The issue of environmental protection focuses on preventing and reducing pollution phenomena caused by those human activities inducing negative effects such as global warming and the greenhouse effect. The energy sector has the greatest contribution to these phenomena in terms of greenhouse gases emissions.

The paper proposes an application in the energy sector for assessing CO2 emissions resulted from burning classic solid fuels and alternative and biomass fuels at a Combined Heat and Power (CHP) using two methods, either by calculations based upon data obtained from analytical laboratory investigations or by direct measurement at the source.

The investigations were carried out to highlight the influence of the addition of biomass (sawdust) to conventional solid fuel (lignite) for reducing CO2 emissions, recovering unburned carbon content present in the slag, improving the lignite energy properties, in order to use the biomass and slag waste and reduce the CO2 emissions.

Problema protecției mediului se concentrează pe prevenirea și combaterea fenomenelor de poluare provocate de unele activități umane, cum sunt cele privind încălzirea globală și efectul de seră. Sectorul energetic are cea mai mare contribuție în ceea ce privește emisiile de gaze cu efect de seră.

Lucrarea își propune o aplicație în domeniul energetic pentru evaluarea emisiilor de CO2 rezultate la arderea combustibililor solizi clasici și alternativi cu biomasă, la o Centrală Electrică de Termoficare (CET), prin două metode, atât prin calcul utilizând datele obținute în urma investigațiilor analitice de laborator, cât și prin măsurare directă la sursă.

Investigațiile au fost efectuate pentru a evidenția influența adăosului de biomasă (rumeguș) la combustibilul solid clasic (lignit) pentru reducerea emisiilor de CO2, recuperarea conținutului de carbon nears prezent în zgură, îmbunătățirea proprietăților energetice ale lignitului, toate în scopul valorificării deșeurilor de biomasă și de zgură și a reducerii emisiilor de CO2.

**Keywords:** energy sector, coal, biomass, waste, carbon, CO2 emissions

1. Introduction

The phenomenon of climate change is a direct consequence of the increase of greenhouse gases - particularly CO2 – contained into the atmosphere. In the energy sector burning fossil fuels - coal, oil, natural gas - generates significant amounts of CO2. From this point of view, the solutions to reduce the greenhouse gases emissions are: decreasing fossil fuel consumption and at the same time promoting renewable energy sources that are clean, whose use would limit the emission of gases that cause the greenhouse effect [1].

In order to fulfill the commitments assumed by the Kyoto Protocol, Romania has adopted a strategy of exploiting sustainable, renewable energy resources – these resources will be promoted and their contribution will increase up to 11.2% in 2015 [2]. The European Commission encourages the use of renewable resources for electricity generation, aiming to reduce the dependence on oil and coal, and also to reduce the greenhouse gases emissions, in particular CO2 emissions. The biomass is one of the renewable resources with zero CO2 contribution (because when it is formed it absorbs CO2 from the atmosphere). This has always been a major source of energy worldwide, since the beginning of civilization. In developing countries and in rural areas, the biomass resulted from wood and agriculture, still represent a significant proportion of the materials used for heating.

The substitution of the traditional fuel with an alternative one in industrial installations leads to important changes in the combustion, heat consumption, thermal efficiency and the emission of CO2. Such examples are furnished by recent research carried out in the cement industry [3-5].

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Monitoring and reporting the CO₂ emissions, in the case analyzed in this paper, can be done using one of the following methods [6-8]:
- The calculation method determining the emissions resulted from technological flows, based upon the operating data obtained with measurement systems and additional parameters resulted from laboratory analysis.
- Method of measuring the emissions using direct measurement of the CO₂ concentration and residual gas flow.

