On the possibility to repay of associated gas torches by using plasma-chemical conversion of methane

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

Novosibirsk State University, Department of Applied Physics

Abstract: We present the research result of processes happening in supersonic jets of light hydrocarbons, when the light hydrocarbons are activated by an electron beam. It has been demonstrated that at higher stagnation pressures, i.e. on advanced stage of condensation, the number of heavy particles increases. It has been confirmed that the observed effect at high braking pressures due to the synthesis of heavy particles.

Keywords: conversion, GTL-production, clusters, supersonic jet, plasma reactions..

1. Introduction

The main components of the associated gas (70 - 90% by the volume) are methane and, in much smaller quantities, ethane, propane and so on. All of these substances under normal conditions (T> 0 ° C) are in a gaseous state. Methane, propane and butane are the basic components of associated gas. They make up about 10% by weight of the oil. Oil production technology in the northern Russia that exists in present, does not include the process of associated petroleum gas into the liquid, and it is mainly burned. Petroleum gas flare that burn petroleum gas are the usual elements in areas of oil production. Only in the Khanty-Mansi Autonomous Area - Yugra, which is extract from the depths of almost 60% of Russian oil, these flares are more than a thousand.

Technologies of processing of volatile hydrocarbons are present for years. They are primarily based on catalysts in Fischer-Tropsch process, and are determined for the stationary production. These technologies are mostly not applicable to the remote oil fields processing. The transportation of the large-tonnage commercial product should be considered as well. The only available high-performance transport of liquid products from the field is an oil pipeline.

In the last two decades researchers of different countries have made attempts to develop direct method of conversion of natural and associated gas in heavy hydrocarbons, bypassing the stage of synthesis gas. As the number of carbon atoms increases the melting point and boiling point of hydrocarbons. Liquid under normal conditions are hydrocarbons C_6H_X and higher. In terms of reducing transport costs the most profitable product of processing of associated gas are liquid hydrocarbons obtained directly at the site.

The requirement of compactness and mobility does not allow using the existing chemical technologies for processing of associated gas to large stationary reactors. One solution of the problem - the conversion of volatile hydrocarbons into the liquid, which could be added to the produced oil for transportation by existing pipelines for processing. The requirement for the liquid: vapor pressure less than 0.6 atm. One promising approach is considered - the initiation of plasma chemical reactions in the flow of a mixture of light hydrocarbons. Charged particles provide large cross sections and, therefore, a high reaction rate. For plasma conversion does not require large size and weight of the reactor.

Nevertheless the attempts to develop the technology of conversion of liquid hydrocarbons into petroleum fractions, based on the plasma-chemical methods have not been successful. The main reason for the negative results, evidently, is the apparent "equilibrium" of processes that occur in the flow, for example, weakly ionized plasma of methane. Therefore, heavy hydrocarbons formed in the discharge with the participation of radicals disintegrate soon after synthesis. Inference: it is necessary to use other physical mechanisms for the initiation synthesis processes. Such mechanism, we believe, can be cluster formation in a supersonic flow of weakly ionized plasma.

2. Plasma chemical technologies

The earliest investigations were focused on

possibilities to use the discharge plasma for the initiation of the gas-phase reactions [1-2].

The Institute of Thermophysics SB RAS has patented the idea to activate the supersonic gas reagent jet with the high-energy electron beam. Using electron beam resulted in the significant movement of the distribution function of electron energies towards higher energies compared to the discharge. I.e. at the same implied power, the proportion of electrons with the energies above the dissociation threshold of the flow particles, significantly increased.

Experiments [3-4] have shown that the proposed method provides an efficient generation of radicals. That has been used to produce hydrogen out of methane, and to sediment the silicon coatings out of silane. We have proved the high efficiency of the method at the point of initiation of the process of fragmentation reactions. The attempts to use this method for the synthesis of heavy hydrocarbons, however, did not provide the expected result. Model calculations have shown the low efficiency of this process. The generated radicals quickly perish in the binary reactions and the increase of the number of activating electrons leads not only to the increase of the radicals' number, but also stimulates the disintegration of the already formed heavy molecules. Thus, to achieve our objective we have to find the additional catalytic mechanisms that will trigger the synthesis process.

