MATHEMATICAL MODELLING OF CHEMICAL REACTIONS IN A PLASMA JET REACTOR

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ABSTRACT

The pyrolysis of ethane in a hydrogen plasma jet has been modelled by dividing the stream into three zones two of them being characteristic for the chemistry of the process. Assuming chemical equilibrium conditions for the high temperature zone and chemical kinetics for the intermediate zone, computed data were in good agreement with the experiments.

1. INTRODUCTION

The pyrolysis of hydrocarbons is an important trend of industrial applications of plasma processes. Nevertheless very few data are available on plasma chemistry in general and on the chemistry of pyrolysis in plasma especially/1/. Based on experiments on pyrolysing hydrocarbons in a plasma jet published earlier/2/, attempt has been carried out on the detailed chemical modelling.

2. THE MODEL

Due to the very complex feature of the phenomena investigated assumptions were used in constructing the model. The plasma jet is divided into three coaxial streams:
/i/ a high temperature stream in the centre of the jet, where those components are formed, which are thermodynamically most stable,
/ii/ an intermediate temperature stream, where pyrolytic

reactions occur,
/iii/ the cold stream, where practically no change takes place in the chemical composition /external zone/. Accordingly it was assumed, that in the high temperature zone chemical equilibrium is quickly established. In contrary the chemical composition of the intermediate zone is strongly time dependent characterized by chemical kinetics. The external zone is viewed as chemically invariant.

As mathematical model for the high temperature zone the concept of the minimum of free enthalpy was used. For the intermediate zone a model based on continuity equations including a detailed reaction mechanism was applied. Mathematical details inclusive of solving the stiff differential equations have been published/3/,

3. RESULTS AND DISCUSSION

The pyrolysis of ethane has been chosen for modelling experimental data shown in Table 1.

Experimental data　　　Table 1.

Run No.	Feed moles/hr	H/C ratio	Enthalpy kcal/mole	Conversion %	Selectivity to CH_4	C_2H_2	C_2H_4
137	35	136	18.7	54	37.6	52.7	8.7
134	35	136	35.9	56	38.7	52.5	7.6
122	35	136	39.3	78	39.8	47.9	11.1
141	55	73	14.0	32	37.3	48.0	19.4
129	55	73	17.7	37	35.0	53.6	9.5
120	55	73	29.2	54	30.9	55.9	10.1
144	78	104	8.2	27	44.8	45.3	6.5
132	78	104	14.2	14	44.3	47.7	9.8
126	78	104	19.0	47	41.8	48.5	7.9

As first step of the computation chemical equilibrium calculations were carried out at the corresponding experimental conditions. Results indicated that from all possible species practically acetylene is the only component in the equilibrium composition above 2000 K temperature.

As a second part of the computation the kinetic model was used. The reaction mechanism has been compiled of taking into account the possible reaction between 1000-2000 K./4-6/ The reaction mechanism at present consists of 57 elementary steps and of 16 species, characterized by the main reaction channels shown in Fig.1.

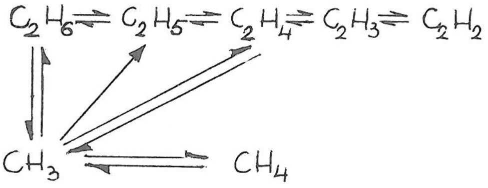

Fig.1. The main reaction channels

The computed selectivities for one typical run at 1500 K are given in Table 2.

Computed selectivity   Table 2.

Time,sec	Selectivity to			
	CH_4	C_2H_2	C_2H_4	CH_3
$1.02_{10}-5$	0.34	0	0.62	0.04
$1.36_{10}-5$	0.32	0	0.65	0.03
$1.96_{10}-5$	0.30	0	0.67	0.03
$3.00_{10}-5$	0.29	0	0.68	0.025
$6.45_{10}-5$	0.29	0	0.69	0.02
$1.03_{10}-4$	0.29	0	0.71	0
$1.05_{10}-3$	0.31	0.04	0.65	0
$1.07_{10}-2$	0.33	0.11	0.56	0
$1.01_{10}-1$	0.38	0.27	0.35	0
$9.27_{10}-1$	0.48	0.42	0.10	0

Selectivities against temperature at 10^{-1} sec reaction time are displayed in Fig.2.

