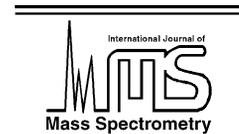




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Combustion and carbonisation exhaust utilisation in electric discharge and its relation to prebiotic chemistry

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Abstract

The municipal waste carbonisation inside a high temperature combustion chamber using direct heating by exhaust gas flow in an oxygen free atmosphere is an interesting alternative in the waste management scenario. The process has a lot of similarities with biomass pyrolysis. During carbonisation inside an oven at lower temperatures ($\sim 350^\circ\text{C}$) the main process is cracking, producing liquid hydrocarbons as levoglucosane and similar tar compounds, then at higher temperatures ($\sim 650^\circ\text{C}$) hydrogen is formed, while at very high temperatures ($\sim 950^\circ\text{C}$) carbon char/active carbon is formed instead of ash. The heat from the process can be recuperated.

The method for flue gas cleaning with possible application to combustion and carbonisation process uses non-thermal plasma based pilot system for 50–250 m³/h of gas flow. The applied method very efficiently cleaned the exhaust gas from a variety of non-wanted compounds, utilising whole combustion exhaust. CO₂ removal efficiency was as high as 40–99%. The process is connected with nitrogen fixation, removal of NO_x, VOC, PAH, –SH and SO_x, PCDD, PCDF and other is done with high efficiency and without wastewater production. The final solid amino acids condensation product (proteinoid) made in electric discharge seems to be convenient as a nitrogen containing fertiliser. (Int J Mass Spectrom 223–224 (2003) 613–625) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Combustion chamber; Pyrolysis; Gas discharge; Exhaust cleaning; Fertiliser

1. Introduction

Millions of tons of waste are produced world-wide every day. Waste has become a critical problem for industrial society, particularly in big cities and densely populated areas. However, still only about 10% of waste is recycled, most of it goes to landfill (64%)

or is incinerated (18%). However, disposal capacities continue to decrease in spite of the reduction in the volumes of waste produced.

In incineration, (partly) combustible waste, usually containing carbon, reacts with oxygen from air. The oxidation reaction takes place at high temperature, the main products being CO₂, H₂O, some SO₂ and non-combustible residue (ash). Supplemental fuel is required to reach the high temperature needed. Since

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solid waste varies in composition, it is virtually impossible to combust solid waste with a stoichiometric amount of air. In practice, excess air is used, which affects the temperature, the efficiency of eventual heat recovery, and the composition of the combustion products. In general, excess air may range from 50 to 200%. The main problems are linked to air and water pollution and are caused by components in the waste that are emitted (heavy metals oxide aerosol in sub-micron range) as well as compounds that are formed during the combustion process (dioxins, HCl, NO_x, etc.). Air pollution control remains a major concern in the implementation of incinerator. Standard methods of flue gas cleaning comprise:

- acids (HCl and SO_x) removal using injection of lime & water;
- non-selective catalytic reduction for NO_x removal on the bases of ammonium spray;
- particulate removal using electrostatic precipitator or bag filters followed by dioxin removal from collected fly ash after-treatment by heating at oxygen free atmosphere.

Alternative method of combustion exhaust cleaning using non-thermal plasma systems for gas flow of about 100 m³/h was tested for several exhaust types relative long time by our group, the results were described in [1]. The energy consumption for conversion of 1 m³ of the combustion exhaust into solid amino acids condensate is 2.3–4.7 W h/m³, i.e. 8.3–16.9 kJ/m³.

The use of non-thermal plasmas for incinerator flue gas cleaning was tested by [2] as an early application for the technology. Incinerators have flows ranging from approximately 2000 m³/h for small specialist incinerators (such as for burning medical waste) to up to approximately 200,000 m³/h for large municipal solid waste (MSW) incinerators. The specific energy for exhaust cleaning was of 33.3 W h/m³ (or 120 kJ/m³) and percentage destruction higher than 85%.

The municipal waste carbonisation inside high temperature combustion chamber using direct heating by exhaust gas flow in oxygen free atmosphere is an alternative to waste incineration. Carbonisation

in comparison to incineration of waste creates only two molecules of CO₂ instead of 10 molecules from one average molecule of waste. The process has a lot of similarities with biomass pyrolysis [3]. At lower temperatures (~350 °C) the main process is cracking producing condensable liquid tar compounds, then at temperatures (~650 °C) hydrogen is formed, at high temperatures (~950 °C) the carbon char/active carbon is formed instead of ash. In spite of several advantages the carbonisation of waste is rarely used because of environmentally hardly acceptable gas exhaust.

This was the reason we focus our attention to complex treatment of carbonisation exhaust. Non-thermal plasma-based technique offers an innovative approach to this subject and was tested by several authors [4–9]. A multifunctional dry gas cleaning pilot system for 50–250 m³/h of gas flow was applied; the system uses spontaneously pulsing transition type of discharge. The applied method cleaned very efficiently the exhaust from variety of non-wanted compounds, utilises CO₂, produces liquid hydrocarbons in process similar to hydro cracking method, produces proteinoid condensate suitable for use as fertiliser, what also improve the running cost of method. The final carbonisation product, active carbon, was tested by several authors [10]. We have tested carbon for wastewater treatment and as additive to soil.

2. Experimental

2.1. Used discharge for non-thermal plasma generation

The spontaneously regularly pulsing direct current electric discharge in streamer to spark transition regime was used. The discharge operates in corona geometry; synergetic effect of electrode surface catalysis is present in discharge gap. The strongly shining streamer channels migrate quickly along the stressed electrode of each discharge tube.

The multifunctional discharge system used for the tests on pilot scale operates on gas flow volume of

50–250 m³/h and comprises in discharge system plurality of 24 discharge tubes connected parallel each other. One discharge chamber consists of the copper rod with an internal thread (stressed electrode) and coaxial cylinder (non-stressed electrode) with inter-electrode distance of 6 mm. The length of one discharge tube is 50 cm.

