21st International Symposium on Plasma Chemistry (ISPC 21)
Sunday 4 August – Friday 9 August 2013
Cairns Convention Centre, Queensland, Australia

# Mass spectrometry peculiarities for supersonic clustered flows of methane and argon-methane mixtures

M. D. Khodakov[1], A. E. Zarvin[1], N. G. Korobeishchikov[1], V. V. Kalyada[1]

[1] *Novosibirsk State University, Department of Applied Physics*

**Abstract:** It has been confirmed that methane clustering starts at a lower stagnation pressure compared to argon clustering, which leads to a prolonged delay of cluster formation in argon. It has been demonstrated that it is reasonable to use specially selected gas mixtures for obtaining high-intensity methane cluster flows.

**Key words:** mass spectrometry, cluster, supersonic jet, methane, ionization.

## 1. Introduction

Interest in studying the processes of methane chemical transformations, its conversion into heavy and, first of all, liquid hydrocarbons or oxygenates right at gas mining sites is conditioned by technological needs [1] and remains strong for years. Unfortunately, synthesis of heavy hydrocarbons from natural oil gas using plasma-chemical methods, when the source material is affected by the self-maintained [2-3] or the non-self-maintained discharge [4-5] has not yet been conducted. Considerable success has only been achieved in the sphere of destruction processes, e.g. when producing hydrogen from methane [6-7].

Numerous attempts were made to combine plasma chemistry with other mechanisms that boost synthesis processes [8-9]. We particularly attempted [10] to juxtapose electronic-beam activation of methane supersonic flow with cluster formation in order to initiate electron-stimulated condensation as well as electronic cross-linking of molecules within the cluster, which causes hydrogen atoms to come out of the cluster as the result of their interaction with the electronic beam, and the remaining radicals are bound into stable molecules of heavier hydrocarbons.

The purpose of this paper is to identify the conditions for the formation of intensive cluster methane flows in order to continue searching for ways of optimizing the plasma-chemical hydrocarbon synthesis process.

## 2. Modeling experiment

Experiments were conducted using the gas-dynamic complex LEMPUS-2 at the Applied Physics Department of the Novosibirsk State University research facility.

In order to test the equipment and methodically check the truthfulness of the obtained results, compare them to the known models and experimental data, measurements in supersonic argon flow were conducted. High-purity argon was used, and the parameters of system are: nozzle-skimmer distance 33 mm, electron energy 40 eV, emission current 2 mA, supersonic nozzle (d * = 0,185 mm, d = 3,6 mm, L = 17 mm), 1 mm skimmer. Typical argon mass spectra obtained with the detector ExTorr XT300M at the jet axis behind the supersonic nozzle is presented in Fig.1. As it was expected a series of $Ar_n^+$ peaks (where n=1-7) in order of decreasing intensity was detected.

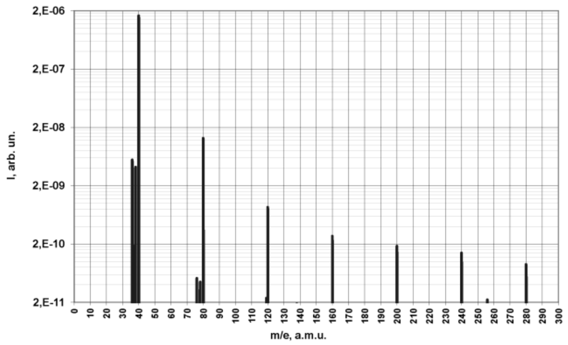

Fig. 1 The mass spectrum of argon. $P_0$=300kPa

Thus, the following and analogous experimental data obtained when varying the stagnation pressure of the nozzle unit settling chamber from 100 to 400 kPa in the stationary flow behind supersonic (according to Hagena, the average cluster size exceeds 2,500 atoms) nozzle confirm the presence of oligomeric argon component in the size of argon clusters, which apparently is the superposition of the true small clusters that failed to reach the average size, and the pieces of large clusters that broke to bits during ionization in the mass spectrometer. The obtained results also testify to the authenticity of the detected mass specters.

