

The Ecological Management of Fumes Released by Bio Fuel Incineration

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Abstract: The result of bio fuel incinerating process is energy, fumes and solid waste. Incineration in sealed areas allows for the release of fumes. To increase ecological features, four variants of initial burning temperature in sealed area have been tested, 20°C, 200°C, 550°C and 800°C, respectively, combined with a process of chemical washing of the gases. The analysis of the effluent has shown that along with the increase of temperature, an increase of SO₂, CN, and N₂ concentrations was also recorded in the released fumes. We noticed the disappearance of NH₃ and H₂S starting with the variant of 200°C, and the gradual reduction of R-CN, aromatic hydrocarbons and NO₂ concentration, when temperature increased up to 800°C. At the same time, gas purification via humid process has diminished the initial concentration of the fumes by 97%.

Key-Words: burning process, bio fuel, fumes, toxic compounds, chemical washing gases

1. Introduction

The study of the chemical composition of some waste made of bacteria masses has concluded that their elementary composition (54.66-59.21% C_{org}, 22.92-30.73% H₂O)[2],[3],[9] is similar to that of alkanes (C=75-82%; H=17-24%; O=0.5-1,0%) or wood polysaccharides (C=44.45%; H=6.17%; O=49.38%) [10]. This conclusion led to the idea that they may be used as fuel and release equivalent amount of energy [1].

Besides the elementary composition of the material, its pollutant potential was defined, the analytical data revealing a 3-5% load of nitrogen, sulphur, chloride, CN, phenols, aromatic hydrocarbon compounds. With respect to their thermo energetic properties, batches of this material have heating powers of: 5180 Kcal/kg (batch 1), 5052 Kcal/kg (batch 2), 5088 Kcal/kg (batch 3), 5173 Kcal/kg (batch 4), ranking it in terms of energetic potential between the beech wood and oil-based fuel, recommending thus its use as bio-fuel [5],[6]. To put to value such a material as an energy source requires testing many variants of combustion with a view to an economic and ecological management of the combustion products.

2. Material and methods

This paper describes a method of using solid residues (inactive biologic mud) from sewage in

chemical industry, through classic ignition systems [2,3]. The results of the ignition consists in energy, gases and ash, this paper describing the matter of ignition gases management. Ignition chambers are equipped with gases recycling systems, which decomposes initial matter until it's elementary composition. Unlike fuel cells [9,11,12], these systems are indirectly energy producers, through initiation of ignition in ceramic chambers and by improving the caloric potential of some conventional combustibles.

The material used was sampled either dry in mud dump or wet in the wastewater treating beds of some treatment plants in the chemical industry.

In order to choose the methods of valuing/removing such waste, the samples were subjected to physical and chemical analysis so as to determine the elementary composition of the organic matter [C, H, O (STAS - 8959/71), N-(Kjeldahl), S- in the calorimetric bomb, P-Jeffery methods], as well as to dose, via spectrophotometric methods, their toxic substance content (e.g. R-SH, R-CN, CN, phenols, aromatic hydrocarbons, heavy metals). Such toxic substances may reach the environment as a result of their combustion or other method. Moreover, after having determined their elementary composition, which justifies the use of bacteria masses as bio fuel, the energetic capacity of the organic waste batches were tested in the calorimetric bomb.

The heating power was determined by the complete burning in the calorimetric bomb of a known quantity of the mud analysed, in oxygen atmosphere, at some 25 atm pressure, as per STAS No. 5269-1969.

All variants of valuing bacteria masses as bio fuel were tested under laboratory conditions by using some burning installations with pyrolon combustion area and absorption of the elements of the gas emission in chemical washing solutions by means of EMIMAT equipment. In order to optimize and make the process more environmentally friendly [4,7,8] the combustion tests were carried out under different conditions, i.e. varying initial temperatures of the incineration area between 20 and 800 °C. The results of the test consisted in analysing the combustion gas chemical composition, measuring the thermo energetic results of this bio fuel, and

identifying the optimal conditions for burning and purging of the emissions so as to avoid the release of any toxic gas or discomforting fumes in the atmosphere when burning begins.

