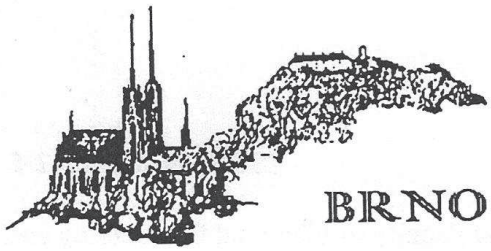
Faculty of Electrical Engineering and Computer Science
Technical University of Brno

and

High Energy Density Research Center
Russian Academy of Science, Moscow

3 rd Czech-Russian Seminar on Project Contact No 101(98)

„Electrophysical and Thermophysical Processes in Low-Temperature Plasma“



Czech Republic

November 16-19, 1999

3rd Czech-Russian Seminar on
„Electrophysical and Thermophysical Processes in Low-Temperature Plasma“

sponsored by

Project Contact No 101
Ministry of Education, Youth and Sports, Prague, Czech Republic

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ABB Brno, Czech Republic

OEZ Letohrad, Czech Republic

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Dept. of Power Electrical and Electronic Engineering FEECS, TU Brno
Technická 8, 616 00 Brno, Czech Republic

ISBN 80-214-1342-5

Published by Faculty of Electrical Engineering and Computer Science TU Brno

Brno 1999

UTILISATION OF CO_2, FIXATION OF NITROGEN AND EXHAUST GAS CLEANING IN ELECTRIC DISCHARGE WITH ELECTRODE CATALYSIS

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ABSTRACT

The method reported here provides a contribution to CO_2 utilisation, nitrogen fixation and combustion exhaust cleaning using synergetic effect of electric discharge with heterogeneous catalysis on electrodes. The efficiency of CO_2 removal is about 40%. The process of CO_2 removal is always accompanied by NO_x removal and is connected with O_2 formation.

The final product of process is powder with fractal microstructure, low specific weight, water insoluble. The main component (95%) of solid product is amorphous condensate of amino acids with about 5% of metal organic compound with catalytic properties. The product was analysed using IR absorption spectrometry, HPLC and thermogravimetry. The following amino acids were observed in the final product: alanine, serine, glycine, aspartic acid, lysine, arginine, methionine, histidine and DNA base cytosine. The condensate has character of statistical protein. Its creation seems to play important role during formation of life in pre-biotic Earth.

Metal organic part of the product comprise oxamidato complexes further converted into porphyrine pigments (as are chlorophyll and haemoglobin) and linear oligo-pyrrole pigment with stereo structure similar to phycobiliproteines. These pigments participate in nitrogen fixation and photosynthesis of amino acids in various micro organisms.

The multifunctional system for removal process was tested on various sources of exhaust (internal combustion engine, brown coal boiler, bituminous pulverised coal boiler, gas boiler, glass oven, VOC sources) in full scale or by-pass gas flow volumes. The observed carbon utilisation efficiency in above described multifunctional discharge systems is high (40-65% of CO_2 is utilised). The energy consumption for conversion of 1 m^3 of the gaseous mixture CO_2-N_2-H_2O into amino acids condensate is 2.3-4.7 Wh/m^3, i.e. 8.3-16.9 kJ/m^3. The continuous conversion of exhaust gases into amino acids does not impose limitations on the energy and industry production and can be successfully used for greenhouse gases limitation and exhaust gas cleaning. The final product seems to have possible use as nitrogen containing fertiliser.

