SENSIBILIZATION OF PLASMACHEMICAL CH₄-CONVERSION BY C₂H₆-ADDITIONS AT PYROLYTICAL CONDITIONS IN A SHOCK TUBE

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ABSTRACT
The influence of ethane additions up to 5% on methane pyrolysis was investigated by means of a single pulse shock tube. The ethane sensitizes the product formation but not the methane decomposition. The effect is discussed by two chain mechanisms based on the improved formation of C₂H₅ radicals.

1. INTRODUCTION
In continuing previous investigations concerning the kinetical modelling of plasmapyrolytical methane conversion by means of a single pulse shock tube /1/, the aim of the present paper is to verify whether the methane pyrolysis can be sensitized by small additions of ethane, i.e. to check, small ethane additions affect the pyrolytical methane decomposition and/or the product formation in a significant manner. This intention refers to earlier results of Iljin and Jeromin /2/ showing that an addition of a 3 - 4% propane-butane mixture improves the pyrolytical methane conversion by which the total conversion degree was increased from 42 to 62%, the acetylene- and ethylene concentrations were enlarged from 9,5 to 13% and 10,2 to 14%, respectively. Such an effect is important for improving the application of the methane pyrolysis for industrial purposes. Furthermore, sensitizing effects are essential also from the theoretical point of view concerning the question of homogeneous plasmacatalytical mechanism under thermal conditions. With respect to previous investigations on modelling plasmapyrolytical processes by the shock tube technique /3/, these method seemed suitable to describe sensitizing effects in the plasma pyrolysis, too.

2. EXPERIMENTAL
The investigations were performed on a single pulse shock tube which construction and operation properties were described in detail previously /4/. By means of such a device it is possible by the shock wave to heat a chemical system to elevated temperatures at thermal equilibrium in 10⁻⁸ s and to quench the pyrolytical system by adiabatic
expansion in a rarefaction wave. The time of pyrolysis is determined by the difference in time between the arrival of the reflected shock wave and the appearance of the expansion wave on the reaction place. In analogy to plasma pyrolysis the reaction system consisted of a mixture of methane and ethane diluted in argon up to 10\%. The overall concentration and pressure were $N \approx 1.8 \times 10^{-5}$ mol cm$^{-3}$ and $p \approx 2.6 \times 10^5$ Pa, resp. The concentrations of the $C_2H_6$-additions up to 5\% of the initial CH$_4$ concentration were in the same order of magnitude as the maximal C$_2$H$_6$-yields occurring during the CH$_4$-pyrolysis. The temperatures and pyrolysis times were altered within $1500 \leq T \leq 2100$ K and $0.3 \text{ ms} \leq t \leq 4 \text{ ms}$ in analogy to plasma pyrolytical reaction conditions. The quenching rate varied in the range of $10^5 \text{ s}^{-1} < dT/dt < 10^7 \text{ s}^{-1}$; the analysis of the hydrocarbons was performed by usual GC-technique with a sensitively of 100 ppm.

3. RESULTS

- The differences in the decay curves (see fig. 1) indicate that methane and ethane have a different pyrolytical sensitivity, whereas ethane is pyrolysed at once, the methane pyrolysis starts later, e.g. until 1 - 2 ms at $T \approx 1500$ K. At higher pyrolysis temperatures the shape of the decay curves of methane and ethane approaches each other. This feature is expressed also by the different values of the constants in the Arrhenius equation.

- A part from a prolonged induction period at $T \approx 1500$ K, no influence of the ethane additions on the methane decay can be observed.

- From the curves of fig. 1 it can be seen that ethane is mainly converted to ethylene whereas from methane besides ethylene, ethane and acetylene are formed also with different reaction rates.

- The addition of ethane to the methane system causes a partly significant increase of the ethylene and acetylene yields (see table 1). From the values of table 1 it is seen, that the sensibilization effect consists mainly in an increase of the ethylene concentration up to the eight-fold. The influence of added ethane on acetylene formation is smaller regarded to ethylene but some times even higher than the concentration of added ethane.

- The sensibilization effect initiated by the ethane additions is independent on the pyrolysis temperature; it concerns the ethylene formation at lower temperatures and at higher temperatures, where ethylene disappears, the acetylene formation.
Table 1: Comparison of product yields in the CH₄- and CH₄/C₂H₆-system.

