AN ALTERNATIVE FOR VALORIZATION OF WASTES AS ENERGY SOURCE

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Abstract:

The efficient use of renewable energy resources is one of the most important elements of energy sustainability at the European Union level. The growing demand for energy will continue to support the use of other materials as resources of energy than conventional ones, coal, crude oil and natural gas. This paper investigates the feasibility of valorizing wastes with energetic potential in a multi-component alternative solid fuel. Biomass - vegetable waste (BW), meat and bone meal (MBM) and slag/bottom ash from lignite combustion, in combination with a low-rank, lignite, was used to prepare tri-component mixtures (MBM+Lignite +Slag and MBM+BW+Lignite) indifferent variable proportions, and further characterized to assess their potential for use as energy source. The thermal behavior of the mixtures was assessed by thermogravimetric analysis; the resulting ashes were characterized by scanning electron microscopy. Also, the environmental impact as emissions level after their combustion was considered. In terms of an effective way of removing wastes (e.g. slag/bottom ash and MBM), the most promising proposed solid mixture was the combination MBM(50%): Lignite(25%): Slag (25%), with a high energetic value, > 2700 kcal/kg, a volatile matter content > 35 % wt, and the ash in half amount compared to its initial mass. The study's findings illustrate the possibility of turning solid waste to raw material by converting them into energy, and promote the development of long-term waste management and recovery solutions.

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1. INTRODUCTION

Finding alternative energy sources, together with preserving the quality and integrity of the environment is a major concern today worldwide (Perera et al., 2013). Also, an improved management of waste will help to reduce the anthropogenic impact at local and regional level and thus reduce the health and environmental problems (Di Fraia et al., 2020). Therefore, turning the industrial and agricultural waste into a raw material to be further valorized by energy recovery will lead to a more efficient use of the natural resources and a sustainable development (Delreux and Happaerts, 2016). Waste may originate from various sectors, either from industry (i.e., metals, wood, glass, paper, plastics) or agriculture and food production (i.e., fruit and vegetable residues, wastes from food processing). Despite posing disposal and environmental challenges, many of these waste proved their potential as source of energy.

Biomass, which refers to any plant derived organic matter such as dedicated energy crops, agricultural food and feed, crops, agricultural crop wastes and residues, aquatic plants, appears to be a promising source for power generation, biomass-based fuels being more attractive since these give no net CO₂ emissions to the atmosphere (Bilandzija et al., 2016). Even if methods that used pure biomass have been developed (i.e., pyrolysis, gasification, and combustion) and studied, the co-combustion of biomass and coal is still the most reliable technology for biomass energy conversion (Wang et al., 2018; Kazagic et al., 2018). Most of the studies aiming to achieve sustainable solutions for an optimum solid fuel, refer to combustion of biomass with high-rank coal (Lei et al., 2017) and less to biomass co-firing with low-rank sub-bituminous coal, brown coal or lignite (Kakaras, 2000), but none included a multi-fuel concept.

Another potential candidate as alternative fuel is the meat and bone meal (MBM), obtained from slaughterhouse waste and used in the past for feeding cattle, sheep and other animals. Since 1994, within the EU this practice has been banned (Council Decision of 27 June 1994), and new options for valorization of MBM has been searched. Studies have shown that MBM can be reliable as component in several solid energy matrix (Ariyaratne et al., 2011). In combinations with different types of coal or biomass, it represents a feasible disposal solution by energy recovery (Gulyurtlu et al., 2005; Vamvuka et al., 2017; McDonnell et al., 2010). Although MBM is already widely used as an alternative fuel, there are less scientific investigations of optimum usage of MBM in a multi-compound solid fuel.

Slag/bottom ash resulting from lignite combustion is also a waste that pose serious problem and creates environmental pollution through the air by particular matter PM10 and PM2.5, water and soil. This material contains an appreciable amount of unburned carbon, which can be recovered and further used as an energy source; the carbon-free ash can be utilized in cement, concrete and mortars, bitumen asphalt binder for road construction and more recently in catalysts development (Rybak et al., 2017; Asl et al., 2018; Jatav et al., 2019). Even lignite is no longer used in the West European countries, there are countries like Romania, Poland and Ukraine that face with this issue. A solution with a positive economic impact is to obtain an alternative type of solid fuel with energy potential based on slag - bottom ash.

