RESEARCH MEMORANDUM

CHEMICAL AND PHYSICAL PROPERTIES OF MODIFIED HI-CAL-2

By Harrison Allen, Jr., Glen E. McDonald, and Barbara J. Pusanski

Lewis Flight Propulsion Laboratory
Cleveland, Ohio
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SUMMARY

The following chemical and physical properties were determined from a sample of modified Hi-Cal-2:

Elemental chemical analysis, percent
- Boron: 54.71
- Carbon: 31.42
- Hydrogen: 13.42

Net heat of combustion of liquid fuel to gaseous carbon dioxide and water, and amorphous boric oxide at 25°C, Btu/lb: -23,700

Density, g/ml
- at 0°C: 0.851
- at 20°C: 0.837

Freezing point: No true freezing point found

Self-ignition temperature, °C: 142

Flash point, °C: 55

Vapor-pressure curve
\[ \log P_{mm} = -\frac{11,965}{2.303RT_{abs}} + 8.1516 \]

Extrapolated boiling point, °C: 225

Decomposition temperature, °C: >157

An infrared spectrum was obtained, and oxygen and water stability were determined.

INTRODUCTION

As part of Project Zip, Bureau of Aeronautics, Department of the Navy, the chemical and physical properties of a sample of modified Hi-Cal-2 (NACA fuel 55Z6), prepared by the Callery Chemical Company, were evaluated at the NACA Lewis laboratory. A Hi-Cal-2 fuel similar to the one evaluated in reference 1 was modified by an extraction process. That portion soluble in hydrocarbon was separated from the insoluble portion, and the modified Hi-Cal-2 fuel was obtained upon removal of the
hydrocarbon solvent. Elemental chemical analysis, heat of combustion, density, freezing point, self-ignition temperature, flash point, stability with oxygen, stability with water, infrared spectrum, vapor pressure, and thermal decomposition were determined for this modified Hi-Cal-2 fuel. Although the precision of measurement of some of these properties was not equal to that obtained for hydrocarbons, this special release research memorandum was prepared to make the data available as soon as possible.

PROCEDURE AND RESULTS

Chemical analysis. - The material, modified Hi-Cal-2, was handled in a helium-inerted dry box or under an atmosphere of helium to insure against any oxidation prior to analysis. The sample was a straw-colored liquid.

The elemental chemical analysis followed the procedures set forth by Project Zip Standard Test Specifications Committee (ref. 2). Total carbon and hydrogen were determined by the microcombustion train to be 31.42 percent and 13.42 percent, respectively. Total boron and carbon, determined by the nitric-acid-oxidation method, were found to be 54.71 percent and 31.25 percent, respectively.

Heat of combustion. - A Parr Adiabatic oxygen bomb calorimeter was used to determine the heat of combustion. The procedure to obtain the raw heat of combustion follows the general method recommended by the Parr Instrument Company with modifications as described in reference 3. In addition, another modification has been made to aid the combustion of boron and carbon. The lid of the adiabatic bomb was fitted with a fine platinum tube so that a burst of oxygen was directed into the burning fuel at the moment the glass ampoule burst. In some cases, this additional burst of oxygen has increased the combustion efficiency of the boron as much as 10 percent and carbon 5 percent. The bomb was calibrated with the oxygen line in place, and a correction was made for the heat added to the bomb by the compression of the additional oxygen. The results from three heat-of-combustion determinations for the fuel, including the analyses of the combustion products and the corrections applied to the raw-heating values, are listed in table I. The average net heat of combustion of modified Hi-Cal-2 is -23,700 ±65 Btu per pound based on 25°C reference temperature.

Density. - The density was determined in an open-arm bicapillary pycnometer (ref. 4) with ground-glass connections that were used to effect a seal from the atmosphere. The pycnometer was filled in a dry box using helium as the inert gas, after which the density measurements were made in the customary manner with constant-temperature baths at 0°C and 20°C. The densities were 0.851 and 0.837 gram per milliliter at 0°C and 20°C, respectively.
Freezing point. - The freezing point was determined in an apparatus featuring a closed sample system, electromagnetic stirrer, and a platinum resistance thermometer (ref. 4). No true freezing point was obtained. Upon cooling the sample to -73°C, the increased viscosity of the sample stopped the stirrer. Further cooling with liquid nitrogen produced only a brittle glass-like material. No temperature measurement was taken at this point.

