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# A study of condensed system flame structure

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Abstract - The main source of our knowledge on condensed system (CS) combustion chemistry are the results of flame structure investigations. Recently the great progress in this field of combustion science has been observed. The modern state of this problem is considered. The methods of experimental investigation and modeling of CS flame structure are described. The mechanisms and kinetics of chemical reactions in CS flame are discussed.

## INTRODUCTION

One of the main tasks of combustion theory is to study the combustion mechanism on the molecular level. The main source of our knowledge of combustion chemistry is the results of flame structure studies: spatial distributions of temperature and species concentrations in flames. Flames of gaseous systems are the simplest and well studied flames. There are quite a number of books and reviews on this subject (ref.1,2). An important class of flames are the flames of CS which are able to selfsustaining combustion, e.g. powders, composite solid propellants and their components such as ammonium perchlorate, $RDX$, $HMX$ etc. . Unlike the combustion mechanism of gases, that of CS is more complicated and multistage; it is two-stage in the simplest case : the first stage is the gasification of fuel, the second stage is the conversion of gasification products to final products. The important peculiarities of CS combustion are : 1) the presence of burning surface; 2) narrow flame zone ( about $0.1 - 1$ $mm$ at low pressures) adjacent to the burning surface. The CS burning rate is $0.1$ $mm/s$ at low pressures and $10 - 100$ $mm/s$ at high pressures. CS flames can hardly be stabilized for several tens of seconds in the best case whereas the gaseous flames can easily be stabilized at the burner in a few hours . Therefore it is necessary to use special diagnostic technique with high spatial and temporal resolutions for CS flames. The above mentioned reasons can explain why the CS flame structure has been studied to a smaller extent as compared with the flame structure of gaseous systems . So far the main quantitative method used for studying the internal structure of combustion wave of condensed systems was the investigation of temperature distribution using fine wire thermocouples (ref.3). This method, however, gives information neither on the nature of the principal processes in the combustion zones nor on their kinetics. The main methods applied to the investigation of chemical structure of flame are the following : 1) probing mass-spectrometry and chromatography, 2) spectroscopic methods-absorption and emission, laser induced fluorescence (LIF), Spontaneous Raman Scattering (SRS), Coherent Anti-Stokes Raman Spectroscopy (CARS).

Until recently the number of works on CS flame structure studies was very small. However, as a result of improvement of experimental technique, development of works on flame structure modeling and rise of interest to CS combustion chemistry, the number of works in this field has been increasing now.This work is intended to survey the modern state of studies on chemical structure of CS flames.

## FIRST STUDIES

One of the first works on CS flame structure was that of Heller and Gordon (ref.4) who sampled double-base propellant flame at high pressures ( $10 - 20$ atm ) at a distance of 1 $mm$ and more from the burning surface. Later , Hertzberg (ref.5) reported sampling of ammonium perchlorate and $PMMA$ sandwich flame at low pressure under $CO_2$ - laser irradiation. However, the technique used in these works was imperfect and did not allow the authors to receive reliable results near the burning surface. The last decade studies on the chemical structure of CS flame have been carried out at higher experimental and theoretical level. The number of works markedly increased especially in Russia and USA. A survey of works which have been carried out in Novosibirsk since 1966 till 1986 was presented in ref.6 and that in USA in 1980-1990 was reported by T.Edwards at the International Workshop on Transient Combustion and Stability of Solid Propellants in Milano in 1990 (ref.7). These studies can be divided into three groups:

1. Experimental study of CS flame structure.
2. Experimental study of the structure of gaseous flames modeling the CS flames.
3. Modeling of gaseous and CS flame structure using detailed kinetics.