High voltage source with dc high voltage of both polarities up to 20 kV, maximum power 600 W and maximum current 30 mA was applied for discharge generation.

2.2. Combustion and carbonisation oven for waste processing and exhaust production

The carbonisation chamber is heated directly using exhaust produced in natural gas oven. The oven is able to burn 10 m³ of gas per hour. Ambient air, used as oxidant, is naturally sucked through the vent in the height of burners. This results to almost stoichiometric combustion, with minimal concentration of oxygen in the flue gas. The carbonisation zone is placed 10 cm above burners; its total volume is 24 dm³. The temperature in the combustion zone can reach 975 °C, produced flue gas 950 °C. A carbonisation process of selected municipal waste arises in carbonisation zone in oxygen free atmosphere. When waste is heated, first volatile part is evaporated, then when the temperature reach 350 °C the thermal cracking starts. In this process the hydrocarbons with lower chains are released. At 500 °C smaller hydrocarbons and its radicals and at 650 °C hydrogen are produced. The waste contains large amounts of water and combustion exhaust additionally CO₂. It together expands the formed carbon char to activated carbon.

Gas mixture exhausted from carbonisation oven contains standard combustion exhaust, gas and liquid phase hydrocarbons and its radicals, oxidants and heterocyclic compounds, sulphur containing compounds, aerosol and some other components. In the subsequent distillation unit the separation of hydrocarbons from gas into the liquid phase take place producing liquid fuel. The process is connected with the recuperation of heat.

2.3. Gas flow and discharge system

The rest gases after distillation are piped to the discharge equipment. In the discharge equipment electrons with temperature up to 6 eV, photons with temperature up to 2000 °C, free radicals, dissociated and excited molecules are formed, but the ambient flowing gas doesn't increase its temperature. Inside discharge gap due to electric activation and catalysis of electrodes water dissociation into H and OH take place and various volume plasmochemical reactions will take place leading to formation of amino acids condensate and other life important organic compounds due to carbon dioxide and nitrogen fixation.

The gas flow system is designed for a gas flow volume from 50 to 250 N m³/h. It is composed of

- two Benzing type fans with low pressure change (Δp from 50 to 300 Pa), first one ACP 160-12 with maximum flow 500 m³/h, second one RR 160, with maximum flow 435 m³/h;
- two flow meters PREMA RPT3 with calibrated measuring range from 10 to 250 m³/h, certified uncertainty 1–2%, with pressure decrease from 5 to 110 Pa;
- discharge chamber.

All components are connected with cylindrical pipes with inner diameter of 15 cm. The schema of pilot scale system is on Fig. 1.

2.3.1. Diagnostic systems

On line diagnostic of air flow parameters is made using 2 ps of Testo 454 before and after discharge system. This make possible to measure gas flow velocity and its distribution, total gas flow evaluated from gas flow velocity distribution, static and dynamic pressure, temperature and humidity.

Gas phase sampling was done using iso-kinetic method. The sample flow into IR gas cells was 30 L/min both before and after discharge reactor. The gained samples were analysed by IR absorption spectrometry.

The infrared absorption spectrometry as a powerful method for identification of various materials in gas,

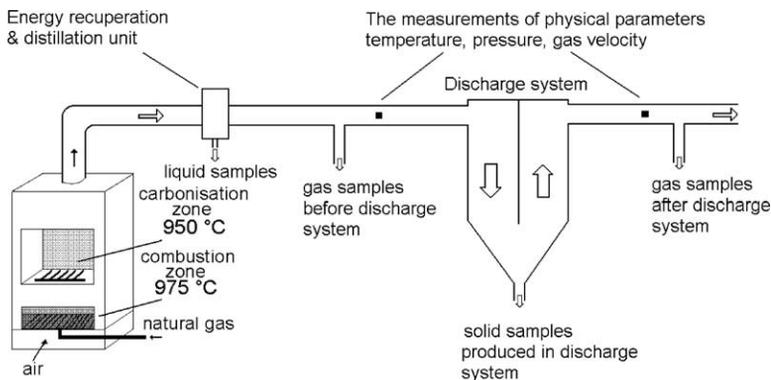


Fig. 1. The scheme of oven used for carbonisation of selected municipal waste and pilot scale discharge system for flue gas cleaning built for gas flow volume of 50–250 N m³/h.

liquid, solid phase and surfaces was used for analysis in all measurements. We have used dispersive IR absorption spectrometer Specord M80 of Zeiss in the range 4000–200 cm⁻¹. Carbon dioxide, carbon monoxide and nitrogen oxides are compounds with intensive infrared absorption bands. Slightly less sensitive is this method for hydrocarbon analysis. Due to action of electrical plasma various plasmochemical reactions take place. The final reaction products and intermediates are in many cases unknown. The infrared spectroscopy is very suitable method for its analysis. We have used various IR techniques. The gases were analysed in 10 cm gas cell with KBr, CaF₂ or KRS5 windows. Liquids were analysed in liquid cell with variable path-length and KRS5 windows. For solid samples the KBr pellet technique was used. The sample is mixed with the KBr powder in the ratio approximately 0.2–1:100 and together pulverised in the vibration mill. The mixture is then pressed under pressure about 22 MPa to the metal ring and by this way the pellet is formed. From pellet the spectra are scanned. This method was used for analysis of solid product formed inside discharge system as well as for analysis of final carbon containing product from carbonisation of waste inside oven.

