

Sandwich Propellant Combustion

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Introduction

- Composite Propellant combustion has been a topic of research for the last 4-5 decades.
- BDP class of models have tried to address the problem in a one-dimensional framework and as a consequence have neglected some important physical phenomena.
- Models proposed in the latter half of the last decade (IISc, Miccio and Buckmaster and co-workers) have tried to understand the interaction between the binder and AP by looking at a simpler problem of sandwich propellant combustion, a two dimensional analogue of composite propellant combustion.

IISc Model:

- Two-dimensional gas phase aero-thermo-chemistry captured by solving N-S eqns along with energy and species conservation and kinetic model of three reaction steps in the gas phase.
- Quasi-steady two dimensional energy equation accounting for regression was solved in the c-phase.
- Surface of the propellant was assumed to planar.
- Importance of two-dimensional conduction in c-phase was brought out.

Miccio Model:

- Five-reaction gas phase model and taking into account the propellant topology, 2-d gas phase species and temperature diffusion has been proposed.
- Despite solving for 2-d unsteady conduction equation in the c-phase, role of c-phase is marginalized.
- Products of AP combustion and AP and binder combustion are the identical.
- Fluid is assumed inviscid, while 2-d diffusion of species & temp is allowed.
- Regression is allowed for in the x-direction - probably forced him to neglect the momentum equation in the y-direction.
- Gas phase specific heat capacity is thrice the c-phase specific heat capacity.
- Assumes spherical AP as a 2-d object while attempting to solve a mono-modal distribution of AP in a binder matrix.

Buckmaster and co-workers Model:

- Allows for an unsteady non-planar regressing surface solves for both gas & c-phase with appropriate jump conditions across the gas-solid interface.
- The gas phase model has a AP monopropellant flame and final diffusion flame.
- No comparisons with experiments are made, reason being non-availability of experimental data for a periodic sandwich propellant.
- But at pressures above LPDL of AP, heat loss (refer Nir) from the edges of a sandwich propellant are minimal and can be neglected.
- Quenched profiles (refer Price et. al.) of sandwich propellants which shows that at pressures above LPDL of AP, regions of AP which are situated far off (5 to 8 times the conduction layer thickness) from the interface are flat, indicating negligible edge heat loss.

- Assumption of constant density leads to large errors as the temp. in the gas phase increase by at least three fold from surface to the edge of the flame.
- Despite solving for the full c-phase equations, importance of c-phase heat transfer not been brought out.

Major deficiency with all the above mentioned studies is inappropriate attention being paid to the prediction of AP monopropellant combustion.

A successful model for sandwich propellant combustion is possible only if all appropriate aspects of AP combustion are predicted with reasonable accuracy. Hence, this presentation is divided into two parts;

Part A - Results of AP monopropellant combustion including stability.

Part B - Importance of c-phase heat transfer and two diffusion flames in combustion of sandwich propellant.

Part A: AP Monopropellant Combustion

Pioneering works like those of BDP and Guirao and Williams and many others.

Major draw backs with all these being

- Due attention not being paid to the stability of AP monopropellant combustion
- Prediction of the initial temperature sensitivity of burn rate has been quite different from the experimental values obtained by Boggs et. al.
- Predictions regarding LPDL of AP combustion have also been incorrect as will be shown later.
- This presentation, however, aims to examine afresh all features of AP combustion while including the unsteady conduction in the condensed phase ignored by most earlier investigators.

Experimental Observations Utilized in arriving at Parameters chosen

- Burn rate pressure index of 0.77 as reported by Boggs et. al. and Beckstead et. al.
- Initial Temperature Sensitivity of burn rate 0.0015 - 0.0021 K-1 as reported by Boggs et. al.
- AP combustion is stable within 14 MPa.

Objectives:

- Predict Pressure index of burn rate
- Initial Temperature Sensitivity of burn rate
- Low Pressure Deflagration Limit
- All the above with Stability of propellant combustion included

Conservation Equations and Solution Procedure

One-dimensional unsteady conservation equations solved for in the gas phase are the mass, energy and species conservation equations.

One-dimensional unsteady condensed phase energy conservation eqn. is solved for in condensed phase.

Pressure is assumed to be constant in the gas phase.

Computational domain --- region above and below the pyrolysing surface.

Surface fixed coordinate system with condensed phase included --- allows for intrinsic instability based on choice of parameters.

- Conservation equations are solved in Primitive variables using finite volume discretization, with vectors being evaluated at cell faces and scalars at cell centers.
- Condensed phase and gas phase solved independently after obtaining surface temperature
- Density is obtained from equation of state after solving for energy and species
- Lewis number assumed to be unity
- Diffusivities of all species identical

Kinetic Details

Surface decomposition process AP $(1-f)$ APP + (f) APD

'f' fraction of AP decomposing at the surface to AP decomposition Products (APD)

APP is pyrolysis product of AP (NH_3 (gas) + HClO_4 (gas))

Occurs in a liquid layer making pyrolysis exothermic

'f' is connected to the thickness of the liquid layer as

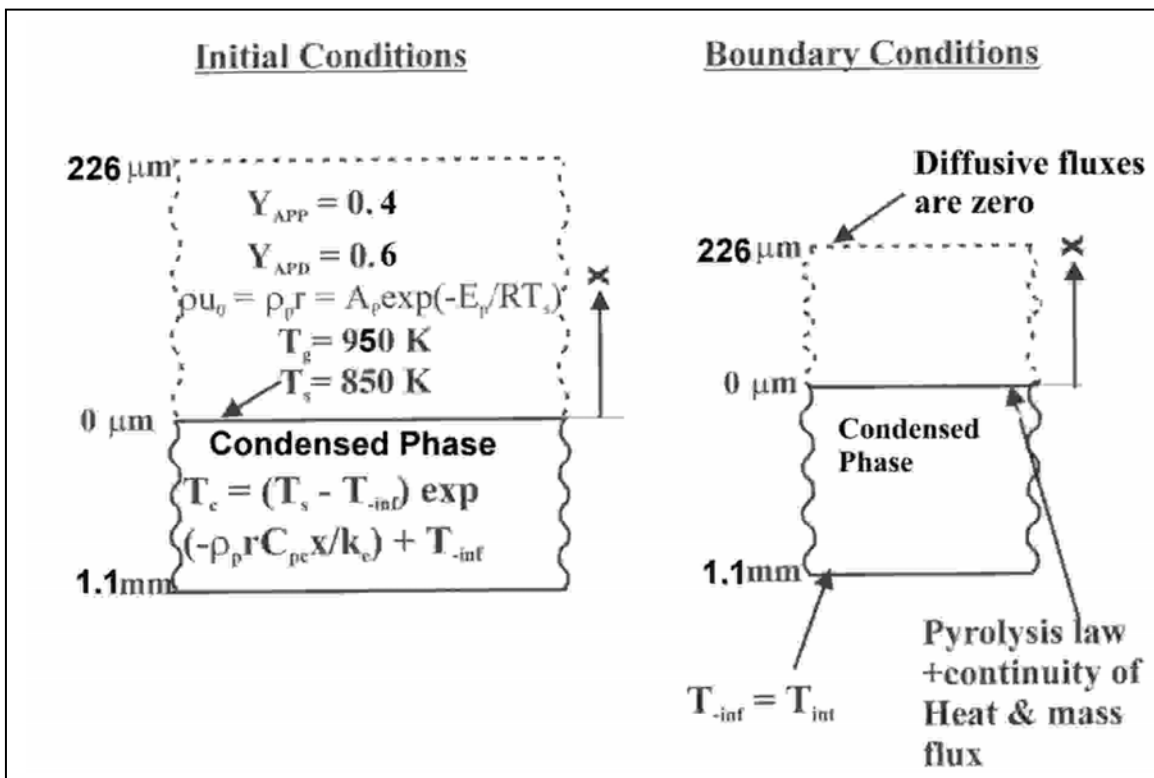
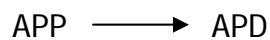
'f' is 0.5 for $T_s > 850$ K (Surface temp. at 2.07 MPa & $r=3.3$ mm/s)

