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FAE INITIATION PROJECT
Progress Report No. 1
(1 January to 31 March 1975
15 April 1975

F. E. Walker

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INTRODUCTION

The problem of FAE is of great interest not only because of its potential value as a weapon for aerial destruction of enemy ground forces and other selected targets, but also because of the devastating effects resulting from accidental spills and leaks of flammable fuels into the open air in industry and during transportation. The latter effects have been very thoroughly described in an overview article by Strehlow. (1)

Once the cloud of fuel-air mixture is formed one can expect various types of damage to be caused, depending on the type of process that will take place. Simple burning of the mixture does not produce as much damage as the detonation wave, and the prediction of what process will actually occur forms the subject for many investigations.

It is now well established that the process depends very much on the uniformity of mixture formed in the cloud, its composition measured in volume or weight percent of air and most of all on the ignition source, i.e., its size, strength and manner of energy release. Due to the unconfined nature of the process, there is also a question of whether a transition-to-detonation can occur from a relatively weak ignition source which would initially start only a deflagration process. Although there is no proof of that phenomenon in an actual fuel-air cloud the transition to detonation has been observed in acetylene-oxygen mixtures with relatively weak ignition sources.
and in an unconfined spherical mode.\(^{(2,3)}\) It was also found that a relatively weak source can initiate a blast wave which first decays to a wave velocity lower than the C-J detonation, but which will pick up speed and accelerate to a final theoretical detonation velocity.\(^{(4)}\)

More detailed discussion of what has already been done in the field of FAE and what is being proposed here will follow in subsequent sections of this report.

**LITERATURE SURVEY OF WORK DONE ON FUEL-AIR-EXPLOSION AND RELATED PROBLEMS.**

I. **Sandia Laboratories - Albuquerque\(^{(5,6,7)}\)**

Benedick et al. looked into initiation of an "unconfined" detonation in plastic bags and out in the open. They investigated several fuel-air mixtures and determined their detonability limits (see Table 1).

They have also looked into the sensitivity of fuel relative to the multiple bonding between carbon atoms. They found that triple bonded fuels are much more sensitive than double and more so than single bonded ones.

In a private communication Benedick suggested that acetylene \((C_2H_2)\) may be a good sensitizer to fuels to expand detonability limits. He also expressed a belief that all that is needed for a successful FAE is a very strong initiator set off in the vicinity of the F-A cloud. The initiator must be strong enough so that its blast wave will start detonation in the cloud.
II. Naval Weapons Center - China Lake (8, 9, 10)

Lind and Josephson started to study properties of various fuels and then took up the task of proper dispersion in the air and ignition. The fuels which they have investigated are listed in Table 1. They concentrated on ethylene oxide and determined more carefully detonation properties (pressure and velocity) as obtained from different initiating boosters.

Now (10) they are concentrating on work with PO because EO was found to undergo easy polymerization. Ref. 9 contains valuable information on various properties of fuels mentioned above.

III. Eglin AFB (11-14)

Collins and Parsons have looked into the critical energy concept, i.e., the amount of energy needed to initiate the detonation process in unconfined fuel-air mixtures. The fuels are listed in Table 1. Their study was conducted in plastic bags similar to (5) with PETN-based detasheet as initiators. They achieved considerable sensitization of MAPP by adding 6% of n-propyl nitrate.

Additional fuels were reported in an internal report (13) which provides valuable information in the forms of tables and graphs of detonation limits and velocities for propylene oxide-air mixtures.

Another internal report (14) describes their effort in developing techniques to investigate controlled, unconfined fuel-air detonations. These are: the bag technique for gaseous F-A mixtures, the spray technique for liquid fuel droplet-air mixtures, and the combination of spray and bag techniques for low vapor pressure liquids.
IV. McGill University - Montreal (15-17)

Although not directly associated with the FAE problem, the group at McGill was actively involved in the study of initiation of spherical detonation waves. Their work was done on low pressure oxy-acetylene mixtures, and their initiator was a monitored laser spark.

Their point is that initiation of spherical gaseous detonation depends not just on the amount of energy but moreso on the rate of energy deposition, i.e., on the power density \( \frac{E}{tv} \). Comparing various ignition sources which on the energy scale indeed gave different critical values, they managed to get a close agreement between their power density values. This power density depends on the initial pressure of the mixture. There is some question about the volume of explosive mixture actually affected and the uniformity of the power deposition.

