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Studying the Influence of Aluminium in ADN/HTPB-Based Solid Propellants

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Ammonium Dinitramide (ADN) combustion has been the subject of great interest over the past few years due to consideration as a green oxidizer in solid rocket propellants. This study is focused on predicting the flame structure of an ADN/HTPB and ADN/HTPB/Al sandwich propellant. Initially, one-dimensional reactor modelling was carried out to implement the detailed chemical kinetics for AP and ADN monopropellant. Detailed understanding on the different combustion zones of ADN monopropellant was studied with implementation of one-dimensional reactor modelling. The results of one-dimensional studies were found to have good correlation with the previous literature. The sensitivity analysis was performed to understand the major species and dominant reaction in different burning zones. Initially, sandwich model was tested on AP/HTPB sandwich propellant and subsequently it was noticed that the findings were identical. The burn rate results of the AP/HTPB sandwich model were validated with the existing literature and were found to be in close match. Followed by this ADN/HTPB sandwich propellant was simulated using a detailed combustion chemistry using 215 reactions and 51 species were used to predict the flame structure across a wide range of pressure. The physiochemical reactions that occur during the combustion of ADN and HTPB are thoroughly examined by employing a complete gas phase combustion model. The computational framework is based on mass, species concentration, and energy conservation equations. For a pressure range of 0.6-6Mpa, the flame structure of the sandwich propellant in different combustion zones was studied. The simulations were also carried out with the addition of aluminum in a homogenized manner in ADN/HTPB sandwich. The gas phase temperature was found to increase with the addition of aluminum. The addition of nano aluminum was observed to have an influence on the flame structure and enhance the performance significantly.

I. Nomenclature

ADN	=	Ammonium Dinitramide	*Al-Mg*	=	Aluminum-Magnesium Powder
AP	=	Ammonium Perchlorate	*GAP*	=	Glycidyl Azide Polymer
HTPB	=	Hydroxyl-terminated Polybutadiene	*NiO*	=	Nickel (II)Oxide

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Al = Aluminum
CuO = Copper (II) Oxide
HCl = Hydrochloric acid

II. Introduction

These days, the effectiveness of energetic materials is assessed along with any existing or possible consequences on the natural environment and human wellness. Ammonium perchlorate (AP, NH_4ClO_4) has been utilised as a solid rocket propellant oxidizer for decades due to its high oxygen balance, energy density, and stability, along with its relative simplicity of handling. However, due to the presence of chlorine in AP, its combustion produces considerable amounts of hydrochloric (HCl) acid as a resultant product. HCl is a poisonous and corrosive gas, so therefore emissions are hazardous to the environment and human health. To reduce the environmental and health impact researchers have found the potential replacement of AP with Ammonium Dinitramide (ADN, $H_4N_4O_4$). ADN is categorised as a green propellant as it does not produce any harmful Chlorinated gases. ADN propellants, either with or without metallic fuels, are the most conceivable "green" alternatives to AP based solid rocket propellants. Such propellants are appealing not just for their environmental friendliness, but also for their ability to surpass the inherent performance constraints of AP/HTPB (where HTPB is used as fuel/binder) propellant. High density and positive oxygen balance make it a promising high-energetic oxidizer for solid propellants. The study proposed by Jingjing Li et al [1] delves into the preparation and combustion behavior of micro composite particles of aluminum (Al) dotted by ammonium dinitramide (Al@ADN) using an in-situ crystallization growth method. The results provide crucial insights into the impact of ADN on the oxidation of aluminum and variations in combustion performance based on the ADN-to-Al ratio. Investigations conducted by Fujisato et al [2] showcased influence of additives on ADN combustion. This research identifies copper (II) oxide (CuO) and nickel (II) oxide (NiO) as promoters of burning rate. The complex interplay of various additives on ADN combustion is explored, providing valuable insights into their roles and effects on propellant performance. The research carried out by Gogulya M.F et al. [3] presented the detonation behavior of ADN and ADN/Al mixtures. The sensitivity, detonation velocity, and the impact of aluminum particle size on ADN/Al was discussed. The findings shed light on the potential classification of ADN as a Group-2 explosive and highlight avenues for further research. Influence of the Copper (II) oxide on the thermal decomposition was studied by H. Matsunaga et al. [4] This study proposed the detailed thermal decomposition mechanism of ADN with major focus on the catalytic role of CuO and its contribution to key intermediates species and combustion products. M.Comet et al. [5] introduced a new family of detonating compositions using ADN as an oxidizer and red phosphorus or titanium hydride as fuels, this research explores their explosive properties. The study positions these compositions as environmentally friendly substitutes for primary explosives containing heavy metals. The experimental study carried out by F. Cristilli et al. [6] scrutinizes the burning behavior of ADN-based composite propellants incorporating mechanically activated Al-Mg (Aluminum-Magnesium) powders. The findings underscore pressure sensitivity, flame temperatures, and the significant impact of activation treatments on propellant ballistics. Addressing environmental concerns, research conducted by V. Weiser et al. [7] explored the combustion behavior of aluminum particles within ADN/GAP composite propellants, presenting a greener alternative to traditional formulations. The work highlighted the distinct thermal and chemical conditions, emphasizing pressure-dependent burning rates and agglomeration phenomena. Further, S. Sims et al. [8] explored the augmentation of burning rates in ADN/GAP propellants through the addition of metallic fibers. The incorporation of Al-Mg alloy fibers leads to a substantial increase in burning rate, showcasing potential applications in hypersonic propulsion. The study carried out by Fujisato et al. [9] addressing environmental concerns related to ammonium perchlorate, this study explores ADN-based propellants using thermoplastic elastomer and hydroxyl-terminated butadiene polymer as binders. The findings emphasize the influence of binders on combustion characteristics, necessitating further optimization. However, due to hygroscopic nature, challenges in storage, and incompatibility with existing curing chemicals for ADN, its utilization is currently constrained, which requires addition of various additives for thermal stability and reduction of sensitivity.

Most of the research on the thermal decomposition of the ADN monopropellant and its flame structure has been reported by various researchers in recent decade by using the simplified and detailed chemical kinetics mechanism. However, the performance and the detailed flame structure related to various compositions of ADN with fuel and binder are still needed to be explored and required integration of different detailed chemical kinetic mechanism. The sandwich-type propellant approach presented by M.W Beckstead et al. (BDP model) [10], particularly represents the multi-layered arrangement of propellant grains or solid rocket motors, provides an important foundation in propellant modelling. It estimates combustion properties with high accuracy, such as different species percentages in

the flame location, temperature patterns, pressure characteristics, along with burning rates by using simplified mechanism.

With motivation to develop the sandwich model with detailed chemical kinetics for various composition of ADN, metallic fuel and binder, the present work investigates the influence of aluminium in the ADN/HTPB propellant formulations at different operating conditions. Different flame structures with and without metal additions in the ADN based propellant is explored with the sandwich propellant model. Along with that variation in species concentration and burn rate at different pressures is studied. The sandwich model with detailed gas phase reactions and intricate dynamics has been validated for AP/HTPB under different pressures, and further adopted for ADN/HTPB. The current study further develops understanding with aluminium particles behaviour during combustion in ADN/HTPB composite propellant formulation. Apart from this, the sensitivity analysis has been conducted for predicting the sensitivity coefficient of high temperature sensitive reactions which play a key role in the three flame zones suggested by P. Thakre et al. [11] of the ADN burning along with metal addition.

III. Methodology

The methodology used in the present study is divide into two sections. The first section describes the overall approach of 1D Modelling for the solid and gas phase for the ADN monopropellant. Along with that sensitivity analysis sheds the light on major sensitive reactions. Followed by this second section describes about the sandwich model setup which is simulated using Converge-CFD solver.