3. Experiments in conditions of condensation

We know that in a supersonic jet clusters could be formed due to a sharp drop of the temperature of the gas downstream up to the cryogenic level. The forces that hold the molecules in the cluster can lead to a change in the threshold of activation and ionization energy of molecules in the cluster, and broaden the energy levels. A large retention time of particles in the cluster increases the probability of energy transfer. For example, in the source [6-7] it has been shown that, when the argon mixtures with methane, monosilane and other molecular additives, are activated by the electron beam of supersonic jets, the highly efficient energy exchange occurs. This effect is detected at a certain stage and is due to the presence of condensation in the flow of mixed clusters. We seemed logical to evaluate the possibility of using clustered methane jets to increase the efficiency and controllability the plasma chemical jet synthesis of heavy hydrocarbons. Previously [8], we investigated the process of clustering in the absence of electronic activation. In this case was demonstrated the possibility of controlled formation of clusters, including mixed, with average sizes ranging from a few to thousands of atoms or molecules.

The activation of flow with clusters can cause the following processes:

a) flow heating, consequently, decrease condensate fraction, by reducing the concentration of clusters, and by decreasing their average size;

b) electron - stimulated condensation, in which the ionized particles becomes nuclei of clusters, so that the number of clusters and the fraction of condensate are increase;

c) electron stitching of molecules in the cluster, in which hydrogen atoms emitters due to the interaction with the electron beam with a cluster, and the remaining radicals are linked to the stable molecules of heavy hydrocarbons.

The research was performed using the LEMPUS experimental complex (Fig.1) of Novosibirsk State University [8-9]. We used molecular beam mass spectrometry apparatus and activating electron gun. The working gas used natural gas composition. The stagnation pressure P_0 varying from 1 kPa to 10^3 kPa. For activating of gas jet the focused electron beam with diameter 1 - 3 mm and electron energy 3 - 5 keV was used. Electron beam crossed the supersonic jet perpendicular to its axis at distance 5 - 20 mm from nozzle.

It is known that the condensation of the mixture of gases starts with the easy condensing components [6]. Ethane and heavier hydrocarbons condense much better than methane. Therefore the number of ethane molecules in the cluster, at least at the initial stage of condensation, can significantly exceed the number of methane molecules. Activation of the jet by electrons leads primarily to an earlier beginning of condensation, as well as a greater drop in gas density due to expansion of the flow due to thermal heating

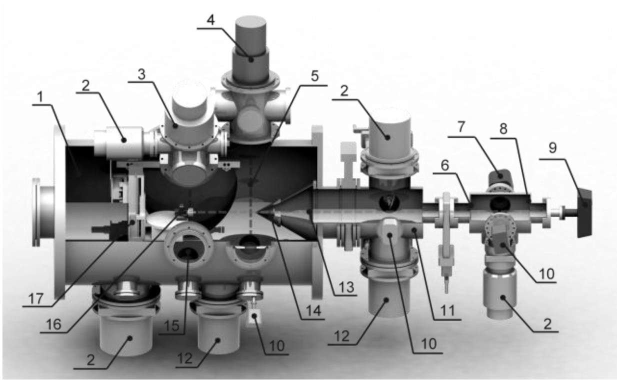

Fig.1 A schematic diagram of the experimental setup LEMPUS-2: 1 - expansion chamber, 2 - turbomolecular pumps, 3 - electron gun with a heated cathode, 4 - electron gun with a hollow cathode; 5 - focused electron beam axis , 6 - collimating aperture 7 - sorption vacuum pump; 8 - detection chamber; 9 - quadrupole mass spectrometer, 10 - Vacuum gauge, 11 - post skimmer chamber, 12 - cryogenic pumps, 13 - nozzle-skimmer- collimator-detector axis, 14 - skimmer, 15 - optical windows, 16 – stagnation chamber and nozzle, 17 - 3 component pointing device.

Condensation leads to release a stream of additional energy, resulting in the jet expands and the density at the axis decreases. In addition, the displacement of molecules from the jet axis by clusters also leads to a drop in the density of monomers, and the intensity of mass peaks of the monomers with increasing P_0 even slightly reduced. Thus, while the electron beam heats the gas, the formation of clusters in a supersonic flow occurs quite efficiently. Than larger the particle, than less effect on their quantity of activating electrons. We can assume that the electron energy is spent not on the collapse of large clusters, as, for example, for yhe formation of chemical bonds in the Van der Waals particles.

Fig. 2 shows dependence of the intensities of ion peaks from the stagnation pressure with electron activation (dark) and without activation (light). The normalization of the intensities of mass peaks in the intensity of the peak m/e = 16 can reverse the effects associated with the fall of the density due to expansion of the flow, and more accurately determine the effect of activating the beam of electrons on the composition of the stream. Found that the ratio of peak m/e = 15 and m/e = 16 when activated by electrons remains practically unchanged. Consequently, we can assume that the mass peak m/e = 15, i.e. CH_3^+, is formed directly in the ionizer of the mass spectrometer for dissociative ionization of methane. The CH_3 radical is formed by electron gun activation of methane jet, dying in the course of the reactions directly in the gas stream and to the sensor of the mass spectrometer does not reach. Ionized components of the plasma flow, including the ion CH_3^+, pass through a grounded conductive molecular beam skimmer system in small quantities, so the ability to contribute to the mass spectrometer signal from the ionized component of the flow is not considered.

