



Experimental Study on Ammonium Nitrate(V)-based Solid Propellants for Fracturing Wells

**Justyna Hadzik,^{*1} Piotr Koślik,¹ Zenon Wilk,¹
Antoni Frodyma,² Łukasz Habera²**

¹ *Institute of Industrial Organic Chemistry,
Annopol 6, 02-236 Warsaw, Poland*

² *Oil and Gas Institute – National Research Institute,
Lubicz 25 A, 31-503 Cracow, Poland*

**E-mail: justyna.hadzik@ipo.waw.pl*

Abstract: This paper investigates the possibility of using ammonium nitrate(V)-based solid propellants for fracturing wells in borehole mining. Various modified propellant compositions with ammonium nitrate(V) and polyurethanes were prepared. Using laboratory rocket motors (LRMs) and underwater tests in pressure chambers, the energetic parameters (*i.e.*, maximum pressure of the gaseous products and pressure impulse) for the selected AN-propellants were determined. Furthermore, thermodynamic analyses for these propellants were performed. The influence of the proposed additives on the energetic parameters (*i.e.*, calorific value and specific energy) was shown. The gas volume generated per unit volume of propellant, which is an important parameter in the process of hydraulic fracturing, was estimated.

Keywords: fracturing wells, solid propellants, ammonium nitrate(V), polyurethanes, thermodynamic analyses

1 Introduction

Ammonium nitrate(V) (AN) is one of the main components of many explosives, including Ammonals, Ammonites, Dynamites and ANFO. The interest in ammonium nitrate and the possibilities of its application in explosives are dictated primarily by its low price, low sensitivity to mechanical factors, *i.e.*, friction and impact, high durability, and simple production technology. Ammonium nitrate(V)

can also act as an oxidizer in solid propellants. The oxidizers commonly used in propellants are ammonium chlorate(VII) and potassium chlorate(VII). Currently, ammonium nitrate(V) is the cheapest oxidant, readily available, and a safe energetic material that does not burn without the help of catalysts. Furthermore, it does not contain metal ions or chlorine and, when completely decomposed by heating to gaseous products (water vapour and nitrogen oxides), does not release chlorine compounds that are harmful to the environment [1-3]. For economic and environmental reasons, ammonium nitrate(V)-based solid propellants are alternatives to the currently used propellants.

There have been many ammonium nitrate compositions proposed and developed that have found application, especially in gas generator compositions. Inventions exist that relate to fracturing rock formations, and particularly to propellant assemblies for creating fractures in wells [4-11]. Fracturing using propellant systems is recognized as a cheap alternative to conventional hydraulic fracturing in circumstances where heavy pumping equipment is not available. Usually, fracturing of wells with propellants is used in an initial stage, preceding conventional hydraulic fracturing, and to improve the injectivity of the borehole. This method has a number of advantages: the length of the fractures ranges from 1.0 m to 5.0 m and it eliminates compatibility problems between the formation fluid and the fracturing fluid. Moreover, it takes up less space, and needs less specialized equipment and fewer employees.

Many experiments [12-16] have shown that exerting pressure in a borehole by burning propellants can be used effectively to create multiple fractures in the rocks surrounding the borehole. The number of fractures created depends on the rate of pressure rise in the borehole. If the rate of pressure rise is low (which is the case in hydraulic fracturing), a single- or double-wing fracture develops in a direction perpendicular to the minimum principal stresses in the rock mass. In cases where a higher rate of pressure rise is applied, several fractures are created. The fractures are developed mainly in radial directions. The number of fractures depends on the rate of pressure rise, rock elasticity and strength, borehole size (depth and diameter), and the stresses prevailing *in situ*. This information is defined at the design stage of the deposit development. In order to perform well fracturing in borehole mining, the required pressure has to be greater than the rock-mass pressure. Based on this data, the amount of propellant necessary to achieve the pressure required to break the resistance of the rock can be determined. The basic parameter describing the amount of propellant in a fracturing tool is the loading density (mass of propellant in free space).

