# Analysis of thermo-chemical parameters and ignition testing of modified heterogeneous propellant

Justyna HADZIK*, Piotr KOŚLIK, Zenon WILK – Institute of Industrial Organic Chemistry, Warsaw, Poland, Department Krupski Młyn

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## Introduction

The problem relates to selection and testing of solid propellants for operations associated with the intensification of oil and gas, including from shale formations. The assumption was modification of heterogeneous propellant MPH type to the stage, where its properties and performance characteristics are appropriate for dry fracturing technology. The advantage of composite propellants is their higher resistance to temperature and pressure, allowing their use at higher operating parameters reigning in the well. Further modification by the addition of ceramic powders in the form of silica or corundum stabilize slits, so that the flow of gas or oil is free.

To optimize the modified compositions used tools for thermo-chemical parameters analysis (program ICT Thermodynamic Code Version 1.0). The influence of the proposed additions to the energetic parameters for studied propellant (i.e. impulse, calorific value, coefficient thrust) was shown. The volume of gaseous products generated per unit volume of propellant, which is important parameter in the process of hydraulic fracturing was estimated.

The results of numerical analyzes were evaluated in an experiment of the study heterogeneous propellant sample in combustion process. Results of ignition testing MPH propellant with a cumulative jet performed in ballistic pressure vessel were presented. These studies are the primary way to determine the conditions that must be preserved in the process of initiating combustion of propellant. They allow to determine the important parameters characterizing the combustion process (maximum pressure, pressure impulse), but also to determine whether it occurred. Stimulation of propellant by means of energetic impulse (eg. cumulative jet) initiates the process of their rapid transformations. It reveals sudden rise of temperature and pressure with the creation of large amounts of gases (approx. 900 l with 1 kg of propellant).

## Results of thermodynamic analyzes

For analysis it is necessary to know qualitative and quantitative composition of heterogeneous propellant MPH and its modified compositions (Tab. 1).

Thermodynamic analysis was performed to determine parameters such as oxygen balance, volume of gaseous products, heat of explosion (calorific of propellant) under standard conditions and a constant volume (V = const., loading density of propellant 0.2 g/cm$^3$). Under constant pressure (p = const.) was determined: specific impulse in frozen and equilibrium conditions, thrust coefficient (p = 0.1 MPa), characteristic velocity and temperature of combustion chamber products (p = 7 MPa). The results are summarized in tables (Table 2: MPH with $SiO_2$ additions, Table 3: MPH with $Al_2O_3$ additions).

Corresponding author:
Justyna HADZIK – M.Sc., e-mail: justyna.hadzik@ipo.waw.pl

Table 1

**Compositions of MPH and MPH modified $SiO_2$ and $Al_2O_3$ additives**

| Propellant composition | Contents [%] | | | | | |
|---|---|---|---|---|---|---|
| | MPH | MPH +10% | MPH +20% | MPH +30% | MPH +40% | MPH +50% |
| Potassium perchlorate | 83 | 74.7 | 66.4 | 58.1 | 49.8 | 41.2 |
| DOA (dioctyl adipate) | 3.5 | 3.15 | 2.8 | 2.45 | 2.1 | 1.75 |
| E5 (epoxy resin) | 5.5 | 4.95 | 4.4 | 3.85 | 3.3 | 2.75 |
| BCN (liquid rubber butadiene-carboxylic acid nitrile) | 8 | 7.2 | 6.4 | 5.6 | 4.8 | 4 |
| $SiO_2$/ $Al_2O_3$ | - | 10 | 20 | 30 | 40 | 50 |

