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**cw CO<sub>2</sub> LASER POWERED PYROLYSIS OF METHANE**

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The cw CO<sub>2</sub> laser-photosensitized (SF<sub>6</sub>) pyrolysis of methane with high content of the sensitizer affords ethylene and acetylene the yields of those are shown to depend upon the laser output and the focussing conditions of the laser radiation.

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There is current interest in the IR laser-induced reactions among those the laser-powered homogeneous pyrolysis<sup>1-3</sup> has arrested a great deal of attention due to its strictly gas-phase occurrence and the elimination of heterogeneous steps so often significant in conventional pyrolyses. One of the pyrolytic reactions important from the practical point of view is thermal decomposition of methane studied frequently under conditions of shock-tube and conventional pyrolysis. The literature on the methane pyrolysis was surveyed<sup>4-6</sup> and the data compiled point out the importance of heterogeneous catalysis of the decomposition that can take place either on the hot wall surface or at the carbon particles formed in the gas phase. Even though the mechanism of the thermal decomposition of methane was studied in detail, the data on the product distribution covering a wide range of the reaction progress under various conditions are not in abundance<sup>7-10</sup>. Despite that the process has already been optimized<sup>7,9</sup> for the production of acetylene no pyrolysis of methane induced by laser was up to our knowledge studied with the aim to find out whether strictly homogeneous conditions of the laser pyrolysis are favorable for either ethylene or acetylene production.

In this paper we present the study of the cw CO<sub>2</sub> laser-photosensitized (SF<sub>6</sub>) decomposition of methane in order to get the knowledge of the dependence of the product distribution upon a few parameters that can affect<sup>11,12</sup> the temperature distribution of the laser-induced process.

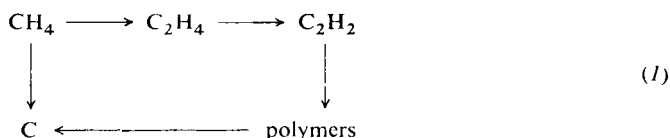
**EXPERIMENTAL**

A cw CO<sub>2</sub> laser<sup>13</sup> operated at the P(20) line of the 00<sup>0</sup>1→10<sup>0</sup> transition (944.2 cm<sup>-1</sup>) with different power ranging between 4–7 W was used for the irradiation of gaseous mixtures of SF<sub>6</sub> sensitizer and methane. The experiments were carried out with a cylindrical glass reactor of 10 cm path length and 3.6 cm inner diameter fitted with NaCl windows. The laser beam was

focussed with a Ge lens (f.l. 5 cm) at different positions of the reactor in horizontal configuration. The preparation of the  $\text{CH}_4\text{-SF}_6$  mixtures for the irradiation and the measurement of the reaction progress by using the gas-chromatography (water-deactivated alumina) were performed by the technique described elsewhere<sup>13,14</sup>. Sulfur hexafluoride (Montedison, Milano, I.E.C. Standard) and methane (Moravské naftové doly, Lužice, 98.7% purity) were commercial samples.

## RESULTS AND DISCUSSION

The pyrolysis of methane studied in a wide temperature range is known<sup>4-9</sup> as a process that yields below 1 500 K mainly ethane and hydrogen. Above this temperature the pyrolysis is viewed<sup>4-9</sup> as a sequence of reaction steps (Eq. (1))



the importance of those is influenced mainly with temperature, conversion, inert gas dilution, and reactor surface. An increase in the reaction temperature results in a higher conversion and higher yields of polymers and carbon<sup>10</sup>. The dilution with an inert gas and extremely short contact times ( $10^{-3}$ – $10^{-4}$  s) along with very high temperature ( $\sim 1\,900$  K) are the conditions<sup>7,9</sup> that favor acetylene over carbon and polymers and afford as high yield of acetylene as about 90 percent. These results sound very promising in the light of future prospects of a comeback of basic chemical acetylene<sup>15</sup>. No attempt to optimize the methane pyrolysis for high amounts of ethylene was made until now. However, it is known that ethylene can be formed<sup>9</sup> in rather high yields ( $\sim 30$  percent) with inert gas dilution and extremely short contact time ( $\sim 10^{-3}$  s) at temperatures 1 800–1 900 K. For the formation of the major (Eq. (1)) and minor (propylene, allene) products heterogeneous catalysis both on the reactor surface and on the carbon nuclei formed in the gas phase is important. The  $\text{CO}_2$  laser-powered pyrolysis of methane the results with which are shown below excludes the possibility of the heterogeneous catalysis on the reactor surface.

