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NEW YORK UNIVERSITY

College of Engineering

RESEARCH DIVISION

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ACETYLENIC COMPOUNDS FOR ROCKET FUELS

TECHNICAL REPORT No. 5

for the period 1 June 1953 to 1 December 1953

PREPARED FOR
OFFICE OF NAVAL RESEARCH
AND

BUREAU OF AERONAUTICS, DEPT. OF THE NAVY
CONTRACT NO. NONR-285(04)
PROJECT NO. NR 092-159

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December 15, 1953

Chief of Naval Research
Navy Department
Washington 25, D. C.

Contract Nonr-285(04)

Dear Sir:

I should like to submit for your inspection and approval the fifth technical report under the subject contract covering work done during the fifth six-months period of the contract, 1 June 1953 - 1 December 1953.

Very truly yours,


John Happel
Project Director

JH:imc

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Technical Report No. 5

December 1, 1953

For the Period June 1, 1953 - December 1, 1953

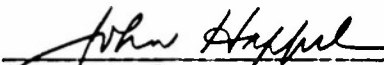
ACETYLENIC COMPOUNDS FOR ROCKET FUELS

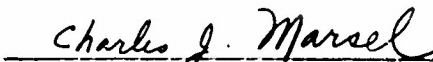
Prepared for the Office of Naval Research

and

the Bureau of Aeronautics, Dept. of the Navy

Contract Nonr - 285(04)
NR - 092 - 159


John Happel
Project Director


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Report No. 175.15

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SUMMARY

To date some forty acetylenic compounds have been prepared and screened for application as fuels in liquid bipropellant rocket systems at the New York University Laboratories. Previous results of this program are summarized in the four technical progress reports issued at six months intervals. The most important properties for preliminary evaluation was considered to be ease of ignition (as judged by hypergolicity and later ignition delay) and specific impulse. After the first year of the subject program emphasis was placed on the acetylenic hydrocarbons because of their good physical characteristics and high specific impulse. It was discovered that certain acetylenic hydrocarbons could be prepared which also have good ignition characteristics, a fact not previously appreciated or reported by other organizations.

This report deals in general with the applicability of acetylenic hydrocarbons for use in jet propulsion systems. Although the primary object of this contract is to develop fuels for bipropellant systems, calculations and a limited number of tests by other laboratories indicate that the acetylenic hydrocarbons also have interesting possibilities for monopropellant and ram jet systems. Actual rocket evaluation tests have been made on one of the acetylenic hydrocarbons, methyl divinyl acetylene with encouraging results. It is believed that further studies may result in the development of compounds of even greater promise.

In the recent cooperative test program on determining ignition delay on six fuels, as initiated at the Bartlesville meeting of the Petroleum Derivable Fuels Conference, the sample of methyl divinyl acetylene submitted by New York University showed up very favorably. One very promising property of this material is its excellent low temperature ignition characteristics; it has an ignition delay value of 5.5 milliseconds at -65°F with RFNA as measured by the CRC tester. Addition of certain acetylenic hydrocarbons to JP-4 can improve the ignition characteristics of this fuel, according to test data obtained by the Naval Research Laboratory. For example, dimethyl divinyl diacetylene rendered JP-4 hypergolic with both white and red nitric acid when present in concentrations as low as 15% by volume, at room temperature.

Values for the theoretical specific impulse were calculated for a series of straight chain monoyne, diyne and triyne hydrocarbons, including a conjugated and unconjugated set for the latter two series. Conditions favoring best values of specific impulse are maximum concentration of acetylene bonds in a molecule, and non-conjugation. As representative values, using WFNA, stoichiometric quantities of oxidizer, and frozen equilibrium, diacetylene has an I_{sp} of 237.6 and 1,4-pentadiyne a value of 234.5. Pilot plant quantities of two acetylenic hydrocarbons, methyl vinyl acetylene and methyl divinyl acetylene, were furnished to Reaction Motors, Inc. for testing in a small 80 lb. thrust rocket motor. These materials had a measured maximum I_{sp} of 210 and 209 respectively, using RFNA; these values are higher than a corresponding point for JP-4. In addition, RMI has the following comments to make: Starting - smooth

hypergolic starts on all tests; Combustion - smooth combustion except at extreme O/F ratio where combustion was somewhat rough; Shutdown - smooth.

A series of shock sensitivity tests, involving detonation of a partially-confined liquid sample by a #6 blasting cap, were carried out through the cooperation of Picatinny Arsenal, and are fully reported. The fragmentation of the lead pipe containing the liquid sample is an indication of the force of detonation. It was gratifying that the results of these detonation tests correlated quite well with the drop weight test as used in our laboratory, and that both methyl vinyl acetylene and methyl divinyl acetylene may be considered relatively safe in handling.

