Autoignition - A Liquid Propellant Explosive Potential Limiting Phenomena

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ABSTRACT

During the design phase of large liquid launch vehicles, personnel safety considerations and facility and equipment design criteria must account for the unlikely but potentially possible series of failures that would lead to unplanned, hazardous mixing of bulk quantities of propellants. Massive explosion and destruction might be a suspected result.

Simple theory of chemical energetics would predict explosive forces greater than equivalent weights of TNT (trinitrotoluene). Judicious use of "buffer" zone land and facility or equipment "hardening" requirements dictates that new projects estimate potential explosive yields by precise, realistic analysis.

This paper highlights the work done by NASA to develop and confirm a precise analytical theory and predictive model for liquid propellant explosives. It covers a span of almost fifteen years work, most performed under Contract NAS10-1255 with the University of Florida. Dr. Eric A. Farber of the University and Mr. J. H. Deese of NASA-Kennedy Space Center conceived and conducted tests to establish a theory that autoignition occurs when propellants mix in a certain "Critical Mass" or greater. The author participated in the latter phases of this work and was technical manager of Contract NAS10-8591. This contract was completed in May 1975 by Battelle Laboratories and describes quantitatively the physical phenomena taking place prior to autoignition.

The work confirmed that autoignition occurs and prevents the mixing of more than the "Critical Mass" and therefore limits the explosive yield to several thousand pounds (kilograms) which is highly significant when total propellant loads reach hundreds of thousands of pounds (kilograms).

The results were useful in establishing explosive safety criteria for Space Shuttle facilities and operations.

INTRODUCTION

Space vehicle cryogenic fuel and oxidizer pairs do not ignite spontaneously when small quantities are purposefully or accidentally mixed together. However when some failure mode, such as rupture of a separating bulkhead, or bulkheads, causes large quantities to mix, a significant probability of spontaneous detonation exists. The phenomena of autoignition has been confirmed and quantitatively described by work performed at the Kennedy Space Center, the University of Florida and most recently by the Battelle Pacific Northwest Laboratories.

The latest work was completed in May 1975 and no further effort is planned, since sufficient confidence in predicting TNT equivalence for large quantities of LOX/LH₂ has been established. A slightly weaker test data base exists for LOX/RP-1, but for this combination safety margins allow sufficient confidence for presently anticipated usage.

It is appropriate now to summarize the knowledge gained from more than ten years of effort as it has become accepted and is no longer a center of research attention.

Launch complex layouts are determined by interelement distance scales fixed by acoustic hazards and explosive hazards. Hazards pertain both to personnel and to other facilities and equipment. Static tests were instrumented to give acoustic level predictions but explosive levels, generally expressed as TNT equivalence (percent of equal mass of TNT), were attainable by the more expensive project of purposefully detonating flight vehicle stages in statistically significant numbers of ground tests. An analytical understanding or a valid empirical model was necessary to avoid the unacceptable cost and waste of large numbers of explosive tests for large mix quantities.

During Saturn V planning phases, Mr. J. H. Deese of NASA Facilities Design initiated a contract with Dr. E. A. Farber, of the University of Florida, to explore a mathematical model approach to TNT equivalence and other explosive phenomena of liquid rocket propellants. It is well known that small quantities of propellants appropriately mixed and ignited externally yield TNT equivalence greater than 1.00, which is in accord with the theoretical thermodynamic potential of such "clean" reactions. As apparent mix quantities grow to several hundreds of pounds (or kilograms), to tens and even hundreds of thousands of pounds the explosive potential grows progressively less by TNT equivalence.

One rather obvious explanation, is that when large quantities are allowed to mix under the failure
modes of interest the percentage actually mixed may be progressively less. Postulating a Yield Function and a Mixing Function and examining their relationship proved fruitful, but led to time dependence inconsistencies where tests were not of comparable designs. Mixing was determined not only by relative density, temperature and other physical properties of the propellant pair, but by time from initial fluid mass contact. It is possible to derive some good information, however, discounting time, since it is not the overriding factor where the experiment conditions tend to proceed to roughly comparable time states before initiation.