Finding the best way to convert a waste in raw material is not an easy task to accomplish. Therefore, the aim of this work was to investigate the sustainable potential as solid fuel of several waste, namely biomass- vegetable waste (BW), MBM and slag/bottom ash from lignite combustion, in combination with a low-rank, lignite, in a tri-component mixture (MBM+Lignite +Slag and MBM+BW+Lignite), and three variable proportions (I: 25% wt+50% wt+25% wt; II: 50% wt+25% wt+25% wt; and III: 25% wt+25% wt+50% wt), as

an alternative for waste management and energy conversion. The main criteria of selecting the materials were (i) to be an inexpensive material or waste, and (ii) to be readily available, and thus the resulted alternative fuel to be within the concept of sustainable energy through the use of local energy sources and resources. The tri-component solid energy sorts were physically and chemically characterized to determine their viability as fuels and also to find the optimum compositional mixture that makes it competitive with a classical fossil fuel.

2. MATERIAL AND METHODS

2.1. Raw Material

Lignite and slag/bottom ash from lignite combustion, were obtained from a thermal power plant, the CET Govora situated in Vâlcea county (Romania). The biomass vegetable waste (BW), which is a mixture of grape processing residues and apricot kernels, were delivered by a fruit processing company, the SC Annabella SRL, in Vâlcea county (Romania), a company interested in finding a feasible solution to valorize biomass wastes in order to recover the generated energy costs. Low risk meat and bone meal (MBM) was obtained from the SC Diana SRL Râmnicu Vâlcea (România), a company involved in meat processing.

2.2. Preprocessing steps

Since the main task of the work is achieving an alternative solid fuels from a mixture of components with high variability in composition, a special attention was given to the pretreatment steps before mixing. A great impediment for having a positive energy balance at the end is represented by the high humidity level of the raw materials/wastes involved. Therefore, a drying procedure has been applied to the raw materials prior to the thermo-chemical processing. We used for this step a solar dryer device (Fig. 1) with moisture extractor (Ionete et al., 2018), avoiding additional energy consumption for drying waste (BW and MBM).

Figure 1. Solar dryer with humidity extractor for specific organic wastes (Ionete et al., 2018)

The dehumidification of the organic samples was achieved by exposing the samples to the influence of sunlight, followed by the extraction of moisture continuously under the atmosphere of the drying chamber and its free or forced condensation. Solar drying of organic waste is encouraged by climate change since in Romania, for at least 8 months in 2019, was provided the necessary temperatures (average $T = 15^{\circ}\text{C}$) to reach the optimal level of dehumidification, $<5\%$. Next, the samples were milled in a ball mill (*Planetary mill Pulverisette 7, Fritsch*) and sieved up to 0.200 mm .

2.3. Experimental Methods and Measurements

Various analytical investigations were carried out while combining three distinct types of materials to create a new possible solid fuel. Determination of C-N-H-S/O was performed after the samples were brought into the dry state by an elemental analyzer EA Flash 2000 (*Thermo Fischer Scientific, UK*), using both GC-combustion and GC-pyrolisis methods. The samples followed in part the typical elemental investigation of classical solid fuels ([ASTM D5373 - 16](#); [BS EN 15104:2011](#)). The advantage of using this equipment is that simulates the combustion conditions of a thermal and electrical plant, by using the combustion temperature of 950 °C in an oxygen atmosphere ([ASTM D5373 - 16](#); [BS EN 15104:2011](#)). Valuable information can be revealed from the content of energetic elements like C and O. Also, the content of N, S and C can estimate the potential pollution through a process of combustion/co-combustion of alternative fuel from wastes with oxidative emissions like NO_x, SO_x and CO_x. To better assess the impact of using the proposed tri-component solid fuels, the emission factor (EF), more precisely, the specific carbon content, kg CO₂/GJ, was calculated using the following equation:

$$EF = \frac{\frac{M_{CO_2} \times C}{M_C \times 100}}{Q_i} \quad (1)$$

where: M_{CO₂} = 44g/mol, M_C = 12g/mol, C = elemental content (%wt), and Q_i= inferior calorific power, (kcal/kg).