As an extension of this study they also proposed a phenomenological model for coupling between chemical kinetics and blast hydrodynamics. This model brought out the essential features of the three propagation regimes of the reacting blast corresponding to different magnitudes of the source energy: decay to a C-J wave, decay to a sonic wave and intermediate decay to less than C-J velocity but slowly recovering and gaining speed, approaching C-J from below.

V. University of Michigan - Ann Arbor (18-21)

A rather comprehensive analytical comparison between strong blast waves and C-J detonations was worked out by Nicholls and his group at the University of Michigan. They put forward the concept of the critical radius separating the inner blast wave zone from the outer
detonation zone. This concept agrees very well with the critical radius proposed by Lee and his group at McGill. (15) They, in fact, extended Bach's analysis to the system containing liquid fuel drops in a gaseous oxidizer and derived the complementary expression for the critical initiation energy in that system.

Their experimental work was done in a specially-designed, sectored detonation tube into which fuel droplets were fed in a proper fuel-air ratio. Among the liquid fuels which were being investigated are two types of kerosene, 2- and 1-nitropropane and propyl nitrate. Their results show good agreement with their theory, in that critical threshold energies and critical radii were predicted with remarkable accuracy. MAPP gas was the only gaseous fuel that was investigated in their experiments. These results, compared with the field bag tests of Collins (12) show a good agreement.

Their experimental findings also agree well with Bach's (15) predictions that depending on the initiating energy level the original blast wave would either decay to the C-J detonation wave or to an acoustic wave, or, for the range in between, to a wave slower than the C-J velocity, but one which would then accelerate to that.

A considerable theoretical effort was also made by this group to determine analytically the ground motion and dynamic air impulse which are generated by such fuel-air explosions and which are the main cause of the damage.
VI. Picatinny Arsenal - Dover, N.J. (22-24)

Their experimental effort was directed towards determining the chemical aspects of the shock initiation of fuel droplets and towards establishing a criteria of which fuel would be easier to initiate.

Their investigation was carried out with several liquid fuels, which are physically very similar but chemically rather different:

- ethyl nitrate \((C_2H_5NO_3)\)
- propyl nitrate \((n-C_3H_7NO_3)\)
- nitromethane \((CH_3NO_2)\)
- butyl alcohol \((n-C_4H_9OH)\)
- nitrobenzene \((C_6H_5NO_2)\)

They found that nitrates have the weakest RO-NO₂ bond and they were the easiest ones to ignite and explode with as low a shock Mach number as 3.3 in oxygen. Other fuels had stronger NO₂ and OH bonds and, therefore, did not yield to initiation. Thus, their conclusion was that chemical stability is an important factor controlling the autoignition mechanism of fuel droplets.

Later their studies were extended to a few gaseous fuels in order to compare the ease of thermal decomposition between nitrates, nitro compounds and hydrocarbons (ethyl nitrate, nitromethane and butane, respectively). Their finding was again that nitrates should ignite and explode easier, because they have significantly higher rate constants than the nitrocompounds and hydrocarbons and they form alkoxy radicals rather than alkyl radicals, as is the case for the other fuels.
At higher shock strength they found ignition to occur in the boundary layer with no blast waves being formed, suggesting a new mode of ignition for the nitrates.

VII. Atlantic Research Corporation (25)

The work of G. von Elbe at ARC was directed toward the study of the effects produced by free radicals on the combustion process in hydrocarbon-air mixtures. The free radicals were injected into the system through the use of fluorine and fluorine-producing compounds. The ignition lag in propane-air mixtures was found to be virtually eliminated when free radicals were added in proper amounts.

Investigation was conducted with propane, methane, hexane, and diethyl ether. Results were also given for butane and cyclohexane from other investigators. (26) The ignition temperature was shown to be greatly affected by the concentration ratio $[F_2]/[O_2]$, and the "explosion peninsula" was shifted considerably with increase of fluorine concentration towards a lower temperature and pressure.

It was found that free radicals do play a significant role in the combustion and explosion process, and an additive such as fluorine will enhance the chain branching mechanisms which in turn will provide easier ignition and explosion.

