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METHOD OF PRODUCING THRUST BY HYDROGENATION OF AN ACETYLENIC HYDROCARBON

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This invention relates to a bipropellant combination for use with rockets and other propulsion devices. More specifically, the invention relates to the hydrogenation of unsaturated hydrocarbons to produce a novel propellant system for rockets and other propulsion devices, particularly those devices which afterburn the exhaust products of the rocket such as air turborockets and ramrockets.

The liquid propellants in use today may be divided into two general classes, referred to as monopropellants and bipropellants. The monopropellants consist of a single material; acetylenic compounds such as isopropenyl acetylene and methyl acetylene form one group of monopropellants which have high heats of combustion, a property useful in the present invention. The bipropellants involve the reaction of two materials, stored in separate containers, which are injected into the reaction chamber as needed. The bipropellants typically consist of an oxidizer and a fuel, with the emphasis in recent years directed towards oxidizers and fuels having a high energy content. Liquid oxygen, hydrogen peroxide, fluorine and nitric acid have been utilized as oxidizers while hydrogen and various hydrocarbons have been utilized as fuels for various bipropellant systems.

In selecting a bipropellant system for a rocket it is important that the propellant system develop a high specific impulse. Specific impulse may be defined as the pounds-force of thrust developed per pound mass of propellant exhausted. The velocity and height which a rocket will attain at cutoff are related to the specific impulse; the velocity varying directly and the height with the square. Thus, it can be seen that doubling the specific impulse of the fuel system would double the velocity at cutoff, but quadruple the height at cutoff. The high specific impulse desired may be obtained by selecting a system which has a high energy, the high energy being reflected in a high rocket chamber temperature, or which has exhaust products low in molecular weight or a combination of both high energy and low molecular weight exhaust products. Higher energy systems (i.e., those systems having high rocket chamber temperatures) are usually complex as their use necessitates substantial cooling of the rocket motors, thus adding weight and expense to the propellant system.

The bipropellant system of the present invention develops a high specific impulse with a low chamber temperature. Hydrogen is a diatomic molecule having a low molecular weight and in which large quantities of energy may be stored. The specific impulse is high because of the low molecular weight of the reaction products caused by the large proportion of hydrogen present as a reaction product. It can be seen that it may be possible to decrease the molecular weight of a system, thus increasing the specific impulse, by adding an excess of hydrogen. Although this may be done in the present system, its use with an oxidizing system is limited as the molecular weight of oxidizing bipropellant systems cannot be lowered to the value obtained with the present system because the addition of large excesses of hydrogen to the oxidizing system would give mixture ratios of reactants which would be outside the flammability limits and thus the reaction could not proceed. The chamber temperature developed by the present bipropellant system is low enough to enable the operation of the rocket motor uncooled.

The present system has a further advantage over the oxidizing systems in that the exhaust products of the present system have a high heat of combustion and may be afterburned with atmospheric air for additional performance.

Therefore, it is an object of this invention to provide a bipropellant system which has a low adiabatic reaction temperature, a low molecular weight and a high specific impulse.

A further object is to provide a method of propulsion which utilizes the hydrogenation of unsaturated hydrocarbons.

A still further object of this invention is to react liquid hydrogen and an unsaturated hydrocarbon in a rocket motor to provide a force by which a missile may be propelled.

Additional objects and advantages of this invention, if not specifically set forth, will become apparent to one skilled in the art during the course of the following description.

Broadly, this invention comprises a bipropellant system consisting of liquid hydrogen and an unsaturated hydrocarbon. The liquid hydrogen and unsaturated hydrocarbons are stored in separate vessels until needed, at which time they are injected into a reaction chamber of a rocket or other propulsion device to provide a suitable propellant. The present system utilizes the hydrogenation of the unsaturated hydrocarbons rather than the usual oxidation processes used in the bipropellant system presently known. The heats of hydrogenation of the unsaturated hydrocarbons are quite high, thus rendering the present hydrogenation system effective for propulsion.

Acetylenic compounds such as acetylene and 1,5-hexadiyne appear to be particularly desirable unsaturated hydrocarbons. In reacting the acetylenic compounds with hydrogen, it is desirable to obtain as products methane and hydrogen instead of carbon and hydrogen since the bipropellant system is more effective when the products of the reaction are in the gaseous form rather than the condensed form. Also, methane has a negative heat of formation and higher heats of reaction are obtained when methane is the product. In the sign convention used throughout this application, acetylene has a positive heat of formation; the elements, a heat of formation of zero; and carbon dioxide, a negative heat of formation. Typically, when acetylenic compounds are hydrogenated, methane is not formed as the product since the temperatures created tend to decompose the methane into carbon and hydrogen; however, it is possible to circumvent this situation by making use of Le Chatelier's principle and adding a relatively large excess of hydrogen. This excess of hydrogen together with the high pressure generally found in rocket systems will favor the formation of methane even at the higher temperatures. In fact, at a given temperature and pressure there is a minimum concentration of hydrogen above which solid carbon cannot exist in equilibrium with other products. Although, as will be shown later, the addition of about one mole of hydrogen to about one mole of unsaturated hydrocarbon will generally increase the specific impulse over that of the unsaturated hydyrocarbon monopropellant, even though virtually no methane is formed, the optimum results will not be approached until the sufficient excess of hydrogen is added to cause almost complete formation of methane and little or no carbon.