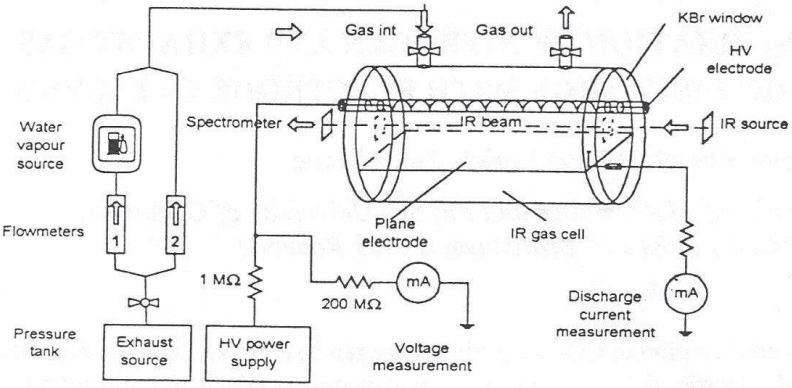
INTRODUCTION

Up to 85% of all forms of energy (electricity and heat production, industry and transport) is produced in combustion processes. This was the reason for focussing our attention on the creation of multifunctional equipment for combustion exhaust cleaning.

Non-thermal plasma techniques offer an innovative approach to the solution of some of these problems. The mean electron energy in a non-thermal plasma is considerably higher than that of the components of the ambient gas. Excited species, metastables, radicals and photons are formed. Due to interaction of plasma with electrode surface heterogeneous catalytic effects gain increasing importance. A non-thermal plasma with above described properties can be generated in an electric discharge realised in corona to spark transition regime.

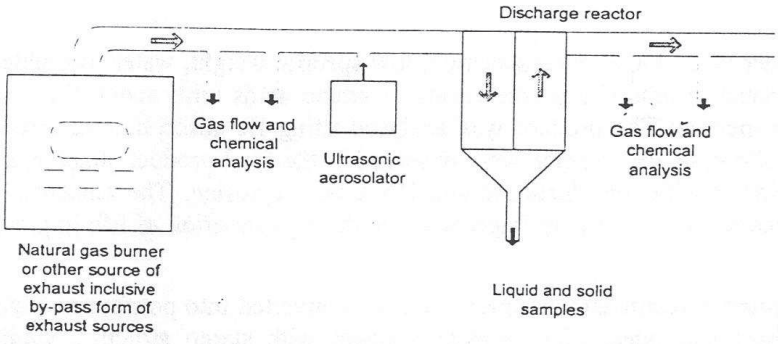
EXPERIMENTAL

For understanding of various aspects of multifunctional equipment for CO_2 utilisation, nitrogen fixation and combustion exhaust cleaning it was necessary provide experimental works on three stages as follows:



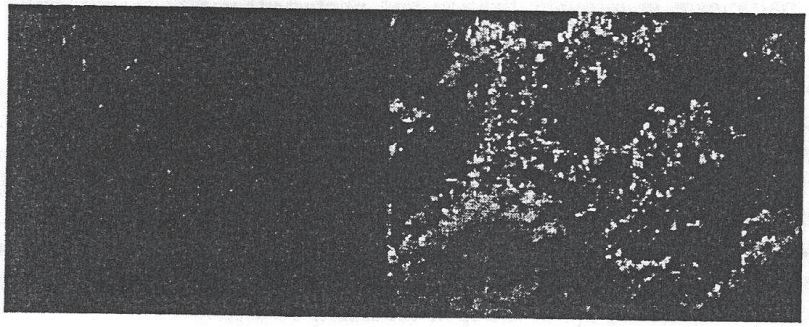
1. GAS CELL DISCHARGE TUBE MEASUREMENTS ARE SCOPED FOR

- step by step kinetic studies for estimation of optimal residence time
- analysis of electrode surface for further understanding of catalytic process
- more detailed understanding of product development in connection to the origin of life on Earth



2. SMALL PILOT SCALE SYSTEM IS SCOPED FOR

- improvement of system from technical point of view
- long term measurements
- production of appropriate amount of solid product
- estimation of energy cost of the system



3. DETAILED ANALYSIS OF PRODUCT

- tests scoped to use of solid condensation product as potential fertilizer
- analysis of ways suitable for natural decomposition of product
- interaction of product with soil and soil bacteria