The high performance liquid chromatography (HPLC) is very sensitive method for the separation and analysis of many types of amino acids, peptides, and protein substances. We have used this method for

analysis of solid product formed in discharge system in the laboratory of Professor B.M. Rode. To detect several basic amino acids present in the product, we have used an Agilent 1100 apparatus with diode array detector by means of comparison of peak retention times to those of pure amino acids using UV-Vis spectroscopic identification at 195 nm for samples and 550 nm for reference. The solid samples from discharge system were dissolved in ultra pure water (0.01681 g in 1 mL). Unfortunately, the samples were not completely dissolved even after several minutes of shaking and subsequent addition of 1 mL of 10% HCl. Method of direct separation was applied to this system. The best condition to analyse samples were using Agilent Hypersil ODS Column (5 μm/200 × 2.1 mm) with the mobile phase consisting of: solvent A (buffer) – 10 mM KH₂PO₄, 5 mM Na⁺C₆H₁₃SO₃⁻ in ultra pure water, pH 2.5 adjusted by H₃PO₄ and solvent B—acetonitrile gradient grade (FLUKA). The flow rate of mobile phase 0.35 mL/min and column temperature 35 °C. The applied gradient was

- 0–5 min: 100% solvent A;
- 5–20 min: 100–80% solvent A, 0–20% solvent B (linear growth);
- 20–22 min: 80% solvent A, 20% solvent B;
- 22–25 min: 80–100% solvent A, 20–0% solvent B (linear decrease);
- 25–35 min: 100% solvent A.

The Proton-Reaction-Transfer Mass Spectrometry (PTR-MS) technique was recently developed in the laboratory of Professor W. Lindinger, Institute of Ion Physics, University of Innsbruck, for the purpose of on-line trace gas monitoring with concentrations in range from pptv to ppmv. The method is very effective for monitoring low concentrations of volatile organic compounds (in range from pptv to ppmv).

In our case the best alternative for analysis of low concentration hydrocarbons were on line gas phase analysis of gases before and after discharge system using PTR-MS. As this method was not possible to apply (pilot system is installed in Bratislava and PTR-MS system in Innsbruck) we have as only alternative used following method. Our solid proteinoid product from discharge system has absorption ability. A part of gas and liquid products are attached in this solid product. The product was produced in Bratislava and analysed in Innsbruck. We have used so-called headspace measurement, where the solid sample from discharge system was dissolved in the water. The concentration of saturated vapour of compounds present in this solution was measured. The buffer gas and water used as solvent was also analysed for background information. The mass spectra were measured in cycles (one cycle is the mass 21 and the masses from 30 to 160 amu). Each mass was measured 0.2 s and one complete cycle took 68.38 s. During the first 20 cycles (1–20), there was no solution in the vessel, so only pure nitrogen from pressure tank enters the spectrometer. Later (cycles 23–49), we have filled the vessel with the pure water, and finally, with the solution of analysed sample (cycles 58–96).

3. Results and its discussion

The selected municipal waste carbonisation inside high temperature combustion chamber using direct heating by exhaust gas flow was applied for waste processing. It was possible to process about 4–10 kg of crushed selected municipal waste, while the full time of processing was close to 2 h. The process has a lot of similarities with biomass pyrolysis. First the waste

was dried, then at temperatures $\sim 350^\circ\text{C}$ the main process was cracking producing condensable liquid tar compounds, then at temperatures $\sim 650^\circ\text{C}$ hydrogen is formed, at high temperatures $\sim 950^\circ\text{C}$ the carbon char/active carbon is formed instead of ash.

To study in details the carbonisation processes in real conditions, we have made a group of measurements of carbonisation process applied to several types of waste. The produced carbonisation gases undergo cleaning inside pilot scale non-thermal plasma based system. We have tested several typical types of waste, mostly rest of food as bones, bread and rolls, eggs shells, chicken rests, potato peels, leaves, rests of vegetables, nut shells, garlic rests, plastic (without chlorine) and a mixture of waste. The composition of carbonisation exhaust differs with time, temperature, i.e., with the stage of carbonisation process. Additional changes occur due to type of processed waste, after distillation, after non-thermal plasma-based processing.

At present stage of analysing system, it was possible to us to make only part of planned methods. It means that we were able to analyse collected solid product from discharge system. At present the gas phase analysis was made only using IR absorption spectrometry of samples introduced into gas cells what limits the number of measurement to one measurement comprising all sorts of analysis per a day.

Full period of measuring process was 3 months. During this time we have collected and analysed carbon product from carbonisation oven for each type of waste separately. Carbon product was analysed permanently every day using KBr pellet technology.

In the case of solid discharge product we have collected this product, but to take up the sample of this product it was necessary to open the discharge system, what was possible to make only on the end of measurements (i.e. after 3 months). Additionally from each measurement the amount of solid product was relative small. This was the real reason for setting the length of measurement period to 3 months. During 3 months (i.e. about 150 h of discharge works) we have collected about 50 g of solid product. It means that it was not possible to analyse solid product from discharge

system for each type of waste separately, only the mixture of solid products formed in discharge system from carbonisation gases of all studied types of waste.

Additionally, the distillation unit did not work properly during first period of measurements, what caused that it was not possible to analyse separately the liquid product. But a part of this product was mixed with solid product inside discharge system. This product was analysed using KBr pellet technique in Bratislava. Additionally this product was analysed using HPLC method for amino acid content and by PTR-MS analysis for trace gases adsorbed in solid product in Innsbruck. Both methods were applied to water solution obtained by macerating of product in water.

In Fig. 2, we see IR absorption spectra of exhaust gases after carbonisation oven (before distillation and heat recuperation unit), before and after discharge system. From spectra before and after discharge system, we can see the very high efficiency of CO₂, CO, gas phase CH_x and NO₂ removal (close to 99%).

In Fig. 3, we see IR absorption spectra of solid product from discharge system after action electric discharge on carbonisation gases. We can see small difference in composition of product on stressed and

non-stressed electrode. In the case of stressed electrode dominates proteinoid character of product. On non-stressed electrode product we see also a part of tar liquid products (levoglucosane) separated from gas by electric wind and changed to solid due to polymerisation induced by the discharge action. Comparison of solid samples with calibration IR absorption spectra of 27 pure amino acids help us to find amino acid components of solid product. Two very probable ones (arginine and lysine) we see on Fig. 4.

