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[54] **HIGH REACTIVITY FUELS FOR SUPERSONIC COMBUSTION RAMJETS**

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[63] Continuation-in-part of Ser. No. 87,344, Nov. 5, 1970, abandoned.

[52] **U.S. Cl.** **149/22;** 44/57; 44/68; 44/76; 149/87; 149/109.4

[51] **Int. Cl.** **C10l 1/30**

[58] **Field of Search** 149/22, 87, 109.4; 44/57, 44/68, 76

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[57] **ABSTRACT**

The invention relates to highly reactive fuel compositions primarily intended for supersonic combustion ramjet engines. In particular, the invention provides highly reactive fuel compositions capable of efficient oxidation and thrust production even within the low combustor residence time of a supersonic combustion ramjet engine. The fuel compositions comprise specific blends of a major fuel component and an additive which, on pyrophoric combustion thereof, produces sufficient heat energy to spontaneously ignite and burn the major fuel component at a substantially increased rate.

2 Claims, No Drawings

HIGH REACTIVITY FUELS FOR SUPERSONIC COMBUSTION RAMJETS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. patent application, Ser. No. 87,344 now abandoned, of the same title, filed Nov. 5, 1970, by the same inventors; the aforesaid application being hereby abandoned.

BACKGROUND AND SUMMARY OF THE INVENTION

In recent years increased interest has developed in the use of liquids for fuels in a supersonic combustion ramjet engine, known in the art as a "scramjet" engine. Although the static temperatures and pressures in the "scramjet" combustor are often similar to their subsonic counterparts, the typical residence time for ignition and combustion are considerably shorter. In the scramjet engine the effects of a higher vehicle velocity coupled with the exclusion of baffles, turbulence generators, etc., produce substantially lower fuel residence times in the supersonic combustor. Thus, in general, the fuel for a supersonic combustion ramjet must be more reactive than that for a subsonic combustion ramjet. Scramjet fuel compositions should also have a high heating value per unit mass; high density, which in turn defines the heating value per unit volume; good storage and thermal stability characteristics; high heat capacity if the fuel is to be used for regenerative cooling; low cost; and low toxicity. However, for scramjet engines with low takeover Mach numbers, e.g., $M_0 = 4$–6, the requirement for high reactivity is of greatest importance.

An acceptable supersonic ramjet engine fuel composition must ignite spontaneously and burn efficiently within the extremely brief residence time (~0.5 msec) available for oxidation in the air flow through the supersonic combustor. Fuels previously employed in subsonic ramjet engines, while having desirable cost, handling, and high heat content characteristics, cannot satisfy the high reactivity requirement of the scramjet at the combustor static temperatures and pressures typical of scramjet take-over conditions. Although heavy hydrocarbon fuels have high heat content per unit volume and are easily handled and stored, these fuel compositions often fail even to ignite in the scramjet engine.

Substances capable of acceptable ignition and combustion within the low residence time in the scramjet engine are generally expensive, toxic, and difficult to store and handle. Many of these readily ignitable substances are actually pyrophoric in nature, that is, the substance ignites spontaneously on exposure to an oxidizing source. For instance, the boranes and alkaylated boranes meet the reactivity requirement but are undesirable due to cost, handling, storage, toxicity, and other considerations. Pentaborane and other lower boranes are pyrophoric at room temperature and also have a relatively low density. Aluminum alkyls also meet the reactivity requirement but are pyrophoric and have low energy densities.

The invention provides fuel compositions combining the desirable characteristics of the hydrocarbons with an essentially pyrophoric additive blend. Particularly, the present fuel compositions substantially exhibit desired cost, handling, storage, and density properties while being capable of ignition and efficient combustion within the low residence times encountered in a supersonic combustor.

