PROJECT ADMINISTRATION DATA SHEET

Project No. E-16-690 (R6221-0A0)          GTRC/C11 DATE 10/10/86
Project Director: E.W. Price                School/XXX Aerospace Engineering
Sponsor: Morton Thiokol, Inc.              Aerospace Group

Type Agreement: Purchase Order No. 0587 and Modification 1
Award Period: From 7/1/86 To 6/30/88 (Performance) 6/30/88 (Reports)
Sponsor Amount:
Estimated: $130,000
Funded: $65,000

Cost Sharing Amount: $N/A
Cost Sharing No.: N/A
Title: Study of Oscillatory Interactions of Solid Propellant Combustion and Combustor Flow.

ADMINISTRATIVE DATA
1) Sponsor Technical Contact: Dr. D.A. Flanigan
Director, Advanced Technology Morton Thiokol, Inc.
3340 Airport Road
Ogden, UT 84405
(801) 625-4997

2) Sponsor Admin/Contractual Matters: Mr. Carl M. Hammond
Vice President, Finance and Administration Morton Thiokol, Inc.
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Chicago, Illinois 60606-1560
(312) 807-2151

Defense Priority Rating: N/A
Military Security Classification: N/A
(or) Company/Industrial Proprietary: N/A

REQUIREMENTS
See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with N/A None Proposed

COMMENTS:
1. This is a fixed-price best efforts purchase order.
2. Modification 1 revises the terms and conditions of the agreement.

SPONSOR'S I. D. NO. 0221200086010

FORM OCA 65:285
GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 07/16/91

Project No. E-16-690
Center No. R6221-0A0

Project Director PRICE E W
School/Lab AERO ENGR

Sponsor MORTON THIOKOL INC/

Contract/Grant No. 0587
Contract Entity GTRC

Prime Contract No.

Title STUDY OSCILLATORY INTERACTIONS OF SOLID PROPELLANT COMBUSTION & COMBUSTOR

Effective Completion Date 880630 (Performance) 880630 (Reports)

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Comments

Subproject Under Main Project No.

Continues Project No.

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TO:  Dr. D. A. Flanigan  
    Director, Advanced Technology  
    Aerospace Group  
    Morton Thiokol, Inc.  
    3340 Airport Road  
    Ogden, UT 84405

FROM:  E. W. Price, Principal Investigator  

SUBJECT:  Summary of Recent Activities on Contract P. O. 0587, Mod. 1

1. John Deur has returned to MTI Huntsville as of September. We are working on a final draft of his Ph.D. thesis. The topic of the thesis is pressure-coupled combustion response, and the thesis develops an analytical-computational model that pictures a burning surface comprised of different kinds of areas in which the governing combustion processes are quite different. The dynamic response is modeled for each kind of area, and the total combustion zone admittance is based on a weighted sum of contributions of the different kinds of areas. Unlike earlier statistical models, the kinds of areas are different not by virtue of particle size, but, instead, by virtue of the surface characteristic and overlying flame complex. In the work completed for the thesis, one kind of surface area was AP, with a coupled AP self-deflagration combustion zone. The other kind of area is that portion of AP and binder surface adjoining the oxidizer-binder contact lines, where response is dominated by the leading edge of the O-F flame (and hence involves diffusion of O and F species). The thesis uses an edge-burning "laminate propellant" model, i.e., a propellant with alternating layers of AP and binder. This choice was made to:

a) simplify geometrical configuration while preserving a relevant flame complex;

b) postpone statistical aspects of the problem until the physics of the combustion response were represented more realistically than in past models; and

c) exploit an extensive background of experimental work on sandwich burning available in this laboratory.

Some novel results from the analysis include calculation of the dynamic response of AP, calculation of the oscillatory mixing field in the gas phase above the oxidizer-binder interface lines on the burning surface, and calculation of the effects of mixture ratio oscillations arising from the differences in dynamic...
response of oxidizer and binder in regions where they "see" the same oscillating O-F flame. The all-up model is a rather nightmarish assemblage of sub-problems that had to be solved, and then suitably coupled together. Because it addresses combustion physics more realistically than previous models, it should be the starting point for a new generation of dynamic response models (as of now, John Deur is the only person who can run the computer program).

2. A new student, Kuldeep Prasad, has been learning about dynamic response and combustor instability, and is now embarked on a more rigorous analysis of sandwich burning. This analysis will model the gas phase with Navier Stokes flow (reacting) and energy conservation (steady and nonsteady, 2-D). This analysis was stimulated by the heterogeneous propellant combustion problem, and a desire to deal more fully with representation of the O-F flame dominated part of the Deur-Price model. However, the problem has broad relevance to all combustion problems involving gas phase flame dominated combustion of heterogeneous systems. Because of the difficulty of the problem, assistance is being obtained from two other faculty members with needed expertise (W. C. Strahle on analytical modeling, and L. N. Sankar on computational methods). This is a classical problem that has only recently become tractable, because of the advances in large high speed computers. Mr. Prasad is intensely interested and has the right background and talents for the problem.

3. Related to the above two studies, we have started a gas burner experiment that simulates the combustion zone of the O-F flame dominated region. The gas burner provides co-axial flows with the inner flow a fuel-rich mixture of methane, O2, and N2, and the outer flow an oxidizer-rich mixture. The flows emerge through a porous plate. The goal is to study the region of the flame that stands in the near surface mixing region, although the whole range of flame shapes vs operating conditions is being mapped as an aid to second generation burner design. The advantage of the gas burner is that the flame complex is large enough to resolve and is stationary for ease of observation. In addition, inflow gases, mixtures, and flow rates can be pre-determined and widely varied. This research is being done by Mr. Hau-Jei Chiang, who is privately sponsored. It is a useful complement to the Thiokol-sponsored work, and was stimulated by that work. We will report progress to MTI for these reasons.

4. There are several other experimental activities that are proceeding at rather modest pace with no major results to report.

   a) Fabrication of laminate propellants has been pursued to the point of making and burning laminates with 4 AP laminae and 3 PBAN laminae. Dry-pressed AP laminae have been prepared in thicknesses down to 300 μm and a target of 200 μm seems attainable. However, flatness is difficult to maintain, which poses a problem in getting uniformity of binder lamina thickness (for 200 μm AP laminae, a binder thickness of 25 μm is needed, and it doesn't take much deviation in AP flatness to cause large percentage variations in 25 μm). Thus, the target goal of 200 μm AP thickness will almost surely pose problems with sample uniformity. Aside from that, the success to date indicates that laboratory samples of laminate propellant can be made, and combustion tests indicate they burn as expected. A long-term goal would be to conduct T-Burner tests with pressure, lamina thickness and frequency as primary variables.
b) A collection of scanning electron micrograms of quenched sandwiches is being assembled from file and new tests to determine the appropriate area allocation to AP self-deflagration and to O-F flame controlled combustion in the Deur-Price model. This involves assessment of "smooth band" width on quenched samples vs pressure and lamina thickness. The "smooth band" is a region of the AP surface adjoining the binder in which dissociative sublimation of AP occurs.

c) Samples of the Shuttle motor nozzle ablative (nose ring) are being exposed to high heat flux in a high power CO\textsubscript{2} laser to determine the feasibility of doing research on ablation-insulation materials without the cost of motor or burner firings.
Dear Dave:

This is a sort of "highlights" report on research activities on our IR & D contract P. O. 0587, Mod. 1. We are pursuing four lines of investigation, with different levels of effort and substantial effort using students supported on their own or state funds.

1. The primary effort is on analytical-computational modeling of pressure-coupled oscillatory response of combustion for heterogeneous propellants. John Deur has finished his "modular" model, which describes the combustion response as the sum of contributions from different kinds of micro areas of the burning surface that are controlled by different parts of the micro-flame complex. At present the model is tailored to AP-hydrocarbon binder propellants, and the micro areas are a) AP surfaces that are dominated by the AP self-deflagration process, and b) areas of binder surface and immediately adjoining AP surfaces that are dominated by the leading edge of the O-F flame. The model has three main parts that calculate the contributions of AP-dominated areas, of O-F flame dominated areas, and of the diffusion flames that burn the outflows from the AP flames and leading edge O-F flames. John Deur's treatment is an assemblage of "simplified" calculations put together to model a complex combination of processes (there is nothing simple in the whole scheme; the much more detailed modeling of the complex real process of transient combustion that are sought in this model simply forces simplifying assumptions at a detailed level that was substantially ignored in earlier approaches). John's analysis shows the contribution of oscillatory combustion of AP that constitutes 50-80% of the propellant surface, and shows the effect of oscillations in combustion of that portion of the binder and AP surface that is dominated by the near-surface part of the O-F flame (portions of the surface that adjoin the AP-binder contact lines on the burning surface). This is referred to as the "KLLEF-dominated" region of the surface, the "KLLEF" being the kinetically limited leading edge of the O-F diffusion flame. It is this surface coupled region that is so difficult to model realistically, and where John Deur has devised a sequence of modeling steps and approximations to gain a result not available previously. The model permits evaluation of the effect of pressure coupled composition oscillations that are predicted by the model (with associated oscillations in molecular weight and flame temperature). The model can also be used to determine the effect of pressure and particle size, although it presently is formulated to describe "two
dimensional" propellants (edge burning laminates). A decision has not been made whether extension of the model to propellant microsurface will be carried out at GIT or by John Deur, who has returned to Thiokol Huntsville.

2. Because of the many approximations used to model the dynamic response of the KLLEF-dominated region (and the poor prospects of measuring the dynamic response), it was decided to carry out a much more rigorous analysis that would resort to finite difference solutions of the two-dimensional reacting viscous flow equations (methods and computers suitable for solution of this problem have become available only recently). We have an outstanding student named Kuldeep Prasad who is doing this problem, with the aid of a faculty committee consisting of myself, Prof. W. C. Strahle (analytical methods), and Prof. L. N. Sankar (numerical methods). This will be Mr. Prasad's thesis topic, and he is making good progress. Operation of the program will be too costly for use as part of an engineering stability analysis. Its purpose is to:

- Provide a more rigorous means to determining the oscillatory response function vs frequency and pressure for a limited set of parameters,
- Provide a means to check adequacy of simpler models that are used in stability analyses,
- Permit parametric studies to determine the effect of kinetic and transport properties on flame behavior, and
- In the process of 1-3, we will learn a lot more about the physics of pressure coupled response, a phenomenon that is not amenable to detailed experimental study on the micro scale present in propellant combustion.

3. As a parallel to the analytical-computational approach described in paragraph 2, a gas burner experiment has been developed that produces a kinetically limited leading edge flame at atmospheric pressure, where its dimensions are large enough to permit some experimental measurements. This burner produces two coaxial gas flows with a mixing fan between the flows simulating that above the oxidizer-fuel contact line on the propellant surface. By using an appropriate combination of an oxidizer-rich and a fuel-rich flow, flames occur in the mixing fan that simulate the KLLEF and diffusion flames in propellant combustion. The gas burner experiment is convenient for study of KLLEFs, not only because the flames are large enough to observe under these conditions, but also because it is easy to control the gas flow composition and velocity. For the present, the study is aimed only at steady state behavior. It is planned to obtain theoretical solutions of this problem from the study in paragraph 2 and use the results of the two studies as checks on each other. The gas burner studies are being conducted by a student (Jimmy Chiang) who is independently funded. However, we believe this experiment is pertinent also to other problems of broad fundamental importance (to all combustion systems involving mixing flows or vaporizing reactants). We have prepared a proposal for a continuing program of research and allocated some DOD-supplied equipment funds for a second-generation experimental set-up with suitable instrumentation. Because of pertinence to the present Thiokol project we will continue to report progress here. Mr. Prasad and Mr. Chiang will work closely together to assure
that their results can be compared. Depending on progress, availability of other outside funding, and agreement of Thiokol, portions of the gas burner study may be funded from the Thiokol contract (we also have a promising senior student working on the project, who will be a state funded graduate student next fall, and a candidate to work on the Thiokol contract in subsequent years).

4. We have been exploring the possibility that our 1200 watt CO$_2$ laser can be used to study char formation and properties of nozzle ablatives. If the approach is feasible, it will permit systematic studies of the effect of such variables as heating rate, ply angle, fiber variables, polymer variables and physical constraint. We have found that we can produce char formation rates comparable to the rocket motor environment, for small sample surfaces (5 mm by 6 mm). We have sectioned the charred regions and are examining methods of sample preparation and microanalysis. Al McDonald has arranged for us to receive samples of carbon cloth, cured phenolic, and shuttle nozzle ablatives. We are having to learn more about past work on ablatives and materials (e.g., thermal decomposition of phenolics, fiber characteristics of carbon cloth, and loads on fibers and char layers), and we are finding reports hard to get. We are going ahead with testing to find what we can do with the laser and our microanalysis equipment, realizing that a fully meaningful test may involve more than we now recognize.

Sincerely,

/2

Edward W. Price
Regents' Professor
School of Aerospace Engineering

cc: R. Kruse
    B. Stokes
    J. Deur
April 30, 1991

Mr. Bob Casey
MS-S76A
The General Electric Company
600 Main Street
Johnson City, N.Y. 13790

Dear Mr. Casey:

Enclosed, please find a TK50 tape containing the initial update of the TMAN program carried out under the Purchase Order No. BBM005601. Please note that the updated program contains the following modifications:

1. The program has been modified to include coupled stability and control derivative matrices as functions of flight speed.
2. The input data file 'helo_model.dat' contains AH-64 specific data derived from the FLYRT program for the case: W=14660 lbs, sea level standard day, V=-50 to 175 knots in steps of 5 knots.
3. The program has been modified to allow for direct inputs from the pilot.
4. The modified program can be run with Maneuver1A option only at this time to simulate 'Slalom' and 'Terrain Following' maneuvers.

We plan to implement the following over the next two-month period:

1. Include a simplified stability augmentation system model in the TMAN program.
2. Include total aerodynamic force and moment data as functions of trim flight condition and modify the TMAN aerodynamic force and moment calculations as trim forces and moments plus perturbation forces and moments.
3. Carry out simulation for typical direct inputs from the pilot and compare simulation results from the TMAN program with those from the FLYRT.
I have attached a copy of the 'read_me.1st' file and the list of commands we have used to generate the tape copy. If you have any questions or comments, please call me at (404)894-3043. Thank you for giving me the opportunity to work on this project.

Sincerely,

J.V.R. Prasad
Asst. Professor
The new simulation program consists of the routines:

- Simulation.for (all subroutines)
- sim_common.for (definitions of COMMON blocks)
- controller_gains.dat (4 controller gains)
- helo_model.dat (AN-64 coefficients)

and optionally

- commands.dat (for canned commands)
- sim.com (compiles program)
- changesrec.vax (documents all changes made to the program)

The format of the data files is documented within the source code in subroutines Initialize_model and Command_input.

Output files are

- `<Name>_aux1.dat` (equivalent to the former Auxiliary1.dat)
- `<Name>_aux2.dat` (equivalent to the former Auxiliary2.dat)
- `<Name>_aux3.dat` (equivalent to the former Auxiliary3.dat)
- `<Name>_aux4.dat` (equivalent to the former Auxiliary4.dat)
- `<Name>_out1.dat` (equivalent to the former For008.dat)
- `<Name>_out2.dat` (equivalent to the former For016.dat)
- `<Name>_iolog.dat` (logs all keyboard inputs)

and after improper termination of program:

- temp.dat (logs internal parameters from subroutines Helo_equ_of_motion and Integrate_and_transform)

The program is very sensitive to slight deviations from the trim conditions and has to be used with care in order to avoid fast diverging conditions.