## MASS-SPECTROMETRIC STUDIES OF CS FLAME STRUCTURE

At present the most effective and universal experimental technique for studying the CS flame structure is the method of mass-spectrometric probing of CS flames (MSPCSF) which was improved in our laboratory in 1975 (ref.6-8). It allows to record all stable species present in the flame as well as the structure of CS flame with the resolution sufficient to study CS combustion at low pressures. The use of spectroscopic methods requires certain parameters which are not available. The MSPCSF method consists in the following : a burning strand of solid propellant moves with a speed exceeding the burning rate towards the probe so that the probe is sampling continuously the gaseous species from all the zones including those adjacent to the burning surface. The sample is transported to the ion source of a time-of-flight (TOF) or quadrupole (QMS) mass-spectrometer. The mass spectra of samples are recorded with simultaneous filming of the probe and burning surface. The data allow one to identify stable components, to determine their concentrations and spatial distributions, i.e. to study the flame microstructure.

The apparatuses of two types have been developed for studying the flame structure. The sample is transported to the ion source as a molecular flow using a microprobe with an inlet orifice of 10-20 $\mu m$ in the first type of setup and as a molecular beam using a sonic probe with the inlet orifice 100-200 $\mu m$ in the second type. The former set up has a high spatial resolution and negligible disturbs the flame that allows one to study the flame with a narrow combustion zone up to 0.1 *mm*. However, in this case, radicals recombine and quenching can become a problem. The latter set up allows detecting the radicals, but more strongly disturbs the flame and therefore has a smaller spatial resolution. Fig. 1 shows the last model of the second type setup, developed in our laboratory (ref.9).

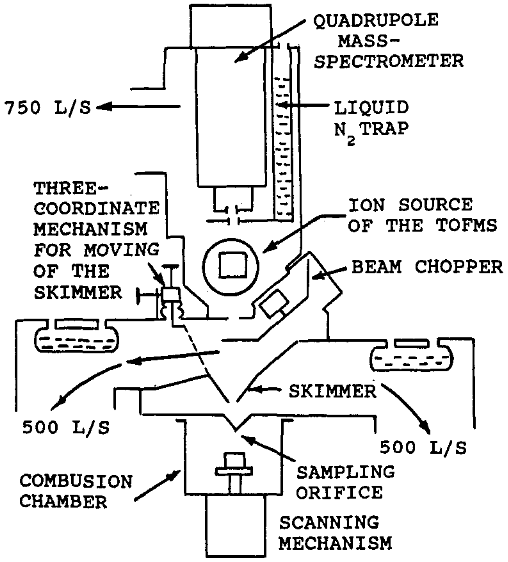

Fig. 1 The set up with molecular beam inlet system for sampling of flames.

TABLE 1. Condensed systems which flame structure has been studied by probing mass-spectrometry.

| $N^o$ | System | Pressure, atm | Type of setup | Ref. |
|---|---|---|---|---|
| 1 | $AP$ | 0.6 (T=260°C) | 1 | 12 |
| 2 | $RDX$ | 0.5 | 2 | 13,14 |
| | $HMX$ | 1 | | |
| 3 | $AP-CTPB$, sandwiches | 0.6; 0.08 | 1 | 15 - 18 |
| | $AP-CTPB$, | 0.3 | | |
| | $HMX-AP, CTPB$ | 0.5 | | |
| 4 | $RDX$ composite propellants | 1 | $CO_2$ - laser heating 200 W/cm$^2$ | 19 |

