

HYDROCARBON GAS HYDRATES and THEIR DETONATION HAZARD

A.A.Vasil'ev, A.I.Valishev, V.A.Vasil'ev and L.V.Panfilova

Lavrent'ev Institute of Hydrodynamics SB RAS
Novosibirsk State University
Novosibirsk 630090
gaset@hydro.nsc.ru

INTRODUCTION

As a result of geological explorations, a huge fuel reserves as gas-hydrates have been found in bowels of the Earth and at the bottom of World ocean. The reserves of hydrocarbon raw material (mainly as methane) in gas-hydrate state are estimated in $2 \cdot 10^{16} \text{ m}^3$, which noticeably exceeds all known reserves of gas, petroleum and coal taken together. Now hydrate problem attracts attention in many countries: the national programs dealing with the investigation and perspectives of their utilization have been initiated in Japan, France, England, Canada, Norway, India, USA, etc.

Gas-hydrates are solid crystalline compound looking like snow or friable ice. They are formed from water molecules and from some individual gas G (common formula of hydrate is $G \cdot n\text{H}_2\text{O}$ with $n \geq 5,67$). Water molecules form a spatial skeleton construction at freezing – crystalline lattice of «the host» – with interior cavity, inside which the molecule of individual gas G_i (molecule – «visitor») can be placed.

According to the modern classification there are six types of cavities: small – D' and D, large – T, P, H, E. The surface of D'-cavity is «cross-linked» from three tetragonal, six pentagonal and three hexagonal edges (structural formula – $4^3 5^6 6^3$). The following formulas are characteristic for other cavities: D – 5^{12} , T – $5^{12} 6^2$, P – $5^{12} 6^3$, H – $5^{12} 6^4$, E – $5^{12} 6^8$. The D-cavity (12-heral pentagonal dodecahedron) is energetically preferred among all cavities.

For today the following hydrate structures are known – cubic, tetragonal, hexagonal and rhombic, in which the spatial lattices of «host» are united. The cubic structure CS-I has a space-centered lattice with the parameter 1.20 nm; $6\text{T} \cdot 2\text{D} \cdot 46\text{H}_2\text{O}$ is a formula of the crystalline cell (2 small cavities D with an average free diameter 0.52 nm and 6 large cavities T with a diameter 0.59 nm). The structure CS-I is characterized by values $n=46/6$ (type 1) or $n=46/8$ (type 2) depending on the filling of cavities. The cubic structure CS-II has face-centered a diamond-type lattice with the parameter 1.74 nm; a formula of the cell is $8\text{H} \cdot 16\text{D} \cdot 136\text{H}_2\text{O}$ (16 small cavities D with an average free diameter 0.48 nm and 8 large cavities H with a diameter 0.69 nm) with characteristic values $n=136/8=17$ (type 1) or $n=136/24$ (type 2). «Windows», which connect the separate cavities, have an average diameter $0.20 \div 0.28$ nm. The tetragonal structure TS-I has the formula of a cell $4\text{P} \cdot 16\text{T} \cdot 10\text{D} \cdot 172\text{H}_2\text{O}$ and it is characterized by value $n=8.6$ at filling of cavities P and T. The hexagonal structure HS-I has the formula of a cell $2\text{T} \cdot 2\text{P} \cdot 3\text{D} \cdot 40\text{H}_2\text{O}$ and it is characterized by values $n=40/4=10$ (type 1) or $n=40/7$ (type 2). The hexagonal structure HS-III has the formula of a cell $\text{E} \cdot 2\text{D}' \cdot 3\text{D} \cdot 34\text{H}_2\text{O}$ and it is characterized by value $n=34$ at filling of cavity E. The rhombic structure $4\text{H} \cdot 4\text{P} \cdot 4\text{T} \cdot 14\text{D} \cdot 148\text{H}_2\text{O}$ has value $n=148/12$ at filling of cavities H, P, T.

