Detonation properties of explosive proppants based on slurry nitromethane plus ammonium perchlorate mixtures

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Abstract. In this paper, the results of investigation on detonation properties of heterogeneous mixtures of ceramic proppants with slurry liquid explosives (LE) such as nitromethane (NM) plus ammonium perchlorate compositions are presented. The mixtures discussed are promised to be used for far field fracture stimulation of oil bearing formations subjected to hydraulic fracturing. Experimental results on detonation velocities of LE-proppant mixtures in long tubes up to 25 diameters versus internal diameters are presented. Results of experimental comparison of detonability of LE studied with pure NM in proppant matrix are also represented. The objective of the study was to assess detonability and detonation parameters of these mixtures at various initial conditions.

1. Introduction

Explosive mixtures of nitromethane (NM) with solid particles are well known for a long time [1]. Introduction of inert microparticles in nitromethane is known to increase its sensitivity to impacts and reduces the critical charge diameter [2–6]. Such mixtures exhibit a number of useful properties relevant to their use in fracturing as the explosive proppants (EP). Firstly, its small critical detonation diameter permits the mixture to be pumped and detonated in narrow cracks (to fractions of millimeter) or proppant pack pores. Secondly, the two components are reactive which would warrant their complete burnout. A thickening agent (polymethylmethacrylate) is an obligatory component of such mixtures to prevent sedimentation of the solid particles. Variation of its concentration allows the liquid explosives (LE) viscosity to vary from that of a normal liquid to a thick gel.

Comparison of the results of tests carried out with the stoichiometric and rich mixtures led to an unexpected result. Detonation velocities of mixtures with coarse ammonium perchlorate (AP) particles are higher throughout nearly entire range of tube diameters tested. Keeping in mind that the fine AP (9 µm) is about two orders of magnitude more expensive than the coarse AP (90 µm), we can assert that the heterogeneous mixture can be made quite cheap. Critical diameters experiments demonstrated that the critical diameter increases monotonically...
Table 1. Mean grain sizes of proppants used.

| Grade of BorProp | 40/80 | 16/20 | 12/18 | 10/14 |
|------------------|-------|-------|-------|-------|
| Mean grain size, mm | 0.30  | 1.03  | 1.34  | 1.73  |

as the mixture gets richer and the AP particle size increases. Only three mixtures had a critical detonation diameter which was smaller than that of pure nitromethane. They are stoichiometric mixtures containing 9 and 35 µm AP particles and a rich mixture (with equivalence ratio 1.2) containing AP particles 35 µm in size.

2. Experiments

As a preliminary tests are clearly demonstrates a possibility of using above LE mixtures as a component of EP in oil well applications the following questions must to be answered before the practical using of such mixtures. Is it possible to support a self sustaining detonation regime in LE–proppant mixtures? How the detonation parameter depends on ceramic proppants particle sizes, mixture richness, AP particle size and crack width (charge diameters)? How the detonation property of EP depends on LE–proppant ratio in their mixture?

A following gelled explosive mixtures were selected for tests: NM with 1 wt % of saturated polymethylmethacrylate (PMMA) + AP particles 9 and 35 µm in size. AP fraction of 9 µm is quite expensive, therefore most of the following experiments with 35 µm particles were performed taking in mind future practical applications. Four commercially grade fractions of ceramics proppants of various grain sizes were choose for experiments (table 1). When fabricating LE–proppant mixtures we took into account the open grain porosity of the proppant. Therefore, before mixing with LE the proppant grains were wetted with nitromethane to reduce the voids and absorption of NM from AP–NM mixture.

The weight fractions of the proppant and LE were calculated as follows. First, the pore volume between proppant particles per unit volume of the mixture was assessed, and then the weight of LE needed to fill the pore volume was calculated assuming that the proppant grains contacted each other and could not be compacted without their crushing. The results of measurements of the required ratios for different fractions of the proppants are demonstrated that for BorProp 16/20, 12/18 and 40/80 the LE–Proppant mass ratio is 0.388, for BorProp 10/14 is 0.369. Only stoichiometric mixture NM–AP was used taking into account such additional fuel as gelling agent saturated in NM (PMMA). The NM absorbed by internal porosity of proppant grains was not taking into account, because we believe to minor role of this component in detonation front reactions. However, it was chosen just to equalize the vapor pressure in the resulting mixture and to avoid additional admixing in the mixture if some other wetting agent would choose. Example of mixture used is shown in figure 1.

