

## ANALYTICAL INVESTIGATIONS ON CHOPPED WASTE OF BIOMASS AND SLAG RECYCLING FROM THE ENERGETIC DOMAIN

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### **Abstract:**

In an economy increasingly globalized a country's energy strategy is done in the context of changes and developments taking place worldwide. Due to increasing energy demand, energy has developed rapidly without the problem of environmental protection. Total energy demand in 2030 will be around 50% higher than in 2003. The current world energy situation compel mankind to find new energy sources in order to replace fossil fuels currently used widely. It is considered that in perspective, energy from biomass will be ranked second only to energy from fossil fuels [1].

Special attention was given to recovery of the waste and biomass burning from the perspective of preserving natural resources and reduce the amount of waste generated [2]. The quality criteria for the recovery of waste are usually connected to the structural properties of the residue and the content of hazardous substances and the amount of unburned fuel or the solubility of heavy metals, etc.. [3]

This paper presents the results of same laboratory tests on different samples of coal and waste mixed blends of biomass and small clay.

Test samples were subjected to specific laboratory solid (moisture, ash, elemental analysis, calorific value) necessary for evaluating and reporting CO<sub>2</sub> emissions in accordance with the law [4]

Analytical investigations were performed to highlight the following aspects:

- The influence of biomass present in the fuel mix to reduce CO<sub>2</sub> emissions, [2]
- The use of biomass mixed with slag often recover unburned carbon content in the process of energy production, [2]
- The influence of carbon (total carbon, organic carbon) in calculating CO<sub>2</sub> emissions [4].

Following laboratory tests found a better relationship between organic carbon (TOC) and CO<sub>2</sub> emissions than total carbon that is present in fuel [4].

**Keywords:** recovery, recycling, waste, biomass, slag

## **1. INTRODUCTION**

In an economy increasingly globalized a country's energy strategy is done in the context of changes and developments taking place worldwide. Due to increasing energy demand, energy has developed rapidly without the problem of environmental protection. Total energy demand in 2030 will be around 50% higher than in 2003. At EU level, it was found that the largest amount of CO<sub>2</sub> emissions results from the production of electricity and heat. [1]. Coal-based energy production in the EU has generated approximately 950 million tons of CO<sub>2</sub> emissions in 2005, representing 24% of the total EU CO<sub>2</sub> emissions. With regard to Romania, a CO<sub>2</sub> emission from different sectors of activity also highlights the major contribution of the energy sectors transport and which means that these are areas in which implementation measures and various actions to reduce CO<sub>2</sub> emissions are necessary [1].

European signatory countries (including Romania) have committed to reduce CO<sub>2</sub> emissions (responsible for the greenhouse effect) by 8% during 2008-2012. The alternative is the development and wide application of technologies based on renewable energy sources to reduce dependence on fossil that resources. The difference between fossil fuels and renewable energy sources is that the last ones are available locally. These sources can be grouped into the following categories: sun, wind, water, geothermal and biomass energy. It is believed that in the future, energy from biomass will take the second place after the energy from the combustion of fossil fuels [2]. In order to meet the commitments under the Kyoto Protocol Romania has adopted the strategy of turning to renewable energy and the use of renewable energy potential that will have increase and to go up to 11.2 % in 2015

Special attention was given to small capitalization waste from biomass burning and natural resource conservation in light of fossil fuels and reducing the amount of waste generated [3]. The quality criteria for recovery of waste is usually related to structural properties of the residue, the content of hazardous substances and the amount of unburned fuel or the solubility of heavy metals etc. [5]

## **2. EXPERIMENTAL PART**

Experiments that led to the elaboration of the work deals with two aspects: reuse of small waste (slag) in the technological process; turning waste biomass (sawdust)

There were analyzed various samples of coal, biomass, biomass mixed with coal, ash and slag, slag mixture of biomass used in various industrial units of energy (CET GOVORA, CET Iasi, Thermo ROMAG Tr Severin; CET Bacau, etc.). The samples of evidence used in the laboratory experiments are presented in Table. 1