An oxygen bomb incorporated into a calorimetric system (*IKA 5000, Germany*) was used for determining the energy values, namely the higher (HHV) and lower (LHV) values. Specific method conditions were used: ~1 g of NIST standard material, benzoic acid, cotton yarn, high purity of O₂, 5.0 (*Messer Gas, Romania*), combustion at T > 900°C. Measurement were made in triplicate to validate the results; RSD < 5% was taken into account ([Constantinescu et al., 2017](#)). To validate the combustion profile of the proposed alternative fuels, a thermogravimetric analysis was performed with a SDT Q600 (*TA Instruments, USA*) analyzer, in an aluminum crucible, with inert atmosphere of N₂ having the flux rate of 100 mL/min, in a temperature range from ambient to 1050°C, with an increasing temperature rate of 10°C/min. The mass of the samples used for this investigation was between 9 to 12 mg. The microstructure for each sample that involved slag/bottom ash, in fact its behaviour in combination with MBM and L (in different composite variations), was also evaluated by using a scanning electron microscope with LaB₆ cathode (*Zeiss Evo 50 XVP, Germany*). The feasibility of the proposed system was also assessed by an environmental analysis. Elements investigation was performed by atomic adsorption spectroscopy with an air+ acetylene flame using a NOVAA300 AAS (*Analytic Jena, Germany*) and with graphite furnace for Cu determination using a ZEEnit 650 instrument (*Analytic Jena, Germany*). For quantitative analysis of metals (Cd, Cu, Cr, Zn, Ni, Ca, Al, Pb, Fe, Mn, and As), a multi-element standard solution XVICertiPUR - mixture of 21 elements in diluted nitric acid (*Merck, Darmstadt, Germany*) was used as certified reference material. Since, the MBM was used as one of the ingredients in the proposed waste-alternative fuel mixtures, an investigation of dioxin and furans levels in the initial raw material was performed by GC-MS (*GC-MS Varian CP 3800, Varian Inc., USA*) technique ([Vremere et al., 2011](#)). Hexane-assisted extraction, filtration and concentration to dryness in a rotary evaporator were applied. The residue obtained was dissolved in acetonitrile. The method described in EPA 8280 was used for analysis ([EPA - Method 8280B](#)). Also, the potential risk induced by using MBM was assessed based on the overall

toxicity equivalent concentration (TEC) (Safe, 1998) according to the relation:

$$TEC = \sum(C_i \cdot TEF_i) \quad (2)$$

where: C_i is the concentration of individual congener (dioxin) in the mixture, and TEF_i is their relative potencies or toxic equivalency factor.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of fuels/waste- raw materials

The fuels/waste used in performing the tri-component solid fuels included biomass-vegetable waste (BW), meat and bone meal (MBM), slag/bottom ash from lignite combustion and coal - lignite. For each component, proximate and elemental analysis was carried out, as well as the energetic values (Table 1).

Table 1. Properties and characteristics of investigated raw waste materials

Investigation type	Lignite	MBM	Slag	BW
Moisture ^{ar} %wt	37.21 ± 4.50	18.52 ± 2.24	39.76 ± 4.81	1.48 ± 0.18
Ash ^{ar} %wt	28.20 ± 0.85	6.49 ± 0.19	80.77 ± 2.42	2.13 ± 0.06
Volatiles ^{ar} %wt	21.06 ± 0.63	81.43 ± 2.44	10.59 ± 0.32	78.79 ± 2.36
Fixed carbon ^{db} %wt	50.74 ± 1.52	12.08 ± 0.36	8.64 ± 0.26	19.08 ± 0.57
Carbon ^{db} %wt	21.29 ± 0.61	28.95 ± 0.83	15.56 ± 0.45	49.68 ± 1.43
Nitrogen ^{db} %wt	1.53 ± 0.05	11.09 ± 0.37	0.26 ± 0.01	1.42 ± 0.05
Hydrogen ^{db} %wt	2.06 ± 0.05	6.34 ± 0.16	0.52 ± 0.02	6.42 ± 0.16
Sulfur ^{db} %wt	0.45 ± 0.03	8.88 ± 0.50	0.34 ± 0.02	< 0.005
Oxygen ^{db} %wt	29.75 ± 0.18	38.25 ± 1.10	2.55 ± 0.06	36.60 ± 1.10
HHV ^{db} kcal/kg	2086 ± 25	3730 ± 45	971 ± 12	4813 ± 58
LHV ^{db} kcal/kg	1700 ± 20	3400 ± 41	800 ± 10	4591 ± 55
EF kg CO ₂ /GJ	94.12	71.55	147.73	95.155