The technique used to explore the feasibility of initiation of self-sustaining detonation in a proppant + heterogeneous explosive (NM–AP) mixture was based on “soft firing” method. The LE–proppant mixture was initiated by a detonation wave of a proppant-free mixture of a similar density spreading at an expected velocity in the range from 3 to 5 km/s. A stoichiometric mixture of Al flaked particles (PAP-2) and 100 µm AP particles with 6 wt % nitromethane additive (as a compacting agent) served as the initiator. Low-velocity detonation (LVD) in the initiator mixture was excited via deflagration-to-detonation transition (DDT) in a tube of 10 mm in internal diameter (ID). LVD in the initiator mixture has a wide reaction zone and is qualified as a nonideal detonation (i.e., a detonation wave in which some fraction of the energy is released behind the CJ plane). This approach to detonation initiation is more preferable than the direct
Figure 1. Sample of the 73 wt % BorProp 10/14 + 27 wt % of NM–PMMA–AP stoichiometric mixture.

initiation of detonation with a condensed high explosive (HE), because it significantly reduces the possibility of inducing overdriven detonation in the LE–proppant mixture and, hence, to find out whether the process initiated is non-decaying and self-sustaining or not. The setup used is shown schematically in figure 2(a).

To support or reject the assertion that low-velocity detonation in the LE–proppant mixture is incapable of significantly crushing the proppant granules, fragment catchers made of wetted cardboard were mounted on the two sides of the charge [figure 2(b)].

Optical fibers technique was chosen to obtain detonation velocities. The significant duration (100–250 µs) of the luminosity signals deserves special attention; it provides an indirect evidence of the wide heat release zone. This signifies that the initiates detonation wave is highly nonideal with a large energy fraction released downstream of the CJ plane. A measurement performed on ten bases allows the detonation velocity evolution along the charge length to be traced.

In figures 3 and 4, the enclosure fragments exhibit a shape inherent in destruction by low-velocity detonation, namely, large fragments 40 or 70 mm in size with stepwise longitudinal bends. Long longitudinal bends fragments are normally observed solely when the heat release zone in a detonation wave is wide.

The tube fragments confirm the realization of low-velocity detonation propagation regime. Most of the proppant grains are not crushed after detonation front traverses them which is evidenced by the imprints left by the granules on the enclosure fragments in figure 4.

In the photo of the cardboard catcher fragment (figure 5) at least a major number of proppant grains remain intact. This is accounted for by two reasons: firstly, we failed to find punctures made particles that were finer than the original proppant grains. Only original proppant grains
Figure 2. (a) Tube equipped with optical fibers and igniter cap. (b) Wetted cardboard boxes as fragment catchers.

were found in the ash after the cardboard catcher was burned. This leads to an important from practical point of view inference: Proppant particles keep their integrity after being subjected to low-velocity detonation. “Soft” low-velocity detonation saves proppant particles from destruction.

At first, the detonation velocity of proppant mixtures with LE based on nitromethane and ammonium perchlorate is measured. Experiments were performed in steel tubes 500 and 700 mm long 10 and 18 mm in inner diameter, of wall thickness 3 and 6 mm. Detonation velocity was measured on several bases using the optical fiber technique. The velocity of the initiating detonation wave in a stoichiometric Al–AP mixture was measured along the first base. Only the results of experiments in which the initiating wave velocity deviated from the average value by no more than 200 m/s were compared. The mixture was loaded into the steel tubes, precautions were undertaken to minimize the amount of air bubbles in the mixture. In some tests the detonation velocity was measured also in mixtures of proppants of various trademarks with pure nitromethane. The shape, size and thickness of tube fragments were examined in each test. Whenever the fragment parameters gave rise to doubt concerning stability of the detonation
The major reason of malfunctioning was detonation failure during the wave transition from the initiating tube 10 mm in diameter to the wider test tube 18 mm in diameter. Figure 6 displays the detonation velocity versus distance along the tube length for LE–proppant mixtures of various sorts. The commonly accepted parameter, the number of tube diameters, was chosen as a measure of the distance. It is worth noting that even in homogeneous HE detonation approaches steady state as a rule within 3 or 4.5 calibers. As one can see in figure 6, detonation
Figure 5. The holes in wetted cardboard from proppant grains (frame area is 50 × 50 mm²).

is stabilized within no less than 13 or 20 enclosure calibers. This is because of the fact that the relaxation processes in the inert matrix and reaction releasing heat take much longer time than in the case of homogeneous HE.