1D Model for Gas and solid Phase:

The research approach utilized in this work consisted of a structured methodical sequence of actions to thoroughly examine the chemical kinetics and thermodynamic characteristics of ADN/HTPB with and without Al addition. First, utilizing 1D reactor model in Converge CFD [12], a thorough examination was carried out with the goal of understating thermal characteristics of ADN with use of detailed chemistry. After that, in-depth sensitivity analyses using Cantera reactor model [13] were carried out to determine and assess the crucial reactions affecting in the combustion process of ADN. Followed by that, an analytical approach was developed using MATLAB by implementing equations suggested by [15-17] to solve the solid phase evaporation which accurately compute temperatures on the surface and determine geometrical correlations with respect to the widths between the ADN/HTPB propellant formulation. The utilization of this analytical method was crucial in understanding the thermodynamic processes, which attributes within the solid phase.

Computational Domain:

Lastly, using the Converge-CFD solver [12], a sandwich model arrangement, illustrating the ADN/HTPB composite has methodically prepared to simulate the two-dimensional flame characteristics using detailed chemical kinetics mechanism and boundary conditions adopted from 1D reactor calculations. Fig 1(a) describes the a perfectly mixed sandwich model in the which HTPB particles are surrounded by ADN particles. This demonstrates a small area of binder within two bigger oxidizers regions exposed into the reactive chamber stream at the micro scale, or vice versa arrangement can be done. Fig 1(b) describes the simplified version of Fig 1(a) for the gas phase which contains 12% of HTPB surrounded by 88% of ADN particles on both sides. The overall length of the computational domain is 800µm and the height is 240µm. The geometric distances selected here are obtained through the analytical code (as mentioned in previous section) depending on the mass fractions of the oxidizer and binder. The proportion of ADN and HTPB is varied and solved at different pressures assuming that is the homogeneous mixture. Similarly, method has been implemented with the addition of the homogenously mixed Al fuel in HTPB regions of sandwich model. This enabled a thorough analysis about the flame structure, different species concentrations and flame location in the gas phase combustion.

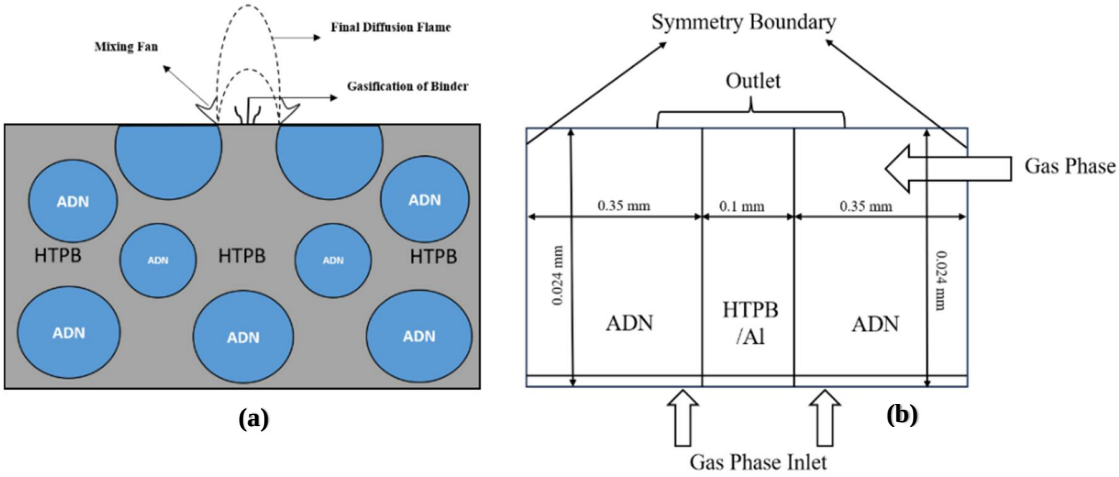


Fig 1: Computational Domain Overview

Through the integration of these approaches, an in-depth understanding of the combustion behaviours and correspondence between HTPB and ADN with and without Al fuel was acquired. Fig 2 summarizes the above-mentioned approach utilized in the present study.

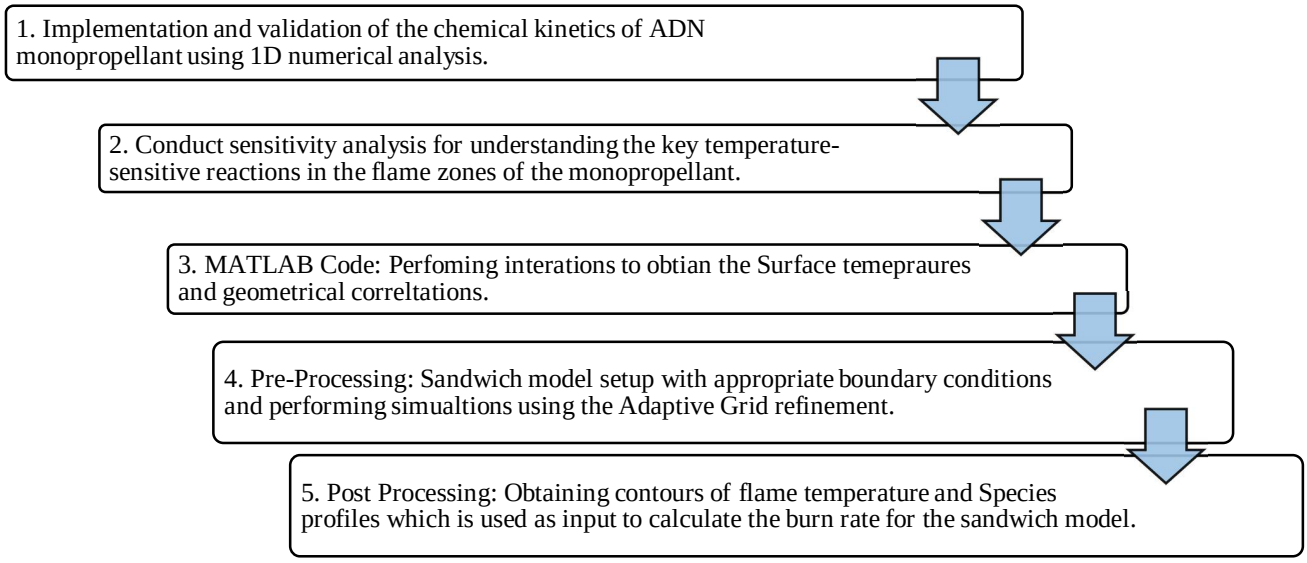


Fig 2: Methodology Flowchart

Sandwich Modelling

A model description that represents the propellant is made up of a homogenous blend of ADN and HTPB, simulate only single region of HTPB surrounded by two sides with ADN. The two-dimensional time-dependent compressible reacting multi-species Euler equations in combination with the detailed chemistry is solved using Converge-CFD [12] solver to model sandwich propellants. A framework for the combination of solid and solid disintegration, is simplified with the series of mathematical equations given by [15-17] introduced in analytical code (mentioned in section III) determines the physical boundary parameters underlying the flow equations in gas phase. The model generated is a chemically driven model, utilizing a solid phase framework to depict a burning interface of propellant. The influence of both pressure and Al composition on the flame pattern and consumption of species during combustion were examined using this framework. The kinetic mechanism defines the chain of reactions which occur in the gas phase, resulting in a reactive combination of species. The principles of mass, momentum, and energy conservation dominate the movement of fluids assuming ideal gas law.