Accordingly, it is the primary object of the invention to provide fuel compositions for supersonic ramjet engines which ignite and burn efficiently within the low residence times of a supersonic combustor.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present fuel compositions essentially consist of blends of a major fuel component usually consisting of a heavy hydrocarbon component which ordinarily would not ignite under scramjet conditions, and an additive component present in a relatively low proportion for initiating ignition and aiding in continued combustion of the composition. The major fuel component may be chosen from a large group of suitable hydrocarbons. Primary considerations for hydrocarbon choice are density, cost, and storability. Straight-chain alkanes, such as n-dodecane ($C_{12}H_{26}$), may be chosen but are not generally as desirable as the highdensity heterocyclic hydrocarbons. In particular fuels such as methylcyclopentadiene dimer (MCPD, $C_{12}H_{16}$) and its hydrogenated derivative, tetra-hydro methylcyclopentadiene dimer (T-HMCPD, $C_{12}H_{20}$), have desirable characteristics. "Shelldyne-H," a proprietary product of Shell Development Corporation, is a heavier hydrogenated hydrocarbon ($C_{14}H_{18}$, molecular weight 186.3) having acceptable handling and density chracteristics. Low molecular weight hydrocarbons have storage and handling difficulties which usually outweigh any advantage to their use.

Essentially pyrophoric additives having the high reactivity necessary to promote rapid ignition of the fuel compositions include mixtures of the alkylated aluminums, such as triethylaluminum (TEA) and trimethylaluminum (TMA), and the boranes and alkylated boranes, particularly pentaborane (B_5H_9) and either a mixture of diethyldecaborane and ethyldecaborane ($C_{3.2}H_{20.3}B_{10}$, HiCal 3-D) or ethyldecaborane alone. Blends of these additive components, particularly TEA and "HiCal 3D," are used in a composition including a heavy hydrocarbon as the major constituent.

Ignition of the present fuel compositions is provided by the additive mixture. For example, in a fuel composition comprising a hydrocarbon, an aluminum alkyl, and "HiCal 3–D," the aluminum alkyl burns initially, the combustion of the aluminum and recombination of alkyl radicals occurring first and producing a small exothermic heat release insufficient to ignite the hydrocarbon. However, the heat released by the rapid aluminum reaction is sufficient to ignite the "HiCal 3–D" which does produce enough heat to ignite the hydrocarbon. Although the organic portion of the aluminum alkyl usually burns subsequent to the combustion of the aluminum portion, this "second phase" combustion which releases the major portion of the heat of combustion of the aluminum alkyl is often too slow to effectively ignite the hydrocarbon.

The addition of an aluminum alkyl to an alkylated borane can shorten t_{ig} of the alkylated borane by as much as 50 percent. For example, 20 percent by weight of triethylaluminum to "HiCal 3–D" shortens the ignition delay of the alkylated borane by nearly 50 percent, due to ignition of the "HiCal 3–D" by the rapid heat release of the aluminum in the TEA as described gener-

ally hereinabove. The optimum amount of TEA added to "HiCal 3-D" appears to be near 20 percent. Since the alkylated borane is thereby ignited much more readily, the large exothermic heat release thus produced causes a proportionally more rapid ignition of the hydrocarbon component of the present fuel compositions.

The present fuel compositions were tested to measure ignition time, t_{ig}, and combustion efficiency, η_c. Ignition delay tests were conducted using air supplied at 2000°R at 15–20 psia to a plenum attached to a converging nozzle having a nominal Mach number of 0.75 exiting into a rectangular test section. The components were injected from a 2mm diameter hole in the tip of a tube located on the axis of the nozzle. In order to evaluate performance of the compositions, static pressures were measured in the plenum, at the nozzle exit, and at several locations in the test section. Parameters affecting performance are found to include the initial air static temperature T_a, and the initial fuel temperature T_f, both of which cause reduction in t_{ig} as they increase. Overall fuel/air ratio does not seem to affect t_{ig}. Mach 1.6 and Mach 2.5 nozzles were also used in the test arrangement described. The results of these tests are summarized in Tables I, II, and III reproduced below.

