The Application of Cooled Probes for the Investigation of the Change of Chlorinated and Unsubstituted Hydrocarbons in Plasma Jets.

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Abtract.

It is described the application of cooled probes for the determination of concentration profiles of chemical compounds in plasma jets containing hydrocarbons. The experiments corroborate results being received by a new modelling methode.

Introduction.

If hydrocarbons are injected in a plasma jet a row of new species arise. On account of the limited reaction times the concentrations of these species are different along the axis of the plasma jet. Because the velocity and the temperature of the plasma gas is not constant in the cross-section of the plasma jet there is a gradient of the concentrations in the radial direction. A simple possibility to determinate the concentrations of species is to take samples of the plasma gas by cooled probes and to analyse them conventionally by gaschromatography. In this paper the construction and the application of cooled probes are described. The probes were used for the determination of the chemical composition of plasma free jets and enclosed plasma jets.

Probes for plasma free jets and experimental results.

Fig. 1 shows the scheme of the device. An Ar plasma jet (1) streamed in a vessel (2) purged by argon. The plasma jet was generated by a 3.5 kW plasmatron (3). The

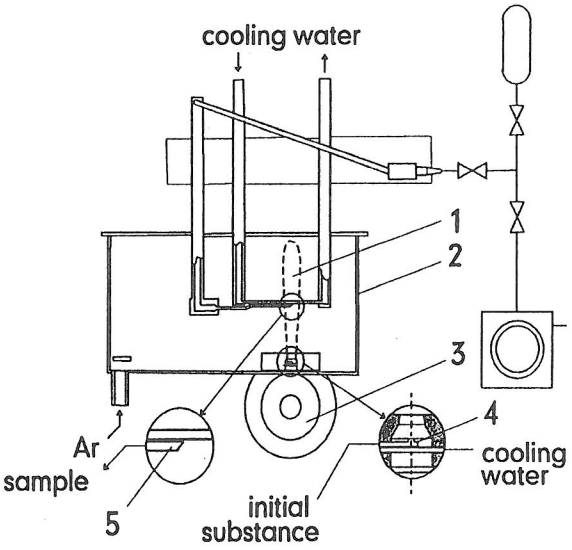


Fig. 1: Plasma Jet Device including a Cooled Probe for the Investigation of a Plasma Free Jet

initial substances (methane 1,5 mol-%, Ne 5 mol-%; plasma gas Ar 438 l h^{-1}) were injected at the axis of the plasma jet by a water-cooled capillary tube (4) (Ø 1 mm, stainless steel). In order to detemine the chemical composition, samples of the plasma gas were taken by a water-cooled probe (5) (capillary Ø 1 mm, stainless steel) brought in the plasma. The samples were analysed by gaschromatography and mass-spectrometry. By moving the probe in radial and axial direction we received the corresponding spatial (quench-) profiles of the chemical components of the plasma. Fig. 2 shows the measured spatial distribution of the concentration of ethine in the plasma jet as a function of the reaction time t. The reaction time resulted from the the velocity v(z) of the plasma gas at the axis z which we had determined previously by a rotating mirror methode [1] to be

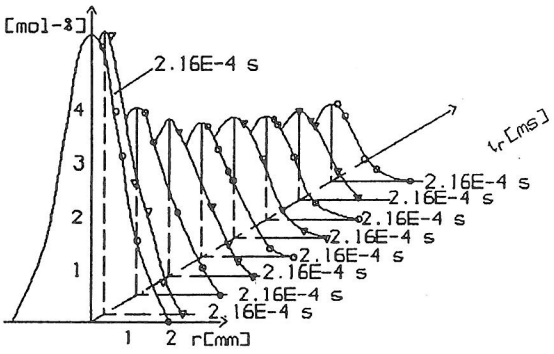


Fig. 2: Spatial Distribution of Ethyne in the Plasma

$v(z)=156 - 1{,}42\ z\ [m\ s^{-1}];\ t = 7{,}067 \cdot 10^{-4}\ [5{,}05 - \ln(156 - 1{,}415)]\ [s^{-1}];\ [z] = mm$

On account of diffusion and convection the concentrations of all chemical species decreased along the axis. Their effect were determined by the decrease of the concentration of the neon along the axis caused only by these physical processes. So the concentration of other species were corrected for the case that no radial diffusion and convention took place. Fig. 3 shows the measured concentrations of neon and ethyne (corrected values) along the axis of the plasma jet.