'f' is 0 for $T_s < 825$ K (Melt Temperature)

$f = 0.5 - 0.02(850 - T_s)$

Allows for intrinsic variation of LPDL with Initial temperature

Single reaction gas phase chemical kinetics model



Choice of Parameters

Table of Thermo-physical Properties of AP

Property	Value	Reference
AP Heat of Formation	-2517545 J/kg	JANAF ²⁴
Specific Heat Capacity of Condensed Phase, C_{pCAP}	1602 J/kg	Based on average values of JANAF ²⁴
Thermal Conductivity of Condensed Phase, k_{CAP}	0.21 W/m K	Based on average values of Zanotti et al ²⁵
Density of Condensed Phase, ρ_{CAP}	1957 kg/m ³	Density of Orthorhombic Phase Shoemaker ²⁶
Surface Temperature, T_s	850 K at a pressure of 2.07 MPa and burn rate 3.3 mm/s	Beckstead and Hightower ²³ , Powling ²⁷ , Mitani and Niioka ²⁸
Melt Temperature, T_m	825 K	Beckstead and Hightower ²³

Table of Reaction Rate Parameters, Thermodynamic and Transport Data

Property	Value	Comments and References
C_{pg}	1273.6 - (P - 2.07) * 1.7 J/kg	Tuned to obt. an adiabatic flame temp. variation (obt. from equilibrium calculations) of 1394 to 1412 K at an initial temp. of 299 K.
D_p (1000 K)	4.0075×10^{-5} kg/ms	In the same range as Guirao and Williams ¹¹ , $D_p \sim T^{0.68}$
Mol. Wt. of APP	117.5	
Mol. Wt. of APD	27.8	Obtained from NASA SP-273
Heat of formation of APP	-482220 J/kg	Calculated with inputs from Narahari ²⁹
Heat of formation of APD	-3898200 J/kg	Calculated with inputs from Narahari ²⁹ and NASA SP-273
A_{SAP}	7864 kg/m ² s	Tuned to get a burn rate of 3.3 mm/s for a T_s of 850 K
E_{SAP}	50.24 kJ/kg mole	Obtained through parametric study
A_{gAPF}	8.55×10^5	Obtained through parametric study
E_{gAPF}	27.45 kJ/kg mole	Obtained through parametric study
n_{gAPF}	2	At the pressures encountered in AP combustion 2 nd order reaction are important

Table of Sensitivity Study

Experimental value of $n=0.77$, $sp=0.0015 - 0.0021 K^{-1}$

	Burn Rate Pressure Index	Temperature Sensitivity of Burn Rate
$E_{gAPF}/R = 3800 K^{-1}$	0.8	$0.0026 - 0.00235 K^{-1}$
$E_{gAPF}/R = 3300 K^{-1}$	0.77	$0.00247 - 0.00227 K^{-1}$
$E_{gAPF}/R = 2800 K^{-1}$	0.73	$0.00236 - 0.00221 K^{-1}$
$E_{sAP}/R = 6542 K^{-1}$	0.74	$0.0025 - 0.00235 K^{-1}$
$E_{sAP}/R = 6039 K^{-1}$	0.77	$0.00247 - 0.00227 K^{-1}$
$E_{sAP}/R = 5536 K^{-1}$	0.79	$0.0025 - 0.00223 K^{-1}$
$f = 0.7 (-560 kJ/kg)^{-1}$	0.693	$0.0028 - 0.0024 K^{-1}$
$f = 0.6 (-205 kJ/kg)^{-1}$	0.77	$0.00247 - 0.00227 K^{-1}$
$f = 0.5 (+147 kJ/kg)^{-1}$	0.81	$0.0023 - 0.00218 K^{-1}$

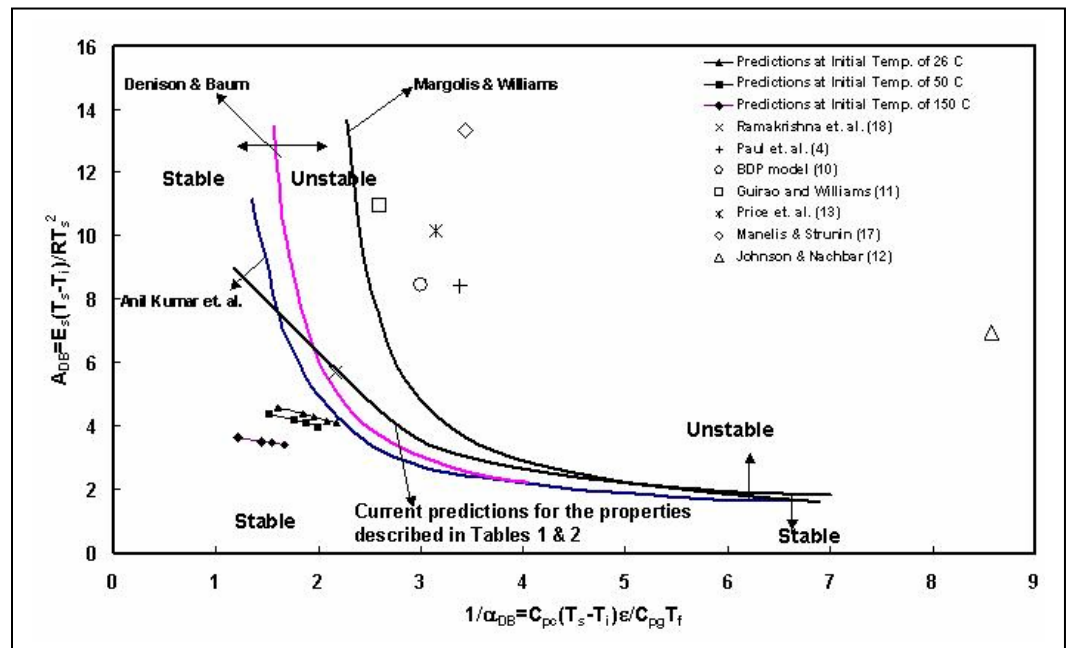
[1] Values indicated within brackets refer to the surface heat release at 2.07 MPa and $T_i = 26 C$