Further to model the chemistry in converge different combustion models are available out of which SAGE combustion model is implemented in the present study because of its efficient solving capabilities [18]. The burning and laminar diffusion flames are precisely modelled by the SAGE detailed chemistry solver. With the use of SAGE combustion solver simulations were less computationally expensive and were found to have good results for sandwich propellant modelling applications. SAGE combustion chemistry solver makes use of the CVODE solver to simplify the ODE equations. Reaction rates were calculated depending upon Arrhenius rate of reaction expression which is highly influenced by local conditions in the cell zones. The local conditions such as temperature, pre-exponential factors and activation energy were found to have effect on the reaction rates. Along with that SAGE solver integrates with the transport solver to understand the species development in the overall combustion. It improves computing efficiency by independently parallelizing. Each computational time-step computes accurate species masses percentages and rates of reaction, considering modifications as sources and assuring exact flame dynamics under a variety of situations. The SAGE combustion solver solves the detailed mechanism for ADN is devised through [14&19] for ADN/HTPB combustion, which included 206 reactions with 45 chemical species. Similarly, Al reactions obtained from [20] are added in the reaction mechanism with final mechanism which consist of 215 reactions and 51 species. Transport and thermodynamic data for the multi-component gas phase mixture are necessary for the mechanism, which is obtained from the literature and open-source resources given by S. Gordon et al. [21].

Boundary Conditions for sandwich model.

The sandwich propellant modeling within Converge -CFD involves setting up a computational domain that represents the layered structure of the propellant. This includes defining appropriate boundary conditions such as specifying inlet velocities, pressures, and temperatures. Additionally, symmetry boundary conditions are applied to account for the interactions between the propellant layers. The two front and back sides of single cell in the third dimension are selected as symmetric boundary to perform a two-dimensional simulation. The three sides of numerical domain's exit are characterized through a Dirichlet pressure, Neumann velocity, and Neumann backflow constraints. Variations in the atmospheric pressure are determined by the Dirichlet pressure in parametric research. The condensed phase surface temperature and mass fluxes are computed using analytical method mentioned in previous subsection to provide inlet temperature as well as mass fluxes for the layers of gas phase reactive ADN/HTPB. The initial temperature in the solid phase was taken as 300K at 20 bars for the ADN/HTPB sandwich model. With the use of the analytical code mentioned in the above sections, solid phase was solved to obtain the surface temperature at the gas phase. The surface temperature was found to be 800K and 850K at the burning surface of ADN and HTPB respectively. Same methodology is utilized at different pressures ranging from 6-60 bars. In the case of ADN/HTPB/Al sandwich the surface temperatures were obtained were found to be 800K and 990.42K at the burning surface of ADN and HTPB/Al respectively. The transformation of phase and growth of Al particles are neglected in the current modelling. Only the gas phase reactions are solved in the current simulations. Along with this high spatial resolution, Adaptive mesh Refinement was utilized, which allows for the detailed analysis of combustion behavior, and fluid dynamics phenomena at a microscale level. Ultimately, the advanced capabilities of Converge CFD combined with precise boundary conditions enable a thorough investigation of sandwich propellant behavior.

Validation of the Sandwich Model

To validate the present approach of the sandwich propellant model in the commercial Converge CFD solver, the previously studied sandwich AP/HTPB model by [22 and 23] is tested. To obtain the accurate surface temperature at the burn surface and geometry conditions, an analytical code [15-17], discussed in previous subsection is used for AP/HTPB. This code makes use of the mass ratios of oxidizer and binder, energy balance and heat transfer within the sandwich model to iterate the accurate surface temperature and massflux of the propellant. The code was then used to perform several iterations at different pressures and same was compared with the literature study. This parametric study enabled helped to select the desired sandwich propellant model. At first AP/HTPB based sandwich model is simulated using the detailed chemistry given by Jeppson et al. [19] at 20 bar pressure. Results of the flame temperature were deduced from the simulated sandwich AP/HTPB case and used as an input parameter in MATLAB code (extended code from previous one), which solve the burn rate related equations given by [15-17]to obtain the burn rate for the AP/HTPB sandwich model. Fig 3 shows the comparison of AP/HTPB combustion burn rate at different pressures compared to previous modelling and experimental work which concludes that they are in good correlation with the previous work. The results show that the approach used in present study is accurate and reliable.