Table 2

**Thermodynamic parameters of MPH modified with $SiO_2$ additions**

| Properties | 10 % $SiO_2$ | 20 % $SiO_2$ | 30 % $SiO_2$ | 40 % $SiO_2$ | 50 % $SiO_2$ |
|---|---|---|---|---|---|
| Theoretical density [g/cm$^3$] | 2.014 | 2.033 | 2.053 | 2.072 | 2.093 |
| Oxygen balance [%] | -7.29 | -6.48 | -5.67 | -4.86 | -4.05 |
| Gases volume [cm$^3$/g] | 402.8 | 358.2 | 313.6 | 268.9 | 224.2 |
| Gases volume generated per unit volume of propellant [cm$^3$/1ml] | 811.24 | 728.22 | 643.82 | 557.16 | 469.25 |
| Mole number of gaseous product [mol/$kg_{expl.}$] | 16.465 | 14.643 | 12.819 | 10.993 | 9.165 |
| Heat of explosion [J/g] | 3145.2 | 2781.3 | 2417.5 | 2053.7 | 1690 |
| Specific impulse in frozen conditions [Ns/kg] | 1802 | 1651 | 1491 | 1321 | 1142 |
| Specific impulse in equilibrium conditions [Ns/kg] | 1821 | 1659 | 1495 | 1323 | 1142 |
| Thrust coefficient | 1.626 | 1.658 | 1.693 | 1.706 | 1.737 |
| Temperature of combustion chamber products [K] | 2699.4 | 2462.1 | 2207.6 | 1996 | 1731.3 |
| Characteristic velocity [m/s] | 1108 | 996 | 881 | 774 | 657 |
| Heat of formation [kJ/kg] | -4251.36 | -5463.1 | -6674.85 | -7886.59 | -9098.33 |

Table 3

**Thermodynamic parameters of MPH modified with $Al_2O_3$ additions**

| Properties | 10 % $Al_2O_3$ | 20 % $Al_2O_3$ | 30 % $Al_2O_3$ | 40 % $Al_2O_3$ | 50 % $Al_2O_3$ |
|---|---|---|---|---|---|
| Theoretical density [g/cm$^3$] | 2.1 | 2.216 | 2.345 | 2.491 | 2.656 |
| Oxygen balance [%] | -7.29 | -6.48 | -5.67 | -4.86 | -4.05 |
| Gases volume [cm$^3$/g] | 402.8 | 358.2 | 313.6 | 268.9 | 224.2 |
| Gases volume generated per unit volume of propellant [cm$^3$/1ml] | 845.88 | 793.77 | 735.39 | 669.83 | 595.47 |
| Mole number of gaseous product [mol/kg$_{expl.}$] | 16.465 | 14.643 | 12.819 | 10.993 | 9.165 |
| Heat of explosion [J/g] | 3154.3 | 2799.6 | 2444.9 | 2090.3 | 1735.8 |
| Specific impulse in frozen conditions [Ns/kg] | 1803 | 1653 | 1489 | 1319 | 1141 |
| Specific impulse in equilibrium conditions [Ns/kg] | 1817 | 1658 | 1495 | 1323 | 1142 |
| Thrust coefficient | 1.65 | 1.709 | 1.681 | 1.712 | 1.744 |
| Temperature of combustion chamber products [K] | 2629.1 | 2327 | 2233 | 1977 | 1716.9 |
| Characteristic velocity [m/s] | 1093 | 967 | 886 | 771 | 654 |
| Heat of formation [kJ/kg] | -4379.13 | -5718.63 | -7058.14 | -8397.64 | -9737.15 |

Selected thermodynamic items were presented in graphical form (Fig. 1 – 4).

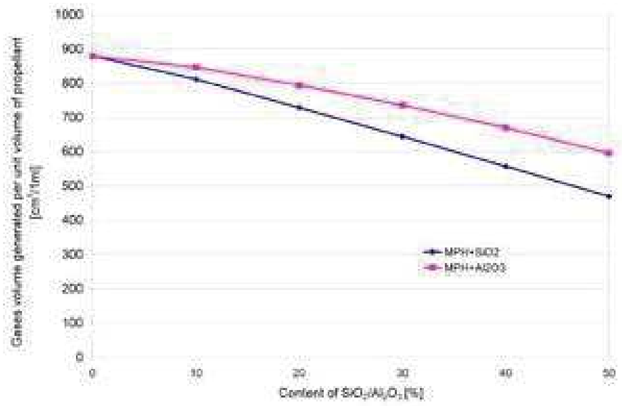


**Fig. 1. Influence of 10 – 50 % $SiO_2$ and $Al_2O_3$ additives per volume gases generated per unit volume of MPH propellant**

