

SAFETY ENGINEERING OF ANTHROPOGENIC OBJECTS

ASSESSMENT OF THREAT ARISING BY EXPLOITATION OF ACETYLENE

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Abstract

In the paper base reactivity parameters of acetylene are considered. The terms of safe usage of acetylene are interpreted and related to their molecular structure. Unusual susceptibility of acetylene to exothermic self-decomposition is analysed. Chemical composition and parameters of acetylene decomposition at various initial states are estimated in thermodynamic calculations. Combustion and explosion of acetylene/air and acetylene/oxygen mixtures are estimated in full range of acetylene concentration.

Key words: acetylene, self-decomposition, combustion and explosion parameters

INTRODUCTION

Acetylene is a technical gas preserving their usability in many areas of technology and everyday life. Acetylene mixtures with oxygen offer exceptional energy outcome (high heat of combustion) as well as a stream of high-temperature combustion products. Due to mobility acetylene containing devices become to be an easy-to-delivery energy source. Reliably to ignite acetylene effectively burns at wide concentration ranges. But in reverse, exceptional reactivity and flammability constitute a considerable combustion and explosion hazard. A unique feature, in comparison to other hydrocarbons, is the susceptibility of acetylene to exothermic self-decomposition. That imposes special precautions for storage and transport of acetylene cylinders. Safety of exploitation of acetylene is regulated by technical documents [1 ÷ 3] and is a subject of numerous investigations, e.g. [4 ÷ 7] and others.

However, the hazardous incidents that occasionally are also accompanied with life losses are still noted [7, 8]. The proper recognition of a hazard and right forecast of possible upshots is a primary task in ensure of safe technical specification of anthropogenic objects [9].

In the paper exceptional reactivity, low ignition energy and wide flammability range of acetylene are recalled and discussed. A special attention is paid the phenomenon of self-decomposition of acetylene. The process is self-excited and occurs violently with massive emission of energy. The molecular structure of acetylene that leads to that special behavior is discussed. Exact parameters of acetylene decomposition at constant pressure and volume are estimated. As in practical applications acetylene is reacting at various concentrations in relation to air or oxygen evaluation of combustion and explosion parameters of acetylene mixtures with air and oxygen is performed.

1. EXCEPTIONAL REACTIVITY OF ACETYLENE

2.1. Extreme ignitability and flammability of acetylene

The specific characteristic of acetylene, in comparison to other hydrocarbons, is their low minimal ignition energy. The facility to ignite is closely related to extreme combustibility as well as explosion and detonation hazard of acetylene/oxidizer mixtures. Several parameters characterizing combustion and flammability properties of acetylene are set up in Table 1.1.

Compound	Minimum ignitron energy	Flammability limits versus volume concentration in air, %		Maximal velocity of laminar flame
	mJ	lower	upper	cm/s
Methane, CH ₄	0,28	5,3	15	45
Acetylene, C ₂ H ₂	0,019	2,5	82 100*	160
Ethane, C ₂ H ₆	0,24	3,0	12,5	40,1
Propane, C ₃ H ₈	0,25	2,2	9,5	39,0
Hexane, C ₆ H ₁₄	0,248	1,2	7,5	38,5
Benzene, C ₆ H ₆	0,225	1,4	7,1	40,7
Hydrogen, H ₂	0,018	4	75	315

*) with admitting of self-decomposition of acetylene

Table 1.1. *Minimal ignition energies, flammability limits and maximal velocity of laminar flame of exemplary hydrocarbons and hydrogen [10 ÷ 12]*

Characteristic feature of acetylene is their low minimal ignition energy that is at least ten times lower than that of typical hydrocarbons. That is a serviceable factor that eases technical application. Acetylene-oxygen or acetylene-air bunches that are formed during welding, cutting etc. are easy to ignite and effectively burn-out enabling full fuel consumption. But by the same exceptional ignitability imply increased hazard degree.

The outstanding propriety of acetylene in comparison to other hydrocarbons is their high value of laminar combustion velocity (Table 1.1). It is lower than for hydrogen, but still quite close to sound velocity. High value of combustion velocity sets important hazard by uncontrolled firing. The transformation occurs violently, and formation of detonation waves is to be accounted. Especially, that may succeed by combustion proceeding in semi-closed spaces, by reflection from obstacles etc. In fact, hydrogen and acetylene mixtures with oxygen, nitrogen oxide and other oxidizers diluted by nitrogen were that in which the detonation phenomenon was discovered and firstly registered (Berthelot and Vieille 1883, Mallard and Le Chatelier 1883, independently).