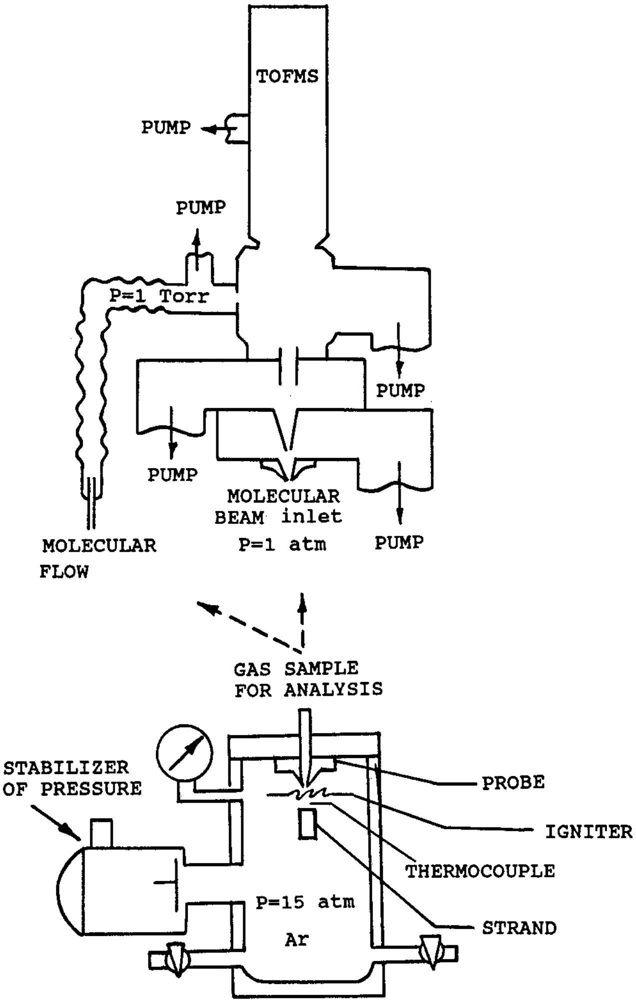

Fig. 2
The set up, which was used for investigation of double base propellant flame at high pressures.

A characteristic feature of this set up is the introduction of a sample as a molecular beam both into the ion source of TOFMS and QMS. It allows one to extend the potentialities of MS analysis of a sample on studying the CS flame structure; i.g. to detect simultaneously stable species by TOFMS and one lable particle by QMS. The range of working pressures is 0.1-100 atm. Fig. 2 shows the set up of the first type, which was used for investigation of double-base propellant flame at the pressure 15 atm (ref.10). Quantitative aspects of the results of MS sampling investigations of the CS flame structure are essentially defined by the accuracy of determination of errors of the sampling technique. In the case of flame with narrow zones of combustion ( 0.1 *mm*) the zone width is comparable with the external diameter of the probe tip. This case was studied in our laboratory (ref.11). In order to analyze this problem, model flat methane-air flame (flame zone width 0.5 *mm*) has been studied at atmospheric pressure using several methods : 1) microprobing MS (with the outer diameter of the probe tip 0.5 *mm*); 2) SRS using spectrometer with intracavity spontaneous Raman scattering; 3) microthermocouple. The conclusion is the following. If you make a correction for sampling site relative to the burning surface, the errors in the measurement of the concentration profile of stable species will amount to less than 10 – 15 %. It is quite sufficient for quantitative processing of the probe data on the flame structure : establishment of reaction mechanism and estimation of reaction rate constants. Table 1 shows CS which flame structure has been studied by probing MS.

Systematic investigations have been carried out in the Institute of Chemical Kinetics and Combustion in Novosibirsk and in the Pennsylvania State University. The chemical structure of the high temperature zone of *RDX* flame has been studied in most details. Fig.3 shows data on chemical flame structure for *RDX* at 0.5 atm (ref.13).

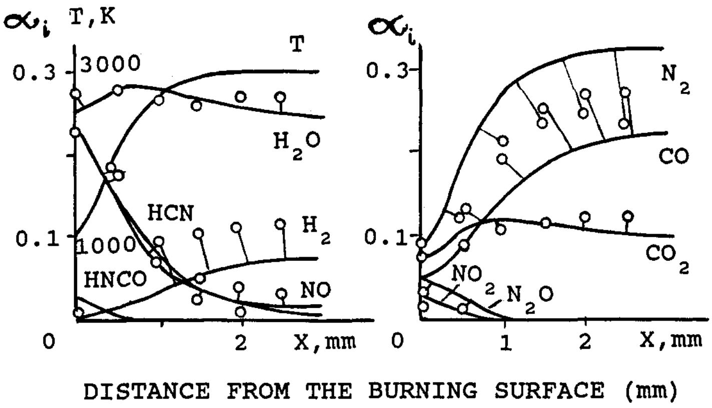

Fig. 3 Hexogen flame structure (dots - experiment, lines - theory (ref. 13).