3. Results and discussion

3.1. Fumes released by incineration of bio fuel initially introduced in not-heated areas

It was noticed that the initiation of the burning process, when bio-fuel samples introduced in the combustion installation at 20°C are burnt, progresses difficultly due to the temperature range needed to ignite the compounds which led to the initial release of thick smoke containing incompletely burnt particles.

Table 1 - Fumes released by incineration at the 20°C initial temperature of sealed area

Gaseous emissions	Initial temperature of incinerating area - 20°C							
	Batch 1		Batch 2		Batch 3		Batch 4	
	Bio fuel material status							
%	wet	semi-dry	wet	semi-dry	wet	semi-dry	wet	semi-dry
CO ₂	56,940	122,865	41,802	137,100	79,012	165,180	56,600	168,650
H ₂ O	5,010	10,820	4,800	15,740	11,158	23,670	7,740	23,040
R-CN	0,250	0,542	0,255	0,836	0,210	0,450	0,121	0,362
CN ⁻	0,080	0,175	0,092	0,301	0,078	0,165	0,040	0,120
H.A	0,095	0,201	0,085	0,279	0,095	0,201	0,026	0,076
NO ₂	2,460	5,300	1,151	3,775	2,350	4,985	1,434	4,265
RSH	0,480	1,040	0,236	0,774	0,360	0,764	0,009	0,028
H ₂ S	0,080	0,169	0,066	0,216	0,090	0,191	0,021	0,062
NH ₃	0,992	2,138	0,190	0,623	1,120	2,376	0,712	2,118
SO ₂	0,102	0,218	0,098	0,321	0,115	0,244	0,025	0,075
Cl ₂	0,005	0,011	0,010	0,032	0,008	0,017	0,003	0,001

When a 200°C temperature was exceeded, the particles on the tube walls ignited and burning gases became transparent.

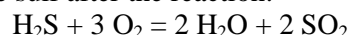
Gases emitted by burning were then subjected to the wet purging system. The physical and chemical analysis of the absorbent solutions showed that consist of R-CN, R-SH, NH₃, NO₂, SO₂, aromatic hydrocarbons, H₂S, and cyanides, in a descending order.

3.2. Fumes released by bio fuel incineration at 200 °C pre-heated sealed area

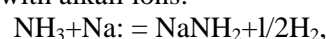
The experiment was performed again by using the results in the preliminary tests, which indicated a more rapid and complete burning if the areas where mud was burnt had been pre-heated at over 200°C. Hence, the samples were introduced in pyrolon pipes, heated by means of Bünsen burners, at some 200°C.

Under such conditions, the samples ignited quickly and only the integral mud samples released little smoke due to high moisture. Substances released were generally similar to those in the preliminary test, except sulphuretted hydrogen and ammonia fumes were not gathered. Having consulted the analytical data obtained from solutions in gathering containers of the installation has led us to the following findings:

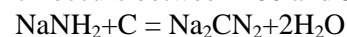
- sulphuretted hydrogen oxidized at sulphur dioxide la bioxid de sulf after the reaction:



- ammonia passes probably into sodamide and then in cyan ions or directly into cyanide, upon contact with alkali ions:



reaction which occurs between 200 and 300°C;



reaction which occurs between 400 and 500 °C;

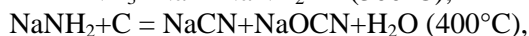
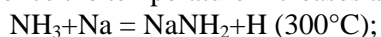
Table 2 – Fumes released by bio fuel incineration at 200 °C pre-heated areas

