Swirl and Fuel Composition Effects on Boron Combustion in **Solid-Fuel Ramjets**

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The objective of this experimental investigation was to determine the influence of swirl flow and fuel composition on boron combustion efficiency, combustion products, and specific thrust. A solid-fuel ramjet combustor that was directly connected with an air heater and an air supply was used. The experiments were conducted with and without inlet flow swirl. HTPB fuels containing up to 40% boron or boron carbide in varying compositions were applied. An exhaust particle sampling technique in connection with a chemical analysis procedure was developed in order to measure the composition of the condensed combustion products. The principle of the sampling method was based on quenching the reaction products on a cold surface. The results show that boron combustion efficiency and specific thrust are strongly increased for swirl flow conditions. Boron combustion efficiency increases with increasing amounts of boron in the fuel until a maximum at about 20% boron is reached. Further addition of boron leads to a decrease in combustion efficiency. The observations also lead to a similar behavior of specific thrust. The results for boron carbide fuels were similar, but no maximum in combustion efficiency has been observed.

Nomenclature

= area based on initial fuel grain diameter measured characteristic velocity for hot air before ignition

measured characteristic velocity after ignition

calculated characteristic velocity

thrust coefficient flame holder diameter

internal diameter of fuel grain afterburning chamber diameter

nozzle exit diameter

= thrust

f fuel-to-air ratio \dot{m}_a mass flow air

mass fraction of B₂O₃ m_{B203} $m_{\rm B}$ mass fraction of B mass fraction of B₄C $m_{
m B4C}$ \dot{m}_{tot} total mass flow

pressure of surrounding atmosphere

 P_a nozzle stagnation pressure

radial location S swirl number

 T_o combustor inlet temperature

axial distance

 ΔH heat of combustion per mole ΔH_{c} heat of combustion per g air ΔH_m = heat of combustion per unit mass ΔH_{ν} heat of combustion per unit volume

heat capacity ratio

boron combustion efficiency η_{B}

= combustion efficiency based on thrust η_{TF}

viscosity μ = fuel density

Introduction

T is well known that boron is a potential fuel candidate I for airbreathing propulsion systems. Because of its high

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volumetric heat of combustion its application should substantially increase the performance of volume-limited vehicles. Boron carbide is also an interesting candidate. It provides nearly the same volumetric heat release as boron (Table 1) and its price is only about sixty percent of that of amorphous boron. Realizing this potential, however, has often been unsatisfactory because of incomplete combustion of the boron, resulting in low combustion efficiencies. Theoretical and experimental investigations have been conducted by many authors.¹⁻⁸ Most of the experiments were done in well-defined test set-ups in order to investigate thoroughly the fundamental aspects of boron combustion and to give valuable insight into the combustion mechanism. But, for practical applications, it was felt that there was some lack in fuel- and combustororiented experiments. Recent studies demonstrated the influence of swirl, inlet temperature, mass flow and different HTPB and polyethylene fuels.^{9,10} No further fuel modifications were made and no metallized fuels were used. Therefore, an experimental program was started in order to investigate the influence of various fuel compositions in a solid-fuel ramjet combustion chamber in more detail. Because boron is the fuel component that does not burn very efficiently, whereas the fuel binder burns very well, the objective was to consider the combustion efficiency of boron itself. Therefore, the reaction products of the boron combustion had to be determined. This was also done for boron carbide-containing fuels. A second objective was to measure the influence of swirl flow on boron combustion efficiency. Recent measurements¹⁰ of temperature profiles in a solid-fuel ramjet combustor showed that the temperatures in the combustion chamber generally reach higher values with swirl. This is illustrated in Fig. 1 where maximum temperatures of 1760°C are reached with swirl and 1630°C without swirl. The measurements were done in the vicinity of the reattachment point. It is well known that, in order to achieve boron ignition, temperatures above 1900 K are necessary.8 Therefore, we concluded that swirl flow may improve boron ignition and combustion because of the higher temperature level. In addition, swirl flow should improve mixing and residence time behavior leading to better combustion efficiency and improved thrust.

