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 40-65%. The process of CO_2 removal is always accompanied by NO_x, VOC, SX and other component removal and is connected with O_2 formation. The final product of process is powder with fractal microstructure, low specific weight, water insoluble suitable for use as nitrogen containing fertilizer. The main component (95%) of solid product is amorphous condensate of amino acids with about 5% of metal organic compound with catalytic properties. The condensate has character of statistical proteinoid. Its creation seems to play important role during formation of life in pre-biotic Earth.

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.

The early atmosphere consisted mainly of gases released by volcanic activity. The today composition of combustion exhaust is similar to the neutral primitive atmosphere i.e. CO_2, CO, H_2O, N_2, traces NH_3, H_2, CH_X.

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 parallel provide experimental work on various experimental system described in our earlier work [1,2] on three levels 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 IS SCOPED FOR tests of solid condensation product as potential fertilizer, test of products from the point of view of formation of life important polymers

RESULTS AND ITS DISCUSSION

Coming out from combination of measurements as described above we have found out regime of discharge work so, that exhaust gas after discharge system is clean enough and main product is solid condensate of amino acids. From in situ gas cell discharge tube measurements scoped to step by step kinetic studies we have found -NCO, ON-NCO, $-COO^-$, CH_2, NH_2 radicals in 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 work as reservoir of energy for plasmochemical 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, made of flake chains, containing a large amount of hollows. To know more about the structure the microscopic and SEM photographs were made and are on Fig 3. Its composition was analysed by several ways as IR absorption spectrometry, HPLC, X-ray diffraction and thermogravimetric analysis.

From the IR spectra of product 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. Using IR absorption spectrometry we have estimated also smaller amino acids as alanine serine, glycine, aspartic acid and lysine. From comparison of IR reflection spectrum of the non-stressed electrode surface 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 tetrapyrrole compounds are important parts of photosyntetic chromophores and pyrrole and pyrimidine rings are present also in bases of DNA and RNA.

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.

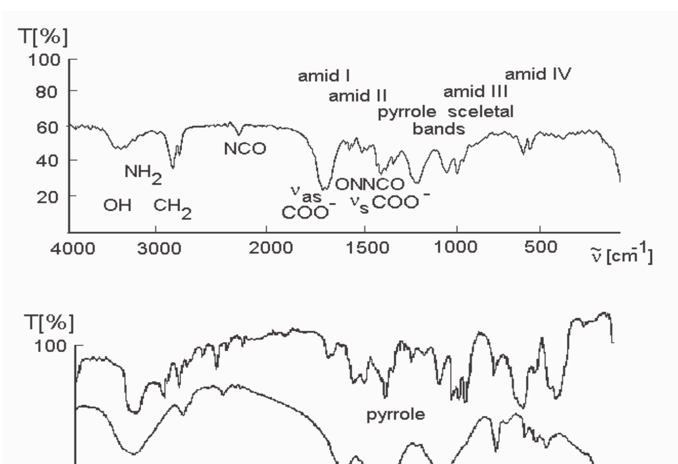


Fig.1 IR absorption spectra of solid condensation product, electrode surface and liquid pyrrole

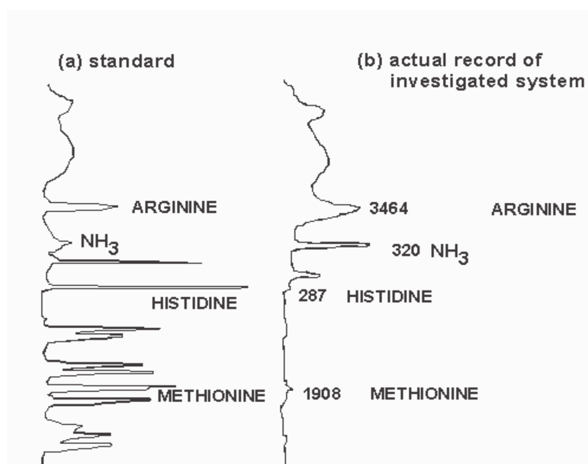


Fig.2 HPLC spectrum of product after conditioning in 6 molar HCl for 24 hours

Reconfiguring of product under the influence of humidity and time lead to the formation of protocells as we see from SEM microscopic photographs on left part of Fig.3 in comparison to protocells published by A.Pappelis & S.Fox in [3] on right part of Fig.3