The above dependences exhibit a tendency for the transient regime distance to decrease as the proppant grain size decreases. Of importance is that the detonation velocity rises in all the mixtures studied, which is indicative of feasibility of self-sustained low-velocity detonation regimes in them.

The initiator device in tests with the tube diameter reduced to 10 mm remained the same. The LE–proppant mixture was initiated by a detonation wave originated in a 18 cm long tube section via DDT-process (with resulting 4 km/s velocity). The wall thickness-to-diameter ratio for tubes available was somewhat higher than that in tubes 18 mm ID, therefore the shape of fragments changed, most of them were long strips (up to 30 cm long), which were specific of low velocity detonations. Like in a tube of the larger diameter the detonation velocity was highly dependent on the proppant grain size (figure 7). Though, mixtures with coarser grains demonstrate a behavior which is close to detonation decay. This signifies that 10 cm diameter is nearly critical for these mixtures.

The tests in both enclosures, 18 and 10 mm ID, show that the average level of measured detonation wave velocities ranges between 2 and 2.5 km and that the mixtures detonate in a highly nonideal regime of propagation with a reaction zone of order of few tens of centimeters wide. The effect of the ratio between the proppant and LE weight fractions in the mixture was assessed from comparative tests performed. In particular, we intended to answer the question
how the compression wave propagation through the matrix with closely contacting proppant grains affects the detonation wave propagation. Therefore, for comparison, in addition to the test with a densely packed mixture in which proppant grains contacted each other without gaps we conducted a test in which the LE fraction was slightly increased (73/27 against 76/24).
Figure 8. Detonation velocity as a function of distance: 1—73/27; 2—76/24; ID = 10 mm.

Figure 9. Comparison of gelled LE–proppant performance with that of pure NM–proppant in tubes of different IDs: 1—12/18 mixture at ID = 18 mm; 2—12/18 and NM at ID = 18 mm; 3—40/80 mixture at ID = 10 mm; 4—40/80 and NM at ID = 10 mm.

Proppant of the 10/14 trademark and 10 mm ID tube were used in these tests. As a result, at the optimal proppant to mixture weight ratio (no gaps between proppant grains) the detonation parameters are the best (blue line in figure 8). Reason—the contacts between proppant grains through liquid are minimized. This suggests that elastic-plastic interactions in the NM–AP
mixture and entrainment of hard proppant grains in the flow (with friction between them) resulting in energy and momentum losses significantly contribute to detonation propagation.

Next step was a comparison of gelled LE–proppant mixture performance with that of pure NM–proppant mixture in tubes of different ID. Tubes with ID 18 mm and 10 mm were used. In figure 9 despite higher detonation velocity, NM mixtures demonstrate the detonation wave decay even in bigger IDs.

3. Conclusion
Experiments demonstrate that detonation velocity of the EP depends heavily on proppant grain sizes. Smaller proppant (0.3 vs 1.7 mm in diameter) shows up to 1 km/s higher detonation velocity. All proppant mixtures support self-sustained LVD regimes with significant nonideal behavior within initial 15–20 mm IDs from the tube beginning. It means that there would be NO destructive pressure rise near the well bore column. Experiments demonstrate stable detonation wave behavior in all mixtures studied. Critical diameters of LE–proppant mixtures are less than 10 mm particularly for 40/80, 16/20 and 12/18 proppants, because of high detonation velocity reserve observed. 10/14 mixture exhibits near critical behavior. Pure NM-proppant mixtures demonstrate detonation wave decay in all cases even in tubes of larger IDs. Detonation wave in a proppant mixture seems to be initiated by a pressure wave spreading through the proppant matrix and differs from an ideal detonation wave by a wider front zone. Pressure level in detonation waves in proppant mixtures is estimated to be enough to avoid the proppant grains destruction. This conclusion supported by analysis of the proppant fragments collected in the cardboard screen. All above conclusions and findings makes ED of investigated type are very promising for the fracturing applications.

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