Ammonium nitrate(V) formulations could be used in the process of stimulation of oil and gas inflow. Due to the nature of ammonium nitrate(V)

(difficult ignition, hygroscopicity) it is necessary to modify and improve the properties of ammonium nitrate in formulations. The most common and effective additive for AN-based propellants is magnesium. There are several references [3, 17-21] that discuss a number of experimental propellant formulations that use magnesium because of its high burn temperature. The combustion of magnesium is highly exothermic, and provides the thermal energy to flash the released water as steam, which then reacts with the metal in a self-sustaining manner. References also describe attempts to use powdered aluminum, but the studied propellant formulations failed to ignite. The difficulty with combusting particles of aluminum is due to the tough shell of aluminum oxide that encases the readily oxidizing metal. In spite of the high cost of magnesium powder, many authors have attempted to use it in formulations of AN-based propellants because of their environmental safety.

In the manufacture of propellants, polymers play an important role, as they act as binders and fuel. There are AN-based propellants described that contain polyurethanes (PU) [22]. Other important factors for the formation of propellant grains are burning rate modifiers and plasticizers [23].

For many years, the Institute of Industrial Organic Chemistry has been working on a wide range of modifications to, technologies for, and ballistic properties and applications of solid rocket propellants [24-27]. The application of AN-propellants for borehole mining does not require a perfected form of the produced propellants (as is the case for rocket systems), but the correct parameters, usually lower burning rate and reliability of ignition at high temperatures and pressures, are of importance. For this purpose a convenient form of propellant, with suitable elements, for the down-hole apparatus used in fracturing, is needed.

2 Experimental

2.1 Materials and preparation

Ammonium nitrate(V) (PULAN[®], produced by Grupa Azoty, Zakłady Azotowe "Puławy" S.A.) was used as a principal component. AN was milled, and the sieve analysis showed the following grain size composition (Table 1).

Table 1. Sieve analysis for ammonium nitrate(V)

Fraction [mm]	Contents [%]
1-0.5	20.5
0.25-0.5	70.9
<0.25	8.6

Two-component polyurethane rubber (VytaFlex 30 type), dioctyl adipate (DOA), magnesium (>0.063 mm) and ferric(III) oxide (Fe_2O_3) were used as additives. All of the components were dried, then the oxidizer was mixed with the catalyst, metal powder and plasticizer until a homogenous mass was obtained, with no visible lumps or discolouration coming from the ingredients. In a suitable vessel, a mix of two polyurethane components was prepared in a homogeneous form. Then, the polyurethane was mixed with the remaining components to an ideal supersaturation mixture. The mixture so prepared was granulated, dried and in the final step compressed to the appropriate form using a hydraulic press that applied 94 MPa pressure. The molded parts were allowed to cross-link at a temperature of 45 °C for 20 h. Samples in a cylindrical form, with masses of about 30 g and diameters of 23 mm or 32 mm were obtained. The densities of the propellant samples were determined by a geometric method, by measuring their mass and deriving the volume from their dimensions (diameter and height). The average densities obtained were slightly lower than the theoretical values as calculated by the ICT Thermodynamic Code, Version 1.0. The contents of the formulations are summarized in Table 2.

Table 2. Formulations of the AN-based propellants

Component [%]	Propellant		
	60/20/15	70/15/10	80/8/8
Ammonium nitrate(V)	60	70	80
Mg	20	15	8
Polyurethane (PU)	15	10	8
Fe_2O_3	2	2	1
Dioctyl adipate	3	3	3
Average density [g/cm^3]	1.38	1.44	1.44
Theoretical density (ICT) [g/cm^3]	1.54	1.59	1.60
Oxygen balance (ICT) [%]	-40.87	-24.91	-14.14

2.2 Measuring arrangements

To determine the energetic parameters for the prepared AN-based propellants, two research methods were proposed. As the first method, in which the maximum pressure of the gaseous products and pressure impulse were determined, a laboratory rocket motor was used (Figure 1 and 2). This method has been described in more detail elsewhere [19, 28-32].

