioxide. For a fuel where the mass composition is known, the carbon mass resulting from complete combustion is calculated by the formula:

$$m_{CO_2} = \frac{g_C}{12} M_{CO_2} \quad (8)$$

In (8), the mass of carbon dioxide has the unit kg CO_2 / kg fuel [3].

For hydrocarbon gases where the composition volume is known, the volume of carbon dioxide resulting from complete combustion, expressed in m^3_N CO_2 / m^3_N fuel, is obtained by adding up the volumes of carbon dioxide from the combustion of hydrocarbons and carbon monoxide, plus the volume of carbon dioxide which possibly exists in the original composition of the fuel:

$$V_{CO_2} = \sum \left(m\, r_{CmHn}\right)_i + r_{CO} + r_{CO_2} \quad (9)$$

In this case, the mass of carbon dioxide, expressed in kg CO_2/ m^3_N fuel, is given by [3]:

$$m_{CO_2} = \frac{M_{CO_2}}{22{,}414} \cdot V_{CO_2} \quad (10)$$

Air pollution by carbon dioxide is a major problem that preoccupies our society, since its effects are extremely important for the climate, flora, fauna and human health. In order to compare the effects of combustion polluting, the emission coefficient is used. The emission coefficient is defined as the ratio between the mass of carbon dioxide resulting from the combustion and the superior or inferior caloric power of the fluid. Therefore:

$$\varepsilon_{CO_2} = \frac{m_{CO_2}}{H} \quad (11)$$

The emission of carbon dioxide ε_{CO2} is expressed in g/ kWh. Depending on whether reporting is done using superior or inferior caloric power, this is denoted as $\varepsilon_{CO2,S}$ or $\varepsilon_{CO2,I}$.

For calculation of the emission of carbon dioxide in the case of combustion of liquid petroleum fuels, when they are composed of only carbon and hydrogen, based by relations (3), (4), (7), (8) and (11), the following original relations have been proposed [4, 5]:

- the emission of CO_2, relative to the inferior caloric value:

$$\varepsilon_{CO_2,I} = \frac{2714 + 550\rho_{15}^{15}}{12.898 + 0.88\rho_{15}^{15} - 2.442\left(\rho_{15}^{15}\right)^2} \quad (12)$$

- the emission of CO_2, relative to the superior caloric value, for liquid petroleum fuels containing no water:

$$\varepsilon_{CO_2,S} = \frac{2714 + 550\rho_{15}^{15}}{14.529 - 0.061\rho_{15}^{15} - 2.442\left(\rho_{15}^{15}\right)^2} \quad (13)$$

Experimental part

The research was performed in the following steps:

- establish sampling points;
- sampling;
- analysis of samples in an authorized laboratory;
- selecting the necessary properties of hydrocarbon fluids for evaluating the carbon dioxide emission coefficient.

Note that these steps require dedicated exploration costs, time spent on organizing and carrying out the work, qualified staff, specific machines and authorized equipment.

Specialized companies have taken samples of combustible gas mixtures, at different points, the fuel gas supply network in representative areas of Romania. Samples of gas mixtures were analyzed in specialized laboratories and authorized using gas analyzers, type ABB TOTAL FLOW 8206. According to chromatography analysis reports, the volumetric composition of mixtures of hydrocarbon gases used for combustion is shown in table 1. Samples whose volumetric composition is shown in table 1, are denoted AG1 ... AG5. Samples AG1 ... AG5 are taken from different areas of Romania.

AG1 ...AG 4 gas mixtures are gases traded in the country.

Crude oil extracted from the reservoir contains a liquid fraction, crude oil, and a gas fraction, associated gas. AG 5 corresponds to a gas mixture composition – so called "associated gas".

Associated gases are also traded in Romanian market.

Table 2 contains values of the relative density of marketed petroleum products. The data in this table are taken from analysis reports, bulletins of gas chromatography, or safety data sheets of supply and distribution firms.

Results and discussions

We used the mentioned relationships to assess the emission of carbon dioxide when burning liquid hydrocarbons.

Of course, there is the relation $\varepsilon_{CO2,S} < \varepsilon_{CO2,I}$ between the coefficients of carbon dioxide emission, relative to the superior and inferior caloric power.