Gaseous emissions	Initial temperature of incinerating area – 200 °C							
	Batch 1		Batch 2		Batch 3		Batch 4	
	Bio fuel material status							
%	wet	semi-dry	wet	semi-dry	wet	semi-dry	wet	semi-dry
CO ₂	60,48	130,15	49,03	160,81	79,20	168,00	55,500	165,120
H ₂ O	5,50	11,80	4,42	14,50	10,42	22,10	8,100	24,100
R-CN	0,22	0,48	0,23	0,75	0,29	0,62	0,181	0,540
CN ⁻	0,09	0,19	0,12	0,38	0,19	0,40	0,019	0,380
H.A	0,09	0,19	0,09	0,28	0,17	0,35	0,064	0,190
NO ₂	2,83	6,10	1,46	4,81	2,40	5,10	1,648	4,900
N ₂	-	-	-	-	-	-	-	-
RSH	0,53	1,15	0,30	0,97	0,38	0,80	0,050	0,150
H ₂ S	-	-	-	-	-	-	-	-
NH ₃	-	-	-	-	-	-	-	-
SO ₂	0,69	1,50	0,16	0,64	0,26	0,55	0,054	0,160
Cl ₂	0,05	0,11	0,01	0,04	0,01	0,020	0,003	0,001

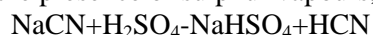
Temperature requirements having been met, the nitrogen compounds can form diazonium or/and nitrosamine salts in the presence of hydrochloric acid released from ferric chloride:



Such compound which, when heated, decompose in phenol and NH₃ or/and N₂, the cycle restarting once the temperature increases as follows:



which, in the presence of sulphur vapours, give:



The most important result of pre-heating the combustion area at 200°C is the decrease by 16% of toxic fumes from burning the four batches of integral or dry mud.

The occurrence of such processes, i.e. that the sulphuretted hydrogen passes into SO₂, the amine nitrogen passes from proteins into and the ammonia into cyanide, is confirmed by gathering increased amounts of such components.

At this stage of the experiment, the findings were as follows: increased amounts of R-SH, SO₂, NO₂, CN and decreased R-CN, NH₃, H₂S concentrations.

As the percentage of toxic fumes maintained around the values of 2-4% of the fresh mud weight and 6-9 % of the dehydrated mud weight, respectively, increasing the pre-heating temperature of the combustion areas up to 550 °C became a requirement.

3.3. Fumes released by bio fuel incineration in 550 °C pre-heated areas

The samples introduced at this temperature ignited instantaneously and released massive quantities of water vapours containing nitrogen oxides, iron chloride, sulphur oxides, cyanides, and manganese pent oxide, carbon dioxide. Moreover, part of the fumes released during the first combustion stage self-ignited after having filled the pipe.

Table 3 – Fumes released by bio fuel incineration at 550 °C pre-heated areas

Gaseous emissions	Initial temperature of incinerating area – 550°C							
	Batch 1		Batch 2		Batch 3		Batch 4	
	Bio fuel material status							
%	wet	semi-dry	wet	semi-dry	wet	semi-dry	wet	semi-dry
CO ₂	67,200	145,080	50,350	165,120	80,141	170,000	54,360	161,600
H ₂ O	5,600	12,050	4,600	15,100	11,410	24,200	8,340	24,800
R-CN	0,106	0,230	0,145	0,480	0,150	0,310	0,135	0,400
CN ⁻	0,134	0,290	0,150	0,490	0,150	0,510	0,154	0,460
H.A	0,046	0,100	0,060	0,180	0,120	0,250	0,054	0,160
NO ₂	2,883	6,220	1,510	4,950	2,600	5,500	1,716	5,100
N ₂	-	-	-	-	-	-	-	-
RSH	0,370	0,800	0,200	0,650	0,260	0,550	0,030	0,090
H ₂ S	-	-	-	-	-	-	-	-
NH ₃	-	-	-	-	-	-	-	-
SO ₂	0,870	1,880	0,220	0,710	0,320	0,680	0,084	0,250
Cl ₂	0,005	0,010	0,014	0,045	0,010	0,020	0,003	0,001

Similarly to the previous case, ammonia reacts with alkali metals forming cyanides. Sulphuretted hydrogen oxidises at SO₂, a part of R-CN burns up to NO₂, CO₂ and H₂O, and the largest part of manganese deposits in the ash as MnO₂.