Experimental Setup and Procedure

The investigations were carried out at our ramjet test facility. The combustor, air heater, and installation are represented in Figs. 2 and 3. The configuration was a connected-

	several fuels					
	ΔH_{ν} , kcal/cm ³	ΔH_m , kcal/g	Δ <i>H</i> , kcal/Mol	ΔH_a , kcal/gair	f, gfuel/gair	ρ, g/cm³
В	32.87	14.06	151.0	1.462	0.104	2.34
B_4C	31.38	12.455	688.64	1.254	0.101	2.52
Be	29.96	16.198	146.0	2.106	0.13	1.85
Li	5.47	10.246	142.21	2.070	0.202	0.534
C	17.6	7.82	93.969	0.680	0.087	2.25
Si	17.04	7.31	205.0	1.499	0.205	2.33
Mg	10.28	5.91	143.84	2.092	0.354	1.74
Al	19.98	7.306	199.55	1.938	0.262	2.702
Zr	18.37	2.83	258.2	1.879	0.664	6.49
Ti	20.48	4.55	218.0	1.588	0.349	4.5
HTPB	9.45	10.16	557.7	0.742	0.073	0.93
PE	10.28	10.49	147.14	0.713	0.068	0.98
PS:	10.45	9.96	1037.35	0.757	0.076	1.05
PMMA	9.31	7.89	789.94	0.963	0.122	1.18
Delrin	5.74	4.07	122.21	0.891	0.219	1.41
Anthracene	12.13	9.55	1702.13	0.754	0.079	1.27
Decacyclene	13.21	9.05	4077.39	0.733	0.081	1.46
Diamantane	11.88	9.82	1849.24	0.707	0.072	1.21
Triamantane	13.01	9.71	2334.19	0.709	0.073	1.34
HCTD	12.63	10.02	1846.5	0.747	0.0745	1.26
PCUD	10.50	10.0	1462.33	0.73	0.073	1.05
CPDO	11.50	10.0	661.03	0.74	0.074	1.15
BINOR S	12.04	9.79	1804.12	0.729	0.0745	1.23

Table 1 Heats of combustion, stoichiometric fuel-to-air ratios and densities of

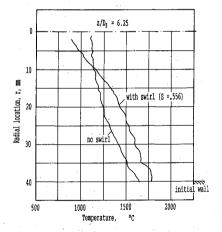


Fig. 1 Combustor radial temperature profiles. 10

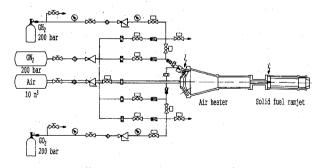


Fig. 2 Schematic diagram of the experimental setup.

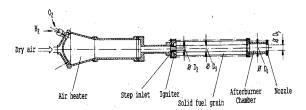


Fig. 3 The ramjet test combustor.

pipe system. The air was taken from a large supply containing pressurized bottles having a maximum pressure of 200 bar. After expansion the air had a temperature of 5°C. The air supply was connected to a vitiated air heater that was equipped with ten hydrogen-oxygen burners. With this device, the air could be heated up to about 1000°C, but in order to keep the water vapor contents low, all experiments were done at 400°C air inlet temperature. The water contents then were about 2-3 vol %. The air did not contain any additional oxygen. The mass flow of air was measured by the pressure drop in a sonic nozzle. It was kept constant for all test runs at an average value of 460 g/s within a range of 3%. In order to get swirling flow conditions, fixed vane swirlers were inserted into the flameholder. The combustion chamber consisted of an 80 mm i.d. fuel block having a length of 300 mm. It was connected with an afterburner chamber having 78 mm i.d. The afterburner chamber was lined with a ceramic material for heat protection. A convergent, uncooled nozzle was used at the end of the afterburner chamber. It was made of hightemperature-resistant steel and had a diameter of 37.5 mm. The low nozzle area ratio of 0.23 was chosen in order to obtain higher chamber pressures resulting in higher regression rates and fuel-to-air ratios. The chamber pressure was 5 bar for the boron combustion tests and 5.2 bar for the boron carbide tests without swirl. The corresponding values for the test runs with swirl were 5.2 and 5.7 bar, respectively. The whole combustor, including the air heater, was mounted on a thrust stand and connected with flexible joints to the supply lines. The thrust could be measured with a low-displacement load cell.

Swirlers

The design and test procedure of the swirlers has been described in a recent publication¹⁰ in more detail. The definition of swirl number is indicated there, also. In most experiments a swirler with a swirl number of 0.54 was used. Figure 4 gives the dimensions and type of swirlers used in this investigation.