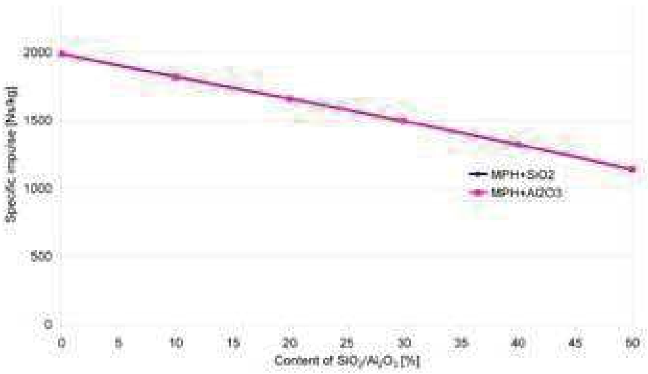


**Fig. 2. Influence of 10 – 50 % $SiO_2$ and $Al_2O_3$ additives for specific impulse of MPH propellant**

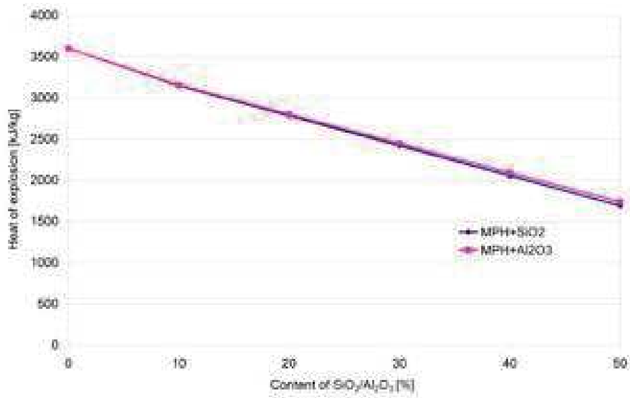


**Fig. 3. Influence of 10 – 50 % $SiO_2$ and $Al_2O_3$ additives for heat of explosion of MPH propellant**

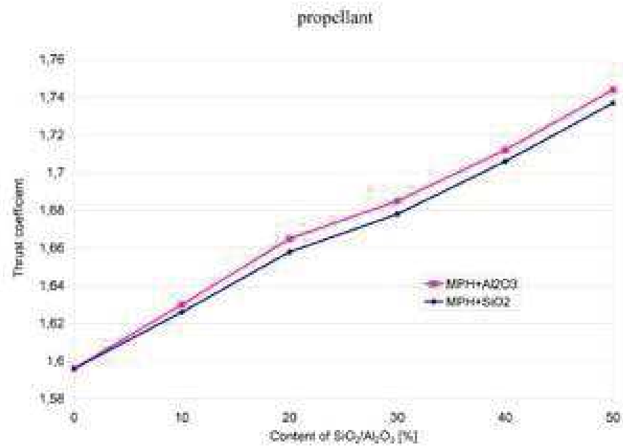


**Fig. 4. Influence of 10 – 50 % $SiO_2$ and $Al_2O_3$ additives for thrust coefficient of MPH propellant**

MPH propellant additives in the form of $Al_2O_3$ and $SiO_2$ reduce the volume of gaseous decomposition products (Fig. 1). The addition of corundum generates larger amount of gases per unit volume of propellant, than addition of silica (with 10 % addition the calculated volume of gas products per unit volume of propellant increases by 4 %, while with 50 % addition of ceramic material increases by 14 %). The value of specific impulse decreases with increasing additives, it does not depend on the type of ceramic powder (Fig. 2). Use of inert materials in modified propellant composed increases the thrust coefficient. Similarly, with addition of corundum, this parameter reaches a higher value than the propellant with addition of silica (Fig. 4). Analyzing the value of heat of explosion – calorific (Fig. 3) influence of kind of additive is not relevant (differences relative to used additives are up to approx. 2 % at 50 % of their content). Whereas, significant decrease in caloric value for propellants with ceramic additives in relation to the pure MPH propellant was occurred (with 50 % addition followed double decrease heat of explosion).