Finally, the fumes released during the pre-heated incineration at 550°C are richer in NO₂, SO₂, CN, CO₂ and H₂O.

At this stage of the experiment, we noticed the complete elimination of ammonia and sulphuretted hydrogen, the increase of SO₂, NO₂, CN quantities, and the reduction of aromatic hydrocarbon, NH₃, R-SH, and H₂S concentrations.

As a rule, concentrations of fumes emissions resulted from 550°C-preheated mud incineration modified passing one into the other, hence quantities have largely remained similar to those in the 200°C preheating. Therefore, we tried to repeat the organic waste incineration test in areas preheated at 800°C

3.4. Fumes released by bio fuel incineration in 880 °C pre-heated areas

During this forth combustion test, the tubes of the incinerating installation were brought to some 800°C by means of Bünsen burners, set at blue flame and at the location of sample.

Table 4 – Fumes released by bio fuel incineration at 800 °C pre-heated areas

Fumes	Initial temperature of incinerating area – 800°C							
	Batch 1		Batch 2		Batch 3		Batch 4	
	Bio fuel material status							
%	wet	semi-dry	wet	semi-dry	wet	semi-dry	wet	semi-dry
CO ₂	68,600	148,150	48,250	158,250	82,500	175,000	58,7200	174,550
H ₂ O	7,040	15,210	4,730	15,501	12,020	25,500	8,4400	25,090
R-CN	0,093	0,201	0,020	0,080	0,047	0,100	0,0500	0,150
CN ⁻	0,220	0,474	0,300	0,980	0,050	1,010	0,3230	0,960
H.A	-	-	-	-	-	-	-	-
NO ₂	1,490	3,210	0,761	2,500	1,420	3,010	1,0630	3,1600
N ₂	1,390	3,910	1,490	4,880	2,120	4,502	1,3280	3,9500
RSH	-	-	-	-	-	-	-	-
H ₂ S	-	-	-	-	-	-	-	-
NH ₃	-	-	-	-	-	-	-	-
SO ₂	0,880	1,900	0,640	2,101	0,840	1,770	0,1010	0,3000
Cl ₂	0,050	0,120	0,015	0,050	0,010	0,020	0,0003	0,0010

The major advantages of this last incineration test are given by the self-combustion of burning gases, which leads to a 50% decrease of the amount of fumes released when using such type of bio-fuel.

Heating was performed until the body emitted visible yellow heat radiations. The samples introduced in the areas brought to 800°C, ignited instantaneously and a sudden and massive gas release was observed. When the tube space was filled, the gases re-ignited. This phenomenon occurred periodically, whenever the critical air and gas mixture was reached, until the end of combustion. The combustion was complete, the walls of the area remaining clean, free of any carbon particles.

Burning gases of fuel in this test contained mainly molecular nitrogen, nitrogen dioxide, sulphur dioxide, and cyanides.

3.5. The importance of the burning area initial temperature to the composition of gases emitted

These determinations can be illustrated by the correlation coefficients, developed in the correlation matrices of the emission composition with the initial temperatures of the burning areas[1], [2].

Despite the fact that the data belong to four batches with composition differences, the four correlation matrices presented the same correlation coefficients between the compound concentrations and temperature. This observation confirms the accuracy of their analytical approach. Thus, correlation coefficients of the order given below were recorded:

- positive, very good ≈ 1.0 , of SO₂ emissions with initial temperatures (R = 0.99);
- positive, high, water quantities with initial temperatures: R=0.95;

- positive, good, of cyanide emission at initial temperatures : $R = 0.98$;
- positive, good, of molecular nitrogen emission with initial temperature: $R = -0.78$;
- negative, significant, of H_2S and NH_3 emissions at initial T° : $R = -0.71$
- negative, significant, of organic cyanide compounds with initial temperatures $R = -0.91$ up to $550^\circ C$ and $R = -0.68$ for the $800^\circ C$ temperature.