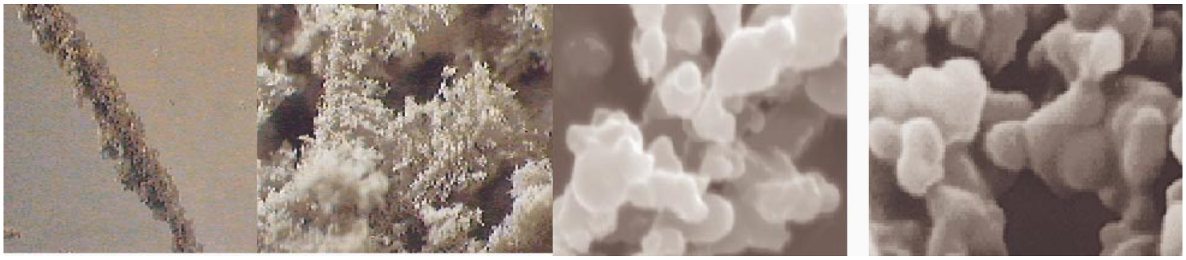


Fig.3 Left part of figure is microscopic photograph of solid product; magnification on left side 150 in middle 500 and on right side SEM photograph with magnification 8000; Right part of figure is SEM photograph of proteinoid protocells published by A.Pappelis & S.Fox [3]

The overview on involved processes is seen on Fig.4 and were published in [2].

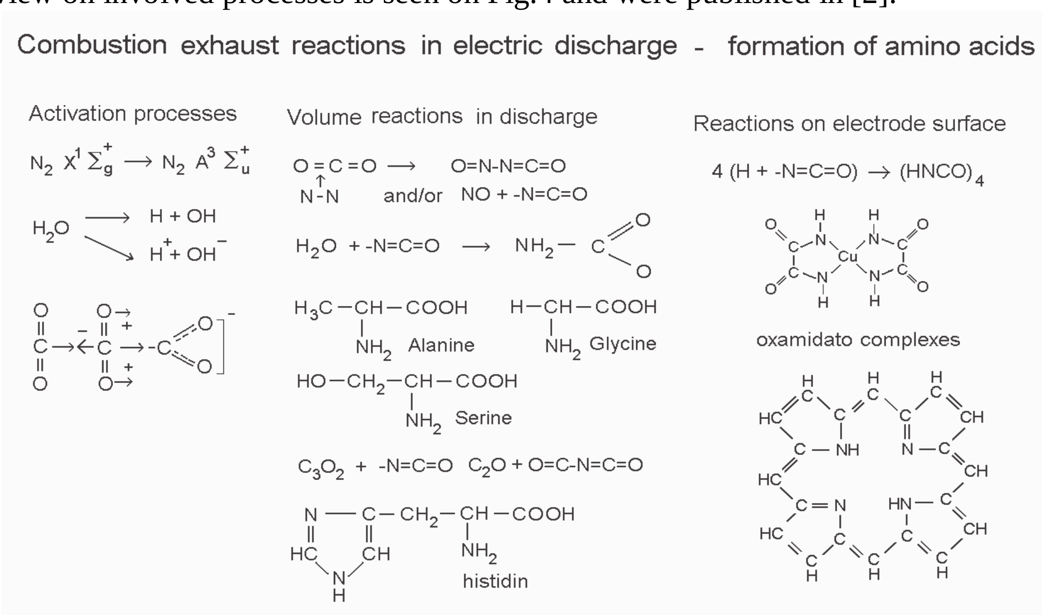


Fig.4 The overview of processes representing conversion of combustion exhaust in electric discharge and formation of amino acid condensation product and catalytic active spots on the electrode surface.

The formation of heterocyclic compounds from radicals and activated species generates several molecules of oxygen in each of the reaction step as we can see for cytosine formation in Fig.5.

