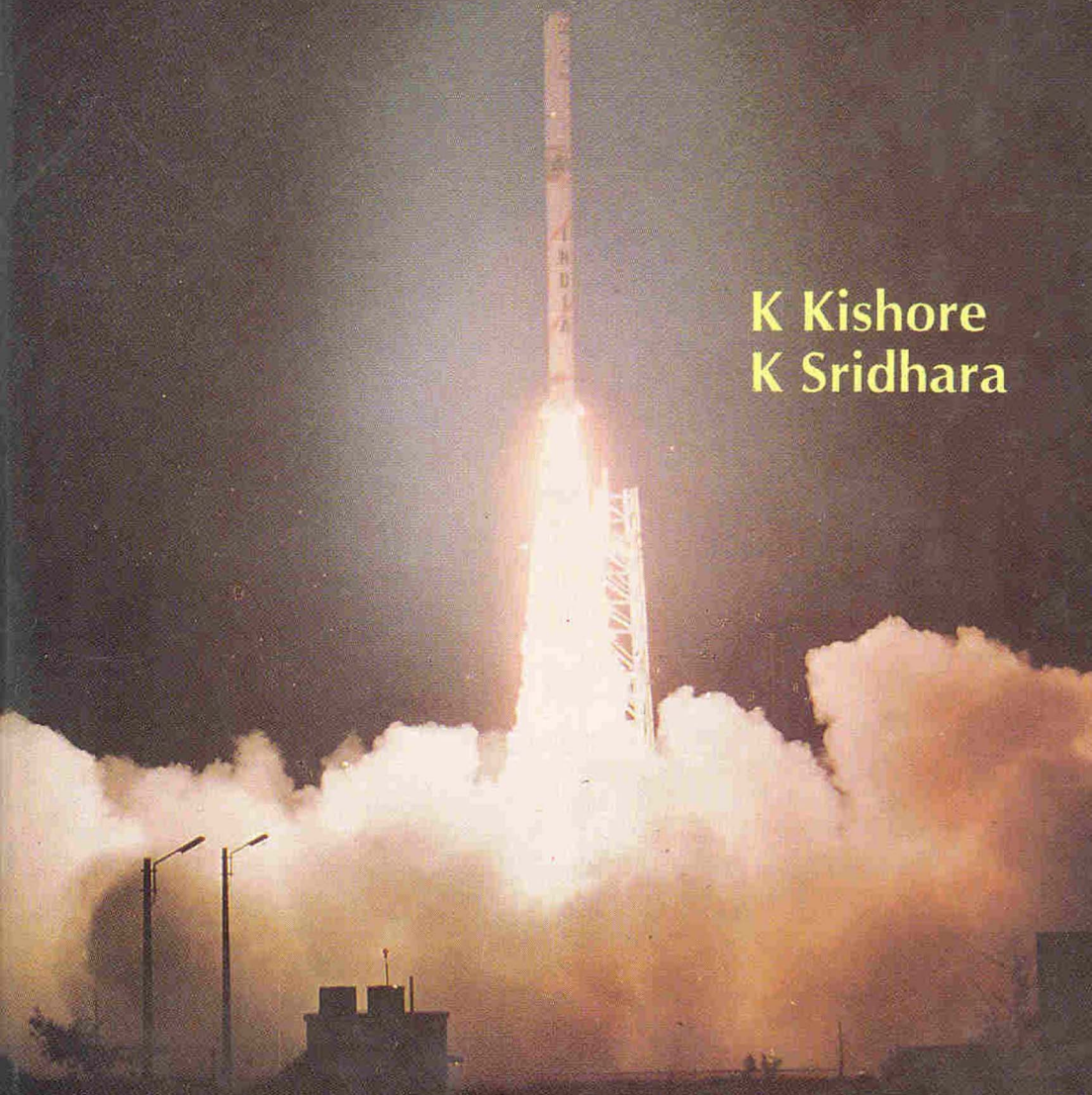




# Solid Propellant Chemistry

Condensed Phase Behaviour of  
Ammonium Perchlorate-Based Solid Propellants

**K Kishore**  
**K Sridhara**



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**SOLID PROPELLANT CHEMISTRY: CONDENSED PHASE  
BEHAVIOUR OF AMMONIUM PERCHLORATE-BASED SOLID  
PROPELLANTS**

**K Kishore & K Sridhara**

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## PREFACE

There are about half a dozen books dealing with propellant chemistry but much of the information available therein is rather old and none of them discusses the condensed phase combustion chemistry of solid propellants in detail. The present monograph is the first of its kind in which the material accumulated over several decades has been sifted from literature and articulated to highlight the importance of condensed phase chemistry which seems to be vital for understanding the key phenomena like burning rate modulation and ageing. Besides, the subtle roles of binders, oxidizers and catalysts have been brought out. It has also been demonstrated as to how condensed phase chemistry is vital in understanding the commonly observed phenomena in solid propellants like extinction, intermittent, plateau and flameless combustions.