All solutions obtained were grid and time step independent

Results and Discussions - Part A

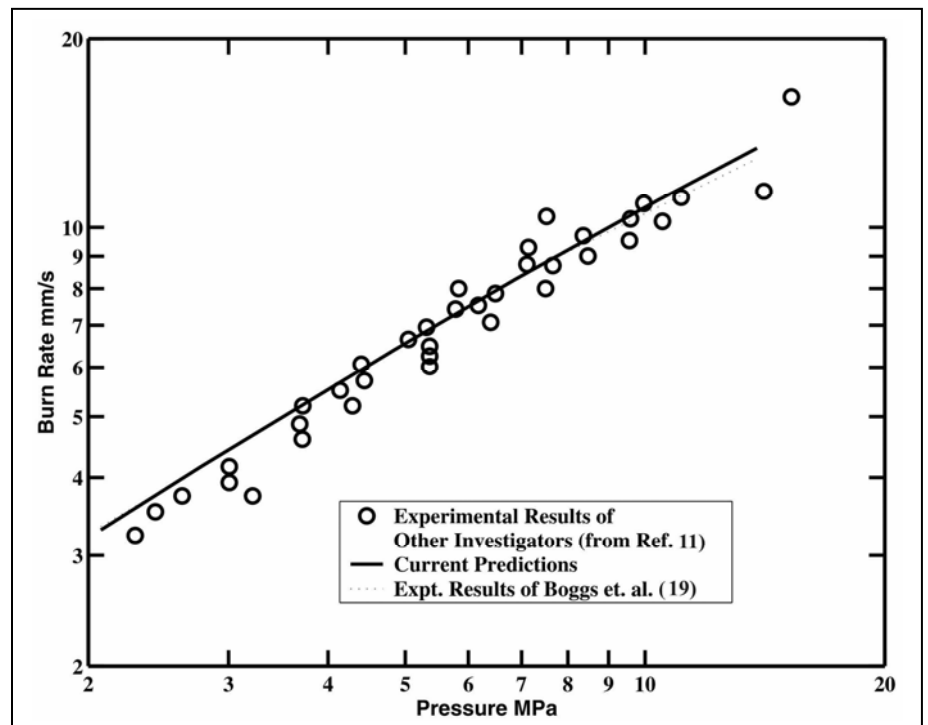
Predicted results of AP combustion on a plot with the stability parameters of Denison and Baum along with the neutral stability curves due to Denison and Baum, Williams and Margolis, Anil Kumar et. al. and current studies.

- BDP Model
 $E_s = 22$ kcal/mole
 $E_g = 30$ kcal/mole
- Guirao and Williams
 $E_s = 28.4$ kcal/mole
 $E_g = 15.5$ kcal/mole
- Paul et. al. $E_s = 22$ kcal/mole $E_g = 31.8$ kcal/mole
- Ramakrishna et. al.
 $E_s = 16$ kcal/mole
 $E_g = 7.94$ kcal/mole
- Current $E_s = 12$ kcal/mole $E_g = 5.96$ kcal/mole



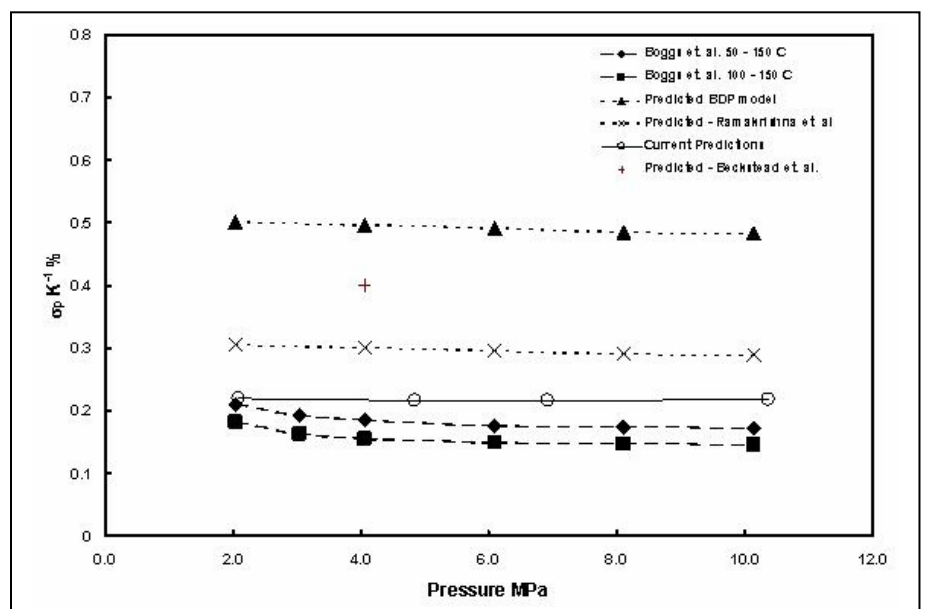
Predicted values of burn rate of AP at various pressures along with experimental results

- Initial Temp. 26 C
- Good agreement with expt. observations of Boggs et al.
- Burn rate pressure index 0.77 up to 7 MPa
- Decreases with increasing Pressure



Predicted initial temperature sensitivity of burn rate as a function of pressure along with experimental and other model results

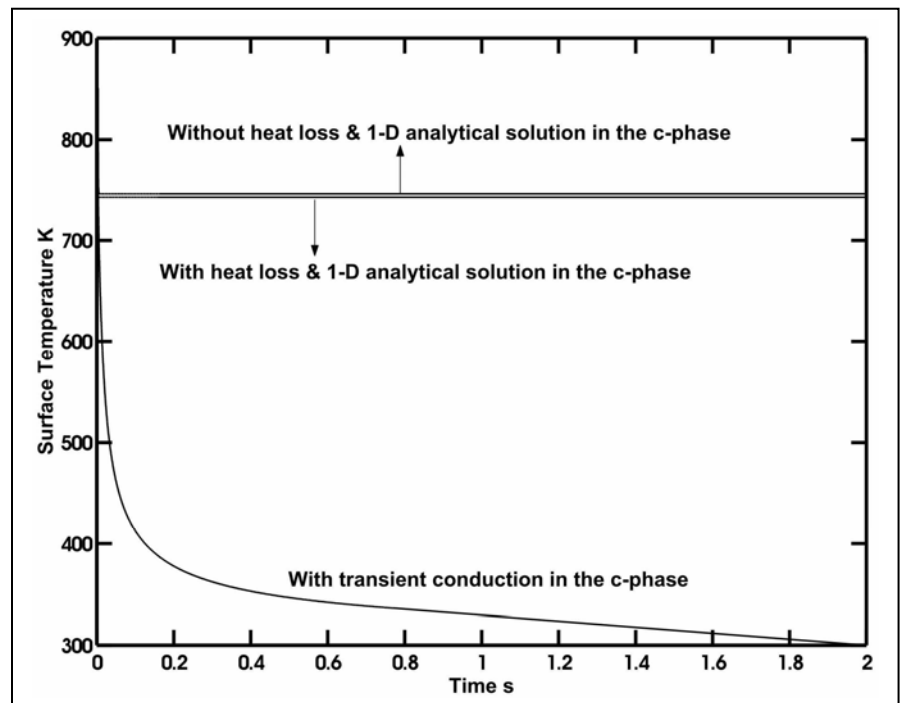
- Predicted values are in reasonable agreement with experimental results.
- Results obtained are better than those obtained by BDP model, Beckstead and Tanaka and our own previous effort.
- Experimental results of Watt and Petersen³⁹ and Friedman et. al.⁴⁰ have not been used here for comparison - presence of small traces of impurity.