<table>
<thead>
<tr>
<th>Yield in arb. units</th>
<th>CH₄-system</th>
<th>CH₄/C₂H₆-system</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>C₂H₂</td>
</tr>
<tr>
<td>1500 K</td>
<td>2 ms</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>3 ms</td>
<td>41</td>
</tr>
<tr>
<td>1600 K</td>
<td>1.5 ms</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>3 ms</td>
<td>22</td>
</tr>
<tr>
<td>1730 K</td>
<td>0.5 ms</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>3 ms</td>
<td>9</td>
</tr>
<tr>
<td>2000 K</td>
<td>1 ms</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3 ms</td>
<td>-</td>
</tr>
</tbody>
</table>

4. DISCUSSION

In respect to the measured curves and from both, the differences in the binding energy of C-H and C-C bonds and the different Arrhenius parameters it can be supposed, that ethane is pyrolysed earlier than methane especially at lower temperatures and shorter residence times according

\[ C₂H₆ + Ar \rightarrow CH₃ + CH₃ + Ar \]  \hspace{1cm} (1)

and \[ CH₄ + Ar \rightarrow CH₃ + H + Ar. \] \hspace{1cm} (2)

The rapid ethylene formation observed in the investigated CH₄/C₂H₆ mixtures can be explained by the well known decomposition of the C₂H₅ radical via

\[ C₂H₅ + Ar \rightarrow C₂H₄ + H + Ar. \] \hspace{1cm} (3)

High concentrations of ethylradicals are generated by reaction of methylradicals according

\[ CH₃ + CH₄ \rightarrow C₂H₅ + H₂ \] \hspace{1cm} (4)

\[ CH₃ + C₂H₆ \rightarrow C₂H₅ + CH₄ \] \hspace{1cm} (5)

\[ CH₃ + CH₃ \rightarrow C₂H₅ + H \] \hspace{1cm} (6)

The hydrogen atoms formed in reactions 2, 3 and 6 cause additionally reactions generating the reactive radicals C₂H₅ and CH₃ by
\[ \text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2 \quad (7) \]
\[ \text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2 \quad (8) \]

From reaction 3 - 8 it can be concluded, that in the CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixture the pyrolysis of methane is characterized by an autocatalytic process consisting of two chain reactions connected with each other. These two mechanisms are maintained by the most reactive radicals H and CH\textsubscript{3}. In consequence of this, ethylene in the CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} system is formed by a smaller number of reaction steps than in the pure CH\textsubscript{4} system.

The experimental fact, that the methane decay essentially remains unchanged by ethane additions is due to the competition of an acceleration of the CH\textsubscript{4} decay via reactions 4 and 8 and a re-formation of CH\textsubscript{4} molecules from both, the reaction 5 and the quenching process / 5 /.

The observed increase of the acetylene yields in the CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixtures especially at T \( \gg 1700 \) K is caused by the ethylene decay according
\[ \text{C}_2\text{H}_4 + \text{Ar} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{Ar} \quad (9) \]

Because of the high concentration of H atoms in the CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} system and with respect to their recombination to H\textsubscript{2}, additional acetylene formation mainly during the quenching process via
\[ \text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \quad (10) \]
\[ \text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} \quad (11) \]

has to be considered. Furthermore, reactions 10 and 11 are assumed to be responsible for inhibition of soot formation in the hot phase.

5. CONCLUSIONS

1. Small additions of ethane up to 5\textsubscript{\%} in a methane system do not affect the plasmapyrolytical methane decay. However, a sensibilization of the pyrolytic product formation concerning the ethylene and acetylene yields can be observed.

2. The observed sensibilization is based on an amplification of the autocatalytic product formation by ethane additions during the methane pyrolysis.

3. From the present investigations by the shock tube technique it can be expected that a similar sensibilization effect can be achieved at plasmapyrolytic conditions.

4. The observed sensibilization effect can be assumed as a proof that homogeneous catalytic effects occur under thermal reaction conditions.
REFERENCES


/ 2 / Iljin, D.T. and Je.N. Jeromin, "Chemical reactions of organic compounds in electrical discharges" (russian), Nauka Moskov 1966, p. 32


Fig 1: Pyrolytical conversion of CH$_4$ at two different temperatures. Product concentrations $c_i$ related to initial methane concentration $c_{CH_4}$ versus residence time $t$. Dotted lines: CH$_4$-system, full lines: CH$_4$/C$_2$H$_6$-mixture.