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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C06B 47/00

A1

(11) International Publication Number: **WO 92/07808**

(43) International Publication Date: 14 May 1992 (14.05.92)

(21) International Application Number: PCT/US91/08008

(22) International Filing Date: 24 October 1991 (24.10.91)

(30) Priority data:
605,266 29 October 1990 (29.10.90) US

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(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

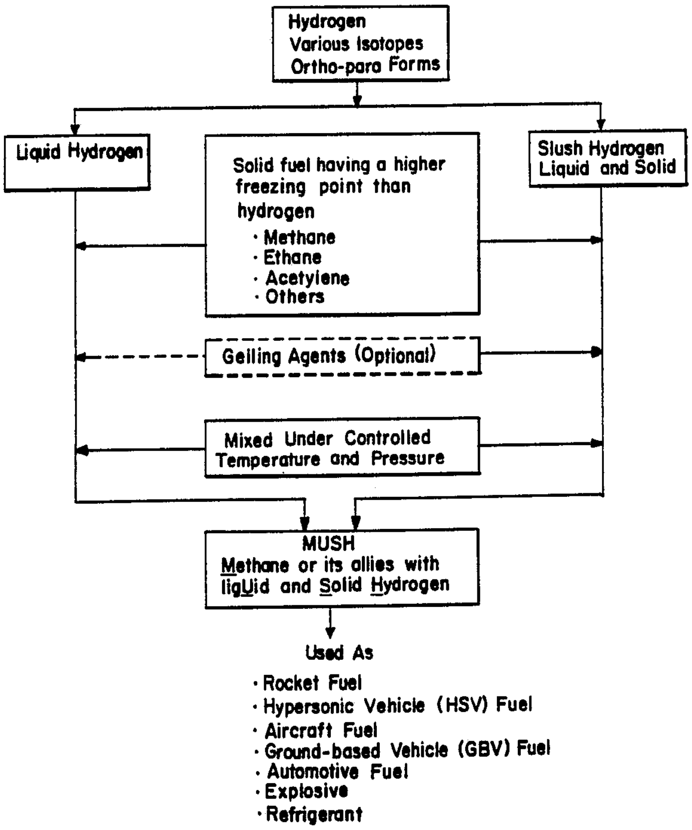
Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CRYOGENIC FUELS

(57) Abstract

A cryogenic fuel mixture which can be utilized as an improved rocket fuel, hypersonic vehicle fuel, aircraft fuel, ground based vehicle (GBV) fuel, ship or underwater vehicle fuel, automotive fuel, explosive or refrigerant is described. The mixture comprises a cryogenic hydrogen liquid or slush mixed with a second fuel in fuel value proportions and having a freezing point higher than that of hydrogen. An oxidizer such as liquid oxygen (LOX) may be combined with the hydrogen or second fuel under controlled pressures and temperatures such that a monopropellant is provided. In a preferred form of the invention the hydrocarbon fuel is methane. The fuel may be combusted with any oxidant, including, but not limited to, oxygen, air, oxidizers such as fluorine, or any other chemical oxidant.

PRODUCTION OF HYDROGEN AND FUEL SLURRY



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CRYOGENIC FUELS

Technical Field

This invention relates to high performance fuels and more particularly to cryogenic fuel mixtures or slurries suitable for use as propellants for rockets, hypersonic vehicles, ground based vehicles (GBVs), ships and underwater vehicles.

Background Art

High performance propellants, especially for rockets and hypersonic air vehicles have four basic requirements: high energy density, excess heat capacity, fast reaction requirements, and ease of storage and handling. To a lesser extent, these same requirements also apply to the fuels for GBVs. An additional requirement for GBVs is that the fuel be clean burning.

These fuel requirements have led to a cryogenic fuel called slush hydrogen. In general, slush hydrogen is a mixture of liquid hydrogen and solid hydrogen at the triple point pressure (1.02 psia) and temperature (13.8K) of hydrogen. The mixture is usually about 50% of each phase, liquid and solid, although varying ratios of liquid and solid phase may be present. This fuel, because of its high energy content (*i.e.*, high heat of combustion, high specific impulse content), is a highly desirable rocket, spacecraft and aircraft fuel.

U.S. Patent Nos. 3,455,117 to Prelowski, U.S. Patent No. 3,521,457 to Hemstreet, U.S. Patent No. 3,521,458 to Huibers, and U.S. Patent No. 3,354,662 to Daunt all disclose methods for producing slush hydrogen. Another related patent is U.S. Patent No. 4,305,256 to Anderson which involves a process for making a cryogenic gel having a methane component.

Fuels for spacecraft must have certain characteristics which are compatible with requirements for space flight. These include a high energy content per pound. Consequently, hydrogen is a highly desirable spacecraft fuel because it has both a high heat of combustion and a high specific impulse.

Another advantage arising from the use of solid hydrogen is the increased amount of refrigeration that is available in the stored product. This is particularly due to solid hydrogen's heat of fusion. This increased refrigeration is especially desirable for long duration missions where the utmost in storage duration capability is required. To date, however, in spite of these advantages it has not been practical to use solid hydrogen by itself because of the difficulty of handling it and pumping it through transfer lines.

Hydrogen carried as a compressed gas also is not suitable for this purpose since the weight of the required tankage tends to nullify any advantages of the high heat of combustion of the hydrogen. Hence, it has been the practice to use hydrogen in its liquid form when it is used as a spacecraft fuel.

One of the limitations of the use of liquid hydrogen, however, arises from its low density (4.42 lbs. per cubic foot). Liquid hydrogen, in fact, has the smallest density of any liquid known. This necessitates the requirement for large volume containers which requires large volumes within the spacecraft where space is at a premium. Moreover, at a pressure of one atmosphere, liquid hydrogen boils at a temperature of only approximately 20.39 K. Consequently, to prevent the influx of heat to the hydrogen and to prevent its vaporization at this extremely low temperature, it is necessary to store the liquid hydrogen in a container that is well insulated. This, of course, adds to the spacecraft's weight.

Ideally, therefore, from an energy standpoint alone, it would be preferable to use solid hydrogen because it has a greater density at its triple point (5.41 lbs. per cubic foot) as opposed to liquid hydrogen at its boiling point. Thus, a given sized tank can contain about 20% more weight of solid hydrogen as compared to the liquid form. This not only conserves space but because of its smaller bulk, less insulation is required. This reduces the spacecraft's weight requirements.

In recent years there has been considerable interest in the use of slush hydrogen. In general, slush hydrogen has satisfactory fluid handling properties and also possesses some of the higher density and storability features of the solid form of hydrogen.

A problem with slush hydrogen as a fuel is its relatively low density. With a 50% solid-liquid mixture, slush hydrogen has a density of approximately 5.1 lbs/ft^3. Although this density is an improvement over the density of normal boiling point liquid hydrogen alone, it presents significant limitations as a fuel.

Because of this low density a very large vehicle is required just to contain the hydrogen slush fuel. This necessitates the requirement for large volume containers and in general large volume vehicles. Consequently, such large vehicles are less efficient and costly due to increased drag, weight, and structural requirements.

Another disadvantage of slush hydrogen as a fuel is the difficulty in handling and storing the fuel and in pumping the fuel through transfer lines. Slush hydrogen has a relatively low density (about 8% that of water) and exists normally at relatively low pressure, about 1 psia. This relatively low pressure can lead to the in-leakage of air and other gases and the attendant formation of explosive mixtures.

Yet another disadvantage of slush hydrogen as a fuel is its instability with respect to heat input. Any heat entering the hydrogen slush through for example, pumping energy or inadequate insulation, goes directly to melt the solid hydrogen portion of the slush hydrogen mixture. When enough heat has accumulated to raise the temperature a fraction above the triple point temperature of hydrogen, all the solid hydrogen is melted and a slush no longer exists. Additionally, the solid portion of the hydrogen slush tends to aggregate unless mixing occurs. Mixing adds energy to the mixture, melting the solid, thus defeating the need to minimize energy input to the fuel to minimize boiloff and solids loss.

There is then considerable interest in the art in improving the fluid handling properties, density, temperature stability, and storability features of hydrogen as a cryogenic fuel and especially of slush hydrogen as a propellant fuel. The present invention is directed to a cryogenic fuel slurry which may include cryogenic hydrogen or slush hydrogen as a major component but with the addition of elements to improve its performance, stability, storability, and handling characteristics as a fuel.

Disclosure of Invention

In accordance with the present invention, a cryogenic slurry suitable for use as a high performance fuel and a method of producing such a fuel is provided. The cryogenic fuel slurry includes as a major component hydrogen or slush hydrogen in combination with other elements which improve the performance and handling characteristics of the hydrogen slurry for use as a fuel.