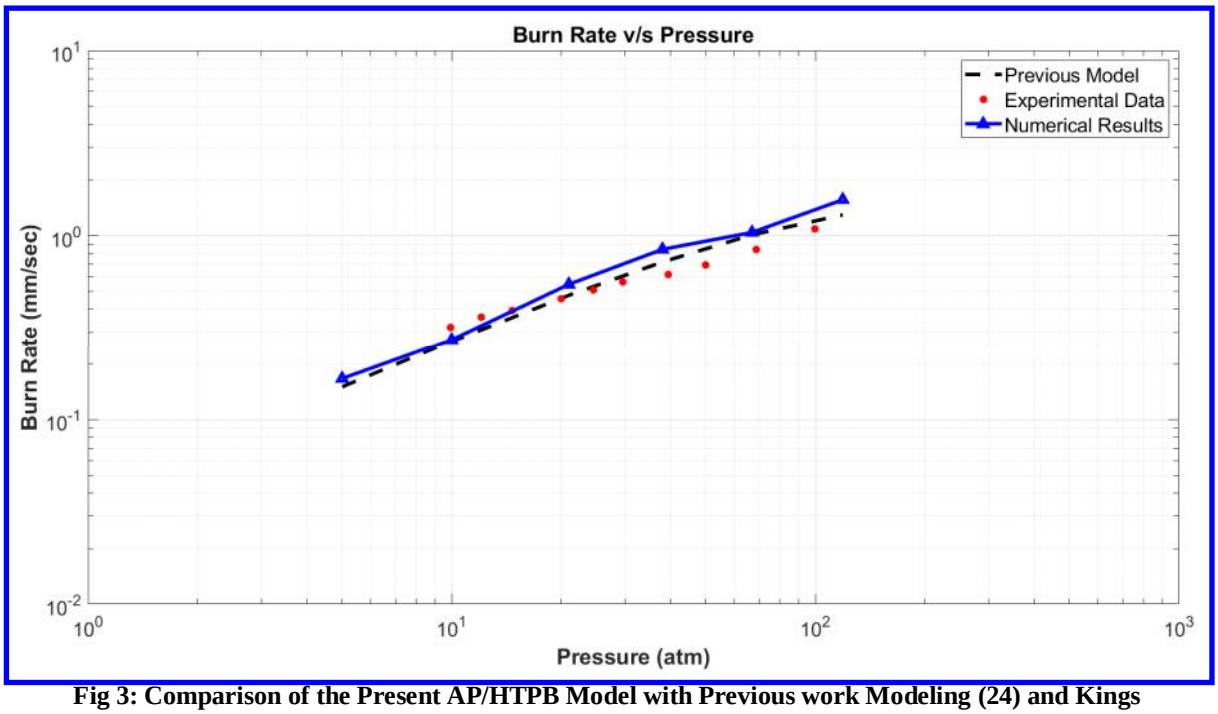


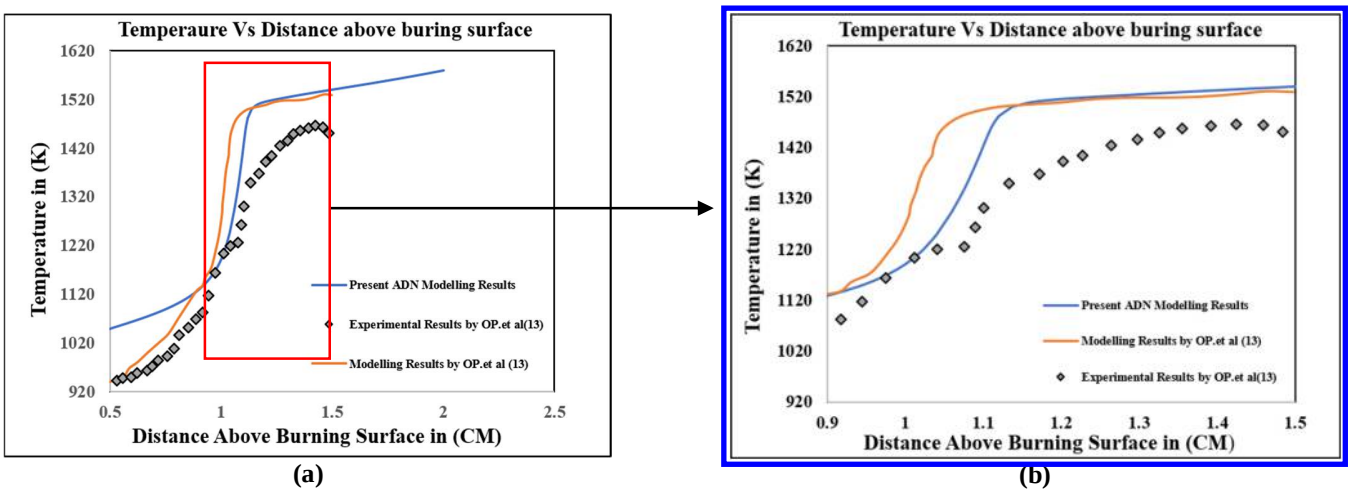
Fig 3: Comparison of the Present AP/HTPB Model with Previous work Modeling (24) and Kings Experimental data (25 and 26)

IV. Results and Discussions

Verification of the Reaction Mechanism for ADN monopropellants:

The ADN monopropellant detailed kinetic mechanism is obtained from O.P. et al. [14], however the thermodynamic and transport data are obtained from different literature sources. Hence, it is essential to verify the utilized chemical kinetic mechanism for ADN. Hence, 1D simulations are performed using converge-CFD for experimental and modelling conditions used by O.P. et al. [14] for operating pressure of 0.6 MPa and initial temperature of 920 K. The obtained results for temperature above burning surface are obtained and compared with results from O.P. et al. [14] in shown in Fig 4(a&b). In initial region the current mechanism with thermodynamic and transport data overpredicts the temperature in the initial region, closer to the surface, while beyond 0.9 cm (zoomed region in Fig 4b) it has reasonable agreement in temperature trends with modelling and experimental data from O.P. et al.14].

To investigate further a sensitivity analysis was performed. The use of sensitivity analysis in this work centers around how the pressure, temperature, oxygen content, reaction processes, and fuel mix affect flame structure, ignition delay factors, and flame stability during the combustion of ADN monopropellant. From the Fig 5 it can be seen that NH_3+OH is a crucial reaction which has highest positive sensitivity factor which confirms that the NH_3 and OH species has influence in both hot and cool flame zones. Followed by this HONO +OH and NO+OH(+M) reactions with negative sensitivity factor plays a significant role in the thermal decomposition of ADN with generation and consumptions of HONO. Similarly, NH_2+NO which leads to formation of N_2 and H_2O has positive sensitivity factor affecting the hot zone of ADN combustion. With the use of sensitivity analysis and the temperature profiles a prediction was given for the initial temperature rise starting from 0-0.5 cm. The 1D calculations assumes a homogenous mixture of the selected propellants in the gas Phase. After understanding the performance of chemical kinetics for ADN monopropellant given by [14], it was further integrated with the HTPB and Aluminum reactions to perform the sandwich modelling. Further the equilibrium temperatures obtained by 1D model are compared with NASA CEA flame temperature at different operating pressures in Fig 6. This concludes that the detailed chemistry in for ADN monopropellant can be used reliably and the same is implemented in the Sandwich propellant modelling.



(a) (b)

Fig 4: Temperature Vs Distance Validation Profile at 0.6Mpa for ADN Monopropellant

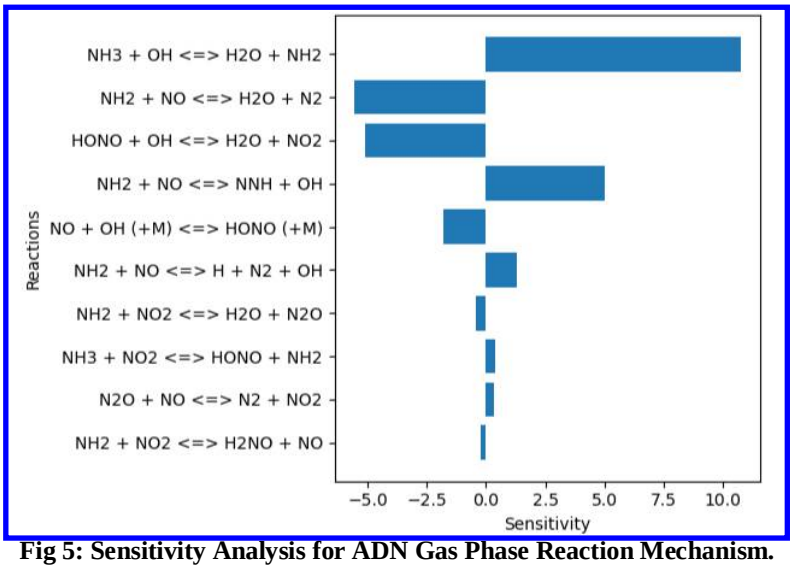


Fig 5: Sensitivity Analysis for ADN Gas Phase Reaction Mechanism.

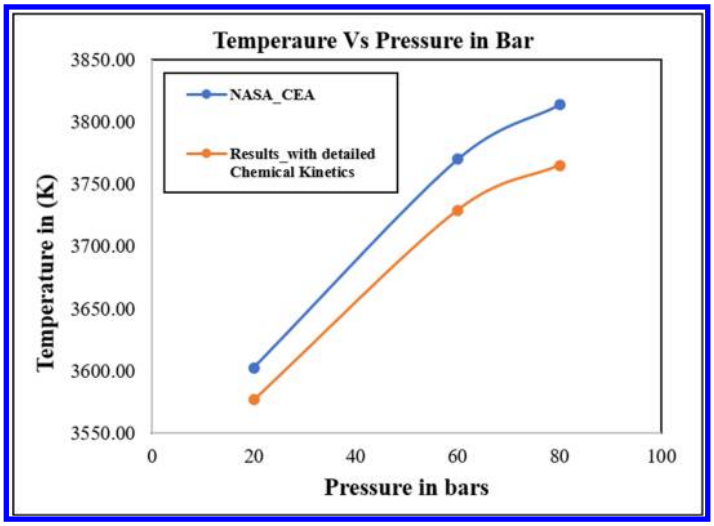


Fig 6: Comparison of the adiabatic flame temperature using detailed reaction Mechanism.

