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Assis Resende, Salatiel; Costa e Silva, Valdir; Mota de Lima, Hernani

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Estudo de combustíveis não-convencionais para misturas explosivas

Salatiel Assis Resende
M.Sc., PPGEM, Departamento de Mineração
Universidade Federal de Ouro Preto/UFOP
Ouro Preto, Minas Gerais, Brasil
salattiel@gmail.com

Valdir Costa e Silva
PPGEM, DEMIN,
Universidade Federal de Ouro Preto/UFOP
Ouro Preto, Minas Gerais, Brasil
valdir@demin.ufop.br

Hernani Mota de Lima
PPGEM, DEMIN,
Universidade Federal de Ouro Preto/UFOP
Ouro Preto, Minas Gerais, Brasil
hernani.lima@ufop.br

Abstract

The use of ammonium nitrate and fuel oil (ANFO) results in low cost blasting. Such costs may be further reduced by replacing fuel oil with alternative fuels such as biomass (biodiesel, rice straw, corn cob, sugar cane bagasse) and tires residue. This paper investigates the use of other fuels instead of fuel oil by measuring the detonation velocity (VOD) and verifying the importance of these fuels in an explosive mixture. Except for biodiesel, all the tests conducted for the mixture of ammonium nitrate and alternative fuels showed poor performance when compared with ANFO. The achieved percentage of detonation velocity (VOD) of the mixtures in relation to the ANFO were 55.4% for ammonium nitrate + rice straw, 64.9% for ammonium nitrate + corn cob, 70.1% for ammonium nitrate + sugar cane bagasse, 74.4% for ammonium nitrate + tires residue and 93.7% for ammonium nitrate + biodiesel. This study indicates that the methodology proposed can be applied as a reference for determination and preparation of explosive mixtures of fuel and oxidizing agents since in all the tests conducted the detonation of the charges occurred.

Keywords: ANFO, blasting, alternative fuels, biomass

Resumo

A utilização do ANFO (ammonium nitrate fuel oil) implica um reduzido custo de desmonte. Tais custos podem ser mais baixos ao se substituir o óleo diesel por combustíveis alternativos como biomassa (biodiesel, palha de arroz, sabugo de milho, bagaço de cana-de-açúcar) e resíduo de pneu. Esse artigo investiga o emprego de novos combustíveis, em substituição ao óleo diesel presente no ANFO via medição da velocidade de detonação e verificação do efeito desses combustíveis na mistura explosiva. Com exceção do biodiesel, todos os ensaios provenientes da mistura entre o nitrato de amônio e os combustíveis alternativos apresentaram desempenho insatisfatório comparado ao ANFO. Os percentuais obtidos de velocidade de detonação das misturas em relação à do ANFO foram de 55,4% (NA + Casca de arroz), 64,9% (NA + Sabugo de milho), 70,1% (NA + bagaço de cana), 74,4% (NA + resíduo de pneu) e 93,7% (NA + Biodiesel). Ainda, a metodologia adotada pode ser aplicada como referência para determinação e elaboração de misturas explosivas (agentes oxidantes e combustíveis), uma vez que, nos ensaios realizados, ocorreu a detonação das cargas.

Palavras chave: *ANFO, desmonte, combustíveis alternativos, biomassa.*

1. Introduction

The importance of ANFO as an industrial explosive due to cost, safe handling and ease of use has prompted a large amount of work attempting to quantify the influence of physical properties (parameters of the explosive) to the detonation properties (parameters of the explosion). Studies of the detonation properties of ammonium nitrate and various fuels have been conducted by COOLEY (1955), DERIBAS (1999), MIYAKI *et al*. (2007), ZYGMUNT (2009) and BUCZKOWSKI e ZYGMUNT (2011). Fuels used in these studies include: coal dust, confectioners sugar, aluminium powder, TNT and fuel oil.

Clark (1987) reported a comprehensive review of ANFO detonation velocity as a function of charge diameter, charge confinement, fuel oil content, particle size, particle size distribution, loading density and moisture content. He also showed experimental curves for sensitivity to initiation (measured as the minimum detonator size required to initiate a detonation reaction) as a function of fuel oil content, charge density, particle size, particle size distribution, bulk density, number of crystalline transitions (prill density) and diatomaceous earth content. The general conclusions taken from Clark's study include:

• Detonation velocity is strongly dependent on charge diameter for charges less than 100mm in diameter. Detonation velocity continues to increase in charges up to 1016mm in diameter. Results are not reported for larger charge diameters.