This paper presents two methods:

- **the calculation method** it based on determining in laboratory the physico-chemical and energy characteristics of the solid fuels used in the installation, namely: technical analysis (moisture and ash), elemental analysis (C, H, S, N) and determining the low and upper calorific value. Based on the data obtained from laboratory investigations we calculate the *emission factor*, EF and oxidation factor, FO, and then the emission of CO₂, E_{CO₂}, with the relationship:

\[
E_{CO₂} = \text{operating data } \times EF \times FO \quad [t]
\]  

- **the direct measurement method** which consists in the analysis of flue gases at the emission source, by a gas analyzer equipped with a special IR cell for measuring the CO₂ emissions, CO₂ measured, in kg/Nm³, and determining of the total flue gas flow, Q_{total f.g.}, in Nm³, related to the combustion installation. By applying the relationship below we directly obtain the emission of CO₂, E_{CO₂}:

\[
E_{CO₂} = \text{CO₂ measured } \times Q_{total f.g.} \times 10^{-3} \quad [t]
\]

### 2. The experimental method

The experiments that led to this research address the following issues:
- the influence of biomass in the solid fuel (lignite) mixture and implicitly the reduction of CO₂ emissions;
- verifying the possibility of re-using in the technological process the waste slag at the bottom of the furnace resulting from the combustion process in admixture with the biomass;
- evaluating the content of CO₂ by calculation and direct measurement on an energy installation for the selected fuel mixtures.

The work includes laboratory experiments as well as an application on monitoring the CO₂ content by calculation and direct measurement at an industrial facility in the energy field (case study).

The samples used in laboratory experiments, agreed with representatives of Combined Heat and Power, are presented in Table 1.

The samples were put to solid fuels specific tests: soaked humidity (W_s); hygroscopic humidity (W_h); total humidity (W_t), ash (A), elemental analysis (carbon-C, hydrogen-H, sulfur-S, nitrogen-N, oxygen-O) as well as determining the calorific value: upper (Q_s) and lower (Q_l).

In order to determine the elemental analysis (C, H, S, N) a Thermo Fisher Scientific Elemental Analyzer – EA Fleash 1112 was used and the calorific value was determined using a Parr bomb calorimeter 6200. The presented analyses were conducted in compliance with existing national and international standards [9-14].

The analytical results for the tested samples were recalculated for the initial fuel state (assigning to it the index i) in accordance with standard STAS 398-82 [15].

The case study on CO₂ monitoring was done by comparative analysis (calculation and direct measurement) to a unit representing a Combined Heat and Power Plant (CHP).

The installation can operate, in terms of fuel supply, both on coal and coal in addition to renewable energy sources (biomass / sawdust).

Measurements were performed at the chimney stack of a boiler of 420 t/h steam (installation category B / IMA 1) [8].

For calculating the oxidation factor, the emission factor and evaluating the CO₂ emissions a set of 6 separate samples of solid fuel mixed with biomass and waste samples of technological nature.

### Table 1

<table>
<thead>
<tr>
<th>Sample No. Nr. probă</th>
<th>Analyzed sample Proba analizată</th>
<th>Sample No. Nr. probă</th>
<th>Analyzed sample Proba analizată</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Coal (lignite)</td>
<td>6</td>
<td>Coal + 10% Biomass</td>
</tr>
<tr>
<td></td>
<td>Cârbune (lignite) – C</td>
<td></td>
<td>Cârbune + 10% Biomasă – CB2</td>
</tr>
<tr>
<td>2</td>
<td>Biomass (sawdust)</td>
<td>7</td>
<td>Coal + 17% Biomass</td>
</tr>
<tr>
<td></td>
<td>Biomasă (Rumeguș) – B</td>
<td></td>
<td>Cârbune + 17% Biomasă – CB3</td>
</tr>
<tr>
<td>3</td>
<td>Slag Zgură – Z</td>
<td>8</td>
<td>Slag + 33% Biomass</td>
</tr>
<tr>
<td>4</td>
<td>Ash Zăluș – K</td>
<td>9</td>
<td>Slag + 40% Biomass</td>
</tr>
<tr>
<td>5</td>
<td>Coal + 5% Biomass</td>
<td>10</td>
<td>Slag + 60% Biomass</td>
</tr>
<tr>
<td></td>
<td>Cârbune + 5% Biomasă – CB1</td>
<td></td>
<td>Zgură + 40% Biomasă – ZB3</td>
</tr>
</tbody>
</table>
side burning (slag and ash) were taken over a period of 24 hours. In parallel, there were six direct measurements of CO₂ emissions at the chimney stack.

The amount of solid fuel used at the moment of measurement was 2859.44 t / day. According to current standards [16,17], the concentration of CO₂ at source (chimney stack) was measured with one analyzer Testo 350 XL, a special cell equipped with infrared. For the other gases the equipment uses electrochemical cells, specific for each gas.