Note: ar- as received; db- dry basis; EF- calculated emission factor

The physico-chemical characterization was done using classical gravimetric methods for the study of fuel behavior. The Ash content was determined in the oven at 550°C temperature for biomass or 850°C temperature for lignite, the volatiles content were determinate at 900°C for 7 minutes, while the moisture was determined at 70°C and 105°C.

The highest concentration of ash in the case of slag/bottom ash was predictable, since is a residual product resulting from the combustion of lignite in the boilers of a thermal power plant. As regard the content of volatile matter, the results were somewhat encouraging, and was a first signal of their potential "precursors" for future alternative fuels. MBM and BW have recorded significantly high levels of volatile matter compared to lignite.

The high nitrogen content registered in MBM, 11.09%, will surely cause problems in a combustion process by the generation of pollutant emissions (NO_x nitric oxides like NO₂ and NO). Hydrogen, an energy potential element, was found in high quantities within the MBM and BW, leading thus to high calorific values, confirmed to be significantly higher than for a conventional fuel (e.g., lignite). Sulfur level of Slag and BW do not highlight problems, since is below that of fossil fuels, except in MBM samples which recorded values 20 times higher than lignite. MBM is an animal waste naturally containing

amino acids such as methionine, cystine and cysteine, explaining thus the high sulfur level ($S > 8\%$ wt). As for oxygen and hydrogen, the levels are high, corresponding to potential alternative fuels, and is comparable to those found in the literature (Magdziarz and Wilk, 2013; Yilmaz et al., 2018; Constantinescu et al., 2018), which also led to significant calorific values (HHV), of 3730 kcal/kg for MBM, to 4813 kcal/kg for BW, significantly higher than of lignite, ~ 2086 kcal/kg.

Since there is a considerable concern on human exposure to various chemicals that may affect the endocrine and/or carcinogenic system, the risk for health induced by waste like MBM was evaluated based on the equivalent total toxicity concentration (TEC), defined by the concentration of the individual congener dioxins/furans, mixed carcinogens, multiplied by their relative power factors or toxic equivalence factors (TEF_i) (Van den Berg M; et al., 2016). The results are shown in Table 2.

The most toxic dioxin is represented by the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), for which a toxic equivalency factor (TEF) of 1 was attributed and used. The dioxin concentrations are calculated as the sum of the toxicity equivalents, TEQs that are relevant for the most toxic dioxin, TCDD. The TEC values for PCDDs and PCDFs were 0.7903 ng/kg and 0.3008 ng/kg, respectively. The total TCDD of 0.089 ng/kg was below the level set for the cleaning level (13 ng/kg). This 2,3,7,8 - TCDD clearance level set in MBM certify no risk of using it for an innovative solid energy sort.

Table 2. The content of dioxin and furans in MBM^{db}. TEF for assessing the risks to human health of 2,3,7,8 - substituted PCDDs and PCDFs and TEC