**Table. 1 - Samples used for experiments**

Sample	
C1-Coal (lignit)	K2-Ash
C2-Coal (lignit)	K3-Ash
C3-Coal (lignit)	M1-33%B+67%Z
109 B-Biomass	M2-40%B+60%Z
110 B-Biomass	M3-60%B+40%Z
Z2-Slag	CB1-5%B+95%C
Z3-Slag	CB2-10%B+90%C
	CB3-17%B+83%C

The samples were used determination of the following specific analysis for solid fuels:

- Impregnation humidity ( $W_i^i, \%$ ) according to SR 5264:1995
- Hygroscopic humidity ( $W_h^i, \%$ ) according to SR 5264:1995
- Total moisture ( $W_t^i, \%$ ) according to SR 5264:1995
- Ash ( $A_i, \%$ ) according to ISO 1171:2010
- Elemental analysis ( $C_t^i, C_o^i, H^i, S^i, N^i, \%$ ) according to ASTM D 5373:2008, ISO 10694:1998 ISO 351:1996
- Calorific value upper and lower ( $Q_s^i, Q_i^i, \text{kcal/kg; kJ/kg}$ ) according to ISO 1928:2009

Recalculation of analysis results in different states (initial, dry basis) was performed in according to STAS 398/92.

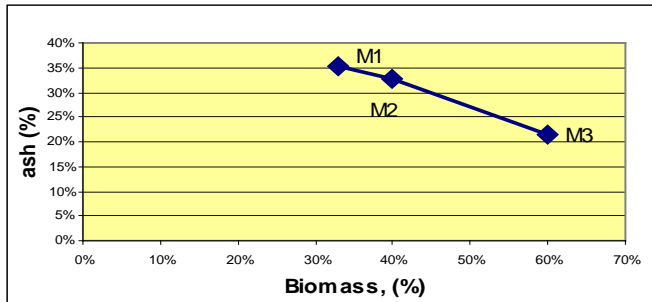
### **3. RESULTS AND DISCUSSION**

Table. 2 contains the results of tests on samples presented in Table 1. Laboratory experiments also show the effects of adding biomass in coal and slag mixture.