To know more about solid polymeric proteinoid product formed inside discharge system, the product was additionally investigated using HPLC method. This method gives the possibility to know amino acidic component of proteinoid formed in discharge. The results that we have gained from the comparison of peaks from HPLC analysis with peaks from pure compounds are summarised in Table 1.

As we can see, the retention time of several amino acids (glycine, aspartic acid and serine) is very short, so in the chromatograph of our sample the overlaying of injection and sample peaks occurs and it causes that we are not able analyse them. They could be hidden in the injection peak, so to detect these compounds,

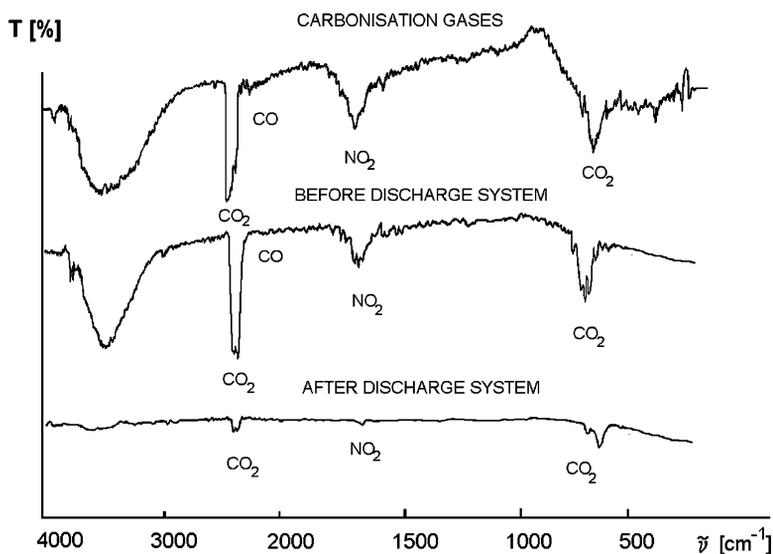


Fig. 2. IR absorption spectra of exhaust gases from top after carbonisation oven, before and after discharge system made in gas cell with KBr windows.

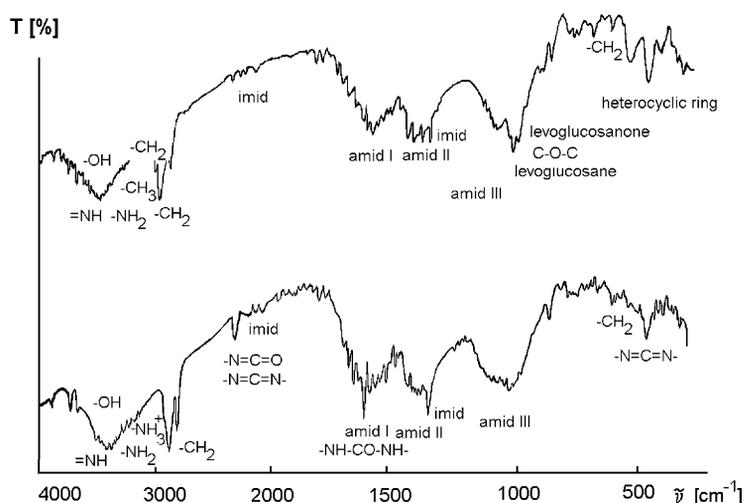


Fig. 3. IR absorption spectra of solid product collected from non-stressed electrode (on the top) and stressed electrode (on the bottom) made using KBr pellet technique.

we would have to evolve new separation method (different composition of mobile phase, different gradient applied) or to use the derivation method. So, the absence of their peaks is not the evidence of their absence. It is the case of lysine, the interference of lysine peak with unknown impurity occurs.

Additionally we must also emphasise, that the product was not completely dissolved before the analysis. On the other hand, the coincidence of peaks for our sample and pure compounds (alanine, arginine) is still not the evidence of the presence of these compounds. This evidence is in the case of arginine

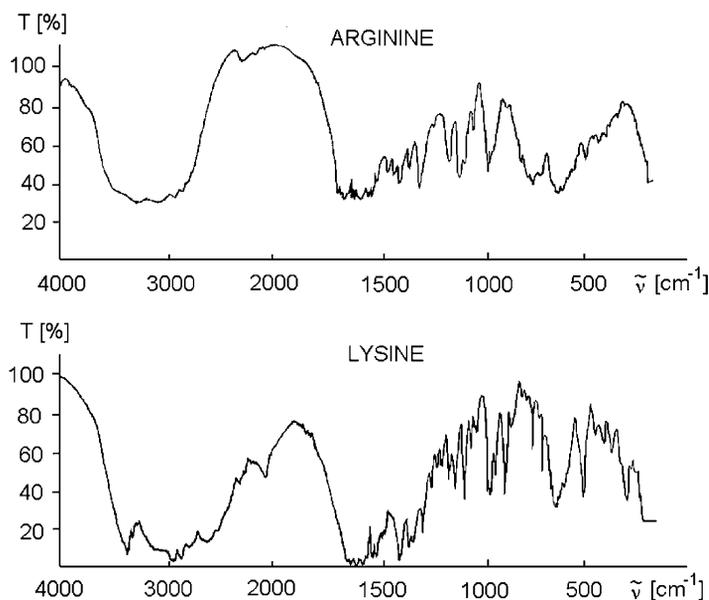


Fig. 4. IR absorption spectrum of arginine and lysine made using KBr pellet technique.