Congeners	Concentration ng/kg	TEF	TEC ng/kg
<i>Polychlorinated dibenzo-p-dioxins (PCDDs)</i>			
2,3,7,8-tetrachlorodibenzo-p-dioxin TCDD	0.089 ± 0.033	1	0.089
1,2,3,7,8 pentachlorodibenzodioxin PeCDD	0.421 ± 0.019	1	0.421
1,2,3,4,7,8 hexachlorodibenzodioxin HxCDD	0.854 ± 0.132	0.1	0.0854
1,2,3,6,7,8 hexachlorodibenzodioxin HxCDD	1.055 ± 0.185	0.1	0.1055
1,2,3,7,8,9 hexachlorodibenzodioxin HxCDD	0.835 ± 0.064	0.1	0.0835
1,2,3,4,6,7,8-heptachlorodibenzodioxin HpCDD	0.588 ± 0.220	0.01	0.00588
1,2,3,4,6,7,8,9 octachlorodibenzodioxin OCDD	1.221 ± 0.007	0.0003	0.0001221
<i>Polychlorinated dibenzo-p-furans (PCDFs)</i>			
2,3,7,8-tetrachlorodibenzofuran TCDF	0.247 ± 0.006	0.1	0.00247
1,2,3,7,8 pentachlorodibenzofuran PeCDF	0.135 ± 0.021	0.03	0.00135
2,3,4,7,8 pentachlorodibenzofuran PeCDF	0.356 ± 0.011	0.3	0.0356
1,2,3,4,7,8 hexachlorodibenzofuran HxCDF	0.653 ± 0.137	0.1	0.0653
1,2,3,6,7,8 hexachlorodibenzofuran HxCDF	0.385 ± 0.187	0.1	0.0385
1,2,3,7,8,9 hexachlorodibenzofuran HxCDF	0.878 ± 0.085	0.1	0.0878
2,3,4,6,7,8 hexachlorodibenzofuran HxCDF	0.637 ± 0.258	0.1	0.0637
1,2,3,4,6,7,8 heptachlorodibenzofuran HpCDF	0.412 ± 0.008	0.01	0.000412
1,2,3,4,7,8,9 heptachlorodibenzofuran HpCDF	0.558 ± 0.289	0.01	0.00558
1,2,3,4,6,7,8,9 octachlorodibenzofuran OCDF	1.124 ± 0.261	0.0003	0.0001124
SUM	10.448		0.06418333

Note: db – dry basis

Also, to anticipate a potential gaseous emission rich or not in metals, following a future combustion process, to control the environmental impact of using the proposed wastes as raw material in a multi-component fuel, the evaluation of heavy metals content (Table 3) was performed. In case of MBM, high levels were quantified for calcium and aluminum. Also, high content of iron, without concern because these levels are normal, were recorded in lignite and slag.

Table 3.Metals content of investigated raw waste materials

Metal	Raw materials type			Reference values[28]	
	MBM ^{db} mg/kg	Slag/bottom ash ^{db} mg/kg	Lignite ^{db} mg/kg	Alert threshold mg/kg	Intervention threshold mg/kg
Cd	0.40 ± 0.08	0.23 ± 0.05	0.39 ± 0.08	3 ÷ 5	5 ÷ 10
Cu	5.75 ± 1.03	18.70 ± 3.36	36.80 ± 6.62	100 ÷ 250	200 ÷ 500
Cr	1.20 ± 0.25	43.50 ± 9.13	37.00 ± 8.00	100 ÷ 300	300 ÷ 600
Zn	107.70 ± 19.40	31.13 ± 5.60	41.24 ± 7.42	300 ÷ 700	600 ÷ 1500
Ni	2.20 ± 0.60	32.38 ± 8.42	44.60 ± 11.60	75 ÷ 200	150 ÷ 500
Ca	150.20 ± 36.00	-	-	-	-
Al	169.90 ± 43.66	-	-	-	-
Pb	19.86 ± 3.65	20.70 ± 3.80	8.90 ± 1.64	50 ÷ 250	100 ÷ 1000
Fe	-	7472.00 ± 1868.00	5350.00 ± 2.22	-	-
Mn	-	103.80 ± 21.80	156.00 ± 32.76	1500 ÷ 2000	2500 ÷ 4000
As	-	75.14 ± 19.46	37.00 ± 9.60	15 ÷ 25	25 ÷ 50

Note:db- dry basis

The levels of cadmium and lead, extremely toxic heavy metals, do not exceed the worrying value for any of the investigated raw materials. Arsenic, which could create problems both in gaseous emissions and in ash resulting from the single combustion of the slag or lignite, was not detected in MBM. Pollution with As could lead to degenerative, inflammatory and neoplastic changes in the skin, respiratory system, blood, lymphatic system and reproductive system. Precisely this effect of reducing the negative impact of metals on the environment, could result from mixtures containing MBM with Slag and Lignite or MBM with BW and Lignite.