The acetylenic hydrocarbons offer promise for application as monopropellants. Experiment Inc. has kindly evaluated a group of acetylenic hydrocarbons, as furnished by this laboratory, by means of their fuse wire ignition test. The test determined the monopropellant pressure at minimum energy for ignition using a fuse wire as a point source of ignition; the lower the pressure, the better the ease of ignition. While the test work was not complete it indicated that several acetylenic hydrocarbons, methyl vinyl acetylene and 1,5-hexadiyne, should ignite quite readily as monopropellants. The theoretical specific impulse as monopropellants was calculated for a series of straight chain acetylenic hydrocarbons of the monoyne, diyne and triyne series. Acetylene itself has the highest value of specific impulse of all the hydrocarbons studied (222), with methyl acetylene having a value of 195. In the

diyne series, 1,4-pentadiyne has maximum thrust with a value of 196. The Wyandotte Chemical Co. is now testing samples of 1,6-heptadiyne and 3-butyne-1-ol, furnished by the N.Y.U. laboratories, for possible application as monopropellants.

The acetylenic hydrocarbons also appear to offer promise as fuels for the ram jet and the ram rocket or ducted rocket. Experiment Inc. has kindly measured minimum spark ignition values for five acetylenic hydrocarbons furnished by New York University. Based on the correlation developed by Experiment Inc. between minimum spark ignition energy and impulse efficiency, the acetylenic hydrocarbons show a considerably higher impulse efficiency than the paraffins; the impulse efficiency of methyl divinyl acetylene is probably 20-25% greater than that of JP-4. Acetylenic hydrocarbons may also be used in a ram rocket, since their monopropellant decomposition products, carbon and hydrogen, are completely combustible. Values of specific impulse for a series of acetylenic hydrocarbons in such an application have been calculated.

In summary, it may be said that acetylenic hydrocarbons appear to have interesting possibilities as fuels in bipropellant and possibly other jet propulsion systems. Evaluation tests of various types by a number of different organizations as well as the N. Y. U. Laboratories support this conclusion.

HYDROCARBONS AS BIPROPELLANTS

Ignition Delay Measurements

operational ignition delay test program, agreed at a meeting of the Petroleum Derivable Fuels Conference. The compounds listed below were received, and evaluated in the California Research Corporation apparatus:

Naval Air Rocket Test Station	- Triethyl Amine
Philips Petroleum Company	- N,N,N',N' - tetramethyl propane 1,3-diamine
Shell Chemical Company	- Dioxaphospholane blend
California Research Corp.	- Ethyl mercaptal of Acetaldehyde
Standard Oil of Indiana	- Methyl disulfide

and our own compound, Methyl Divinyl Acetylene

Table I consists of values of ignition delay obtained for the six compounds mentioned above.

The conditions for running the tests were:

1. Oxidizer - RFNA
2. Transducer - Instrument supplied by the Berkeley Scientific Corporation.
3. "Stop" probe height - 2-3/4 inches above the point of the fuel cup.
4. Drop Height - 6.0 millimeters.

The variables "stop" probe height and drop height are discussed in Appendix A.

The RFNA used in testing the compounds listed was that supplied by NARTS.

In each case reported in Table I, the ignition delay value is the average of at least three runs. Values are in milliseconds.

Table I

Ignition Delay Results, Cooperative Test Program

<u>Compound</u>	<u>Temperature</u>			
	<u>-65°F</u>	<u>-40°F</u>	<u>32°F</u>	<u>75°F</u>
Shell Dioxaphospholane Blend RF 311	2.7	2.7	2.6	1.8
Ethyl Mercaptal of Acetaldehyde	15.0	(117.4)* 8.4	3.3	3.2
N,N,N',N' Tetra methyl propane - 1,3-diamine	7.2	6.0	5.9	5.4
Methyl Disulphide	10.5	5.0	4.5	6.9
Triethyl amine	28.7	24.3	28.9	24.9
Methyl divinyl acetylene	5.5	6.8	11.1	10.4

*Ignition delay values for Ethyl Mercaptal of Acetaldehyde at -40°F fell into two groupings. Of eight runs, five grouped about 117.4 mss and three grouped about 8.4 mss.

It might be mentioned that the reproducibility obtained with the cylindrical ignition delay tester seemed to depend upon the particular fuel in question. With the majority of fuels, the accuracy of any result was within 10% of the average.