VIII. Miscellaneous

Some of the pertinent information on the chemistry of various fuels for the FAE problem can be obtained as referenced - thermal decomposition of nitromethane $(\text{CH}_3\text{NO}_2)$(27) and hydroazoic acid $(\text{HN}_3)$(28) and various kinetic data on gas-phase unimolecular reactions. (29)
The search for decomposition reactions of other candidate fuels has not yet been completed and will, therefore, be reported on in the next communication.

Resume of the Literature Survey

In summary, the literature survey revealed that most of the work done so far was to determine the detonability limits of various fuel-air mixtures and to establish the energy thresholds which would initiate the system. A list of fuels is shown in Table 1, together with their limits of detonability and, where available, threshold energies.

PRESENT EFFORTS

Very much in line with the work of von Elbe, present efforts are to supplement the existing work on the FAE problem by investigating the possibility of controlling the flammability and/or detonability of the fuel-air mixture by controlling the production of free radicals, atoms and ions in that mixture. This can be achieved by doping or inhibiting the initial medium with the proper chemical components which would enhance or hinder the process of radical formation.

We intend to study the possibility of causing ignition by using mixtures of gases which upon contact would spontaneously react. If one of the component gases is initially inhibited with a third gas, then upon bringing the two reacting gases together no reaction would result until the radical inhibitor is used up. Once the inhibitor is gone, the reaction would take place, and, if the two gases were properly mixed, the reaction would proceed instantaneously and explosively.
To get more information on the effectiveness of such a chemical system and a better understanding of spontaneous ignition, an experimental system is being set up in our laboratory. As shown in the accompanying diagram (Fig. 1), the system consists of feed lines from bottles containing different gases and a stainless steel test chamber. The latter is fitted with a photodetector, a thermocouple and a pressure transducer for proper diagnosis of the events taking place. Initial studies will be conducted with tetrafluoro-hydrazine ($N_2F_4$) and silane ($SiH_4$) with cis-2-butene ($CH_3CH:CHCH_3$) as the inhibitor.

When we learn how to control and properly delay the advent of explosion, we will apply this system to a fuel-air mixture, with and without doping by other radical-forming or gettering agents.
Table 1. Detonability Limits

<table>
<thead>
<tr>
<th>Fuel</th>
<th>% in Air Volume</th>
<th>Energy Threshold Kcal (% in air)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>2.5 - 5</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Propane</td>
<td>3 - 7</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Propane</td>
<td>4 - 6</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Propylene</td>
<td>3.5 - 8.5</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Propylene Oxide (PO)</td>
<td>4.8 - 9.5</td>
<td>3.</td>
<td>8</td>
</tr>
<tr>
<td>Propylene Oxide (PO)</td>
<td>2.7 - 14.4</td>
<td>3.5</td>
<td>12</td>
</tr>
<tr>
<td>50% EO + 50% PO</td>
<td>4.8 - 17</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Ethylene Oxide (EO)</td>
<td>6 - 24</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Methyl Acetylene</td>
<td>6.5 - 10</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>MAPP</td>
<td>2.9 - 10.2</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>MAPP</td>
<td>2.9 - 9.7</td>
<td>0.209 (4.3)</td>
<td>19</td>
</tr>
<tr>
<td>MAPP</td>
<td>3.3 - 9.8</td>
<td>19. (4.5)</td>
<td>12</td>
</tr>
<tr>
<td>Nitro-propyl nitrate (npn)</td>
<td>2.2</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>6% npn + 94% MAPP</td>
<td>2.8 - 10.1</td>
<td>12.</td>
<td>12</td>
</tr>
<tr>
<td>npn + petroleum ether</td>
<td>(4.8% by weight)</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Dimethyl amine</td>
<td>6.5</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>10</td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>
Fig. 1. Schematic diagram of the experimental set-up to test the delayed ignition of spontaneously ignitable gases.
REFERENCES


17. Lee, J. H., Knystautas, R., Guirao, C. M. and Lam, E., "Direct Initiation of Explosions in Flammable Mixtures," to be presented at the Fourth International Symposium on Transport of Hazardous Cargoes by Sea and Inland Waterways, which is to be held in New Orleans, LA, on April 13-17, 1975.


Budget Summary

A tabulation of the financial status of the FAE account follows:

<table>
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<th>Month</th>
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<th>Spent ($K)</th>
<th>Total Obligated</th>
<th>Balance ($K)</th>
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<td>41.43</td>
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<tr>
<td>March</td>
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<td>35.08</td>
<td>1.6</td>
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