Test cases used are Slalom2 and Terrain2, both similar to those described in K. Beiges thesis.

At the moment only Maneuver1A is implemented. Due to changes in the data structure, errors in variable definitions will occur when adding other maneuvers.

Andreas Lipp  
4/29/91
The following commands have been used to create the tape copy:

$ALLOCATE MUA0:
$INITIALIZE MUA0: GTTMAN
$MOUNT MUA0: GTTMAN
$COPY *.*.* MUA0:
OSCILLATORY INTERACTION OF SOLID PROPELLANT
COMBUSTION AND COMBUSTOR FLOW

by

E. W. Price, J. M. Deur, C. Markou and R. K. Sigman
School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

prepared for

Morton Thiokol, Inc.

under Contract P. O. 0587, Mod. 1

June 1987
OSCILLATORY INTERACTION OF SOLID PROPELLANT
COMBUSTION AND COMBUSTOR FLOW

ABSTRACT

Progress is reported on a combined analytical and experimental study of oscillatory combustion of AP-HC binder composite propellants. To avoid the diversion to statistical three-dimensional description, much of the effort is related to edge-burning of propellants made up from alternating laminae of oxidizer and fuel. The burning surface is pictured as consisting of areas that respond to pressure oscillations in the same way as self-deflagrating AP, and other areas that respond to oscillations in the near-surface part of the oxidizer-fuel flamelets. The net response is the sum of the contributions of these two kinds of areas, plus the quasi-steady response of the outer diffusion flames to the oscillatory outflow from the underlying flames. Analyses were made of the AP flame response, and of the response of the O-F flame dominated areas, using pseudo-one-dimensional models. Notable features of the results are a) presence of composition oscillations in the flame, and b) maximum AP response at a lower frequency than maximum for the O-F flame dominated part of the surface. The principal result of experimental work was successful fabrication and combustion photography of small "laminate propellant" samples.

INTRODUCTION

The present project is aimed at a more rational basis for dealing with the problem of combustion instability in solid rocket motors. The technical focus is on better understanding of the dynamic response of heterogeneous propellant combustion to oscillations in the pressure environment. The first year of study focussed on better understanding of the nature of the microscopic combustion zone, including clarification of the complex flamelet structures and the three-dimensional coupling between flame complex and the heterogeneous surface, with due regard for the heterogeneous propellant microstructure. Much of this effort was based on AP-hydrocarbon binder systems, and extensive reliance was made on results of edge-burning laminate configurations (Ref. 1) in order to simplify analysis and interpretation of experimental results.

In the second year of this project, the experimental work on combustion zone
microstructure continued at a modest level; experimental results had predicted a singular aspect of combustion zone behavior referred to as "KLLEF detachment" that, in turn, would be manifested as an anomaly in burning rate behavior of bimodal AP propellants. Propellants formulated to exhibit such behavior were prepared and exhibited the novel burning rate behavior (Fig. 1), thus providing a test of validity of the concept of the singular behavior in particular, and the concept of combustion zone microstructure in general (the combustion zone microstructure is shown in Fig. 2, and the singular behavior is explained in Fig. 3). These details of combustion zone structure are important because they are believed to contribute in a major way to the oscillatory response to pressure oscillations, and involve details not present in existing oscillatory response models. In particular, the flame behavior involved in the singular behavior in Figs. 1 and 3 (KLLEF detachment) is expected to be a major factor in oscillatory response at low pressures. With this in mind, it was proposed in the report of the second year of the contract that experimental measurements of combustion response be made over the range of conditions for which transitional behavior of the steady state flame has been observed (Figs. 2, 3). Such tests would further evaluate the validity of the postulated singularity in flame zone behavior, and evaluate the postulate that the total flame zone response is significantly enhanced by this singular attribute of the flame complex (KLLEF attachment and detachment).

In the second year, analytical studies were also started on oscillatory behavior of various regions of the burning surface. This was the start of a new concept of describing dynamic response, in which the responsive burning surface (Fig. 4) is viewed as being made up of different kinds of areas classified according to which part of the flame complex dominates dynamic response. In particular, it has been assumed (as a beginning) that the surface consists of areas of AP that are dominated by the AP self-deflagration (the amount of area depending on pressure, particle size). Some of the AP area is more strongly affected by the portion of the 0-F flame (referred to here as the "KLLEF") that is nearest the surface. Thus, the 0-F flame-dominated areas involve binder surface and the AP surface area in close proximity to the binder. Allocation of AP surface to the AP flame-dominated category and 0-F flame dominated category is based on propellant microstructure and results of experimental studies (Ref. 1) (e.g., the AP flame dominated area is evident in the central area of AP particles in Fig. 4, while the smoother areas around the outer periphery are 0-F flame
dominated). Thus for AP-HC binder propellants the combustion zone response is described as the combined response of

1. AP flame dominated areas
2. Primary O-F flame (KLLEF) dominated areas
3. Quasisteady response of the extended diffusion flamelets to the oscillatory output of the other areas (these outer flamelets are viewed as not coupled to the surface).

From our understanding of the combustion zone, this description pertains to the range of pressure and particle size corresponding to the upper branch of the burning rate curve in Fig. 1, and current analytical effort is focused on this domain. The importance of adaptation of response models to the domain of lower pressure and smaller AP particles remains to be determined by T-Burner tests proposed earlier. It seems likely than an entirely different response function model will be required somewhere below 300 psi.
Principal areas of progress for this year are summarized below.

**Theoretical**

1. Development continued on the "modular" concept of combustion zone response, in which the burning surface is subdivided into different areas whose dynamic response is dominated by different components of the flame complex. For typical AP-HC binder propellants at typical motor pressures, the surface is divided into areas of the AP surface that burn relatively independently of the oxidizer-fuel (O-F) flame, and areas of oxidizer and binder where surface pyrolysis and surface coupled effects are dominated by the kinetically-limited leading edge of the O-F flame. Dynamic response of these two kinds of surfaces are calculated by different models consistent with the different governing processes, and the net response is an area-weighted average. The amount of area allocated to each type of response is based on experimental observations from quenched samples, wherein the region of the self-deflagration of AP is revealed by the presence of residue of reactive froth and surface nucleation (Fig. 4). The rest of the AP surface ("smooth band") is assigned to the O-F flame dominated region (Ref. 1).

2. The pressure-coupled response function for AP self-deflagration was calculated using the Denison and Baum quasi-steady gas phase homogeneous propellant-one dimensional (QSHOD) model. Fig. 5 shows the response function for the chosen set of parameters. Details of choice of parameters and application of the DB model are shown in Attachment A, which is the thesis proposal of Mr. John Deur.

3. An elementary approach to modeling the dynamic response of the O-F flame dominated surface was carried out. This model assumes that the O-F flame is a flat, uniform temperature flame above adjacent areas of oxidizer and fuel. It is assumed that the oxidizer and fuel areas affected by this flame respond independently to the flame oscillations, each area according to its own pyrolysis kinetics. The difference in pyrolysis characteristics leads to a difference in oscillations of pyrolysis rate of oxidizer and fuel, and hence to oscillations in mixture ratio in the mixture entering the O-F flame (KLLEF portion). The analysis (Attachment A) leads to a response function with contributions from
conventional (DB-QSHOD) response, and contributions due to mixture ratio oscillations (which take the form of molecular weight oscillations and a contribution to flame temperature oscillations). These contributions are found to be sizeable for propellants that are fuel-rich (e.g., propellants with unimodal oxidizer particle size used in research studies). The contributions tend to be small and "self canceling" for propellants with binder content near 10%. In addition to Attachment A, the results of this analysis are reported in a paper to be presented at the Joint Propulsion Specialists Conference on June 30, 1987.

4. In order to make a more realistic description of dynamic response, it is necessary to address the multidimensional aspects of the KLLEF-dominated areas. To simplify this problem, attention has been focused on a "two-dimensional" propellant consisting of laminates of oxidizer and fuel, burning edgewise to the laminae. A long-term objective is to model the all-up reacting flow problem for this configuration, but the present approach is less ambitious using the classical Burke Schumann approach, the diffusion equations are adapted to calculate the oscillating diffusion field immediately above the contact line between pyrolyzing oxidizer and fuel surfaces. This is the mixing field in which a KLLEF stands, and the quasi-steady oscillation of the KLLEF will be estimated, based partly on the calculated oscillations of its "parent" mixing field. Progress in this effort is reported in Attachment A.

Experimental

Experimental work has been concerned primarily with efforts to make and burn laminate propellants, and plans for oscillatory combustion tests.

1. Consistent with the adoption of a two-dimensional analysis of oscillatory combustion as a goal, limited efforts have been made to fabricate small samples of laminate propellants. The primary difficulty is in preparation and handling of thin laminae of AP, which are made by pressing AP powder in a steel die at about 20,000 psi. The present apparatus was used successfully to make laminae 1 inch in diameter and 400 µm thick. Several laminate samples were made with PBAN binder approx. 50 µm thick, with 5 AP laminae and 4 binder laminae. It is proposed that larger samples (more laminae) would be made by laminating several such 5-layer samples together. Thus, while tedious, sample preparation is
possible. Several of the 5-4 laminae were burned in the window bomb at 500 psi. The samples burned evenly in the desired manner. A new video camera set-up was used in the tests and gave very satisfactory resolution of the burning sample.

2. Some exploration was made of the possibility of getting T-Burner tests run on the bimodal propellants used previously to demonstrate the effect of KLLEF detachment on steady state burning rate (Fig. 1). A proposal for such tests was part of last year's report, but tests were not planned at GIT because no T-Burner facility was available. Efforts to arrange for tests have been unsuccessful. These tests are considered important as a means to assess the possibly critical role of oscillatory KLLEF detachment as a driving source for instability. The tests are also needed to determine the range of conditions under which the "modular" theory will be applicable.

3. Concurrent with the above efforts, design has begun on an experiment to measure oscillatory combustion response using an oscillating CO$_2$ laser beam as a controlled stimulation of the burning surface. Such an experiment would have the advantage of low cost per test, and the possibility of testing over a frequency range in each test. Such experiments are made feasible by the current development of a 1200 watt CO$_2$ laser facility in our laboratory. A preliminary description of the experiment is contained in a project proposal nearing completion. In the experiment, samples would be burned in a small flushed test cell while being exposed to a uniform oscillating laser beam. The combustion response would be calculated from the pressure oscillations measured in the test cell. An interesting further feature of the experiment is the possibility of studying large amplitude response (the laser heat flux can be comparable to the heat flux from the flame). On the present program, the experiment could be applied to AP self-deflagration, laminate propellant combustion, and the bimodal formulation discussed earlier in this report (Fig. 1). This laser combustion experiment is being developed on another current (ONR) contract, and independent funding will be sought in the future. However, application to the present project is anticipated, and relevant progress will be included in reports on this contract.

REFERENCES

Fig. 1  Burning rates for bimodal AP propellants, showing break in the burning rate curves corresponding to KLLEF detachment on small particles at low pressure. Coarse AP was 400 μm, and fine AP size is indicated in the figure.

Fig. 2  Principal features of the combustion zone microstructure and processes as suggested by accumulated results: 1, binder lamina; 2, interface plane between binder and oxidizer; 3, oxidizer surface adjoining binder (smooth band); 4, leading edge of the oxidizer burning front; 5, oxidizer region that regresses at the normal AP self-deflagration rate; 6, AP flame; 7, leading edge region of the AP flame; 8, oxidizer flame, modified by the anomalous decomposition in the smooth band (flame may be quenched); 9, oxidizer-fuel diffusion region, with stoichiometric surface indicated by broken line; 10-11, kinetically limited leading edge flame (KLLEF) (fuel-rich and oxidizer-rich sides); 12, diffusion flame; 13, tip of diffusion flame.
Fig. 3 Trend in surface and oxidizer-binder combustion zone structure with thickness of the binder lamina (flames for different binder thickness superimposed).

a) Very low pressure (p<0.4 MPA) (stoichiometric tip is retracted for binder thickness #1)

b) Low pressure (0.4<p<2.0 MPA)

In case 1 of part a, the stoichiometric tip is retracted too far for holding of the premixed flame.
Fig. 4  Quenched surface of a propellant having bimodal oxidizer distribution, coarse size being 400 μm. Large oxidizer particles show a "frothy" central area where burning is dominated by the AP self-deflagration (surface similar to that of large quenched single crystals burned with no binder). The dark outer boundary of the large particles (referred to as "smooth" band in sandwich burning studies) is believed to represent surface characterized by (endothermic) dissociative sublimation, with exothermic AP reactions suppressed by heat loss to the adjoining binder. Combustion over this region and the adjoining binder is dominated by the leading edge of the O-F diffusion flame (KLLEF).
Fig. 5  Pressure coupled response for ammonium perchlorate.
A Surface Coupled Flamelet Approach to Dynamic Response in Heterogeneous Propellant Combustion

A Thesis Proposal
Submitted in Partial Fulfillment of the Requirements for the Ph.D. Degree

By

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CHAPTER 1
INTRODUCTION

1.1 COMBUSTION RESPONSE

1.1.1 ACOUSTIC ANALYSIS OF SOLID PROPELLANT ROCKETS

One of the most serious problems that can affect the development of a solid propellant rocket motor is that of combustion instability, an unbounded interaction between the combustion processes of the solid propellant and the fluid dynamic processes in the motor cavity. Because of the pressure dependence of the combustion processes, the possibility always exists for the coupling between these phenomena and the pressure fluctuations in the internal flow field of the motor. Because of the adverse effects such an interaction can produce, it is common practice to perform a stability analysis of a motor design early in its development program.

1.1.2 COMBUSTION AS A BOUNDARY CONDITION

An acoustic analysis of the motor flowfield, with combustion response added as a boundary condition, has been the normal method of the stability calculation. In such an analysis, the gas in the cavity is assumed to be a non-reacting, homogeneous medium with only low amplitude, wavelike motions present. This allows the use of linearized governing equations, where each variable present has been decomposed into mean and perturbation components. There are obvious benefits, from the standpoint of simplicity and cost, in using such an analysis, and they are reasonably effective, particularly in the case of a motor with a conventional non-aluminized ammonium perchlorate-hydrocarbon binder propellant, in showing the potential for small, spurious
pressure excursions to grow to significant magnitude with a particular design.

A key input to such an acoustic analysis is information concerning the combustion processes, in particular how they respond to small perturbations in pressure. Such perturbations are always present in mechanical systems such as a missile in flight or even a motor being fired on static test stand. If the propellant's combustion processes respond in a manner which will induce a growing pressure wave in the motor cavity, serious consequences may result.