3. Results and discussion

The laboratory experiments show the effects of the addition of biomass in the mixture of solid fuel (lignite) and slag sample.

The analytical results obtained on the examined samples are shown in Table 2. In addition, coal - C is specified, and the emission factor, EF, in t CO₂/TJ, calculated with the relationship:

\[ \text{EF} = \left[ \left( \frac{M_{\text{CO}_2}}{M_c} \right) \times \frac{(C/100)}{10^6/Q_i} \right] \]

where: \( M_{\text{CO}_2} \) - molecular weight CO₂; \( M_c \) - atomic weight of carbon.

For mixtures of coal and biomass (CB1, CB2, CB3) the emission factor was calculated according to the proportion of coal and taking into account that the biomass had a 0 value for it [8].

Based on the analyzed main key indicators, for the sample - CB3 (coal + 17% biomass) compared to the tested coal sample, (C), considered as standard, the following results were obtained:

- the carbon content increases with approx. 3%;
- the percentage of ash decreases with approx. 4%;
- the low caloric value increases with approx. 200 kJ / kg;
- the amount of CO₂ emissions factor decreases in proportion to the biomass percentage.

Thus, using a mixture of biomass and lower quality fuel leads to the increase quality of the raw material used in the energy sector.

For the samples of slag mixed with biomass, ZB1, ZB2 and ZB3, it was found that in the presence of biomass the unburned carbon in the slag sample can be recovered (Z), and the lower caloric power of the slag increases from 4127 kJ/kg to 6828 kJ/kg. Unfortunately, the obtained lower caloric value is still too low to allow the use within the combustion installation of only the slag + biomass mixture and, consequently, at the request of the end user, the tests involving these mixtures were abandoned.

Based on laboratory results, the beneficiary finally decided that the experiments would use only a mixture of coal and 17% biomass, CB3 mixture.

**Case study**

In the case study we presented the results obtained by the two methods of assessing CO₂ emission mentioned above, for the mixture of coal with 17% biomass, CB3, which gave the best results.

3.1. Based calculation method

Table 3 presents the technical and elemental analysis for the 6 samples taken within 24 hours of operation in the CHP, for solid fuel CB3.
Mixed fuel samples were subjected to laboratory tests in order to determine the indicators presented in Table 3; in addition to the total carbon content (C_t) and the organic carbon content (C_o) was determined, in accordance with ISO 10694 SR: 1998 [12] used to calculate the emission factor (EF).

Also, six samples were taken from the slag and ash in order to determine the content of unburned carbon in the slag (C_nslg) and, respectively, in the ash (C_nash) for calculating the oxidation factor (FO). The results are shown in Table 4.

Following laboratory analytical investigations, was calculated the oxidation factor, FO, the emission factor, EF, and, respectively, the CO₂ emissions, E_CO₂. The index i represents the recalculation of the fuel for the initial state.

The oxidation factor, FO, was calculated by the relationship:

\[ FO = 1 - \left( \frac{A_i}{C_o^i} \right) \times \left[ 0.2 \times \left( \frac{C_n^i}{100} \right) + 0.8 \times \left( \frac{C_n^i}{100} \right) \right] \]

where: A_i - ash content; C_o^i - organic carbon content; C_n^i - unburned carbon content within the slag; C_n^i - the content of unburned carbon in the ash;

The emission factor, EF was calculated with equation (3), where C_i is replaced C_o^i.

The CO₂ emissions (E_CO₂ in t CO₂) were calculated with the following equation:

\[ E_{CO₂} = M_{fuel} (t) \times Q_i^i (kJ/kg) \times EF (tCO₂/TJ) \times FO \]

where: M_{fuel} - quantity of solid fuel.

Also, these provided information on the CO₂ emissions resulting from the use of natural gas as support for mixed fuel combustion - CB3 (coal + 17% biomass). The amount of CO₂ resulting from the burning of natural gas was: \( E_{CO₂} \) (natural gas) = 135.42 t CO₂.