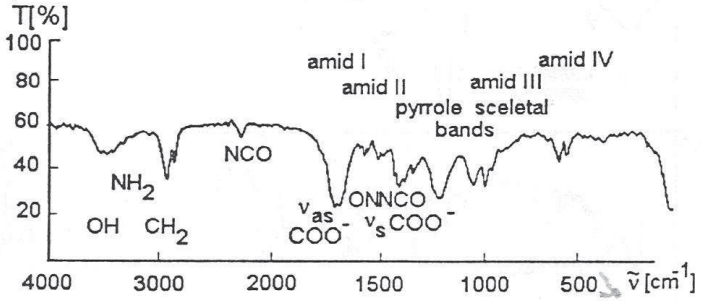
RESULTS AND ITS DISCUSSION

Coming out from combination of measurements as described above we have found out regime of discharge so, that exhaust gas after discharge system is clean enough and main product is solid condensate of amino acids. A typical feature of our experiments is that during polycondensation of solid product appearing close to the surface of non stressed electrode oxygen is set free. From the gaseous products during step by step kinetic studies content of -NCO, ON-NCO, $-COO^-$, CH_2, NH_2 radicals is seen from IR spectrum. We propose formation of these radicals through formation of electronically excited N* followed by its incorporation into CO_2. The electronic state described as N_2

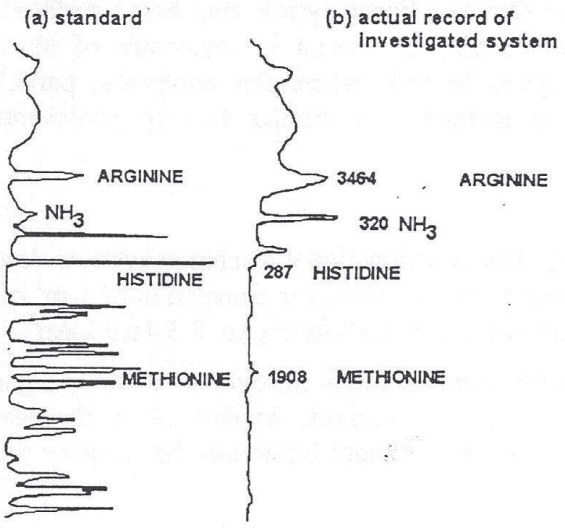
$A^3\Sigma^+_u$ has a lifetime between 1.3-1.9 s and that is why it can participate, with a high probability, in chemical reactions. With prolongation of residence time the gas product is converted under the assistance of catalytic properties of electrode surface into solid product. The gas became cleaner, which is connected with pressure depression.

The product is powder with fractal structure on microscopic level, with low specific weight, of grey-beigish colour, made of chains of flakes, containing a large amount of hollows. For visual observation of the structure the microscopic photographs with various magnification were made (see experimental part). Its composition was analysed by several ways as IR absorption spectrometry, HPLC, X-ray diffraction and thermogravimetric analysis

Using IR absorption spectrometry we have estimated smaller amino acids as alanine serine, glycine, aspartic acid and lysine. From the IR spectra of product additionally comes out that polymer chains are highly branched and cross-linked, contain large amount of amid groups especially in α position and variety of intra and intermolecular hydrogen bonds.



The IR absorption spectrum of product containing amorphous amino acid condensate made using the KBr pellet technique



HPLC spectrum of product after conditioning in 6 molar HCl for 24 hours

From HPLC spectrum we have additionally estimated the amino acids arginine, histidine and methionine.

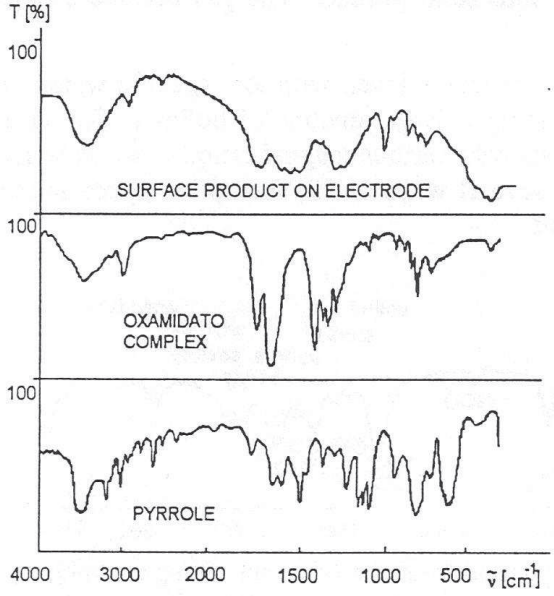
The individual amino acids are incorporated inside polymer randomly without any rules.