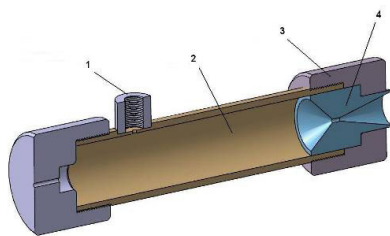


Figure 1. Laboratory rocket motor (LRM) in cross section:
1. measuring connector,
2. motor casing, 3. motor head, 4. nozzle

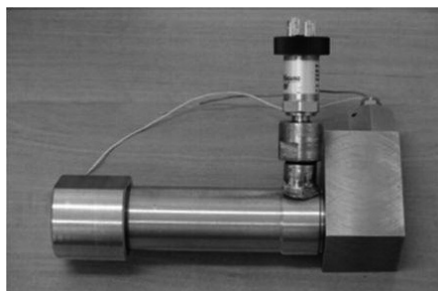


Figure 2. Actual view of LRM

The volume of the chamber was 75 cm³. In these experiments, a steel nozzle with a diameter of about 1.6 mm was used. The sample being examined (23 mm diameter) was placed in a vertically-located motor casing. The head igniter conductors were threaded through the nozzle, and then the motor head was tightened.

The second experimental method was concerned with the study of the initiation step of the samples and the process of their combustion, in aqueous environmental conditions that usually occur in boreholes. AN samples with 32 mm diameter were tested in a pressure chamber with internal volume about 1160 cm³. The samples were protected in a heat-shrinkable shield (Figure 3). In addition, the time and burning rate were estimated.

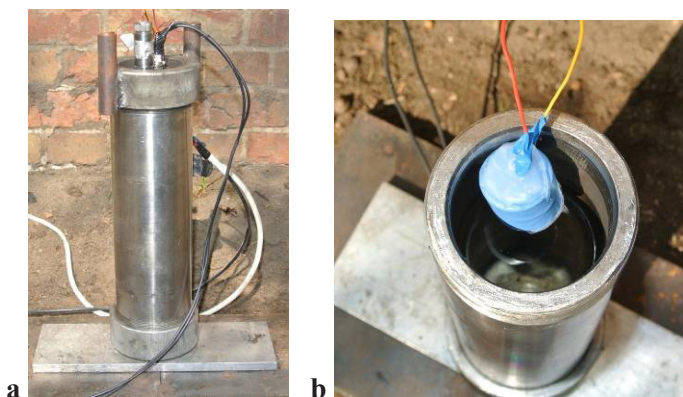


Figure 3. a) View of test stand; b) Placing the sample into the pressure chamber

In this method, the loading density of the propellants, which depended on the quantity of water in the chamber, was a variable parameter. The measuring arrangement in both methods consisted of digital oscilloscopes (GwInstek GDS-2204 with maximum sampling rate 1 GS/s, and Agilent model 54622A), which recorded the signal from the pressure sensor. Piezoresistive pressure sensors ADZ NAGANO series SML-31.0 (Table 3) were used.

Table 3. Technical parameters of the ADZ NAGANO series SML-31.0 sensors used in the experiments

Parameter	Unit of measurement	Sensor value
Measuring range	MPa	0-25 and 0-60
Sampling	ms	< 1
Output	V	0.5-4.5

3 Results and Discussion

2.1 Thermodynamic calculations

For a preliminary assessment of the energetic parameters of the proposed AN-based propellants (Table 2), thermodynamic analyses using the ICT Thermodynamic Code, Version 1.0, were performed. Calculations under standard conditions ($V = \text{const.}$) and with an assumed loading density of about 0.1 g/cm^3 were carried out. The results are summarized in Figures 4-7.