• Increasing the stiffness of charge confinement up to a critical value will increase the VOD of a charge of given diameter and density.

• Critical diameter (the minimum diameter at which a detonation will propagate) decreases as the stiffness of the charge confinement increases.

• Maximum heat of detonation is found in an oxygen balanced ANFO mix of 94.2% AN and 5.8% FO. Maximum VOD is found at a slightly lower FO content. However, VOD decreases significantly more rapidly with decreasing FO content (due to NO_x formations) than it does for increasing FO content (due to CO formations).

• Detonation velocity increases with increasing charge density.

• Detonation velocity increases with decreasing particle size.

The detonation velocity (VOD) of wave that propagates through the explosive is a parameter that defines the rate of energy releasing. Parameters affecting the detonation velocity include the charge density, the diameter of the hole, confinement, the primer, and aging of the explosive. For the first three parameters, the detonation velocity increases significantly with increasing values (JIMENO *et al.* 2003). Detonation velocity is used to determine the efficiency of an explosive reaction. The greater the detonation velocity the more the breakage will occur, since the explosive detonation pressure is directly proportional to the square of VOD. Currently VOD is the sole property of detonation, which can be determined easily in the holes. Probably for this reason great importance has been attributed to it (SANCHIDRIÁN, 2009). The VOD of explosives is measured to calculate the pressure produced in the hole during the detonation of the explosive, to compare the performance when launched with different primers, different accessories and materials used for the containment of buffer, and to verify whether the explosives and the accessories are activating in accordance with the value provided by the manufacturer (SILVA, 2006).

In Brazil few companies share the market of explosives for mining and construction (MUNARETI *et al.*, 2002). Allied to this reality, the lack of information on the use of ANFO for most of the mines and quarries makes the same become dependent on products and prices set by explosive manufacturing industries. The use of ANFO implies a reduced cost of blasting. However, such costs can be even lower when replacing diesel oil by alternative fuels such as biomass (biodiesel, rice straw, corn cob, sugar cane bagasse) and tires residue. According to Silva (2006), these materials combine with excess oxygen to prevent the explosive mixture formation of NO, NO_2, and toxic chemicals, reducing the temperature of the reaction "heat robbers".

On the other hand, the explosive mixture containing an oxidising agent (ammonium nitrate, calcium nitrate, potassium nitrate, sodium nitrate etc.) ensures the oxidation of carbon, which prevents the formation of CO. This also makes their disassembly more environmentally satisfactory.

This paper investigates the use of new fuels to replace diesel oil in the ammonium nitrate fuel oil (ANFO) by measuring the detonation velocity and verifies the efficacy of these fuels in the explosive mix.

2. Materials And Methods

The materials (fuels) used in this study were sugar cane bagasse, rice straw, corn cob, tires residue and biodiesel – considered fuels capable of reacting with an oxidizer, generally oxygen in a combustion reaction.

The methods adopted include: choice of materials, thorough preparation, sampling, elementary analyses, determination of chemical balance and oxygen balance AN + fuel mix and detonation field tests to determine VOD recording.

Primary samples were randomly taken in order to guarantee that all parties have the same chance of being selected. Particle size of the samples were then reduced in order to increase the surface area (CLARK, 1987). Residues of tires were acquired in a company dealing with retreading tires.

The increments (Figure 1) were subjected to homogenization and quartering technique in order to obtain the proper amount for elemental analysis.