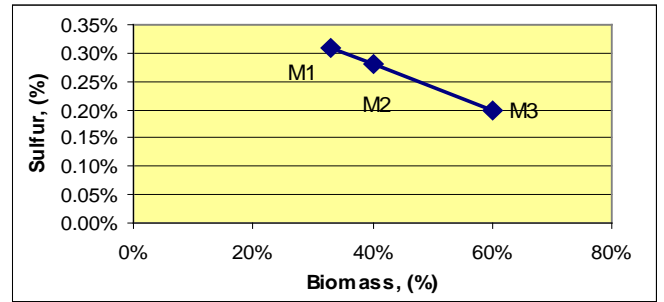
**Table 2- Characterization tests**

Sample	W <sub>i</sub> <sup>i</sup>	W <sub>h</sub> <sup>i</sup>	W <sub>t</sub> <sup>i</sup>	A <sup>i</sup>	S <sub>t</sub> <sup>i</sup>	C <sub>t</sub> <sup>i</sup>	C <sub>o</sub> <sup>i</sup>	H <sup>i</sup>	N <sup>i</sup>	O <sub>s</sub> <sup>i</sup>	Q <sub>i</sub> <sup>i</sup>	Q <sub>i</sub> <sup>i</sup>	TOC <sup>dry</sup>	Fe (C <sub>t</sub> <sup>i</sup> )	Fe (C <sub>o</sub> <sup>i</sup> )
	%									kcal/kg		kJ/kg	%	t CO <sub>2</sub> /TJ	
C1-Coal-lignite	34.44	7.36	41.80	20.56	1.89	22.41	17.06	2.81	0.81	2171	1779	7448	29.31	110	84
C2- Coal-lignite	35.05	7.64	42.69	21.31	1.56	21.79	17.30	2.60	0.69	2141	1754	7346	30.19	109	86
C3- Coal-lignite	34.78	7.39	42.17	21.54	1.58	22.03	17.12	2.60	0.72	2161	1778	7444	29.60	109	84
109B-Biomass	39.00	3.74	42.74	0.61	0.01	30.01	-	3.92	0.09	2927	2471	10346	-		
110B-Biomass	39.07	4.25	43.32	0.54	0.01	29.81	-	3.88	0.10	2915	2458	10291	-		
Z2-Slag	35.71	1.11	36.82	0.00	0.48	9.82	9.08	0.23	0.56	1214	987	4131	14.37		
Z3-Slag	35.54	1.24	36.78	0.00	0.46	9.34	8.95	0.20	0.56	1211	985	4125	14.15		
K2-Ash	0.00	0.68	0.68	0.00	0.00	2.16	0.61	0.00	0.00	-	-	-	0.61		
K3-Ash	0.00	0.53	0.53	0.00	0.00	3.14	0.42	0.00	0.00	-	-	-	0.42		
M1-33% B+67% Z	36.80	2.35	39.15	35.35	0.31	15.50	11.66	1.15	0.50	1471	1182	4947	19.16		
M2-40% B+60% Z	37.03	2.20	39.23	32.83	0.28	17.15	12.58	1.40	0.47	1606	1303	5456	20.69		
M3-60% B+40% Z	37.68	2.41	40.09	21.55	0.20	21.94	16.10	2.93	0.35	2019	1631	6828	26.88		
CB1-5%B+95%C	35.48	8.01	43.49	20.78	1.62	22.13	16.56	2.74	0.75	2145	1746	7312	29.30		
CB2-10%B+90%C	37.63	6.62	44.25	18.82	1.38	22.36	17.20	2.76	0.79	2212	1808	7568	30.84		
CB3-17%B+83%C	37.78	7.72	45.50	17.20	1.23	24.57	18.45	2.81	1.17	2235	1821	7624	33.85		

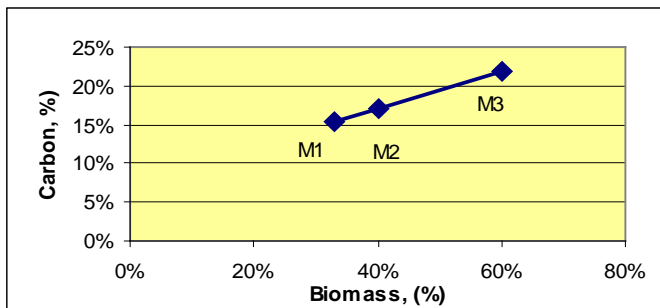
In Figures 1, 2, 3 and 4 is presented the influence of biomass on ash content, sulfur, carbon and lower calorific value for biomass+slag mixture samples (M1, M2, M3)



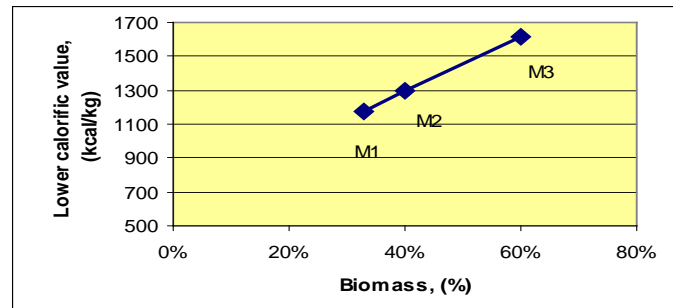
**Figure 1** – Variation of ash content in biomass slag mixture



**Figure 2** - Variation of sulfur content in the mixture of slag with biomass



**Figure 3** - Variation of carbon content in biomass slag mixture



**Figure 4** - Lower calorific variation in biomass slag mixture

From the above chart we can see that the addition of biomass in the clay has the following effects: on one hand the ash and sulfur content decreases and on the other the carbon content and the calorific value increases.