Huge reserves of gas hydrates attract attention not only in connection with the perspective of their utilization as a fuel and chemical raw material, but also as a possible serious «violator» of ecology. The natural gas-hydrates exist near to the barrier of their phase stability and consequently they are quite sensitive to changes of thermodynamic conditions. Even insignificant changes of thermobaric conditions (of natural or artificial origin) can cause

the decomposition of natural gas-hydrates and uncontrollable emission of great amount of hydratic methane into the atmosphere. Its capable to intensify the greenhouse effect multiply (specific absorption of a thermal radiation of the Earth by methane is approximately 20 times above, than that by a carbonic gas).

The problem of fire and explosion hazards of huge clouds of methane-air mixture produced from methane hydrate at its decomposition is very important as well. It is should particularly emphasized, that the gas volume in hydrate state is much less than volume of the same gas under normal conditions (about 165 m³ of methane is «compressed» in 1 m³ of hydrate). The similar clouds can always appear at emergency, because the gas is easily extracted from the hydrate.

In this paper the calculated parameters of detonation hazard of mixtures CH₄ – air (oxygen) – H₂O and C₂H₂ – air (oxygen) – H₂O are presented. Methane is the main component of natural hydrates, and acetylene is chosen as the specific standard, because its mixtures with oxygen are considered traditionally as the most dangerous mixtures from an initiation point of view, i.e. they are characterized by minimum values of the critical initiation energy at comparison with others fuels.

ASSUMPTIONS and CALCULATIONS

It is possible to make some estimations for several variants of hypothetical hydratic charges as the mixtures of the simplest hydrocarbon (methane or acetylene), air (oxygen) and water. The number of variants is determined by the water phase to be considered: 1) as a gas; 2) as fine-dispersed droplets of liquid water; 3) as fine-dispersed ice sprayed likely homogeneous two-phase «dusty-gas» cloud; 4) as fine-dispersed hydratic ice. Variant Nos.2–4 differ from variant No.1 by the fact that the energies of the liquid-gas (No.2) and solid-liquid-gas (No.3) phase transitions and the additional energy of formation of the hydrate (No.4) are taken into account in them.

For approximated calculations the characteristic sizes of particles – snowflakes of a hydrocarbon hydrate sprayed in air (oxygen) can be assumed to be negligible. Under such assumption it is possible to neglect all physical relaxational processes (acceleration and fragmentation of particles, detachment of a boundary layer, etc.), which occur actually. Such sprayed hydrate can be considered as hypothetical gas with new enthalpy and entropy of components in the initial stage.

As a result, a portion of the chemical energy of a mixture will be expended on the phase transition, which will cause a change of the main parameters of combustion and detonation.