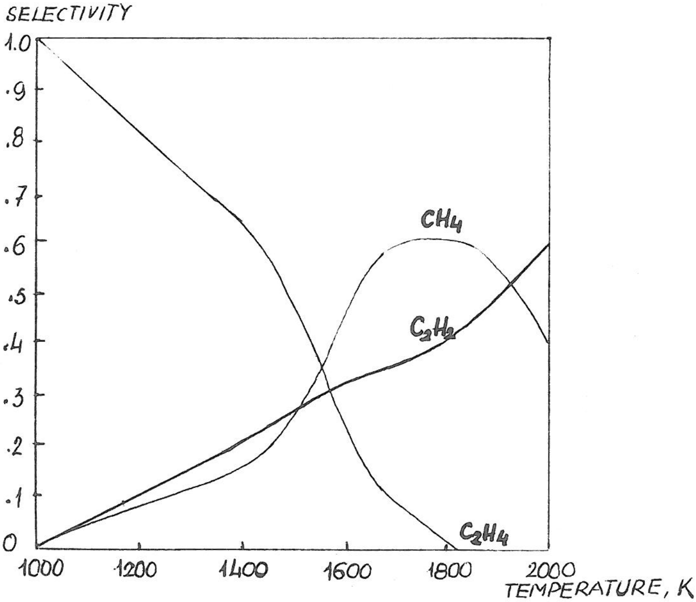

Fig.2. Computed selectivity vs. temperature

The analyis of the computed data and comparison with the experiments lead to the following conclusions:

- There is a clear indication for the competition of the two main channels - one the dehydrogenation of ethane, the other via CH_3 radical - leading to acetylene.
- Above 2000 K temperature chemical equilibrium is achieved within a few milliseconds. Therefore it has been a reasonable assumption that the high temperature zone of the jet could be modelled by chemical equilibrium computations.
- That is not the case for the intermediate temperature region, residence times usual in jets require chemical kinetic models.
- There is indication, that a substantial part of the chemical reactions proceeds in the pyrolytic zone.

With this knowledge further informations can also be obtained. Experiments with acetylene as feed have been performed at similar conditions. By assuming that temperature and velocity profiles of the streams for both feeds were similar the measured conversion values enabled us to make a quantitative estimation of the distribution of the total stream into parts corresponding to the three zones defined by the model. Consequently the selectivities for the pyrolytic zone can also be determined from the measured overall selectivities. These values are given in Table 3.

Feeds and the pyrolytic zone selectivities Table 3.

Run No.	Feed ratios of each zone w_1/w	w_2/w	w_3/w	$\frac{\text{selectivity to } CH_4}{\text{selectivity to } C_2H_4}$
137	0.46	0.07	0.47	2.5
134	0.44	0.30	0.26	4.9
122	0.22	0.40	0.38	5.8
141	0.68	0.05	0.27	2.5
129	0.63	0.13	0.24	3.1
120	0.46	0.19	0.35	4.1
144	0.73	0.11	0.16	4.1
132	0.65	0.14	0.21	5.9
126	0.53	0.27	0.20	8.6

w_1, w_2, w_3 and w stand for the low, intermediate high temperature and total stream respectively.

It can be seen that on increasing the specific enthalpy of the feed the ratio of the low temperature zone to the total stream dicreases, while that of the intermediate zone increases. No specific change in the high temperature stream can be observed.

The CH_4/C_2H_4 selectivity ratio values show an increasing tendency with increasing specific enthalpy. The numerical values of the selectivities even allow us to make an approximate estimation of the kinetically equivalent isotherme temperature of the pyrolytic zone, its value being in the temperature range of 1000-1500 K for the investigated cases.

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