Earlier predictions including our own had failed to predict $\dot{\phi}_p$ and this is resolved through invoking a number of factors, the most important of them being the lower activation energy as obtained in high heating rate results of Brill et al.

Surface temperature history for a pressure below LPDL (2.0 MPa) at an initial temperature of 20 C.

- Quasi-steady condensed phase without heat loss - BDP model
- Quasi-steady condensed phase accompanied by a heat loss - Guirao and Williams
- Possible to obtain steady burning at any pressure, despite the loss of liquid layer and consequent loss of activity on the surface.



Solution obtained with transient conduction in the c-phase without heat loss and with the liquid layer model, the surface temperature starts to decrease as the pyrolysis process becomes endothermic. This makes the surface temperature decrease even further making the pyrolysis process even more endothermic. These processes continue till the propellant ceases to burn.

Conclusions - Part A

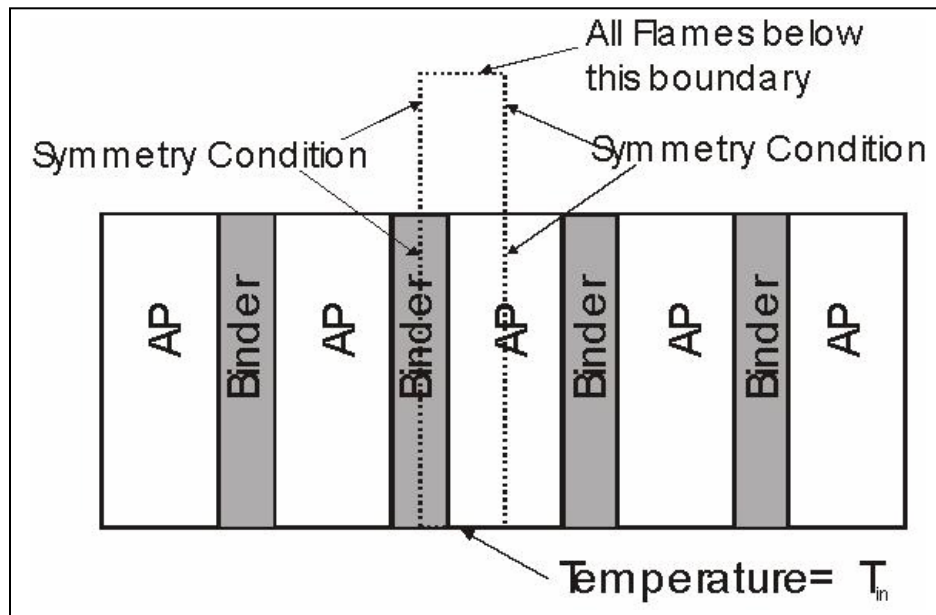
Computations with simple single step gas phase reaction model & surface model have been carried out with a view of simulating all aspects of AP combustion

- $n=0.77$ from 2.07 to 6.9 MPa and decreases from 6.9 MPa to 13.8 MPa
- sp obtained is 0.0021 K^{-1} in good agreement with experimental value of $0.0015\text{-}0.0021 \text{ K}^{-1}$
- LPDL predicted correctly and shown to be not caused by either heat loss or linear instability but due to transient heat conduction into the solid
- *Identifying stability to be a very important criterion in AP combustion*

Future Work: Research of AP combustion at pressures $> 14 \text{ MPa}$ where AP exhibits Mesa Burning - could be related to stability related issues.

Part B: Sandwich Propellant Combustion

Mathematical Formulation



Two dimensional unsteady equations of mass, momentum, energy and species conservation along with condensed phase energy equation.

Unsteady non-planar surface regression is allowed for.

Similar to AP Monopropellant Combustion.

Kinetic Details

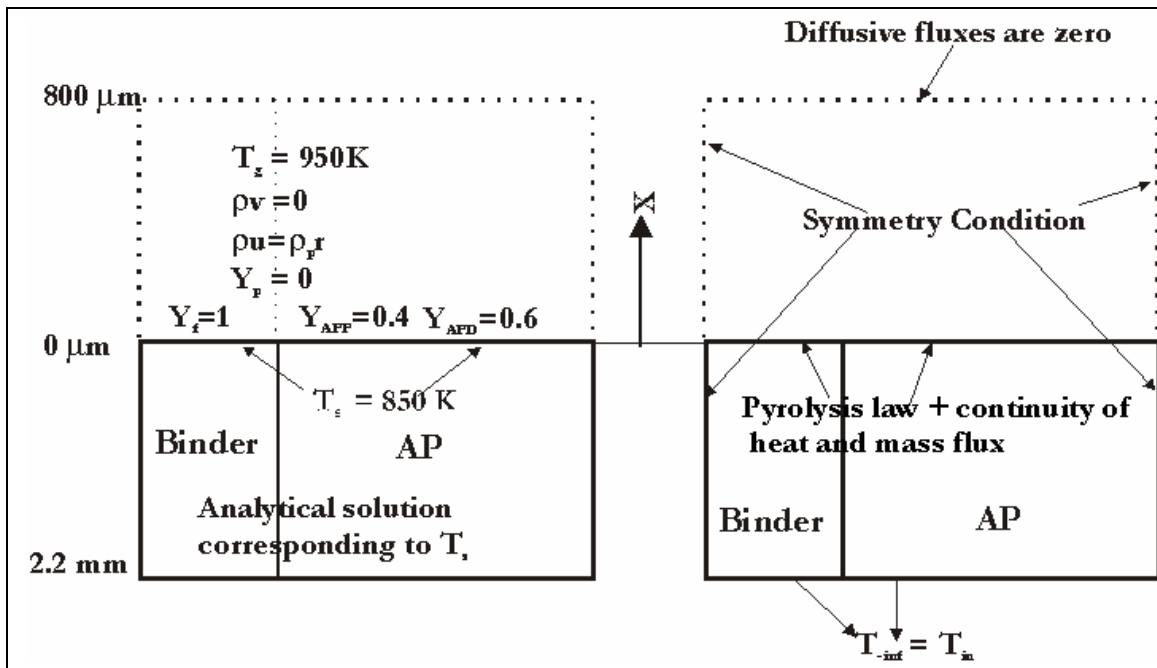
Surface decomposition process and the decomposition process for AP are taken as described previously.