The special feature of acetylene is also their high upper flammability limit. Two aspects of limiting acetylene flammability are to be discerned. In standard definition combustion occurs by fuel reactions with oxidizer. The maximal values of acetylene concentration at which the combustion may be supported by acetylene reactions with oxygen are of 80% to 82% ([2], [10, 13]). On the other hand, combustion is the process in which energy is produced the fuel being a source. In the case of acetylene, the energy-producing reactions may occur independently to oxidizer (oxygen) presence. Acetylene may emit energy solely, as result of their decomposition, without oxygen presence. Therefore, in many literature sources the value of 100% is stated as the upper flammability limit of acetylene ([12, 14]).

2. MOLECULAR STRUCTURE AS THE SOURCE OF UNUSUAL SUSCEPTIBILITY OF ACETYLENE TO SELF-DECOMPOSITION

2.1. Self-decomposition susceptibility as a special threat arising by exploitation of acetylene

The susceptibility to auto-decomposition creates serious threats in exploitation of acetylene. At increased temperature, by compression as well in contact with contaminants the break of intermolecular bonding and decomposition to elemental carbon and hydrogen is observed. The limiting temperature of auto-decomposition of acetylene is of 180-190°C

however the loss of stability may occur at even lower temperatures [2]. The reaction may start at even ambient temperature after compression to pressure of about of 15 bar [7].

The excessive compliance to spontaneous decompositions prompts of additional safety demands different from usual requirements such as to avoid of open fire, electrostatic discharge, etc. In particular, the susceptibility to generation of energy without contact with oxidizer imposes of special precautions by storage and transport of acetylene. Due to statistical distribution of internal energy of individual acetylene molecules, in even normal temperature some number of molecules achieves energy level that exceeds activation energy. Then, they undergo decomposition. The main task of safe exploitation of acetylene is to avoid of accumulation of incidentally liberated energy that proceed in scatted points of the volume filled with acetylene.

To prevent of spreading and accumulation of energy evolved in incidental acts of decomposition of acetylene molecules the casing (cylinders) designed for storage of acetylene are supplied with porous material. After filling acetylene is then parted into micro-volumes displaced in pores. Energy evolved in breaks of acetylene molecules is to be absorbed by surrounding material. Additionally, liquid solvents are introduced. Adjacent molecules of solvent may then immediately intercepted energy emitted in accidental break of acetylene molecule. Commonly used solvents are acetone and more recently dimethylformamide.

The susceptibility to self-decomposition occurring with liberation of energy considerably differ of acetylene from hydrogen. Hydrogen appearing in bimolecular form of H_2 is stable and may be stored and transported in any leak-proof tanks, pressure vessel in gaseous or liquid form, under oxidizer access precluded.

The high reactivity of acetylene demands not only to preserve of suitable safety requirements of usage like prevention of impacts, vibrations, uncontrolled exposition to temperature etc. The special precautions are also to be undertaken in post-accidental procedures. Transport and emptying of damaged acetylene cylinders may provoke of uncontrolled incitement of acetylene decomposition [3].

The specificity of acetylene physicochemical properties is closely related to their molecular structure.

2.2. Characteristic features of molecular structure of acetylene

Carbon atom has six electrons, four of them are taking part in building of intermolecular bonds. Valence electrons are placed 2s (two) and 2p (other two) orbitals. Orbital 2s is of

spherical shape with zeroth momentum while 2p orbitals are perpendicular and adherent electrons (each pair) differ in angular momentum (l_x , l_y , l_z , Fig. 2.1a).

In most common cases the binding orbitals are formed by sharing of electrons of adjoining atoms. In e.g. methane four bonding orbitals are formed each sharing of one electron originating from carbon and the other from hydrogen. Carbon atom gains of four pair of electrons and the octet rule i.e. formation of noble gas valence shell is fulfilled (Fig. 2.1b).