Table 1

The results from the preliminary HPLC analysis of product from discharge system

Amino acid	Retention time (min)	Coincidence with a peak in analysed sample
Glycine	2394	Uncertain
Alanine	3445	Yes
Lysine	12,204	Uncertain
Histidine	11,527	No
Aspartic acid	2243	Uncertain
Arginine	15,251	Yes
Serine	2255	Uncertain
Leucine	17,324	No
Isoleucine	16,904	No
Valine	13,787	No

strongly supported by the results from IR analysis of the same sample.

PTR-MS analysis gives a possibility to analyse very low concentration of several VOC present in studied system. This fact enables us to analyse gases (and liquids) present due to absorption process in solid product formed in discharge system after action of discharge on carbonisation gases. The disadvantage of this method is difficult analysis of such a complicated spectrum. There are hundreds possible compounds, which can form ions with masses we detected. But it help us, that we were able to detect only compounds, which satisfy following criteria: (1) they must have higher proton affinity than water, (2)

they must be soluble, but cannot decompose in the water, (3) their Henry's law constant ($\text{atm m}^3/\text{mol}$) must be high enough. Additionally, because of the conditions in the plasma reactor, we can also exclude air/moisture and light sensitive compounds. The information that we have extracted from these measurements is summarised in the Table 2.

The carbonisation residuum (carbon char) from oven has the character of activated carbon. In the case of each treated waste (bones, bread and rolls, eggs shells, chicken rests, potato peels, leafs, rests of vegetables, nut shells, garlic rests, plastics, mixture of waste without glass and metal) the char remains its texture from original material. The analysis made by IR absorption spectrometry using KBr pellet technique shows differences in the presence of mineral components and form how carbon intercalates with mineral components in produced carbon char. First it is necessary to know, that carbon bonded together with single bonds have no absorption bands in IR spectra. Only presence of C=C conjugated and disorder in carbon body due to presence of radicals is seen in IR spectra. The biggest difference is seen between spectra of bones (top) & vegetable rests (bottom) as we see from Fig. 5. In the case of bones dominates calcium and phosphorus groups bonded to carbon as intercalates. In the case of vegetable rests the conjugated carbon chains, rests of sugar-like structures (C–O–C), rest of magnesium from chlorophyll bonded

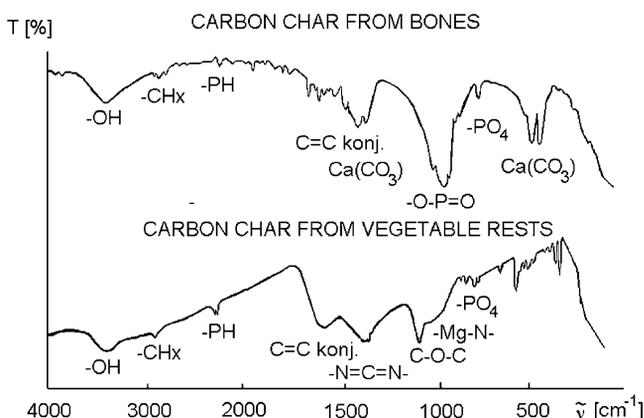


Fig. 5. IR absorption spectra of carbonisation product from bones (top) and vegetable rest (bottom) made by KBr pellet technique.

Table 2

PTR-MS analysis of gas components absorbed in solid proteinoid discharge product following dissolution in water and subsequent vapourisation