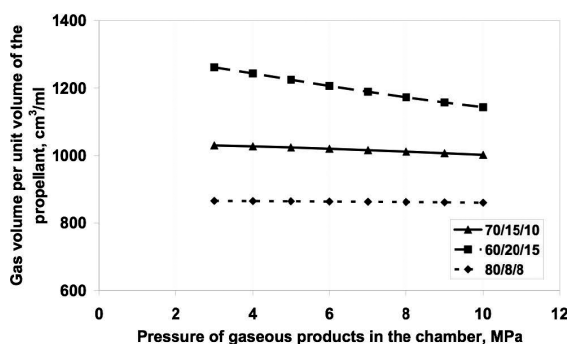


Figure 4. Gas volume generated per unit volume for AN/Mg/PU propellants

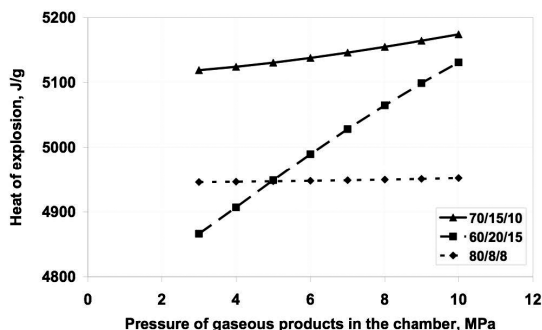


Figure 5. Heat of explosion for AN/Mg/PU propellants

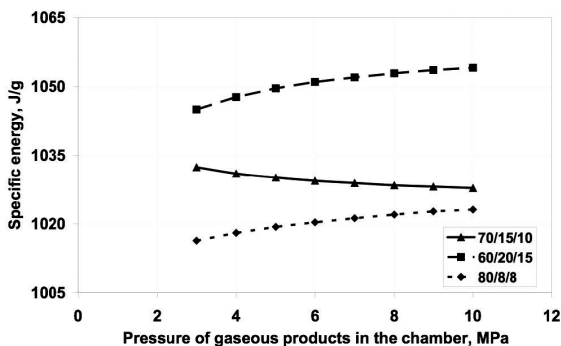


Figure 6. Specific energy for AN/Mg/PU propellants

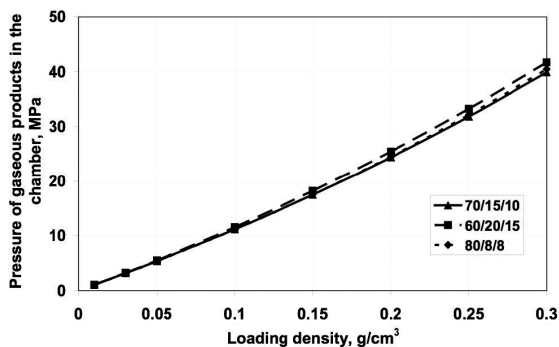


Figure 7. Pressure vs. loading density for AN/Mg/PU propellants

Comparing the ammonium nitrate(V) propellants with respect to their AN content, the lowest thermodynamic parameters were for samples with 80% AN. The highest values of the heat of explosion (calorific) were achieved for the

composition with 70% AN (Figure 5). In turn, the composition with 60% AN featured higher values of the specific energy (Figure 6) and gas volume (Figure 4). The substantial dependence of the gaseous product pressure in the chamber on the loading density is shown in Figure 7. No influence of the AN content in the samples on the combustion product pressure was observed.

2.2 Research in laboratory rocket motors (LRMs)

The results of the combustion processes of the investigated propellants in the LRM are shown in the plots of pressure changes recorded on the oscilloscope during the tests (Figure 8).

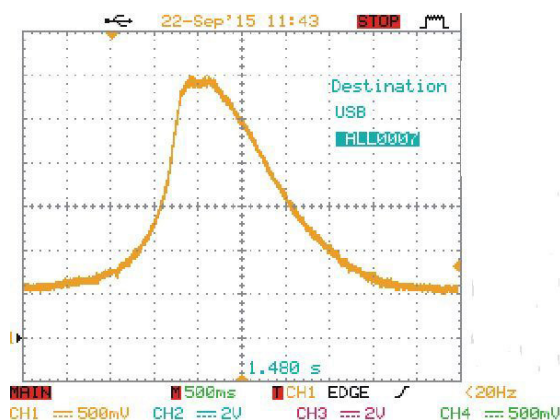


Figure 8. Characteristic pressure curve for the AN/Mg/PU 70/15/10 sample

In Figures 9-11, the $p(t)$ curves obtained for the studied AN-based propellants in the LRM tests are shown. The average values for the pressure impulse of the tested propellants were also calculated, as shown in Figure 12.