Combustion Characteristics of ADN/HTPB:

A sandwich model using the detailed chemical kinetics is simulated at different pressures using the homogenized mixture. Ammonium Dinitramide (ADN) is used as an oxidizer in the sandwiched ADN/HTPB combustion framework, and Hydroxyl-Terminated Polybutadiene (HTPB) is used as a fuel binder. In these formulations, burning happens via diffusion flames, which depends entirely on an oxidizer and fuel being mixed in different compositions. Fig 7 shows the typical diffusion flame characteristics with temperature contours at 20 bar pressure. Fig 7 shows the elliptic labeled curves which differentiate the diffusion and the premixed flame as shown in Fig 8 with contours of Flame Index parameter. Here the flame Index varies from -1 to 1 in which 1 represents the premixed flame and -1 represents the non-premixed flame. The three distinct flame zones, premixed flame, primary diffusion flame and ADN monopropellant flame are observed. It is observed that ADN monopropellant flame gets attached to the premixed flame which is lifted from the burning surface. Depending on the high temperature sensitive reactions and species which are obtained through the sensitivity analysis, the flame characterization is concluded. The ADN monopropellant flame is formed because of the thermal decomposition reactions taking place at the burning surface this causes the ADN to decompose into species which allows to form a monopropellant flame with rise in temperature from surface to the adiabatic flame temperature of 2000K for ADN monopropellant. Additionally, because of thermal decomposition of ADN atoms into respective species which combines with the pyrolysis products of the HTPB are thought to have been blended and this interactions between them allows to form a premixed flame next to the ADN monopropellant flame. Further the initial diffusion flame, particularly is affixed at the point of interface among the ADN particulate and binder, differentiates into two separate flames. The first phase of diffusion involving the constituents of HTPB degradation as well as ADN breakdown yields an initial diffusion flame of 3000K which is observed through present sandwich model. Additionally, when the combustion entities of remaining HTPB together with ADN interact to move away from the burning surface and propagate as a result, the final diffusion flame forms with ADN/HTPB. By comparing the experimental results by O.P et al. [27] with obtained results from sandwich model, it can be concluded that the burning of the ADN occurs far away from the surface which tends to have very less effect on the burning rate of propellant because of very less change in the surface temperatures, along with that the dark zone region which is occurred in the sandwich model is formed because of the preliminary gaseous products of the ADN and HTPB which produces a luminous jet diffusion flame/primary diffusion flame which take place in the initial region. Further mixing of the remaining byproducts of HTPB and ADN are mixed in the final diffusion flame which increases the heat release rate and intends to speed up the combustion reactions which occurs at farther distances in the range of 4-5cm which is not captured in this model because of the smaller domain in the Y direction.

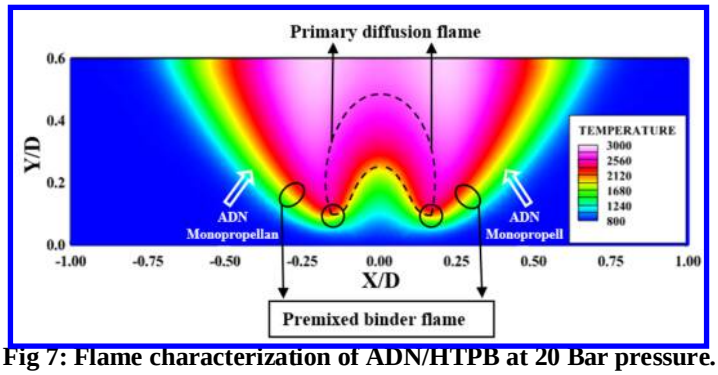


Fig 7: Flame characterization of ADN/HTPB at 20 Bar pressure.

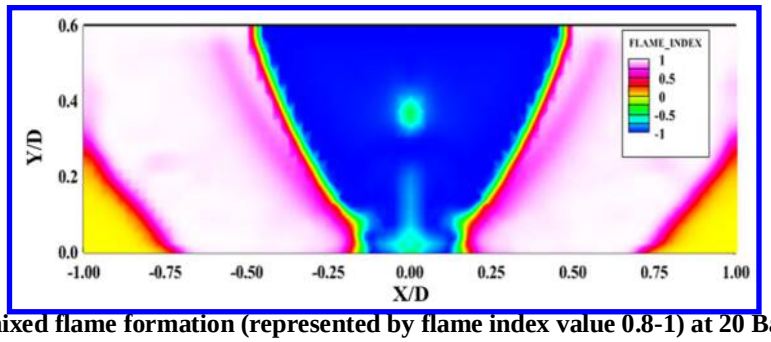


Fig 8: Premixed flame formation (represented by flame index value 0.8-1) at 20 Bar pressure.

As suggested by O.P et al. [27] the properties associated with diffusion flames in ADN/HTPB compositions has very less effects of pressure. The same was observed through present model, Fig 9 shows the typical diffusion flame characteristics with temperature contours at varying pressure. The temperature contours are formed by the combustion products of ADN and HTPB species which mixes in the gas phase region at different pressures. In the present study as the pressure is increased from 6 to 60 bars the flame temperature moves away from the burning surface. It was observed that the ADN combustion surface temperature is marginally elevated than that of the HTPB surface temperature. As a result, a prolonged, wider, hot zone forms, which are located above the solid burning layer along the mixing interfaces within the oxidizer and fuel molecules.

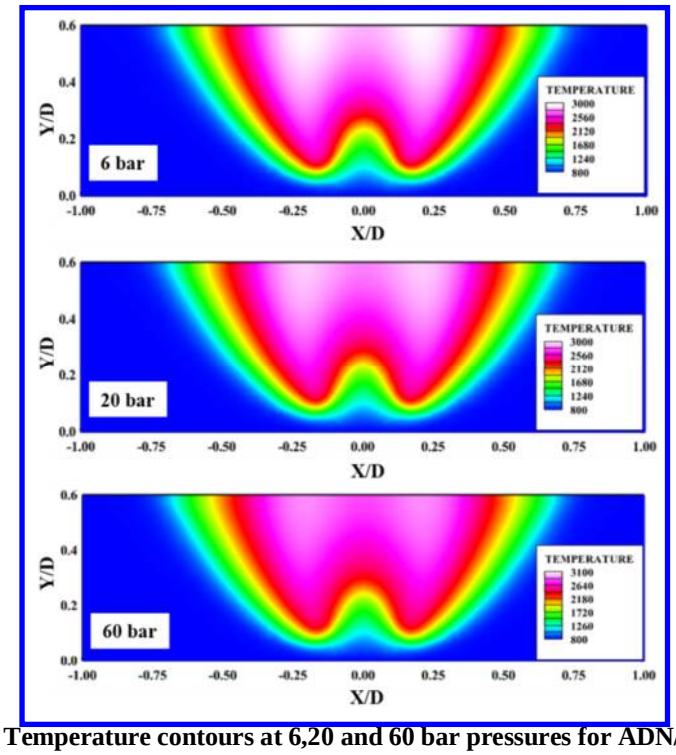


Fig 9: Temperature contours at 6,20 and 60 bar pressures for ADN/HTPB.

Combustion Characteristics of ADN/HTPB/Al:

Blending aluminum, HTPB, along with ADN together in propellant formulation produces a complex flame exhibiting unique characteristics. When compared to traditional propellants, ADN has a considerable impact on combustion and produces an environmentally friendly, lesser smoky flame. The inclusion of aluminum in the mixture produces a strong incandescence in the flame, a brilliant luminosity that increases the energy output of the propulsion system. The unique combustion traits associated with ammonium dinitramide (ADN), hydroxyl-terminated polybutadiene (HTPB), along with aluminum (Al) composite propellants in rocket motors are well established. Each of these components work together to affect numerous facets of the combustion process, notably flame features. A brief description of their combustion behavior including the ensuing flames is provided below. A homogenized mixture of the HTPB/Al which is surrounded by the ADN particles is considered for the ADN/HTPB/Al sandwich model.