AP decomposition flame : $APP \rightarrow APD$

Primary diffusion flame : $F + APP \rightarrow P$

Final diffusion flame : $F + APD \rightarrow P$

Initial and Boundary conditions



Choice of Parameters

Calculations were carried out with variable thermal properties in the gas phase and with temperature averaged thermal properties in the condensed phase.

AP reaction rate, thermo-physical and transport data are as presented previously.

The values of PDF and FDF reaction rate parameters and the pre-exponential factor of binder pyrolysis need to be calibrated against experimental results at various pressures and binder thicknesses to get to appropriate values.

Thermo-physical Properties of Binder (HTPB)

Property	Value	Reference
HTPB Heat of Formation	363170 J/kg	Chemical Engineer's Handbook ⁴²
Specific Heat Capacity of Condensed Phase, C_{pcb}	2900 J/kg	Based on average values of Zanotti et al ²⁵
Thermal Conductivity of Condensed Phase, k_{cb}	0.14 W/m K	Based on average values of Zanotti et al ²⁵
Density of Condensed Phase, ρ_{cb}	920 kg/m ³	Based on average values of Zanotti et al ²⁵

Reaction Rate Parameters For the Diffusion Flames

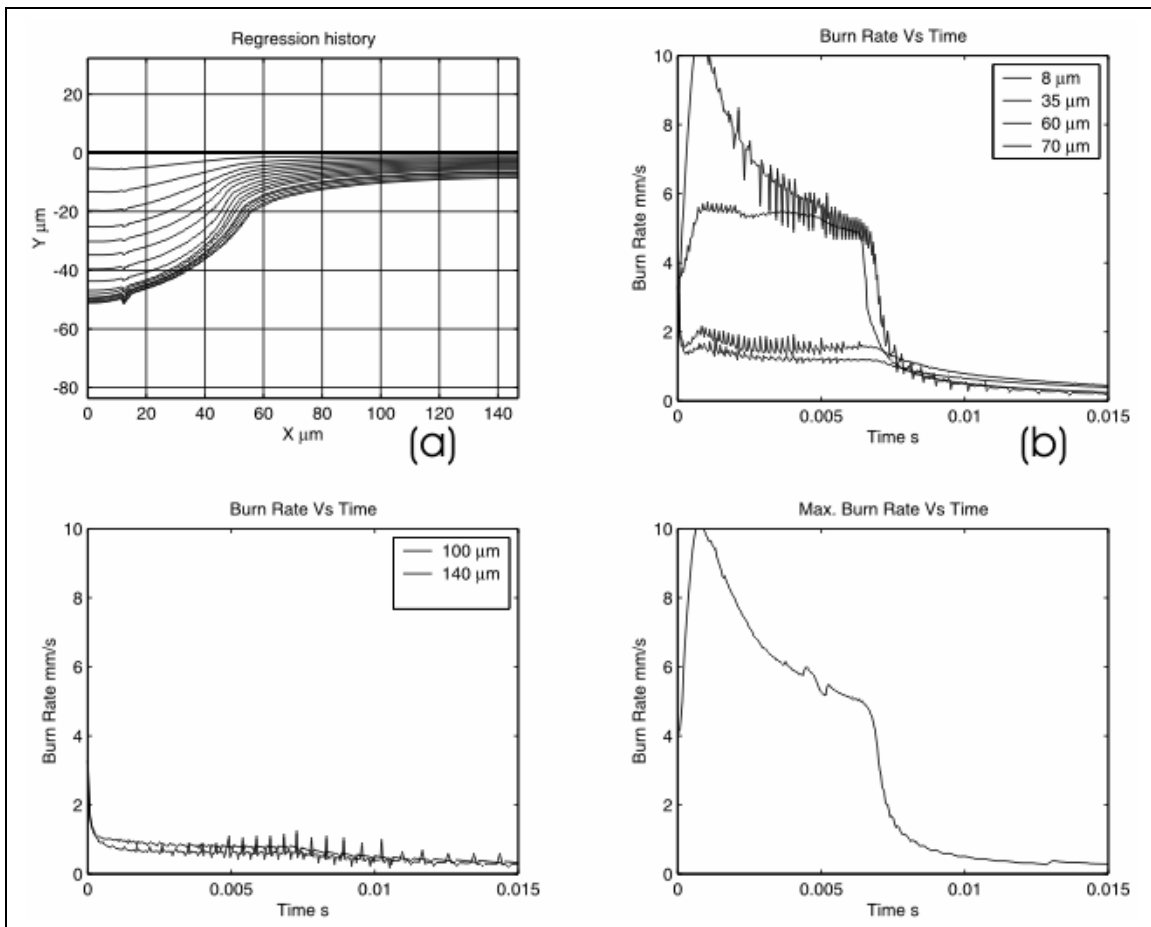
Property	Value	Comments and References
Mol. Wt. of Binder	35	Chemical Engineer's Handbook ⁴²
Mol. Wt. of Products	26.7	Obtained from NASA SP-273
Heat of formation of Binder	3076000 J/kg	Cal. with inputs from Narahari ²⁹
Heat of formation of Products	-6424228 J/kg	Cal. with inputs from Narahari ²⁹ and NASA SP-273
A_{sb}	1750 kg/m ² s	
E_{sb}	47.31 kJ/kg mole	Brill ⁴³
A_{gPDF}	1×10^9	
E_{gPDF}	119.8 kJ/kg mole	
n_{gPDF}	2	
A_{gFDF}	2.5×10^6	
E_{gFDF}	59.9 kJ/kg mole	
n_{gFDF}	2	

Results and Discussions – Part B

- Calculations were carried out for two different pressures 2.1 MPa and 1.4 MPa
- The thickness of the binder in all the calculations being 25 μm .
- Calculations were carried out for two different values of the
- pre-exponential factors of the two diffusion flames.
- PDF : 1×10^9 to 4×10^9
- FDF : 2.5×10^6 to 5×10^6

