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NON-THERMAL PLASMA TECHNIQUE APPLIED TO WASTE CARBONIZATION

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Abstract

Pyrolysis in an inert atmosphere with direct heating was applied for thermochemical waste degradation. The system enables poly-generation of energy and materials (heat, hydrogen, liquid hydrocarbons), the amorphous nano-sized carbon is formed from the carbonized material. The method for flue gas cleaning uses non-thermal plasma based pilot system for 50-250 m³/hour of gas flow. The applied method cleaned very efficiently the exhaust gas from variety of non-wanted compounds, CO₂ removal efficiency is as high as 40-99% and is connected with solidification of gas into proteinoid polymeric material.

Introduction

Millions of tons of waste are produced worldwide every day. Waste has become a critical problem for industrial society, particularly in big cities and densely areas. However, still only about 10 % of waste are recycled, most of it goes to landfill (64 %) or is incinerated (18 %). The municipal waste carbonization inside high temperature combustion chamber using direct heating by exhaust gas flow in oxygen free atmosphere is an alternative to waste incineration [1]. Carbonization in comparison to incineration of waste creates only 2 molecules of CO₂ instead of 10 molecules from one average molecule of waste. During waste carbonization 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. Formed active carbon, was tested by several authors [2]. We have tested carbon for wastewater treatment and as additive to soil. In spite of several advantages the carbonization of waste is rarely used because of environmentally hardly acceptable gas exhaust. This was the reason we focus our attention to complex treatment of carbonization exhaust. Non-thermal plasma based technique offers an innovative approach to this subject and was tested by several authors [3-9]. A multifunctional dry gas cleaning pilot system for 50-250 m³/hour 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 [15-19], utilizes CO₂, [10-12] produces additional liquid hydrocarbons in process similar to hydro cracking method, produces solid proteinoid condensation product suitable for use as fertilizer and/or absorber material.

Experimental

The carbonization chamber is heated directly using exhaust produced in natural gas oven with stoichiometric combustion and almost oxygen free flue gas. The carbonization zone (maximum temperature 950°C is placed 10cm above burners (temperature 975°C) A carbonization process of selected municipal waste arises in carbonization chamber in oxygen free atmosphere. When waste reach 350°C first volatile part is evaporated, then the thermal cracking starts producing hydrocarbons. 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 carbonization 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. The process is connected with the recuperation of heat. The non-condensable exhaust gases after distillation flow to the discharge equipment through cylindrical pipes with inner diameter of 15cm. The necessary gas flow is produced with 3 fans (flow 500 m³/h, Δp from 50 to 300 Pa) and measured using flow meters PREMA RPT3 with calibrated measuring range from 10 to 250 m³/h. On line diagnostic of air flow parameters is made using 2 pc 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.

The multifunctional discharge system used for carbonization exhaust treatment operates on gas flow volume of 50-250 m³/hour and comprises in discharge system plurality of 24 discharge tubes connected parallel each other. The spontaneously regularly pulsing direct current electric discharge in streamer to spark transition regime was used. 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. The schema of pilot scale system is on Fig. 1

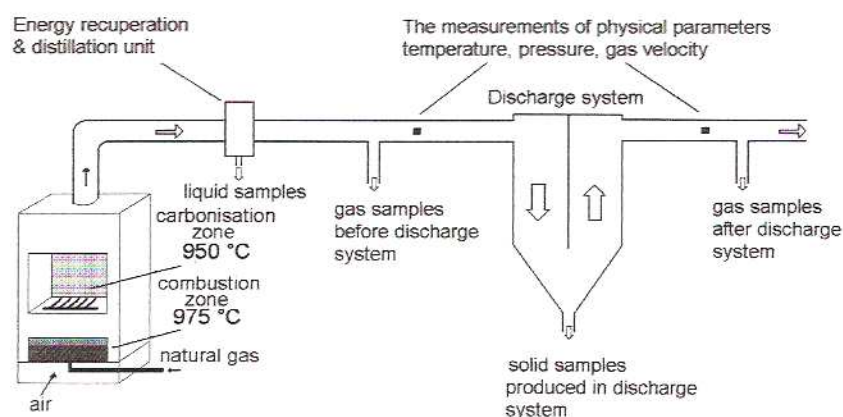


Fig. 1 The schema of oven used for carbonisation of selected municipal waste and pilot scale discharge system for flue gas cleaning built for gas flow volume of 50-250 Nm³/hour

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

Results and its discussion

To study in details the carbonization processes in real conditions we have made a group of measurements of carbonization process applied to several types of waste. The produced carbonization 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, leafs, rests of vegetables, nut shells, garlic rests, plastic (without chlorine) and a mixture of waste. The composition of carbonization exhaust differs with time, temperature i.e. with the stage of carbonization process. Additional changes occur due to type of processed waste, after distillation, after non-thermal plasma based processing.