In defence and space laboratories and also in some private companies, a large number of scientists and engineers are involved in work on propellants. This monograph will be extremely useful for this large community, not only in helping them to assess the progress made in AP-based composite solid propellants but also to grasp the key phenomena in an organised manner. It will also serve as a useful information source for those who wish to enter the fascinating field of solid propellant combustion. Besides, there are many academic institutions and universities where propellant chemistry is taught either as an independent subject or under the general courses in combustion or fuel science and technology. This monograph will serve as a good reference book not only for those opting for these courses but also for those engaged in basic research in propellant chemistry. This monograph is aimed at catering to the information needs of readers at postgraduate and research levels. The readers of course are required to have some exposure in propellants.

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Bangalore  
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**K Kishore**  
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# CHAPTER 1

## INTRODUCTION

Man's desire to explore outer space and build a strong defence edifice has culminated in the development of space vehicles and missiles in which composite solid propellants (CSP) are the major source of chemical energy<sup>1,2</sup>. Being complex mixtures, their combustion behaviour too is quite complex and is not yet fully understood. CSP<sup>3-6</sup> are heterogeneous mixtures consisting of a large proportion of oxidizer, usually ammonium perchlorate (AP), and a fuel-cum-binder, generally hydroxy-terminated polybutadiene (HTPB) or carboxy-terminated polybutadiene (CTPB). In addition, they contain curing agents, plasticizers and bonding agents for improving their mechanical properties, and metallic fuel additives and burning rate modifiers for improving specific impulse and burning rate, respectively. A typical CSP composition is given in Table 1.1.

**Table 1.1. Typical composition of CSP<sup>6</sup>**

<i>Ingredients</i>	<i>Weight, %</i>
Ammonium perchlorate	60 - 84
Butadiene polymer	12 - 16
Aluminium	2 - 20
Curing agent(s)	0.2 - 1.0
Stabilizers	0 - 1.0

The chemistry of a CSP formulation and its combustion is an engrossing complex phenomenon and has been the subject of many studies<sup>7-14</sup>. The combustion profile of the propellant can be classified into several zones, such as heated zone, chemical reaction zone, burning surface zone and porous zone, all in the condensed phase, and fragment flowing zone and product zone in the gas phase<sup>15</sup>. The combustion of CSP occurs to varying degrees in both condensed

and gas phases<sup>16</sup>. There are two schools of thought regarding the combustion of CSP. According to one school, the gas phase processes are believed to control the burning of the propellant; the gaseous species emanating from the pyrolyzing surface are considered to intermix and react exothermally in the gas phase to form final products, liberating heat and establishing an equilibrium flame temperature. Part of the heat generated in the flame is transferred to the surface to be used up in pyrolyzing and gasifying the surface layer, so that the combustion process recurs steadily. In modelling gas phase combustion processes, the reactions occurring therein are considered to be fast and the heat transfer from the flame to the surface is considered to be the rate-controlling step.

The other school of thought<sup>16-18</sup>, which also includes the Bangalore group<sup>19-26</sup>, believes that the condensed phase reactions occurring at or just below the burning surface are important. The decomposition/degradation in addition to the gas phase reactions of the oxidizer and the binder, and the cross-reactions between their products are exothermic in nature and contribute significantly to the total energy of the propellant. Condensed phase processes also include melting and gasification phenomena at the surface. Knowledge about the chemistry of condensed phase reactions, which is a key process, will facilitate understanding of vital phenomena like burning rate modulation and ageing. An organized comprehension of the condensed phase chemistry will also provide a better insight into the extinction phenomenon and intermittent, plateau and flameless combustion.

Kishore and coworkers<sup>19-27</sup> demonstrated both qualitatively and quantitatively the existence of condensed phase reactions. In AP/polystyrene (PS) model propellant<sup>19-26</sup>, mass spectroscopic analyses have indicated that the mass spectrum of CSP is different from the additive spectra of AP and PS individually. Likewise, the enthalpy of propellant decomposition, which is a nucleation-controlled phenomenon<sup>28</sup>, is larger compared to the additive enthalpies of the individual components<sup>29,30</sup>. This excess enthalpy of the condensed phase is about one third of the calorimetric value (total heat of combustion)<sup>18,23,24,31</sup>. This is corroborated by a master plot of the thermal decomposition rate against the burning rate of propellants, which suggests that the burning rate increase/decrease is about one third of the order by which the rate of thermal decomposition increases/decreases in the presence of additives<sup>21,22,25</sup>. Separation of the binder portion from the quenched

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