Applying the calculation method, by making use of relations (3) (4) and (5) were calculated the oxidation factor, FO, the emission factor, EF, and the total CO₂ emission, E_CO₂ for the 6 samples of mixed fuel. The obtained values for CO₂ emission were shown in Table 5 (referring to 24 operating hours CHP).
3.2. Measurement based method

In order to measure the concentration of CO₂ in the Combined Heat and Power (CHP) were performed 6 sets of measurements at the chimney stack belonging to the 420 t/h boiler for a period of 24 hours, tests made with a portable flue gas analyzer - TESTO 350 M / XL equipped with a special cell in the IR [9]. The measured values represent average hourly values.

The measurements were performed for the following parameters: temperature, pressure, analysis of O₂ and CO₂. The analysis of gas (O₂, CO₂) was done in accordance with SR ISO 10396: 2008.

The measured values, given in Tables 6 and 7, were recalculated at standard conditions of temperature (273.15 K) and pressure (101 325 Pa).

For evaluating the CO₂ emission for 24 hours, the total flue gas flow, Q_{total f.g.} in Nm³, was calculated with the relationship:

\[ Q_{\text{total f.g.}} = Q_{\text{fuel f.g.}} + Q_{\text{natural gas f.g.}} \]  

where: Q_{fuel f.g.} is the flue gases flow for the solid fuel mixture; Q_{natural gas f.g.} is the flue gas flow for natural gas.

Using the relations presented in [18], taking into account the mass of solid fuel used within 24 hours (2859.44 t), its composition (Table 3) and the excess air ratio, \( \lambda = 1.4 \) the volume of the flue gases resulting from burning solid fuel CB3, \( V_{\text{fuel f.g.}} \) and then \( Q_{\text{fuel f.g.}} \).

The \( Q_{\text{natural gas f.g.}} \) was calculated according to [18], depending on the mass of natural gas burned in 24 hours (72.82 t) and the excess air ratio, \( \lambda = 1.17 \).

The values obtained for flue gas flows are shown in Table 8.

---

### Table 6

<table>
<thead>
<tr>
<th>Sample Proba</th>
<th>Gas temperature Temperatură gaze [°C]</th>
<th>Environment temperature Temperatură ambientă [°C]</th>
<th>Absolute pressure Presiune absolută [Mbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>158.7</td>
<td>431.7</td>
<td>274.8</td>
</tr>
<tr>
<td>2</td>
<td>158.8</td>
<td>431.8</td>
<td>275.7</td>
</tr>
<tr>
<td>3</td>
<td>158.8</td>
<td>431.8</td>
<td>275.6</td>
</tr>
<tr>
<td>4</td>
<td>158.9</td>
<td>431.9</td>
<td>276.5</td>
</tr>
<tr>
<td>5</td>
<td>158.8</td>
<td>431.8</td>
<td>275.6</td>
</tr>
<tr>
<td>6</td>
<td>158.9</td>
<td>431.9</td>
<td>276.2</td>
</tr>
</tbody>
</table>

### Table 7

<table>
<thead>
<tr>
<th>Sample Proba</th>
<th>O₂ [%]</th>
<th>CO₂ [%]</th>
<th>CO₂ [ppm]</th>
<th>CO₂ [mg/Nm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.99</td>
<td>7.96</td>
<td>79600</td>
<td>156016</td>
</tr>
<tr>
<td>2</td>
<td>13.05</td>
<td>7.89</td>
<td>78900</td>
<td>154644</td>
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<tr>
<td>3</td>
<td>13.29</td>
<td>7.80</td>
<td>78000</td>
<td>152880</td>
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<tr>
<td>4</td>
<td>13.1</td>
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<td>78100</td>
<td>153076</td>
</tr>
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<td>5</td>
<td>13.11</td>
<td>7.79</td>
<td>77900</td>
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</tr>
<tr>
<td>6</td>
<td>13.11</td>
<td>7.81</td>
<td>78100</td>
<td>153076</td>
</tr>
</tbody>
</table>