The key word in the above discussion is response. A quantity of some importance to the stability analysis of a solid rocket motor is the pressure coupled response, defined as:

\[ R_p = \frac{r'/r}{p'/p} \]  

(1)

The pressure coupled response is a frequency domain property of a propellant; in other words, it is a function of oscillation frequency, indicating different magnitudes and phases of response at different imposed pressure oscillation frequencies. A quantity related to this response function and, mathematically, the correct boundary condition for an acoustic analysis of a motor cavity is the acoustic admittance, which replaces the regression rate in the pressure coupled response with the normal velocity out of the combustion zone as follows:

\[ A = \frac{u'/\bar{u}}{p'/p} \]  

(2)

1.1.3 COMBUSTION MODELING

A great deal of effort has been invested in developing models for the
The combustion of solid propellants, both to better understand the processes involved as well as obtain the necessary inputs to perform stability analyses of rocket motors. These models fall into two categories, steady state and non-steady state. As the names imply, it is the latter category of models which leads to the response functions needed to perform stability analyses, while the former generally derive expressions for the mean regression rate or other properties of interest such as the temperature sensitivity. However, the steady state models provide key insights into the combustion processes of solid propellants and often serve as the basis of the combustion models employed in non-steady state calculations.

1.1.4 DIFFICULTIES IN COMBUSTION MODELING

There are many difficulties which face the combustion modeler in developing an accurate, tractable, and affordable model of the burning of a solid propellant. Because of the assumptions involved in performing an acoustic analysis of the motor cavity, the description of the gas motions in the vicinity of the walls of the motor cavity, where the combustion zone is located, is generally inadequate. Likewise, the complexity of the combustion process means that, for a model to remain tractable, the gas oscillations can only be treated in a limited manner.

For example, the analyses involved are typically restricted to allowing only one-dimensional gas motion, perpendicular to the propellant surface. Thus, the combustion region is subjected to variations in pressure, density, and temperature, but no crossflow velocities, steady or perturbation. This leaves the acoustic admittance as the appropriate boundary condition, but at the expense of perhaps significant details of the combustion process.
In some cases, such as the dynamic behavior of the quench limits of a kinetically limited flame residing in a mixing fan, rigorous analytical solutions are not presently possible. Here, recourse must be made to approximate treatments if any solution is to be obtained.

Of course, any model requires the use of parameter values, such as surface temperatures, that can only be obtained from experimental sources. However, because of the inhospitable conditions in the combustion zone and the small scales involved, such measurements may not be available or so prone to error that they are of little utility. While emerging from the microscopic details of a single combustion site on the surface of a heterogeneous propellant, one is faced with yet another problem, that of how to represent the random aspects of the surface structure present in a well-mixed propellant.

This last problem can be dealt with, to some degree, by looking first not at a true heterogeneous propellant, but rather a simple analog to such a propellant. The oxidizer-binder laminate, shown in Figure 1, allows examination of the multi-dimensional heat transfer, mixing, and combustion aspects of the propellant combustion problem, but in two rather than three dimensions and without the complexity of the overall propellant surface.(3)

1.2 OXIDIZER-BINDER LAMINATE COMBUSTION ZONE DETAILS

The combustion zone of such a laminate is still very complex, as Figure 2 illustrates. To gain a clearer understanding of how this structure was determined and what it means to the combustion modeler, a short description of the experimental results obtained through previous studies conducted by Price and co-workers follows.(4)
1.2.1 OXIDIZER SURFACE

Considering the Ammonium Perchlorate (AP) surface first, it is important to remember that AP burns independently at pressures above roughly 2 MPa, and Figure 2 has been drawn to represent a situation above this limit. If the pressure represented were below this pressure cutoff, the AP would form a shaft around the thin region of the AP-binder interface combustion region. At very high pressure, about 6 MPa and above, the AP region away from the interface would form a stepped-down plane about the interface region, because at such pressures the AP burns at a higher rate than the AP-binder system. Finally, it is important to note the flaky appearance of the surface of the AP in the self-deflagration region as seen in Scanning Electron Microscope (SEM) images taken of quenched samples. It is believed that this surface texturing is the remnant of a froth layer present during self-deflagration. Exothermic reactions are believed to occur in such layers.

Looking at the AP surface immediately adjacent to the binder, it has been found that, in addition to protruding relative to both the binder and the oxidizer surface further away from the interface, the surface texture of this region is also different, having a smooth appearance. It is believed that this difference in character is due to differences in the modes of decomposition of the oxidizer in these regions. Because conventional polymer binders decompose endothermically and are relatively cool, there is a degree of lateral heat transfer from the hotter, exothermically decomposing oxidizer to the binder. This results in the AP in the interface region seeing less net heat than it would without the presence of the binder heat sink, leading to a different decomposition path, probably dissociative sublimation.
This leaves the leading edge region of the oxidizer surface. Here again, heat transfer is the explanation for the observed behavior. Whereas the oxidizer surface further out is receiving heat solely from self-deflagration and that closer in is being retarded by the lateral heat transfer into the binder, the AP in the leading edge region is getting heat feedback from self-deflagration as well as the AP-binder flame while losing less heat to the binder because of its greater distance from the interface. The result is the maximum net heat back into the solid and, consequently, the greatest regression.

1.2.2 AP FLAME

Above those AP areas undergoing principally self-deflagration, an AP monopropellant flame is postulated. Its existence is postulated as experimental evidence is lacking owing to resolution problems based its presumed close proximity to the surface. A degree of uncertainty also surrounds the quench limit of the flame as it approaches the interface region; quenching is assumed to occur, altering the AP behavior in the interface region even more, but the details necessary to fix the location for modeling purposes have yet to be determined. The heat release for the exothermic decomposition of the AP is believed to be partitioned between this flame and the froth layer mentioned previously, in a manner dependent on pressure and, hence, important to dynamic response.

1.2.3 BINDER SURFACE

The binder layer between the oxidizer slabs is composed of a polymeric material, which pyrolyzes endothermically. The layer is relatively thin in
order to approximate the typical thickness that would be expected in a propellant with a high solids loading. It will be discussed later why, for energy balance considerations, the binder is recessed relative to the oxidizer.

1.2.4 INTERFACE PLANE AND MIXING REGION

There is no evidence of heterogeneous reactions in the interface plane between the AP and the binder. Thus, extending from the surface at the interface is a mixing region of unreacted binder and oxidizer decomposition products. In Figure 2, the outward bulged dotted line represents the stoichiometric surface in the mixing region. The bow is due to the dilute nature of the oxidizer compared to the binder. As with any diffusion process, pressure and the inflow conditions of the binder and oxidizer product gases greatly influence the process.

1.2.5 KINETICALLY LIMITED LEADING EDGE FLAME

At some point in the mixing fan, a sufficient temperature is reached to support a kinetically limited flame, from which the name Kinetically Limited Leading Edge Flame (KLLEF) is derived. This flame serves as the leading edge of the final diffusion flame, and it is through this relationship that the existence of the KLLEF is postulated, since all free standing diffusion flames must have some type of kinetically limited edges. As with the AP flame, spatial resolution problems limit the possibilities of actually observing the KLLEF.

Although the KLLEF is itself dominated by kinetic processes, this is not to say that diffusion does not play an important part in determining the
location and extent of the flame, since it's the diffusion process which is responsible for providing the pre-mixed gas. The KLLEF is centered at the stoichiometric surface in the mixing fan and extends some finite distance on either side, until, at some point in the mixing region where the gas becomes too fuel rich or fuel lean, quench limits are approached.

Because the diffusion process, which determines KLLEF location, and the quench limit phenomena are both pressure dependent, the KLLEF position and extent will be affected strongly by any pressure disturbances. Likewise, as the binder and oxidizer decomposition processes are also strongly dependent on pressure, the mixture ratio of the gases leaving the surface will fluctuate creating further changes in the KLLEF.

The location and extent of the KLLEF as well as their variations with pressure are important because of the heat that the KLLEF returns to the interface region of the surface. It is the dominant heat source in this region, as the diffusion flame is too far out to have more than a limited effect and the AP flame is quenched. The KLLEF continues to be an important heat source to the AP surface outwards toward the leading edge region, and its fluctuations will have to be considered in the modeling of that region as well.

1.2.6 FINAL DIFFUSION FLAME

Standing on the base of the KLLEF and extending out along the stoichiometric surface of the oxidizer-binder mixing fan is the final diffusion flame. Here, it is postulated that, for a typical non-aluminized, AP-hydrocarbon binder propellant, the final combustion of binder and oxidizer vaporization products takes place. One problem with this description is the
generally fuel rich nature of a solid propellant; the classical description of a diffusion flame resting on or near the stoichiometric surface, with no oxidizer species on the fuel side of the flame and no fuel species on the oxidizer side, may not be strictly the case in this situation. However, history and simplicity warrant that, for the time being, this distinction will not be made.

The amount of oxidizer and binder decomposition products consumed in the diffusion flame is strongly dependent on how much of these materials were consumed in the diffusion flame holder, the KLLEF. Even the existence of a diffusion flame depends on this question. Figure 3 shows low and high pressure test cases involving three sandwiches with varying binder thicknesses. At both pressures, as the binder thickness is increased, the stoichiometric surface expands further, both laterally and vertically. Being affected overall by kinetic factors, the KLLEF remains roughly at the same absolute location, but its location varies considerably relative to the stoichiometric surface. In the low pressure case, one of the curves has been drawn to show the stoichiometric tip, the convergence of the mixing regions for the two interfaces of the sandwich, below the projected KLLEF position. Without any flame holders, the diffusion flame can't exist; and, with its location now in a region which is too oxidizer rich to support a sufficient flame temperature, the KLLEF has also extinguished. The high pressure examples have been drawn to illustrate that, for the particular thin binder sandwich being considered, the lower KLLEF height, due to the effect of the higher pressure on the kinetics of the flame, means that the extinguishment of the diffusion flame will not occur under the conditions which resulted in extinguishment at lower pressure. Clearly, the pressure dependence of the above will have a significant impact.
on the response characteristics of the sandwich combustion zone, particularly near the mean pressures where stoichiometric tip retraction, as the above phenomenon can be labeled, occurs.

It has been previously mentioned that the KLLEF dominates the heat feedback to the surface in the interface region, while the AP flame does the same further out in the AP self-deflagration region. Thus, the surface decomposition processes are relatively insensitive to changes in the diffusion flame. However, this final flame can still have an impact on the overall acoustic admittance of the combustion process, where the responses of all components of the combustion process are averaged together.

The purpose of this research is to take this picture of sandwich combustion, based principally on steady state experimental studies, and develop a model for the combustion response of a sandwich propellant which accounts for the dynamic coupling of the component flamelets and their respective dominated surfaces. As the next chapter will show, this concept of surface coupled flamelets has not been previously employed in describing the combustion of heterogeneous propellants.
As noted in the introduction, combustion models fall into two broad categories, steady state and non-steady state. Since, in many instances, steady state models form the basis of many of the non-steady analyses, it is logical to begin with a few of the best known examples of steady state models.

2.1 STEADY STATE MODELS

2.1.1 GRANULAR DIFFUSION FLAME MODEL

One of the first models to examine the combustion of heterogeneous propellants was devised by Summerfield and co-workers. Generally referred to as the Granular Diffusion Flame (GDF) model, this treatment is based on a competitive, quasi-steady two reaction process, a pre-mixed flame of oxidizer and fuel decomposition products dominating at low pressures and a diffusion flame dominating at higher pressures. The pre-mixed flame is described as a stream of gas proceeding vertically at a fixed velocity based on the average mass flow rate in which a second order reaction is occurring. The latter is taken to have a degree of completion of, on average, zero, indicating an assumption of complete reaction near the surface. The diffusion flame is postulated to consume "pockets" of binder decomposition gases, with characteristic dimensions and masses, which are created at the surface and proceed to react through the surrounding oxidizer decomposition gases. The dimensions of the pockets are related to, but not the same as, the dimensions of the corresponding oxidizer crystals. The pocket concept associated with the diffusion flame gives rise to the model's name. These flame models are
employed to calculate two flame lengths which are then summed to provide the length at any pressure, assuming thus that at any pressure the overall combustion process is controlled in part by kinetics and in part by diffusion.

Decomposition at the surface is controlled by heat conduction from the flame, with a single net heat release, combining an exothermic value for the oxidizer with an endothermic heat release for the binder, needed to fit the one-dimensional governing energy equation. The surface is assumed to be dry, such that all mixing occurs in the gas phase, with no sub-surface reactions.

A net energy balance of the system, with the flame model providing the flame thickness for the assumed linear temperature gradient in the gas phase, is solved for the regression rate of the propellant as a function of pressure. The expression obtained is of the following form:

\[ \frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1/3}} \]  

In practice, this expression has been used mainly as an alternative to St. Robert's law, with laboratory data fixing the values of the two parameters. Although this is then an empirical expression, its foundation is in a physical model, albeit a very simple one.

2.1.2 HERMANCE MODEL

Another early steady state model, and perhaps the first to attempt to predict the regression rate effects of formulation changes, was proposed by Hermance.(7) As with the GDF model, this is a one-dimensional treatment of the combustion of heterogeneous propellants. The model breaks the combustion zone into three regions: the surface, the intermediate gas phase mixing region, and the gas phase flame zone. The energy equations for each region must be matched.
with one another at their boundaries, the boundary conditions requiring matched temperatures and heat fluxes at each interface. The resultant coupled equations are solved in an iterative fashion to obtain the rate, surface temperature, and flame temperature.

The propellant surface supports not only endothermic binder and exothermic oxidizer decomposition processes, but also an exothermic heterogeneous reaction between the binder and decomposed oxidizer. The latter is postulated to occur in a fissure region surrounding the oxidizer crystal, this providing the identifying feature of the model. Each reaction contributes to the overall mass flux at the surface with the contributions weighted by area factors. The oxidizer and binder factors are taken to equal their volume fractions. The heterogeneous reaction factor is based on a characteristic length associated with the fissure development during the course of combustion. The fissure length is a function of an empirical ignition delay and the time necessary for the oxidizer crystal to reach a statistically determined average intersection diameter with the presumed planar propellant surface. This figure is based on a mathematical study of geometric planes passing through randomly packed beds of spheres. (10)

Diffusion of the oxidizer and binder decomposition gases is the key process occurring in the intermediate region. As in the GDP model, the calculation of the flame standoff distance is a key element of the model. In this case, it is a function of the average velocity of the gases leaving the surface and a characteristic reaction delay time, which is a function of the reaction rate in the gas phase.

In the final region, oxidizer and binder decomposition products react in a planar flame with a heat release taken to be a propellant property, i.e.,
not a function of pressure or regression rate. Heat from the combustion process is conducted back to the surface.

A key reservation about this model is the postulated fissure development. In reality, fissure development of the type described by the model is now known not to occur in ammonium perchlorate based propellants; yet, it is a major factor in the model, particularly at high pressures.(6)

2.1.3 BECKSTEAD, DERR, AND PRICE MODEL

For the most part, the above models have been superseded by the model originated by Beckstead, Derr, and Price (BDP).(8) This model makes some advances over its predecessors with a condensed phase treatment employing a simplified treatment of surface geometry and a more intricate flame structure in its gas phase model.