MAIN RESULTS and DISCUSSION

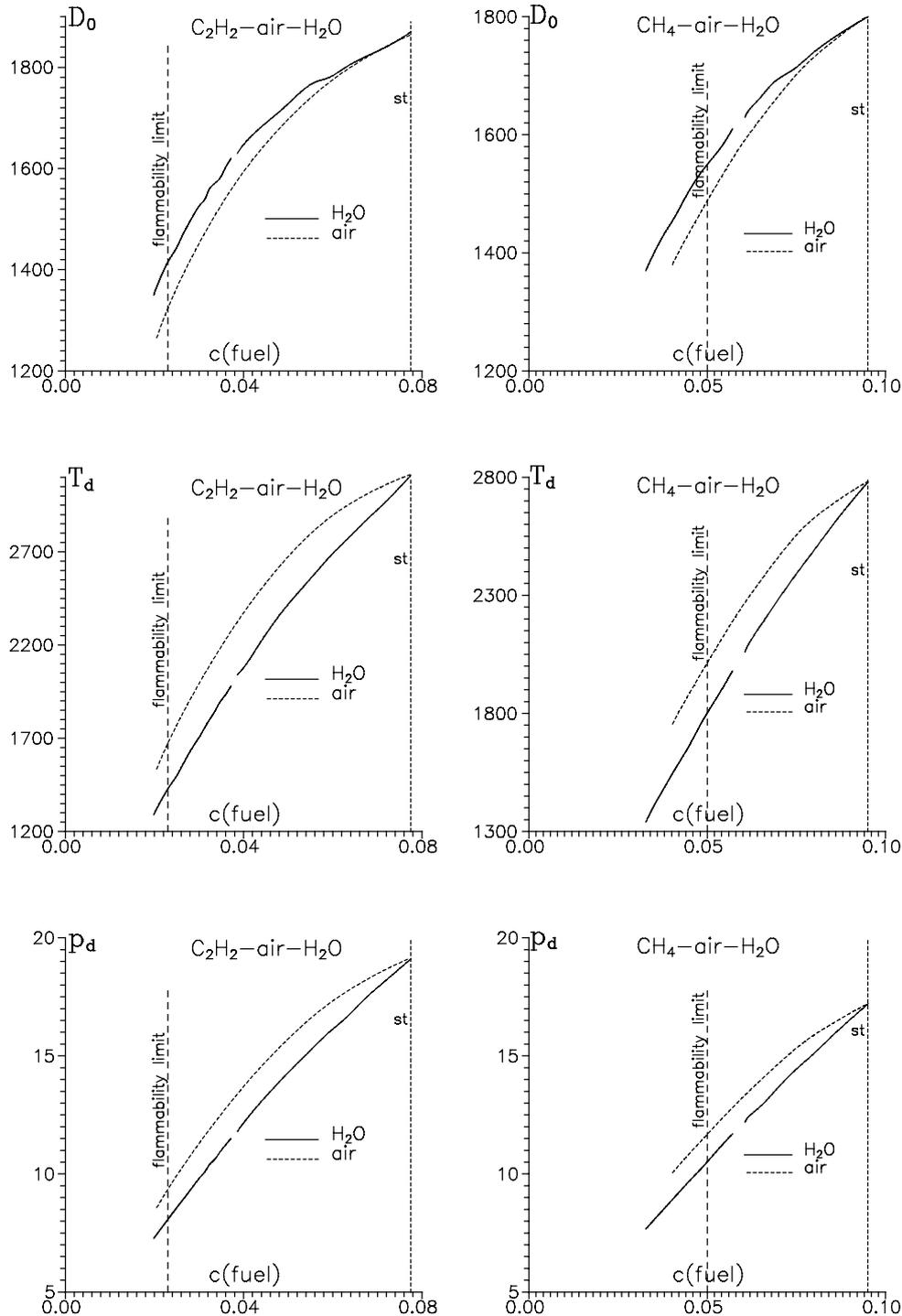
Some results are reported for mixtures at stoichiometric fuel/oxidizer ratio. The amount of H₂O was varied from zero up to such value, at which the molar fraction of fuel in a mixture achieves the lower flammability limit (on concentration), passing through the values that correspond to mentioned above structures of hydrates.

The calculation are carried out with the help of the Computer Program «SAFETY». The pressure p₀=0.1 MPa and the temperature T₀=273 K are used as the initial parameters.

On Figs.1–6 the most important detonation parameters are presented for C₂H₂ (left figs.) and CH₄ (right figs.) mixtures. The dotted curves on all Figures correspond to fuel-air or fuel-oxygen mixtures (FAE or FOE) without H₂O, the solid curves correspond to calculation for variant 1, i.e. gradual dilution of stoichiometric mixtures with the vapour of water (gaseous); dashev curves on Figs.5–7 correspond to calculation for variants 3 (or 4). Vertical dashed lines with symbols on Figs.5–7 refer to fuel concentration in the appropriate typical hydrate structures. The lower flammability limit and detonation limit in corresponding FOE and FAE