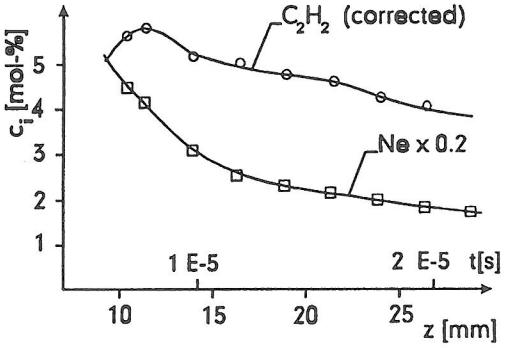


Fig. 3: Distribution of the Concentrations of Ethyne and Neon along the Axis of the Plasma Jet

In the interval T = 4000... 4300 K we assumed the decay of ethyne in the plasma jet as a reaction of 2nd order [2]. In this case the rate constant of this reaction is

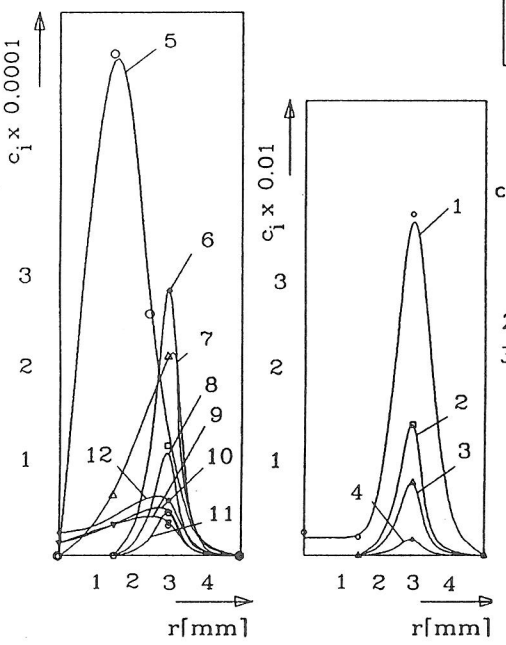
$$k(T) = \frac{1}{t_2 - t_1}\left(\frac{1}{c_2} - \frac{1}{c_1}\right)$$

(c_1 and c_2 are the concentrations of C_2H_2 at the reaction times t_1 and t_2, respectively). The needed values of the temperature T(z) of the plasma gas along the axis z were

determined previously by spectroscopy . Using T(z) and the decreasing part of the axial concentration profile of C_2H_2 ($t > 8 \cdot 10^{-5}$ s) k(T) was determined to be

$$k = 10^{14} e^{-\frac{250\ kJ/mol}{RT}}\ cm^3 s^{-1} mol^{-1}$$

This agrees with the corresponding k(T) of the NIST tables [3].



1 - ethyne
2 - 1-butene-3-yne
3 - ethene
4 - 1,3-butadiyne
5 - 1,2-dichloroethane
6 - methane
7 - chloroethene
8 - chlorobenzene x 10
9 - 1,3,5-hexatriyne x 10
10 - 1,3-hexadiyne-5-ene x10
11 - dichloroethylbezene x5
12 - chloroethylbenzene x 5

Fig. 5: Distribution of the Concentrations of the Species in the Cross-section of the Plasma Jet (initial substance 1,2-Dichloroethane, Reaction Time $t = 10^{-4}$ s)