The cryogenic fuel slurry of the invention generally stated comprises a mixture of liquid hydrogen and another solid fuel added to the hydrogen in fuel value proportions and having a higher freezing point than that of hydrogen. In a preferred form of the invention, the cryogenic fuel slurry includes a slurry of liquid hydrogen, solid hydrogen, and a solid hydrocarbon fuel such as methane contained in the liquid hydrogen.

In addition to the addition of a solid hydrocarbon fuel such as methane to the cryogenic fuel slurry, oxidizers such as subcooled liquid oxygen (LOX) can also be added or slurried to the slurry to improve the combustion characteristics of the fuel. In the case of GBVs, the oxidizer can be used to reduce the formation of pollutants and contaminants from atmospheric oxidation of the fuel. Additionally, a gelling agent may be added or slurried to the cryogenic fuel slurry of the invention to significantly improve the handling characteristics of the fuel. Moreover, chemical reaction retardants may be introduced to improve the safety and handling characteristics of the fuel/oxidizer mixture.

The combination of cryogenic fuel and oxidizer mixtures provides a cryogenic monopropellant. In a preferred form of the invention liquid oxygen and methane are mixed under such conditions described herein so that the methane remains in the liquid state. Thus miscible mixtures of LOX/L-CH_4 may be formed of very wide mixture ratios. Such a cryogenic liquid mono-propellant may have LOX/L-CH_4 concentrations equal to the stoichiometric ratio, not equal to this ratio, and even extending beyond the lower explosive limit (LEL) or the upper explosive limit (UEL) of O_2/CH_4 mixtures.

Additionally, processes for producing a cryogenic fuel slurry or mixture in accordance with the invention are also disclosed.

Other objects, advantages and capabilities of the present invention will become more apparent as the description proceeds.

Brief Description of the Drawings

Figure 1 is a schematic drawing showing production of hydrogen and a fuel slurry mixture in accordance with the invention;

Figure 2 is a schematic drawing showing production of hydrogen and an oxidizer slurry in accordance with the invention;

Figure 3 is a schematic drawing showing production of an oxidizer and fuel monopropellant in accordance with the invention;

Figure 4 is a chart showing the liquid temperature range of different cryogenic liquids;

Figure 5 is a chart that compares the liquid density of various cryogenic fluids in U.S. engineering units and metric units;

Figure 6 is a chart that compares the cooling power of various cryogens on a weight basis expressed in U.S. engineering units and in metric units; and

Figure 7 is a chart that compares the cooling power of different cryogens on a volume basis. In this and other figures "MUSH" represents the combination of methane plus slush hydrogen. "MOX" represents the combination of methane and oxygen. "HOX" represents the combination of hydrogen and oxidizers. "METHROGEN" is the general name chosen to represent the combination of METHane plus hydROGEN.

Best Mode for Carrying Out the Invention

As used herein the following definitions are applicable:

slush - a solid/liquid mixture of an essentially pure component. Both the solid and liquid present are merely different physical phases of essentially the same chemical species.

An important distinction in the use of the term slush is that it refers to a solid/liquid mixture of an essentially pure component. Both the solid and liquid present are merely different phases of essentially the same chemical species. For instance, one skilled in the art of handling slush systems would consider the slush to be a physical mixture of solid and liquid phases of a pure or single component.

Physical conditions at or near the triple point or melting point of the pure component must be maintained for the slush mixture of solid and liquid phases to exist in stable equilibrium. In the case of hydrogen slush, the triple point conditions are approximately 13.8 Kelvin, and 1.02 psia pressure.

A snowy slush, for instance, would be a mixture of solid (ice) and liquid (water), such as partly melted or watery snow.

slurry - a free flowing pumpable suspension of fine solid material in liquid. A slurry or suspension are terms used to describe a mixture of a solid and liquid phases of different chemical species. An example of a slurry is coal slurry, which is a mixture of solid coal suspended in liquid water. The solid component of a slurry is usually considered by one skilled in the art as insoluble or only partially soluble in the liquid phase.

In the simplest terms, then, a slush refers to solid and liquid mixtures of the same component (*e.g.*, snowy slush), while slurry refers to solid and liquid mixtures of different components or even multi-components (*e.g.*, a coal slurry).

gel - a two phase colloidal system consisting of a solid and a liquid in more solid form than a sol.

sol - a colloidal solution consisting of a suitable dispersion medium, which may be gas, liquid, or solid, and the colloidal substance, the disperse phase, which is distributed throughout the dispersion medium.

slush hydrogen - a mixture of liquid hydrogen and solid hydrogen. The mixture is usually about 50% of each phase, although varying ratios of liquid and solid phase as well as different ortho/para hydrogen ratios, or isotopic modifications of hydrogen, may also be present. Although the process of the invention may be applied to normal hydrogen, that is, hydrogen having about 25% para and 75% ortho content, it is much more practical to employ the process only with para hydrogen. This is because at the low temperatures used herein hydrogen tends to spontaneously convert from the ortho form to the para form while evolving considerable amounts of heat (*i.e.*, heat of conversion). As used herein the term slush hydrogen preferably includes hydrogen having approximately 99.79% para hydrogen and 0.21% ortho hydrogen. This is by way of example however, and not by limitation, as any ratio of ortho/para concentration may be present for the practice of the invention. Additionally, any ratio of the isotopic forms of hydrogen, that is protium, deuterium, and tritium may be used for the practice of the invention.

With reference to Figure 1 in a preferred embodiment the invention broadly stated comprises, a cryogenic fuel slurry including liquid hydrogen, solid hydrogen and a solid fuel having a higher freezing point than that of hydrogen mixed under conditions of controlled temperature and pressure. The solid fuel is preferably a solid hydrocarbon such as methane or its allies and may also be another hydrocarbon or a multi-component mixture of hydrocarbons. This fuel is referred to herein as MUSH. The generic term for such combinations is METHROGEN. As will hereinafter be more fully explained, gelling agents may also be added to the mixture for combination with a hydrocarbon component of the slurry to improve the handling characteristics of the slurry. Any oxidizer is suitable for combustion.

With reference to Figure 2, an oxidizer such as cryogenic oxygen and/or fluorine may also be slurried to the hydrogen slurry or slush. This fuel is referred to herein as hydrogen and oxidizers (HOX). Chemical reaction retardants such as inert gases may also be slurried to the hydrogen fuel slurry to improve the safety and handling characteristics of the slurry. Moreover, gelling agents may be added to the hydrogen fuel slurry for combination with a hydrocarbon component of the slurry such as methane to improve the handling characteristics of the slurry.

With reference to Figure 3 a cryogenic monopropellant may also be formed by a cryogenic combination of an oxidizer and a hydrocarbon such as methane. This monopropellant is termed herein as methane and oxygen (MOX).

As a main component of a cryogenic fuel slurry formed in accordance with the invention, a solid fuel of a higher freezing point than that of hydrogen is suspended or contained in the liquid hydrogen component of the cryogenic slurry in fuel value proportion. As shown in Figure 4, this may include a hydrocarbon such as methane, ethylene, ethane, acetylene, propylene, propane, or butane. The solid other fuel may be a single component such as methane or a multi-component mixture including a number of different solid components. Air, oxygen, or any chemical oxidizer may be used for combustion.

Table 1 lists the relative properties of various cryogenic liquids.

TABLE 1. RELATIVE PROPERTIES OF CRYOGENIC LIQUIDS

	mol wt g/mol	liquid density lb/ft^3	g/cc	vapor density lb/ft^3	g/L	Liq-vap expansion	H L-G B/ft^3	H L-G B/lb	H vap B/lb	Cooling Power B/lb	Cooling Power B/ft^3
H2	2.02	4.4	0.071	0.083	1.33	53.0	848	192.7	1725.1	1917.8	8438
MUSH	3.58	7.76	0.124							1198	9300
He	4	7.8	0.125	1.06	16.99	7.4	69	8.8	663.3	672.1	5242
CH4 5	16	26.5	0.425	0.115	1.84	230.4	5804	219	173.3	392.3	10396
Ne	20.2	75.4	1.208	0.593	9.50	127.2	2797	37.1	121.5	158.6	11958
MOX	21.33	36.42	0.583							295	10740
N2	28	50.4	0.808	0.276	4.42	182.6	4329	85.9	100.6	186.5	9400
02	32	71.2	1.141	0.279	4.47	255.2	6515	91.5	83	174.5	12424
Ar 10	39.9	87.4	1.401	0.36	5.77	242.8	6135	70.2	48.2	118.4	10348

Figure 5 compares the liquid densities of various cryogens. Figures 6 and 7 compare the cooling power of various cryogens on a weight and volume basis respectively.