Particle Sampling Procedure

In order to retain condensed combustion products, a particle sampling technique was applied. Figure 5 shows the experimental arrangement. A motor-operated water-cooled rod was driven into the afterburner chamber for three seconds. The burning particles were quenched at the cold surface and

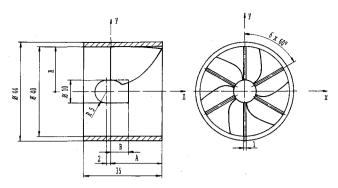


Fig. 4 Swirler design.

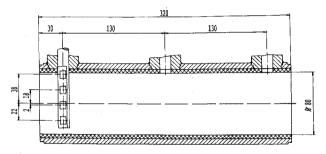


Fig. 5 Particulate sampling arrangement.

collected in four small cavities that were milled into the rod. The rod had a triangular cross-section in order to avoid excessive flow disturbance. The moment of sampling was the same for all test runs. The sample was taken two seconds after steady-state combustion was established. After the test run the particle sampling system was removed from the test rig, the combustion products were subjected to wet chemical analysis, and the rod was cleaned for further use in the next run. In most of the experiments the contents of the four cavities was mixed because the results of the chemical analysis indicated only minor differences between the cavities. The described sampling procedure is a method for collecting solids. Gaseous species can also be captured on cold surfaces, but there has to be sufficient time to allow for condensation.

Chemical Analysis

In order to judge combustion performance, overall efficiency based on combustion chamber pressure or thrust is determined experimentally. The combustion efficiency based on thrust is defined by

$$\eta_{TF} = \frac{(C_{\text{exp}}^*)^2 - (C_{\text{air}}^*)^2}{(C_{\text{theor}}^*)^2 - (C_{\text{air}}^*)^2} \tag{1}$$

$$C_{\rm exp}^* = \frac{F}{\dot{m}_{\rm tot} C_{\rm F}} \tag{2}$$

$$C_{\rm air}^* = \frac{F}{\dot{m}_a C_F} \tag{3}$$

$$C_F = \sqrt{\gamma^2 \left[\frac{2}{\gamma + 1}\right]^{2\gamma/\gamma - 1}} + \left[\frac{2}{\gamma + 1}\right]^{\gamma/\gamma - 1} - \frac{P_a}{P_t} \quad (4)$$

 C_{theor}^* was calculated by a computer program, 11 whereas all other characteristic velocities were determined by thrust measurements.

In addition, in this investigation a boron combustion efficiency was determined by chemical analysis of the boron combustion products. During the combustion process, the following condensable species may be formed:

- 1) Boron oxides B₂O₃, B₂O₂
- 2) Boron acids H₃BO₃, HBO₂

- 3) Boron carbides e.g. B₄C
- 4) Boron nitride BN
- 5) Soot C
- 6) Water H₂O
- 7) Unburnt boron B

During condensation on a cold surface, the following species occur:

- 1) Boron oxides + acids B₂O₃ · xH₂O
- 2) Boron carbides e.g. B₄C
- 3) Unburnt boron B
- 4) Boron nitride BN
- 5) Soot C

We defined a boron combustion efficiency by

$$\eta_{B} = \frac{\text{reacted boron}}{\text{total boron}} = \frac{\text{reacted boron}}{\text{reacted boron} + \text{unreacted boron}}$$

in terms of mass fractions one obtains

$$\eta_{\rm B} = \frac{0.3107 \ m_{\rm B203}}{0.3107 \ m_{\rm B203} + m_{\rm B} + 0.7829 \ m_{\rm B4C}} \tag{5}$$

the coefficients being the conversion factors from boron compounds to boron.

In wet chemical analyses one cannot distinguish between different boron oxides and acids, so we decided to summarize the components and calculate the results as boron oxide B_2O_3 . A similar situation occurred with the boron carbide. There are several existing boron carbides such as B_4C , $B_{13}C_2$, $B_{24}C$, and so forth. The results in this case are given as B_4C . We also did not separate C and H_2O but considered the sum $C + H_2O$ as remainder in the chemical analysis. For combustion efficiency calculations, the B_4C was considered to belong to the unreacted boron because B_4C can be burnt to B_2O_3 and CO_2 :

$$B_4C + 4O_2 -> 2B_2O_3 + CO_2$$

The formation of B_4C itself contributes slightly to the heat generated, because the reaction

$$4B + C -> B_4C(s)$$

is exothermic having a reaction enthalpy of -18.1 kcal/mole. Also the reaction

$$B + 0.5N_2 -> BN (s)$$

is exothermic having a reaction enthalpy of -59.27 kcal/mole. This is also small compared to the enthalpy of -303.64 kcal/mole generated by direct combustion of boron with oxygen:

$$4B + 3O_2 -> 2B_2O_3$$

The chemical analysis procedure makes use of the well-known mannitol method and for separation of the components modified methods taken from literature 12 were applied. The samples were ground and about 100 mg were weighed and treated for 15 minutes with 40°C warm water. This avoids losses of boric acid, which is volatile with water vapor. Under these conditions the boric acid and boron oxide were dissolved and the remainder contained a mixture of boron, boron carbide, and soot. The suspension was filtered through a 0.45- μ membrane filter and the residue was flushed with water. Then 3.6 g of mannitol were added to the resulting boric acid solution and the mixture was titrated with 0.1 n NaOH with phenolphtalein as indicator. From this the amount of B_2O_3 in the sample was determined.

The residue of the filtration was boiled with 10 ml of 10% H_2O_2 solution and 20 ml of a 1.3% $K_2S_2O_8$ solution under reflux conditions for 30 min. The solution was filtrated, neu-

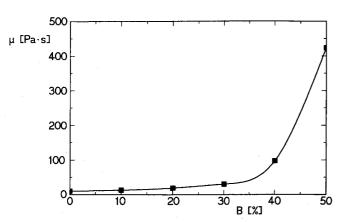


Fig. 6 Effect of boron contents on fuel mixture initial viscosity.

tralized against methyl red, treated with mannitol, and titrated with 0.1 n NaOH against phenolphtalein. From this the amount of B in the sample was determined.

Another 100 mg of the sample were weighed and mixed with 1 g Na₂CO₃ in a platinum crucible. After 20 min of heating, the melt was cooled down and dissolved in about 80 ml of H₂O. The solution was treated with dilute HCl and the CO₂ was boiled off. After neutralization against methyl red, the solution was treated with mannitol and titrated with 0.1 n NaOH against phenolphthalein. From this, one obtains the total boron amount of the sample from which the boron carbide was calculated.

Several samples were tested for BN by melting the sample with NaOH in a crucible and determining the NH₃ that evolved, but no boron nitride was found.

Fuels

The fuels were made of HTPB R-45 M and boron or boron carbide. The amorphous boron powder had boron contents of 95–97%, the average particle size was $0.7-1.0 \mu$ and the specific surface area was 8-13 m²/g. The boron carbide had an average particle size of 0.7-0.9 μ and a specific surface area of 17-22 m²/g. The curing agent was tolylene diisocyanate (TDI). In order to reduce the amount parameters that can influence the investigation, we decided not to use any further additives such as plasticisers or wetting agents. Under these conditions, fuels containing up to 40% boron or boron carbide could be manufactured. The HTPB was heated and degassed and then the boron or boron carbide was added. The ingredients were mixed intimately with a high-shear stress impeller mixer. The mixture was heated up and degassed under vacuum again. Finally, the TDI was added and another degassing procedure took place. In order to get an idea which mixtures could be cast, viscosity measurements were made with HTPB-boron mixtures of increasing boron contents. A typical result is shown in Fig. 6. The initial viscosity rises strongly with increasing boron amount. Mixtures having a higher viscosity than 200 Pa·s were considered not to be processable. The fuels were cast into molds under vacuum in a casting machine. The fuels were cured at a temperature of 60°C. After curing the mandrel was removed. The fuel density was determined by a buoyancy method and the heat of combustion was determined in a bomb calorimeter at 30 bar oxygen pressure.

Combustion Efficiencies

The results of the combustion efficiency measurements are indicated in Fig. 7 for boron containing fuels. The results of two series of the test runs are given, one with swirl and one without swirling flow. The effect of fuel composition on boron combustion efficiency as calculated from Eq. (5) is plotted. In addition, the fuel-to-air ratio for each data point is given. The combustion efficiency increases at first with increasing

amounts of boron in the fuel. Then it reaches a maximum near to 20% boron. Further addition of boron to the fuel leads to a decrease of combustion efficiency and the values are even less than with small amounts of boron. Without swirling flow the combustion efficiencies are always between 30 and 40%. A significant change results when swirling flow is introduced. This can also be seen by inspecting the exhaust plume during a test run by photographic techniques. Without swirling flow, the plume has an orange-red color and some particle tracks of unburnt boron are to be seen. With swirl, the plume has the typical green color of boron combustion products. An evaluation of boron combustion efficiencies, then, leads to values between 50 and 60%, which is distinctly higher than without swirl.