## 3. Mass spectrometry of pure methane molecular beams

As the estimates show, methane is condensed slightly better than argon, so it would be natural to expect analogous mass spectra that includes methane monomers and oligomers in supersonic flows of methane. However, even the very first experiments proved us wrong. The detected mass spectra (Fig.2) showed the presence of $C_1^+$ peak group, i.e. $CH_n^+$, where n = 0 – 5 as well as group $C_2^+$. The absence of methane oligomers in the mass spectra can be caused by extreme stability of large methane clusters to electronic ionization, or vice versa, practically 100% destruction of clusters to monomers that occurred during the ionization of large clusters.

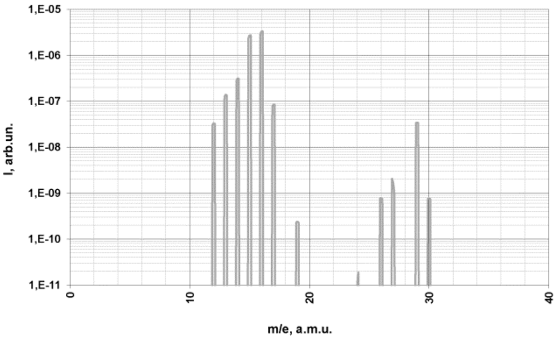

Fig. 2 The mass spectrum of methane. $P_0$=300kPa

## 4. Mass spectrometry of argon-methane mixture molecular beams

Experimental data on argon-methane mixtures obtained for three mixtures with three different concentrations (2.5%, 5%, 10%) of methane in argon within a broad stagnation pressure range is of our principal interest here. Choosing argon as the carrier gas is conditioned by the following reasons. Since small amounts of methane are contained in argon, methane gas dynamics will be analogous to those of a monoatomic gas. Argon does not enter into chemical reactions with methane; it is heavier than methane, therefore methane monomers not engaged in condensation process must be pushed away from the jet axis by argon. Argon is condensed slightly worse than methane, thus, condensation nuclei will be represented mostly by small methane clusters [11], and the emitted condensation heat will be absorbed by the buffer gas, argon. Mass specters obtained at an stagnation pressure of 300 kPa in one of the studied modes are presented in Fig. 3, a – c.

As the obtained results show, the amplitude of group $C_1^+$ peaks is increased together with the growth of methane concentration in the mixture, changes slightly with the growth of argon monomer, and is decreased almost by two orders of magnitude with the growth of argon dimer. The ratio of summed amplitudes for methane and argon peaks significantly differs from their concentrations in the initial mixture: the amount of methane in the flow turns out to be higher and grows as the initial methane concentration is increased. Mass peaks are found in the spectra, which correspond to masses of methane and are steadily detected along the whole examined range despite their comparatively small amplitude. At the same time a part of methane oligomer peaks can also be identified with the mixed argon-methane clusters. One more characteristic of the mixture mass specters is the presence of protonated ions from one of methane molecules that build up the cluster. Protonated peak intensity falls down with the growth of methane concentration in the mixture. This reaction occurs during ionization of particles, hence methane protonated ions are formed inside the mass spectrometer's ionizer and can be used as a marker indicating the presence of methane on the condition that the 'coat' formed by the carrier gas does not get too thick. Despite the low peak amplitudes and a comparatively large variety of data, the doublet's protonated peaks usually reach