As an illustration, a cryogenic fuel slurry may include a mixture of liquid hydrogen and a solid hydrocarbon which is added in fuel value proportions. A 50/50 mixture of solid methane and liquid hydrogen can be utilized as an example. This liquid would have a density of approximately 13.06 lbs/ft^3 or 1.73 (173%) times as great as the density of 50/50 solid/liquid slush hydrogen alone.

Adding solid methane to liquid hydrogen does decrease the energy density over that of liquid hydrogen alone. The energy density of a 50/50 hydrogen/methane mixture would be approximately 39,000 BTU/lb-m, compared to that of liquid hydrogen alone of approximately 51,000 BTU/lb-m. It should be noted that other measures of energy such as specific impulse (ISP) and specific fuel consumption (SFC) are usually less affected, especially when the oxidant is air rather than pure oxygen. A 24% decrease in energy density however, achieves a 173% increase in propellant bulk density. Vehicle drag and structural weight can now be much smaller than with hydrogen alone, more than offsetting the small decrease in energy density of the hydrogen-methane slurry. Furthermore, the hydrogen-methane slurry will possess slightly reduced reaction kinetics, but this is more than offset by an even higher heat content for meeting hypersonic vehicle fuel requirements.

Additionally, due to the high zero point energy of hydrogen, slush hydrogen is an extremely fragile system with respect to heat input. Any heat entering the system through imperfect insulation, or pumping energy, for instance, goes directly to melt the solid hydrogen portion of the slush hydrogen mixture. This, of course, immediately destroys the purpose of slush hydrogen. When enough heat has accumulated to raise the temperature a fraction above the triple point temperature of hydrogen, all the solid hydrogen has melted, and only liquid hydrogen remains. The system has been destroyed as far as being a slush. In the hydrogen-methane system to the contrary, a solid methane phase will exist even to the boiling point of liquid hydrogen and beyond, owing to the much higher freezing point of methane. The hydrogen-methane cryogenic slurry will be a very stable system compared to a slush hydrogen system.

In addition to the low energy density (by volume) possessed by slush hydrogen, slush hydrogen has another flaw: the solid fraction tends to aggregate unless mixing occurs. Mixing adds energy to the mixture, melting the solid, thus defeating the need to minimize energy input to the fuel to minimize boiloff and solids loss. Slush hydrogen-methane will maintain the solid methane even if vigorously mixed or pumped, since the boiling temperature of hydrogen ($T=20$ Kelvin approximately) is substantially below the freezing temperature of methane ($T=90$ Kelvin, approximately).

The addition of a solid fuel such as methane to hydrogen in a cryogenic slurry thus in itself provides a substantial improvement over hydrogen slush as a fuel. Moreover, methane gelling agents which form weak addition or coordination compounds, or clathrates, with methane, can be added to the mixture to produce a gel of cryogenic fluids. As is apparent, a gel would provide improved handling characteristics in a cryogenic fuel.

Prior attempts to produce a gel of cryogenic fluids have largely not been successful due to the basic nature of a pure, single component cryogen. A gel requires some unusual intermolecular potential to form a colloidal suspension. Such molecular forces are generally absent in cryogenic liquids because of their basic molecular simplicity and symmetry. The more complex molecular species such as the higher hydrocarbons have generally become solids at cryogenic temperatures due to their inherently higher molecular weight.

The present invention can make gel formation in cryogenic fluids possible because a methane component or its allies is usually present. Because of this, various gelling agents which form weak addition or coordination compounds, or clathrates, with methane or its allies may be used. The gelling agent may be selected from the class consisting of water and methyl alcohol, since both exhibit the above enumerated qualities. Because methyl alcohol does not adversely affect the energy balance of the gelling process to as large an extent as water, it can be present in the gelled, cryogenic system in substantially greater proportion than water without detracting from the efficiency of the process. Further, applicants acknowledge the possibility that liquids can be gelled with gelling agents which do not become liquid or gaseous at ambient temperature, such as silica.

The gelling agent is present preferably so that it forms between about 0.1% to about 25% (by weight) of the resulting gel and is selected so that it is a solid at the temperature of the liquid cryogenic and preferably a liquid or a gas at ambient temperature.

In addition to a solid fuel component and gelling agents, various oxidizers may be added to the cryogenic fuel slurry to provide oxidants which would normally need to be added to the fuel separately. One such suitable oxidizer would be liquid oxygen (LOX). Another suitable oxidizer would be a mixture of oxygen and fluorine (FLOX). Mixtures of FLOX are well known. With FLOX as an oxidizer, the oxidation mixture would preferably be a cryogenic slurry of oxygen and fluorine, in which one member is in the cryogenic liquid state, and the other is in the solid state. This arrangement provides a suitable density and establishes chemical passivation of the fluorine. The oxidation components may also be included in the cryogenic fuel slurry in the form of a gel.

The combination of oxidizers with the cryogenic fuel slurry would produce a "cryogenic monopropellant" in which the majority of the fuel and oxidizer can be contained in a single cryogenic storage tank. An example is the cryogenic oxygen-methane mixture described above MOX. Also included in this disclosure are gels of the above.

It is not necessary that the cryogenic monopropellant be a solid/liquid slurry. Miscible liquid cryogenic solution monopropellants also result from this invention. For instance, LOX at one standard atmosphere pressure has a normal boiling point of 90.18 Kelvins. The freezing point (triple point) of methane is 90.7 Kelvins. Thus, liquid oxygen at one atmospheric pressure exists at a temperature below the freezing point of methane. A methane/LOX mixture at these conditions would comprise substantially liquid oxygen, solid methane, and a small fraction of dispersed methane in solution in the liquid oxygen.

However, if the pressure above the boiling LOX is elevated, the temperature of the LOX rises accordingly. Raising the pressure of LOX may be accomplished by autogenous means, with a pressurant gas, or by mechanical and hydro-mechanical pressurization. An increase of pressure from 14.696 psia to approximately 15.303 psia is sufficient to raise the temperature of LOX to equal or exceed the freezing temperature of methane. Accordingly, elevated pressures may be used to produce a homogeneous, miscible mixture of LOX and liquid methane in almost any concentration of the two. In a similar way, elevated pressures of LOX may be used to achieve liquid/liquid mixtures of LOX plus other hydrocarbons and mixtures of hydrocarbons including, but not limited to methane. Some of these possible mixtures will hereinafter be described. Other suitable oxidizers in addition to LOX may include GOX, F_2, OF_2, FLOX, N_2F_4, ClF_5, ClF_3, N_2O_4, Mon-25, IRFNA, H_2O_2, N_2H_4 and other oxidizers.

For illustrative purposes, the following hydrocarbons may be used singly or in any combination with LOX or another oxidizer as described above: Methane, Ethane, Ethylene, Propane, Propylene, Propyne, Acetylene, and others. Carbon may be also added to LOX as a dispersed pure phase as elemental carbon itself, or as carbon monoxide.

System thermodynamic parameters may be chosen to make such illustrative mixtures become liquid/liquid or liquid/solid systems, as one desires.

It is pointed out that methane is of special interest as the preferred hydrocarbon additive to LOX or LH2 because:

(1) Methane has the highest H:C ratio of all the hydrocarbons. Methane is a preferred means of storing and transporting hydrogen.

(2) The proximity of the methane freezing point to the LOX Normal Boiling Point facilitates achieving liquid/liquid mixtures of methane and LOX.

It is noted that the freezing point of ethylene, ethane, propane and propylene also lend themselves to forming liquid/liquid mixtures with LOX. The H:C ratio of these hydrocarbons is however, lower than that of methane.

It is possible with fuel slurries and mixtures constructed in accordance with this invention to form liquid/liquid mixtures of LOX and certain hydrocarbons. It is also possible to combine any ratio of hydrocarbon or hydrocarbons with LOX. Possible mixtures could include, but are not limited to:

(1) Stoichiometric mixtures of LOX and a hydrocarbon or hydrocarbons.

(2) Oxygen rich or oxygen lean mixtures of LOX and a hydrocarbon or hydrocarbons.

(3) Mixtures that are outside the lower explosive limit (LEL) or the upper explosive limit (UEL) of the hydrocarbon or hydrocarbons and LOX mixtures. By forming liquid/liquid mixtures whose concentration of components is not within the explosive limits, relatively safe, stable mixtures of LOX and hydrocarbons are made possible.