3.2. Physico-chemical characterization of the tri-component waste/coal-based mixtures

Considering the compositional profile shown by the four selected materials, MBM, BW, Slag and Lignite, two tri-component mixtures, namely MBM+Lignite+Slag and MBM+BW+Lignite, were prepared in variable proportions, and further tested, with the aim to obtain a low cost waste based fuel, with efficient co-combustion and environmental friendly. A series of 6 mixtures were prepared from the selected raw materials, which may constitute a reliable solution of eliminating waste (MBM, Slag, and/or BW) by energy recovery. The mixtures followed three compositional proportions, of (% , wt) 25:50:25, 50:25:25 and 25:25:50, thus to cover a varied range of data that will offer information (Table 4) on the durability of the proposed fuel solution.

Table 4. Properties and characteristics of the proposed tri-component mixtures

Investigation type		MBM+Lignite+Slag			MBM+BW+Lignite		
	Parameter	I ^(*)	II ^(**)	III ^(***)	I	II	III
Proximate analysis	Fixed carbon %wt	13.42±0.40	12.14±0.36	11.46±0.34	15.28±0.46	15.18±0.46	17.08±0.51
	Volatiles %wt	39.16±1.17	51.58±1.55	33.61±1.01	56.22±1.69	98.12±2.94	67.27±2.02
	Ash %wt	47.42±1.42	36.28±1.09	54.93±1.64	28.50±0.86	17.06±0.51	15.65±0.47
	Moisture %wt	21.11±2.55	20.29±2.46	19.04±2.30	16.88±2.04	22.09±2.67	17.01±2.06
Ultimate analysis	Carbon %wt	25.32±0.73	26.91±0.77	22.31±0.64	32.66±0.94	34.99±1.00	34.22±0.98
	Nitrogen %wt	3.22±0.11	5.10±0.17	2.94±0.09	3.44±0.12	6.20±0.21	5.51±0.18
	Hydrogen %wt	3.78±0.09	4.40±0.11	2.98±0.07	4.77±0.12	5.59±0.14	5.61±0.14
	Sulfur %wt	2.20±0.12	3.31±0.19	2.00±0.11	2.16±0.12	3.80±0.21	4.96±0.28
	Oxygen %wt	18.06±0.54	24.00±0.72	14.84±0.45	28.47±0.85	32.36±0.97	34.05±1.02
	HHV kcal/kg	2493±30	2791±33	2162±26	3412±41	3759±45	3982±48
	LHV kcal/kg	2120±25	2433±29	1876±23	3129±38	3444±41	3600±43
	EF kg CO ₂ /GJ	93.628	88.883	95.128	56.223	98.123	67.277

Note: I: 25%wt+50%wt+ 25%wt; II: 50%wt+25%wt + 25%wt; III: 25%wt+25%wt+50%wt

As for other energetic solid waste blends (Constantinescu et al., 2017; Ylmaz et al., 2018; Constantinescu et al., 2018), the proposed tri-component solid energy sorts mainly based on waste materials, reveals a positive evolution, both in terms of high energy levels and decrease of elementary components (S, N, and C) with potential environmental negative impact. The multicomponent-based waste solid fuels, namely MBM+Lignite+Slag and MBM+BW+Lignite, registered high energy values, of 2162 to 2791 kcal/kg and from 3412 to 3982 kcal/kg, respectively. Since MBM is an organic, biological nature, rich in sulfur-containing amino acids, sulphur level was relatively high. This phenomenon was also previously reported, and a solution for correcting possible SO₂ emissions would be the inclusion of a sustainable adsorption material, such as limestone (McDonnell et al., 2010). The levels of N and S, initially high in the MBM samples, significantly decreased in the proposed mixtures due to their low content in slag/bottom ash and lignite.

As for the volatile matters, all six tested mixtures have recorded higher values than for lignite, a classic fossil fuel used to produce more than 35% of the total annual energy required for Romania (Transelectrica Report, 2019). The same trend is also observed for the energetic values.

All six innovative tricomponent solid energy sorts have recorded values of volatile matters V^{ar} , but also of increased calorific value HHV^{ar} higher than those of lignite, a classic fossil fuel used to produce more than 35% of the total annual energy required for Romania (Ionete et al., 2018).