Mass	Concentration c (ppbv)	Possible source ions	Possible compounds with calculated concentration in liquid phase (mol/L) ^a
33	5.7	CH ₅ O ⁺	Methanol (1.3E-06)
41	4.4	C ₃ H ₅ ⁺	Fragments of various HCs
42	3.2	C ₂ H ₄ N ⁺	Acetonitrile (9.3E-08)
45	84.0	C ₂ H ₃ O ⁺ , CH ₃ N ₂ ⁺	Vinyl alcohol, acetaldehyde (1.3E-06) or 1,2-ethanediol (0.0014) ^b
54	0.4	C ₃ H ₄ N ⁺	Acrylonitrile (2.9E-09)
56	3.1	C ₃ H ₆ N ⁺	2-Propyn-1-amine (1.9E-06)
59	42.5	C ₃ H ₇ O ⁺	Acetone (1.1E-06)
60	1.7	C ₂ H ₆ NO ⁺ , C ₃ H ₁₀ N ⁺ , C ₂ H ₅ O ₂ ⁺ , C ₃ H ₉ O ⁺ , C ₂ H ₈ NO ⁺	Methyl formamide (8.647E-05), acetamide (0.00015),...
63	0.9	C ₂ H ₇ S ⁺ , C ₂ H ₇ O ₂ ⁺	1,2-Ethanediol (0.000015), ethylthiol,...
68	0.4	C ₄ H ₆ N ⁺ , C ₃ H ₂ NO ⁺	Methyl acrylonitrile (1.619E-09) or 3-butenenitrile (9.975E-09)
69	13.8	C ₄ H ₅ O ⁺	3-Butyn-2-one, but-3-ynal,...
70	1.9	C ₄ H ₈ N ⁺ , C ₃ H ₄ NO ⁺	Butyronitrile (3.6E-08), propanenitrile, or 2-oxo, propiolamide
73	29.7	C ₃ H ₅ O ₂ ⁺ , C ₄ H ₉ O ⁺	Butyraldehyde (2.6E-07), methyl ethyl ketone (5.2E-07), acrylic acid (8.0E-05), tetrahydrofuran (4.2E-07)
74	2.2	C ₄ H ₁₂ N ⁺ , C ₃ H ₈ NO ⁺ , C ₂ H ₄ NO ₂ ⁺ , C ₂ H ₄ NS ⁺	Propionamide (4.9E-08), acetoxime (2.8E-08),...
81	0.6	C ₄ H ₅ N ₂ ⁺	Pyrazine, pyrimidine or pyridazine (2.1E-07 all three ^c)
83	17.4	C ₄ H ₇ N ₂ ⁺ , C ₆ H ₁₁ ⁺ , C ₅ H ₇ O ⁺	1-Methylpyrazole (2.2E-07), 1-aminopyrrole, 2H-pyran, 2-cyclopentenone,...
84	4.0	C ₅ H ₁₀ N ⁺ , C ₄ H ₆ NO ⁺ , C ₃ H ₆ N ₃ ⁺	Trimethylacetone (5.6E-08), 5-methylisoxazole (6.4E-08), 4-aminopyrazole (0.003),...
87	5.7	C ₅ H ₁₁ O ⁺ , C ₄ H ₇ O ₂ ⁺ , C ₆ H ₁₅ ⁺ , C ₄ H ₁₁ N ₂ ⁺	1-Pentanal (3.9E-08), crotonic acid (1.3E-05), 2-pentanone (6.8E-08),...
88	0.5	C ₅ H ₁₄ N ⁺ , C ₄ H ₁₀ NO ⁺ , C ₃ H ₆ NO ₂ ⁺	Butyramide (2.5E-05), amylamine (2.1E-08), morpholine (4.3E-07),...
97	7.1	C ₅ H ₅ O ₂ ⁺ , C ₇ H ₁₃ ⁺ , C ₆ H ₉ O ⁺ , C ₅ H ₉ N ₂ ⁺	2-Cyclohexene-1-one (2.1E-08), furan-3-carboxaldehyde (3.7E-08),...
98	0.9	C ₆ H ₁₂ N ⁺ , C ₅ H ₈ NO ⁺ , C ₄ H ₄ NO ₂ ⁺	Capronitrile (7.5E-08), 1H-pyrrole-2,5-dione (2.6E-06), furfurylamine (1.2E-05),...
99	1.9	C ₄ H ₃ O ₃ ⁺ , C ₆ H ₁₁ O ⁺ , C ₅ H ₇ O ₂ ⁺ , C ₅ H ₁₁ N ₂ ⁺ , C ₅ H ₇ S ⁺	5-Hexen-2-one (2.2E-08), cyclohexanone (2.1E-07), 3-hexyn-1-ol,...
101	3.8	C ₄ H ₅ O ₃ ⁺ , C ₅ H ₉ O ₂ ⁺ , C ₆ H ₁₃ O ⁺	Hexanal (1.8E-08), 2-hexanone (4.1E-08), D-valerolactone (2.8E-08),...
107	2.3	C ₇ H ₇ O ⁺ , C ₄ H ₁₁ O ₃ ⁺ , C ₈ H ₁₁ ⁺ , C ₃ H ₇ O ₄ ⁺	Diethylene glycol (0.0011), D(L)-glyceric acid,...
111	4.3	C ₆ H ₇ O ₂ ⁺ , C ₈ H ₁₅ ⁺ , C ₇ H ₁₁ O ⁺	2-Acetylfuran (4.4E-07), benzenediol, <i>o</i> (<i>p</i>)-benzosemiquinone,...
112	0.6	C ₄ H ₆ N ₃ O ⁺ , C ₅ H ₆ NO ₂ ⁺ , C ₆ H ₁₀ NO ⁺ , C ₅ H ₁₀ N ₃ ⁺ , C ₇ H ₁₄ N ⁺	Pyrrrole-2-carboxylic acid (0.0033), histamine (0.0011), heptanenitrile,...

Table 2 (Continued)

Mass	Concentration <i>c</i> (ppbv)	Possible source ions	Possible compounds with calculated concentration in liquid phase (mol/L) ^a
113	1.2	C ₆ H ₉ O ₂ ⁺ , C ₄ H ₅ N ₂ O ₂ ⁺ , C ₇ H ₁₃ O ⁺ , C ₆ H ₁₃ N ₂ ⁺ , C ₅ H ₉ N ₂ O ⁺ , C ₅ H ₅ O ₃ ⁺	Furan-3-carboxylic acid (1.1E–05), 4-ethoxypyrazole (4.1E–06), ...
115	2.6	C ₆ H ₁₁ O ₂ ⁺ , C ₇ H ₁₅ O ⁺ , C ₈ H ₁₉ ⁺ , C ₆ H ₁₅ N ₂ ⁺ , C ₄ H ₇ N ₂ O ₂ ⁺	2,5-Hexanedione (5.9E–05), piperazine, 1,4-dimethyl-(0.00024), ...
125	1.3	C ₇ H ₉ O ₂ ⁺ , C ₉ H ₁₇ ⁺ , C ₆ H ₇ N ₂ O ⁺ , C ₇ H ₉ S ⁺	<i>p</i> -Methoxyphenol (2.3E–06), 2,5-hexanedione, <i>o</i> -toluenethiol, ...
126	0.5	C ₆ H ₈ NO ₂ ⁺ , C ₇ H ₁₂ NO ⁺ , C ₅ H ₈ N ₃ O ⁺	Furanmethamine, <i>N,N</i> -dimethyl-(1.7E–07), <i>N</i> -methyl-hydroxypyrid-4-one (4.1E–05), ...
127	1.0	C ₈ H ₁₅ O ⁺ , C ₆ H ₇ O ₃ ⁺ , C ₉ H ₁₉ ⁺ , C ₇ H ₁₁ O ₂ ⁺ , C ₆ H ₁₁ N ₂ O ⁺	4-Propoxypyrazole (2.4E–06), 3-furancarboxylic acid, methylester (2.9E–08), levoglucosenone, ...
129	4.8	C ₈ H ₁₇ O ⁺ , C ₇ H ₁₃ O ₂ ⁺ , C ₈ H ₅ N ₂ ⁺ , C ₆ H ₉ O ₃ ⁺ , C ₆ H ₁₃ N ₂ O ⁺	3,5-Heptadione (8.1E–05), 1,3-dicyanobenzene (9.5E–06), 1-octanal, ...
130	0.5	C ₈ H ₂₀ N ⁺ , C ₉ H ₈ N ⁺ , C ₆ H ₁₆ N ₃ ⁺ , C ₆ H ₁₂ NO ₂ ⁺	Cycloleucine (0.00032), 2-piperidinecarboxylic acid (0.00020), ...
137	0.4	C ₁₀ H ₁₇ ⁺ , C ₈ H ₉ O ₂ ⁺ , C ₈ H ₁₃ N ₂ ⁺ , C ₅ H ₁₃ O ₄ ⁺	Phenylacetic acid (9.8E–06), 2-pyridinepropaneamine (0.00028), ...
139	0.5	C ₆ H ₇ N ₂ O ₂ ⁺ , C ₇ H ₇ O ₃ ⁺ , C ₈ H ₁₁ O ₂ ⁺ , C ₇ H ₁₁ N ₂ O ⁺ , C ₉ H ₁₅ O ⁺	2-Phenoxyethanol (1.1E–05), <i>p</i> -ethoxyphenol (1.1E–05), 1,3-benzodioxol-5-ol, ...
143	6.5	C ₈ H ₁₅ O ₂ ⁺ , C ₇ H ₁₁ O ₃ ⁺ , C ₉ H ₁₉ O ⁺ , C ₁₀ H ₂₃ ⁺ , C ₁₁ H ₁₁ ⁺	2,6-Dimethyl-4-heptanone (5.6E–08), homofuranol, 5-nonanone, ...
144	0.6	C ₁₀ H ₁₀ N ⁺ , C ₉ H ₂₂ N ⁺	1-Naphthylamine (5.4E–06), 5-aminononane, ...
157	7.0	C ₁₀ H ₂₁ O ⁺ , C ₁₀ H ₉ N ₂ ⁺ , C ₁₂ H ₁₃ ⁺ , C ₁₁ H ₂₅ ⁺ , C ₉ H ₁₇ O ₂ ⁺	4,4'-Dipyridyl (0.0028), decanal, <i>D</i> (L)-menthol, 4-decanone, ...
158	0.7	C ₇ H ₁₂ NO ₃ ⁺ , C ₈ H ₁₆ NO ₂ ⁺ , C ₇ H ₁₆ N ₃ O ⁺ , C ₁₁ H ₁₂ N ⁺ , C ₁₀ H ₂₄ N ⁺	Butanenitrile, 4,4-diethoxy- (1E-05), tranexamic acid, 2,6-dimethylquinoline, ...