In a preferred embodiment of the present invention, liquid hydrogen and liquid acetylene are utilized as the propellants. Although it has not been practical to utilize acetylene as a monopropellant, its use in a bipropellant system is advantageous. One reason for not using acetylene as a monopropellant in air turborockets is its high adiabatic decomposition temperature of about 3100° K., which is much too high for use with turbine-blade systems. The hydrogenation of acetylene on the other hand not only lowers this temperature, but also substantially increases the specific impulse over that calculated for acetylene as a monopropellant. In utilizing the present hydrogenation system, liquid hydrogen and liquid acetylene or other acetylene compounds are stored in separate vessels. The hydrogenation may be initiated by any of the normal procedures used with monopropellants, such as by injecting liquid hydrogen and liquid acteylene into the reaction chamber, adding a small amount of oxygen or air and providing a suitable spark. After the reaction is initiated the desired measured quantities of liquid hydrogen and liquid acetylene are added to sustain the reaction. In an alternative method the hydrogenation may be initiated by injecting liquid acetylene without liquid hydrogen into the reaction chamber with the oxygen and a spark. After the acetylene reaches its decomposition temperature, measured quantities of liquid hydrogen and liquid acetylene are injected into the reaction chamber to sustain the hydrogenation. The latter method has a disadvantage in that the decomposition temperature of acetylene is higher than the decomposition temperature for an acetylene-hydrogen mixture. This hydrogenation reaction produces a thrust which may be utilized in propelling a missile. Further, since the reaction products obtained from the hydrogenation are principally methane and hydrogen, which have high heats of combustion, added propulsion may be produced by afterburning these reaction products with atmospheric air. Thus it is apparent that the present hydrogenation system is particularly advantageous when utilized in an air breathing type of rocket system such as an air turborocket or a ramrocket. The important properties for both acetylene and hydrogen are presented in Table I.

TABLE I

Physical Properties

LIQUID ACETYLENE AND LIQUID HYDROGEN

Acetylene (B.P. −84° C.):

$\Delta H_f°$ (25° C.) (gas) = 54.19 kcal./mole

ΔH_{vap} (−84° C., 1 atm.) = 1.52 kcal./mole

$\Delta H_f°$ (25° C.) (liq.) = 52.67 kcal./mole

ΔH_c (25° C.) (net) (liq.) = 20,600 B.t.u./lb.

Hydrogen (B.P. −252.8° C.):

$\Delta H_f°$ (25° C.) (gas) = 0.00 kcal./mole

ΔH_{vap} (−252.8° C., 1 atm.) = 0.216 kcal./mole

c_p (liq.) = 2.5 cal./gm.° K.

$\Delta H_{-252.8°C.}^{25°C.} = 2.5\ (298.1 - 20.3) = 694$ cal./gm. = 1.388 kcal./mole

ΔH_f (−253° C.) (liq.) = −1.6 kcal./mole

ΔH_c (25° C.) (net) = 49,600 B.t.u./lb.

In Table II are shown the calculated parameters for various mole ratios of liquid acetylene to liquid hydrogen. In each case one mole of acetylene was used. The calculations were made by the injection of liquid reactants at a

chamber pressure of 20 atmospheres exhausting to one atmosphere. Frozen equilibrium was assumed.

TABLE II

Reactants	T, ° K.	Mol. Wt.	I_{sp}, secs.	Products in Moles			ΔH_c, B.t.u./lb.
				C	H_2	CH_4	
$C_2H_2+H_2$	2,150	14.0	260	2.0	2.0	0	22,650
$C_2H_2+1.5\ H_2$	1,900	11.6	261	2.00	2.5	0	23,600
$C_2H_2+2.0\ H_2$	1,750	10.0	267	2.0	3.0	0	24,500
$C_2H_2+3.0\ H_2$	1,500	8.40	268	1.8	3.6	0.2	26,100
$C_2H_2+4.0\ H_2$	1,350	7.47	270	1.55	4.1	0.45	27,000
$C_2H_2+5.0\ H_2$	1,275	6.85	271	1.26	4.52	0.74	28,700
$C_2H_2+6.0\ H_2$	1,225	6.53	273	0.83	4.66	1.17	29,800
$C_2H_2+7.0\ H_2$	1,175	6.00	278	0.68	5.36	1.32	30,800
$C_2H_2+8.0\ H_2$	1,140	6.00	275	0.00	5.00	2.00	31,600
$C_2H_2+9.0\ H_2$	1,050	5.50	272	0.00	6.00	2.00	32,400

It will be noticed from Table II that the addition of one mole of liquid hydrogen to one mole of liquid acetylene will increase the performance over the pure monopropellant decomposition process by 24 specific impulse points. Further, if the number of moles of hydrogen to liquid acetylene is increased, the specific impulse also increases, reaching a maximum where about 7 to 8 moles of hydrogen are added. It should further be noted that the addition of liquid hydrogen tends to eliminate the formation of carbon as one of the reaction products. The complete elimination of carbon is advantageous for the reasons noted above and because the afterburning properties will be improved.