The results of analysis obtained values of gas volumes relate to theory. In practice, propellant additives in the form of silica and/or corundum must have a different grain composition, so that part of their remain unreacted and in the form of ballast filled the gap.

## Experimental part

Experimental part includes the examination of MPH propellant in a pressure vessel. The proposed research methodology used to assess the initiating capability the combustion process with the simultaneous measurement of pressure and effectiveness of the shape charges (based on the penetration pile of the control plates) – comp image test system in the Figure 5.

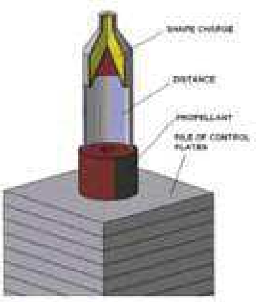


**Fig. 5. Test system of initiating propellant ignition with the assessment of effectiveness of the shape charge**

For the test was used a sample of MPH propellant with a weight 124.2 g and the following dimensions: external diameter 40 mm, inner diameter 10 mm, height 60 mm. Test sample was initiated by the axial – direction shape charge ŁOKTC-H-PP-Sz-130 70 type. The distance between charge and propellant was 48 mm. Pile of control plates were made of steel S250 format 50 x 50 mm and a height of 10 mm. Number of plates used in the present test was 12 units.

Pressure measurement was performed using parallel sensors: a piezoelectric (PCB Piezotronics type, series M102B06 – Tab. 4) and resistance (SML type, series ADZ Nagano 31.0 – Tab. 5).

**Table 4**

**The sensor characteristics of PCB M102B06 series**

| **Measuring range for ± 5V output** | **3450 kPa** |
|---|---|
| Measuring range for ± 10V output | 6895 kPa |
| The sensitivity | 1.45 mV/kPa |
| Maximum pressure | 68950 kPa |
| The resolution | 0.014 kPa |
| Slew time | ≤ 1.0 $\mu$s |
| Sensitivity to acceleration | ≤ 0.0014 kPa/(m/s$^2$) |
| The maximum temperature (instantaneous) | 1650°C |
| The maximum instantaneous acceleration | 196000 m/s$^2$ in peak |

**Table 5**

**The sensor characteristics of Nagano ADZ SML 31.0 series.**

| **Measuring range** | **6 MPa** |
|---|---|
| Output signal | 0.5 - 45 V |
| Slew time | ≤ 1.0 ms |
| Signal linearity | 0.15 % |

Pressure sensors were powered by a portable 3-channel IEPE signal conditioner dedicated to PCB ICP sensors series VIBAMP PA-3000. Direct measurement of pressure was recorded using a digital oscilloscope (GwINSTEK GDS-2204 – the maximum sampling rate 1GS * s-$^1$). View of the measurement test system is shown in Figure 6.

a) b)

**Fig. 6. a) view of test system, b) view of sensors in the tank measuring flange**

**Results of MPH propellant in the pressure tank examination**

During the MPH propellant ignition test with a shape charge, formed and speeding jet cumulative initiated propellant and then perforated pile of control plates the depth of 30 mm. The propellant has been burnt completely. The measurement result is an interpretation of an illustrative pressure curve *P (t)* (Fig. 7).