Figure 8 shows the results for boron carbide containing fuels. Although a little bit different in shape, the curves show a similar behavior. No maximum is to be seen. The combustion efficiency is highest at low boron carbide contents and decreases with increasing boron carbide contents. The decrease is higher for nonswirling flow for higher boron carbide loads. The difference in efficiency between swirling and nonswirling flow is about 30%, which is significantly higher than for boron containing fuels. There is some scattering in the values, but often the results of the test runs were quite reproducible. This can be demonstrated, for instance, by three data points at 20% boron for the swirling flow condition.

Table 2 shows the influence of different swirlers on combustion efficiency for two different fuel compositions. The swirlers are characterized by the swirl number, but it must be noted that the swirlers are also different in type. For comparison also the data for nonswirling flow are given. As indicated, the combustion effciency increases with increasing swirl number.

In order to compare conventional combustion efficiencies with boron combustion efficiencies, the measured data were plotted in Fig. 9. The data comprise swirl and nonswirl con-

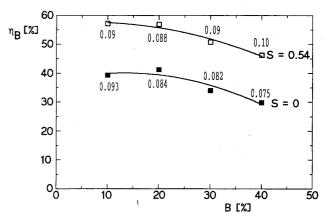


Fig. 7 Boron combustion efficiency vs fuel composition.

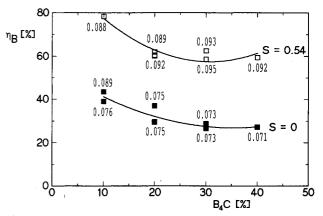


Fig. 8 Boron combustion efficiency vs fuel composition.

Table 2 Influence of different swirlers on combustion efficiencies

Fuel composition, %B	Combustion efficiency,		
70 B	Swirl no.	76	
10	0.0	39.3	
10	0.3	48.8	
10	0.54	57.1	
10	0.7		
30	0.0	34.0	
30	0.3	28.2	
30	0.54	50.7	
30	0.7	52.4	

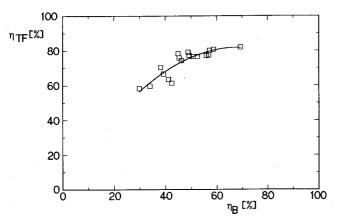


Fig. 9 Combustion efficiency based on thrust vs boron combustion efficiency.

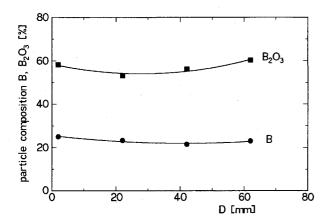


Fig. 10 Radial distribution of solid combustion products $m_a=440.9$ g/s; $T_o=380.2^{\circ}\mathrm{C}$.

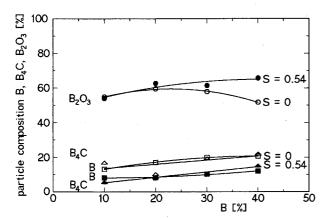


Fig. 11 Effects of fuel composition on combustion products.

ditions and are given for boron fuels. The combustion efficiency based on thrust increases with increasing boron combustion efficiency. So a high boron combustion efficiency is also a good indicator for a high combustion efficiency of the whole fuel. The lowest boron combustion efficiency measured in this series of the test runs was 30% (without swirl) the highest was 69% (with swirl).

Chemical Composition of Solid Combustion Particulates

The radial distribution of the composition of the solid combustion products in the afterburning chamber is given in Fig. 10. The data points represent the chemical composition of the deposits in each of the four cavities of the sampling rod. The data for unburnt boron and boron oxide are given. The test run conditions are also indicated. The profiles are very flat and within the limits of measurement errors, the composition is nearly constant across the afterburning chamber. This result was confirmed by other test runs and led to the decision to mix the contents of all four cavities for evaluation of all other test runs.

The dependence of the composition of the combustion products on fuel composition is indicated in Fig. 11. The measurement data are valid for boron containing fuels with and without swirling flow. Generally the percentage of B, B_2O_3 , and B_4C increases with increasing boron contents of the fuel except for the B_2O_3 curve. The mass fractions of B_2O_3 are always higher for swirling flow than without swirl. The unburnt boron and the B_4C mass fractions are higher without swirl. This leads to the situation that generally there are more burnt products and less unburnt products in the swirling flow case, and this results in significantly higher combustion efficiencies.