Farber defined the yield function as the fraction of the theoretical maximum yield which is actually obtained: \[ y = \frac{Y}{Y_{\text{Theor. Max.}}} \]

pressed in energy or total impulse form but damage predictions must account for different pressure-time trace form in liquid propellant explosions than solid high explosives. A mixing function \( X \) is the volume mixed at time \( t \) multiplied by a turbulence factor, a boiling factor, and a freezing factor, empirical characteristics of the fluids: \[ X = V_m F_T F_B F_F \]

A mathematical model was developed with three parameters to relate \( X \) to \( y \):
\[
\frac{b}{b+c} = \chi^d. \quad \text{A statistical function follows then, a modified Dirichlet bivariate surface with four parameters. It is written, using } a \text{ as the scale on quantity parameter:}
\]
\[
f(X,y) = \frac{d!}{(a+b+c)!} \chi^{d-1}(1-\chi^d)^{a-1}y^{b-1}(1-y)^{c-1}
\]

Where \( \Gamma \) is the Gamma Function, with restrictions \( y > 0, \chi > 0, y \neq \chi^d, d \neq 0 \). The parameters can be estimated from the individual test data and averaging by the transformation \[ u_i = 1 - \chi_i^d, v_i = \frac{y_i}{\chi_i} \]

Confidence limits can be established in conventional manner from the statistical function. For detailed development consult pages 7 and 8 of Reference 1.

Application of the model and the statistical function can be used as a rough estimation tool for any rocket propellants or any energy reactant fluid pair. But more precise use requires the data to be specific as to propellant type and that some description of failure mode and resulting mixing influence be considered. When the Saturn V launch vehicle was taken as whole and failure modes causing tankage rupture on the launch pad (to lift-off) were considered, the average yield prediction was 3.5 percent and the 95 percent confidence limit was 9 percent or less. This was considerably less than the 60 percent estimate used as a restriction at the time, and to which Saturn V facilities were designed. Figure 1 shows the cumulative data used in model development.

It was against this background that work leading to development of autoignition and Critical Mass theory proceeded. The prospect of reducing the explosive equivalence from 60 to approximately 10 percent was very attractive but required substantiation by more thorough and precise analysis.

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**Figure 1** Estimated Explosive Yield as a Function of Propellant Weight

- **Solid points** - Self Ignition
- **Pyro Data**
- **ADL Spill Tests**
- **Missile Failures**
- Upper Bound (95% Confidence Limit)
Design of Prediction Model Experiments

In order to understand the relationships of the yield function, mixing function, time dependence, chemical and physical reactant properties, and quantity effects, a "Seven Chart" approach was developed. The first chart predicted the maximum theoretical energy release as a function of fuel-oxidizer ratio and included a tertiary (LOX/LH₂/RP-1) mixture as well as the binary mixtures. The second chart related the yield potential to fuel-oxidizer ratio, this being different because of reaction rate differences. Chart 3 related the remaining amounts of LOX and LH₂ as a function of time from a relatively low turbulence contact mode, LH₂ of course tending to vaporize rapidly. Three thousand pounds (1,350 Kg) of hydrogen was observed to vaporize from a 4400 pound (2000 Kg) tertiary mixture within ten seconds. Chart 4 related yield potential to time and predicted a maxima at approximately seven seconds for the experiment just described. The mixing function-time relationship, Chart 5, proved the most difficult to analyze. High speed photographs, simulation by wax cast models, vibration mixing for repetitive contact dynamics, and finally a fine wire (low thermal inertia) thermocouple grid were used to "map" progressive mixing dynamics. The three dimensional thermocouple grid proved to be the most powerful tool but the high speed recording and data reduction were expensive and time consuming. The grid was useful in studying the detonation process itself with rapid propagation and state changes being discernable through skillful data trace analysis. Combining the yield potential function and mixing function led to the expected yield function-time relationship, Chart 6.