Self-ignition temperature. - The self-ignition temperature was determined in the Setchkin apparatus (ref. 5), which consists of a heated glass flask into which the fuel is dropped. Ignition attempts were made as the temperature was decreased. The glass flask was not cleaned between ignitions. When the lowest point giving ignition was reached, the value was rechecked with a series of clean flasks. The self-ignition temperature was 142°C. Delay times up to a maximum of approximately 5 seconds were experienced.

Flash point. - The flash point was determined in a modified Pensky-Martens type closed-cup apparatus. The sample cup had a volume of only 3 cubic centimeters and was half filled with liquid sample. The temperature rise of the cup was held to less than 1°C per minute. Inasmuch as boron burns with a green flame, the flash could be easily seen. The flash point obtained for modified Hi-Cal-2 was 55°C.

Oxygen stability. - The apparatus (ref. 6) used to measure the oxidation rate of modified Hi-Cal-2 consisted of a 50-milliliter flask connected to a 100-milliliter gas burette equipped with a mercury leveling bulb. A 2.53-gram sample of the fuel was placed in the flask in a dry box. The flask was removed from the box and connected through stopcocks to the gas burette. The burette was filled with 75 milliliters of oxygen at room temperature and atmospheric pressure. The stopcocks were turned to allow the oxygen to diffuse into the flask. The volume of gas in the burette was recorded twice daily along with the atmospheric pressure and the room temperature. The principle of this experiment is based on the assumption that the rate of reaction is proportional to the rate of disappearance of oxygen as measured by the volume change in the gasometer. This also involves the assumption that only liquid and solid, but no gaseous, products are formed.

Figure 1 shows the variation in volume of gas, reduced to standard temperature and pressure, absorbed by the sample with the time in hours. At the end of a two-week period, the average rate of gas absorption was 0.015 milliliter of gas per gram of fuel per hour. As can be seen from the figure, the daily readings of the burette fluctuated even after the volumes had been reduced to standard conditions. No positive explanation can be given for these fluctuations; however, if the experiment were run at a constant temperature, the fluctuations might have been reduced or eliminated.
After the oxidation experiment was completed, the gas remaining in the apparatus was removed and analyzed. In addition to the gases known to be present (helium and oxygen), infrared analysis showed that the residual gas contained about 4 percent ethane. The fact that gaseous products may be produced by the reaction indicates that the measurement of volume-change may be unsatisfactory for determining the rate of oxidation of boron-containing fuels.

Water stability test. - The water stability of modified Hi-Cal-2 was determined in an apparatus similar to that used in reference 6. It consisted of a three-necked flask, distilling receiver, and gas burette in a thermostated bath. After the flask was purged with dry nitrogen, 1.47 grams of sample were admitted. One hundred milliliters of water were added through the distilling receiver. The mixture was then stirred vigorously by a magnetic stirrer for the remainder of the test. The time and the volume of the gas evolved (presumably hydrogen) were recorded. The results are shown in figure 2. The initial phase of the hydrolysis is shown on an expanded scale in figure 2(a). The rate of gas evolution during the first 2 minutes was 3 milliliters per minute, decreasing to 0.6 milliliter per minute during the second hour. From the second hour to 70 hours, the rate was a constant 0.028 milliliter per minute. The total volume of gas (assumed to be wet hydrogen) evolved during the 70 hours was 122.1 milliliters at approximately 27° C and 739 millimeters pressure.

Infrared spectrum. - The spectrum was obtained with a Baird double-beam recording spectrophotometer. The precision of the instrument is ±1 percent of the transmission value and ±0.02 μ for the wavelength. The sample was examined in a 0.06-millimeter cell. Figure 3 shows the spectrum of modified Hi-Cal-2; the spectrum is similar to that of a sample reported to be ethyl decaborane.

Vapor pressure and decomposition. - The thermal-stability apparatus consisted of a 200-milliliter cylindrical glass bulb attached to a mercury manometer with approximately 18 inches of glass capillary tubing. This tubing was wound with a nichrome heating coil to prevent condensation. A steel tube furnace was fitted closely around the glass sample bulb; a thermocouple attached directly to the bulb measured the temperatures.

A sample of modified Hi-Cal-2 was placed in the bulb in a helium-inerted dry box. The bulb was attached to the capillary tubing and then degassed at -196° C. The bulb was next placed in the furnace and heated at the rate of approximately 30° C per hour. Pressure and temperature measurements were recorded at 15-minute intervals.