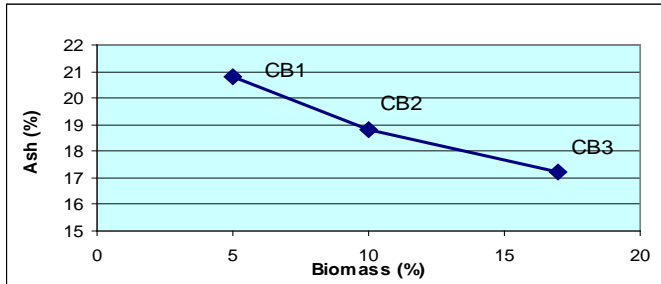
For the samples (M1 and M2) the addition of biomass by 33% and 40% increases the carbon content by 6% in compared with Z2 and Z3 slag samples and the low calorific value is about 1200 kcal/kg. The sulfur content did not suffer significant changes. For the sample M3 the addition of biomass was 60% and a reduction in ash content approx. 10% was achieved in compared with samples M1 and M2, a decrease of 0.15% sulfur content and the lower calorific value significantly improved by about 500 kcal/kg compared to samples M1 and M2 and about 16% compared with samples Z2 and Z3 slag

Burning solid fuels (lignite) is associated with the generation of a variety of residues and by products. According to their source, residues from combustion plant can be divided into waste resulting from the combustion process and waste from the operations and equipments such as coal mills and water treatment units. [3]. In order to be stored the granular waste, must meet the following additional criteria: TOC = max 5% and pH <6. Waste slag and ash waste enter in this category. [4].

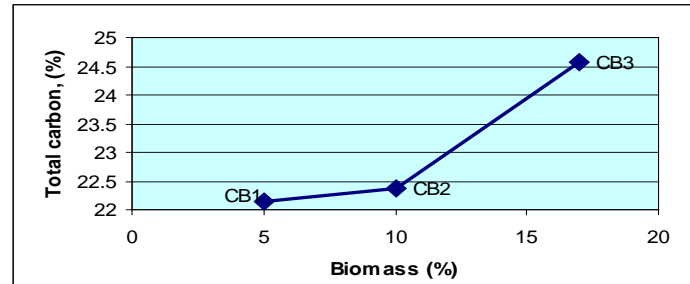
In the experiments were determined both total carbon content and organic carbon content. The test results are presented in Table 2. From the results it is found that samples of slag (Z2, Z3) have organic carbon content (TOC) of about 14% dry basis. This value is unburned carbon slag. The

Samples can be exploited in the process using biomass as filler (M1, M2, M3.) Ash samples (K2, K3) show that carbon content (total and organic) is less than 1% dry basis. The ash waste can be reused/recovered in the production of cement and concrete, as aggregate, asphalt or as a filler in many products, regeneration of mines, etc.

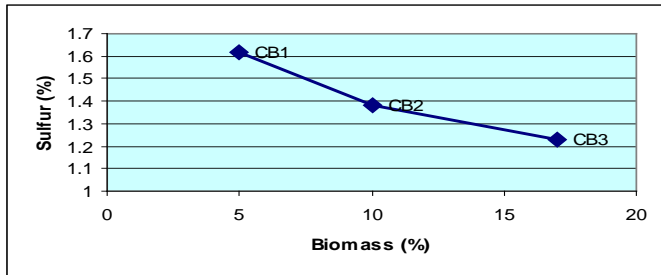
Figures 5, 6, 7, 8 and 9 present the influence of biomass on ash content, sulfur, carbon and lower calorific value of coal mixture samples+biomass (CB1, CB2, CB3).



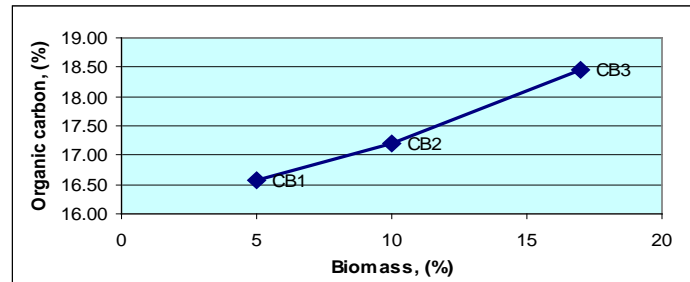
**Figure 5** - Variation in ash content of coal with biomass mixing