The oxidizer and binder are assumed to pyrolyze exothermally and endothermically, respectively, and their mass fluxes are weighted to obtain the net flux from the surface. The weighting is based on surface area fractions of the oxidizer and binder calculated with an assumed geometry of a partially exposed, perfectly spherical oxidizer crystal protruding or recessed relative to the presumed flat binder surface. The degree of exposure is measured by the diameter of the exposed crystal at the binder plane, with the value taken to equal the same statistical planar intersection value used by Hermance. Another key to the calculation is the protrusion height of the crystal above the surface, this is found via a geometric argument with an empirical ignition delay added. The ignition delay introduces a degree of pressure dependance into the situation, with the oxidizer protruding at low pressures and recessed at high pressures. The final equations for the oxidizer
area fraction and the standoff distance are, respectively:

\[ S_{ox}/S_t = \zeta (6(h/D_{ox})^2 + 1)/(6\zeta (h/D_{ox})^2 + 1) \]  

(4)

and

\[ h/D_{ox} = 1/2 (1 + 1/\sqrt{3})(1 - r_{ox}/r_f) + r_{ox}\text{ign}/D_{ox} \]  

(5)

The overall mass flux is expressed in terms of the oxidizer's regression rate by applying the requirement that, on the average, the ratio of oxidizer to binder consumption equals the ratio of mass fractions in the propellant. Thus, in the final expression for the mass flux off the surface, the binder rate only appears as a minor term in Equation 5 above. This leaves the oxidizer pyrolysis as the rate controlling process.

Turning to the surface energy balance, a number of simplifying assumptions are applied. In the original version of the model, both the surface temperature and condensed phase specific heat are taken as averages of the corresponding oxidizer and binder values. Further, heat transfer back to the surface is assumed to consist solely of conduction, i.e., no radiation heat transfer is considered. Under these assumptions, the surface energy balance is:

\[ m_t c_p (T_s - T_o) = -m_{ox} (S_{ox}/S_t) Q_L \]

\[ -m_f (S_{f}/S_t) Q_f + \beta_{pf} Q_{pf} m_f e^{-\xi_{pf}} \]

\[ + (1 - \beta_{pf}) m_{ox} (S_{ox}/S_t)[Q_{Ap} e^{-\xi_{Ap}} + Q_{f_f} e^{-\xi_{ff}}] \]

where the three terms on the left hand side of the expression represent the heat conduction from the model's three flame regions.
The flame structure alluded to above is shown in Figure 4. There are basically two flame paths, binder and oxidizer surface decomposition products react in the primary flame to form inert products or oxidizer decomposition products react initially in an AP monopropellant flame and then proceed to react with the binder gases in a final diffusion flame.

The primary flame takes the binder decomposition products and reacts them with perchloric acid from the AP decomposition as described by the following energy balance:

$$\dot{Q}_p = c_p (T_f - T_0) + \alpha Q_L + (1 - \alpha) Q_f$$

A key term related to the primary flame is its standoff distance. The primary flame is a premixed flame; hence, the standoff distance is the sum of a length associated with diffusion and another based on kinetics. The latter is calculated from an expression derived by Hermance in his model, illustrating the cross-pollination that occurs in combustion modeling. The expression for the diffusion distance is based on the Burke-Schumann analysis of cylindrical diffusion flames. This is multiplied by an "average flame height factor" to give the equivalent, based on heat transfer considerations, one-dimensional value needed in the model from the two-dimensional analysis. The final expression for the primary flame height is:

$$\epsilon_{pf} = c_p m_{t}\left(\frac{\delta_{pf}}{\lambda k_{pf} \rho_{pf}}\right) + c_p m_{t} A_{xf} X_{pf}/\lambda$$

The AP monopropellant flame is described as a premixed flame in which AP decomposition products, ammonia and perchloric acid, react to form diatomic oxygen and inert products. The energy balance and flame height equations for this flame are, respectively:
\[ Q_{AP} = c_p (T_{AP} - T_o) + Q_L \] (9)

and

\[ \xi_{AP} = c_p m_{ox}^2 / (\lambda k_{AP} p \delta_{AP}) \] (10)

The AP flame height is similar to the kinetics term of the primary flame height expression. Unlike the primary flame which is assumed to have a parabolic shape rising from the rim of the exposed oxidizer crystal, the AP flame is assumed to be flat, spreading out above the AP surface until it intersects the primary flame.

The final diffusion flame, which follows the AP monopropellant flame, reacts the oxygen from that flame with the remaining binder decomposition products. Because the AP products have passed through one flame already and because the diffusion flame must be above the AP flame, the energy and flame height equations are somewhat more complicated:

\[ Q_{ff} = c_p / a [(T_s - T_o) - a(T_{AP} - T_o) + (1 - a)Q_f/c_p] \] (11)

and

\[ \xi_{ff} = \xi_{AP} + c_p m_{ox} A_{fh} \chi_{ff} / \lambda \] (12)

Although the flame height is calculated from the Burke-Schumann analysis, the shape of the final diffusion flame is assumed to be parabolic.

With two flame paths, some method of determining what fraction of the decomposition products enter each flame has to be incorporated into the model. This is accomplished by a simple geometrical projection of the primary and AP flames onto the plane of the propellant surface. The ratio of the projected areas is the parameter.
The key to understanding this parameter is its dependence on the flame height equations and, hence, strong dependence on pressure. At low pressures, the primary flame diffusion and reaction distances are, combined, typically shorter than the AP flame standoff distance. The primary flame is dominant in this regime. As pressure increases, the reaction distances fall, while the primary flame's diffusion distance increases. The result is an increasing importance given to the AP and final diffusion flames.

As in the Hermance model, an iterative scheme is needed to solve for the surface regression rate. Actually, the surface energy equation is solved for the surface temperature, which is then used in the Arrhenius rate equations of the oxidizer and binder to obtain the rate.

Since its original development, the BDP model has been modified several times (6,11,12,13) to allow it to deal with bimodal and trimodal, monodisperse propellants, aluminum combustion, catalyst effects, differentiated binder and oxidizer surface temperatures, and a corrected flame shape calculation. While aluminum combustion is not of interest in the present discussion, the restricted treatment of multimodal propellants is of interest, particularly for comparison to the Petite Ensemble Model (PEM) which will be discussed later.

Extending the BDP model to bimodal and trimodal propellants is very simple, all that is required is to sum up the weighted expressions for the area ratios, Equation 4, to produce a net oxidizer fraction term.(11) The only other change has to do with a characteristic dimension needed in the calculation of the diffusion flame height. This dimension is related to the width of the concentric pipes in the original Burke-Schumann analysis. In the original BDP model, the length is linked to the linear distance between
centers of adjacent oxidizer particles. However, this restricts the model to propellants with oxidizer mass fractions less than 0.7. With the change to bimodal and trimodal propellants, this performance is improved by allowing the fines to rest inbetween the coarse particles. By using statistical information, namely that the intersection area of a plane through a randomly packed bed of spheres is equal to the volume fraction of the spheres in the bed, and the assertion that the volume of binder associated with any crystal is proportional to the surface area of that sphere, so each sphere to be fully wetted, it is possible to derive a new expression for this characteristic dimension.

Allowing differences in surface temperatures is also simple, but results in a greater complexity in the system of equations. Essentially, there exists a system of equations for each different oxidizer size, as each has a different surface temperature, as well as for the binder, which also has a different surface temperature. To illustrate the complexity involved, the following are the surface energy balances for an oxidizer (indicated by its size counter (i) and composition counter (j)) and the binder, respectively:

$\begin{align*}
    m_{oxij} S_{oxij} c_p (T_{soxij} - T_o) &= -m_{oxij} S_{oxij} Q_{Lij} \\
    + \beta_{pfij} (m_{oxpfij} S_{oxpfij} + m_{fpfij} S_{fpfij}) Q_{pfij} e^{-\xi_{pfij}} \\
    + (m_{oxij} S_{oxij} - m_{oxpfij} S_{oxpfij}) Q_{APIj} e^{-\xi_{APIj}} \\
    + (m_{oxij} S_{oxij} - m_{oxpfij} S_{oxpfij} + m_{fij} S_{fij}) Q_{fijfij} e^{-\xi_{fij}} \\
    - m_{fpfij} S_{fpfij} Q_{fij} e^{-\xi_{fij}}
\end{align*}$

(13)
and

$$m_f c_p (T_{sf} - T_o) = -m_f Q_f$$

$$+ \sum_{i,j} (1 - \beta_{pfij})(m_{oxpfij} S_{oxpfij}/S_f)$$

$$+ m_{pfij} S_{pfij}/S_f) Q_{pfij} e^{-E_{pfij}}$$

(14)

Once the surface temperatures are found, the corresponding rates can be calculated and summed to yield the average rate as per the following:

$$\bar{r} = \frac{1}{P_p} \sum_{k} m_k S_k$$

(15)

The effect of catalysts has been incorporated into the BDP model through the primary flame reaction rate equation. (13) The modified rate equation reads:

$$r_{pf} = A_{pf} e^{-E_{pf}/RT} p^2 \left[ 1 + \frac{C_{cat}}{A_1 + C_{cat}} \frac{A_{cat}}{A_{pf}} \right]$$

(16)

In the original BDP model, only the first term is used in calculating the flame height from the Burke-Schumann analysis. The differences between the truncated expression and the full series expression can be significant, especially if the flame is fuel rich, a likely possibility in the case of solid propellant combustion. Figure 5 illustrates the differences encountered: (6)

Even with these changes, the BDP model still has several deficiencies. As a physical model of the combustion zone, the BDP model does not approximate the details which have been observed and inferred from recent sandwich
combustion studies, which is understandable since the model was originally presented over fifteen years ago. These differences are particularly noticeable for the flame complex. Although extended to multimodal propellants, the model still cannot handle polydisperse formulations, which all real propellants are. This latter deficiency has been treated in the next model to be discussed.

2.1.4 PETITE ENSEMBLE MODEL

The Petite Ensemble Model (PEM) treats the combustion of polydisperse, multimodal heterogeneous propellants using statistical means. Unlike the previously discussed models, the PEM is more concerned about how the heterogeneity of a propellant, due to its multiplicity of oxidizer modes, can be treated in a statistical fashion than in the details of the combustion processes themselves. The latter processes are described via the BDP model.

The fundamental assertion of the model is that the surface of a heterogeneous propellant can be rearranged into a series of "pseudo-propellants," which can then be treated independently to obtain their individual regression rates. Each such pseudo-propellant is a monomodal, monodisperse propellant with a single species oxidizer; as such, it contains oxidizer particles from all modes in the overall propellant.

The calculation of the steady state regression rate of a heterogeneous propellant via this scheme first requires the description of each oxidizer mode in terms of a distribution function. Oxidizer modes can be described in terms of log normal distribution functions using two variables, the mean oxidizer diameter and a width parameter. The former is simply the
oxidizer diameter that corresponds to the center of the distribution; when a particular oxidizer size is mentioned as being in a propellant, the size indicated is actually the mean size for that mode's distribution. The width parameter describes how closely the oxidizer particles within a mode are graded relative to the mean diameter, the lower the value of the width parameter the narrower the distribution of sizes within the mode. A width parameter value of unity indicates a monodisperse mode; all particles have the mean diameter. Integration of the distribution function over a range of oxidizer diameters provides the mass fraction, relative to the entire mode, of the crystals within the limits of integration. The distribution function has the form:

\[ F_{\text{ox,d}} = \frac{1}{(2\pi \sigma_{\text{ox}})^{1/2}} e^{-1/2\left( \frac{\ln D_{\text{ox}} - \ln D_0}{\ln \sigma_{\text{ox}}} \right)^2} \]  

(17)

The above distribution function describes the characteristics of that mode in absolute terms. However, in a propellant, there will likely be two or more modes, in order to achieve the desired loading or performance. The overall propellant oxidizer distribution function describes all of the oxidizer in the propellant as a sum of the individual mode distribution functions weighted with their corresponding mass fraction in the total propellant. In equation form, this reads:

\[ F_d = \sum \alpha_n F_{\text{ox},n} \]  

(18)

With the overall distribution function defined above, the calculation of the mean propellant regression rate follows from:
Here, the pseudo-propellant oxidizer mass fraction is needed to compensate for the alteration in the dimensions of the distribution function when it is formed by the weighted summation described above. To calculate this quantity, the apportionment of the binder to each oxidizer crystal must be first discussed.

In the PEM, the volume of fuel associated with each crystal is taken to equal a proportionality constant multiplied by the diameter of the crystal raised to a power. In the multimodal version of the BDP model, the diameter was squared, relating the volume of binder with the wetted area of the oxidizer crystal. From calculations made with the PEM, it has been shown that if the exponent equals three, then each oxidizer crystal will burn with the same o/f ratio, while lower exponent values result in fines burning fuel rich and coarses burning fuel lean.\(^{(15)}\) The proportionality constant can be found from a combination of definitions of the total volume fraction of fuel, the mean volume of each oxidizer crystal, the number fraction of oxidizer crystals between any two differentially seperated oxidizer sizes, and the above described power expression.\(^{(6)}\) The terms involving the mean volume and number fractions of oxidizer crystals are based on the same statistical oxidizer diameter used in the Hermance and BDP models.

The final expression for the volume fraction of binder associated with each oxidizer crystal is:

\[
\Delta V_{F,d} = \frac{\pi (1-\xi)/6}{\int_0^{D_{ox}} d_D^{-3} d_D^{n-3}} D_{ox}^n
\]  

\[(20)\]
or, in differential form, for the volume fraction of binder for crystals between two differentially separated sizes:

\[
\Delta V_{F,d} = \frac{(1-\xi)}{D_{ox}^{n-3} d\xi_d} \cdot D_{ox}^{n-3} d\xi_d
\]  

(21)

Returning to the pseudo-propellant oxidizer mass fraction, this can now be found by direct calculation.(6) The expression is:

\[
\alpha_d = \left(1 + \int_{D_{ox}}^{(1-\xi)} \frac{D_{ox}^{n-3} d\xi_d}{\rho_f \rho_0 D_{ox}^{n-3}} \right)^{-1}
\]  

(22)

Returning to Equation 19, the only term left to discuss is the regression rate for each pseudo-propellant. In the PEM model, these rates are found via a modified version of the BDP model.(15) The main differences are to allow not only different oxidizer and binder surface temperatures but also specific heats, as well as variable gas phase conductivities and diffusion coefficients, the latter as functions of the gas temperature. As with the BDP model, a method of describing aluminum combustion has been added, but this is beyond the scope of the present discussion.

In an early description of the PEM model, reference is made to a "snap shot" combustion model based on the BDP scheme.(6) In this technique, the statistical point in time approach employed in the BDP model is replaced with a time integral method which follows the combustion of a typical oxidizer particle from emergence from the surface to complete combustion. The mean mass flux for the particle is:

\[
\bar{m} = \frac{1}{\tau} \int_{0}^{\tau} m \, dt
\]  

(23)
while the height of the crystal above or below the planar fuel surface is:

\[ h = \int_{t_b - t_{\text{ign}}}^{t_f} \frac{m_{\text{ox}}}{\rho_{\text{ox}}} \, dt - \int_{t_b}^{t_f} \frac{m_f}{\rho_f} \, dt \]  

(24)

Likewise, the area ratio term (Equation 4) is determined with the oxidizer diameter replacing the statistical intersection diameter. However, this scheme has not been workable in practice and is only now being reconsidered for inclusion in the model.(16)

One final note concerning the mean rate expression, Equation 19, refers to the direct summation of regression rates that is assumed.(15) Another possible scheme would be an inverse summation for the overall rate:

\[ \frac{1}{\bar{R}} = \int_{D_{\text{ox}}} F_d/\alpha d r d z \, d\ln D_{\text{ox}} \]  

(25)

Calculations using both expressions show that the direct representation works best for "fast" burning propellants, while the inverse expression fits experimental data better for "slow" burning formulations. The direct summation scheme is still the dominant method in obtaining PEM results.