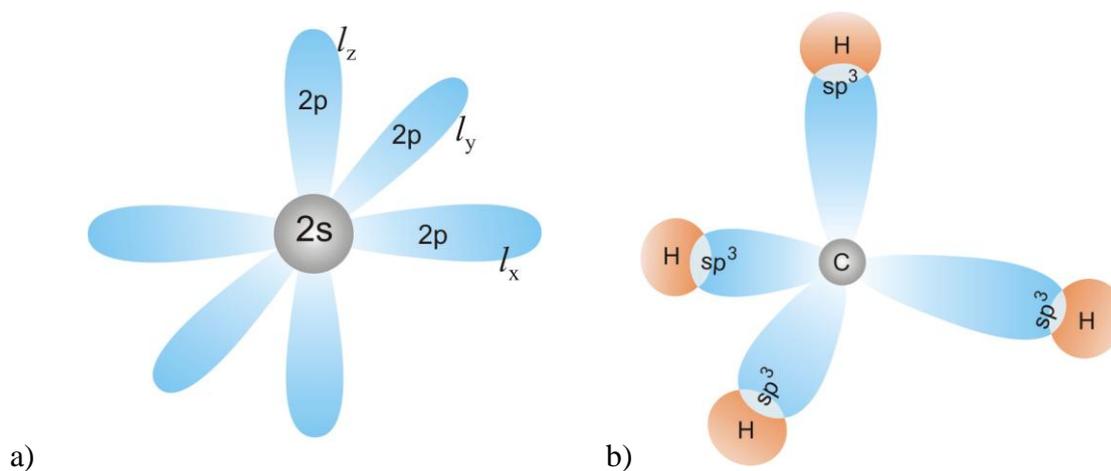


Figure 2.1. Schemes of carbon (a) and methane (b) electron orbital structures

The process of averaging of properties of electrons originating from 2s and 2p orbitals is named as hybridization [15]. Hybridized orbitals in methane are denoted sp^3 what mean that they result from mixing of one orbital 2s and three 2p orbitals. The electron cloud of methane takes a tetrahedral form.

The hybridization, in various forms, occurs by formation of electron bonds in other chemical species containing of carbon atoms. Among many of chemical species in which carbon is present the important is the case when between carbon atoms two bonds are to be formed as e.g. in ethylene (Fig. 2.2).

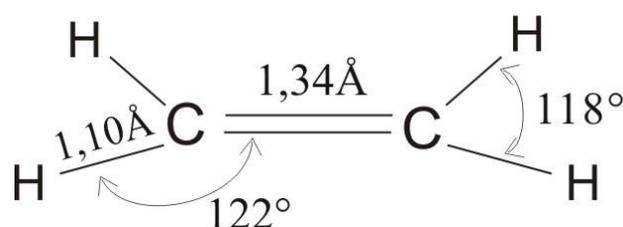


Figure 2.2. Structural chemical formulae of ethylene

Denoted by parallel lines, double in ethylene or triple in acetylene various bindings in multiple bonds differ from each other in a considerable manner. The scheme of acetylene molecule that contains triple bond between carbon atoms is depicted in Fig. 2.3.