At present stage it was possible to us to make only part of planed methods. It means that the gas phase analysis was made was not on-line, only isokinetic sampling followed by ex-post analysis of gas samples after oven,

before and after discharge system was made using IR absorption spectrometry as we see on Fig.2. From spectra before and after discharge system we can see the very high efficiency of CO_2 , CO, gas phase CH_x and NO_2 removal (close to 99%). The carbon product from carbonization oven was analyzed permanently every day using KBr pellet technology for each type of waste separately.

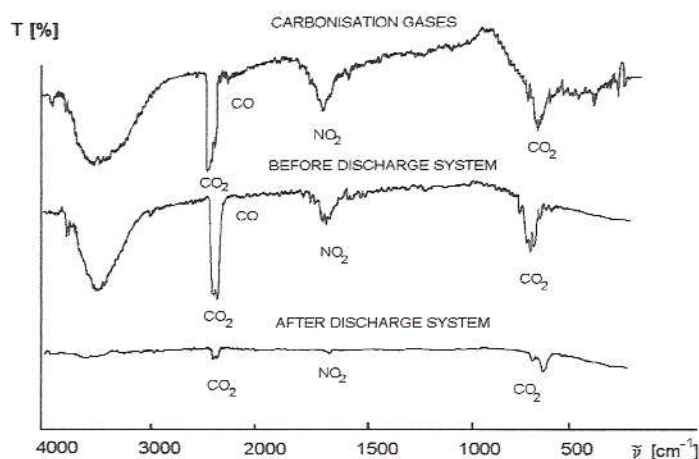


Fig. 2 IR absorption spectra of exhaust gases situated from top after carbonization oven, before and after discharge system made in gas cell with KBr windows

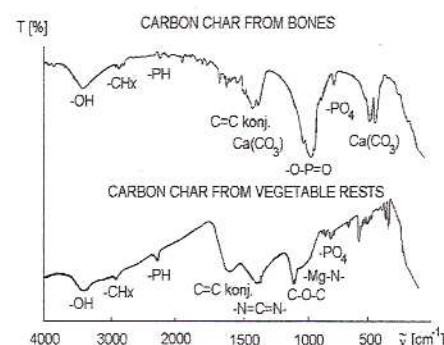


Fig. 3 IR absorption spectra of carbon char from carbonization oven produced from bones (top) and vegetable rest (bottom), the spectra are made using KBr pellet technique.

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, that inside carbon are holes with radius changed in 3 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 $0.3\text{g}/\text{cm}^3$.

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 how carbon intercalates with mineral components in produced carbon char. The biggest difference is seen between spectra of bones (top) & vegetable rests (bottom) as we see from Fig. 3. 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 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 analysis made externally using AAS method shows following information about carbon char:

pH=8.7, P=7.1 g/kg, Na=13.4 g/kg, K=14.8 g/kg, Ca=29.0 g/kg, Mg=37.7 g/kg, Fe=25.3 g/kg, N=15.9 g/kg.

On the Fig.4 we see IR absorption spectra of solid product from discharge system after action electric discharge on carbonization 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, an condensable part of exhaust) 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.

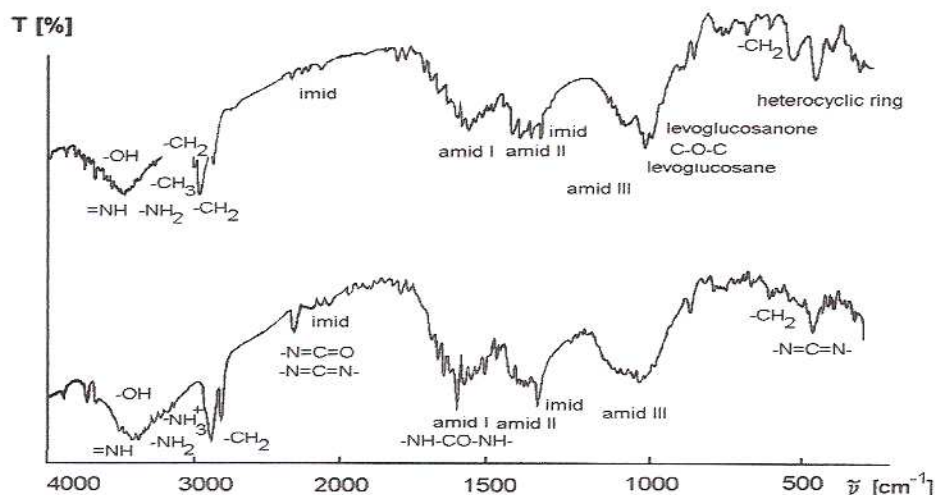


Fig. 4 IR absorption spectra of solid product collected from non stressed electrode (on the top) and stressed electrode (on the bottom) made using KBr pellet technique

Conclusions

As we have used for carbonization the stoker fired type of oven, the waste treatment described in this contribution comprises several thermal decomposition forms of work (slow and fast pyrolysis, carbonisation) so produced exhaust comprises condensable as well as non-condensable portion of gas.