Besides incorporating the BDP combustion model with the same faults noted earlier, the PEM can also be faulted for its assertion that the propellant surface can be rearranged into pseudo-propellants without regard to the effects that differing combustion zones, for different sized oxidizer crystals, may have on the overall combustion process.

2.1.5 "FASTEST PATH" SCHEME

One final steady state methodology is the "Fastest Path" scheme.(17,48)
This is not a model, but rather a proposed mechanism. The basic concept is that combustion will proceed along the path of fastest progress, which may not be a vertical ray through the propellant. Instead, based on the ignition delays of the particles surrounding the current leading edge of the combustion front and the separation distances between these particles, combustion will continue in the direction which represents the minimum time delay. Particles which are bypassed may not be ejected from the surface, but rather may be subject to multiple ignition points which will increase their rate of consumption. A Monte Carlo technique can be seen as a likely method of modeling the arrangement of particles about the current particle under consideration with a trial method then employed to find the fastest next step.

2.2 NON-STEADY STATE MODELS

Until now, all of models under discussion have been steady state methods of describing the combustion of heterogeneous propellants. One reason for examining these schemes as a prelude to a discussion of non-steady combustion model is that some, such the PEM, serve as the basis of existing non-steady models. Further, as will be seen, combustion response models which do not employ existing steady state models tend to deal with combustion in a very simple fashion. So, in many respects, the model which is to be developed in the present research will have more in common, at least in terms of a detailed description of the combustion zone, with the above steady state methodologies than with the response models that will now be discussed.

2.2.1 HOMOGENEOUS MODELS

Non-steady combustion models can be divided into two broad categories, homogeneous and heterogeneous. The homogeneous models are similar in many
respects with regards to basic assumptions and, to a remarkable degree, final results. (18)

Common assumptions for most homogeneous theories include a condensed phase which is one-dimensional, semi-infinite, inert, isotropic, and, as the name implies, homogeneous. The surface generally pyrolyzes via an Arrhenius expression, and the heat returning to the surface from the flame zone follows the Fourier heat conduction law. The assumption with the biggest impact, in that it removes much of the importance, for the sake of simplicity, of the gas phase analysis in any model, is that the gas phase is quasi-steady, i.e., it responds very quickly to any small changes that are imposed on it.

The typical result of these assumptions is an analysis focusing on the transient aspects of the thermal lag in the condensed phase as it impacts the surface energy balance. The final result of most of these models is an expression generally referred to as the Universal Two Parameter Response Function:

\[ R_p = \frac{nAB}{AB-(A-1)+k+A/k} \]  

Although, in most models, the two parameters (A and B) have specific definitions in terms of propellant properties (albeit having different definitions in different models), it is common practice to use this expression to empirically fit response data, finding values of A and B which correspond to the best fit. It is interesting to note that, in many cases, the values of A and/or B eventually found by empirical fitting can not be reconciled with the original parameter expressions found in the various models, indicating limitations in those models.

In the context of the combustion zone discussed earlier, it should not be
surprising that homogenous models are not adequate to describe the combustion response for a heterogeneous propellant. However, the simplicity of the resultant two parameter expression makes it sufficiently desirable to attempt, at least, to find some application in more complex situations. This will become clear when the discussion of the current analysis commences.

2.2.2 HETEROGENEOUS MODELS

Heterogeneous response models vary in the manner with which they represent the changes of propellant properties in the condensed phase or on the surface. These techniques can be labeled as: "sandwich" models, "edgewise sandwich" models, and postulation models.

In sandwich models, the heterogeneity of the condensed phase is described in terms of a sequence of alternating layers of pseudo-propellants which are traversed in the process of combustion. The key models of this type are those of Williams and Lengelle (19) and Cohen and Strand (20). In both cases, the properties of the condensed phase are assumed to vary vertically in a sinusoidal fashion, this representation being chosen to allow closed form solutions to be obtained for the combustion response. Obviously, such an arrangement is totally unrealistic and still ignores the effects of surface heterogeneity on the combustion process. Deur and Glick (21) have also devised a sandwich model but, by using an explicit numerical method with randomly chosen layer compositions, have eliminated the difficulties associated with the sinusoidal variation of properties. Although ad hoc corrections are made to account for interactions between burning particles on the surface, the scheme has proved less than satisfactory.

The application of the Petite Ensemble Model (PEM) to non-steady
combustion is the principle model of the edgewise sandwich variety. (15) As previously discussed, this model rearranges the surface of a heterogeneous propellant into sets of pseudo-propellants which are then analyzed via existing one-dimensional combustion models independently and their resultant behavior summed by a statistical scheme. In the case of the pressure coupled response, the equation used is:

\[ R = \frac{1}{R} \int_{D_{ox}} R_{p,d} r_d F_d \, d \ln D_{ox} \]  

Besides providing the scheme for summing the pseudo-propellant responses, the steady state PEM is employed to calculate the needed pseudo-propellant properties, e.g., temperature, sensitivity, required for the homogeneous response function calculations. A variety of homogeneous models have been tried with the PEM driver to calculate the pseudo-propellant response functions. Of course, the problems with the steady state PEM carry over to the non-steady state version.

The term postulation model has been used to refer to schemes which obtain the pressure coupled response of a heterogeneous propellant via a set of heuristic arguments with no true basis in analysis. One model, extensively used in industry, is attributed to Cohen. (22) In this scheme, it is assumed that the response of a propellant is equal to the sum of the responses of the pseudo-propellants which are defined in terms of the propellant's oxidizer modes. For pseudo-propellants of similar composition, i.e., employing the same type of binder and oxidizer, the response functions are assumed to have the same shape, which is calculated from a homogeneous model. The peak frequency of each pseudo-propellant's response is equal to the layer frequency, defined as the ratio of the mean regression rate to the oxidizer diameter, and the
normalized peak magnitude is assumed to equal the ratio of that oxidizer mode's concentration divided by its oxidizer diameter. This scheme is, at best, a method of obtaining a response function when only limited information and resources are available and can not be considered in the context of trying to gain an insight into the combustion behavior of solid propellants.
CHAPTER 3
A SURFACE COUPLED FLAMELET APPROACH TO COMBUSTION RESPONSE MODELING

It is clear that no existing model provides the detailed description of the combustion zone presumably required to adequately model the combustion response of a solid propellant. For this reason, the present analysis is undertaken. However, the complete description of the combustion zone of a heterogeneous propellant is still beyond the scope of this work. Instead, the combustion response of the analogous laminate propellant, described in physical detail earlier, will be modeled.

3.1 MODULARITY

Another simplification will be made by performing this analysis in a modular fashion. This means that the loosely coupled regions of the combustion zone will be treated separately. Thus, analyses will be performed for the AP self-deflagration dominated region, the Kinetically Limited Leading Edge Flame (KLLEF) dominated region, and the diffusion flame contribution. Further, primarily one-dimensional treatments of these regions will be formulated, with corrections for two-dimensional aspects made where required, in order to maintain simplicity and computational ease. Once the component models are available, a summation scheme will be devised to sum their individual contributions to yield the overall acoustic admittance.

3.2 PRELIMINARY ANALYSES

3.2.1 STEADY, ONE-DIMENSIONAL PYROLYSIS OF OXIDIZER-BINDER LAMINATES

A brief examination will be made of a steady, one-dimensional model of
laminate combustion. The purpose of this analysis is to determine the protrusion of one laminate material relative to the other, while also finding the difference in the surface temperatures of the materials. This analysis sets the stage for the non-steady laminate model to be discussed later, in that it introduces the assumption that the KLLEF is the dominant heat source in the O-F interface region on the surface and that, because of the geometry of the flame location and lateral extent of the surface region being considered, the KLLEF can be modeled to some degree as a planar flame in this region. Because of this, the heat flux returning to the surface from the flame can be expected to be relatively uniform in the immediate interface region between oxidizer and binder.

It has been observed (4,24) that the typical binder lamina is recessed in comparison to the AP oxidizer in these laminates, leading to the question whether this phenomenon is a result of some feature of the flame sheet or complex, lateral heat transfer between oxidizer and binder, or different pyrolysis characteristics of the two materials. It is the last possibility which will be examined in the brief analysis which follows.

Figure 1 shows the arrangement for the problem under consideration. Although the two slabs are shown in contact, this is not precisely correct as each is treated as independent of the other and as being infinite in extent so as to allow a one-dimensional analysis. The heat source is described by the "flame" temperature and the standoff distance from one of the slab surfaces. (The other standoff distance is calculated through the following analysis.) The problem is formulated under the assumption that steady state conditions exist, such that a single regression rate is shared by the two slabs.

The surface energy balance for either slab for the above described
conditions is:

\[ \lambda_g \frac{dT}{dx} \bigg|_{o+} = m \left( Q + c_p(T_s - T_o) \right) \]  \hspace{1cm} (28)

Ignoring the effects of convection, the temperature gradient at the surface will be approximated by the linear relation:

\[ \frac{dT}{dx} \bigg|_{o+} = \frac{T_f - T_s}{s} \]  \hspace{1cm} (29)

The two slabs are related through the common regression rate, which is simply the mass flow rate divided by the condensed phase density:

\[ r = \frac{m}{\rho} \]  \hspace{1cm} (30)

Thus, the steady state requirement of a common rate can be written as:

\[ \frac{m_{ox}}{\rho_{ox}} = \frac{m_f}{\rho_f} \]  \hspace{1cm} (31)

The mass flow rates are obtained from an Arrhenius expression:

\[ m = A e^{-\frac{E}{RT_s}} \]  \hspace{1cm} (32)

Equations 28 through 32 can be combined to yield relations for the standoff distances and the surface temperature of one of the slabs as a function of various thermodynamic quantities and the surface temperature of the other slab. In particular, these equations can be combined into a set of three expressions for computational purposes. The expressions for the standoff distances of the oxidizer and the binder slabs are identical in form as shown below:

\[ s = \frac{\lambda_g (T_f - T_s)}{A \left[ Q + c_p(T_s - T_o) \right]} e^{\frac{E}{RT_s}} \]  \hspace{1cm} (33)
By using the properties for either of the components, the corresponding standoff distance can be obtained. The surface temperature of the binder slab is found via the following equation:

\[
T_{sf} = \frac{E_f}{Rln(A_f/r_p f)}
\]  (34)

Since the relative standoff distance and relative surface temperature are the results of interest, some rearrangement of the above equations can be performed to yield:

\[
T_{sox} - T_{sf} = \left( E_{ox}/\ln \left( A_{ox}/r_{pox} \right) - E_f/\ln \left( A_f/r_p f \right) \right) 1/R
\]  (35)

\[
\frac{s_{ox}}{s_f} = \frac{T_f-T_{sox}}{T_f-T_{sf}} \frac{Q_F+c_f(T_{sf}-T_o)}{Q_L+c_{pox}(T_{sox}-T_o)} \frac{A_f e^{E_f/RT_{sf}}}{A_{ox} e^{E_{ox}/RT_{sox}}}
\]  (36)

and

\[
s_{ox} - s_f = s_f (s_{ox}/s_f - 1)
\]  (37)

In order to solve the above system of equations, values for the various constants have to be obtained. Recourse is made to the literature with somewhat checkered results. For some variables which have been measured experimentally, significantly different results are reported by different investigator. To obtain values for some of the variables where experimental results are not available or significantly different between investigators, the remaining well characterized parameters have been used to calculate acceptable values from the above equations or parametric studies will be conducted over a range of possible values.
Table 1 shows the ranges of those variables found in the literature, along with the corresponding references and any pertinent remarks.

The most difficult variables to find values for are the pre-exponentials or pre-factors for the rate expressions. This is mainly an experimental problem in accurately measuring the axis intercepts, the pre-exponentials, for rate curves with high slopes, i.e., high activation energies, since even small errors in measuring slopes will lead to large intercept errors.\(^{(25)}\) To alleviate this problem somewhat, Figure 6 has been prepared and offers a reasonable way to obtain a pre-exponential from a given rate, activation energy, and surface temperature. The ellipses show reasonable ranges of values for AP and polymeric binders based on values reported in the literature.

The heats of vaporization for polymers are also difficult to obtain owing to the rather complex degradation process required before the polymer fragments can enter the gas phase.

To a lesser degree, the heat of vaporization for the ammonium perchlorate oxidizer represents a difficulty due to the unknown degree that the oxidizer decomposition is split between sublimation and self-deflagration at higher pressures. Ammonium perchlorate exhibits a range of heats of vaporizations owing to its changes in decomposition processes as a function of pressure. At low pressures, when AP undergoes a process of dissociative sublimation, an endothermic value on the order of 495 cal/g is noted.\(^{(27)}\) At higher pressures as self-deflagration takes over, the process becomes exothermic with a value of -1075 cal/g possible, assuming total heat release at the surface.\(^{(32,33)}\) In the context of the interface region, it is argued that the mode of AP decomposition changes from deflagration to sublimation as the interface is approached due to lateral heat transfer from the oxidizer into the binder.\(^{(4)}\)
Using reasonable sets of oxidizer and binder parameter values, the relation between relative standoff distance and relative surface temperature can be illustrated as shown in Figure 7 as a function of the poorly known binder heat of vaporization. The conditions in Figure 7a were chosen to correspond to a sandwich experiment at 3.5 MPa. For reasonable values of the binder heat of vaporization and assuming equal standoff distances, the oxidizer surface will have a higher temperature than that of the binder. If lateral heat transfer were allowed, heat would flow from the oxidizer into the binder, causing the oxidizer to protrude and the binder to be recessed in the interface region (Figure 8a). The width of the affected region would be comparable to the thermal wave thickness in one-dimensional pyrolysis. If the binder thickness were on the same order, the entire lamina would be recessed (Figure 8b). This follows observed behavior from experimental work (4).

In research by Price and co-workers (4), it is proposed on the basis of several observations and arguments that the protrusion of the AP is enhanced by the local shift in AP decomposition towards sublimation. The present analysis (Figure 7b) indicates that a less exothermic or endothermic process leads to a protrusion of the AP relative to the binder, with a corresponding lowering in the relative surface temperature.

At higher pressures, the extent of heat release at the AP surface becomes greater and, at a sufficiently exothermic value, matches the heat needed to raise the AP approaching the surface from the initial temperature to the required surface temperature. When this occurs (Figure 9), the oxidizer standoff distance approaches infinity. Physically, the AP decomposition is providing sufficient heat to maintain the required surface temperature without the need for the external heat source or flame. Based on the equations in this
analysis, the limiting value of the oxidizer heat of vaporization is -198 cal/g for a surface temperature of 870 K.

Within the limits of the one-dimensionality and general simplicity of the above analysis, two points emerge. First, the experimentally observed phenomenon of recessed binder laminae relative to oxidizer laminae in sandwich studies can be duplicated analytically with consideration of only the differing pyrolysis characteristics of the two materials. Second, for what are believed to be acceptable ranges of the chemical kinetics and energetics variables for typical propellant ingredients, ammonium perchlorate and PBAN, the oxidizer surface temperature is normally higher than the binder surface temperature. If two dimensional heat transfer were considered, the temperature difference would be predicted to be smaller.