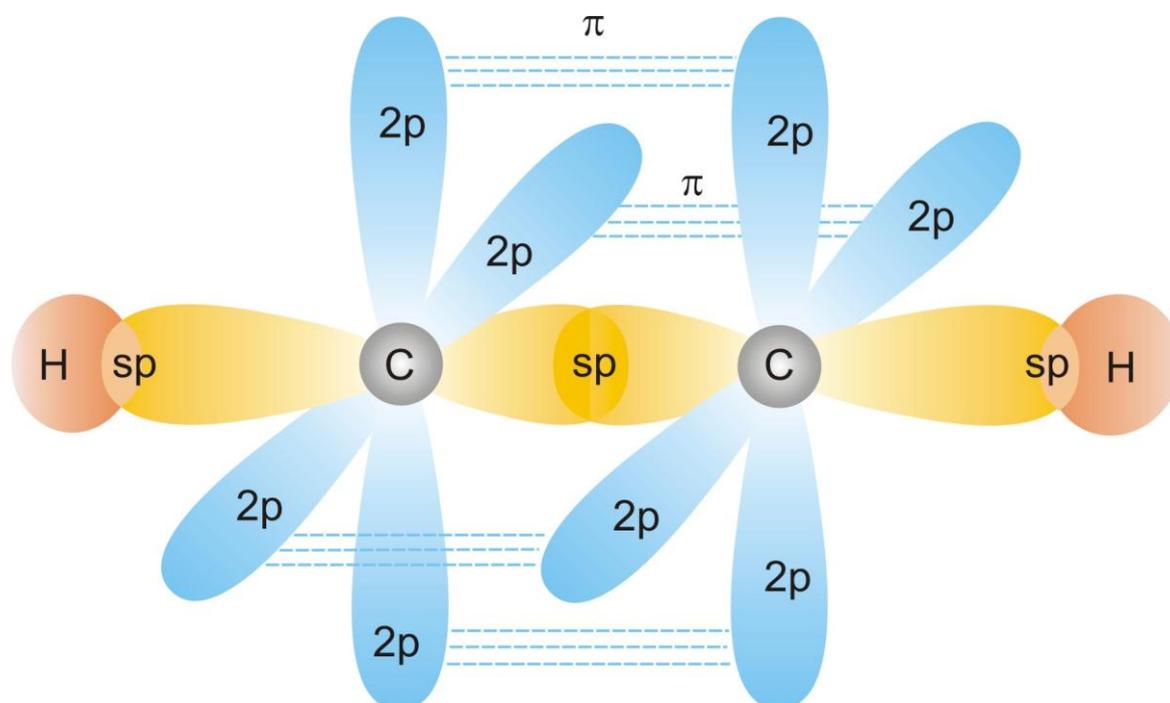


Figure 2.3. Space structure of bonding orbitals of acetylene

The H–C and one C–C bonds in acetylene are formed in hybridized way. In H–C bond hydrogen atom brings one electron and one is shared with carbon. Two electrons from different carbon atoms create the C–C orbital. In both cases common binding electron clouds are formed ([15]). The resulting hybridization is of sp type (Fig. 2.3).

Accounting of hybridization, the number of electrons adjacent to each carbon atom increases to 6 but it is still less to attain of noble shell configuration. The completion of octet rule occurs as result of interaction between electrons remaining in 2p orbitals (two at each carbon atom). But the arising bonds are significantly different from hybridized H–C and C–C orbitals. In general, the electrons remain in their initial displacement and only long-range interactions are emerging. That kind of chemical bond is named as π (Fig. 2.3).

The energy saving attained by formation of π bonds is considerably lower in comparison to other kinds of binding orbitals. As π bond does not create of common electron cloud as it occurs in hybridized orbitals the energy gain is owned only due to completion of eight folded orbital.

The comparison of energetic efficiency of various kinds of chemical bonds may be made upon values of enthalpy of formation. The enthalpy of formation ($\Delta_f H$) is equal to energy that is liberated or was delivered by formation of a considered chemical substance from elements in standard state i.e. H_2 , O_2 , N_2 , He, Ar, Ne, $C_{(s)}$ (graphite), $Al_{(s)}$, $Mg_{(s)}$, $Hg_{(l)}$ etc. The final energy effect does not depend on the way in which the transformation takes place. The negative value of enthalpy of formation denotes that by formation from elements in standard state the energy was liberated. Formation enthalpies of several hydrocarbons are quoted in Table 2.1.

Species	Chemical formula	Molecular mass g/mol	$\Delta_f H(298,15K)$ kJ/mol	$\Delta_f H(298,15K)$ kJ/kg
Methane	CH_4	16,04260	-74,60	-4650,1
Ethane	C_2H_6	30,06940	-84,00	-2793,5
Propane	C_3H_8	44,09620	-104,68	-2373,9
Butane	C_4H_{10}	58,12300	-125,65	-2161,8
Heptane	$C_7H_{16(g)}$	100,20340	-187,80	-1874,2
Ethylene	$H_2C=CH_2$	28,05360	52,40	1867,9
Propylene	$H_2C=CH-CH_3$	42,08040	20,40	484,8
Acetylene	$HC\equiv CH$	26,03780	227,40	8733,5

Table 2.1 Enthalpy of formation of exemplary hydrocarbons [12, 14, 16]

The relatively large negative formation enthalpy of methane is to be noted. That means that partition of methane molecule is subjected to delivery of external energy. The molecular structure of methane is stable, methane holds up millions of years in the earth's crust. On the other hand, all species containing double-bonded carbon atoms have positive enthalpy of formation. That means that alteration of their chemical structure may be accompanied with positive energy effect. It may be mentioned that positive formation enthalpy of un-saturated hydrocarbons makes easier the technology of polymerization.