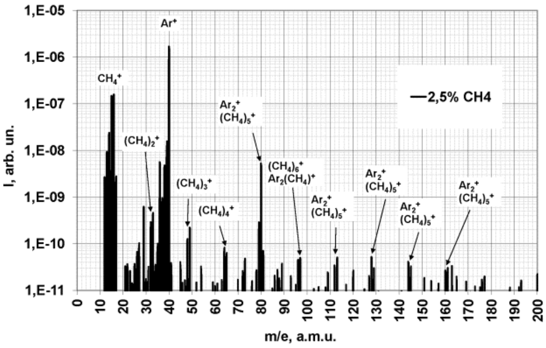

Fig. 3, a

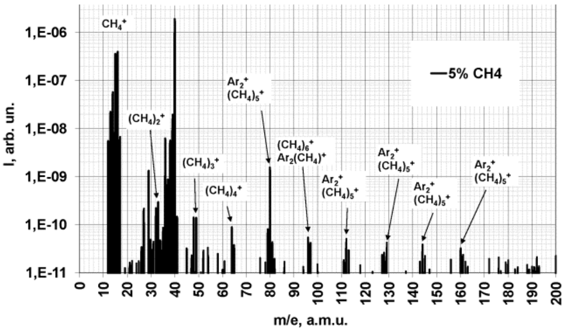

Fig. 3, b

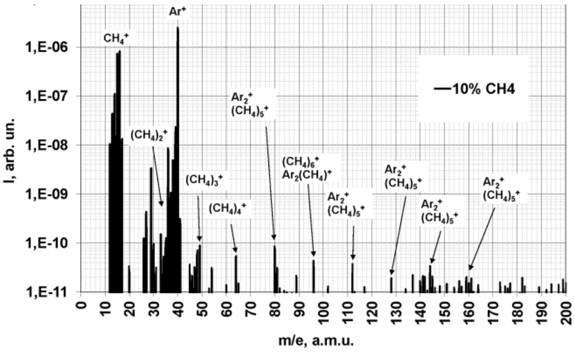

Fig. 3, c

maximum height at the lowest initial concentration of methane in the mixture. It can also be noted that the ratio of separate group $C_1^+$ mass peaks is approximately the same as in pure methane flow. A part of low-amplitude mass peaks had not been identified and was regarded as noise.

Let's consider the change of mixture mass specters at the fixed nozzle – skimmer distance selected in order to minimize the influence of skimmer interaction and the influence of the background gas coming from the flooded space surrounding the jet as well as to maximally move away of the intensive cluster formation area depending on the stagnation pressure. Fig. 4 shows the comparison of argon and methane monomers in pure gases and in three working mixtures with normalization in relation to the amount of methane in the mixture. In general, the dependency changes for argon monomers are insignificant and do not greatly deviate from the pure argon data. As it was expected, at an early condensation stage, when forming condensation nuclei, argon monomer mass peak amplitude is slightly lowered as methane concentration grows, which can be explained by the increase of the emitted condensation heat together with the correspondent carrier gas temperature growth and the corresponding reduction of density on the jet axis. The decrease of monomer signals starting with stagnation pressure values of about 100 kPa characterizes the transition to the so-called developed condensation mode [12], when the amount of condensate stops increasing and an extensive growth of cluster size starts. Argon monomer amplitude in this area is higher at greater methane concentrations, which can testify to the formation of argon coat on argon clusters. The dependencies of methane monomer amplitudes pass through the maximum values at higher $P_0$ compared to argon: at 120 kPa for a mixture with minimum methane concentration and 200 for a mixture with maximum methane concentration, which is apparently explained by the stop of methane condensate amount growth at pressures that are higher at greater concentrations. It is also obvious that in case of cluster formation absence and at the initial stage of cluster formation methane monomer mass peak amplitudes grow identically. Layering occurs at transition to the developed condensation mode; at that moment in the maximum amplitude area relative intensity of methane monomer signal is higher at its lowest concentration in the mixture even in comparison with pure methane.

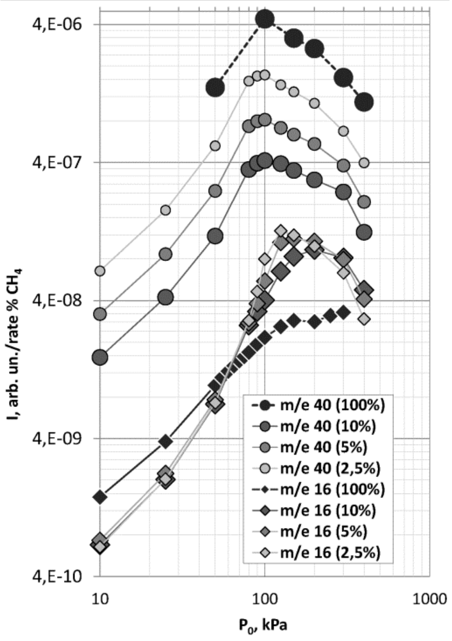

Fig. 4 Dependence monomers amplitude on stagnation pressure

After normalizing methane mass peak amplitudes according to the analogous sum for argon it was confirmed (Fig. 5) that when switching to the developed condensation mode, starting approximately with $P_0$ = 90 kPa, within a relatively narrow range of stagnation pressures methane concentration on the molecular beam axis rises drastically compared to the initial value; besides, an almost eight-fold increase occurs for all three mixtures, after which this new ratio of partial concentrations for mixture components remains constant after further increase of stagnation pressure.