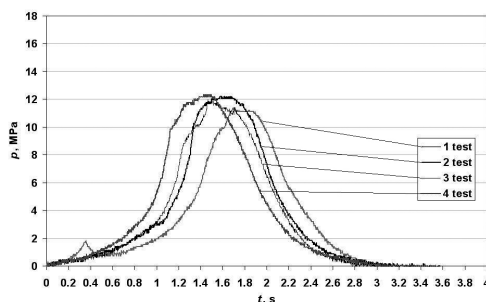


Figure 9. $p = f(t)$ plots for AN/Mg/PU: 60/20/15 propellant

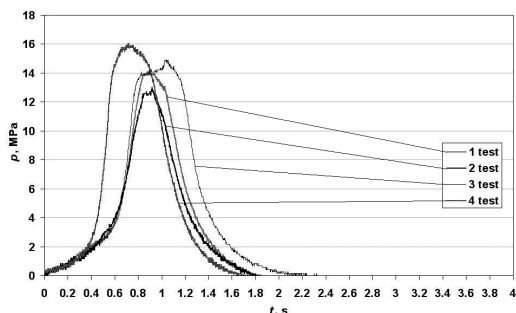


Figure 10. $p=f(t)$ plots for AN/Mg/PU: 70/15/10 propellant

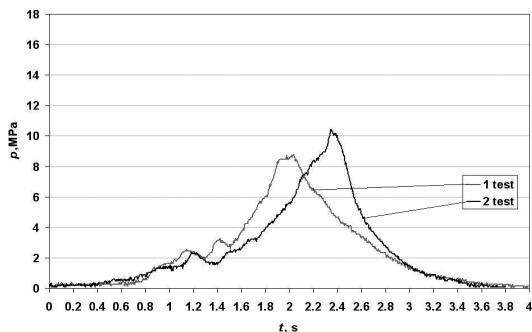


Figure 11. $p=f(t)$ plots for AN/Mg/PU: 80/8/8 propellant

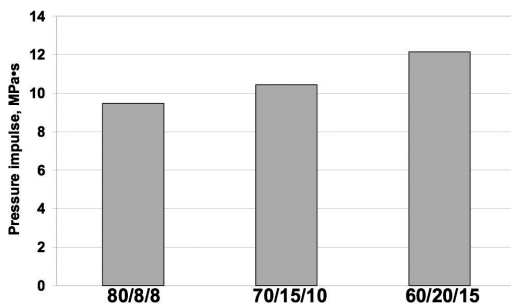


Figure 12. The average values of the pressure impulse for AN/Mg/PU propellants

Based on the results obtained in the LRM, the optimal formulations of AN-based propellants in terms of energy parameters were formulations with 60% or 70% AN, with polyurethane rubber (10-15%) and modified by the addition of magnesium powder (15-20%). These achieved higher values of the maximum pressure and

pressure impulse. The average values of the maximum pressure obtained for the AN/Mg/PU 60/20/15, 70/15/10 and 80/8/8 propellants were 11.87 MPa, 14.47 MPa and 9.53 MPa, respectively. The lowest pressure impulse values were obtained for samples with 80% AN. Also, the burning times for samples with 80% AN in the LRM were the longest. The highest values of the maximum pressure and the shortest burning times were observed for the AN/Mg/PU 70/15/10 propellant. Slightly higher values of the pressure impulse were achieved for the AN/Mg/PU 60/20/15 propellant. This was caused by the slower burning rate of these samples, which was associated with a large area under the test curve. However, it was found, during the combustion tests of AN/Mg/PU 60/20/15, that this formulation created more residue. This is probably connected with a more negative oxygen balance and an incomplete reaction of this formulation. Therefore, the AN/Mg/PU 70/15/10 formulation, with an oxygen balance closer to zero, was selected for further investigation.

2.3 Underwater tests in pressure chambers

The aim of these studies was to show the loading density's impact on the propellants' parameters (pressure of the gaseous products, time and burning rate). Different actual values of the loading densities (0.18 g/cm^3 , 0.22 g/cm^3 , 0.25 g/cm^3 , 0.28 g/cm^3 and 0.3 g/cm^3) were obtained.

The results of the underwater tests of the AN/Mg/PU 70/15/10 formulation are shown in the plot of pressure changes recorded on an oscilloscope during its combustion in a pressure chamber (Figure 13).