^a This concentration is calculated according to Henry's law from gas phase concentration of given compound, and of course only for those compounds, for which Henry's law constant is available. In many cases, there is more than one species that could contribute to given mass in spectrum, and we are not able to exclude them. Here, calculated liquid phase concentrations are theoretically maximum concentrations (100% contribution of given species to gas phase concentration of given mass).

^b In many cases, we are not able to choose only one possible compound contributing to production of ions of given mass. If there are more than two or three possible compounds, we decided to present only the most common or environmentally relevant species (for illustration).

^c These three heterocyclic compounds differ only by the position of nitrogen atoms in cycle, and their Henry's law constant is also almost identical, so this concentration can be used for all these compounds, even as their total concentration, because it is more probable, that all of them are in the sample.

to carbon through nitrogen (Mg–N–, –N=C=N–) are most important features of spectrum. Structures with phosphoric acid are present only in small amounts, probable from DNA and RNA of plant cells.

The produced carbon char in all cases has amorphous character, what was supported also by scanned SEM photographs. From several magnification of SEM it was seen, those inside carbon are holes with radius changed in three order of magnitude. The walls of carbon cells were sub-nanometer sized. The active surface was $257 \text{ m}^2/\text{g}$ measured by BET method using absorption of N_2 . The estimated density of amorphous carbon sample was approximately $0.3 \text{ g}/\text{cm}^3$. Gained carbon char absorb also hydrogen coming from room temperature, details were not possible to estimate due to absence of appropriate diagnostics. The char is at present tested for wastewater treatment and as additive to soil improving vegetation growth for about 2 years.

4. Conclusions

As we have used in described system stoker fired type of oven, the waste treatment described in this article comprises in one system several forms (slow and fast pyrolysis, carbonisation) of work. The consequence was slowly changing exhaust composition during process development in total length of about 2 h, what put increased claims to exhaust treatment. Non-thermal plasma-based system seems to suit to such increased requirements. In the case of carefully separation of waste connected with recycling of all metal, glass, demolition, industrial and chemical waste it is possible to look on the rest part of waste as on biomass. It is truth that such rest “biomass” is possible to compost, but the large amount and possible biological contamination causes that incineration (in our case carbonisation) seems to be necessary. By comparing incineration and carbonisation, we have to see several aspects of this process.

In the case of incineration the energy of waste is fully converted to heat. To secure the constant level of energy release necessary for further energy re-use purposes the combustion should work in excess of

oxygen (200% stoichiometry). As the burning process is very non-homogeneous it causes:

- in the oxygen surplus zones the oxidation of metals creating it oxides (there are able to sublime already at temperature close to 500°C , what is very negative fact);
- in the oxygen shortage zones the formation of non-combusted compounds as polycyclic aromatic compounds PAH, dioxins PCDD, furans, PCDF.

In the case of carbonisation the waste is directly heated by combustion exhaust from help methane burner in combustion chamber in oxygen free atmosphere. It seems that such process must be disadvantageous, but it is not truth. The release of energy from waste is postponed to the temperature when cracking begins ($\sim 350^\circ\text{C}$). Then it is released as chemical not as energy of heat. The system create use-full liquid hydrocarbon (there are separated in distillation unit) suitable to be used as biofuel (levoglucosane and other components). The cracking itself is exothermic process (braking of chemical bonds), so the part of energy used earlier for heating of waste is possible to recuperate. The exhausts during this phase of process are similar to combustion exhaust enriched on large portion of rich variety of hydrocarbons. The treatment of such exhaust in non-thermal plasma systems was the main part of this article.