## MODELING OF CS FLAME STRUCTURE. KINETICS AND MECHANISM OF CHEMICAL REACTIONS IN CS FLAMES

Modeling of flame structure for several CS has been carried out using detailed kinetic mechanisms and system of differential equations describing one-dimensional flow of reacting gas. Table 2 shows most important works. *RDX* and *HMX* flame structure has been modeled in most detail. C.F.Melius from National Sandia Laboratory used "Chemkin" code and detailed kinetic mechanism (131 stages) to model *RDX* flame structure at 0.5 and 17 atm (ref.21). He compared the predictions of chemical kinetic model, shown in Fig.4, with the experimental data for 0.5 atm (ref.14) and noted remarkably good agreement between them. He compared his mechanism to that of Ermolin et al and found that they are very similar.

TABLE 2. Condensed systems which flame structure have been modeled using detailed kinetics.

| $N^o$ | System | Ref. | $N^o$ | System | Ref. |
|---|---|---|---|---|---|
| 1 | $AP$ | 20 | 4 | $HMX, RDX$ | 21 |
| 2 | $AP - CTPB$ | 16 | 5 | $HMX, NG$ - binder<br>$HMX$ - binder | 22 |
| 3 | $RDX$ | 13 | 6 | $AN$ - binder, $TMETN$ | 23 |

There is some difference in the paths of the reactions. After Melius the main path proceeds via the channel $CN \rightarrow NCO$, whereas after Ermolin et al it proceeds via the $HNCO \rightarrow NH_2$ one. Melius also found that $C_2N_2$ transforms into HCN rather than into the intermediate product of the chain process as it follows from Ref.13,21. Ermolin et al. modeled high temperature flame zone using experimental data as boundary conditions (ref.13), whereas Melius (ref.21) modeled both low and high temperature zones using some assumptions about the chemical composition of species at the burning surface. He considered reaction of *RDX* vapors decomposition followed by formation of $NO_2$ and $CH_2O$ and their further reactions yielding $NO$ and $HCN$ in the low temperature flame zone. It is necessary to note that $CH_2O$ has not been observed in *RDX* flame zone in experiment of ref.13, obtained by set up $N^o$ 2. But the zone of $CH_2O + NO_2$ reaction has been registered in the *HMX* flame zone for combustion of sandwich based on $HMX, AP$ and $CTPB$, using set up $N^o$ 1 (ref.17). But so far there is no experimental confirmation of the existence of the zone of *HMX* (or *RDX*) vapor decomposition. Theoretical predictions show that the zone width is about several $\mu m$. This example demonstrates the main difficulty of CS flame structure study which appears due to narrow flame zone adjacent to the burning surface.

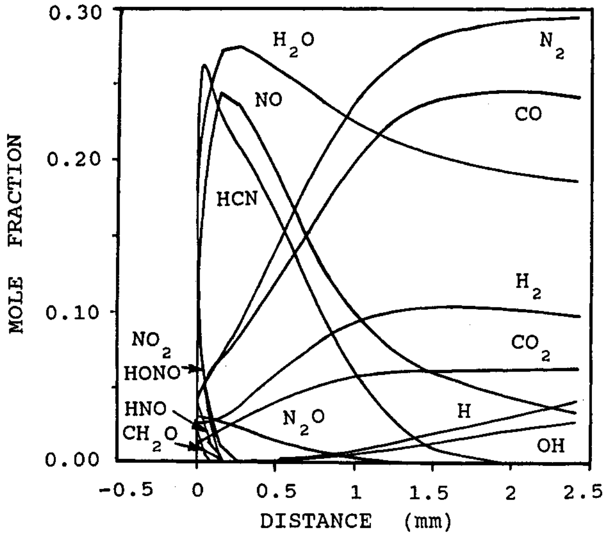

Fig. 4 Major species concentration (mole fraction) profiles as a function of distance (mm) from the burning surface for the *RDX* flame at 0.5 atm (ref.21).