Table 1
VOLUMETRIC COMPOSITION OF SOME GASEOUS HYDROCARBON MIXTURES

Volumetric fraction of component *i*, r_i, %	**AG 1**	**AG 2**	**AG 3**	**AG 4**	**AG 5**
Methane, CH_4	99.23	98.3037	98.9838	99.12	75.00
Ethane, C_2H_6	0.146	0.6133	0.3244	0.32	9.24
Propane, C_3H_8	0.019	0.3124	0.1241	0.10	6.23
i-Butane, *i*-C_4H_{10}	0.006	0.0392	0.0311	0.02	3.46
n-Butane, *n*-C_4H_{10}	0.003	0.0126	-	0.01	-
i-Pentane, *i*- C_5H_{12}	0.002	-	0.0158	0.02	1.10
n- Pentane, *n*- C_5H_{12}	0.001	-	-	0.01	
Hexanes, C_6H_{14}	0.002	0,0019	0.0057	0.02	1.77
Heptanes, C_7H_{16}	0.001	-	0.0117	0.04	-
n- Octanes, *n*- C_8H_{18} and C_{9+} fraction	0.002	-	0.0043	-	-
Nitrogen, N_2	0.522	0.6445	0.1832	0.16	-
Oxygen, O_2	0.001	-	-	-	-
Carbon dioxide, CO_2	0.065	0.0724	0.3159	0.18	3.20

Table 2
VALUES OF RELATIVE DENSITY OF PETROLEUM PRODUCTS AVAILABLE

Oil product	**Relative density, ρ_{15}^{15}**
Liquefied petroleum gases (GPL auto)	0.506...0.55
Liquefied petroleum gases	0.571...0.572
Efix gasoline	0.7497
Euro plus gasoline unleaded	Min 0.720; max 0.775; fixed value 0.7494
Efix diesel fuel	0,8409
Euro 5 diesel fuel	Min 0.820; max 0.845; fixed value 0.8398

Compound	AG 1	AG 2	AG 3	AG 4	AG 5
Carbon dioxide volume from complete combustion V_{CO_2}, [m^3_N CO_2 / m^3_N comb.]	0.9966	1.007585	1.004947	1.0091	1.4513
Carbon dioxide mass m_{CO_2}, [kg CO_2/m^3_N comb]	1.94851	1.977983	1.97277	1.9809266	2.849
Inferior caloric power, H_i [kJ /m^3_N]	35 765	36 676	35 815	36 012	47 253
Superior caloric power, H_s [kJ /m^3_N]	39 778	40 778	37 890	40 044	51 734
Carbon dioxide emission coefficient, $\varepsilon_{CO_2,I}$, [g/kWh]	196.13	198.82	198.296	198.02	217.05
Carbon dioxide emission coefficient, $\varepsilon_{CO_2,S}$, [g/kWh]	176.345	174.622	187.44	178.09	198.26

Table 3
RESULTS OF COMBUSTION CALCULATION IN THE CASE OF SAME HYDROCARBON MIXTURES

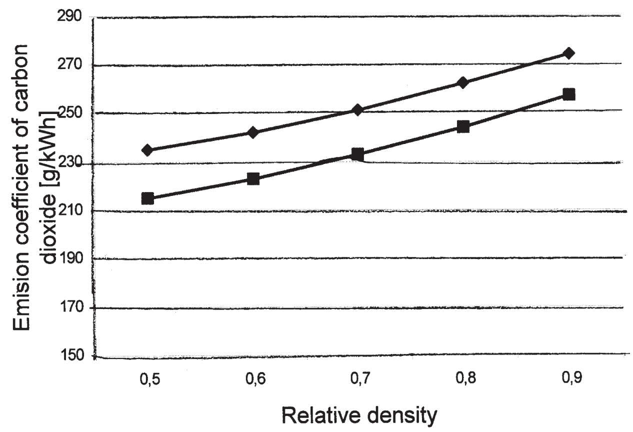

Fig. 4. Variation coefficient of carbon dioxide emission depending on the relative density of the liquid hydrocarbons

To calculate the combustion parameters for gaseous hydrocarbon mixtures we used the volumetric composition from the chromatography analysis of samples (table 1), applied to (6, 9-11). The results obtained are reported in table 3.

Methane combustion has an associated coefficient of carbon dioxide emission of $\varepsilon_{CO2,I}$ = 198 g CO_2/ kWh and $\varepsilon_{CO2,S}$ =178 g CO_2/ kWh, when using the inferior and respectively the superior caloric power.

Table 3 shows that the values of coefficients of carbon dioxide emission corresponding to gas mixtures AG1… AG4 have values similar to pure methane combustion, which is normal since the volume fraction thereof is very high.

For associated gas AG5, having a lower methane content, these coefficients have higher values.

For liquid petroleum fuels, the relative density is known ρ^{15}_{15}, thus the coefficients of carbon dioxide emissions $\varepsilon_{CO2,I}$ and $\varepsilon_{CO2,S}$ are computed using (12) and (13).