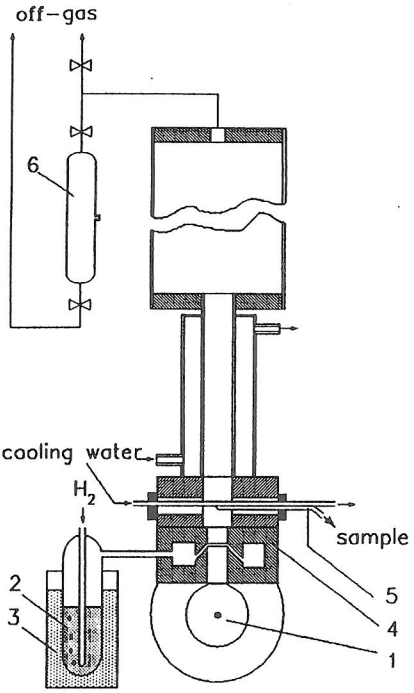


Fig. 4: Plasma Jet Device including a Cooled Probe for Investigation of a Plasma Jet

Probes for enclosed plasma jets.

Plasma jets containing chlorinated hydrocarbons (CHC) were enclosed in a cylindrical reactor because toxic substances were formed (Fig.4). The plasma jet were produced by a 3.5 kW plasmatron (1) (Ar plasma, 425 l h^{-1}). The initial substance (1,2-dichloroethane) was vaporised by piping H_2 gas (50 l/h) through the liquid 1,2-dichloroethane (2) being in a thermostatic bath (3). The vapor was injected into the plasma jet by means of a circular slit nozzle (4) (Ø 6x0.1mm). After the injection of the CHC the (calculated) medium mass temperature was $T \approx 4000K$. The water-cooled probe (capillary tubes,

Ø1 mm, stainless steel) was led through the wall of the reactor .It was manoeuvrable in the radial direction. The gaseous samples put by the probe were fed into sample tubes (as indicated in fig. 1). These samples and samples of the off-gas (6) were analysed by gaschromatography and gaschromatography-mass-spectrometry .

Fig.5 shows the measured radial concentration profiles of the formed species at a reaction time of $t = 1 \cdot 10^{-4}$ s.It can be recognized that 1,2-dichloroethane was mainly changed into hydrocarbons (C_2H_2 , C_2H_4 , CH_4) and in small amounts into chlorinated hydrocarbons (mainly chloroethene and chlorobenzene). For $t_r \geq 5 \cdot 10^{-4}$ s these chlorinated hydrocarbons were decomposed completely. The chlorine was changed into HCl.

A Modelling of the change of methane in a Ar plasma jet and the comparison with the experiment.

By means of modellings the amount of formed species in dependence on the reaction time t_r can be predicted. Recently Trusov [4] [5] showed a new methode of modelling using a variation principle under irreversible thermodynamic conditions. He assumed that in the viewed homogeneous and closed chemical reacting system

-the time gradient for the chemical potential is only determined by the thermodynamical functions of the system components .

-the transition to the thermodynamic equilibrium is considered as a transition of a certain physical system to the minimum of the potential energy Π of the system.

-the dynamics of the chemically reacting system under the influence of the potential energy Π determinates a trajectory of the minimum energy dissipation.

The change of the uncompensated amount of heat Q^i is

$$-\delta \Pi = \delta Q^i ; \qquad Q^i = T S^i = \int_0^t T \sigma \, d\zeta \qquad \text{(irreversible process)}$$

T = temperature of system,

S^i = entropy

The potential energy Π and the material balance φ_j are given by

$$\Pi = \sum_{i=1}^{k} \mu_i c_i \qquad \varphi_j = \sum_{i=1}^{k} c_i \nu_{ij} - b_j \qquad j = 1...m$$

σ - entropy production due to the chemical reactions,

c_i - concentration of the component i,

μ_i - chemical potential

k - number of the components in the homogenous system,

ν_{ij}-stoichiometric coefficients,

b_j - amount of the j^{th} element,

m - number of elements in the system.