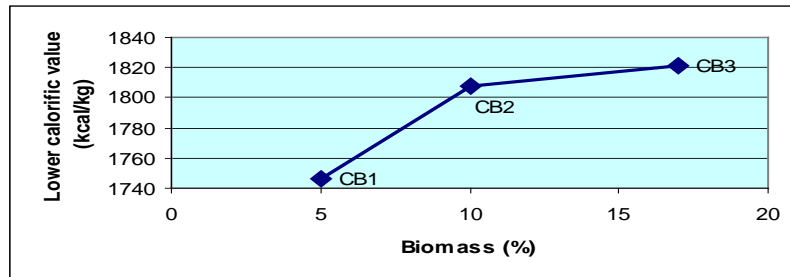
**Figure 6** - Variation in total carbon content of coal with biomass mixing



**Figure 7** - Variation of sulfur content in the mixture of coal with biomass



**Figure 8** - Variation of organic carbon content in the mixture of coal with biomass



**Figure 9** - Variation of the lower calorific in the mixture of coal with biomass

For samples CB1, CB2, CB3 was found that through the addition of biomass, the carbon content and the calorific value increase and in the same time the ash content and the sulfur content reduce. By the addition of biomass in sample CB3, ash content decreases by approx. 4% compared to sample CB1. Carbon content presents an increase of about 2% for CB3 sample where we compared with CB1 sample. Lower calorific value does not suffer major changes (approximately 1800 kcal/kg) due to moisture content.

The addition of biomass in CB1, CB2 and CB3 samples increase the amount of moisture (impregnation and total). An essential condition in order to use biomass as a filler is that moisture content should be between 40 and 60%.

These measures eliminate the possibility of lifting the dust from the transported solid fuel and reduce the possibility of self-ignition. [3]

For the analyzed samples the oxidation factor (fo) were calculated and the emission factor (Fe) both necessary for the assessment of CO<sub>2</sub> emissions. CO<sub>2</sub> emissions were calculated using the following relationship [4]:

$$\text{CO}_2 \text{ emissions} = \text{fuel flow (t)} * \text{net calorific value/net (kJ/kg)} * \text{emission factor (tCO}_2\text{/TJ)} * \text{oxidation factor} \quad (1)$$

The oxidation factor (fo) and the emission factor (Fe) were directly influenced by carbon content and lower calorific value/net. For coal samples C1, C2, C3 were both calculated fo and Fe taking into account the average value of carbon (C<sub>i</sub><sup>i</sup>) in both unburned clay samples Z2 and Z3 and ash samples K2 and K3. The results are presented in Table. 3

**Table 3 - fo and Fe values for samples C1, C2, C3 according to C<sub>i</sub><sup>i</sup> unburned**

Sample	C <sub>i</sub> <sup>i</sup> %	A <sup>i</sup> %	C un slag, %	C un ash, %	fo	Q <sub>s</sub> <sup>i</sup> (kcal/kg)	Q <sub>i</sub> <sup>i</sup> (kJ/kg)	Fe t CO <sub>2</sub> /TJ
C1	22.41	20.56	9.58	2.65	0.9630	1779	7448	110
C2	21.79	21.31	9.58	2.65	0.9605	1754	7344	109
C3	21.03	21.54	9.58	2.65	0.9605	1778	7444	109
Mediate					0.9613			

Table 4 presents the results for fo and Fe taking into account the total organic carbon from the unburned carbon samples (C1, C2, C3) and the average values of organic carbon from slag (Z2, Z3) and ash (K2, K3)

**Table 4 – fo and Fe values for samples C1, C2, C3 according to C<sub>o</sub><sup>i</sup> (TOC)**

Sample	TOC <sup>i</sup> %	A <sup>i</sup> %	TOC un slag, %	TOC un ash, %	fo	Q <sub>s</sub> <sup>i</sup> (kcal/kg)	Q <sub>i</sub> <sup>i</sup> (kJ/kg)	Fe t CO <sub>2</sub> /TJ
C1	17.06	20.56	9.02	0.52	0.9732	1779	7448	84
C2	17.30	21.31	9.02	0.52	0.9727	1754	7344	86
C3	17.12	21.54	9.02	0.52	0.9721	1778	7444	84