By increasing the temperature up to $\sim 550^\circ\text{C}$, the release of hydrocarbons decreases and the composition of exhaust changes to typical combustion exhaust. The treatment of typical combustion exhaust in non-thermal plasma systems we have already described in earlier articles [1,11,12,16–19]. The important property of exhaust treatment is the formation of life important organic compounds in non-thermal plasma-based systems of our construction.

Further heating of waste to temperature higher then $\sim 650^\circ\text{C}$ causes formation of hydrogen. It is again conversion of energy from waste to chemical energy of hydrogen. It is necessary to find most suitable way how to store the released energy from hydrogen. We see at least three possibility how to do it on line as follows:

- store of hydrogen in produced active carbon,
- use of produced hydrogen in fuel cells connected to system;
- conversion of hydrogen in non-thermal plasma-based system to more suitable liquid compound as is hydrazine.

The final active carbon char after release of all gas phase component is reached at temperature $\sim 950^\circ\text{C}$. The formed carbon was detailed analysed for several types of treated waste. The preliminary test of char use in future was tested for hydrogen storage, wastewater cleaning and as balancing additive to soil improving the vegetation growth.

The method of carbonisation exhaust cleaning in non-thermal based pilot system for $50\text{--}250\text{ m}^3/\text{h}$ of gas flow was tested in regime when the released gases are rich on compound produced during cracking (the most

negative phase of processing). The applied method cleaned very efficiently the exhaust gas from variety of non-wanted compounds and similar as in the case of only combustion exhaust, the system utilises gases to solid product. The efficiency of treatment is very high. CO_2 and NO_x removal efficiency vary in $40\text{--}99\%$. The process is connected as in the case of combustion exhaust with nitrogen fixation process. The final solid amino acids condensation product (proteinoid) made in electric discharge seems to have similar properties as the one produced in combustion exhaust described earlier [1,11,12,15]. The energy consumption for conversion of 1 m^3 of the gaseous exhaust into amino acids condensate is $2.3\text{--}4.7\text{ Wh/m}^3$, i.e. $8.3\text{--}16.9\text{ kJ/m}^3$.

The knowledge of cracking process during waste carbonisation gives us the possibility to understand some processes taking later place in discharge system

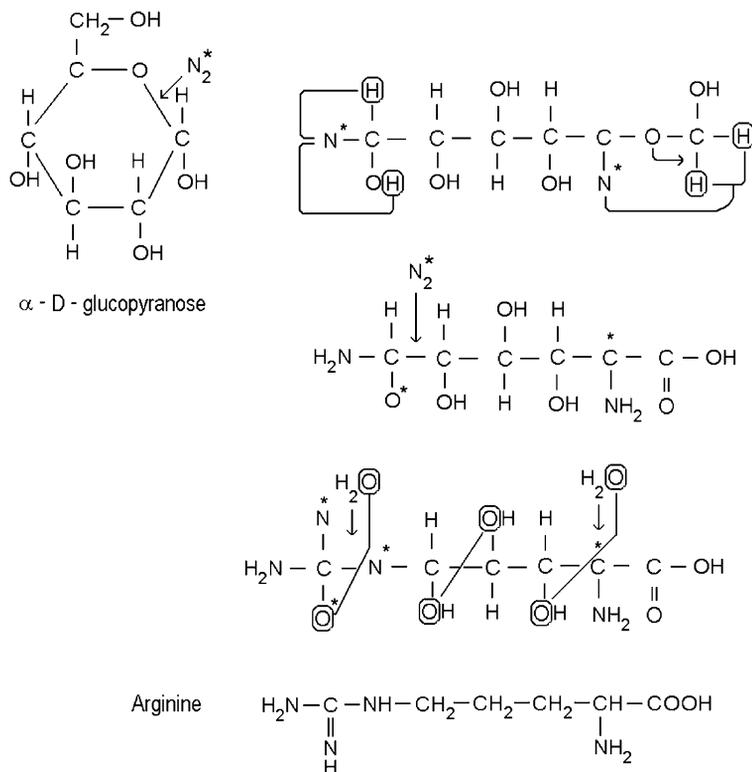


Fig. 6. Formation of arginine from α -D-glucopyranose in non-thermal plasma system.

during solidification of carbonisation exhaust. The large part of municipal waste is composed of several polysaccharides. Thermal de-polymerisation and cracking leads to formation of α -D-glucopyranose. A part of carbonisation gases is due to partial oxidation converted to levoglucosane or levoglucosanone that condense in distillation unit. A part remains unchanged and follow into discharge system. The reactions taking place inside non-equilibrium plasma conditions in electric discharge are strongly influenced by the presence of electric field and heterogeneous catalysis on the electrode surface. The involved chemistry during final product formation can be divided into three important steps: (1) activation, (2) formation of energy rich intermediate species, (3) final product formation. The most important activation step is excitation of molecular nitrogen by repeated electron impact in electric discharge using in total energy close to 6.5 eV. The described electronic state $N_2^*A^3\Sigma_u^+$ has a lifetime between 1.3–1.9 s [13] and that is why it can be involved with a great probability into chemical reaction.

By comparing HPLC results, IR spectra of product (Fig. 3), IR calibration spectra of arginine and lysine (Fig. 4) it comes out that the most probable amino acid in product is arginine. The formation of arginine from α -D-glucopyranose in electric discharge under influence of metastable excited molecular nitrogen $N_2^*A^3\Sigma_u^+$ is possible to see from following Fig. 6. Similar process applied on cyclohexanone we have published in [15].

Similar processes responsible for formation of amino acids in strong and middle reducing primitive atmosphere during origin of life in Earth were described by Miller [14]. Combustion as well as carbonisation exhaust are from the point of view of composition relevant to neutral pre-biotic atmosphere.

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