However, uncontrolled polymerization of stored materials may lead to incidents of fire or explosive nature [4]. Especially, the threat may arise when outflow of energy liberated in breaking of doubled bonds will be hindered (by casing, obstacles, etc.). The thermal explosion [10] may then to succeed.

Auto- polymerization of acetylene is also to happen. Some portion of energy is required to initiate the reaction [2]. However once process starts it accelerates and takes explosive form. The issue is that by acetylene polymerization only one π bond (Fig. 3.3) is to break. The remaining π orbital is still unstable and a potential source of energy. Then, origination of polymerization leads to further and full decomposition of acetylene molecules that is accompanied will excessive liberation of energy and is to occur violently.

2.3 Parameters of acetylene decomposition

In simple way the decomposition reaction of acetylene may be written as



where the evolved energy is equal to enthalpy of formation at constant pressure (Table 2.1). However, any chemical reaction is to fulfill of thermodynamic rules and obey the principle of minimization of thermodynamic potential (Gibbs energy) of the reacting mixture. Therefore, also other substance in diversified concentrations are to be formed what leads to lowering of energy balance of the reaction.

The more exact estimation of parameters of self-decomposition of acetylene may be of purpose by assessing of possible upshot of accidents in which uncontrolled decomposition of acetylene is to occur. Extended thermodynamic calculations were performed for to estimate chemical composition, temperature, energy, and other parameters of acetylene decomposition at various conditions. The results of evaluations are presented in Table 2.2. Three cases of acetylene decomposition were considered: decomposition at constant pressure, at constant volume and, when the initial pressure of acetylene is equal of 10 bars.

Parameter	Decomposition at constant pressure $p_0 = 0,1 \text{ Mpa}$ $\rho_0 = 1,0868 \text{ g/cm}^3$	Decomposition in constant volume $p_0 = 0,1 \text{ Mpa}$ $\rho_0 = 1,0868 \text{ g/cm}^3$	Decomposition in constant volume $p_0 = 1 \text{ Mpa}$ $\rho_0 = 10,868 \text{ g/cm}^3$
ΔQ , MJ/kg	7,805	8,006	8,508
T , K	2892	3222	3341
p , Mpa	0,1	1,166	11,75
Species	concentration	concentration	concentration
	mol/kg	mol/kg	mol/kg
H	4,2898	3,3476	1,4153

H ₂	36,2458	36,6199	36,9054
C(g)	0,0007	0,0012	0,0003
CH ₃	0,0057	0,344	0,1333
CH ₄	0,0029	0,0257	0,2464
C ₂ H ₄	0,0003	0,0045	0,0498
C ₂ H ₆	-	-	0,0001
C(s), graphite	76,9014	76,7410	76,3317
Σy _(g)	40,5452	40,0333	38,7507

Table 2.2 Decomposition parameters of acetylene, $T_0 = 288,15\text{K}$

In last line of the Table 2.2 the total number of decomposition products in gaseous phase ($\Sigma y_{(g)}$) is quoted. With lowering of accessible volume, the content of products in gaseous phase is to decrease. Evaluations were performed with the MWEQ program based on the principle of minimization of thermodynamic potential of the reacting mixture [17]. The method enables of estimation of concentrations of components present in even vestigial concentrations, but in the Table 2.2 only products of concentration exceeding of 0,0001 mol/kg are quoted.

The exact evaluations confirm expected diminish in decomposition energy in comparison to the roughly estimation (2.1). The lowest decomposition energy is observed by transformation occurring at free atmosphere.

Despite of some differences in values obtained in calculations, in any technical conditions decomposition of acetylene imposes of severe threat in regard both to the high temperature and large amounts of emitted energy.