3.2.2 ACOUSTIC ADMITTANCE IN THE KLLEF DOMINATED REGION

The next step from the above analysis is to proceed with a non-steady examination of the same region, to model the surface response in the KLLEF dominated region for latter incorporation into the complete model for non-steady laminate combustion. The goal of this analysis is the derivation of a relation between the acoustic admittance and the propellant pressure coupled response, to show the effects of small perturbations in the composition of the material vaporizing off the laminate surface in the interface region under the influence of an oscillating KLLEF. The fluctuations in the o/f ratio stem from the variations in the heat transferred back to the surface due to the KLLEF oscillations, which cause different changes in the mass flux rates of the oxidizer and binder owing to their differing pyrolysis characteristics.

To provide the simplest path to the final desired expression, the
propellant pressure coupled response, along with the individual responses of
the binder and oxidizer, will be determined via one of the many one-
dimensional, quasi-steady gas phase models, specifically that of Denison and
Baum (34). It is rather immaterial which model is chosen since Culick (35) has
shown that all models with the quasi-steady gas phase assumption yield some
permutation of the same two parameter expression:

\[ R_p = \frac{n_{AB}}{A_{B}(A+1)+k+A/k} \]  \hspace{1cm} (38)

where:

\[ A = \frac{E}{RT_s} \left( T_s - T_o \right) \]  \hspace{1cm} (39)

\[ B = \frac{1}{\sigma_p (T_s - T_o)} \]  \hspace{1cm} (40)

and \( k \) is the positive root of:

\[ k^2 - k - \frac{\Omega}{\lambda_{pw}} = 0 \]  \hspace{1cm} (41)

with:

\[ \Omega = \lambda_{pw}/m^2c_p \]  \hspace{1cm} (42)

Although the details of the analysis leading to this result will not be
repeated here, the assumptions underlying this treatment are listed below,
along with short discussions concerning each assumption's applicability to
the problem under consideration.

1. Both condensed and gas phase processes are one-dimensional. Clearly,
   for the problem being considered here, the condensed phase is not one
dimensional; and, as a consequence, neither is the gas phase. However, as a means towards simplifying the overall analysis, the overall propellant response used for these calculations will be that of an equivalent homogeneous propellant, while the individual behaviors of the binder and oxidizer will be brought in as required.

2. The gas phase is quasi-steady, i.e., due to the short characteristic time of the gas phase relative to that of the solid, the gas phase will adjust to low frequency (<1000 Hz) disturbances very quickly. As noted above, this is the assumption which leads to the similarity in the expressions for the pressure coupled response found at the conclusion of most one-dimensional analyses, irrespective of how the gas phase is modeled.

3. The propellant is homogeneous, semi-infinite, and isotropic. Again, this is somewhat contradictory with the problem that is being examined; however, on the grounds of simplicity, the overall propellant response and those of the component binder and oxidizer will be calculated via the two parameter expression. Some remarks will be made later on the hypothesized effect of two-dimensionality on these results.

4. There are no condensed phase reactions. Again, this is a common assumption, which, ignoring the immediate surface regions of the binder and oxidizer, is generally accepted.(36)

5. The vaporization of propellant is via an Arrhenius rate law. Particularly in the case of polymer binders, the use of this simple functional expression is becoming less acceptable, owing to increased knowledge concerning the complex process by which such materials decompose.(37) However, within the context of the other assumptions being made, the degree of inaccuracy is no more severe.
6. Condensed and gas phase thermal properties are constant and equal for all species. In the current calculations, the properties of the overall propellant will be considered constant when making calculations of the overall propellant response. Likewise, the properties of the binder and oxidizer will each be taken to be constant when making calculations of their individual responses.

7. The flame is pre-mixed and laminar. The KLLEF is a pre-mixed flame, although whether it is laminar is still an open question. In any case, it is important to note that only a single flame, the KLLEF, is being modeled here; it will be its effects on the differing surface regions which give rise to the different sub-analyses to be discussed later.

8. Reactant species are in perfect stoichiometric proportions such that complete combustion occurs. Because of the difficulties in obtaining high solids, i.e., oxidizer, loadings in solid propellants, these propellants are typically fuel rich and consequently do not normally burn to completion. Further, even if the mean distribution were stoichiometric, local variations due to imperfect mixing and fluctuations in vaporization rates, the latter being the focus of the current analysis, will result in localized, in both space and time, variations in o/f ratio. However, the assumption is a common one used to simplify the analyses in most models and so will be used here with these reservations.

9. The flux of each reactant species is fixed fraction of total mass flux. Again, the purpose of this analysis is to examine the effects of fluctuations in o/f ratio. However, these fluctuations will be small.

10. The gas phase molecular weight is constant. The same remarks as made for the previous point apply here as well.
11. Perturbations in pressure, mass flux, and temperature are small. This and the remaining assumptions are typical of most combustion models, and no further comments will be made concerning them.

12. The flame can be modeled as a thin sheet, with a constant flame temperature, where complete combustion occurs. This is in keeping with the one-dimensional nature of the Denison and Baum model. However, in the slab burning problem, the KLLEF is known to be finite in extent and, as it spans a range of o/f ratios in the interface mixing region, has a range of flame temperatures. In order to use the Denison and Baum model, the flame temperature has to be taken as an average of the actual range of temperatures seen in the KLLEF and the extent of the surface coupled region must be effectively smaller than the extent of the corresponding KLLEF.

13. There are no net product mass fluxes back to surface.
14. There is no back reaction.
15. Changes in the heat content of the gas mixture are negligible compared to heat transfer by conduction and heat production by chemical reaction.
16. The Lewis number is unity.
17. Combustion is by a single step reaction of arbitrary order.
18. There is no erosive burning.
19. Diffusion is due solely to concentration gradients, i.e., thermal diffusion is negligible, with all diffusion coefficients equal.
20. Inertial and viscous momentum conservation terms are small.
21. Vaporization from the surface is far from equilibrium such that return flux of molecules from gas phase can be ignored relative to the flux away from surface.
Returning to the development of the relationship between the acoustic admittance and the pressure coupled response, the acoustic admittance has been previously defined as:

\[ A = \frac{u'}{p'}/u \]  \hspace{1cm} (43)

with the pressure coupled response being:

\[ R_p = \frac{r'}{p'}/r \]  \hspace{1cm} (44)

It is important to note that the velocity defined in Equation 43 is that at the upper boundary of the combustion zone, while the rate in Equation 44 is the surface regression rate. Only under quiescent conditions can the two be readily related. Under such conditions, the two can be related by the continuity relation for a unit flow area which reads:

\[ m = \rho u \]  \hspace{1cm} (45)

This expression can be linearized by substitution of each variable by an expression of the form:

\[ x = \bar{x} + x'\varepsilon \]  \hspace{1cm} (46)

with only linear terms in the perturbation variable being retained.

The result, after division by the mean flow rate (Equation 45), is:

\[ \frac{m'}{m} = \frac{\rho'}{\rho} + \frac{u'}{u} \]  \hspace{1cm} (47)

Division by the non-dimensionalized perturbation pressure and substitution for \( A \) and \( R_p \) with Equations 43 and 44 yields:
\[ R_p = \frac{\rho' / \rho}{p' / \rho} + A \]  

(48)

The density perturbation quantity can be replaced by performing logarithmic differentiation on the ideal gas equation of state:

\[ p = \rho RT/M \]  

(49)

The result, equating the differentials of the variables with their perturbation quantities, is:

\[ \frac{\rho'}{\rho} = \frac{T'}{T} + \frac{M'}{M} \]  

(50)

which upon substitution in Equation 48 is the desired expression relating acoustic admittance to pressure coupled response:

\[ A = R_p - 1 + \frac{T'/T}{\rho'/\rho} - \frac{M'/M}{p'/p} \]  

(51)

The pressure coupled response in Equation 51 is that of the overall propellant while the temperature and molecular weight terms will incorporate the effects of mixture ratio fluctuations.

The first of these terms will consist of two parts, flame temperature fluctuations resulting from mass flux perturbations and from mixture ratio perturbations.

The former is a result of the lagging response of the condensed phase temperature distribution to the changing heat transfer conditions resulting from the imposed pressure changes. As a consequence, in order to maintain mass continuity, the flame temperature must oscillate as predicted by the following equation from Denison and Baum:
\[ m' / m = n p' / p + \left( \frac{N+2}{2} + \frac{E_f}{2RT_f} \right) T_f' / \tilde{T}_f \] (52)

King (38) shows, through a comparison of the Zeldovich-Novozhilov (ZN) and Denison-Baum models, that the multiplier of the temperature term is related to the temperature sensitivity of the mean regression rate by the following expression:

\[ \alpha_p = \left( \frac{N+2}{2} + \frac{E_f}{2RT_f} \right) \frac{1}{T_f} \frac{c_{pc}}{c_{pg}} \] (53)

The other temperature term is a direct result of the changes in flame temperature due to composition changes. Figure 10 shows the typical variation of equilibrium flame temperature with oxidizer mass fraction for a PBAN-AP propellant at 6.89 MPa based on calculations made with a standard thermochemistry program. \(7\) The slope of this curve is the desired relation between flame temperature and mixture ratio perturbations and is shown in Figure 11. For ease of computation, it is desirable to have an explicit relation to represent this curve over the range of mixture ratios of interest; for reduced smoke propellants, this range is from roughly 75 to 95 percent oxidizer. Fitting a general third order polynomial to this range on Figure 11 results in the following expression and corresponding coefficients:

\[ T_f' / \alpha' = A \alpha^3 + B \alpha^2 + C \alpha + D \]

A = 1601.4
B = -15923.5
C = 22186.0
D = -8281.3

The desired relation is not that between flame temperature and oxidizer frac-
tion, but rather between temperature and pressure. Thus, an expression relating mixture ratio to pressure is desired. To obtain such an equation, the definition of the oxidizer mass fraction is used:

$$\alpha = \frac{m_{ox}'}{m_{oxy} + m_f}$$  \hfill (55)

This is linearized employing Equation 46 to become:

$$\alpha'/\alpha = \left( \frac{m_{ox}'/m_{oxy}}{p'/p} - \frac{m_f'/m_f}{p'/p} \right) \frac{m_f}{m_{oxy} + m_f}$$  \hfill (56)

which, after dividing by the non-dimensionalized perturbation pressure, becomes:

$$\frac{\alpha'/\alpha}{p'/p} = \left( \frac{m_{ox}'/m_{oxy}}{p'/p} - \frac{m_f'/m_f}{p'/p} \right) \frac{m_f}{m_{oxy} + m_f}$$  \hfill (57)

Employing Equation 44, the definition of the pressure coupled response, the expression becomes:

$$\frac{\alpha'/\alpha}{p'/p} = (R_{pox} - R_{pf}) \frac{m_f}{m_{oxy} + m_f}$$  \hfill (58)

where the term on the far right is the fuel mass fraction which can be replaced by the equivalent oxidizer mass fraction expression to yield:

$$\frac{\alpha'/\alpha}{p'/p} = (R_{pox} - R_{pf}) (1 - \alpha)$$  \hfill (59)

The overall temperature perturbation term can thus be written:

$$\frac{T_f'/T_f}{p'/p} = (R_{pp'} - n) \frac{c_{pc}}{\sigma \bar{T}_f c_p} + \frac{T_f'}{\alpha} \frac{\bar{T}_f}{\bar{T}_f} (R_{po} - R_{pf})(1 - \alpha)$$  \hfill (60)

where the ratio of mean oxidizer fraction to flame temperature is needed to balance out Equations 54 and 59.

Since the Denison and Baum model ignores the effects of gas phase
molecular weight shifts, only the molecular weight perturbation due to mixture ratio fluctuations can be calculated. As can be anticipated, this derivation follows that for the corresponding flame temperature perturbation term, starting from a plot of molecular weight versus percent oxidizer shown in Figure 12. A slope plot from this curve is provided as Figure 13, leading the following curve fitting equation:

\[
\frac{M'/a'}{A^3 + B^2 + C + D}
\]

\[
A = -78.7
\]
\[
B = 167.3
\]
\[
C = -115.4
\]
\[
D = 26.0
\]

Following the same steps as used in deriving Equations 56 through 59, the overall molecular weight contribution is found to be:

\[
\frac{M'/\overline{M}}{p'/\overline{p}} = \left( R_{po} - R_{pf} \right) \frac{M'}{\overline{M}} \frac{\alpha}{\overline{\alpha}} (1 - \overline{\alpha})
\]

Summarizing the equations necessary to investigate the effects of fluctuating o/f ratio, Equations 38 through 42 are needed to calculate the pressure coupled responses of the overall propellant, oxidizer, and binder. Equation 60 provides the flame temperature corrections due to the o/f changes, while Equation 62 does the same for the molecular weight effects. Finally, Equation 51 relates these two quantities with the propellant's pressure coupled response to obtain the corrected acoustic admittance for the KLEF dominated region.

An examination of these equations reveals a large number of parameters both for the individual binder and oxidizer as well as the overall propellant.
This poses an interesting problem, because normally in the literature one finds either data pertaining to a propellant being treated as a homogeneous entity or information concerning the properties of binders or oxidizers. The problem thus becomes one of finding a consistent set of data for both the overall propellant and the constituent binder and oxidizer. The path taken here has been to examine some of the more commonly referenced papers to assemble a table of typical values, the result being Table 2.

Because the concept of a pressure coupled response is not normally applied to binders and oxidizers singularly, some thought has to be given to the definitions of pressure exponent and temperature sensitivity. Both of these quantities are normally defined in terms of steady state variables as stated below:

\[ \sigma_p = \left. \frac{\partial \ln r}{\partial \ln \rho} \right|_p \] \hspace{1cm} (63)

and

\[ n = \left. \frac{\partial \ln \rho}{\partial \ln \rho} \right|_{T_0} \] \hspace{1cm} (64)

In the context of a one dimensional analysis, steady state implies that the propellant, oxidizer, and binder have to be regressing at the same rate.

Since this condition must be met at all pressures and bulk initial temperatures, the behavior of the oxidizer and binder with regards to Equations 63 and 64 must agree with that of the overall propellant. Thus, all three share the same pressure exponent and temperature sensitivity. For the calculations which will be shown in this paper, the pressure exponent will be taken directly from Table 2, while the temperature sensitivity will initially be calculated via Equation 53, again employing information from Table 2.
With the above parameter values and the information in the previously presented figures, calculations showing the relative importance and behavior of the various constituent terms of Equation 51 can now be made.

Figure 14 shows the real and imaginary parts of the overall propellant pressure coupled response as a function of frequency for propellants with 80, 85, and 90 percent solid loadings respectively, a range wide enough to encompass both "laboratory" and "practical" propellants. At this point, it's important to introduce a difficulty that was noted during the early stages of this research. The important aspect of all of the curves is their relatively low peak values compared to experimental response curves seen in the literature. (41)

Looking at the A and B parameters, which determine the shape and relative magnitude of the response, one finds that, for this propellant, the A value is 8.46 and the B value ranges from 1.76 (80%) to 2.25 (90%). Referring to Cohen's paper (41), this A value is not atypical, but the B values are too large by a factor of about two. Looking at Equation 40, the ways to decrease B are limited to increasing the temperature sensitivity and/or surface temperature, since no significant changes can be anticipated for the initial bulk propellant temperature. Of the two choices, the surface temperature can only be changed a small amount, because of the constraints imposed on the surface temperatures of the binder and oxidizer as discussed in the previous steady state analysis.