Before Chart 7, the "Expected Yield" can be developed, the time from mixing start to detonation must be determined. With planned initiated tests this is simple, but where spurious initiation sources or autoignition takes place this is a much more difficult matter, with some degree of randomness inherent. Examination of all available data gave a mean of about three seconds and a standard deviation of about one second. The region of Chart 6 bracketing this time interval then becomes Chart 7, the relation of primary interest. Better statistical estimates were possible with a larger, more controlled sample.

When the "Expected Yield" from past tests was compared to test results, it was noted that the yield (remember that this is defined as a percent) drops off with increasing propellant quantity available for mixing. Several tests had clearly detonated prior to planned initiation. It was possible in the Project Pyro tests, Reference 2, that the process for breaking the fuel and oxidizer separation wall could have induced initiation sources. The time delay suggested however a self ignition termed "autoignition" from that time on. The following were considered as possible initiating causes for autoignition, crystal fracture from mechanical or thermal stress, static electricity from internal friction of fluid layers or static electricity from fluid-gas interface friction. It was known that small quantities of mixed propellants would not autoignite. Since large quantities autoignite, it was apparent that the transition point or region should be determined by experiment and the results then used to better predict large quantity yields. A quantity of propellant mix (at stoichiometric ratio) that would certainly (probability of 1) autoignite was postulated and termed "Critical Mass", an analogy to nuclear reactions.

Since explosive tests are time and resource consuming, the experimental design for obtaining quantitative demonstrations requires judicious selection of test explosive mix amounts, replications and instrumentation schemes. Further theoretical work and model work was conducted to better estimate this transition region. The dynamics of the greater mix region were of immediate interest. In tests with LH₂/RP-1, chosen for obvious inertness, and later confirmed with the actual propellants, the mixing was found to be not only non-linear with time but also not monotonically increasing. The idealized sketch, Figure 2, illustrates the descent at velocity v of a cylindrical plug (cross section) into the surface of the denser propellant, at time t₀ and at a later intermediate time, and finally an oscillatory period when density differences and gas bubble phenomena cause the plug to rise above and below an equilibrium position (depth) denoted by y and a₀ in the figure. A differential equation can be written and solved by iterative techniques that will describe the plug motion as damped sinusoidal. Mixed volume, vapor generated and other parameters of interest may be related to the fluids used, the initial and continuing time dependent introduction conditions of the less dense propellant, and the film heat transfer coefficients. Mixing function predictions were found to be in good agreement with model tests, an example being Figure 3.

Electrostatic charge buildup was measured in the turbulent mix region during model tests and voltage levels observed were on the order of ten thousand volts/cm thus on the order of gas breakdown field strength.

The total Saturn V vehicle was to be analyzed with the primary objective a total stacked vehicle explosive equivalence and a secondary objective of estimating a fireball expansion rate for the third stage, the S-IVB. Propellant dispersal systems are activated when flight trajectory error due to a flight system failure threatens damage to any life or property. Figure 4 shows the general arrangement of Saturn V, with propellant dispersal details shown. These are intended to prevent explosive potential in flight. The "worst case" of total explosive release is taken to be the rupture of the tanks in the stacked stages, common bulkheads on the second and third stage, dual bulkheads on the first stage. The introduction of propellants would be vertical under gravity assist plus small velocity from rupture overpressure.