These correlations are also confirmed by the analytical data – illustrated in Figures 1 and 2 – of which increased concentrations H_2O , NO_2 , SO_2 , CN , and N_2 in burning emissions at the same time with the initial temperature of the burning area.

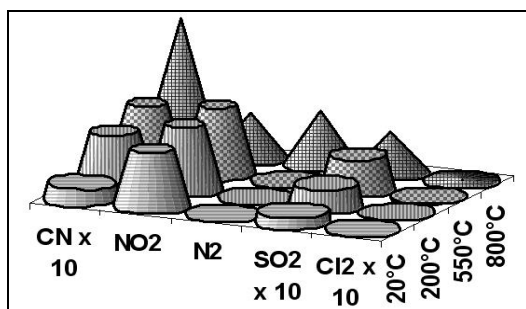


Fig. 1 – Rising concentrations of some fumes at initial temperature of the burning area

Moreover, it was noticed that ammonia and sulphuretted hydrogen from the $200^\circ C$ variant disappeared and the R-SH, RCN, aromatic hydrocarbons concentrations decreased towards the $800^\circ C$ temperature.

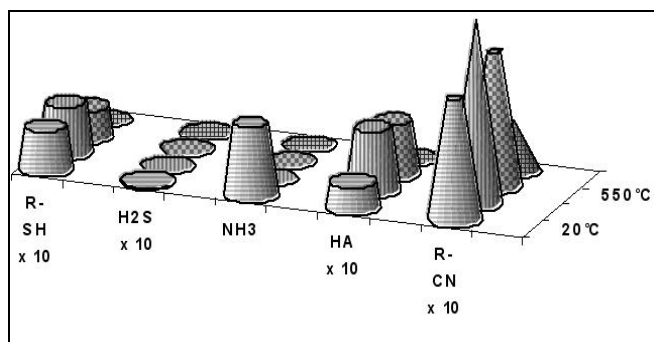


Fig. 2 - Falling concentrations of some fumes at initial temperature of the burning area

3.6. Management of bio-fuel incineration products

3.6.1. Purging burning gases by neutralization

Procedures of treating incineration-related gaseous effluents consist of neutralization of acid gases (NO_x , SO_x , CO_2) by means of a base (limewater) and condensation of heavy metals and

their compounds. This can be performed in two ways:

- gas neutralization can be carried out in the wet stage after filtration, the neutralization products being carried off with the washing water and solid wastes, e.g. fly ash;
- acid gas neutralization before filtration in the dry stage for dry, semi-dry and semi-wet procedures.

3.6.2. Purging gaseous effluents by chemical washing

The gaseous effluent released from mud burning in pyrolysis installations was directed via two successive modules, with containers with solutions of substances, which should retain by dosing and eliminating, the identified fumes by physical and chemical analysis and elementary analysis of bio-fuel.[5],[6],[7]

Washing containers contain the following solutions:

- ACN – sulphuric acid 1%;
- SO_2 – disodium tetrachloro Hg;
- CN – sodium hydroxide 0.01 N;
- NO_2 – Griess reactive (mixture of sulphonylic acid with α -naphthylamine);
- R-SH – silver nitrate 1%;
- Cl_2 – potassium iodine 2%;
- H_2S – cadmium acetate 5%;
- NH_3 – sulphuric acid 0.1 N;
- HA - nitrant mixture (H_2SO_4 conc. + HNO_3 conc. 1:1);
- $HMnO_4$ - sulphuric acid 10%;
- CO_2 – barium hydroxide.

After having gathered the gases resulted from burning the fuel, under various conditions of temperature of the burning area, we made the following observations: 90% of fumes were retained during the first absorption stage and a total purging of some 97% after completing the second absorption stage.