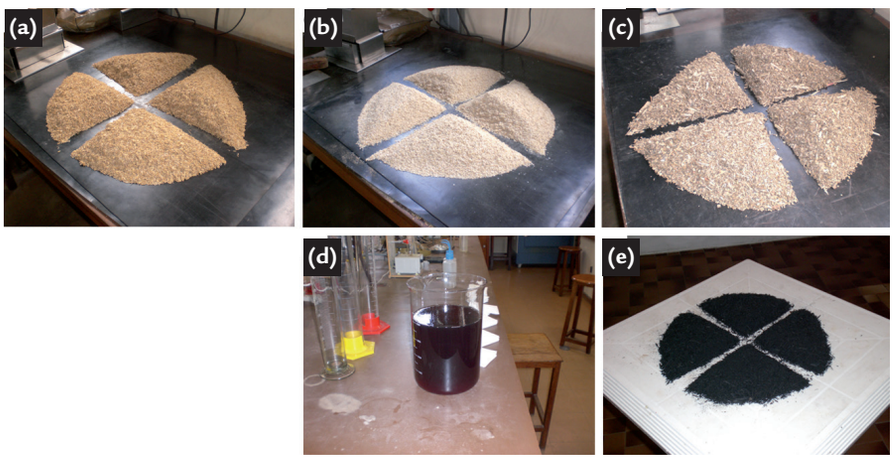

Figure 1
Increments of fuel that will be used to compose sample
a) – rice straw,
b) – corn cob
c) - sugar cane bagasse,
d) – biodiesel, and
e) – tires residue.

Sample Preparation

The basis was a sample primary mass exceeding 2 kg for each solid fuel made by drying in an oven in order to reduce moisture. The homogenization was performed in the same canvas, quartered with a Jones splitter, and conical piled until generating an amount of 5 g for each fuel. A sample of 4 litres of biodiesel composed of 96% diesel and 4% biofuel in mass was collected randomly at pump stations. The sample was placed in a beaker and stirred. An aliquot of 5 ml was collected and sent for elemental analysis along with other fuels.

Elementary analysis

According to Dick et al. (2005) for explosive mixtures, the energy released is optimized for oxygen balance of zero. In order to determine the detonation reaction, prior knowledge of the chemical composition of these fuels is recommended. The elemental analysis of fuels aims to determine the chemical composition thereof for the preparation of a formula to establish a minimum allowing reaction between the fuel and oxidizing agent (ammonium nitrate). The analysis was performed in a Perkin Elmer elemental analyser. Table 1 shows the results of elemental analysis with the mass percentage of each element present in each sample.

Table 1
Percentage by mass of each element present in the samples

	Elementary chemistry analyses			
	C (%)	H (%)	N (%)	O (%)
Corn cob	42.87	6.20	0.61	50.32
Rice straw	34.02	4.73	0.41	60.84
Sugar cane bagasse	43.28	6.00	0.94	49.78
Tire residue	85.60	6.73	0.45	7.23
Biodiesel	60.86	9.12	0.15	29.87

Calculation of stoichiometric formula

The stoichiometric formula indicates the elements that form the substance as well as the proportion in number of atoms of these elements expressed in whole numbers and the smallest possible (Feltre, 1995).

Table 2 shows the minimum formula of each fuel from the elementary chemical analysis.

Table 2
Minimum formula of each fuel used.

Materials	Mass Composition (%)				Stoichiometric formula
	C	H	N	O	
Corn cob	42.87	6.20	0.61	50.32	$C_{82}H_{142}NO_{72}$
Rice straw	34.02	4.73	0.41	60.84	$C_{97}H_{161}NO_{130}$
Sugar cane bagasse	43.28	6.00	0.94	49.78	$C_{54}H_{89}NO_{46}$
Tires residue	85.60	6.73	0.45	7.23	$C_{222}H_{209}NO_{14}$
Biodiesel	60.86	9.12	0.15	29.87	$C_{463}H_{832}NO_{170}$

Determination of the chemical reaction of oxygen and balancing

The most explosive ingredients are composed of elements such as oxygen, nitrogen, hydrogen and carbon (DICK *et al.*, 2005). In addition, metal elements such as aluminium may be used. For explosive mixtures, the energy released is optimized for zero balance oxygen. Zero oxygen balance is defined as the point where the mixture has sufficient oxygen to oxidize all that is combustible but that has no excess oxygen that can react with nitrogen to form nitrogen oxides, and is not deficient in oxygen, forming carbon monoxide. Thus, it becomes necessary to balance the equation. Theoretically, for an oxygen balance equal to zero, the reaction products of detonation are H_2O, CO_2 and N_2. However, small quantities of NO, CO, CH_4 and NH_2 can be generated.