A series of tests were planned and conducted in 1971 and 1972 at Kennedy Space Center, to define the predictive relationships for LOX/LH₂ and LOX/RP-1. Replicated tests of six pounds (2.7 Kg), 60 pounds
60 pounds (27 Kg) and 240 pounds (108 Kg) were conducted by dumping stoichiometric mix amounts of one propellant into another. The mixing took place in ground level dewar after introduction of second constituent from tiltable elevated dewar. Figure 5 shows the result of a 240 pound (108 Kg) autoignition explosion. The tests at the smaller quantities did not autoignite: two tests of twenty of LOX/LH₂ at the 240 pound (108 Kg) quantity did autoignite. The important measurements of electrostatic charge built up in each test were done with wire screen grids. The results are shown (normalized) in Figure 6. The solid lines represent the upper and lower limits established from the data. The lower limit reaches the charge level at which autoignition occurred in the two tests at approximately 2300 pounds (1050 Kg) extrapolation. This confirmed the estimate made earlier for LOX/LH₂ that this amount could mix before explosion was a certainty. It can be seen from the line slopes that scatter is greater for smaller quantities, or said another way that the Central Limit Theorem of statistics tends to make for better prediction confidence at larger quantities. Sufficient replication could demonstrate autoignition at the lower or intermediate levels but the coincidence of agreement of both the two in twenty autoignitions at 240 pounds (108 Kg) and the 2300 pound (1050 Kg) lower limit extrapolation with previous prediction provided enough confirmation of the theory. No autoignition occurred with LOX/RP-1. Lower limit extrapolation was 2900 pounds (1320 Kg) to a charge level equated to a 25,000 pounds (11,400 Kg) test during Project Pyro. Slightly lower confidence exists therefore for LOX/RP-1 but until such time as large stages are planned with these propellants, no further predictive model work is anticipated.

**Extensions and Use of the Model**

Spill mixtures were modeled and estimated as well, but naturally the geometric and time factors are more complicated mathematically.

Detonation overpressures and velocities were estimated from the models and confirmed by instrumentation of test explosions.

The TNT equivalence estimates of both LOX/RP-1 and LOX/LH₂ mixtures were, as a result of examining all test data, reduced from 60 percent to 20 percent for large stored quantities.

It should be noted that some appreciable probability of autoignition does exist for smaller mixes down to the order of a few pounds (or Kg) and that these and smaller quantities can be detonated with high TNT equivalence by an external initiating cause.

For intermediate quantities, both yield and probability need to be estimated on total analysis of potential failure modes.

**Analytical Confirmation of Theory**

In 1974 the author contracted with Battelle Pacific Northwest Laboratories for a team led by Dr. David Lester to examine existing data and to construct analytical (math) models of phenomena leading to autoignition in LOX/LH₂ and LOX/RP-1. The heat transfer and vapor bubble generation and be-
Figure 4  Schematic Diagram of Saturn V, with Effects of Destruct Initiation Indicated
FIG. 5  The 240 Pound (110 Kg) Test Explosion Sequence
Fig. 5 Charge Ratio as a Function of Propellant Weight (LO$_2$/LH$_2$ Mixtures)
havior models were extensions of the state of the art. Work was carried to a point of substantiating the "Autoignition/Critical Mass" theory in large part. It was hoped that the single electrostatic process which controlled reaction thresholds and/or rates could be isolated. However the results, detailed in Reference 4, showed that several interfacial motion phenomena (for example streaming potential between liquid layers) could produce sufficient possible fields to cause a vapor breakdown. The field strengths were of an order higher magnitude, in general, at the 240 pound (108 Kg) quantity, and two or more orders at 2300 pounds (1050 Kg). A discharge from droplet to droplet above the liquid surface was also near the same order for LOX/LH₂ and was for LOX/RP-1 the only phenomena that could clearly be expected to cause initiation.

One of the two coefficient terms of Dr. Farber's Critical Mass equation was confirmed but the high mix energy term was so configuration dependent that confirmation was prohibitive.

**SUMMARY**

That there is an autoignition process which limits the explosive potential of quantities of the commonly used space booster propellants has been established. Even quantities up to millions of pounds (Kg) can be expected to be limited by the autoignition of a mix region of a few thousand pounds (Kg) which will disperse the remaining propellant and prohibit detonation of the total quantities otherwise suspected. Analytical support has been established to the amount consistent with available resources and currently planned estimation needs.

**REFERENCES**

2. NASA/USAF Liquid Propellant Blast Hazards Program - Pyro Quarterly Reports - URS Corp.