Regarding to his assumptions Trusov formulated his modelling as a variation problem

$$\int_0^\infty \left\{ Q^i - \Pi + \lambda \varphi \right\} dt \rightarrow \min$$

λ = Lagrange parameters, t = reaction time.
The solution of this variation problem is synonymous with the solution of the following system of differential equations

$$\frac{d\,c_i}{d\zeta} = e^{A_i} - 1; \qquad b_j = \sum_{i=1}^{k} c_i \nu_{ij} \qquad j = 1...m \qquad A_i = \mu_i T^{-1} + \sum_{i=1}^{m} \nu_{ij}\lambda_j$$

In these differential equations the reaction time t was substituated by a process variable ζ :

$$d\zeta = L^{-1}\, dt.$$

L(t) is a usually unknown coefficient equal for all components (species) of the system. The solution of these differential equations are the concentrations c_i of all species depending on a process parameter ζ. This set of differential equations can be solved by the program package MAGIC containing the needed database for about 2500 substances.

It is a disadvantage of the described methode that the concentrations c_i are only determinated as functions of a process parameter ζ and first there is no information about the reaction time. The great advantage of this modelling is that we don't need any information about the real particular reactions and the accompanying rate constants.

In order to prove predictions of the described modelling methode the change of methane in a Ar plasma jet was modelled (Initial conditions: T =3800 K, plasma gas Ar 438 l h^{-1}, methane 1,5 mol-%, Ne 5 mol-%). The calculated concentration of C_2H_2 $c_1(\zeta)$ was calibrated in this way that the maxima of $c_1(\zeta)$ and measured concentration $c_1(t)$ (fig. 3) are equal. By comparison of the equal values of $c_1(\zeta)$ and $c_1(t)$ we received the relation $t = f(\zeta)$, which made it possible to present the calculated concentrations as functions of the real reaction times. Fig. 6 shows that the calculated concentration of methane $c_2(t)$ was corroborated by the experimental values in a satifactory way. For comparison of Fig. 3 and 6 it is to take into account that the measured concentrations c_{axis} are local values at the axis of the jet and the calculated concentrations are mean values c_m regarding to the

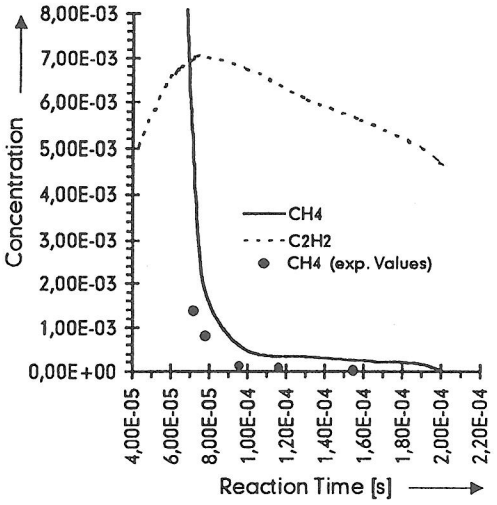


Fig. 6: Change of Methane in a Argon Plasma Jet

cross-section of the plasma jet. If assumed $c(r) = c_{axis} [1- (r/R)^2]$ (Fig. 2) it is $c_{axis} \cdot c_m^{-1} = 6$.

Conclusions.

Cooled probes are useful tools for the chemical analysis of plasma jets. The thermodynamic modelling methode pointed out by Trusov is also practicable for the fast chemical reactions in thermic plasmas.

Literature.

[1] G. Winkelmann, J. Lachmann, Exp.Techn. Phys. 23(1975)2, 203

[2] H.-J. Spangenberg, I. Börger, H. Drost, Klotz, Z. Chemie 267(1986)6, 1081

[3] F. Westly et al., NIST Chemical Kinetics Database V. 6.0 1994, Gaithersburg USA

[4] I. Börger, J. Lachmann, B. G. Trusov, Kinetical modeling of chemical processes during conversion of chlorinated hydrocarbons in thermal plasma, 1995 Minneapolis, USA

[5] B. G. Trusov, A. G. Malanichev, Dokl. AN, Russia. in press.