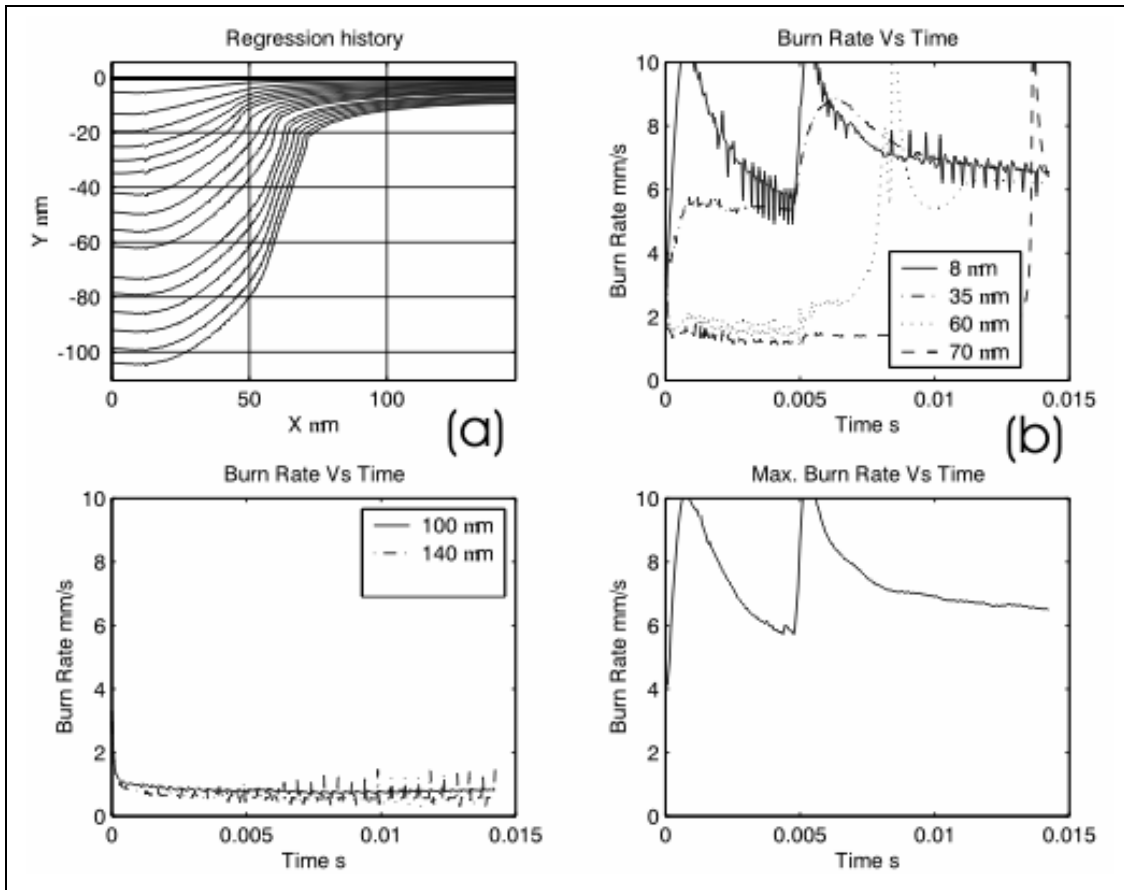
- Calculations were also carried out for identical transport properties for both binder and AP.

Burn profiles and regression rates at a pressure of 1.4 MPa (a) Regressing surface profiles at various times (b) and (c) The variation of burn rates at various sections with time (d) The maximum burn rate variation with time



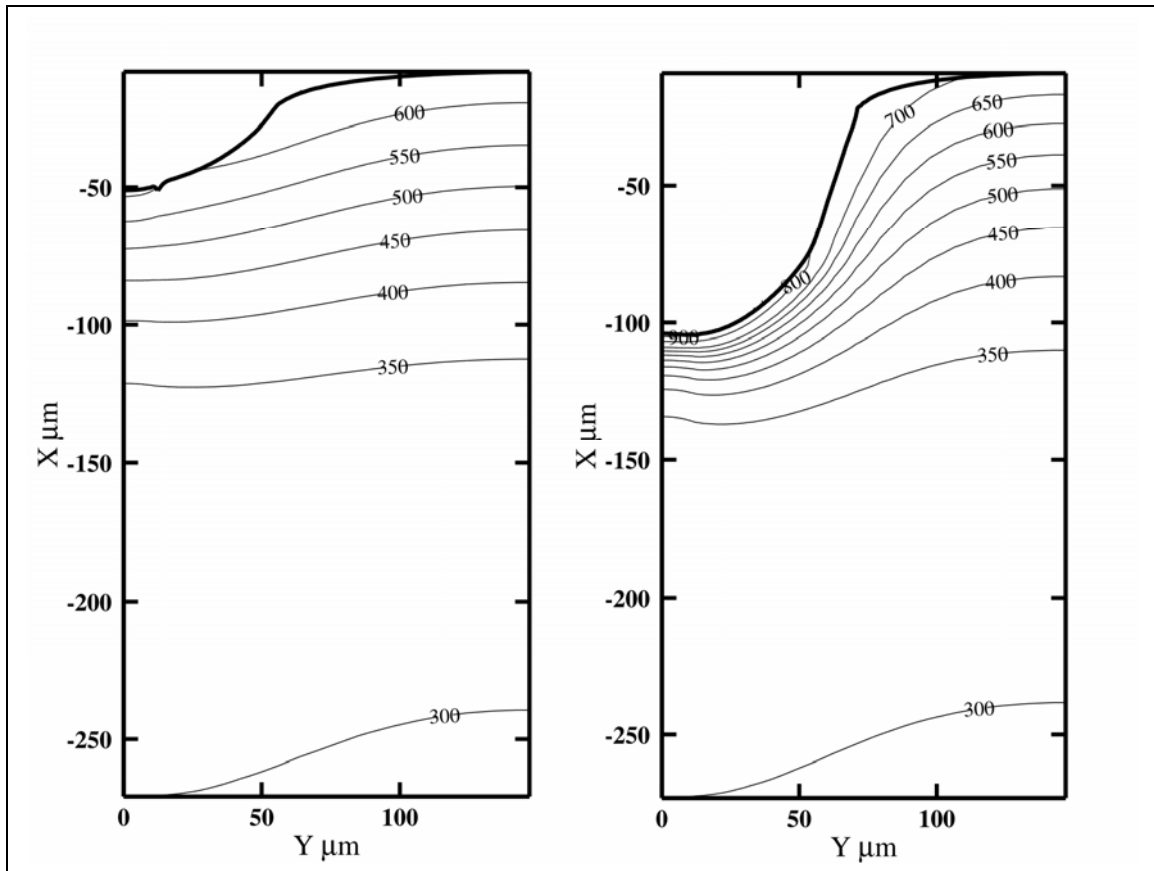
- Pre-exponential factors
 - PDF : 1×10^9
 - FDF : 2.5×10^6
- Burn profiles similar to those observed in the expts. of Price et. al.
- The sandwich propellant has quenched.
- Criterion for steady burning is - change in maximum burn rate for a time period of 4 ms (c- phase thermal relaxation time) should be less than 10%.