This leaves the temperature sensitivity. Based on the information in Table 2 and Figure 10, the temperature sensitivity ranges from 0.001 1/K (80%) to 0.0008 1/K (90%) at a pressure of 6.89 MPa. The literature shows that, in the vicinity of this pressure, a more typical value for a AP-PBAN propellant
is 0.002 1/K. (44)

Since the temperature sensitivity is found via Equation 53, the question now becomes whether this equation should be discarded and replaced by the constant value for the temperature sensitivity noted above or the equation kept with one or more of its parameters altered in such a manner to have the temperature sensitivity at some oxidizer loading match the above value. Since there does not appear to be any greater merit in either scheme, both will be employed, and comparisons drawn on the corresponding results.

With this dilemma resolved, the remaining parameter values from Table 2 and the information in the previously presented figures can now be employed to perform calculations showing the relative importance and behavior of the various constituent terms of Equation 51.

Figures 15 and 16 show the real and imaginary parts of the propellant, flame temperature, and molecular weight responses as a function of frequency for propellants with 80, 85, and 90 percent solid loadings for the case of constant temperature sensitivity and constant gas phase activation energy respectively. In Figure 15, the values of the gas phase activation energy needed to maintain the temperature sensitivity value of 0.002 1/K are shown with each plot, while the different values of temperature sensitivity found with a constant gas phase activation energy of 48640 cal/gmol are provided in Figure 16 with their corresponding plots. In both figures, the temperature and molecular weight responses are labeled as Tp and Mp, respectively.

In both cases, there are non-linear (relative to percent oxidizer) and non-proportional (between the three terms) reductions in all three responses as oxidizer fraction increases.

Of the added terms, the biggest effect is due to the flame temperature
fluctuations; but the effect is only important at lower solids loadings. For the 80 percent case, the peak flame response is 46 percent of the overall propellant peak response. When the loading is increased to 90 percent, the percentage drops to 5.26 for the varying temperature sensitivity case (Figure 16) and only 4.36 for the constant temperature sensitivity plot (Figure 15).

However, with the slight shift in the peak frequency location, the impact on the overall response is still seen, particularly at the lower solids levels, as an influence on the shape and peak location of the acoustic admittance.

The best way to examine the temperature response effect is to examine the behavior of its two component terms independently. Figures 17 and 18 facilitate this for the constant and varying temperature sensitivity cases. In each, the component arising from the lag in the condensed phase response is labeled as 1, while the o/f effect is labeled as 2. The changes in the former curve for the varying temperature sensitivity case are mainly due to drop in overall propellant response when proceeding from 80 to 90 percent solids and the countering increase in the inverse temperature sensitivity. The former drops by 52 percent at the peak response value, while the latter rises by 133 percent. This coupled by the lesser effect of the higher flame temperature, which as its inverse drops by 84 percent, leads to an overall drop for the varying temperature sensitivity case of roughly 59 percent. In the constant temperature sensitivity case, there clearly will not be any effect of varying the temperature sensitivity, but this is balanced by the reduced change in the overall propellant response which now drops only 1 percent from the 80 to 90 percent solids situations. This small change added to that from the inverse flame temperature effect discussed above results in an overall drop of 17
percent between the two extreme loadings cases. It is curious to note, that when comparing the peak values of the flame temperature term to that of the overall propellant response for the varying and constant temperature sensitivity cases, the percentage (7.8) is the same. It is believed that this is just a coincidence.

More dramatic are the changes in the o/f term, mainly because of its dependence on the oxidizer fraction and perturbation relation between that parameter and the flame temperature. The flame temperature effect is still present, but only accounts for approximately 19 percent of the change in response when going from 80 to 90 percent for the constant temperature sensitivity case; the term's significance is slightly smaller for the varying temperature sensitivity case, where it accounts for 16 percent of the overall peak magnitude drop. In the constant temperature sensitivity case, the majority of the effects are due to the mean oxidizer and fuel fraction product (29%) and the perturbation ratio of flame temperature and oxidizer fraction (35%); the difference in the pressure coupled responses of the binder and oxidizer accounts for only 17 percent of the total peak magnitude drop. The varying temperature sensitivity case is just the opposite as the pressure couple response difference accounts here for 33 percent, while the perturbation ratio and mass fraction product account for 28 and 23 percent of the total change respectively. However, in a key sense, the most important term in both cases is the ratio of perturbation flame temperature to oxidizer fraction, the quantity plotted in Figure 11. Referring back to that figure, a very significant change occurs at roughly 88 percent oxidizer. Below that point, positive changes in oxidizer fraction yield positive, in phase changes in flame temperature; but, above that point, the phase relationship is 180
degrees such that positive oxidizer mass ratio fluctuations result in negative flame temperature changes. Thus, at higher loadings, this term subtracts from the solid phase lag term to reduce the overall effect on the acoustic admittance of mixture ratio oscillations. Another component whose importance extends beyond its magnitude contribution is the difference in the binder and oxidizer responses. Because of their different properties, the oxidizer and binder have different frequency response characteristics from each other and the overall propellant. The fact that they enter in as a difference results in further behavior changes. It is these differences which lead to the peak frequency shift in the overall flame temperature response.

The molecular weight term is very similar to the o/f term just discussed, with the exceptions that molecular weight fluctuations are small and monotonically increasing over the range of oxidizer fractions of interest. As with the o/f term, the effect on the difference between response functions is significantly altered from the constant to varying temperature sensitivity cases. In the former, the difference in oxidizer and binder responses at the peak value create only a 2 percent drop when comparing the 80 to 90 percent loadings calculations; while, in the latter, the difference is on the order of 40 percent. Of the remaining terms, the inverse mean molecular weight represents the smallest change, 84 percent from 80 to 90 percent. This is followed by the perturbation ratio at 63 percent and the mass fraction product at 57 percent. Because the molecular weight is inversely related to the density in Equation 49, it enters 180 degrees out of phase into Equation 48, explaining why its negative is plotted. Because of the monotonistic nature of the variation of molecular weight with oxidizer mass fraction over the range of interest, there will be no phase shift as in the case of the flame temperature
relationship. This means that the molecular weight effect will remain out of phase and decrease the overall acoustic admittance for any mean oxidizer loading situation. The significance of this point can't be underestimated. For example, consider the 85 percent oxidizer loading case. Here, the temperature and molecular weight terms so nearly cancel, that the overall effect on the acoustic admittance is negligible.

The analysis presented above is based on two rather extreme assumptions: first, that an essentially two-dimensional problem can be treated as a combination of one-dimensional sub-problems; and, second, that the frequency behavior of each of these component problems can be found via an existing, highly restrictive one-dimensional combustion response model. The obvious reason for proceeding with such an analysis is the simplicity that it affords, but what can be expected if a more thorough two-dimensional analysis is performed? In that case, lateral heat transfer between the slabs of oxidizer and binder will reduce differences in their surface temperatures in the interface region where the KLEFF is the important heat source. In the context of the above analysis, they will then have the same B term (Equation 40), since temperature sensitivity is the same for both. However, the A terms (Equation 39) will be different by roughly a factor of 2 owing to the remaining differences between the oxidizer and binder activation energies. Cohen (41) has shown that, even with the same B, there are still significant differences in relative response peak magnitudes and frequencies; however, the differences become much less noticeable as one proceeds to higher values of B. As the oxidizer and binder response curves approach one another, the response elements dependent on the difference between the two will tend to zero. This eliminates the molecular weight fluctuation effect altogether, but there will
still be some flame temperature effect owing to the condensed phase lag term. However, the latter will now be in phase with the propellant response, thus reducing its importance.

Another question of interest is under what conditions would the effects of mixture ratio oscillations be greatest? Based on the previous section, one answer is at the lower oxidizer loadings. Of course, very few, if any, practical propellants have loadings on the order of 80 percent. However, this figure is not unusual for the so-called laboratory or experimental propellants, where monomodal propellants are produced for particle size experiments. Because of packing constraints, these propellants are restricted to loadings below 80 percent. So, one conclusion that may be drawn from this study is that such propellants may exhibit unusual response behavior relative to more practical formulations due to the effects shown in this analysis.

Another way to modify the results would be to consider oxidizers and binders with different characteristics, in particular activation energies and surface temperatures, so as to modify their relative pressure coupled responses. If the response of the oxidizer were sufficiently enhanced, the magnitude and phase of the flame temperature component could be dramatically altered. There is a relation between the A and B parameters which can be used to show the relative degree of response for different sets of these parameters (35, 42, 43, 18):

\[
\frac{B+1}{(B-1)^2} \geq A
\]  

(65)

The closer the quantity on the left is to that on the right, the greater the overall response. In conjunction with Equations 39 and 40, this could be used to test different oxidizer and binder combinations to see which provides
the maximum disparity in responses. However, this will not be done here.

In conclusion, this analysis shows that the effect of mixture ratio oscillations is generally small for practical propellants, but can be significant for so-called laboratory propellants with their lower solids loadings. The effects are mainly due to flame temperature perturbations resulting from the inability of the condensed phase to respond rapidly to changes in heat flux and to flame temperature fluctuations resulting directly from fluctuations in the o/f ratio. Molecular weight fluctuations result in much smaller effects on the overall acoustic admittance and under most practical conditions are negligible. Two-dimensionality is predicted to lessen the impact of mixture ratio fluctuations, while different combinations of oxidizers and binders (other than the examined AP-PBAN system) will also affect the results.

One final comment concerns the application of this analysis to the complete model. This analysis represents the surface response portion of the module for the KLLEF dominated region. In the next section, the gas phase details of the KLLEF will be modeled. At some point, these two models must be joined to produce a total model of the KLLEF region for insertion in the total response model.

3.2.3 DYNAMIC RESPONSE OF THE INTERFACE MIXING REGION

While the KLLEF is a pre-mixed, kinetically limited flame, its location depends strongly on the details of the mixing fan issuing from the interface between the oxidizer and binder surfaces. Price and co-workers (4) employed this point to discuss the behavior of the KLLEF under steady state conditions with a simple dimensional analysis using a presumed KLLEF profile defined in a
functional manner. A logical extension of that analysis is to describe the mixing region in an explicit fashion, determine the KLLEF location within the region, and then link the KLLEF location with the characteristics of the mixing region in that locale. A further extrapolation starts with a calculation of the response of the mixing region to pressure and inflow property oscillations. Since this work is still in progress, only a brief look at what has been accomplished and what is planned is possible.

The basis of the mixing region analysis is the Burke-Schumann diffusion flame solution. This classic work examines two burner geometries, a concentric cylindrical burner producing an axial-symmetric diffusion flame and a parallel plat burner producing a flat flame. As the problem under consideration is that of alternating slabs of oxidizer and binder, the latter analysis will be used.

As the parallel plate burner version of the Burke-Schumann analysis is rarely seen, a rederivation has been performed. The geometry of the problem is shown in Figure 19, with particular attention drawn to the parameters describing the burner dimensions and to the coordinate system being used. Although the lengthy details of the rederivation will not be recounted here, the assumptions used in the analysis will be discussed below with attention given towards their impact on the laminate problem.

The following assumptions are commonly applied to combustion analyses.

1. No body forces are applied. This assumption ignores the effects of gravity and natural convection, the latter being more important at low flow velocities.
2. Thermal diffusion or Soret and Dufour effects are not considered.
Thermal diffusion is normally small compared to diffusion due to concentration gradients, often by more than an order of magnitude.\(^{(8)}\)

3. Pressure gradient diffusion is ignored. This is again usually a small effect.\(^{(8)}\)

4. Terms involving the bulk viscosity are neglected. A later assumption will ignore the remaining viscous terms. Outside of boundary layers, this is a reasonable assumption.

5. Radiation heat transfer is not considered. Although not necessarily negligible, the simplifications arising from its removal from the system of equations are significant, making the problem more tractable.

The second major set of assumptions used in the derivation are so commonly applied to combustion analyses that they have been given a collective name, the Shvab-Zeldovich formulation.\(^{(8)}\) These assumptions are:

6. Steady state conditions are assumed.

7. Flow speed is low.

8. Viscous effects are considered negligible. In low speed, steady flows, this is an acceptable assumption.\(^{(8)}\) This combined with the above assumptions results in the momentum equation yielding the result that pressure is, approximately, constant.\(^{(8)}\)

9. Binary diffusion coefficients are equal. This allows use of Fick's Law, a commonly postulated diffusion relation.

10. The Lewis number is unity. This is required to simplify the governing equations.

By making one more assumption, a very useful common expression for the conservation of energy and conservation of species can be obtained. This assumption is:
11. Chemical reactions occur in a single reaction step. This may not be strictly true for the complex combustion processes associated with solid propellant decomposition products; but the real processes are not fully known in any case, and the resultant simplification is significant.

With the above assumptions, the energy and species conservation equations can be manipulated to equal, respectively:

\[ v \left( \frac{\rho u T}{\int h_1^T \mathrm{d}T} - \rho \int h_1^T \mathrm{d}T \right) = \frac{\omega_i}{M_i(v_i - v_i)} \]  
(66)

and

\[ v \left( \frac{\rho u a_i}{M_i(v_i - v_i)} - \rho \int a_i \mathrm{d}v \right) = \frac{\omega_i}{M_i(v_i - v_i)} \]  
(67)

By subtracting one of the species equations from the energy equation or subtracting one species equation from another, the non-linear reaction term is removed, producing a simple linear differential equation:

\[ v \left( \frac{\rho u (a_i / M_i(v_i - v_i)) - (a_i / M_j(v_j - v_j))}{M_i(v_i - v_i) - M_j(v_j - v_j)} \right) = 0 \]  
(68)

A further six assumptions take Equation 68 to the final differential equation of the Burke-Schumann analysis.(8)

12. The single reaction is of the form:

\[ v_f \dot{g}_f + v_o \dot{g}_o + \sum v_i \dot{g}_i \]  
(69)
Again, this may not be correct for the case of solid propellant combustion, but it does simplify the analysis a great deal.

13. Flow is one-dimensional out of the ducts. This is basically the same as saying that regression is normal to the surface and that the surface is flat.

14. The mass flow per unit area is constant everywhere. This poses a serious restriction on the regression rates of the oxidizer and binder, which may not be desirable. Analyses do exist where this restriction is lifted, but they are significantly more complex. (46)

15. The product of density and the diffusion coefficient is constant. This is another assumption made to improve tractability.