The results were plotted curves of figure 4, which shows the variation of the coefficients of carbon dioxide emission, ε_{CO2},I and ε_{CO2},s, depending on the relative density of the liquid hydrocarbon; it is found that the emission of carbon dioxide increases, when the relative density of liquid petroleum products increases.

The carbon dioxide emission coefficients are $\varepsilon_{CO2,I}$ = 233 g/kWh and $\varepsilon_{CO2,S}$ = 214 g/kWh for propane, and $\varepsilon_{CO2,I}$ ≈ 240 g/kWh and $\varepsilon_{CO2,S}$ ≈ 221 g/kWh for butane.

As a result, the coefficients of carbon dioxide emissions, when burning liquefied petroleum gas (which is a mixture with different composition of propane and butane), relationships are valid 233 < $\varepsilon_{CO2,I}$ < 240 g/kWh, or 214 < $\varepsilon_{CO2,S}$ < 221 g/kWh.

According to analysis of newsletters from companies supplying liquid petroleum products or from distribution stations (table 2), if the relative density values correspond to gasoline, then the emission factors of carbon dioxide are distributed in the ranges according to data from figure 4: $\varepsilon_{CO2,I}$= 242...251 g/kWh and $\varepsilon_{CO2,S}$ =233...244 g/kWh (fig. 4).

For Diesel fuel, the corresponding values are $\varepsilon_{CO2,I}$ = 262...274 g/kWh and $\varepsilon_{CO2,S}$ = 244...257 g/kWh.

Figure 4 indicates that the carbon dioxide emission increases when the relative density of liquid products increases.

Liquefied petroleum gases have emission coefficients smaller than gasoline and Diesel fuel, which recommends their use as combustion fuel. Moreover, these fuels are currently cheaper than gasoline.

Analysis of carbon dioxide emission from combustion of hydrocarbon fluids will lead to:

$$\varepsilon_{CO_2,I,AG1...AG4} < \varepsilon_{CO_2,I,AG5} < \varepsilon_{CO_2,I,LPG} < \varepsilon_{CO_2,I,Gasoline} < \varepsilon_{CO_2,I,Diesel}$$

Carbon dioxide emission analysis results in the conclusion that the smallest values are for methane and gaseous mixtures corresponding to natural gases (gas mixtures AG1…AG4).

Data from S.C. Enel Energie Muntenia S.A, provided July 2013, indicates the emission of CO_2 in Romania, in 2012, is 408.67 g/kWh, which means that using gaseous and liquid hydrocarbons will result in decreased pollution [10].

Conclusions

The research conducted in this work used data on hydrocarbons fluids commonly used in combustion processes. Specialized companies have taken samples of combustible gas mixtures, at different points, the fuel gas supply network in representative areas of Romania. The data about the petroleum products are taken from analysis reports, bulletins of gas chromatography, or safety data sheets of supply and distribution firms.

Qualitatively, the evaluation of the coefficient of carbon dioxide emission provides a fuel selection criterion. For example, the choice of gasoline, which has the lower relative density is less polluting.

Quantitatively, knowing the amount of carbon dioxide emitted from burning a fuel allows finding the polluting effects of their use. Therefore, to minimize the pollution zone, might resort to appropriate local solutions, although possibly they are more expensive.

In determining the cost or purchase a fuel selection criteria could be emission of carbon dioxide.

The original relations presented, based on mathematical relationships taken from specific publications, for the evaluation of carbon dioxide emission coefficients in the case of liquid petroleum fuels, provides a rapid way of evaluating the effects of pollution when burning these fuels.

The combustion of hydrocarbon fluids and especially those gaseous would lead to a decrease environmental pollution because emission factors of carbon dioxide are lower than those reported currently in Romania.

Nomenclature

g_i - Mass fraction of component *i* in a gas mixture, [kg component *i*/kg fuel]
H - Caloric power, H, [kJ /m^3_N]
M - Molar mass, [kg/kmol]
m - Mass, [kg]
r_i - Volumetric fraction of component *i* in a gas mixture, [m^3_N component *i*/m^3_N fuel]
V - Volume, [m^3]
ε_{CO2} - Carbon dioxide emissions, [g/kWh]
ρ - Density, [kg/m^3]
ρ_{15}^{15} - Relative density (the density of the liquid petroleum fuels relative to the water, at 15 ^{0}C)

Subscript

C – Carbon
CO_2 - Carbon dioxide
H - Hydrogen
I - Inferior
M - Ballast, solid substance which does not burn
N - Nitrogen
O - Oxygen
S_f - Sulfur
S - Superior
W - Water

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