3. COMBUSTION AND EXPLOSION PARAMETERS OF ACETYLENE-AIR AND ACETYLENE-OXYGEN MIXTURES

In practical applications acetylene is used in various concentrations in relation to air or oxygen. Results of evaluation of combustion and explosion of acetylene/air mixtures are presented in Fig. 3.1.

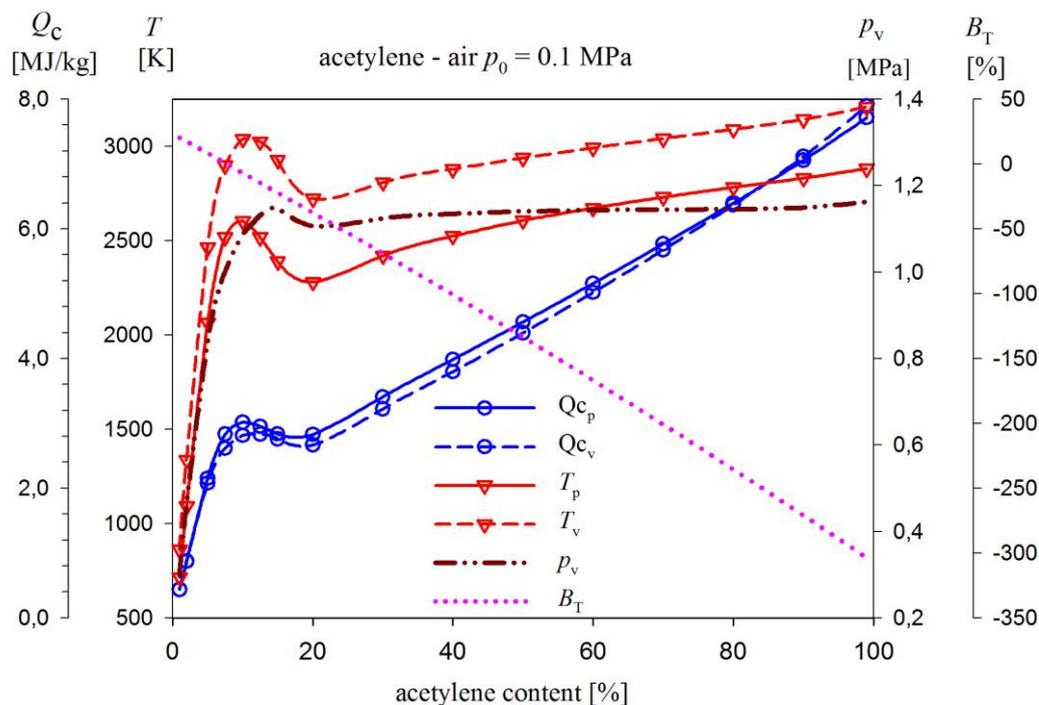


Figure 3.1. Combustion and explosion parameters of acetylene/air mixtures

The initial state of considered acetylene/air mixtures was of initial pressure of 1 bar (0,1MPa) and temperature of $T_0 = 288,15\text{K}$ (15°C). The energy and temperature attained by combustion at constant pressure are denoted by $Q_{c,p}$ and T_p respectively. Simultaneously, in Fig. 3.1 the parameters acquired by restricted expansion of transformation products are depicted. The energy, temperature and pressure of explosion in constant volume are denoted by $Q_{c,v}$ and T_v and p_v . Additionally, the oxygen balance of the mixture (B_T) is displayed.

The course of all parameters, both combustion at constant pressure and transformation in constant volume have two maximums. The first summit is in vicinity of stoichiometric composition of the mixture at which oxygen balance equals zero (7,73%). In combustion products the substances in highest oxidation degree are then formed, as e.g. CO_2 and H_2O . When fuel concentration crosses stoichiometric point, number of subordinate products as CO , CH_3 is increasing as they are formed in lack of oxygen.

In combustion of typical hydrocarbons when fuel becomes to surpass of stoichiometric concentration region, the combustion parameters decrease. The unreacted fuel gathers heat evolved in combustion reactions what leads to diminution of temperature, energy and pressure of reacting mixture. The course of combustion and explosion parameters in vicinity of stoichiometric point of ethane (5,65%) is presented in Fig. 3.2. The symbols and notation are the same as in Fig. 3.1.