In the use of GBVs this arrangement would be cleaner burning than one in which atmospheric air is utilized as an oxidizing agent. In general, atmospheric air contains nitrogen. During oxidation noxious emissions are produced by reaction of the fuel and oxygen with nitrogen in the air.

Air combustion is not a limitation, however. METHROGEN, MUSH and MOX are equally suited for combustion with any oxidant, including atmospheric air in whole or in part.

An improved automotive fuel having the possibility of producing no nitrogen oxide emissions, since only LOX and not atmospheric air is used, is thus possible with the cryogenic fuel of the invention.

Additionally, since the cryogenic fuel slurry of the invention is a monopropellant fuel [e.g., LOX + methane], in the liquid/liquid state, only one set of containment tanks and one set of auxiliary equipment (*e.g.*, insulation, instrumentation, pumps, etc.) would be required.

An additional application of the cryogenic fuel slurry of the invention is an improved explosive for excavation, mining, and demolition. This present arrangement allows a fuel and a hydrocarbon to be safely stored separately, and combined into any mixture or quantity of the two near the time and place of intended use as an explosive. Alternately, the components may be pre-combined.

The cryogenic fuel slurry of the invention can be utilized as an improved explosive for the discharge of projectiles as in a weapon such as a gun or cannon. The LOX and hydrocarbon may be safely stored separately. They can then be metered together in a desired ratio and quantity of the two near the time and place of the intended use as a "gunpowder" or explosive for the discharge of projectiles.

The cryogenic fuel slurry of the invention can be utilized as an improved explosive in any detonating weapon system. For instance, LOX and the selected hydrocarbon or mixture of hydrocarbons may be pre-mixed or metered together near the time and place of intended use as a fuel-air-explosive (FAE) weapon.

The cryogenic fuel slurry of the invention can be utilized as an improved refrigerant. For instance, the cryogenic slurry will provide an improved refrigerant for cooling Infra-Red detectors, focal plane arrays, X-ray detectors and other such instruments or systems whose performance is improved by lower temperatures.

Previously cited U.S. Patents 3,354,662; 3,455,117; 3,521,457; 3,521,458 and 4,305,256 disclose apparatus and methods for making hydrogen slush. Each of these U.S. patents is included herein by reference. In general, a cryogenic fuel slurry can be produced in accordance with the present invention by producing liquid hydrogen and/or slush in accordance with the prior art but with the addition of solid fuel elements in fuel value proportions (*i.e.*, 50-50) oxidizers, and chemical retardants as required to the hydrogen slush. This may be done during manufacture of the slush and can be done for instance by injection of a solid hydrocarbon at elevated pressures as previously described to achieve a liquid/liquid mixture of LOX and hydrocarbon.

In general cryogenic fuels formed in accordance with the invention can be utilized in the art as follows:

A. For cryogenic slurry fuels:
   1. Improved rocket performance.
   2. Improved hypersonic vehicle performance
   3. Improved commercial and military aircraft performance.
   4. Improved propellant handling characteristics, such as greater heat content, improved storage times, virtually no loss storage for fuel cells and spacecraft applications.
   5. Improved ground support facilities by reason of the higher heat content and storability.
   6. Reduced cost of production (compared to slush hydrogen).
   7. Simplified rocket, Hypersonic Vehicle (HSV), and high performance aircraft design resulting from the higher bulk density.
   8. Decreased structure weight due to less tankage, reduced insulation requirements, and less fuel need.
   9. Reduced drag due to less surface area.
   10. Improved energy density (by volume)
   11. Increased radiant heat transfer due to the presence of the carbon and other species in the mixed slurry.
   12. Improved safety due to increased flame visibility.

13. Narrower detonation limit than slush hydrogen.
14. An improved refrigerant.
15. An improved explosive for excavation, mining, demolition, weapons, etc.
16. In addition to the systems containing hydrogen as described above, other fuels such as C_2H_6, C_2H_4, RP-1, N_2H_4, B_5H_9, and B_2H6 may also be successfully used to form a cryogenic fuel slurry in accordance with the invention.

B. For cryogenic slurries of fuels and oxidizers, and liquid/liquid mixtures of fuels and oxidizers formed in accordance with the invention, the following additional benefits can be achieved.

1. Greatly simplified ground support equipment.
2. Greatly simplified vehicle design.
3. Greatly simplified motor (engine) design.
4. Reduced noxious emissions due to the reduction or complete elimination of atmospheric air containing nitrogen.
    a. Reduced NO_x generation due to the reduction or elimination of atmospheric air.
5. Reduced weight for aerospace applications since one fuel system is totally or partially eliminated. By eliminating the fuel system, the system eliminates a pump, valves, flow lines, and on-board power generation requirements which add weight.
6. Controlled burn due to potential addition of flame retardants or inert agents.
7. Improved energy density.
8. Improved motor efficiency due to increased burn temperature since the oxidizer system may use pure oxygen rather than air.
9. An improved automotive fuel having the possibility of producing reduced nitrogen oxide emissions if only LOX is used.
10. An improved automotive fuel resulting from the fact that the cryogenic monopropellant fuel (*e.g.*, LOX + methane) in the liquid/liquid state requires only one containment tank and only one set of auxiliary equipment (*e.g.*, insulation, instrumentation, pumps, etc.).
11. An improved explosive for excavation, mining demolition, weapons, etc., resulting from the liquid/liquid mixture of LOX and hydrocarbon. The fuel and hydrocarbon may safely be stored separately, and combined into any mixture or quantity of the two near the time and place of intended use as an explosive. Alternately, the LOX and hydro-carbon may be pre-combined.

12. An improved explosive for the discharge of projectiles as in a weapon such as a gun or cannon, or for weapons per se, such as fuel air explosive (FAE). The LOX and hydrocarbon may be safely stored separately. They then can be metered together in the desired ratio and quantity of the two near the time and place of their intended use as a "gunpowder" or explosive for the discharge of projectiles. Alternately, the separate components may be pre-combined.
13. An improved refrigerant for cooled detectors, sensors, and systems.

Thus cryogenic fuel slurries formed in accordance with the invention offer significant advantages over prior art cryogenic fuels.

While the invention has been described with reference to preferred embodiments thereof, as will be apparent to those skilled in the art, certain changes and modifications can be made without departing from the scope of the invention as defined by the following claims:

What is claimed is:

1. A cryogenic fuel slurry comprising:
liquid hydrogen; and
a solid fuel slurried with the liquid hydrogen in fuel value proportions and having a freezing point higher than that of hydrogen.

2. The cryogenic fuel slurry as recited in claim 1 and wherein:
the solid fuel is a hydrocarbon.

3. The cryogenic fuel slurry as recited in claim 2 and wherein:
the liquid hydrogen is contained in a hydrogen slush.

4. The cryogenic fuel slurry as recited in claim 3 and wherein:
the liquid hydrogen and solid hydrocarbon fuel are combined in an approximately 50-50 ratio.

5. The cryogenic fuel slurry as recited in claim 4 and wherein:
the hydrocarbon is solid methane.

6. The cryogenic fuel slurry as recited in claim 1 and further comprising:
an oxidizer slurried with the hydrogen and solid fuel mixture.

7. The cryogenic fuel slurry as recited in claim 6 and wherein:
the oxidizer is cryogenic liquid oxygen (LOX).

8. The cryogenic fuel slurry as recited in claim 7 and wherein:
the oxidizer is a mixture of liquid oxygen and fluorine (FLOX) in which oxygen is in the cryogenic liquid state and fluorine is in the solid state.

9. The cryogenic fuel slurry as recited in claim 5 and wherein:
a gelling agent is added to the slurry for combination with methane to cause suspension of the methane.

10. The cryogenic fuel slurry as recited in claim 9 and wherein:
the gelling agent is selected from the class consisting of water and methyl alcohol.

11. The cryogenic fuel as recited in claim 10 and wherein:

the gelling agent is present so that it forms between about .1% to about 25% (by weight) of a resulting gel.

12. The cryogenic fuel as recited in claim 11 and wherein:

the gelling agent is a solid at the temperature of the cryogenic fuel and a liquid or a gas at an ambient temperature.

13. The cryogenic fuel as recited in claim 12 and further comprising:

an inert gas or cryogenic liquid added to the cryogenic fuel to improve the handling characteristics of the cryogenic fuel.

14. A fuel comprising:

a cryogenic mixture of hydrogen slush;

a solid hydrocarbon as a fuel contained within the liquid hydrogen of the hydrogen slush in fuel proportions and having a freezing point higher than that of hydrogen; and

an oxidizer slurried with the hydrogen slush to provide an oxidizer during combustion of the fuel.