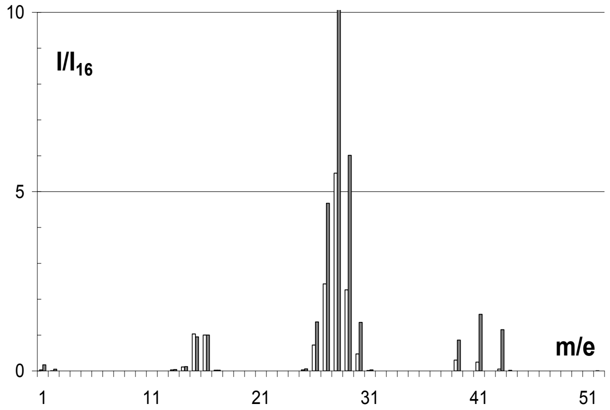

Fig.2 Mass spectrum of the mixture

Finally, the normalized relative intensities of mass peaks with ionization and without ionization $I_{norm} = (I/I_{16})_{aeb} / (I/I_{16})_0$, we obtain the "enrichment" - an amount reflecting the impact of activation on the intensity of the mass peak. In Fig. 3 shows that flow activation by electrons does not affect to the relative intensity of the peaks CH_n, however, it leads to significant changes in the other masses. The increase of the proportion of free hydrogen (H, H_2), as well as the relative proportion of the complexes C_2H_n, C_3H_n, possibly it is a consequence of the restructuring of weakly bound van der Waals bonds in the hydrocarbon chemistry in large complexes

4. Concluding remarks

Analysis of the experimental data shows the following. At the initial stage of condensation the activation of the jet gas by electron beam stimulates the clustering at lower stagnation pressures. At the same time, apparently, the heating of the gas flow proceed, which leads to a gas density drop in the axial region. At higher stagnation pressures, i.e. on advanced stage of condensation, the number of heavy particles increases. One can suggest that the observed effect at high stagnation pressures due to the synthesis of heavy particles from the flow of methane is activated by an electron beam.

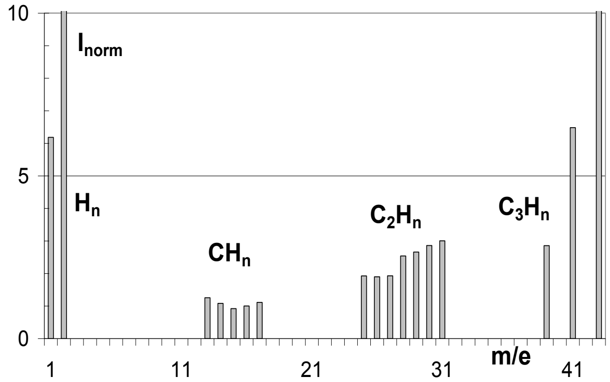

Fig.3 Normalized relative intensities of mass peaks with ionization and without ionization

Thus, the efficiency of ion-cluster interactions in supersonic flows of hydrocarbons opens up the possibility of their use in GTL technology.

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.

5. References

[1] J.R. Fincke, R.P. Anderson, T.A. Hyde, Ind. Eng. Chem. Res., **41**, 1425 (2002).
[2] K.V. Kozlov, P. Michel, H.-E. Wagner, 14th Internat. Symp. on Plasma Chemistry, **IV**, 1849 (1999).
[3] R.G. Sharafutdinov, V.M. Karsten, et al, Surface and Coatings Technology, **174-175**, 1178 (2003).
[4] R.G. Sharafutdinov, A.E. Zarvin, et al, Technical Physics Letters, **31**, 641 (2005).
[5] A. Vinokurov, R. Sharafutdinov, Yu. Tychkov, Chem. and Technol. Fuels and Oils,. **41**, 112 (2005).
[6] A.E. Zarvin, V.Zh. Madirbaev, et al, Tech. Phys., **50**, 1444 (2005).
[7] V.Zh. Madirbaev, A.E. Zarvin, Vestnik Novosibirsk State University. Series: Physics, 2(1), 36 (2007).
[8] N.G. Korobeishchikov, A.E. Zarvin, et al, Plasma Chem. Plasma Proc., 25, 319 (2005).
[9] A.E. Zarvin, N.G. Korobeishchikov, et al, Eur. Phys. J. D, 49, 101 (2008).