Table III indicates the parameters for a representative group of acetylenics. The calculations were made by the injection of liquid reactants at a chamber pressure of 20 atmospheres exhausting to 1 atmosphere and frozen equilibrium was assumed.

TABLE III

Reactants	T, ° K.	Mol. Wt.	I_{sp}, secs.	Products in Moles			ΔH_c, B.t.u./lb.
				C	H_2	CH_4	
Isopropenyl Acetylene	1,380	22	166	483	2.66	0.17	18,820
Methyl Acetylene	1,680	20	191	300	2.0	0.00	19,690
C_2H_2	3,100	25.5	236	2.0	.98	.04	20,600
1-Hexyne	1,090	21.2	148	4.76	2.52	1.24	18,570
Isobutenyl Acetylene	1,250	23.2	147	5.44	2.88	0.56	19,000
1-Butyne	1,330	14.9	171	3.72	2.44	0.28	19,400
1,7-Octadiyne	1,450	21.2	174	8.0	5.0	0	18,700
1,6-Heptadiyne	1,670	22.5	179	7.0	4.0	0	18,550
1,5-Hexadiyne	2,060	26.0	190	6.0	3.0	0	19,000
$C_2H_2+8.0\ H_2$	1,140	6.00	275	0.00	5.00	2.00	31,600
$C_2H_2+O_2$	3,590	------	266	------	------	------	------
1,5-Hexadiyne+17 H_2	1,100	7.46	242	1.0	10.0	5.0	28,300

In Table III above it should be noted that the acetylene-hydrogen combination produces higher results than an acetylene-liquid oxygen combination. Also, the temperature of the acetylene-oxygen is much greater than is the temperature of the acetylene-hydrogen combination; hence, the acetylene-hydrogen combination is to be preferred due to the fact that the rocket engine need not be cooled. In Tables II and III the last column (ΔH_c, B.t.u./lb.) represents the heat of combustion of the reaction products measured in B.t.u.'s per pound. This parameter is important in determining the effectiveness of the reaction products in afterburning. In the afterburning step the reaction products are burned with atmospheric air to produce a further propellant force. The higher the heat of combustion of the reaction products, the greater the effectiveness of these reaction products in the afterburning step. From Tables II and III it can be seen that the reaction products from the hydrogenation of acetylenic compounds, particularly acetylene, plus 7 to 10 moles of hydrogen and 1,5-hexadyne, plus about 17 moles of hydrogen, exhibit high heats of combustion.

Although the acetylene-hydrogen system is preferable in many aspects, this system has a relatively low bulk density and hence would require relatively large storage vessels where a long mission is to be accomplished. For this reason other acetylenic compositions having a higher bulk density may be preferred. It is important in selecting an acetylenic compound to select one which has a relatively high adiabatic decomposition temperature since the addition of hydrogen will lower this temperature. It is seen that 1,5-hexadyne has a high adiabatic decomposition temperature, a higher bulk density than acetylene, and thus may be preferred for some missions even though the spectific impulse is lower than that which is obtained with acetylene.

Since many different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention should not be limited except as defined in the appended claims.

I claim:

1. A method of producing thrust for the propulsion of a rocket which consists of separately introducing into a reaction chamber in said rocket a liquid acetylenic hydrocarbon and an excess of liquid hydrogen under conditions of elevated temperature and pressure to cause the hydrogenation of said acetylenic hydrocarbon to form methane and hydrogen as the major reaction products, said hydrogenation being accompanied by the liberation of heat, and discharging the heated reaction products from said reaction chamber through an exhaust nozzle to create a propelling thrust.

2. A method of producing thrust for the propulsion of a rocket according to claim 1 in which the acetylenic hydrocarbon is acetylene and the hydrogen and acetylene are introduced into the reaction chamber in the proportion of about 7 mols to about 10 mols of hydrogen for each mol of acetylene.

3. A method of producing thrust for the propulsion of a rocket according to claim 1 in which the acetylenic hydrocarbon is 1,5-hexadyne and the hydrogen and 1,5-hexadyne are introduced into the reaction chamber in the proportion of about 17 mols of liquid hydrogen for each mol of 1,5-hexadyne.

4. The method of propelling an air breathing rocket which consists of injecting a liquid acetylenic hydrocarbon and an excess of liquid hydrogen into a reaction chamber in said rocket to cause hydrogenation of said acetylenic hydrocarbon to methane, whereupon the reaction products are predominantly methane and hydrogen at elevated temperature and pressure, exhausting the said reaction products from the reaction chamber through a nozzle to produce an initial thrust, and burning the exhausted reaction products with air to produce an additional thrust.

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