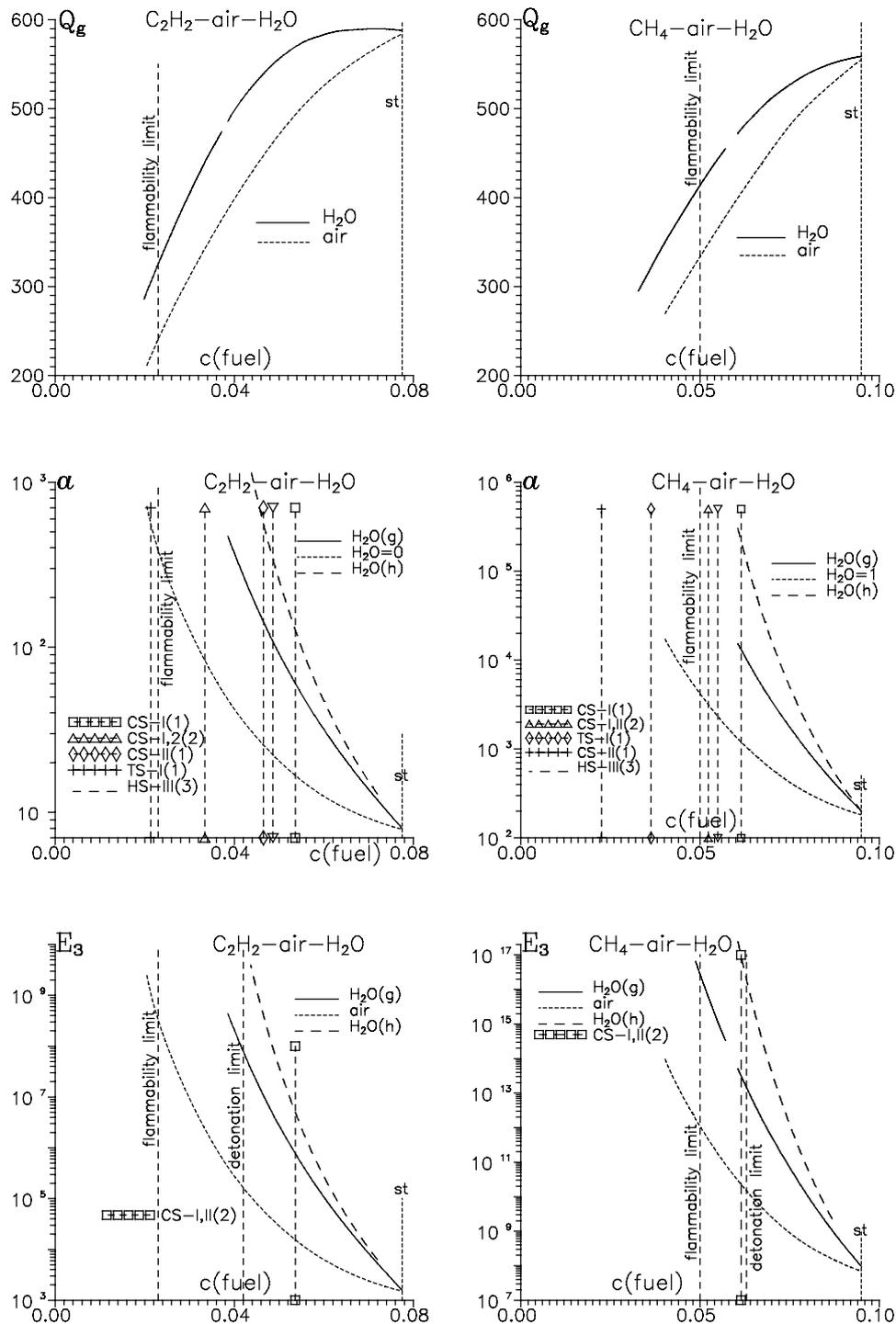
is specified also on some figs as vertical dashed lines with description words.

Its seen, that at dilution by water, the concentrations corresponding to the typical structures of hydrates are placed on both sides from the lower flammability limit. The lines for structures with small values n are situated inside of concentration limits, that indicates on a



Figs.1–3. The detonation velocity D_0 – m/sec, the temperature T K and the dimensionless pressure ($P=p/p_0$) of the products are presented in dependence on molar portion of acetylene (left figs.) or methane (right figs.) in air–water mixture.

possibility of flame propagation in such mixtures. The lines for structures with small values of n are within the concentration limits, which indicates the possibility of flame propagation in such mixtures. The concentrations outside the range of concentration limits correspond to



Figs.4-6. The chemical energy release Q cal/g, the detonation cell size a mm, the critical initiation energies of spherical detonation E_3 J are presented in dependence on molar portion of acetylene (left figs.) or methane (right figs.) in air-water mixture. «st» denotes the stoichiometric concentration; $H_2O(g)$ and $H_2O(h)$ denote water in the gas and hydrate forms, respectively; dashed verticals with symbols at the ends refer to the concentrations corresponding to the typical structures of hydrates.