Ammonium nitrate + corn cob (1)

$$326N_2H_4O_3 + 2C_{54}H_{89}NO_{46} \rightarrow 164CO_2 + 794H_2O + 327N_2$$

Ammonium nitrate + Rice straw (2)

$$289N_2H_4O_3 + 2C_{97}H_{161}NO_{130} \rightarrow 194CO_2 + 739H_2O + 290N_2$$

Ammonium nitrate + Sugar cane bagasse (3)

$$213N_2H_4O_3 + 2C_{54}H_{89}NO_{46} \rightarrow 108CO_2 + 515H_2O + 214N_2$$

Ammonium nitrate + Tires residue (4)

$$1069N_2H_4O_3 + 2C_{222}H_{209}NO_{14} \rightarrow 444CO_2 + 2347H_2O + 1070N_2$$

Ammonium nitrate + biodiesel (5)

$$2344N_2H_4O_3 + 2C_{463}H_{832}NO_{170} \rightarrow 926CO_2 + 5520H_2O + 2345N_2$$

Calculation of explosive mix-mass percentage

The percentage by mass of explosive mixtures was determined taking into account the molecular weight of ammonium nitrate and fuel present in item 2.5 of balanced reactions (Table 3).

Oxidizing agent and Fuel	Composition	Molecular Mass (g)	Mass (%)
Ammonium nitrate	326 $N_2H_4O_3$	326 x 80 = 26080	(26080/30664) x 100 = **85.1**
Corn cob	$2C_{82}H_{142}NO_{72}$	2 x 2292 = 4584	(4584/30664) x 100 = **14.9**
	Total	**30664**	
Ammonium nitrate	289 $N_2H_4O_3$	289 x 80 =23120	(23120/29958) x100 = **77.2**
Rice straw	2 $C_{97}H_{161}NO_{130}$	2 x 3419 = 6838	(6838/29958) = **22.8**
	Total	**29958**	
Ammonium nitrate	213 $N_2H_4O_3$	213 x 80 = 17040	(17040/20014) x 100 = **85.1**
Sugar cane bagasse	2 $C_{54}H_{89}NO_{46}$	2 x 1487 = 2974	(2974/20014) x 100 = **14.9**
	Total	**20014**	
Ammonium nitrate	1069 $N_2H_4O_3$	1069 x 80 = 85520	(85520/91742) x 100 = **93.2**
Tire residue	2 $C_{222}H_{209}NO_{14}$	2 x 3111 = 6222	(6222/91742) x 100 = **6.8**
	Total	**91742**	
Ammonium nitrate	2344 $N_2H_4O_3$	2344 x 80 = 187520	(187520/205764) x 100 = **91.1**
Biodiesel	2 $C_{463}H_{832}NO_{170}$	2 x 9122 = 18244	(18244/205764) x 100 = **8.9**
	Total	**205764**	

Table 3
Calculation of the mass ratio between the oxidizing agent and fuel

Detonation tests

To conduct the detonation tests we used schedule 80 steel pipe, cylindrical 50.8 mm in diameter and 1.000mm long. Mixtures of fuel and dense ammonium nitrate were previously mixed and poured into the tube and kept contained (Figure 2). A silent line was first introduced and later replaced by a detonating cord connected to a booster introduced into the pipe end to ensure the initiation of the explosive column without deflagration of the same. In addition, a coaxial cable of known resistance with one end in contact with the explosive mixture, and the other connected to VOD measuring equipment was used. Upon detonation of the explosive charge, the wave travelling through the explosive column is recorded on the equipment for measuring VOD (Microtrap). Data from each test, contained in the Microtrap were unloaded and stored in a computer before initiating the next trial. Performance evaluation of new compounds was conducted by comparing the results, taking as standard ANFO. The tests were conducted at the premises of the Capitão do Mato Mine owned by Vale and located in the municipality of Nova Lima/Minas Gerais. In order to ensure representativeness, for each mix five tests were conducted totalling thirty detonation tests, among which twenty were recorded by measuring VOD equipment.

Figure 2
Loading the mix in the steel pipe Schedule 80.

3. Results

Figure 3 shows the velocities of detonation for each explosive mixture of the detonation tests conducted.

It can be observed that except for biodiesel, all tests from the mixture of ammonium nitrate and alternative fuels showed poor performance compared with the result of ANFO.