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TABLE I

Results of Subsonic Ignition Tests of Pyrophoric-Hydrocarbon Mixtures

Fuel	Total Temp. (°R)	Total Pressure (psia)	Static Pressure (psia)	Mach Number	Static Temp. (°R)	Fuel Flow (lb/sec)	Air Flow (lb/sec)	Fuel Temp. (°R)	Velocity (ft/sec)	Combustion Delay Dist. (inches)	Combustion Delay Time (msec)
50.0%NDD 12.0%TEA 37.5%HiCal-3D	1927	19.25	13.92	0.695	1757	0.0280	0.843	730	1427	17.0	0.99
50.0%SDH 12.5%TEA 37.5%HiCal-3D	1953	22.97	19.79	0.465	1871	0.0256	0.777	714	985	6.0	0.51
75.0%SDH 12.5%TEA 12.5%HiCal-3D	1945	24.57	20.54	0.512	1848	0.0268	0.892	775	1078	7.0	0.54
87.50%SDH 6.25%TEA 6.25%HiCal-3D	1940	23.47	19.87	0.493	1851	0.0259	0.830	808	1043	7.0	0.56
Shelldyne-H	1959	25.52	21.44	0.505	1863	0.0140	0.916	868	1068	no ignition	
10.0%TEA 90.0%SDH	1959	17.19	11.03	0.823	1725	0.0250	0.823	821	1670	no ignition	
Shelldyne-H	1937	19.78	13.13	0.790	1722	0.0844	0.913	847	1606	no ignition	
12.5%TEA 12.5%HiCal-3D 75.0%SDH	1944	27.07	23.14	0.480	1858	0.0400	0.941	766	1014	6.0	0.50
MCPD	1944	13.05	19.36	0.773	1736	0.0420	0.884	787	1578	no ignition	
6.25%TEA 6.25%HiCal-3D 87.50%MCPD	1943	23.86	20.35	0.482	1854	0.0476	0.831	739	1017	5.0	0.41

TABLE II

Fuel	Mach Number	Initial Air Temperature,°R	Initial Fuel Temperature,°R	Ignition Delay Time, msec
6.7 % TMA 8.9 % HiCal 3-D 87.50% MCPD	2.5	1535	710	0.20
12.5 % TEA 12.5 % HiCal 3-D 75.0 % Shelldyne-H	2.5	1535	710	0.15

TEA = Triethyl aluminum
TMA = Trimethyl aluminum
MCPD = Methylcyclopentadiene dimer
THMCPD = Tetrahydro-methylcyclopentadiene dimer

TABLE III

Fuel % by weight	M_{ci}	ER	T_t (°R)	T_{ci} (°R)	P_t (psia)	T_f (°R)	P_{ci} (psia)	Combustion efficiency η_c
8.2 TMA 9.0 HiCal 3-D 82.8 MCPD	3.23	0.53	4020	1527	459	723	7.63	0.41
12.5 TEA 12.1 HiCal 3-D 75.4 Shelldyne-H	3.24	0.58	3876	1457	448	711	7.37	0.32

Other tests indicate that the following fuel compositions according to the present invention ignite within 0.2 msec for T ≥ 1535°R and M ≥ 2.5, conditions corresponding to a Mach 5 takeover speed at 95,000 feet:

Composition No.	Components by weight per cent
I	10% triethylaluminum 10% HiCal 3-D 80% MCPD
II	6.7% trimethylaluminum 8.9% HiCal 3-D 84.4% MCPD
III	8% trimethylaluminum 9% pentaborane 83% MCPD

As can be seen in Table I, the additive blends of the present fuel compositions cause ignition of a heavy hydrocarbon which will not ignite alone in the available residence time. Triethylaluminum alone is also shown to be insufficient to ignite the heavy hydrocarbon, Shelldyne-H.