In figure 4, the pressure in millimeters is plotted against the temperature in °C. The pressure of the vapor is measured in the first part of the heating curve. At higher temperatures, decomposition occurs
and the total pressure includes the pressure of the gaseous decomposition products. Finally, there is a decrease in the rate of pressure rise as the supply of liquid material is depleted.

In order to determine the temperature of incipient decomposition, the log of the pressure in millimeters is plotted against $1/T, ^{\circ}K$ in figure 5. The straight-line part of the curve represents the region in which the vapor pressure alone is being measured. At approximately $157^{\circ}C$, decomposition commences and adds to the total pressure. Finally, at temperatures above $240^{\circ}C$ the supply of liquid material is depleted and the pressure levels off.

The equation for the straight-line portion of the vapor-pressure curve between $103^{\circ}$ and $157^{\circ}C$ in figure 5 is

$$\log P_{mm} = -\frac{11,965}{2,303RT} + 8.1516$$

where

- $P$ pressure, mm Hg
- $R$ gas constant
- $T$ temperature, $^{\circ}K$

The mean molar heat of vaporization over the temperature range covered by the straight-line part of the curve is 11,965 calories. By extrapolation to a pressure of 760 millimeters of mercury, a boiling point of $225^{\circ}C$ would be obtained.

**DISCUSSION**

The heat of combustion of modified Hi-Cal-2 determined calorimetrically was -23,700 Btu per pound. The heat of combustion, calculated from the boron-carbon-hydrogen analysis and assuming that the heat of formation of modified Hi-Cal-2 is similar to that of ethyl decaborane, is -24,800 Btu per pound. Hence, the boron content and heat of combustion were sufficiently high to make modified Hi-Cal-2 suitable for engine development. This fuel contains sufficient boron to investigate problems associated with boron oxide deposition on engine parts. The boiling point and vapor pressure correspond roughly to that of a $C_{13}$ hydrocarbon and are thus in a range considered for aircraft fuels. Although the marked increase in viscosity at $-75^{\circ}C (-990^F)$ would probably not seriously affect engine development studies, some considerations would have to be given to possible fuel system problems that might occur under low-temperature conditions.

Although the $142^{\circ}C$ spontaneous-ignition temperature for modified Hi-Cal-2 is considerably lower than that found for hydrocarbons (decane and hexadecane have spontaneous-ignition temperatures of about $230^{\circ}C$),
these boron hydride type fuels can react slowly with air at lower temperatures. However, the stability-with-oxygen experiment indicates that this fuel presumably can be handled in air for short periods of time under normal conditions. The flash point ($55^\circ$ C) is also considerably below that of hydrocarbons of similar volatility. Tetradecane has a flash point of about $100^\circ$ C. Thus both the relatively low self-ignition temperature and flash point indicate that modified Hi-Cal-2 would have greater reactivity with air than conventional fuels.

On the basis of the relatively few tests performed, it appears that a fuel having the properties of modified Hi-Cal-2 may be suitable for engine development; however, there is not sufficient information to determine whether the fuel is suitable for propulsion applications.

Lewis Flight Propulsion Laboratory  
National Advisory Committee for Aeronautics  
Cleveland, Ohio, December 2, 1955

REFERENCES


### TABLE I. - HEAT OF COMBUSTION OF MODIFIED HI-CAL-2

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<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
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<td>0.6278</td>
<td>0.4713</td>
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<td>Raw heat, Btu/lb</td>
<td>-17,532.0</td>
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<td>-20,666.7</td>
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<tr>
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<td>Percent carbon burned</td>
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<td>Corrections, cal/g:</td>
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<td>Btu/lb</td>
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<td>Average heat of combustion, Btu/lb</td>
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<td>Standard deviation, Btu/lb</td>
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Figure 1. - Oxygen stability of 2.5-gram sample of modified Hi-Cal-2.
Figure 2. - Concluded. Water stability of modified Hi-Cal-2.

(h) Complete time history.

Volume of hydrogen evolved from 1.47-gm sample, ml.

Time, hr
Figure 4. - Pressure developed by modified Hi-Cal-2 with increasing temperature.
Figure 5. - Pressure-temperature relationship for modified Hi-Cal-2.
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