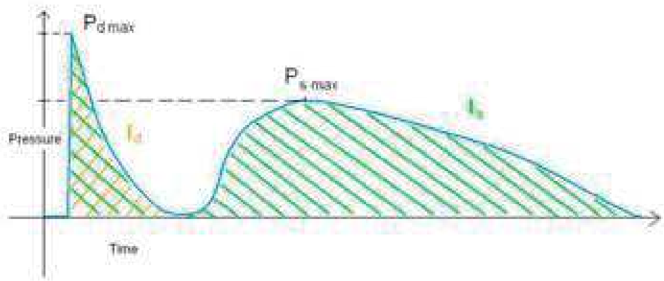


**Fig. 7. Characteristic pressure curve – basic energetic parameters of test arrangement**

Energetic parameters determining the test arrangement:

1. The maximum pressure *Pd* (shock wave generated by the shaped charge).
2. The pressure impulse *Id* (result of calculating the integral of the positive phase of shock wave pressure, which characterizes the work ability of explosive material in charge).
3. The maximum pressure of propellant combustion process (deflagration) *Ps*.
4. Total pressure impulse *Is* (result of calculating the integral of the positive phase the entire pressure curve).

Based on dependence p = f (t) obtained during the initiating and combustion registration of MPH propellant (Figure 8) was determined energetic parameters characterizing the test arrangement (Table 6).

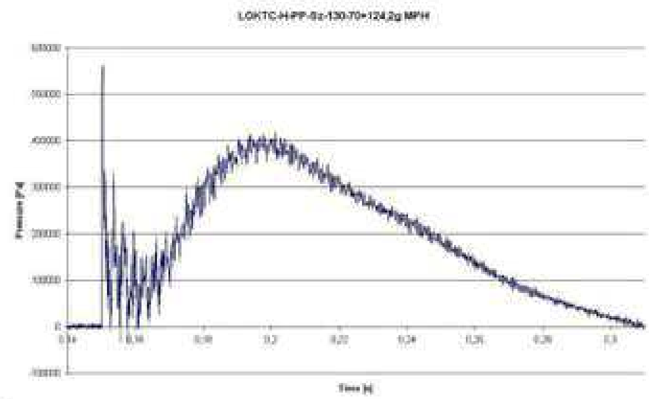

**Fig. 8. Dependence of p = f (t) for arrangement ŁOKTC-H-PP-130–70 with MPH propellant (124.2 g)**

**Table 6**

**Energetic parameters for arrangement shape charge with MPH propellant**

| **Parameter** | **Value** |
|---|---|
| Maximum shock wave pressure $P_d$ | 560 kPa |
| Maximum pressure of propellant combustion process $P_s$ | 419 kPa |
| Shock wave pressure impulse $I_d$ | 563 Pa·s |
| Total pressure impulse $I_s$ | 30719 Pa·s |

**Summary**

Article relates to research performance and energetic parameters, modified heterogeneous propellant, which is a potential to use the openings of oil and gas fracturing treatments. For the purpose of optimizing modified propellants compositions used thermodynamic analysis tools, which support experimental research. Owing these tools it is possible to know the energetic characteristics, composition and quantity of gas products. However, on research stage of propellants under real conditions required is the choice of research methodology, allowing define the process for initiating and decomposition of tested propellants. Proposed research methodology of propellant in a closed pressure system has proved appropriate for assess the effectiveness of ignition and stable combustion of the propellant during tests. Additional registration of pressure changes in ballistic chamber allows to determine the energetic parameters of tested propellant.

**Literature**

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*Justyna HADZIK – M.Sc., graduated from the Faculty of Chemistry at the Silesian University of Technology in Gliwice in the field of Chemical Technology, specialization: – Organic Technology. She completed post-graduate studies in the field of Technology of Explosives. She is an assistant lecturer in the Institute of Industrial Organic Chemistry, Branch Krupski Młyn. Her research interests are related to the development of and research on explosives and blasting agents.

e-mail: justyna.hadzik@ipo.waw.pl, tel.: 32 392 84 74

Zenon WILK – M. Sc., assistant professor, graduated from the Silesian University of Technology in Gliwice, specialization: Conversion and Use of Energy. Post – graduate studies: Chemistry and Technology of Explosive Materials. He got his Ph. D. degree at the Faculty of Mechatronics at the Military University of Technology in Warsaw. He is an expert in the field of technology of explosives, mechanics and modeling the explosion issues, particularly the cumulation phenomenon. He is the head of the Institute of Industrial Organic Chemistry, Branch Krupski Młyn. He was involved in many research and application projects on producing explosives and blasting equipment for borehole mining and specialist works.

e-mail: zenon.wilk@ipo.waw.pl, tel.: 32 382 11 91

Piotr KOŚLIK – M. Sc., graduated from the University of Technology in Wrocław, specialization: Mechanical Engineering - Design, Manufacture and Operation and graduated from the University of Technology in Częstochowa, specialization: Mechanical Engineering – Welding.