Surely, the exact growth value can change when modifying the gas-dynamic system configuration. But even at this stage we can be certain about the prospects of using mixtures in order to achieve maximum flow intensity for any gas of interest.

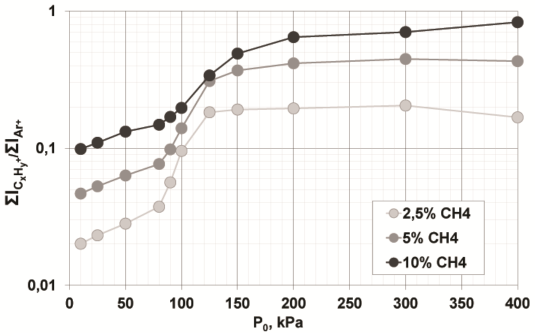

Fig. 5 Dependence of sum methane and argon amplitudes to stagnation pressure

## 5. Conclusion

Thus, by using the new LEMPUS-2 complex an intensive molecular beam of methane clusters was obtained. It has been ascertained that large-size clusters in a supersonic jet of methane are not detected by mass spectrometry of oligomeric pieces, which can be conditioned by their fragmentation into monomers or their destruction stability when they are ionized with 40 – 100 eV electrons. At the same time, in the mass spectra of argon mixtures containing small amounts of methane, both methane oligomers and mixed argon-methane clusters are apparently detected, which testifies to the complex structure of large clusters, whose formation is caused by methane. It has been confirmed that methane clustering starts at lower stagnation pressures compared to argon and leads to an additional delay of cluster formation in argon. It has been demonstrated that it is reasonable to use specially selected gas mixtures for obtaining high-intensity methane cluster flows.

## 6. Acknowledgements

This work has been performed with financial support from the Russian Federation Government Scholarship No. 11.G34.31.0046 (leading scientist K. Hanyalich, NSU) and the Education and Science Ministry of the Russian Federation, project No. 3.749.2011.

## 7. References

[1] A. V. Grunvald, Neftegazovoe delo, http://www.ogbus.ru/2007_2.shtml (in Russian) (2007)
[2] J. R. Fincke, R. P. Anderson, T. A. Hyde, Ind. Eng. Chem. Res., **41,** 1425 (2001)
[3] K. V. Kozlov, P. Michel, H. E. Wagner, 14th Internat. Symp. on Plasma Chemistry, **IV,** 1849 (1999)
[4] R. G. Sharafutdinov, V. M. Karsten, S. Ya. Khmel et al., Surface and Coatings Technology, **174**, 1178 (2003)
[5] R. G. Sharafutdinov, A. E. Zarvin, V. Zh. Madirbaev, V. V. Gagachev, G. G. Gartvich, Technical Physics Letters, **31,** 641 (2005)
[6] A. M. Anpilov, E. M. Barkhudarov, N. K. Berezhetskaya, S. I. Gritsinin, A. M. Davydov, Yu. N. Kozlov, I. A. Kossyi, M. A. Misakyan, S. M. Temchin, V. G. Ralchenko, P. A. Gushchin, E. V. Ivanov, Technical Physics, **56**, 1588 (2011)
[7] A. Ya. Stolyarevsky, Alternativnaya energetika I ecologiya, **2**, 26 (in Russian) (2005)
[8] N. G. Korobeishchikov, A. E. Zarvin, V. Zh. Madirbaev, R.G. Sharafutdinov, Plasma Chem. Plasma Proc., **25**, 319 (2005)
[9] A. E. Zarvin, N. G. Korobeishchikov, V. V. Kalyada, V. Zh. Madirbaev, Eur. Phys. J. D., **49**, 101 (2008)
[10] V. Zh. Madirbaev, A. E. Zarvin, N. G. Korobeishchikov, Vestnik Novosibirsk State University, **3**, 34 (in Russian) (2008)
[11] N. G. Korobeishchikov, A. E. Zarvin, V. V. Kalyada, V. Zh. Madirbaev, Vestnik Novosibirsk State University, **6**, 55 (in Russian) (2011)
[12] S. Ya. Khmel, R. G. Sharafutdinov, A. E. Belikov et al., Preprint of Inst. Thermophysics, **271**, 93 (1994)