15. The fuel as recited in claim 14 and wherein:

the solid hydrocarbon is cryogenic solid methane.

16. The fuel as recited in claim 14 and wherein the hydrocarbon is selected from the group consisting of methane, ethane, ethylene, propane, and propylene, propyne and acetylene, and the oxidizer is selected from the group consisting of LOX, GOX, F_2, OF_2, FLOX, N_2F_4, ClF_5, ClF_3, N_2O_4, Mon-25, IRFNA, H_2O_2 and N_2H_4.

17. The fuel as recited in claim 15 and wherein:

the solid hydrocarbon is a binary or multicomponent mixture of hydrocarbons.

18. The fuel as recited in claim 17 and wherein:

the binary mixture is methane plus ethane.

19. The fuel as recited in claim 16 and wherein:

the oxidizer is cryogenic liquid oxygen (LOX).

20. The fuel as recited in claim 19 and wherein:

the (LOX) and methane are combined at elevated pressures and temperatures to produce a homogeneous miscible solution of liquid oxygen (LOX) and liquid methane.

21. An improved ground based vehicle (GBV) fuel comprising:

a cryogenic mixture of liquid hydrogen and hydrocarbon(s), singly or as multi component mixtures;

a cryogenic mixture of hydrogen slush and hydrocarbon(s), singly or as multi component mixtures.

a cryogenic solution of an oxidizer (OX) and a hydrocarbon having a freezing point higher than that of hydrogen with the OX-hydrocarbon solution slurried to the hydrogen slush in fuel value proportions and with the OX-hydrocarbon solution formed as a liquid/liquid mixture at elevated pressures;

whereby a cryogenic monopropellant fuel is provided.

22. The fuel as recited in claim 21 and wherein:

the hydrocarbon is methane.

23. The fuel as recited in claim 22 and wherein:

the oxidizer (OX) is liquid oxygen (LOX).

24. An improved explosive for weapons or the discharge of projectiles for a weapon comprising:

a cryogenic mixture of liquid hydrogen and hydrocarbon(s), singly or as a multi component mixture.

a cryogenic mixture of hydrogen slush and hydrocarbon, singly or as a multi component mixture;

a cryogenic liquid oxidizer (OX) stored in a first receptacle;

a cryogenic solution containing a hydrocarbon fuel having a freezing point higher than that of hydrogen and stored in a second receptacle;

whereby the (OX) and hydrocarbon may be combined in a desired ratio in fuel value proportions in quantities sufficient to form an explosive.

25. The explosive as recited in claim 24 and wherein:

the hydrocarbon comprises methane.

26. The explosive as recited in claim 25 and wherein:

the oxidizer (OX) is liquid oxygen (LOX).

27. An improved fuel comprising:

a cryogenic mixture of a first fuel selected from the group consisting of H_2, C_2H_6, C_2H_4, RP-1, N_2H_4, B_5H_9, or B_2H_6;

a cryogenic mixture of an oxidizer and a hydrocarbon fuel in fuel value proportions with the oxidizer formed in a solution with the hydrocarbon fuel under controlled pressure and temperatures;

whereby a cryogenic monopropellant is provided.

28. The improved fuel as recited in claim 26 and wherein:

the first fuel is either liquid hydrogen or hydrogen slush;

the hydrocarbon fuel is methane;

the oxidizer is liquid oxygen (LOX); and

a liquid/liquid mixture of methane and (LOX) is formed under condition of controlled pressure and temperature.

29. The improved fuel as recited in claim 26 and wherein:

the hydrocarbon and oxidizer are combined in a ratio which is outside a lower explosive limit (LEL) of the hydrocarbon.

30. The improved fuel as recited in claim 26 and wherein:

the hydrocarbon and oxidizer are combined in a ratio which is outside an upper explosive limit (UEL) of the hydrocarbon.

31. The fuel as recited in claim 26 and wherein:

the improved fuel is utilized as an explosive and the first fuel is held separate from the hydrocarbon fuel and oxidizer mixture until use.

32. The fuel as recited in claim 31 and wherein:

the improved fuel is utilized as a refrigerant.