16. Lateral diffusion is much greater than vertical diffusion.

17. The burner is semi-infinite in the transverse direction. This is the same as saying the slabs are infinitely long.

With these assumptions, Equation 68 becomes:

\[ \rho u_y \frac{\partial \beta}{\partial y} - \rho D \frac{\partial^2 \beta}{\partial x^2} = 0 \]  

where:

\[ \beta = -\frac{\alpha_o}{M_o v_o} + \frac{\alpha_f}{M_f v_f} \]  

and an examination of Figure 19 results in the definition of the following boundary conditions:

\[ \beta = \frac{\alpha_f}{M_f v_f} \quad y = 0, \ a \leq x \leq a \]  

\[ \beta = -\frac{\alpha_o}{M_o v_o} \quad y = 0, \ -b \leq x \leq -a \text{ and } a \leq x \leq b \]  

and
\[ \frac{\partial b}{\partial x} = 0 \quad x = \pm b, \quad y > 0 \]  \hspace{1cm} (74)

This final boundary condition is needed to allow a final solution to be obtained. In the slab problem, there is no such boundary preventing diffusion of the gas beyond the projected edge of the oxidizer slabs in the gas phase. However, since interest is focused on the interface region, it is a simple matter when using this solution to set the oxidizer slab widths to some large value.

It is easier to work with a non-dimensionalized form of these equations. The non-dimensional variables are:

\[ \xi = x/b \]  \hspace{1cm} (75)

\[ \eta = yD/u_y b^2 \]  \hspace{1cm} (76)

\[ C = a/b \]  \hspace{1cm} (77)

\[ \nu = \frac{\alpha_{0,0} / M_0 \nu_0}{\alpha_{f,0} / M_f \nu_f} \]  \hspace{1cm} (78)

and

\[ \gamma = \frac{\alpha_{f,0} \nu_f}{\alpha_{f,0}} \]  \hspace{1cm} (79)

Thus, the system of equations becomes:

\[ \frac{\partial \gamma}{\partial \eta} = \frac{\partial^2 \gamma}{\partial \xi^2} \]  \hspace{1cm} (80)

with boundary conditions:

\[ \gamma = 1 \quad \eta = 0, \quad -C < \xi < C \]  \hspace{1cm} (81)

\[ \gamma = -\nu \quad \eta = 0, \quad -1 < \xi < -C \text{ and } C < \xi < 1 \]  \hspace{1cm} (82)
and

\[ \frac{\partial \gamma}{\partial \xi} = 0 \quad \xi = \pm 1, \eta > 0 \]  

(83)

Equations 80 through 83 are recognizable as the same equations that govern the heat conduction in an insulated rod.(47) The solution is:

\[ \gamma = C(1+v) - v + \frac{2(1+v)}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \cos(n\pi \xi) \sin(n\pi \eta) e^{-\frac{n^2 \pi^2 \eta}{a^2}} \]  

(84)

or, substituting back for the original physical variables:

\[ \frac{\alpha_o}{M_o(-v_0)} - \frac{\alpha_f}{M_f(-v_f)} = \frac{a}{b} \left( \frac{\alpha_{f,0}}{M_f v_f} + \frac{\alpha_{o,0}}{M_o v_o} \right) \]

- \[ \frac{\alpha_{o,0}}{M_o v_o} + \frac{2}{\pi} \left( \frac{\alpha_{f,0}}{M_f v_f} + \frac{\alpha_{o,0}}{M_o v_o} \right) \cdot \]

\[ \sum_{n=1}^{\infty} \frac{1}{n} \cos \left( \frac{n\pi x}{L} \right) \sin \left( \frac{n\pi y}{W} \right) e^{-n^2 \pi^2 yD/u_y b^2} \]  

(85)

It is important to note that the above solution is for the difference in the mass fractions of the oxidizer and fuel gases. It thus allows a map of the concentration field in the entire mixing region to be obtained. In the Burke-Schumann analysis, the flame sheet approximation would now be applied to solve for the flame surface location, taken to be the stochiometric surface, where the fuel and oxidizer mass fractions are both zero. However, as we are interested in mapping the entire mixing region, this step will not be taken.

Since the non-steady behavior of the mixing region is desired, a perturbation analysis is also needed. In the Denison and Baum model, the steady state gas phase reaction equation is linearized by the expansion of all
pertinent variables into mean plus perturbation form. This has been done to Equation 85 with the following result:

\[
\frac{\alpha_0}{M_0(-\nu_o)} - \frac{\alpha_f}{M_f(-\nu_f)} = \frac{a}{b} \left( \frac{\alpha_{f,0}}{M_f v_f} + \frac{\alpha_{o,0}}{M_o v_o} \right) - \frac{\alpha_{o,0}}{M_o v_o} + 2 \pi \left( \frac{\alpha_{f,0}}{M_f v_f} + \frac{\alpha_{o,0}}{M_o v_o} \right).
\]

(34)

\[
\sum_{n=1}^{\infty} \frac{1}{n} \cos \left( \frac{n \pi x}{b} \right) \sin \left( \frac{n \pi a}{b} \right) \sum_{k=0}^{\infty} \frac{1}{k!} \left( \frac{n^2 \pi^2 D_1}{b^2} \right)^k \left( \frac{k p k - 1 p^2}{u_y} \right) y^k
\]

\[
+ \frac{2}{\pi} \left( \frac{\alpha_{f,0}}{M_f v_f} + \frac{\alpha_{o,0}}{M_o v_o} \right) \sum_{n=1}^{\infty} \frac{1}{n} \cos \left( \frac{n \pi x}{b} \right) \sin \left( \frac{n \pi a}{b} \right) \sum_{k=0}^{\infty} \frac{1}{k!} \left( \frac{n^2 \pi^2 D_1}{b^2} \right)^k \frac{k - 1}{u_y} y^k
\]

(86)

\[
\text{where pressure has entered by assuming a linear relationship between pressure and the diffusion coefficient as follows:}
\]

\[
D = D_1 p
\]

(87)

It must again be explained that the inflow velocities are not independent in this analysis, thus imposing severe restrictions on the possibilities of imposed inflow oscillations.

As of this writing, this is the current status of this development. A computer program of the solution is being written, and parameter values are being obtained from the literature. When completed, the code will provide contour maps of the concentration field in the interface region and the corresponding response function information.

3.3.4 Combustion Response in the AP Dominated Region

The combustion response in the AP dominated region has been calculated
under the assumption that the combustion processes involved are analogous to those of a homogeneous propellant. Thus, the Denison and Baum model can be employed to calculate the pressure coupled response, using the thermal and kinetic properties of AP listed in Table 2 and values for the temperature sensitivity \(0.00155 \text{ 1/K}\) and pressure exponent \(0.492\) for AP as a monopropellant.\(^{(49)}\) The resulting pressure coupled response is shown in Figure 20.

A question still exists as to how the effects of heat transfer from outside the self-deflagration region impact this region’s response and whether steps must be taken to correct for any changes resulting from such an effect.

3.3 PROPOSED RESEARCH

3.3.1 KLLEF STUDIES

The next step in this research will be to define the KLLEF location and extent within the interface mixing region. This will be accomplished through extrapolation of the information obtained in previous sandwich burning studies. By doing this, it will be possible to link this location with the diffusion model and study the oscillations in KLLEF location due to diffusion processes.

However, on the whole, KLLEF response behavior is more complicated with kinetics effects, quench limit effects, and interactions with the final diffusion flame, e.g., stoichiometric tip retraction. A thorough model of the KLLEF will have to incorporate models for these phenomena.

Eventually, it is hoped that the KLLEF model can be incorporated explicitly in the surface response model previously discussed. If possible,
the KLLEF model may be embedded into the Denison and Baum model.

3.3.2 DIFFUSION FLAME STUDIES

A model for the final diffusion flame is also needed. The above diffusion analysis is a likely starting point, but the basic question of how the diffusion flame enters into the acoustic admittance must be answered. Because of its location far out in the gas phase, it is doubtful that the diffusion flame has a major effect on the surface response. It will still have an effect, as yet undetermined, on the overall acoustic admittance.

3.3.3 COUPLING STUDIES

With the component models completed, a scheme for fractioning the overall response between the different components must be devised. Such a scheme will have to depend heavily on information from the experimental studies previously performed.

3.3.4 MODEL VERIFICATION AND QUALITATIVE EXTENSION TO PROPELLANTS

Studies with the completed model will focus on determining the model's behavior to a wide range of situations and correlating the model's performance with predicted slab combustion traits, e.g., the predicted anomalies in response near regions of KLLEF detachment. Finally, qualitative extension of the model's results will be made to true heterogeneous propellants.
Figure 1. Oxidizer-Binder Laminate Pyrolysis Model.
Key: 1. binder lamina, 2. interface plane between oxidizer and binder, 3. oxidizer surface adjoining binder (smooth band), 4. leading edge of oxidizer burning front, 5. oxidizer region that regresses at the normal AP self-deflagration rate, 6. AP flame, 7. leading edge of AP flame, 8. oxidizer flame modified by the anomalous decomposition in the smooth band (flame may be quenched), 9. oxidizer-fuel diffusion region with stoichiometric surface indicated by broken line, 10 - 11. Kinetically Limited Leading Edge Flame (KLLF), 12. diffusion flame, and 13. stoichiometric tip of diffusion flame.

Figure 2. Oxidizer-Binder Laminate Combustion Zone. (4)

a. Very Low Pressure (p<0.4 MPa)  b. Low Pressure (0.4<p<2.0 MPa)

Figure 3. Trend in Oxidizer-Binder Combustion Zone Structure with Binder Lamina Thickness. (4)
Figure 4. Flame Structure Postulated in Beckstead, Derr, and Price Model. (9)
Figure 5. Non-Dimensional Flame Standoff Distance Versus Oxidizer Volume Fraction Calculated from BDP Approximate Solution and Exact Burke-Schuman Solution.(6)
Figure 6. Range of Kinetic Parameters.


\[ r = 0.5 \text{ cm/sec} \]
\[ s_{ox} = 50 \mu m \]
\[ L_{ox} = -80 \text{ cal/g} \]
\[ T_{sox} = 870^\circ \text{ K} \]
\[ L_F = 250 (\text{cal/g}) \]

\[ r = 0.5 \text{ cm/sec} \]
\[ s_{ox} = 33 \mu m \]
\[ L_{ox} = 0 \text{ cal/g} \]
\[ T_{sox} = 820^\circ \text{ K} \]
\[ L_F = 250 (\text{cal/g}) \]
Key: a. solid line is surface without lateral heat transfer, while broken line is postulated surface when lateral heat flow occurs, b. surface for thin binder laminate when lateral heat flow occurs (4), and c. surface of thin binder sandwich burning at high pressure (approximately 10 MPa) (4).

Figure 8. Laminate Profiles Based on Experimental Sandwich Experiments and Physical Arguments.
Figure 9. Non-Dimensionalized Standoff Distance Versus Heat of Phase Change as a Function of Surface Temperature.
Figure 10. Flame Temperature Versus Oxidizer Mass Fraction.

Figure 11. Perturbation Flame Temperature Versus Oxidizer Mass Fraction.
Figure 12. Gas Phase Molecular Weight Versus Oxidizer Mass Fraction.

Figure 13. Perturbation Molecular Weight Versus Oxidizer Mass Fraction.
Figure 14a. Real Part of the Propellant Pressure Coupled Response Calculated from the Denison and Baum Model.
Figure 14b. Imaginary Part of the Propellant Pressure Coupled Response Calculated from the Denison and Baum Model.
Figure 15a. Combustion Response in the KLLEF Dominated Region for 80% AP Formulation (Constant Temperature Sensitivity).
Figure 15b. Combustion Response in the KLEF Dominated Region for 85% AP Formulation (Constant Temperature Sensitivity).
Figure 15c. Combustion Response in the KLLEF Dominated Region for 90% AP Formulation (Constant Temperature Sensitivity).
Figure 16a. Combustion Response in the KLLEF Dominated Region for 80% AP Formulation (Varying Temperature Sensitivity).
Figure 16b. Combustion Response in the KLLEF Dominated Region for 85% AP Formulation (Varying Temperature Sensitivity).
Figure 16c. Combustion Response in the KLEEF Dominated Region for 90% AP Formulation (Varying Temperature Sensitivity).
Figure 17a. Flame Temperature Response Components in the KLLEF Dominated Region for 80% AP Formulation (Constant Temperature Sensitivity).
Figure 17b. Flame Temperature Response Components in the KLLEF Dominated Region for 85% AP Formulation (Constant Temperature Sensitivity).
Figure 17c. Flame Temperature Response Components in the KLLEF Dominated Region for 90% AP Formulation (Constant Temperature Sensitivity).
Figure 18a. Flame Temperature Response Components in the KLLEF Dominated Region for 80% AP Formulation (Varying Temperature Sensitivity).
Figure 18b. Flame Temperature Response Components in the KLLEF Dominated Region for 85% AP Formulation (Varying Temperature Sensitivity).
Figure 18c. Flame Temperature Response Components in the KLLEF Dominated Region for 90% AP Formulation (Varying Temperature Sensitivity).
Figure 19. Parallel Plate Burner Geometry for Burke-Schuman Diffusion Flame Analysis.
Figure 20. Pressure Coupled Response for Ammonium Perchlorate.
Table 1. Ammonium Perchlorate and PBAN Properties

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<th>Symbol</th>
<th>Values</th>
<th>Comments</th>
<th>Ref.</th>
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<tr>
<td>r</td>
<td>0.3 - 1.0 cm/sec</td>
<td>over p range 1 - 10 MPa</td>
<td>4,24</td>
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<tr>
<td>s&lt;sub&gt;ox&lt;/sub&gt;</td>
<td>50.0 um</td>
<td>within order of magnitude</td>
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<td>avg. value -95.5 cal/g</td>
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<tr>
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<tr>
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<td>T&lt;sub&gt;o&lt;/sub&gt;</td>
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Table 2. Propellant, Oxidizer, and Binder Parameters.

Common

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<td>$T_f$</td>
<td>(Fig. 10)</td>
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Propellant

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<td>$M$</td>
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<tr>
<td>s</td>
<td>standoff distance</td>
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</table>
S  surface area
\( t \)  time
\( t_{ign} \)  ignition delay
T  temperature
u  velocity
V  volume
w  rate of production by chemical reaction
x  lateral coordinate for Burke-Schumann analysis
X  flame standoff distance
y  vertical coordinate for Burke-Schumann analysis
\( \alpha \)  oxidizer mass fraction
\( \beta \)  Burke-Schumann mass fraction variable, fraction of reactants consumed
\( \gamma \)  non-dimensionalized Burke-Schumann mass fraction variable
\( \delta \)  reaction order
\( \varepsilon \)  perturbation variable
\( \zeta \)  oxidizer volume fraction
\( \eta \)  non-dimensional vertical coordinate
\( \lambda \)  thermal conductivity
\( \nu \)  stoichiometric coefficient, inlet o/f ratio
\( \xi \)  non-dimensional lateral coordinate
\( \rho \)  density
\( \sigma \)  oxidizer mode width parameter
\( \sigma_{p} \)  temperature sensitivity
\( \tau \)  lifetime of oxidizer particle
\( \omega \)  frequency
\( \Omega \)  non-dimensionalized frequency
\( \$ \)  chemical species
Subscripts

AP  ammonium perchlorate self-deflagration flame

d  pseudo-propellant

f  fuel, flame

ff  final diffusion flame

g  gas phase

i  oxidizer size counter, species counter

j  oxidizer type counter

k  propellant ingredient counter

L  oxidizer vaporization

ox  oxidizer

p  propellant

pf  primary flame

s  surface

t  total

Superscripts

'  perturbation

-  mean

o  reference state
REFERENCES