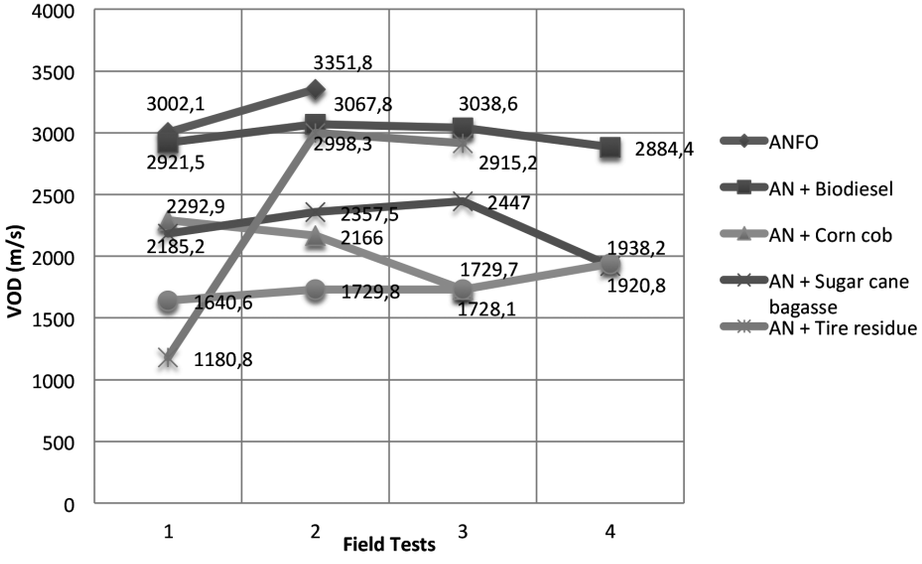

Figure 3
Detonation velocity of the explosive mixes.

Figure 4 shows the variation of the average of the detonation velocity for different mixes used in the tests. It can be observed that the mixing of ammonium nitrate and biodiesel presents a satisfactory outcome in relation to other fuels, but unsatisfactory when compared with ANFO. A mixture of ammonium nitrate and rice straw has the worst result with a detonation velocity averaging around 1759.2m/s. For other fuels, the average detonation velocity varied between 1759.2m/s and 3.177m/s. The achieved percentage of detonation velocity (VOD) of the mixtures in relation to the ANFO were (55.4%) for ammonium nitrate + rice straw, (64.9%) for ammonium nitrate + corn cob, (70.1%) for ammonium nitrate + sugar cane bagasse, (74.4%) for ammonium nitrate + tires residue and (93.7%) for ammonium nitrate + biodiesel.

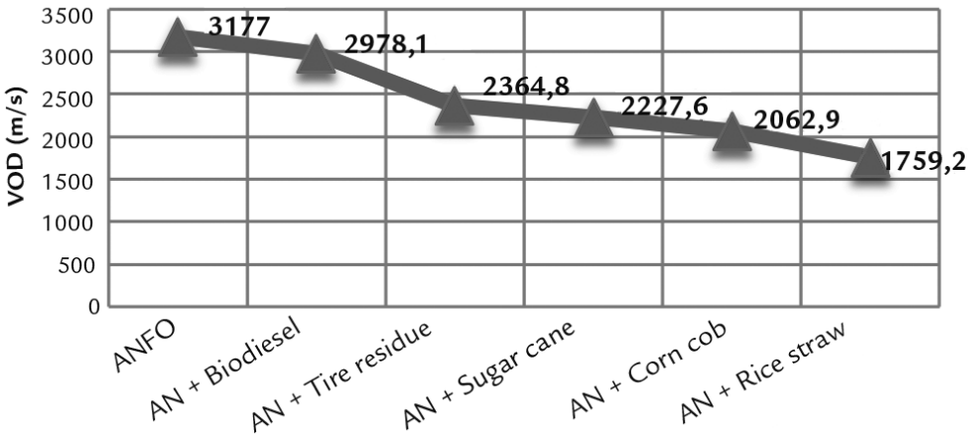

Figure 4
Variation of the VOD for the different mixes

4. Final Comments And Recommendations

Regarding the results presented, biodiesel showed satisfactory performance in relation to other fuels. In the field, during the preparation of the mixtures, better interaction was observed between the liquid fuel (biodiesel) with ammonium nitrate when compared to other solid fuels (corn cob, rice straw, sugar cane bagasse, tire residue).

It is also believed that the results may have been affected by the segregation of solids at the time the tubes were loaded, which likely caused a change in the proportions between the oxidizing agent and the fuels, influencing directly the detonation velocity. This study does not assess the effect of particle size on the VOD. According to Clark (1987), detonation velocity increases with decreasing particle size, certainly by reducing the segregation. Assessing the influence of particle size on VOD for solid fuels is recommended for further studies.

This study, however, indicates that the methodology proposed can be applied as a reference for the determination and preparation of explosive mixes of fuel and oxidizing agents, since in all of the tests conducted, detonation of the charges occurred.

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