As it was shown in modeling *AP* flame structure (ref.24,25), the chain-branching reaction

$$NH_2 + O_2 \rightarrow HNO + OH \qquad (*)$$

is one of the most important stages in *AP* flame chemistry. This reaction was studied experimentally mainly at low temperatures and theoretically in a number of papers and its rate constant is most often taken from the papers by Dean (ref.26,27). In order to reach agreement between experimental and theoretical results on *AP* flame structure a 30-times higher rate constant must be used. Comparison of experimental data of Van Tiggelen et al on $NH_3 - O_2 - Ar$ flame structure at P=35 torr (ref.28) and the data reported by Fuji on the ignition of $NH_3 - O_2 - Ar$ mixture behind reflected shock waves at 1-10 atm (ref.29) with the results of modeling by Ermolin et al. (ref. 24,25) showed the pressure dependence of the rate constant of reaction (*). This conclusion also follows from experimental results and modeling of flame structure of composite solid propellants based on *AP* and *CTPB* (refs.15,16). The pressure dependence of the rate constant is assigned to the neglection of the $NH_2 + O_2 \rightarrow products$ stage parallel to reaction (*). In order to obtain the pressure independent rate constant and explain above mentioned facts it is necessary to extend the kinetic mechanism of $NH_2 + O_2$ reaction

$$\begin{array}{ccccc} NH_2 + O_2 & \rightleftharpoons & NH_2OO & \rightleftharpoons & HNOOH \\ \downarrow & & \downarrow & & \\ NH_2O + O & \longrightarrow & HNO + OH & & \end{array} \qquad (**)$$

and add the mechanism the reactions of the particles $NH_2O_2$, $HNOOH$, $NH_2O$, including three-molecular stages.

## SPECTROSCOPIC STUDIES OF CS FLAME STRUCTURE

The main spectroscopic methods, used in investigation of CS flame structure are shown in Table 3.

TABLE 3. Spectroscopic studies of CS flame structure.

| Method | Species | System | Resolution, $\mu m$ | Ref. |
|---|---|---|---|---|
| Absorption, emission | $OH$<br>$NH$ | $HMX$ - binder<br>P = 15 atm | 15 | 30 |
| LIF | $CN$<br>$OH$ | $HMX$ - binder<br>P = 35 atm | 20 - 50 | 23 |
| PLIF | $OH, NO$<br>$CN, NH$<br>$NO_2$ | $HMX$, laser irradiation<br>P = 1 - 3 atm | 20 | 31 |
| CARS | $CO, N_2, H_2$ | $HMX$ - binder | 200 | 32 |

Figure 5 show the results of investigations of *HMX* flame structure obtained by PLIF (ref.31). Only a few systems have been studied quantitatively by these methods. The main advantage of this technique in comparison with the probing technique lies in its contactless. However the application of these technique to the investigation of narrow flames at high pressure face difficulties because of insufficiently high spatial resolution.

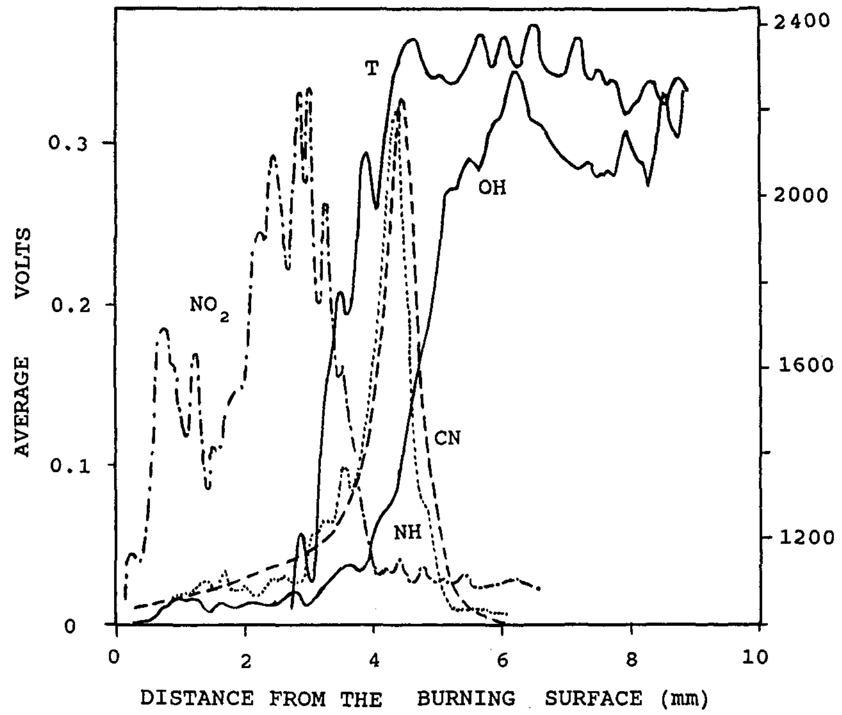

Fig. 5 Species and temperature profiles during steady-state laser supported deflagration of *HMX* (ref.31).