During chemical analysis there remains a difference to 100% not consisting of boron compounds. It is considered to be water and soot. In Fig. 12 the sum of all boron, chemically bonded and unbonded, is indicated in dependence of fuel composition. Also the percentage of nonboron containing combustion products is given. The nonboron containing combustion products decrease with increasing amounts of boron in the fuel, whereas the total boron increases. The amount of nonboron compounds is higher with swirling flow and the total boron is lower.

Thrust Measurements

The results of the thrust measurements are presented in Fig. 13 for boron fuels. The data are given as specific thrust, which means thrust divided by the mass flow of air. This was done in order to eliminate the influence of mass-flow scattering on the results. It is well known from ramjet theory, that the thrust is proportional to the airmass flow. The data are given again for swirling and nonswirling flow conditions. In addition, the fuel-to-air ratio is indicated for each data

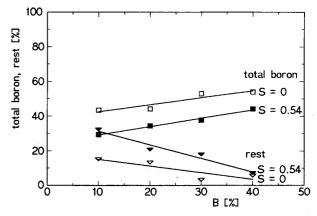


Fig. 12 Effects of fuel composition on combustion products.

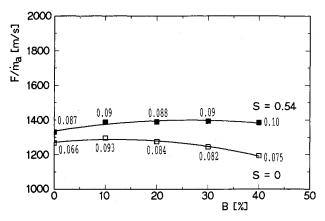


Fig. 13 Dependence of specific thrust on fuel composition.

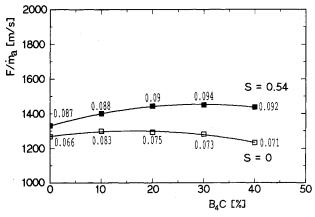


Fig. 14 Dependence of specific thrust on fuel composition.

point. The specific thrust first reaches a maximum value at about 10% boron in the fuel and then decreases with increasing boron contents for the nonswirl case. In the case of swirling flow, the specific thrust increases for low boron contents and there is only a slight decrease for higher boron contents. The thrust is significantly higher with swirl.

Figure 14 shows similar results for boron carbide fuels. The shape of the curves is somewhat different, but first there is also an increase and then a decrease of specific thrust with increasing amounts of boron. The thrust level is even higher than for boron fuels for the swirling flow condition.

Regression Rates

Detailed results of regression rate measurement are not given in this paper because in order to determine exact regression rate relations a large amount of data is needed. But from the data obtained, one can see an indication that the regression rate is reduced by increasing the amounts of boron or boron carbide. The regression rate is higher with swirl than without swirl.

Discussion

The results of this investigation show that there is a general decrease of boron combustion efficiency and specific thrust for amounts of boron or boron carbide higher than 20% in the fuel. There may be several reasons for the thrust decay. At first, the addition of energetic materials such as boron and boron carbide should increase the heat of combustion of the fuel. Therefore, the specific thrust should increase. But when the amount of energetic material is increased, the amount of binder decreases. Because the combustion of binder provides the heat for igniting the boron, and because it is well known that boron does not ignite easily below 1900 K, reduced binder

contents may not generate enough heat for complete boron ignition and combustion. This leads to a decrease in combustion efficiency as measured.

Second, as indicated in Figs. 7 and 8, it has not been possible to keep the fuel-to-air ratio constant in a series of test runs because swirl flow and fuel composition have an effect on regression rate in both directions. The fact that the thrust is strongly dependent on the fuel-to-air ratio may also explain the experimental results. The heat-sink effect of an increasing amount of unignited boron particles in the gas phase or an accumulation of unreacted boron particles, which decrease the heat transfer to the surface leading to a reduced pyrolysis rate of the fuel may be further explanations.

The significant improvement in boron combustion efficiency for swirling flow can be explained by the better mixing and higher temperatures in a swirl flow combustor as indicated in Fig. 1. This causes better ignition and combustion of the boron, which can be observed even visually regarding the plume.

Results and Conclusions

The significant conclusions of this study are:

1) The application of swirl flow increased the boron combustion efficiency and specific thrust considerably up to 15%.

2) Addition of energetic materials such as boron and boron carbide in smaller amounts to the fuel increased the specific thrust considerably up to 10%. Further addition of boron or boron carbide led to a decrease on specific thrust.

3) Determining the boron combustion efficiency in addition to conventional combustion efficiencies gives more information on the combustion process.

4) Boron carbide is an intermediate that occurs during the combustion process.

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