The thermal decomposition of methane carried out under the focussed irradiation of methane with a continuous-wave  $\text{CO}_2$  laser in the presence of an  $\text{SF}_6$  sensitizer proceeds with the laser output 4–7 W only at very high partial pressures of  $\text{SF}_6$ . No measurable rate of the decomposition was observed with the laser output 7 W and the mixtures  $\text{CH}_4$  (3.3 kPa)– $\text{SF}_6$  (4.7 kPa) and  $\text{CH}_4$  (1.3 kPa)– $\text{SF}_6$  (8 kPa). Considering the observation<sup>13,14,16</sup> that a hot zone temperature can be raised by increasing the partial pressure of the sensitizer and decreasing the effective laser beam diameter, the initiation of the laser sensitized decomposition of methane was attempted with more favourable values of these parameters. The results are gathered in Table I and Figs 1 and 2.

The rate of the laser-photosensitized decomposition of methane occurring with higher SF<sub>6</sub> content increases with higher laser output and focussing conditions relating to a decrease in the effective beam diameter. This can be understood in the light

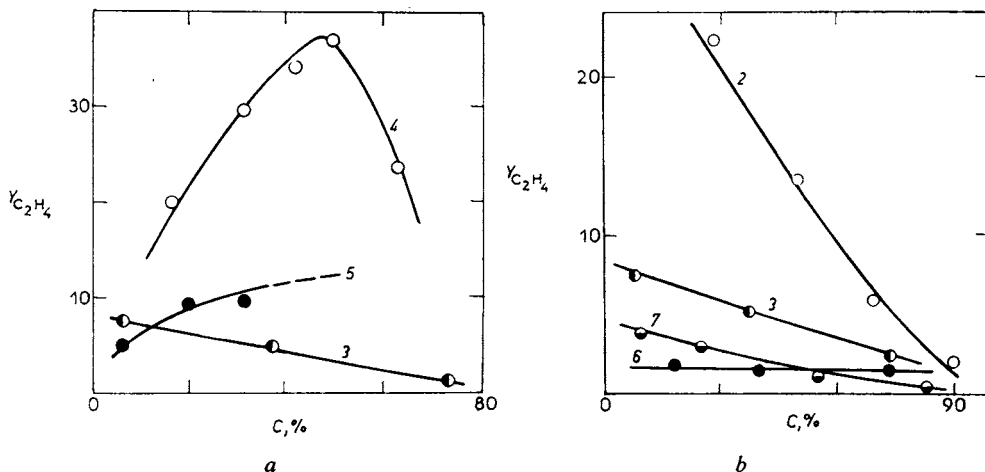


FIG. 1

Yield (*Y*) of ethylene *a* and acetylene *b* as 200 mol product/mol CH<sub>4</sub> decomposed at different conversions with runs 2–7 (Table I)

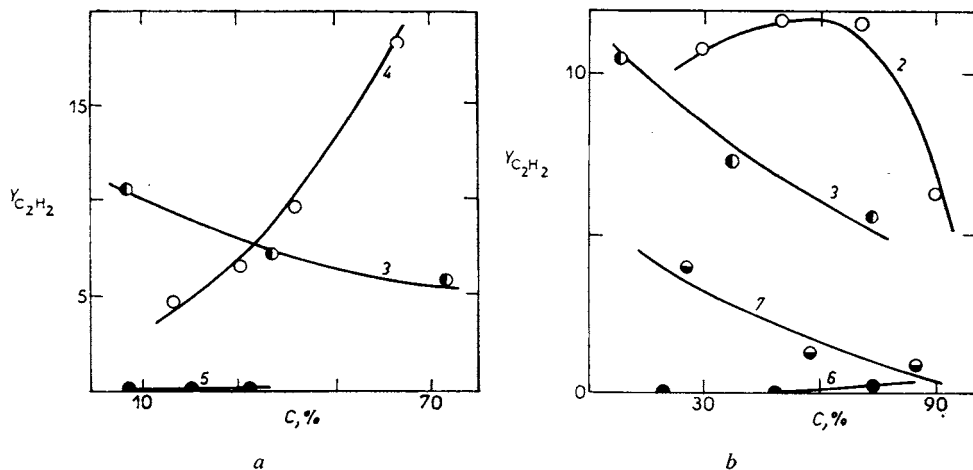


FIG. 2

Yield (*Y*) of ethylene *a* and acetylene *b* as 200 mol product/mol CH<sub>4</sub> decomposed at different conversions with runs 2–7 (Table I)