FIG. 1

PRODUCTION OF HYDROGEN AND FUEL SLURRY

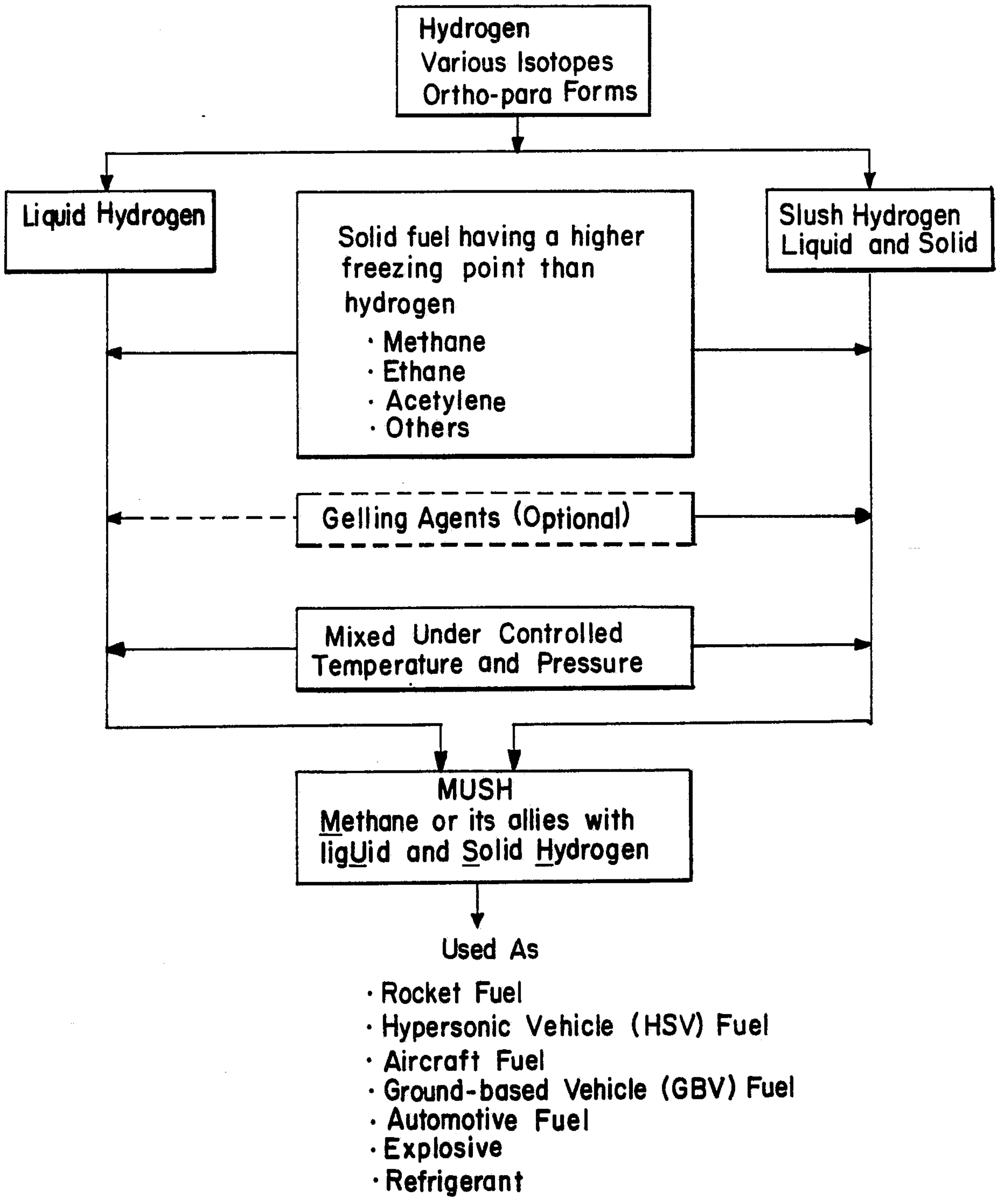


FIG.2

PRODUCTION OF HYDROGEN AND OXIDIZER SLURRY

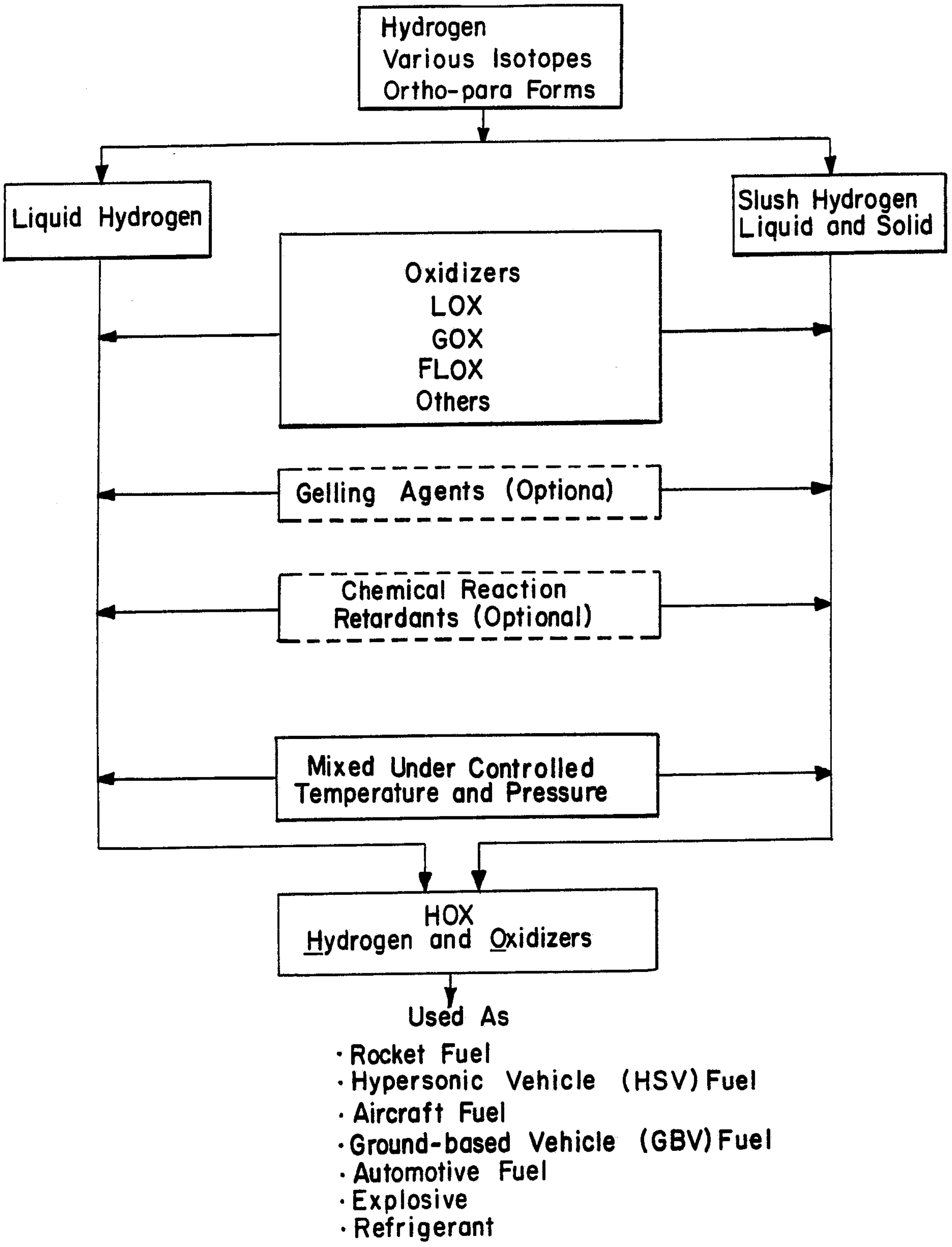


FIG.3

PRODUCTION OF OXIDIZER AND FUEL MONOPROPELLANT

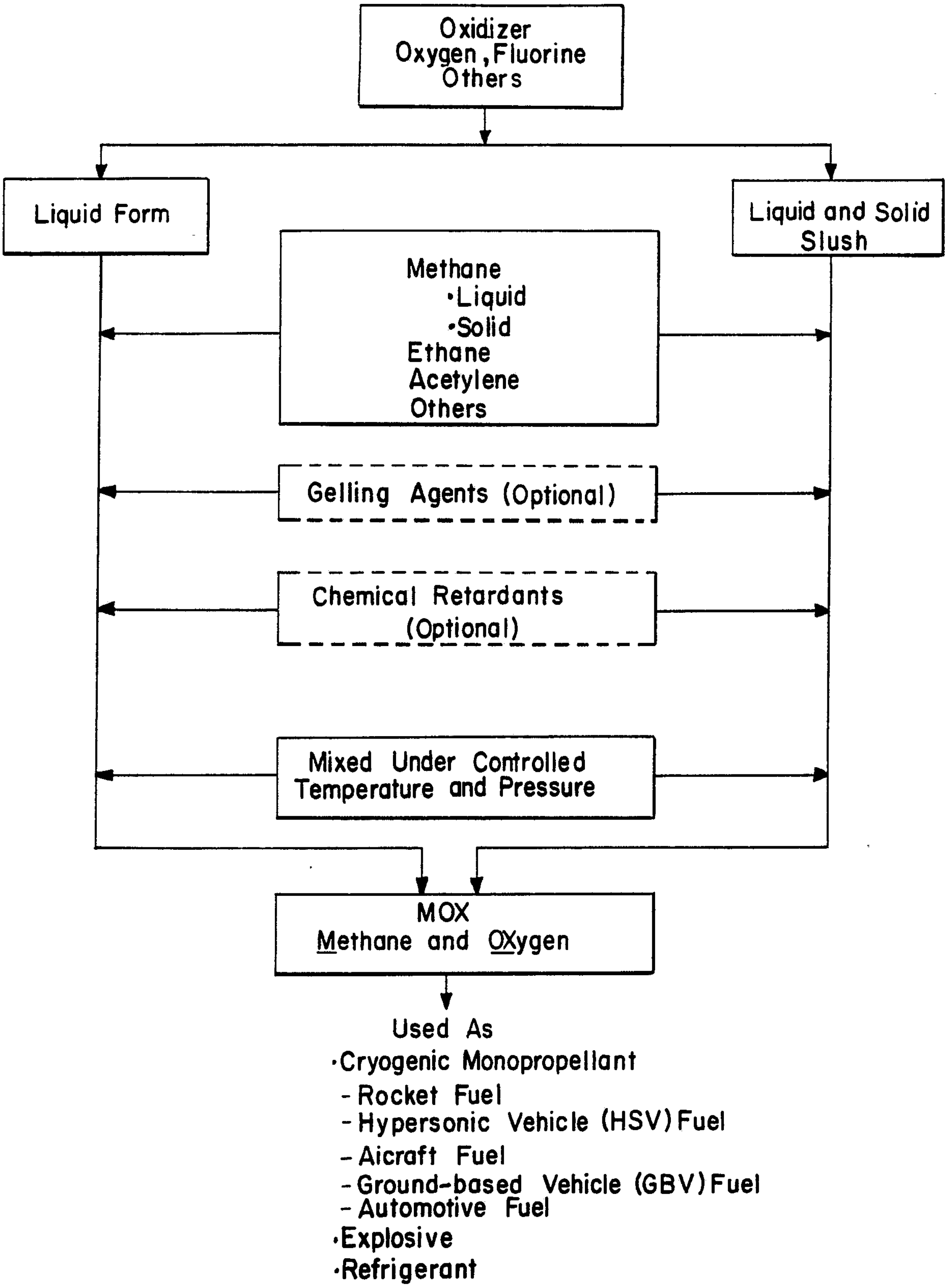
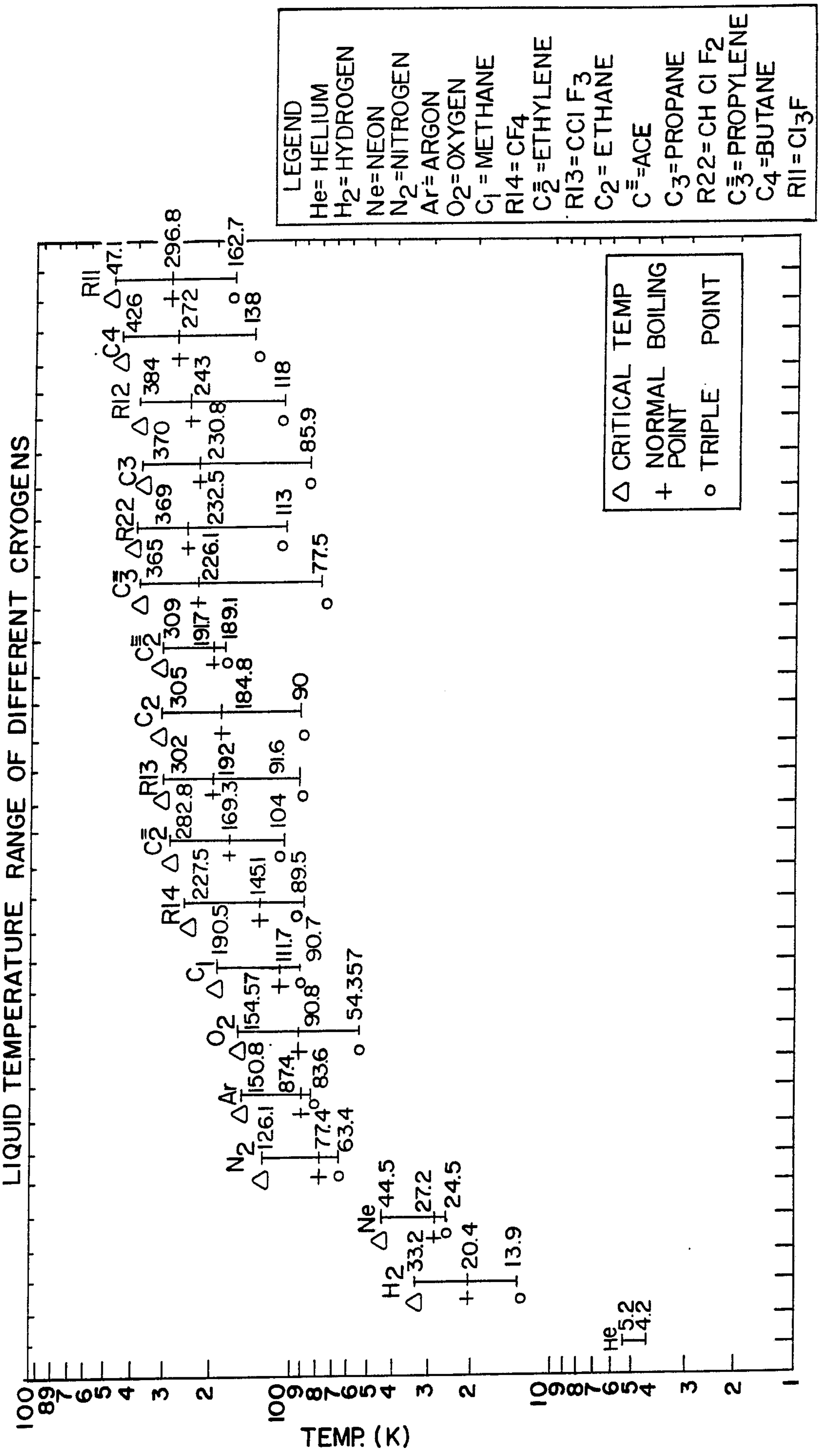