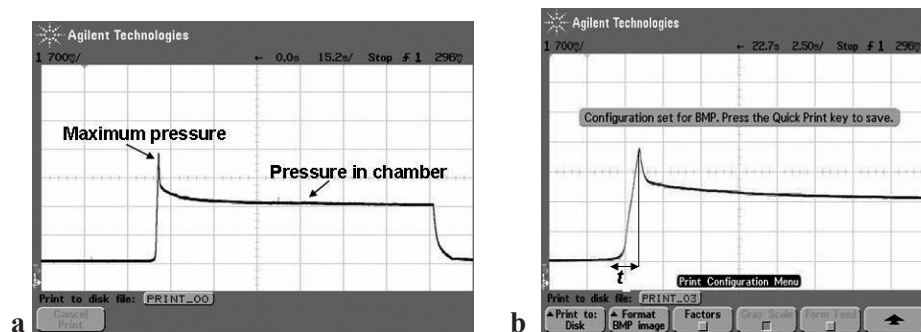


Figure 13. a) Characteristic pressure curve for the tested AN/Mg/PU 70/15/10 propellant; b) Maximum pressure peak in relation to burning time (t) at a larger scale

The $p(t)$ curves obtained for the AN-based propellants studied are shown in Figure 14. In addition, the effects of the loading density on the pressure in the chamber, burning time and burning rate were calculated (Figures 15-17).

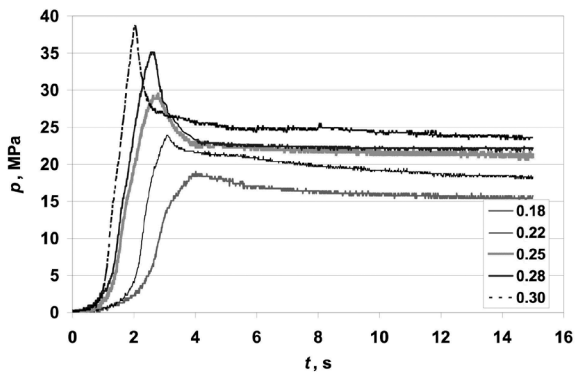


Figure 14. $p=f(t)$ plots for the AN/Mg/PU 70/15/10 propellant

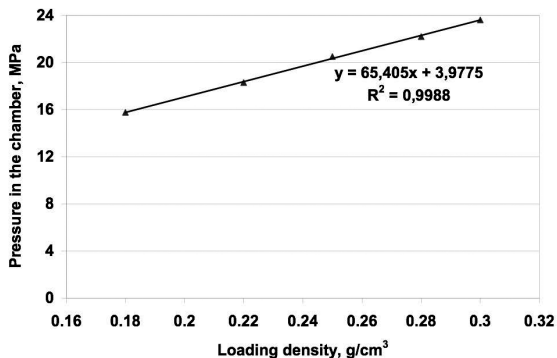


Figure 15. Pressure in the chamber for the AN/Mg/PU 70/15/10 propellant

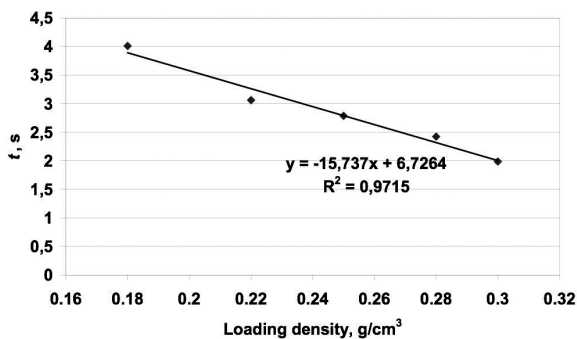


Figure 16. Burning time for the AN/Mg/PU 70/15/10 propellant

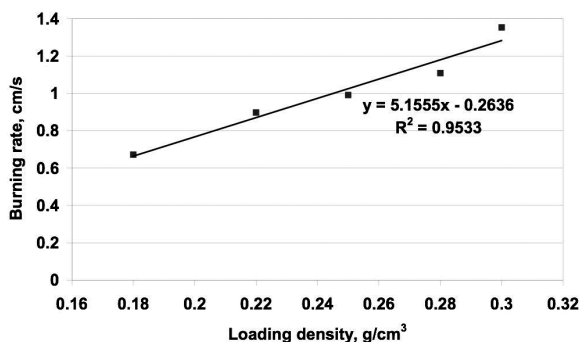


Figure 17. Burning rate for the AN/Mg/PU 70/15/10 propellant

The highest maximum pressures and pressure in the chamber were observed for higher values of the loading densities. For example, for a loading density of 0.3 g/cm³, the pressure of gaseous products generated in the combustion process was about 38 MPa and the pressure in the chamber was about 24 MPa, as shown in Figures 14 and 15. In the thermodynamic calculations, the theoretical value of pressure in the chamber was higher, about 40 MPa (Figure 7). This is probably because of the higher theoretical density of the AN/Mg/PU 70/15/10 propellant (Table 1). Moreover, the shortest burning time (about 2 s; Figure 16) and burning rate at the highest level (Figure 17) were obtained for the highest loading density.