TABLE I  
Representative runs with laser-powered pyrolysis of methane

Run <sup>a</sup>	Laser output W	Focussed <sup>b</sup> cm	$t_{50}$ <sup>c</sup> s <sup>-1</sup>	$\langle T \rangle$ <sup>d</sup> K	Tar and carbon production <sup>e</sup>
1	4	0	2 500 <sup>f</sup>	1 170	no
2	5	0	100	1 290	yes
3	6	0	77	1 300	yes
4	6	1	400	1 240	no
5	6	1.5	1 600	1 190	no
6	6	1	300 <sup>g</sup>	1 250	no
7	7	0	62	1 310	yes

<sup>a</sup> With CH<sub>4</sub> (2.6 kPa)–SF<sub>6</sub> (42 kPa) mixtures. <sup>b</sup> To the position behind the entrance window. <sup>c</sup> Time of irradiation needed for the pyrolysis achieve 50 percent conversion. <sup>d</sup> Mean effective temperature  $\langle T \rangle = E_A / 2.3R (\log A - \log k)$ , where  $E_A$  and  $A$  are the Arrhenius parameters taken from ref.<sup>7</sup> and  $k$  is the first order rate constant. <sup>e</sup> Black deposition at the entrance window and the upper part of the reactor wall. <sup>f</sup> Extrapolated. <sup>g</sup> Irradiation chopped with frequency 63 Hz with equal transmission and obscuration wheel driven by a variable d.c. motor.

of the observation<sup>11,12</sup> that both the alterations in the laser parameters result in an increase of the hot zone temperature. Such an interpretation is in accord with values of mean effective temperature (Table I), even though this parameter has to be lower than true temperature in the irradiated systems.

With run 1 only ethane and ethylene are formed and the decomposition at 12 percent conversion yields about 15 percent of ethylene and 30 percent of ethane. The higher laser output favors formation of ethylene and acetylene and the dependence of their yield upon the progress of the decomposition carried out with different irradiation parameters is given in Fig. 1 and 2. It is seen that with 6 W output the highest yields of ethylene and acetylene are afforded with the irradiation focussed at 1 cm behind the entrance window (run. 4, Fig. 1). No increase in their yields is achieved with higher and lower laser output (compare runs 2, 3 and 7, Fig. 2), or with the chopped radiation (run 6, Fig. 2). Although the occurrence of the laser-powered pyrolysis is to be limited to the gas phase, the conditions used in this work cannot utterly exclude at least some participation of the surface of the entrance window, whereupon some deposition of a black material evidently carbon and tar took place and was apparently the reason for small cracks in the window because of its local overheating. The formation of the black substance was accompanied with a yellowish visible fluorescence. The results with runs 2, 3 and 7 thus cannot be considered as those giving the information about the product distribution in the process in that only heterogeneous catalysis of the methane decomposition on the carbon nuclei in the gas phase takes place.

## REFERENCES

1. Shaub K. M., Bauer S. H.: *Int. J. Chem. Kinet.* 7, 509 (1975).
2. Tardieu de Maleissye J. F., Lempereur F., Marsal C.: *C. R. Acad. Sci.* 275, 1153 (1972).
3. Olszyna K. J., Grunwald E., Kechn P. G., Anderson S. P.: *Tetrahedron Lett.* 19, 1609 (1977).
4. Khan M. S., Crynes B. L.: *Ind. Eng. Chem.* 62, 10, 54 (1970).
5. Chen C. J., Back M. H., Back R. A. in the book: *Industrial and Laboratory Pyrolyses* (L. F. Albright, B. L. Crynes, Eds). ACS Symposium Series 32, Washington, D. C. 1976.
6. Pola J., Farkačová G., Chvalovský V.: *Chem. Listy*, in press.
7. Yampolskii Yu. P., Gordon G. D., Lavrovskii K. P.: *Neftekhimia* 8, 198 (1968).
8. Frolich P. K., White A., Dayton H. P.: *Ind. Eng. Chem.* 22, 20 (1930).
9. Holmen A., Rokstad O. A., Solbakken A.: *Ind. Eng. Chem., Process Des. Develop.* 15, 439 (1976).
10. Schneider I. A., Murgulescu I. G.: *Z. Phys. Chem. (Leipzig)* 218, 338 (1961).
11. Kubát P., Pola J.: *This Journal* 49, 1354 (1984).
12. Kubát P., Pola J.: *This Journal*, in press.
13. Pola J., Farkačová M., Kubát P., Trnka A.: *J. Chem. Soc., Faraday Trans. 1*, 80, 1499 (1984).
14. Kubát P., Pola J.: *J. Chem. Soc., Perkin Trans. 2*, submitted.
15. Paessler P. in the book: *Energy and Feedstocks in the Chemical Industry* (A. Stratton, Ed.). E. Horwood Ltd., Chichester 1983.
16. Tardieu de Maleissye J., Lempereur F., Marsal C.: *Ber. Bunsenges. Phys. Chem.* 81, 235 (1977).

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