At first a sandwich model consisting of 68/14/18 (by wt%.) of ADN, HTPB and Al respectively is simulated at 20 bar pressure. As a result, an increase in the gas phase temperature is observed during the simulation. Fig 10 shows the temperature contour of the sandwich ADN/HTPB with the addition of the Al. This simulation reveals that addition of the Al in 18% by wt. has greater impact on the gas phase temperature when compared with the AP/HTPB propellant in the presence of Al content. The rise in gas phase temperature with the addition of Al is because of the process of phase change from aluminum oxide (gas) to Al_2O_3 (liquid form) generates a tremendous amount of energy in the form of heat (roughly 1073.2 kJ/mol). Along with that the mixing of the gaseous oxidizer species with the Al species contributes to the higher rate of exothermic reactions occurring due to the presence of subsequent reactions. Further to understand the different flame structure for ADN/HTPB sandwich with the Al content an elliptical labelled contour

is shown in Fig 10. This figure describes when the Al is blended with HTPB the structure of the primary diffusion flame is stronger. In this case a torch like diffusion flame with very high temperature of 3400K is completely visible. In comparison with the previous ADN/HTPB sandwich model this model also represents premixed flames, primary diffusion flame and the ADN monopropellant flame. Initially an ADN monopropellant flame with rise a temperature of 2000K is formed above the ADN surface. Moving ahead, a flame with the homogenized HTPB/Al is generated at the center due to pyrolysis products of HTPB/Al at the surface. The byproducts of the HTPB/Al are then interacting with the ADN by products to form a premixed flame which is shown in the Fig 11. Along with that this interaction tends to generate the primary diffusion flames which starts just above the surface. A primary diffusion flame is generated close to the surface which tends to have a flame temperature of 3400K. Through this model it has been observed that with the addition of the Al the primary diffusion flame with a higher temperature is formed very close to the burning surface.

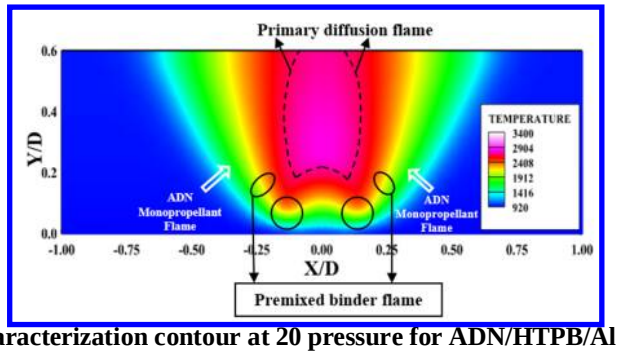


Fig 10: Flame characterization contour at 20 pressure for ADN/HTPB/Al sandwich model.

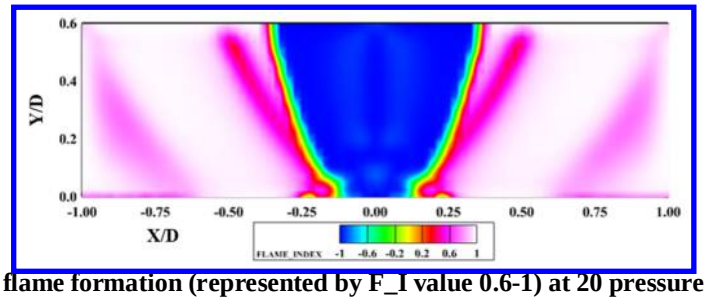


Fig 11: Premixed flame formation (represented by F_I value 0.6-1) at 20 pressure for ADN/HTPB/Al sandwich model.

A sandwich framework of the ADN/HTPB/Al composite propellant is comprised up of layers that facilitate a diffusion flame to develop upon burning surface. The species contour of H_2O, HNO_3, NH_3, N_2O, Al_2O_3, CO, CO_2 and NO shown in Fig 12&13 helps to distinguish multiple flames which occur during the combustion process of sandwich ADN/HTPB/Al. The exhaust gas composition and overall combustion kinematics of the ADN/HTPB/Al combined propellant structure are significantly influenced by this primary diffusion flame. The main components that comprise the primary diffusion flame are the gases carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), and aluminum oxide (Al_2O_3). The emission of water vapor and carbon dioxide through burning is facilitated by the inclusion of hydroxyl-terminated polybutadiene (HTPB). Additionally, the presence of metal atoms burns, producing oxides of aluminum (Al_2O_3). The presence of carbon monoxide is a byproduct of an interaction among the fuel portions, and ammonium dinitramide (ADN) that occurs at the initial stages of burning. Further the premixed flame formation is greatly influenced because of the chemical byproducts of ADN and its thermal breakdown, particularly consist of NH_3, N_2O, HNO_3, and NO. These oxygen-dense chemicals promote more rapid burning rates for propellant by enhancing the mechanisms of combustion. The temperature and chemistry of the flame are affected by NO, which functions as an intermediary in burning pathways. By making more oxygen available, the gas nitrous oxide (N_2O) speeds up the reactions that occur during combustion. Flame characteristics are additionally influenced by ammonia and HNO_3, which generate radicals that facilitate burning. The byproducts produced upon ADN thermal degradation change the combustible circumstances, which in turn affects the premixed flame's kinematics and brightness. Lastly the combination of the HTPB and Al in the sandwich model influences the flame height generated by them called as the Binder flame.

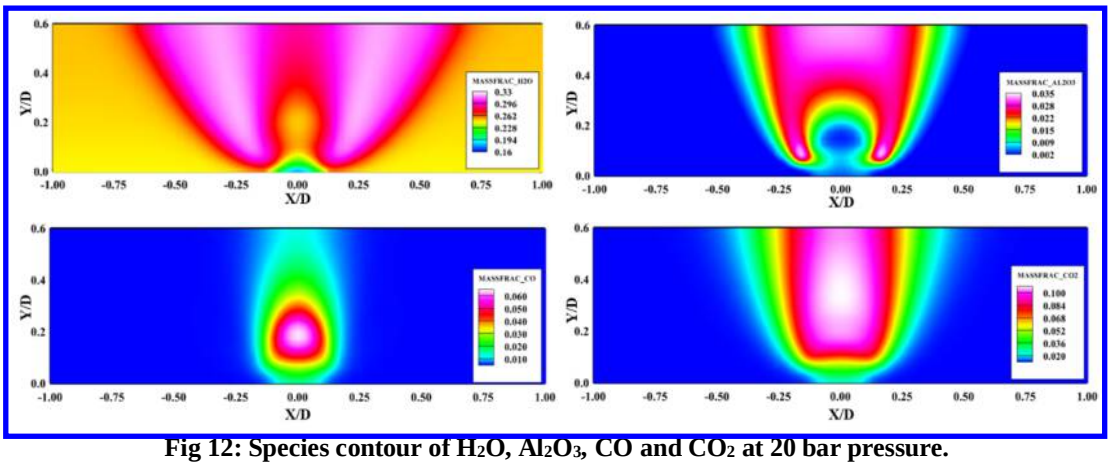


Fig 12: Species contour of H_2O, Al_2O_3, CO and CO_2 at 20 bar pressure.

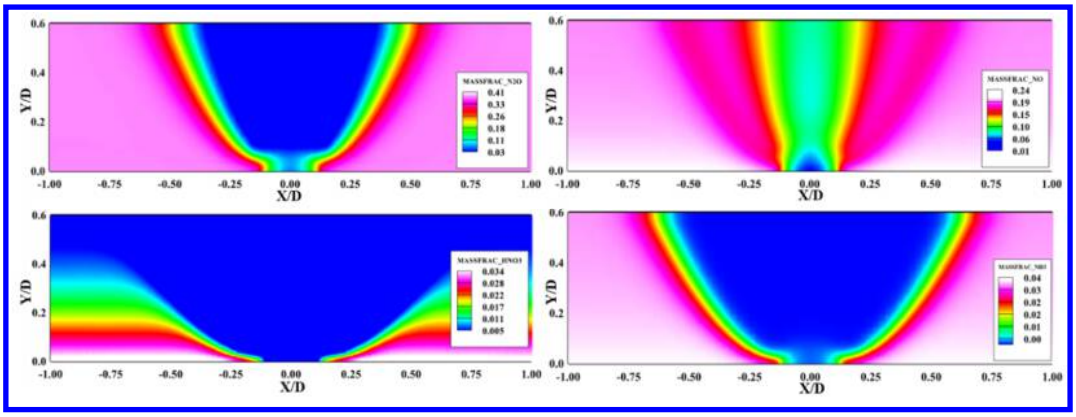


Fig 13: Species contour of NH_3, N_2O, HNO_3, and NO at 20 bar pressure.