Burn profiles and regression rates at a pressure of 1.4 MPa (a) Regressing surface profiles at various times (b) and (c) The variation of burn rates at various sections with time (d) The maximum burn rate variation with time



- Pre-exponential factors
 - PDF : 4×10^9
 - FDF : 5×10^6
- Sandwich propellant burn at a nearly steady rate.
- Increase in the reaction rates of the two diffusion flames made it possible to get steady regression.
- Burn rate of 6mm/s pretty large

Condensed phase temperature profiles at 1.4 MPa

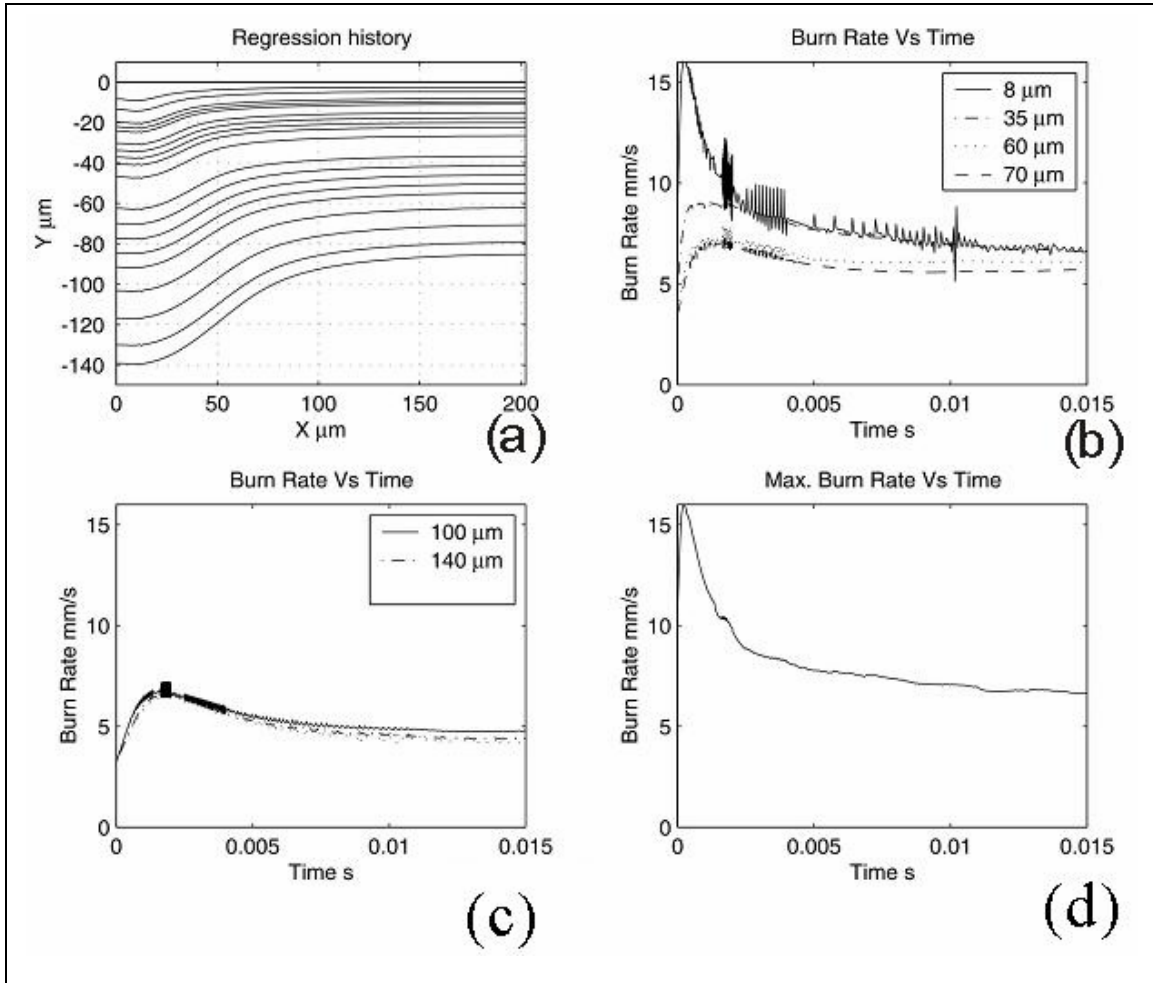


Low diffusion flame reaction rates

High diffusion flame reaction rates

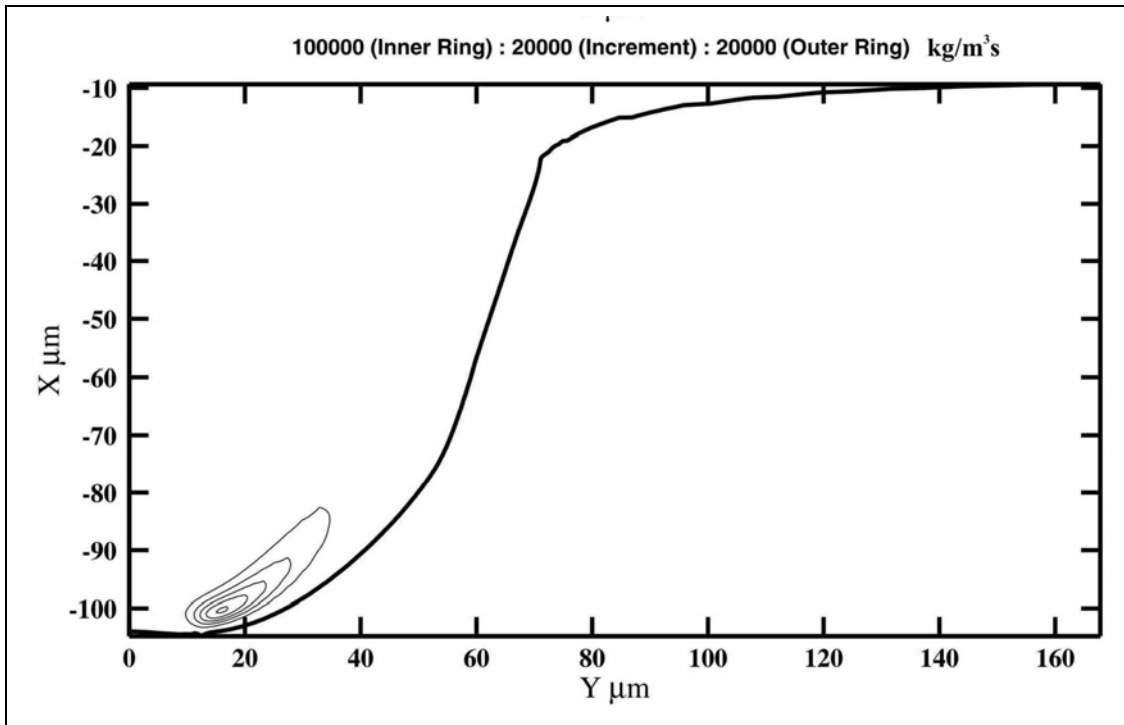
- AP in both the cases - regressing below LPDL.
- Temp. on the edge of AP slab is lower than those at the interface region between AP and binder.
- Lateral flow of heat from the interface region to the edges of AP.
- Combustion is sustained only if the interface region which is close to the diffusion flame does get the required heat flux from the gas phase.