FIG.4

LIQUID TEMPERATURE RANGE OF DIFFERENT CRYOGENS



SUBSTITUTE SHEET

FIG.5

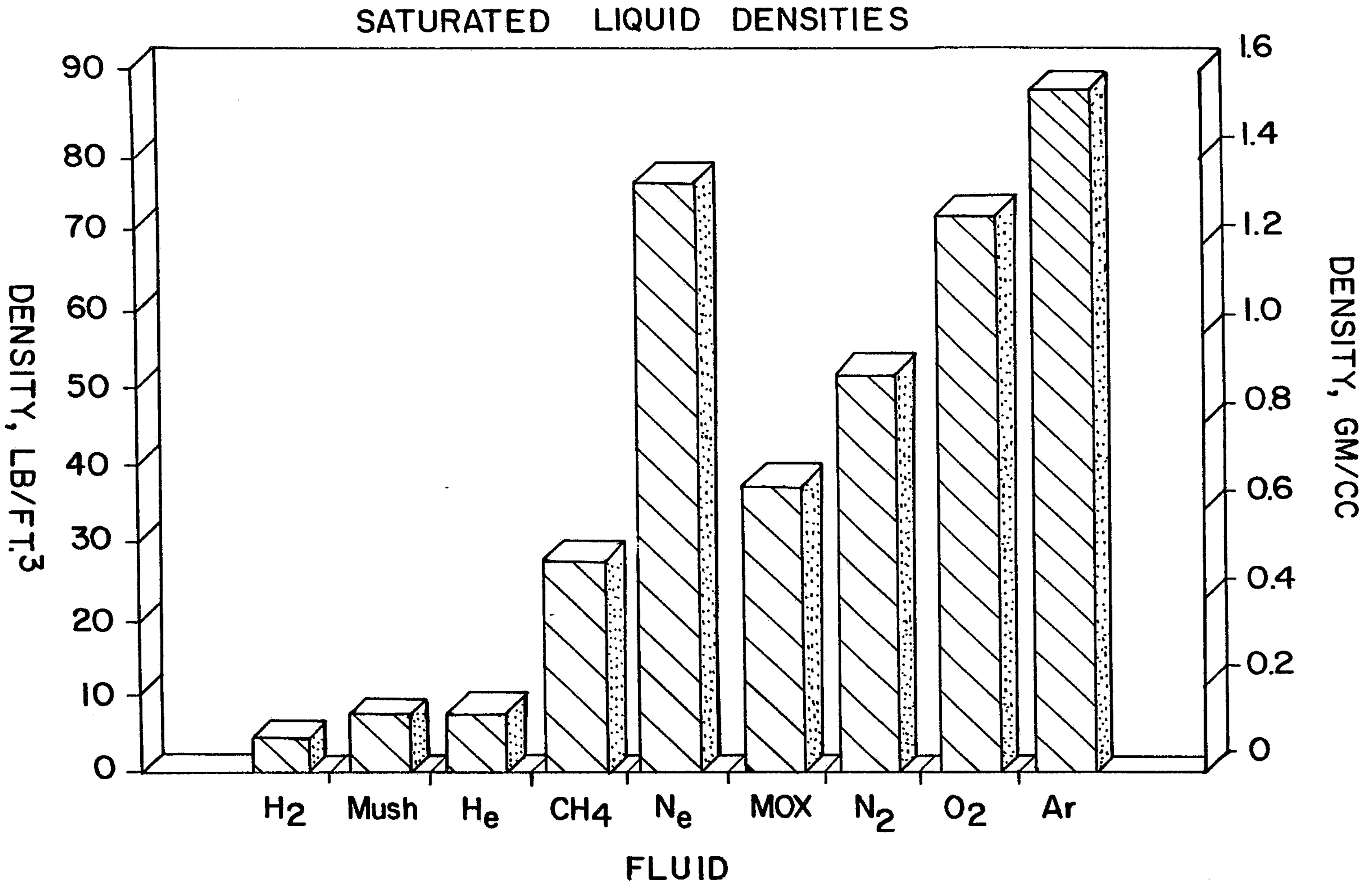

SATURATED LIQUID DENSITIES
DENSITY, LB/FT.^{3}
0
10
20
30
40
50
60
70
80
90
DENSITY, GM/CC
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
H_2
Mush
H_e
CH_4
N_e
MOX
N_2
O_2
Ar
FLUID