As described, slag/bottom ash derived from the lignite combustion is eliminated by recombustion in the mixture, almost one element of novelty, except by the use of this raw material waste mixed with lignite in different proportions. All the energy values, valid for the proposed tri-component based slag fuels (MBM+Lignite+Slag), are superior to individual matrices, slag and lignite, as follow: for hydrogen, from 2.98 to 4.40%wt vs. 0.52%wt in Slag and 2.06%wt in Lignite; for carbon, from 22.31 to 25.32%wt vs. 15.56 %wt (Slag) and 21.29%wt (Lignite); for oxygen, from 14.84 to 18.06%wt vs. 2.55%wt (Slag) and 9.24%wt (Lignite); for volatile materials, from 33.61 to 39.16%wt vs. 10.59 %wt (Slag) and. 21.06%wt (Lignite); and HHV, from 2162 to 2791kcal/kg vs. 971kcal/kg (Slag) and 2086kcal/kg

(Lignite). The ash content of the proposed of the MBM+Lignite+Slag based mixtures is inferior to the Slag matrix, of 36.28-54.93% wt vs. 80.77% wt.

To better assess the properties of the MBM+Lignite+Slag based mixtures, a scanning electron microscopy (SEM) investigation was performed (Fig. 2) for the ash obtained after their combustion at $> 900^{\circ}\text{C}$.

Figure 2. SEM investigations of the Slag/bottom ash-based mixtures

A: Slag/Bottom ash; B: MBM+Lignite+Slag/Bottom ash (I);
C: MBM+Lignite+Slag/Bottom ash (II); and D: MBM+Lignite+Slag/Bottom ash (III)

The results revealed the influence of both MBM and Lignite in the proposed mixture MBM+Lignite+Slag/Bottom ash in its three different proportions (I, II and III). In case of the Slag/bottom ash investigation, irregular particles of coal ash are distinguished, but also unburnt charcoal (Fig. 2A). Figure 2B represents the bottom ash resulted from the combustion of the solid sort MBM+Lignite+Slag/Bottom ash (I). The investigation carried out at $2\ \mu\text{m}$ shows the effect of combustion and cavernous formed on the surface of iron and silicon monolithic due to the "disappearance" of unburnt carbon "caught" in this structure. The increase mass of MBM in the mixture MBM+Lignite+Slag/Bottom ash (II), at 50%, lead to a change in the surface of the bottom ash as shown in Fig. 2C. The surface is much more cavernous because the increasing organic mass content in this mixture leading to a more efficient combustion and initial sunburnt carbon from Slag/bottom ash "caught" in this monolithic of iron, also confirmed by the energy investigations describing the highest HHV level. Figure 2D highlights a slag after combustion of the sort MBM+Lignite+Slag/Bottom ash (III), which is similar to a "coral", being extremely "spinous" on its whole structure. This fact is due to the naturally high quantity of the innovative solid energy sort MBM+Lignite+Slag/Bottom ash (III) in Slag/bottom ash from lignite combustion, at 50%. The organic matter of the very homogeneous mixture on combustion at high temperature has "tried" its "release", thus creating these "coral" structures type to the surface of the remaining slag.

3.3 Combustion behavior of the tri-component waste/coal-based mixtures

Combustion characteristics of waste raw materials, MBM, Slag/Bottom ash, BW and Lignite, as well as the developed innovative solid energy sorts have been evaluated by thermogravimetric analysis (TGA), which give a rapid investigation of the value of fuel in terms of the starting and final temperatures involved in the combustion process, along with other characteristics such as steps of combustion as function of materials composition and the amount of ash at the end of the process. This investigation is very useful for the study of the combustion kinetics. The measurements for all samples were carried out under same conditions of temperature range, atmosphere, heating rate, resulting in a high degree of repeatability. The steps of mass loss during the temperature progress for the tested raw materials was achieved. By comparing the thermal degradation curves shown in Fig. 3 and Fig. 4, it was noted that the raw materials lost most of their mass between $T = 110^{\circ}\text{C} \leftrightarrow 460^{\circ}\text{C}$, except for slag resulted from the combustion of lignite, that are linear on all temperature range, with a 8.9 % maximum mass loss.