Burn profiles and regression rates at a pressure of 2.1 MPa (a) Regressing surface profiles at various times (b) and (c) The variation of burn rates at various sections with time (d) The maximum burn rate variation with time

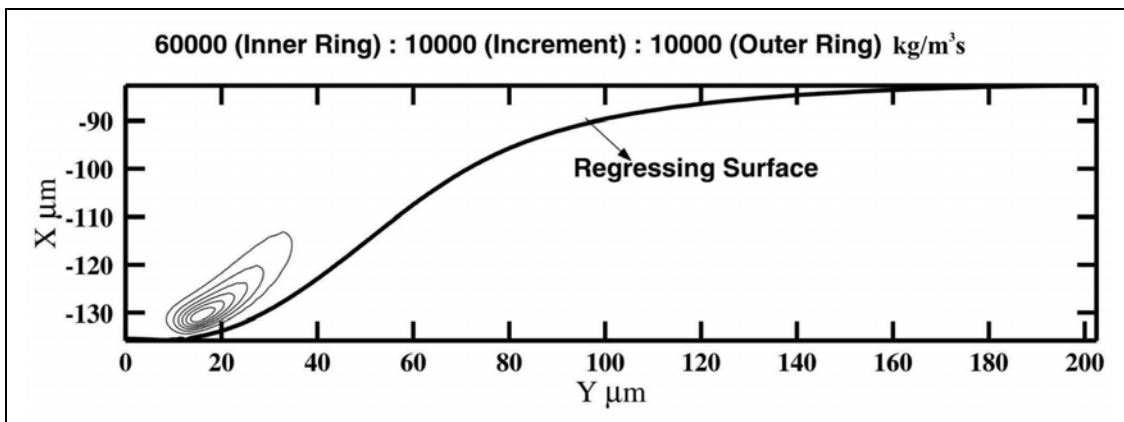


- Pre-exponential factors
 - PDF : 1×10^9
 - FDF : 2.5×10^6
- Burn Rate 6.5 mm/s
- Expt. observed 4mm/s
- Pressures lower than LPDL higher reaction rates are reqd. to obt. sustained regression
- Pressures higher than LPDL even lower values of reaction rates lead to very high burn rates.
- Increasing the rates of reaction of PDF whilst lowering the reaction rates of FDF

Primary diffusion flame reaction rates



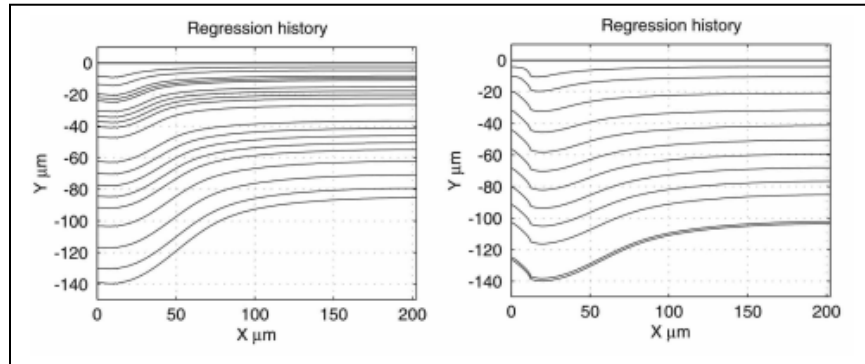
Pressure 1.4 MPa



Pressure 2.1 MPa

- PDF is less important at pressures higher than LPDL of AP.
- Availability of APP being reduced at pressures above LPDL of AP due to the presence of a strong premixed monopropellant flame
- Predicted sandwich propellant behavior over a wide range of pressures were to have reasonable agreement with expt. observations it would be more appropriate to utilize two different diffusion flames rather than a single one as argued by Hegab et. al.

Regressing surface profiles at various times

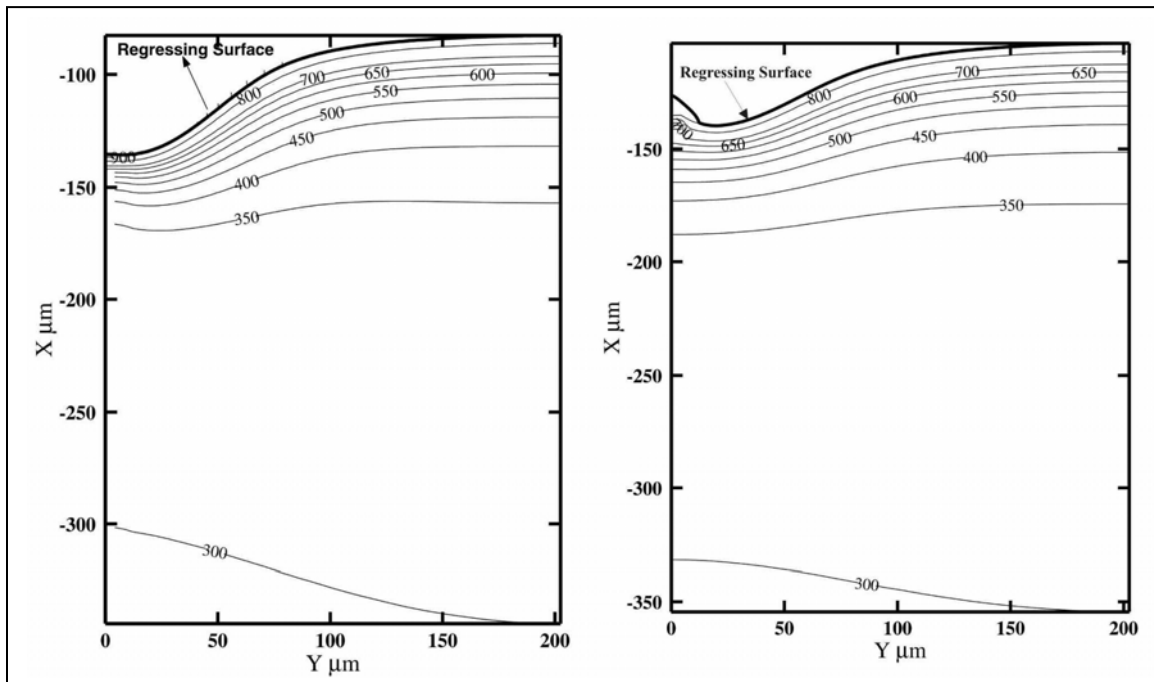


Different thermal properties of AP and binder

Identical thermal properties of AP and binder (AP properties)

- Importance of condensed phase heat transfer is brought out explicitly.
- Marked difference in the profiles obtained is observed, despite the rest of the parameters being identical for both calculations

Condensed phase temperature profiles



- With identical thermal properties for both AP and binder temperature contours must have been horizontal lines.

- Not so because different sections have different burn rate.
- But profiles are flatter than those obtained with different thermal properties of AP and binder.

Conclusions - Part B

Numerical studies of a sandwich propellant geometry with two-dimensional unsteady gas and condensed phase and a non-planar regressing surface have been carried out.

- Importance of AP monopropellant combustion studies has been brought out.
- Necessity of having two different diffusion flames if the predictions of sandwich propellant burn behavior were to have reasonable agreement with experimental observations has been elucidated.
- Importance of condensed phase in influencing the burn behavior of a sandwich propellant has been explicitly brought out.

Future work must focus on determining the reaction rate parameters of the two diffusion flames so as to predict the burn behavior of sandwich propellants under varying conditions of pressure and binder thickness.