## MEASUREMENTS AND MODELING OF CS RELATED FLAMES

Since the CS flame width even at low pressures is comparable to the spatial resolution of diagnostic apparatus researchers came to modeling the CS flames by gaseous flames wide enough. Measurement and modeling of the structure of CS related flames allow one to find chemical mechanism which then can be used for prediction of CS flame structure. The main problem of this approach lies in correct choosing those gaseous components which are the products of gasification process of CS at the burning surface and are responsible for heat release in flame. Table 4 shows studied flames. $HClO_4 - NH_3$ flame models *AP* flame. Other flames, based on $NO_2$ and $N_2O$, model *RDX* and *HMX* flames. Figure 6 shows the results of investigation of $HCN/NO_2$ flame structure (ref.34).

TABLE 4. Measurements and modelling of CS related flames.

| System | Ref. | System | Ref. |
|---|---|---|---|
| $HClO_4 - NH_3$ | 33 | $CH_4 - N_2O$ | 36 |
| $HCN - NO_2$ | 34 | $CH_4 - NO_2$ | 37 |
| $C_2N_2 - NO_2$ | 35 | | |
| $CH_2O - NO_2$ | 36 | | |
| $CH_4 - NO_2$ | | | |

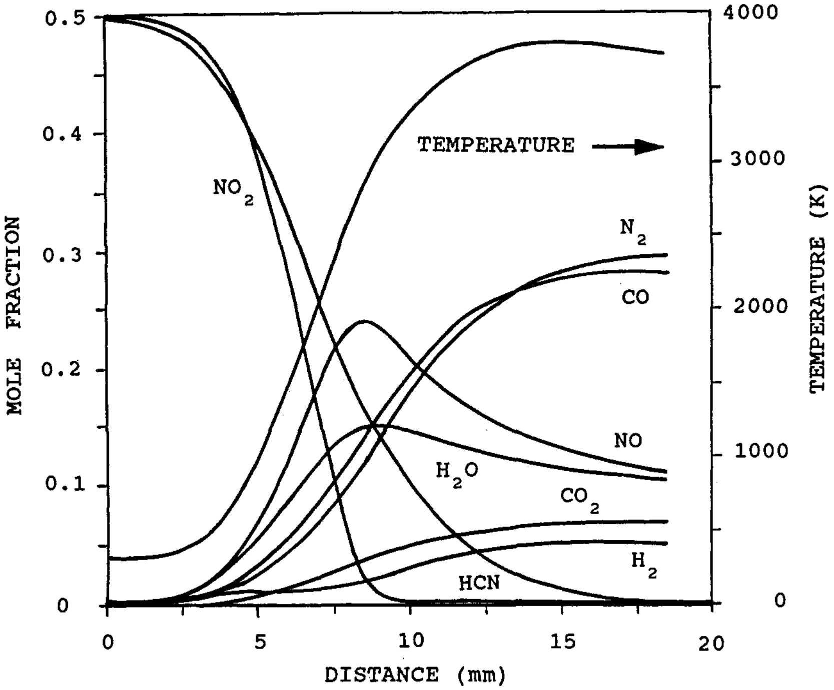

Fig. 6 Calculated temperature and major species concentration profiles of an $HCN/NO_2$ flame at 25 torr (ref.34).

## SUMMARY AND FUTURE PROSPECTS

The study of CS flame structure has become one of scientific directions in combustion science. In future it is useful to improve the experimental technique, to increase the spatial resolution of optical and probing methods, to extend the range of pressures towards higher pressures, to couple the probing and optical methods.

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