### Table 8

<table>
<thead>
<tr>
<th>Sample Proba</th>
<th>( V_{\text{fuel f.g.}} ) [Nm³/kg]</th>
<th>( Q_{\text{fuel f.g.}} ) [t]</th>
<th>( Q_{\text{natural gas f.g.}} ) [t]</th>
<th>( Q_{\text{total f.g.}} ) [t]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.9609</td>
<td>11325.87</td>
<td>1243.46</td>
<td>12569.33</td>
</tr>
<tr>
<td>2</td>
<td>3.9920</td>
<td>11414.95</td>
<td>1243.46</td>
<td>12658.41</td>
</tr>
<tr>
<td>3</td>
<td>3.9630</td>
<td>11331.87</td>
<td>1243.46</td>
<td>12575.33</td>
</tr>
<tr>
<td>4</td>
<td>3.9838</td>
<td>11391.38</td>
<td>1243.46</td>
<td>12634.84</td>
</tr>
<tr>
<td>5</td>
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<td>11416.18</td>
<td>1243.46</td>
<td>12659.64</td>
</tr>
<tr>
<td>6</td>
<td>3.9513</td>
<td>11298.41</td>
<td>1243.46</td>
<td>12541.87</td>
</tr>
</tbody>
</table>
The total emission of CO₂ was then calculated by the relation (2). In this way we could assess the total emissions of CO₂, \( E_{CO_2\ total} \), by direct measurement method at the chimney stack.

The final results of the measurements are shown in Table 9. (The obtained values for CO₂ emission refer to 24 operating hours CHP).

By comparing the results of the two methods presented in Tables 5 and 9, the values obtained by the calculation method are on average approx. 4.2% higher than those obtained by the method of direct measurement, probably due to measurement accuracy and difficult conditions. The differences are within the uncertainty margin of maximum 5%, respecting the conditions set forth in Annex VIII of [8].

The proximity of these values allows us to apply the described methodology in this case study, and any other combustion plant which needs to be analyzed.

Therefore, for a given combustion plant (CHP) and a certain type of fuel used, after the actual measurements of CO₂ within the flue gases and comparing them with the values obtained by calculating CO₂ emissions, forecast values of these emissions can be established, without the need to make any more costly and difficult measurements.

4. Conclusions

- By adding 17% biomass to the solid fuel coal (lignite), we obtained the following results:
  - the carbon content increases by approx. 3% compared to the sample of carbon (C);
  - the ash percentage decreases with about 4%;
  - the low calorific value increases with approx. 200 kJ / kg;
  - the amount of the CO₂ emission factor decreases according to the biomass percentage.
- The obtained results showed that by using biomass mixed with slag, its unburned carbon content is recovered, which further leads to an increase of the low calorific value and thus allows the reuse of slag waste within the technological circuit in the combustion plant;
- By using biomass or coal mixed with slag, the quantity of classic solid fuels used is reduced, the energy properties of classical solid fuels are improved and biomass and slag waste are recovered;
- The tests presented in this paper have shown that the use of biomass yield a decrease in the oxidation factor, the emission factor and also a reduction in CO₂ emissions;
- The CO₂ emission factor can be evaluated both by calculation based methodology and through direct measurement method;
- The research carried out showed that both methods can be used to monitor CO₂ emissions, the obtained results being comparable, the differences are within the margin of uncertainty of maximum 5%, according to the conditions set forth in Annex VIII of Regulation 601/2012.
- Based on this case study, for a given combustion plant (CHP) and for a certain type of fuel used, after the actual measurements of CO₂ from flue gases and by comparing them with the values obtained by calculating the CO₂ emissions forecast values such emissions can be determined, without needing to make actual measurements, which are costly and difficult.

REFERENCES

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14. SR ISO 10396:2008 – Emissions from fixed sources. Sampling for the determination of automatic gas concentrations. \( \text{O}_2, \text{CO}_2, \text{CO}, \text{SO}_2, \text{NO}, \text{NO}_2, \text{NO}_x \). (in Romanian).

The BMC is a tri-annual symposium focusing on the research, development and application of different composite materials with matrices behaving as brittle under normal or special conditions. The present Symposium follows the series of highly successful meetings which originated with EUROMECH 204 Colloquium on Brittle Matrix Composites held in Jablonna, Poland, in November 1985. This meeting was later renamed BMC 1. The Second Symposium (BMC 2) was held in Czedyna, Poland, in September 1988. Starting with the 1991 meeting (BMC 3) all subsequent BMC Symposia were held every three years in Warsaw, Poland.

The Symposium will be held in the Staszic Palace located in the center of Warsaw. The sessions will take place in the Mirror Hall, located on the 1st floor of the building.

Symposium topics are concentrated at problems related to three groups of composites:
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- Ceramic based materials
- High strength composites

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