The data presented in table no. 3 and 4 reveals the correlation between organic carbon/total and fo/Fe. In table no. 5 and 6 are presented fo and Fe recalculated according to the % biomass for mixtures of slag +biomass (M1, M2, M3) admixtures of coal+biomass (CB1, CB2, CB3). By mixing slag with biomass and coal with biomass, the CO<sub>2</sub> emissions reduce. This is due to the fact that biomass is considered CO<sub>2</sub> neutral Fe = 0 (tCO<sub>2</sub>/TJ). [5]. The oxidation factors (fo) recalculation was done considering the average value fo = 0.9613 for coal. By applying different rates (33% B 40% B 60% B) the following results were obtained and these are presented in Table 5.

**Table 5 - fo mixing samples of slag + biomass (M1, M2, M3)**

Sample	fo
M1-33% B+67% Z	0.6441
M2-40% B+60% Z	0.5768
M3--60% B+40% Z	0.3845

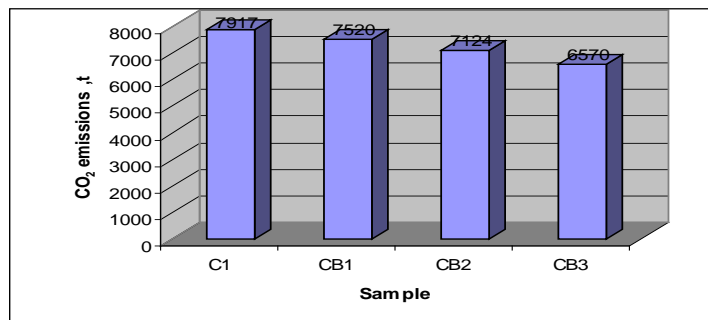
**Table 6 – Fe samples of coal+biomass (CB1, CB2, CB3)**

Sample	Fe t CO <sub>2</sub> /TJ
CB1-5%B+95%C	105
CB2-10%B+90%C	99
CB3-17%B+83%C	91

For sample C1, CO<sub>2</sub> emissions were calculated using the relation (1) considering 1,000 tons. By applying % biomass samples for CB1, CB2, CB3 CO<sub>2</sub> the following emissions were obtained and these are presented in table 7 and figure 10

**Table 7** – CO<sub>2</sub> emission coal mixture samples + biomass (C1; CB1; CB2; CB3)

Sample	Emisia t CO <sub>2</sub>
C1-100%C	7917
CB1-5%B+95%C	7520
CB2-10%B+90%C	7124
CB3-17%B+83%C	6570



**Figure 10** – CO<sub>2</sub> emission samples CB1, CB2, CB3 compared with C1

The data presented shows that the use of biomass leads to decreases of oxidation factor, emission factors and thus a reduction of CO<sub>2</sub> emissions.

#### **4. CONCLUSIONS**

Usage of biomass with clay mixtures and biomass with coal mixtures has the following advantages: reducing the amount of solid fuels, biomass and slag waste recovery, reducing emissions of SO<sub>2</sub> and CO<sub>2</sub>.

The addition of biomass in coal and slag reduces the amount of ash, decreases the content of sulfur, and improves the energetically properties of the process.

An important condition for the use of biomass is that the moisture content should be between 40 and 60%. Using this measure to eliminate the possibility for an accelerated self-ignition is eliminated.

The results demonstrate that using biomass waste mixed with grain (slag) the unburned carbon content is recovered and can be used further in the technological process.

The tests presented in the paper showed that by using biomass a decrease of the oxidation factor, emission factors and also a reduction of CO<sub>2</sub> emissions where obtained.

#### **5. REFERENCES**

- [1] Analysis emissions of greenhouse gases - [www.adrcentru.ro](http://www.adrcentru.ro)
- [2] Energy Strategy of Romania for the period 2007-2020
- [3] Reference Document on Best Available Techniques for Large Combustion Plants (IPPC)
- [4] Order MMGA 95/2005 on the establishment of acceptance criteria and procedures for waste acceptance preliminary to the national list of waste storage and accepted in each class of landfill
- [5] CE Decision no. 589/2007 laying down guidelines on monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87CE
- [6] Directive 75/442/CE which council provides waste management plans