The release of energy from waste is postponed to the temperature when cracking begins ($\sim 350^\circ\text{C}$). The chemical energy is separated in the form of liquid hydrocarbon in distillation unit (levoglucosane and other tar components). The cracking itself is exothermic process (breaking 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 is very effective.

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 [10-12, 15-19]. The important property of exhaust treatment is the formation of life important organic compounds in non-thermal plasma based systems.

Further heating of waste to temperature higher than $\sim 650^\circ\text{C}$ 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 have prepared for tests the following possibility of hydrogen storage:

- absorption/desorption of hydrogen in carbon char with further use in PEM fuel cells,
- conversion of hydrogen in non thermal plasma based system to more suitable liquid compound as is hydrazine and/or hydrocarbons in system similar to hydrocrack (a part of hydrogen storage program was already realized).

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 exhaust cleaning using non thermal based system was tested in regime when the released gases are rich on secondary tar components formed during cracking phase. 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. CO₂ and NO_x removal efficiency vary in 40-99%. The process is connected as in the case of combustion exhaust with nitrogen fixation. The final solid amino acids condensation product (proteinoid) made in electric discharge was based on typical amid group as in the case of combustion exhaust only hydrocarbon part of product was enriched with radicals produced from tar components.

The knowledge of cracking process during waste carbonisation gives us the possibility to understand some processes taking later place in discharge system during solidification of carbonisation exhaust. The large part of municipal waste is composed of several poly saccharides. Thermal de-polymerisation and cracking leads to formation of α -D-glucopyranose. In process of partial oxidation is α -D-glucopyranose converted to levoglucosane or levoglucosanone that condense in distillation unit, only small portion is transported further 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: • activation, • formation of energy rich intermediate species, • 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 6.5eV. The described electronic state $N_2^* A^3\Sigma_u^+$ has a lifetime between 1.3-1.9 sec [13] and that is why it can be involved with a great probability into chemical reaction. From IR spectra of product in Fig.4 and IR calibration spectra of arginine and lysine 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 5. Similar process applied on cyclohexanone we have published in [15].

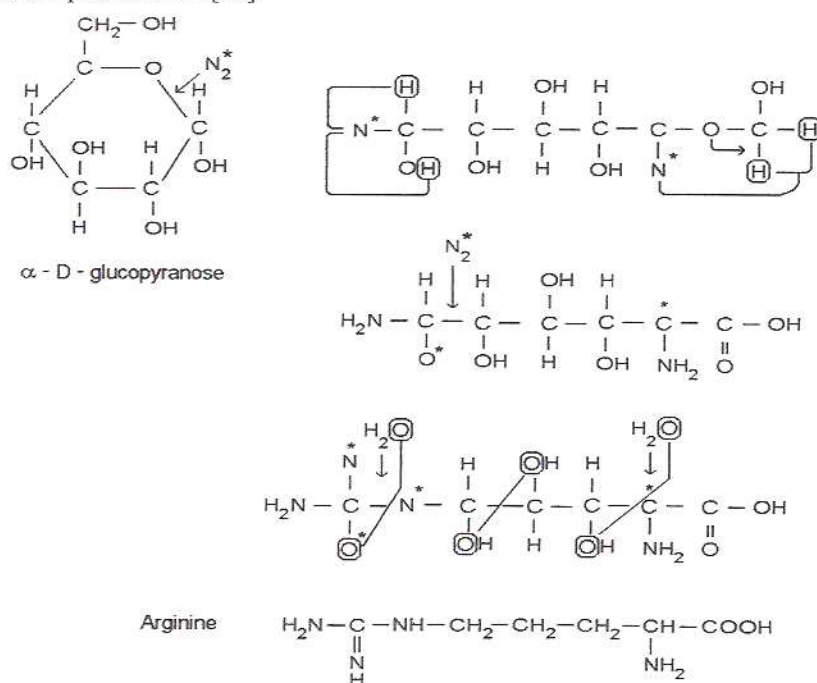


Fig 5 Formation of arginine from α -D-glucopyranose in non-thermal plasma system

Similar processes responsible for formation of amino acids in strong and middle reducing primitive atmosphere during origin of life in Earth were described by S.L. 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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