Figure 3. Comparative TG curves: raw materials vs. MBM+Lignite+Slag/Bottom ash (I; II; III) mixtures

For the Lignite sample the maximum mass loss was 42.4%, registering a quite high total content of volatile materials, ash and humidity, $V^{\text{as}} + A^{\text{as}} + W_t^{\text{as}}$. Until 100°C the lignite sample loss water, approx. 5% wt representing the adsorbed water resting after the initial processing of the material. In the second stage of mass loss, the organic chains are degraded with a high rate and the degradation continues up to 1000°C with a lower rate, resulting a residue representing 57.6% wt of the initial mass. The content of the residue is rich in metals and minerals. BW sample investigated in the dry state do not show a step of water loss, but the first visible step of mass loss were between $200^{\circ}\text{C} - 260^{\circ}\text{C}$, which represent the loss of functional groups ($-\text{OH}$; $-\text{CHO}$; $-\text{CH}_3\text{OH}$) from the structural components: lignin, cellulose, hemicellulose.

Figure 4.Comparative TG curves: raw materials vs. MBM+BW+Lignite (I; II; III) mixtures

Between 350°C-500°C, these structures suffer complete degradation. The TGA investigation of MBM showed a loss of water up to 150°C. Protein backbone and lipids degradation occur in the range 220°C-530°C. BW and MBM have a high content of organic matter completely degraded up to 600°C, which explained the low value of the final residue.

In order to emphasise the rate and temperature of thermal degradation for the raw materials, Table 5 summarizes the temperature corresponding to the following mass loss: 5%, 10%, and 25% together with the final residue at 1050°C (Petreanu et al., 2012). The order of mass loss for raw materials used in the development mixtures, was the following: Slag/Bottom ash> Lignite> BW > MBM.

Table 5.Temperature of thermal degradation for raw materials

Material	Temperature at 5 % mass loss °C	Temperature at 10 % mass loss °C	Temperature at 25 % mass loss °C	Final reziduu at 1050 °C (%)
Slag/Bottom ash	729.00	-	-	91.30
Lignite	111.50	307.18	456.00	57.60
BW	179.30	200.50	279.20	23.20
MBM	108.70	213.00	291.00	19.00

The first stage of mass loss occurred up to 100°C representing the adsorbed water. Comparing the thermal degradation curves in Fig. 3 it is noted that the mixtures MBM+Lignite+Slag (I, II, and III) lost most of their mass between 240 and 460°C. The highest mass loss was found in the case of the MBM+Lignite+Slag (II) sort. According to the TG curves shown in Fig. 3, the combustion of the slag in the proposed tri-component based waste fuels is an effective solution for disposal of this waste, as the process can begin in the range of lower temperatures and the amount of ash is smaller than in the case of it single combustion. According to the TG curves shown in Figure 4, the initial weight loss in the mixtures is recorded up to 110°C which represents the loss of adsorption water. Between 180 and 460°C, the interval II of mass loss is recorded, which represents the

equivalent of the ash content in the innovative mixtures developed. Maximum weight loss temperature was at 500°C corresponding to the volatile matter content. With a 77% maximum mass loss, the proposed tri-component solid energy sort III demonstrated the most balanced combustion behavior.

4. CONCLUSIONS

In this work, an idea for sustainable pathway of waste disposal through energy recovery is presented, proposing and testing a tri-component solid fuel based on wastes (vegetable biomass from food industry, meat and bone meal from meat processing and slag/bottom ash from Lignite combustion) and coal - Lignite. Deliverables were six different solid energy sorts, which were tested in terms of combustion efficiency and pollution and health impact. Of all the developed mixtures, the highest energy value, of 3982 kcal/kg, was registered in the MBM+BW+Lignite multi-component fuel in the compositional combination of 25%:25%:50%, a value significantly higher than of Lignite (~ 2100 kcal/kg) originated from Romania. Also, the elemental analysis noted in this sort a level S < 5% wt, halfway towards the initial level of MBM, ~ 9% wt. In the case of Slag/bottom ash, the combination with MBM and Lignite (MBM+Slag/Bottom ash+Lignite) in proportion of 50%:25%:25%, by the sort type (II), a HHV level > 2700 kcal/kg was obtained, highlighting the sustainability of valorization this waste, with added value, in the circular economy as alternative fuel. Overall, the obtained data are encouraging for converting waste into potential fuels, with comparable or even superior properties than classical fossil fuels.

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Abbreviations: BW - biomass - vegetable waste; MBM - meat and bone meal; SEM - scanning electron microscopy; TGA - thermal gravimetric analysis; C - carbon; H - hydrogen; N - nitrogen; O - oxygen; S – sulphur.

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