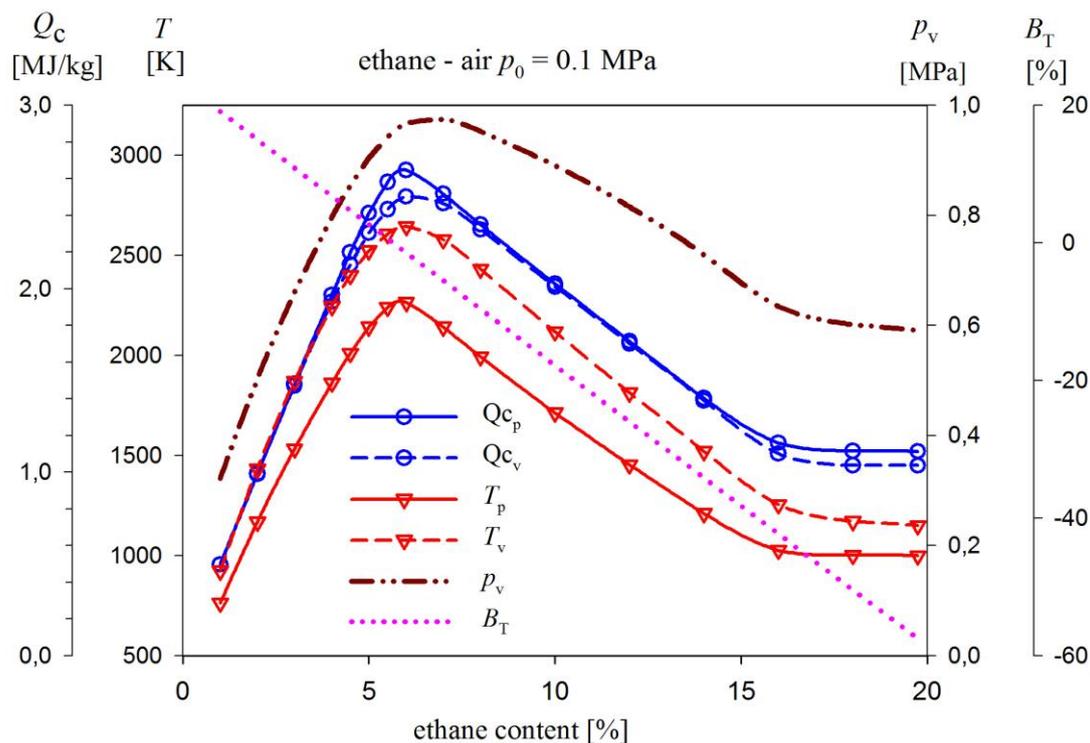


Figure 3.2. Combustion and explosion parameters of ethane/air mixtures

As in majority of fuels, the maximal parameters are attained at ethane concentrations slightly exceeding the stoichiometric point. But by further increase of fuel content, the visible lowering of transformation parameters occurs and the end, the upper flammability limit (12,5%, Table 1.1) is attained.

Acetylene/air mixtures behave in considerably different manner by growing concentrations of acetylene. After crossing the region of stoichiometric concentration the further increase of evolved energy (Q_{cp} and Q_{cv}) as well as of other transformation parameters occurs. The energy evolved in acetylene decomposition is responsible for that effect. In the limit, when acetylene concentration reach of 100% the parameters of combustion and explosion tends to values attained by decomposition of homogeneous acetylene, as presented in Table 2.2. Therefore, a potential threat arising by acetylene exploitation is manly demarcated by parameters of possible uncontrolled decomposition of acetylene.

The course of combustion and explosion of acetylene/oxygen mixtures in dependence of acetylene concentration is presented in Fig. 3.3. The symbols and notation are the same as in Fig. 3.1.