4. Conclusions

Owing to the elementary composition and heating power, close to those of conventional fuels, some organic waste in the chemical industry can be used as fuel in incineration installations with a view to producing energy.

The chemical, physical and energetic properties of solid waste, originated from biological

purification stations, make them suitable for mixtures in construction material industry. The direct consequence of replacing coal powder from standard ceramic mixtures with this material is lower energy consumption in burning ovens and implicitly lower prices of final products.

Incinerating this fuel required a supplementary supply of energy, e.g. natural gas, both to initiate burning until reaching 200°C, and to avoid amine emissions and unpleasant smelling gases, then, the system will work on a self-thermal basis.

The increase initial temperature of burning areas generates, at over 200°C, an optimised combustion, hence at 800°C, fuel burning gases contain mainly molecular nitrogen, nitrogen dioxide, sulphur dioxide, cyanides. Moreover, amines disappear completely, aromatic hydrocarbons, sulphuretted hydrogen, ammonia, alkyl hydrosulphide, organic cyanide compounds.

The efficient purging of burning gases may combine or apply separately one of the following methods:

- gas recycling through a burner provided with a one-piece cylinder, filled with absorbent ceramic slag;

- chemical washing of effluent in solution bath which react to oxides, aldehydes, ketones, tars, aromatic hydrocarbons, etc. found in burning gas composition;

- solid waste of bio-fuel burning – as they consist of fly ash, reaction products (salts), reagents in excess (lime, etc.) to which residue in the heating chamber of the burning installation is added – is accepted for the disposal procedure of burying or, according to its composition, to improve or fertilise agricultural land degraded due to acidity or excessive leaching.

References:

1. Aris, M.S., Hassan, S., Development of thermal insulation material from oil palm waste, *On-Line Proceedings WSEAS (EEESD'05)*, Vouliagmeni, Athens, Greece, July 12-14, 2005;
2. Băra I., Stefan N., Bucureşteanu Maria, The chemical pollution a selective factor in the evolution and adaptation of plants. *Evolution and Adaptation*, Cluj, 1991, 17-26;
3. Bucureşteanu Maria, Niţă, Marilena, Catană C., Reziduurii industriale în ecosisteme amenajate. *Lucr. Conf. Naţ. de Ecologie Arad, Ziridava, XVII*, 580-583
4. Bucureşteanu Maria, Biocombustibili din masă bacteriană - parte a unor mixturi valoroase energetic și economic, *Lucr. Congr. Naţ. „Prezent și perspectivă în biotehnologiile mileniului trei”*, Bucureşti, 2003;
5. Cotrău M., Butuc A., *Toxicitatea gazelor și vaporilor*, M.I.C., Iași, 2004;
6. Durand J.P., 1996, *Traitements des déchets spéciaux industriels*, Séminaire ATEE;
7. Lambisto G., *Environnement et Technique*, 1994, p.29-31;
8. Leroy J.B., *Les déchets et leur traitement* - Presses Universitaires de France, 1994;
9. Mladen Stanojevic, Sanja Vranes, Iskender Gokalp, Preliminary Remarks on Socio-Economic Impacts of Biofuel Production and use in Europe, *On-Line Proceedings WSEAS (EE 06)*, Chalkida, Evia Island, Greece, mai 8-10, 2006
10. Neamțu, G., *Biochimie ecologică*, Ed. Tehnică București, 1983;
11. Pătrașcu R., Minciuc E, Comparative analysis of different combined heat and power generation: fuel cells, gas turbine, internal combustion engine, *On-Line Proceedings WSEAS (EEESD 08)* Algarve, Portugal, June 11-13, 2008
12. Zhengmao Y, Zhijun L., Habib M., Lean Burn Engine Control for Fuel Economy and Exhaust Aftertreatment, *On-Line Proceedings WSEAS (EED 07)*, Tenerife, Spain, Dec. 14-16, 2007.