FIG.6

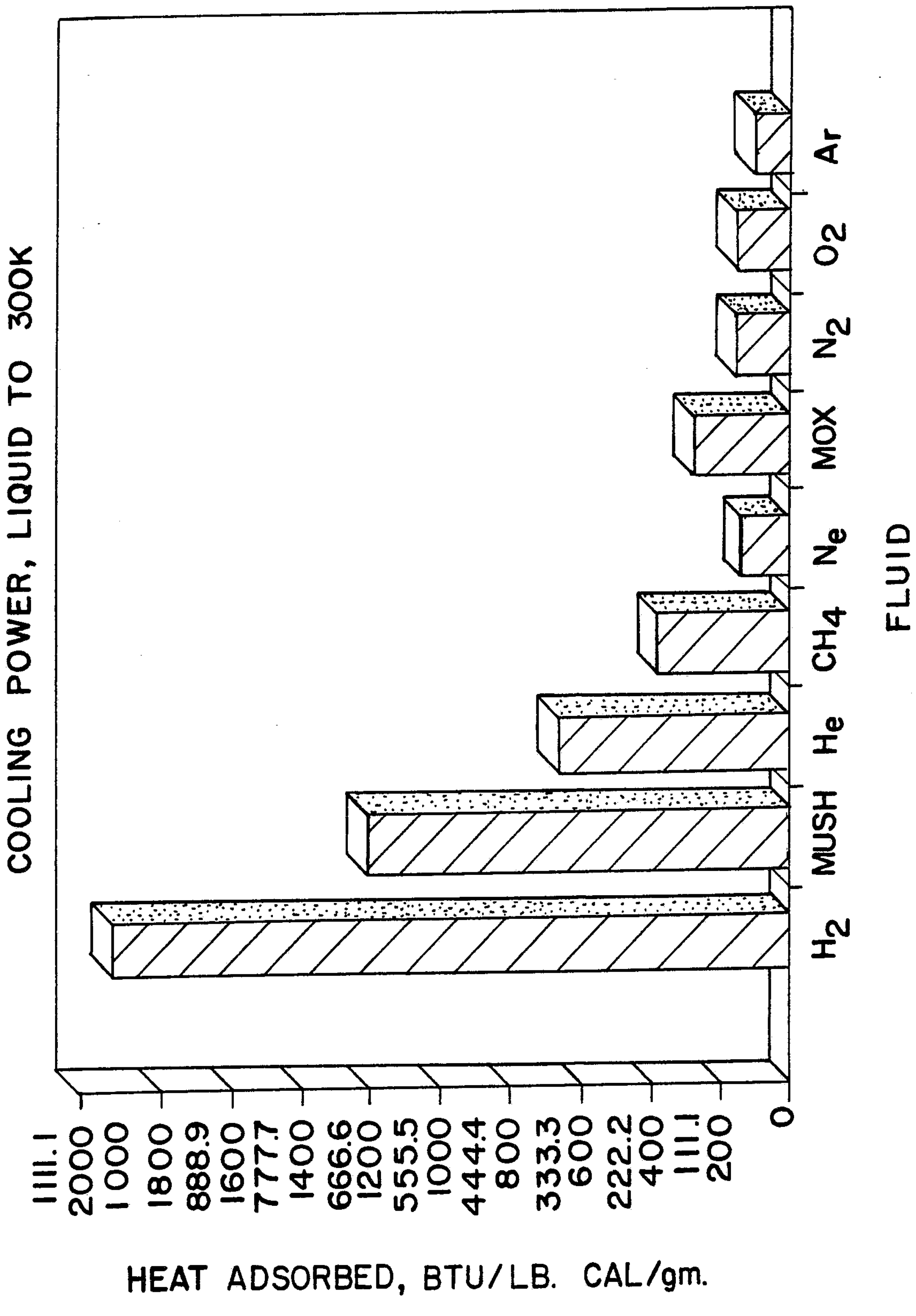
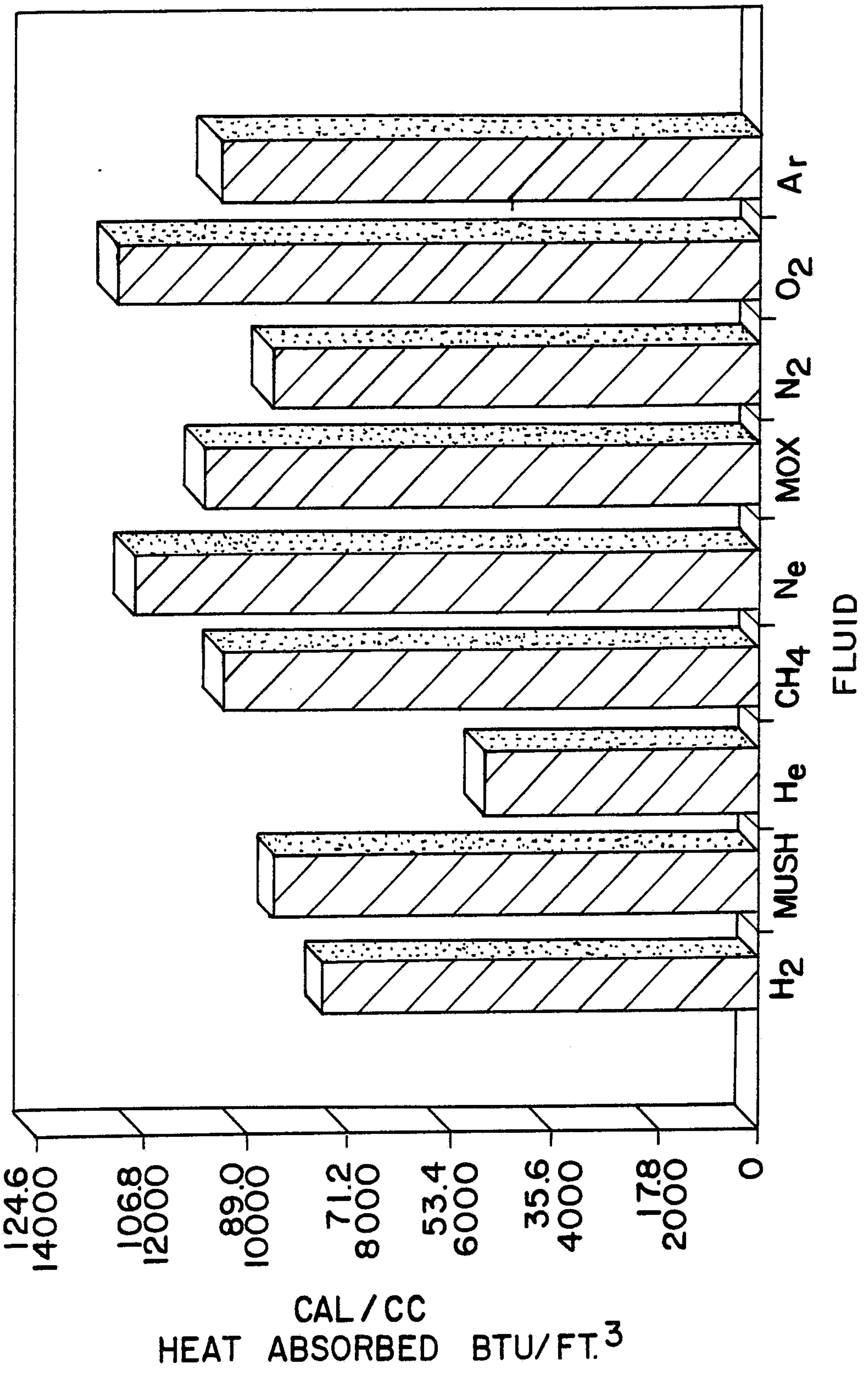

COOLING POWER, LIQUID TO 300K
HEAT ADSORBED, BTU/LB. CAL/gm.
2000
1111.1
1800
1000
1600
888.9
1400
777.7
1200
666.6
1000
555.5
800
444.4
600
333.3
400
222.2
200
111.1
0
FLUID
H_2
MUSH
He
CH_4
Ne
MOX
N_2
O_2
Ar

FIG.7

COOLING POWER, LIQUID TO 300 K



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/08008

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C06B 47/00
U.S.Cl.: 149/1

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	149/1

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3,516,879 (PAINE) 23 June 1970 See column 3, lines 65-67.	1-2
Y	US, A, 4,835,959 (COFFINBERRY) 06 June 1989 See column 7, lines 1-3 and 41-44.	1-5 and 9-13
Y	US, A, 4,305,256 (ANDERSON) 15 December 1981 See lines 1-3 and 9-14 of the Abstract.	10-13
X Y	N, "Carbon Compounds/Liquids Hydrogen Fuels", Technical Report FR02-W396, issued October 1970, 85 pages, see the Abstract (page iii) and pages 71 and 80.	1-3 1-5 and 9-13
A	US, A, 3,377,801 (ALTMAN) 16 April 1968 See col. 4, lines 3-10.	1
A	US, A, 3,691,769 (KEILBACH ET AL.) 19 September 1972 See Fig. 1.	1
A	US, A, 3,069,840 (TOULMAN, JR.) 25 December 1962 See col. 3, line 26.	1

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 06 March 1992	Date of Mailing of this International Search Report 18 MAR 1992
International Searching Authority ISA/US	Signature of Authorized Officer Edward A. Miller

International Application No. PCT/US91/08008

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 2,886,424 (HYSLOP, JR.) 12 May 1959 See col. 2, lines 48-51 and col. 3, lines 48-52.	1

V. ☒ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE** [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ...... , because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☒ Claim numbers 20, 31 and 32, and: GOX, N_2H_4 & MON-25 oxidizers, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

Claims 20 makes no sense in terms of the requirements of independent claim 14. Claims 31-32 cannot be understood as method limitations of a composition. The oxidizers GOX and MON-25 are unknown acronyms or abbreviations, while N_2H_4 is a fuel, not an oxidizer.

3. ☐ Claim numbers__________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING** [2]

This International Searching Authority found multiple inventions in this international application as follows:

See Form PCT/ISA/206 and attached sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-5 and 9-13.

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.