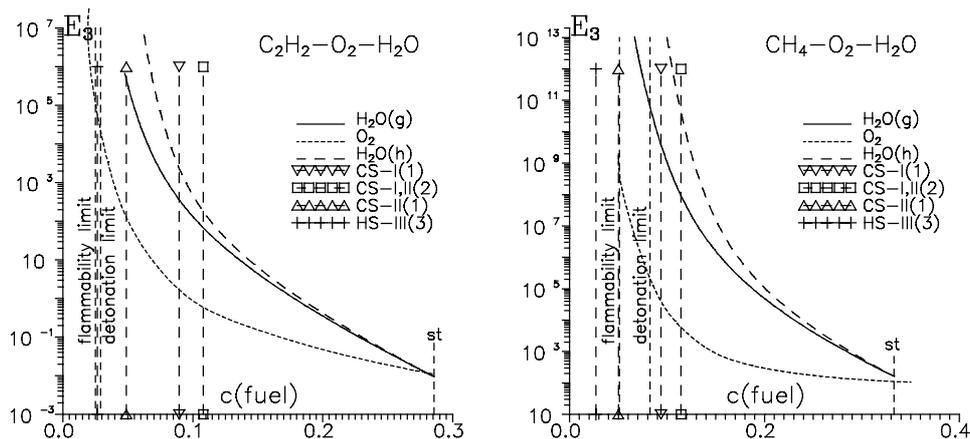


Fig.7. The critical initiation energies of spherical detonation E_3 J are presented in dependence on molar portion of acetylene (left figs.) or methane (right figs.) in oxygen–water mixture.

structures with large values of n , i.e., stationary flame propagation cannot occur at these C_n .

As the hydrate structure CS–I is characteristic for methane and acetylene, the calculations confirm a possibility of burning of such hydrates not only in an oxygen, but also in an air medium. Such parameters as the detonation velocity and the temperature and pressure of the products decrease with increase in the H_2O concentration, whereas the cell size a and the critical initiation energies increase appreciably.

The lowest initiation energies are characteristic for acetylene–oxygen mixture. The addition of water increases the critical initiation energy E , nevertheless, the calculated values of E are such that one can speak about relative easiness of detonation excitation not only of a mixture of a «gaseous» acetylene hydrate with oxygen, but also of a real hydrate ($E_3=180$ J).

In mixture of acetylene – air it is required about 1/3 g TNT for excitation of detonation. The addition of gaseous water up to hydratic ratio requires approximately 180 g TNT, and for real hydrate the mass of an initiating charge must be increased up to 1.35 kg TNT, which indicates on the relative explosion hazard of acetylene–hydrates.

Methane–oxygen mixture without water also has relatively low initiation energies. However, the dilution of FOE by water increases significantly the energy E . For example, to initiate the detonation in mixture with gaseous water, which corresponds to methane hydrate, charge about 22 kgs TNT is required. The TNT mass is increased up to 10 tons at taking into account the phase transition. Concerning to air mixtures, even stoichiometric methane–air mixture requires about 21 kgs TNT for initiation of a detonation. With water added, these values increase so significantly (up to 10^4 tons for gaseous water and up to 10^{13} tons for a real methane hydrate), that the process of detonation excitation in such mixtures becomes unrealizable in practice.

CONCLUSION

The calculated parameters of mixtures methane–oxygen(air)– H_2O and acetylene–oxygen(air)– H_2O are presented from ecology and hazard points of view. The values of the critical initiation energy with reference to hydrates of methane and acetylene have been estimated. The data indicates the burning possibility of hydrocarbon hydrates in oxygen and air. As to a detonation, it is possible to speak about real explosion hazard of acetylene–hydrates, whereas methane–hydrates require the unreal large charges for initiation of detonation.