4 Conclusions

This work investigated the possibility of using ammonium nitrate(V)-based solid propellants for fracturing wells in borehole mining. Because of the advantages of ammonium nitrate(V) described, different formulations of AN-based propellants were prepared.

Initially, studies in a LRM were performed that allowed preliminary estimation of selected parameters of the propellant formulations. Based on these studies, plots of pressure changes during combustion with the maximum pressure of gaseous products were specified. In turn, tests in a pressure chamber enabled more accurate assessments of the energetic parameters (constant pressure in the chamber, time and burning rate). These studies have shown that by changing the loading density, desirable pressure values could be optimized. It is possible to estimate the appropriate pressure values of gaseous products to allow rock fracturing to be performed. The chosen formulation was characterized by

reliable ignition in each case and operational reliability in aqueous and high-pressure conditions.

Moreover, the AN-based propellants investigated generated a large amount of gaseous products and had a lower burning rate, features that are desirable in their applications in gas generators.

Acknowledgements

We would like to thank Mr. Daniel Hadzik for his assistance, endless support, many helpful suggestions and discussions during the tests. This work was supported by the National Centre for Research and Development under Project No. PBS3/B2/0/2015.

References

- [1] Kubota, N. *Propellants and Explosives. Thermochemical Aspects of Combustion*. Wiley-VCH, Weinheim **2007**, pp. 73-74, 95-99; ISBN 3-527-30210-7.
- [2] Rarata, G.; Surmacz, P. Modern Solid Rocket Propellants. (in Polish) *Prace Instytutu Lotnictwa* **2009**, *202*: 112-124.
- [3] Oommen, C.; Jain, S. R. Ammonium Nitrate: A Promising Rocket Propellant Oxidizer. *J. Hazard. Mater.* **1999**, *67*(3): 253-281.
- [4] Tiernan, J. P.; Passamanek, R. S. *Propellant for Fracturing Wells*. Patent US 20080264289 A1, **2008**.
- [5] Seekford, D. B. *Method and Apparatus for Stimulating Wells with Propellants*. Patent US 7565930 B2, **2009**.
- [6] Tiernan, J. P. *Propellant Cartridge with Restrictor Plugs for Fracturing Wells*. Patent US 7487827 B2, **2009**.
- [7] Brooks, J. E.; Kneisl, P.; Zazovsky, A. F.; Duhon, M. C.; Fayard, A. *Propellant Fracturing of Wells*. Patent US 7431075 B2, **2008**.
- [8] Tiernan, J. P.; Spear, G. B.; Landis, D. *Propellant Fracturing System for Wells*, Patent US 8522863 B2, **2013**.
- [9] Page, J. C.; Miskimins, J. L. A Comparison of Hydraulic and Propellant Fracture Propagation in a Shale Gas. *J. Can. Petrol. Technol.* **2009**, *48*(05): 26-30.
- [10] Tiernan, J. P.; Passamanek, R. S. *Propellant for Fracturing Wells*. Patent US 7409911 B1, **2008**.
- [11] Tiernan, J. P.; Passamanek, R. S. System for Fracturing Wells Using Supplemental Longer-Burning Propellants. Patent US 7073589 B2, **2006**.
- [12] Habera, Ł.; Košlik, P.; Wilk, Z.; Frodyma, A. Modern Perforating and Fracturing Devices – the Concept and Firing Ground Tests. (in Polish) *Nafta-Gaz* **2014**, *70*(5): 301-306.
- [13] Frodyma, A. Theoretical and Computational Grounds for Borehole Stimulation