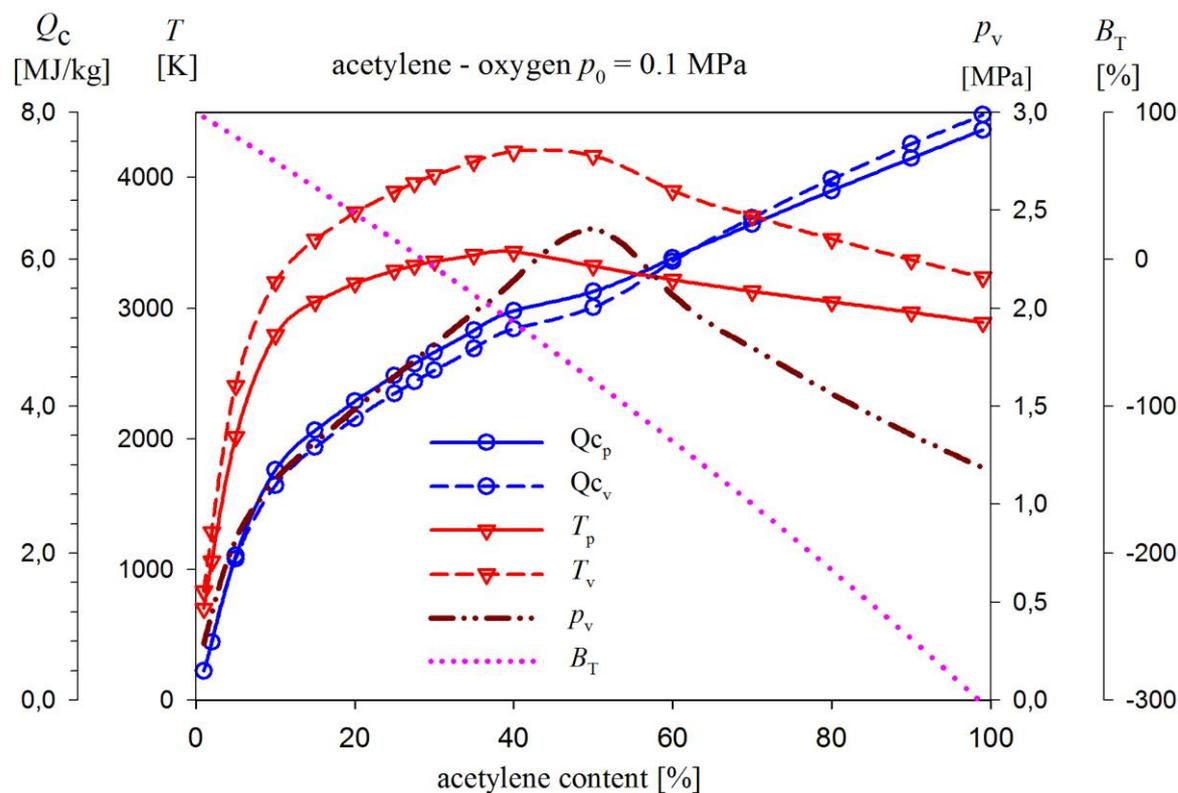


Figure 3.3. Combustion and explosion parameters of acetylene/oxygen mixtures

In reactions with oxygen acetylene is effective in wide range of concentrations. Apart from compositions containing of only few percents of acetylene, combustion temperature exceeds of 3000K. Combustion energy at stoichiometric concentration (28,57%) achieves of about of 4,5MJ/kg however, it is still lower than by auto-decomposition. The pressure maximum is attained at about of 50% concentration of acetylene. 50% is a threshold over which the elemental carbon (graphite) is to be formed. As at higher acetylene concentrations the number of moles in gaseous phase becomes to diminish, the magnitude of explosion pressure (p_v) is to decrease (Fig. 3.3).

CONCLUSIONS

In the paper unusual reactivity, i.e. ignitability, wide flammability limits, proneness to explosion and detonation of acetylene are considered. Exceptionally low ignition energies, wide flammability limits and high velocity of combustion are presented and compared with hydrogen and other gaseous hydrocarbons.

The importance of the susceptibility to auto-decomposition of acetylene is indicated. The susceptibility to self-decomposition poses a fire and explosion hazard quite dissimilar to

properties of other hydrocarbons. The molecular structure of acetylene is examined as the constitutive source of acetylene instability. Exact evaluation of chemical composition and thermodynamic parameters of decomposition products of acetylene is performed.

Combustion parameters of acetylene mixtures with air and oxygen are estimated. Combustion at ambient pressure as well as constant volume explosion parameters are calculated in full range of acetylene concentrations. The obtained results may be employed in estimation of expected exploitation parameters or by anticipation of possible upshots of uncontrolled acetylene transformation.

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