He is an Research Specialist – Technical in Institute of Industrial Organic Chemistry, Branch Krupski Młyn. His research interests are related to use numerical tools in the processes associated with the phenomenon of explosion and to design new solutions blasting agents.

e-mail: piotr.koslik@ipo.waw.pl, tel.: 32 392 84 74

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### ZMIANY PERSONALNE

**Zmiana na stanowisku Prezesa Zarządu PKN ORLEN**

Rada Nadzorcza Polskiego Koncernu Naftowego ORLEN SA na posiedzeniu w dniu 16 grudnia 2015 r. odwołała Pana Jacka Krawca ze stanowiska Prezesa Zarządu PKN ORLEN SA i jednocześnie powołała do pełnienia funkcji Prezesa Zarządu PKN ORLEN SA Pana Wojciecha Jasińskiego. Pan Wojciech Jasiński jest absolwentem Wydziału Prawa i Administracji na Uniwersytecie Warszawskim (1972 r.). Posiada bogate doświadczenie wynikające z pełnienia kierowniczych funkcji w administracji publicznej oraz podmiotach prawa handlowego. W latach 1997–2000 był Członkiem Zarządu, a następnie Prezesem spółki Srebrna. Od 2001 był Posłem na Sejm RP. W latach 2006–2007 pełnił funkcję Ministra Skarbu Państwa. *(kk)*

*(http://www.orlenpoludnie.pl/, 17.12.2015)*

**Polak prezesem kanadyjskiej Helix BioPharma**

Prezesem kanadyjskiej spółki biofarmaceutycznej Helix BioPharma, zajmującej się rozwojem innowacyjnych leków onkologicznych, został dr Zbigniew Markowski. Doświadczony menedżer ma za zadanie wesprzeć ambitne cele spółki, m.in. w zakresie prowadzonych w Polsce i USA badań klinicznych oraz pozyskania finansowania na dalsze badania i rozwój. Polak zastąpi Garego Littlejohna, czasowo pełniącego obowiązki Prezesa.

Dr Zbigniew Markowski zarządzał spółkami zajmującymi się doradztwem w zakresie finansowania inwestycji, przede wszystkim w sektorach farmaceutycznym i finansowym. Pełnił również funkcje nadzorcze w wielu spółkach z rynku kapitałowego. Dodatkowo sprawował funkcje doradcze w polskich ministerstwach. Zbigniew Markowski w latach 2006 – 2016 był Prezesem Zarządu spółki O.M. Finance, firmie doradczej w zakresie rynku finansowo-inwestycyjnego. Od 1988 do 2002 r. pełnił funkcję wiceprezesa Zarządu Prokom Investments SA, gdzie odpowiadał za inwestycje w sektorze finansowym i farmaceutycznym oraz był członkiem zarządu farmaceutycznej spółki BIOTON SA. Od 1995 r. sprawował funkcje Przewodniczącego i Członka Rad Nadzorczych w wielu spółkach notowanych na GPW. Przewodniczył komitetom audytu w spółkach: Ciech SA, II NFI SA, ROBYG SA. Od 1993 do 2005 r. pełnił funkcję Pełnomocnika Ministra Prywatyzacji i Przekształceń Własnościowych oraz Ministra Współpracy Gospodarczej z zagranicą do Spraw Prywatyzacji Jednostek Handlu Zagranicznego. W 1994 r. został powołany na stanowisko Radcy Handlowego Rzeczpospolitej Polskiej w Szwecji. (kk)

*(http://biotechnologia.pl/, 13.01.2016)*

*Dokończenie na stronie 45*