- Jobs with Use of Propellants. (in Polish) *Nafta-Gaz* **2012**, 68(9): 590-601.
- [14] Frodyma, A.; Habera, Ł. The Principles of Propellants Physical Interactions in Borehole and Reservoir Rocks Environment and Their Implications for Stimulation Jobs. (in Polish) *Materiały Wysokoenergetyczne* **2013**, 5: 59-71.
- [15] *StimGun® Technology*. The Propellant Technology Development Group; www.corelab.com/owen/cms/docs/TechCat/book_StimGunTech.pdf; access **2015**.
- [16] Al-Qarni, A. O.; Ault, B.; Heckman, R.; McClure, S.; Denoo, S.; Rowe, W.; Fairhurst, D. From Reservoir Specifics to Stimulation Solutions. *Oilfield Rev.* **2001**, 12: 42-60.
- [17] Sinditskii, V. P.; Egorshv, V. Y.; Levshenkov, A. I.; Serushkin, V. V. Ammonium Nitrate: Combustion Mechanism and the Role of Additives. *Propellants Explos. Pyrotech.* **2005**, 30(4): 269-280.
- [18] Florczak, B. Effect of Additives on Properties of Composite Solid Propellants. (in Polish) *Przem. Chem.* **2012**, 91(9): 1858-1862.
- [19] Nakka, R. *Richard Nakka's Experimental Rocketry Web Site*. www.nakka-rocketry.net; access **2013**.
- [20] Kondrikov, B. N.; Annikov, V. E.; Egorshv, V. Y.; DeLuca, L.; Bronzi, C. Combustion of Ammonium Nitrate-Based Compositions, Metal-Containing and Water-Impregnated Compounds. *J. Propul. Power* **1999**, 15(6): 763-771.
- [21] Doll, D.; Lund, G. K. *High Performance, Low Cost Solid Propellant Compositions Producing Halogen Free Exhaust*. Patent US 5076868, **1991**.
- [22] Ye, Z.; Qian, H.; Lu, C.; Liu, Z. Self-sensitizable Characteristic of Modified Ammonium Nitrate. *Cent. Eur. J. Energ. Mater.* **2005**, 2(4): 55-62.
- [23] Naya, T.; Kohga, M. Burning Characteristics of Ammonium Nitrate-Based Composite Propellants Supplemented with Fe₂O₃. *Propellants Explos. Pyrotech.* **2013**, 38: 547-554.
- [24] Florczak, B.; Sałaciński, T.; Maranda, A.; Sitkiewicz-Wołodko, R. Test of Sensitivity of Two-bases Solid Homogeneous Propellants. (in Polish) *Przem. Chem.* **2013**, 92(8): 1464.
- [25] Florczak, B.; Bogusz, R.; Skupiński, W.; Chmielarek, M.; Dzik, A. Study of the Effect of Nitrated Hydroxy-terminated Polybutadiene (NHTPB) Content on the Properties of Heterogeneous Rocket Propellant. *Cent. Eur. J. Energ. Mater.* **2015**, 12(4): 841-854.
- [26] Bogusz, R.; Magnuszewska, P.; Florczak, B.; Maranda, A. Study of the Effect of Curing Agents on Properties of the Heterogeneous Solid Rocket Propellants. (in Polish) *Przem. Chem.* **2015**, 94(3): 366-368.
- [27] Florczak, B. Viscosity Testing of HTPB Rubber Based Pre-binders. *Cent. Eur. J. Energ. Mater.* **2014**, 11(4): 625-637.
- [28] Wickman, J. *Wickman Spacecraft & Propulsion Company*; www.wickmanspacecraft.com; access **2012**.
- [29] Florczak, B.; Białek, M.; Cholewiak, A. Determination of the Internal Ballistic Properties of Solid Heterogeneous Rocket Propellants. *Cent. Eur. J. Energ. Mater.* **2014**, 11(4): 589-601.

- [30] Hadzik, J.; Koślik, P.; Wilk, Z.; Frodyma, A.; Habera, Ł. Preliminary Researches of Selected Propellants in Their Potential Use in Dry Fracturing. (in Polish) *Materiały Wysokoenergetyczne* **2014**, 6: 5-13.
- [31] Hadzik, J.; Wilk, Z. *Research on Modifiers to Improve Energetic Parameters of Ammonium Nitrate – Based Explosives*. (in Polish) IPO Warszawa/Krupski Młyn, Report No. 10000282, **2015**.
- [32] Hadzik, J.; Koślik, P.; Wilk, Z. Experimental Study on the Ammonium Nitrate-based Solid Propellants. *New Trends Res. Energ. Mater., Proc. Semin., 19th*, Pardubice, Czech Republic **2016**, 575-582.