Flame Structure influence with Al addition:

Followed by this to understand the thermal characteristics of the flame a temperature distribution along the vertical Y direction from the burning surface of at the center of ADN, HTPB and the interface is plotted for both ADN/HTPB as well as ADN/HTPB/Al sandwich model which is shown in the Fig 14,15&16. At first the flame profile of the ADN monopropellant increases swiftly to attain an adiabatic monopropellant flame temperature of 2000K which is presented in the Fig 14 for both ADN/HTPB (represented by ADN_1) and ADN/HTPB/Al (represented by ADN_2) case. Further the HTPB and HTPB/Al which placed in the center of the sandwich model will undergo of thermal decomposition and this will result in production of moderate reactive species which interacts with the thermal decomposition of products ADN and plays a crucial role in formation of the premixed binder/oxidizer flame which is show in Fig 15. Lastly the highly reactive species with major mass fraction will combine to form a high temperature region which is called as the primary diffusion flame. In the case of the ADN/HTPB sandwich model the primary diffusion flame moves away from the surface. In the absence of aluminum, the propellant produces a significantly deeper dome-shaped primary diffusion flame, with a higher proportion of flame height to dimension (Y/D ratio) spanning within 0.2 to 0.3. This formulation features an increased broad and prolonged flame. In contrast, when aluminum is incorporated into the combination, a noticeable difference ensues. The flame gets substantially more compact and tinier, generating a narrower sphere of primary diffusion flame having a lower Y/D ratio, typically ranging from 0.1 to 0.15. The inclusion of aluminum to the ADN/HTPB propellant mixture appears to have an important influence on flame characteristics during burning. The alteration in the size and form of the flame indicates a significant change in the behavior of burning and indicates that the inclusion of aluminum affects the structure of the flame. Fig 16 shows the variation of the heights in which the rise in the temperature for the ADN/HTPB with and without Al addition is presented. The rise in temperature is observed because of energy addition done by the Al species. As Al being a highly reactive and has high heat of combustion which is caused by its interactions with the species of oxidizers and binder which reduces the activation energy needed for the reaction. Also, Al serves as a form of catalyst,

assisting in the disintegration of ADN as well as potential combustion reactions that occur. Because of this catalytic action, propellant burns more rapidly and effectively by accelerating the kinetics of overall combustion.

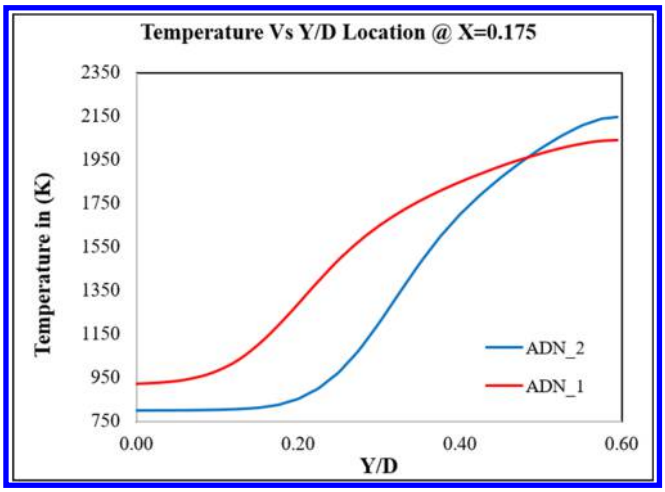


Fig 14: Temperature distribution at center of ADN at 20 bars.

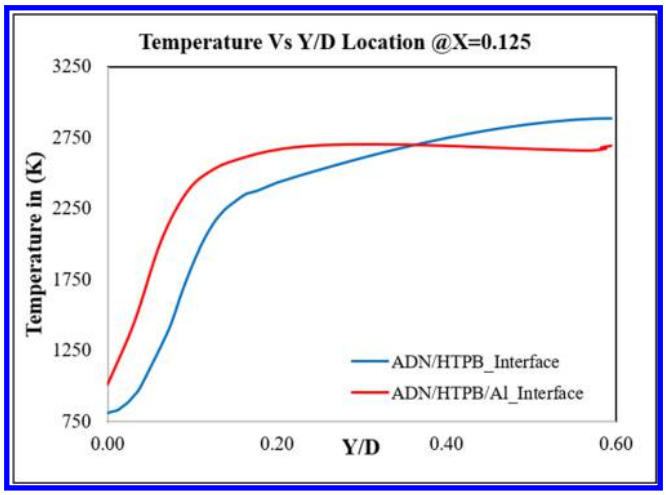


Fig 15: Temperature distribution at the Interface at 20 bars.

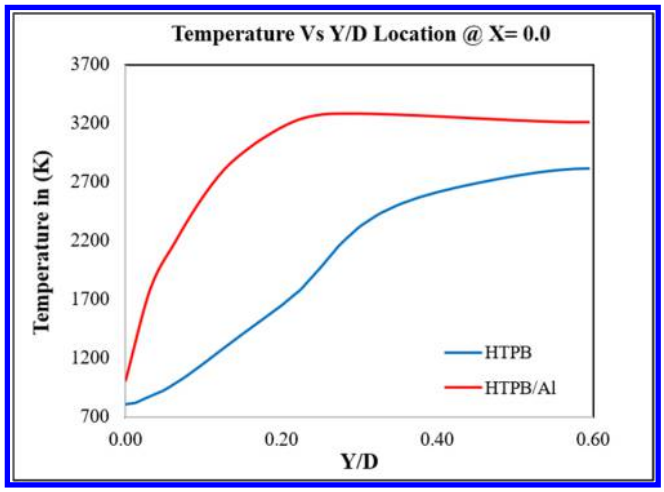


Fig 16: Temperature distribution at the center of HTPB and HTPB/Al at 20 bars.

V. Conclusion and Future work

The computational analysis of ADN/HTPB propellants, incorporating 1D reactor frameworks, sandwich modeling, and detailed chemical reactions interpretation, has significantly improved our understanding of burning behavior and flame characteristics, especially with the addition of aluminum metal powder. The results show that the ADN monopropellant combustion is well studied with the implementation of a one-dimensional reactor model, providing a deeper understanding of the three combustion in the ADN monopropellant. Sensitivity analysis revealed high temperature sensitive reactions, with NH_3+OH reacting significantly in both hot and cool flame zones has greater impact on the monopropellant flame. The integration of aluminum into ADN/HTPB resulted in a higher adiabatic flame temperature in the range of 3300-3850K, which closely matches NASA CEA equilibrium calculations. Followed by this sandwich modeling was conducted on the ADN/HTPB and ADN/HTPB/Al propellant formulations to understand the flame characteristics and structures. The ADN/HTPB sandwich model observed a dark zone region with a primary diffusion flame of 3000K burning away from the surface, while the ADN/HTPB formulation featured a deeper dome-shaped primary diffusion flame with a higher Y/D ratio ranging within 0.2-0.3, providing a broad and prolonged flame. The addition of aluminum significantly impacts the primary diffusing flame pattern, accelerating

overall combustion reactions and decreasing the dark zone region. The flame becomes more compact and tinier, resulting in a narrower primary diffusion flame with a lower Y/D ratio, typically ranging from 0.1 to 0.15. The sandwich model simulations reveal that the ADN monopropellant flame attaches to the premixed flame formed by binder interaction products, revealing complex flame dynamics within these propellant formulations. Further studies will explore modeling a larger Y-direction region to fully understand the properties of the final diffusion flame. Along with that inclusion of solid phase with condensed phase reactions and integrating it with the gas phase region will be focused. Lastly, different binders like GAP and metal additives like Boron or Magnesium will be beneficial. These studies will assess the thermal stability and practicality of using ADN-based propellants, considering practical production considerations and performance enhancement, to replace conventional propellants for a greener environment.