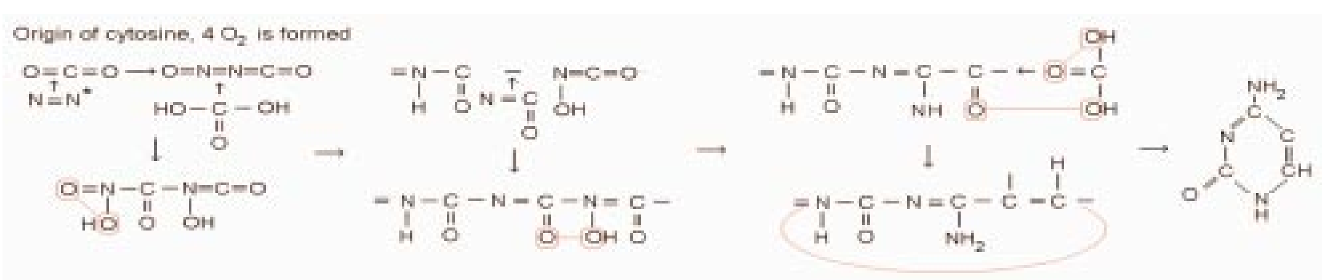
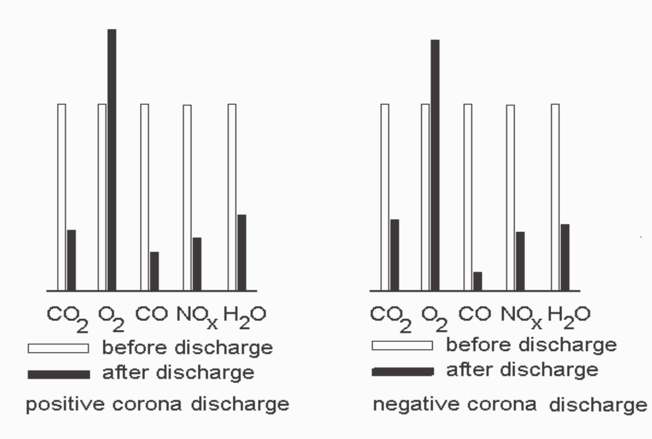


Fig.5 The formation of base cytosine from radicals and activated species leading to the formation of oxygen



We have evidence for oxygen formation. In our experimental flowing system we have generated in this way from oxygen free combustion exhaust 5 and more % of oxygen after discharge system as we see from Fig. 6. Detail are in [2].

Fig.6 The changes of concentration in percentage of initial concentration for exhaust from gas heated glass oven after action of positive and negative corona discharge

We propose that in this way may be ozonosphere originated even earlier then the onset of photosynthesis. The earlier time have also other advantage, the diffusion of oxygen to upper parts of atmosphere was much more probable due to high specific weight of rest primary atmospheric gases.

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

Combustion exhaust is, from the point-of-view of composition, relevant to neutral pre-biotic atmospheres. Similar processes (responsible for the formation of amino acids monomers in primitive atmospheres during the origin of life on Earth) were described by S.L. Miller [4].

- We have shown how aminoacids and other life important substances and polymers can be formed.
- We have produced proteinoid (~100 grams) in abiotic system i.e. by influencing the combustion exhaust (similar to primary atmosphere) and charged water aerosol with repeated electric discharge.
- We have produced oxygen from oxygen free combustion exhaust in electric discharge. We have shown the possibility of oxygen formation before onset of photosynthesis.

REFERENCES

[1] M. Morvová: DC corona discharge in CO2 - air and CO - air mixtures for various electrode materials J.Phys D: Appl.Phys 31 (1998), pp. 1865-1874

[2] M. Morvová, F. Hanic, I. Morva: Plasma Technologies for Reducing CO_2 Emissions from Combustion Exaust with Toxic Admixtures to Utilisable Products, Journal of Thermal Analysis and Calorimetry, Vol.61(2000), 273-287

[3] A.Pappelis & S.Fox at http://www.siu.edu/~protocell/photos.htm

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