Direct-connected supersonic combustion testing produced the results summarized in Tables II and III. Combustion efficiencies, longitudinal wall static pressure (P_w) distributions, and radial profiles of properties in the combustor exit plane were determined at conditions simulating flight at $M_\infty \sim 7.25$ in the tropopause ($T_\infty = 390°R$) at an altitude of ~ 90,000 ft. These carefully instrumented tests, with a proven run-to-run reproducibility of ± 3 percent on combustion efficiency, offer a realistic (but relatively expensive compared to the simpler ignition delay tests) means for evaluating scramjet fuels. Metered cold air was heated in a d.c. arc heater to approximately 5000°R and discharged into a mixing chamber. Unheated secondary air was added to obtain the desired total temperature, T_{t_a} which is nominally 4000°R. With the nominal plenum pressure of 460 psia the conditions at the supersonic nozzle-exit plane were $M_{c_i} = 3.23$, $P_{c_i} = 7.4$ psia, and $T_{c_i} = 1520°R$. To isolate combustor-induced disturbances a 7.27 in.-long cylinder was inserted between the nozzle and the fuel injector. Fuel was injected perpendicular to the air stream from ten 0.030-in.-diameter holes that were equally spaced circumferentially. Immediately downstream of the injector the combustor had a step increase in diameter from 2.74 in. to 3.28 in. The 14.4-in.-long cylinder was followed by a 1.4°-half-angle, 14.4-in.-long conical section, which resulted in an overall combustor exit/injector area ratio of 2. Pitot and cone-static pressure measurements in the combustor exit plane provide the data necessary to describe the flow properties in that plane. Just downstream of the combustor exit, water was sprayed into the stream to quench the reaction rapidly. The heat release and combustion efficiency were obtained by making a calorimetric balance on the exhaust gases, using temperature measurements from a sixteen-point thermocouple rake in the exit of the calorimeter together with all of the water-coolant rates. Water flow to the calorimeter was controlled to yield exit temperatures between 700°F and 1000°F, and to keep the wall temperatures at 400°F–800°F in order to guarantee that all water was vaporized and that reactions were effectively quenched.

Combustion efficiency is defined as the sum of the total heat released upstream of the calorimeter exit plus the sensible heat in the products of combustion when cooled from the colorimeter exit temperature to 212°F (without condensation of water) divided by the lowering heating value of the fuel. The total heat release includes the change in heat flux to the walls with combustion. With this combustor geometry the total heat loss to the walls is approximately 110 Btu/sec for the nominal conditions without fuel flow. With burning, the heat flux increases to about 500 Btu/sec for $ER_{eff} = 1.0$, run lengths between 30 and 45 sec with 10–15 sec for each fuel setting.

We claim:

1. A fuel composition capable of ignition within the low residence times occurring in a supersonic ramjet combustion engine comprising:

a hydrocarbon selected from the group consisting of n-dodecane, methylcyclopentadiene dimer, and tetra-hydro methylcyclopentadiene dimer, the hydrocarbon being present in the fuel composition in a proportion equal to at least 50 percent and not more than 87.5 percent by weight thereof; and, a pyrophoric additive component selected from the group consisting of respective mixtures of trimethylaluminum and ethyldecaborane; trimethylaluminum and pentaborane; triethylaluminum, ethyldecaborane, and diethyldecaborane; and, trimethylaluminum, ethyldecaborane, and diethyldecaborane; the additive component being present in the fuel composition in a proportion equal to not more than 50 percent by weight thereof and wherein the first-named constituent of each mixed additive component constitutes at least 20 percent of the additive component by weight.

2. A fuel composition capable of ignition within the low residence times occurring in a supersonic ramjet combustion engine comprising:

methylcyclopentadiene dimer having a weight percent of at least 80 percent of the total composition; and,

a pyrophoric additive component selected from the group consisting of respective mixtures of trimethylaluminum and pentaborane having relative weight percents of at least 8 percent and at least 9 percent respectively of the total composition; triethylaluminum, diethyldecaborane, and ethyldecaborane having relative weight percents of at least 6 percent of the total composition for triethylaluminum and at least 6 percent of the total composition for the mixture of diethyldecaborane and ethyldecaborane; and trimethylaluminum, diethyldecaborane, and ethyldecaborane having relative weight percents of at least 6 percent of the total composition for trimethylaluminum and at least 8 percent of the total composition for the mixture of diethyldecaborane and ethyldecaborane.

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