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VII. References

1. Jingjing Li, Weiqiang Tang, Zhenhui Liu, Kun Cong, Li Gong, Jianmin Li, Rongjie Yang, Microsized aluminum/ammonium dinitramide core-shell particles to improve the combustion performance of aluminum powders, Journal of Alloys and Compounds, Volume 907,2022,164349, ISSN 0925-8388, https://doi.org/10.1016/j.jallcom.2022.164349.
2. Fujisato, K., Habu, H., Miyake, A., Hori, K. and Vorozhtsov, A.B. (2014), Role of Additives in the Combustion of Ammonium Dinitramide. Propellants, Explosives, Pyrotechnics, 39: 518-525. https://doi.org/10.1002/prep.201300148
3. M.F., Gogulya & Makhov, M. & Dolgoborodov, A. & M.A., Brazhnikov. (2003). Detonation Performance of ADN and Its Mixtures with Al.
4. Matsunaga, H., Izato, Yi., Habu, H. *et al*. Thermal decomposition characteristics of mixtures of ammonium dinitramide and copper (II) oxide. *J Therm Anal Calorim* **121**, 319–326 (2015). https://doi.org/10.1007/s10973-015-4645-6
5. Marc Comet, *[a] Cédric Schwartz, [a] Fabien Schnell, [a] Franck Oudot, [a] Bastien Lallemand, [a] and Denis Spitzer[a] 'New 1208 Detonating Compositions from Ammonium Dinitramide' Propellant Explosives and Pyro techniques DOI: 1209 10.1002/prep.202000288.
6. Cristilli, Francesco & Weiser, Volker & Maggi, Filippo & Imiolek, A & Tagliabue, C & Gettwert, Volker & Dossi, Stefano. (2017). Burning Behavior of ADN-Based Propellants Loaded with Al-Mg Mechanically Activated Powders. 10.13009/EUCASS2017-429.
7. Weiser, Volker & Franzin, Andrea & DeLuca, Luigi & Fischer, Sebastian & Gettwert, Volker & Kelzenberg, Stefan & Knapp, Sebastian & Raab, Angelika & Roth, Evelin & Eisenreich, Norbert. (2017). Combustion Behavior of Aluminum Particles in ADN/GAP Composite Propellants. 10.1007/978-3-319-27748-6_10.
8. Stefan Sims, Sebastian Fischer, and Claudio Tagliabue ''ADN Solid Propellants with High Burning Rates as Booster Material 1213 for Hypersonic Applications'' Propellant Pyrotechnic Explosives doi.org/10.1002/prep.202200028.
9. Fujisato, Koji & Habu, Hiroto & Shibamoto, Hidefumi & Yu, Xiuchao & Miyake, Atsumi & Hori, Keiichi. (2012). Combustion Characteristics of ADN (Ammonium Dinitramide) Based Solid Propellants. TRANSACTIONS OF THE JAPAN SOCIETY FOR AERONAUTICAL AND SPACE SCIENCES, AEROSPACE TECHNOLOGY JAPAN. 10. Pa_89-Pa_92. 10.2322/tastj.10. Pa_89.
10. A model of composite solid-propellant combustion based on multiple flames M. W. BECKSTEAD, R. L. DERR, and C. F. PRICE AIAA Journal 1970 8:12, 2200-2207
11. Piyush Thakre, Yi Duan, Vigor Yang, Modeling of ammonium dinitramide (ADN) monopropellant combustion with coupled condensed and gas phase kinetics, Combustion and Flame, Volume 161, Issue 1,2014, Pages 347-362, ISSN 0010-2180, https://doi.org/10.1016/j.combustflame.2013.08.006.
12. Richards, K. J., Senecal, P. K., and Pomraning, E., CONVERGE 3.1 Manual, Convergent Science, Madison, WI (2023).

13. David G. Goodwin, Harry K. Moffat, Ingmar Schoegl, Raymond L. Speth, and Bryan W. Weber. *Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes*. https://www.cantera.org, 2023. Version 3.0.0. doi:10.5281/zenodo.8137090
14. Oleg P Korobeinichev, Tatyana A Bolshova, Alexander A Paletsky, Modeling the chemical reactions of ammonium dinitramide (ADN) in a flame, Combustion and Flame, Volume 126, Issues 1–2, 2001, Pages 1516-1523, ISSN 0010-2180, https://doi.org/10.1016/S0010-2180(01)00269-3.
15. N. COHEN and L. STRAND. "An improved model for the combustion of AP composite propellants," AIAA 1981-1553. *17th Joint Propulsion Conference*. July 1981.
16. Thomas, James & Petersen, Eric. (2019). Updated Three-Flame Modeling of Composite AP/HTPB Propellants.
17. Neeraj Kumar Pradhan, Arindrajit Chowdhury, Debasis Chakraborty, Neeraj Kumbhakarna, Modified multiflame model for AP-HTPB composite propellant combustion, Combustion and Flame, Volume 259, 2024, 113195, ISSN 0010-2180, https://doi.org/10.1016/j.combustflame.2023.113195.
18. P. Senecal et al., "Multi-dimensional modeling of direct-injection diesel spray liquid length and flame lift-off length using cfd and parallel detailed chemistry," SAE Technical Paper, Tech. Rep., 2003.
19. Jeppson, M.B. & Beckstead, Merrill & Jing, Q (1998). A Kinetic Model for the Premixed Combustion of a Fine AP/HTPB Composite Propellant. AIAA Journal. 44. 10.2514/6.1998-447.
20. Shuyuan Liu, Luyang Han, Pengxiang He, Limin Wang, Jinchao Han, Songqi Hu, Conjugate heat and mass transfer at heterogeneous burning surface of AP/HTPB/Al composite propellant at 2–10 MPa, Applied Thermal Engineering, Volume, ISSN 1359-4311, https://doi.org/10.1016/j.applthermaleng.2023.120362.
21. S. Gordon and B. J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications," NASA Reference Publication 1311 (1996).
22. Radu Cazan and Suresh Menon. "Direct Numerical Simulation of Sandwich Propellant Combustion," AIAA 2003-5082. 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit. July 2003.
23. Lengelle, G. & Duterque, J. & Trubert, J.. (2002). Combustion of Solid Propellants. 63.
24. Kosiba, G.D., 2017. Multidimensional modeling of composite solid propellant combustion (Doctoral dissertation, Rensselaer Polytechnic Institute, Troy, NY). https://hdl.handle.net/20.500.13015/2145
25. M. K. King, "Erosive burning of composite solid propellants: Experimental and modelling studies," J. of Spacecraft and Rockets, vol. 16, no. 3, pp. 154–162, 1979.
26. M. K. King, "Model for steady state combustion of unimodal composite solid propellants," in 16th Aerospace Sci. Meeting, Huntsville, AL, Jan. 1978.
27. Oleg P Korobeinichev, Alexander A Paletsky, Flame structure of ADN/HTPB composite propellants,Combustion and Flame,Volume 127, Issue 3,2001,Pages 2059-2065,ISSN 0010-2180,https://doi.org/10.1016/S0010-2180(01)00308-X.