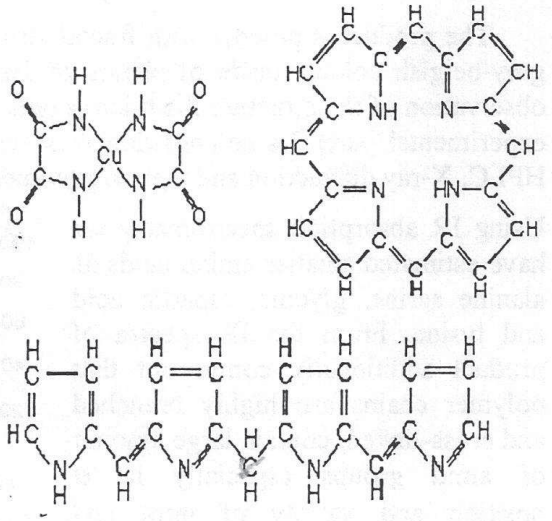
From X ray diffraction was found out amorphous character of polymer.

All this information implicates the proteinoid character in the sense described earlier by Oparin.

The radicals and clusters produced in the discharge, together with the gaseous products (various amines) are stabilised on the surface of the electrodes, usually by di-, tri-, oligo- or polymerisation and/or cyclisation into heterocyclic compounds producing amino acids and various organometallic compounds on the metal surface. These compounds can be successfully analysed using the KBr pellet technique for powder products and IR reflection spectrometry of the electrode surface. The IR spectra of products from the electrodes confirm the formation of amino acids and heterocyclic unsaturated compounds as seen in following spectra. This indicates molecular nitrogen and/or NO_x

fixation into the product. The organo metallic surface product has important catalytic properties, particularly due to its enhanced dielectric constant. From comparison of the IR spectrum of the non-stressed electrode surface, oxamidato complex and liquid pyrrole, the presence of oxamidato complexes with known ferroelectric properties and oligo pyrrole type of compounds with probable catalytic activity can be seen. It is known that linear and cyclic tetrapyrrole compounds are important parts of photosyntetic chromophores (linear phycocynine, cyclic chlorophyl).





Nitrogen fixation participates in the process due to a linear pyrrole-ring based surface catalyst with copper metal. A similar compound (phycocyanin) is present in thylacoids of blue-green algae Spirulina platensis and various types of cyano bacteria where this compound participates in the photosynthesis of amino acids. Oxygen is formed in a similar way to photosynthesis in the multifunctional system.

CONCLUSIONS

The observed carbon utilisation efficiency in the multifunctional discharge systems described above is high (40-65% of CO_2 is utilised). The energy consumption for conversion of 1 m^3 of the gaseous mixture CO_2-N_2-H_2O into amino acid condensate is 2.3-4.7 Wh/m^3, i.e. 8.3-16.9 kJ/m^3.

The amino acids production can be practically used as a new nitrogen containing organic fertiliser. The fixation of nitrogen has unlimited raw material reserves. Application of the new processing might help to solve the reduction of the CO_2 excess without limitation the industry production and development

Similar processes (responsible for the formation of amino acids in primitive atmospheres during the origin of life on Earth) were described by S.L. Miller [1]. Combustion exhaust is, from the point-of-view of composition, relevant to neutral pre-biotic atmospheres.

REFERENCES

[1] Miller, S.L in "Major Events in the History of Life", Ed. By J.W.Schopf (Jones&Bartlett, Boston, Mass., 1992), pp. 1-28