Samples of the acetylenic hydrocarbons listed below were delivered to the Naval Research Laboratory, Washington, D. C. and were tested for ignition delay through the courtesy of Dr. Homer Carhart. Tests were made on mixtures with various concentrations of JP-4, as well as on the neat compounds.

dimethyl divinyl acetylene (2,5-dimethyl-1,5-hexadiene-3-yne)
1,6-heptadiyne
methyl vinyl acetylene (2-methyl-1-butene-3-yne)
methyl divinyl acetylene (2-methyl-1,5-hexadiene-3-yne)
dimethyl divinyl diacetylene (2,7-dimethyl-1,7-octadiene-3,5-diyne)
1,3-hexadiyne

The most promising of these compounds appears to be dimethyl divinyl diacetylene which renders JP-4 hypergolic with both white and red nitric acids when present in concentrations as low as 15% by volume. Methyl divinyl acetylene also appeared quite promising, since it exhibited excellent low temperature ignition characteristics.

In high concentrations with JP-4, the acetylenes reacted vigorously once the ignition barrier had been surmounted. This is in keeping with the very vigorous detonations given by the pure acetylenic hydrocarbons with nitric acid.

Table II gives values for ignition delays of methyl divinyl acetylene / JP-4 blends with nitric acid, as reported by the Naval Research Laboratory.

Fifteen percent of dimethyl divinyl diacetylene in JP-4 rendered it hypergolic at room temperature with both RFNA and WFNA. Data for ignition delays on these blends are presented in Table III.

Ignition delay values for blends of the above two acetylenic hydrocarbons with JP-4 at +35°C are plotted in Figure I.

In conclusion it may therefore be said that ignition characteristics of certain acetylenic hydrocarbons with RFNA compare very favorably with the other fuels tested as part of the cooperative test program outlined at the Bartlesville meeting of the Petroleum Derivable Fuels Conference. Methyl divinyl acetylene, the compound supplied by New York University, showed up very well in this group. One interesting property of this compound is that it exhibits excellent low temperature ignition characteristics.

In order to determine why ignition delay values reported by this laboratory were not in agreement with results of other laboratories using essentially the same apparatus, an investigation into some factors effecting measurement of ignition delay was made. This study is discussed in Appendix A.

Table II

Ignition Delays of Methyl Divinyl Acetylene/JP-4

Blends with Nitric Acids

<u>% JP-4</u>	<u>t(°C)</u>	Ignition Delay (milliseconds)	
		<u>RFNA</u>	<u>WFNA</u>
0	32	8.2 ± 0.4 (5)	10.4 ± 1.0 (5)
0	0	8.5 ± 1.0 (4)	14.3 ± 1.2 (4)
0	-25	5.1 ± 0.3 (2)	8.9 ± 0.5 (4)
25	32	11.6 ± 0.4 (5)	17.6 ± 1.8 (5)
50	32	24 ± 2 (5)	27 ± 3 (6)
50	0	21 ± 1 (4)	26 ± 2 (4)
50	-25	20 ± 2 (3)	127 ± 75 (2)*
75	32	59 ± 6 (5)	NI (4)
75	0	97 ± 28 (3)	---
85	32	NI (3)	---

Vol. of fuel - 0.14 cc; vol. of acid - 1.0 cc. The number of tests with each blend is shown in parentheses following the ignition delay values.

RFNA analyses - 81% HNO₃, 18% NO₂, 1% H₂O.

WFNA analyses - 97.6% HNO₃, 1.2% NO₂, 1.2% H₂O.

*One non-ignition was also observed with this blend.

Table III

Ignition Delays of Dimethyl Divinyl Diacetylene/JP-4

Blends with Nitric Acid

<u>% JP-4</u>	<u>t(°C)</u>	<u>Ignition Delay (milliseconds)</u>			
		<u>RFNA</u>		<u>WFNA</u>	
0	35	3.7	± 0.2 (3)	11.6	± 1.8 (5)
0	0	3.9	± 0.3 (4)	12.4	± 0.5 (4)
25	35	5.9	± 0.4 (4)	19.3	± 1.2 (4)
50	35	9.2	± 0.2 (3)	23	± 1 (4)
50	0	7.5	± 0.3 (4)	22	± 1 (4)
50	-25	15.9	± 0.6 (3)	140	± 62 (4)
75	35	15	± 1 (4)	52	± 7 (3)
75	0	39	± 5 (5)	NI	(3)
75	-25	192	± 5 (2)	---	
85	35	20	± 2 (4)	72	± 3 (3)
85	0	NI	(4)	---	
92-1/2	35	NI	(3)	NI	(2)

Vol. of fuel - 0.14 cc; vol. of acid - 1.0 cc. The number of tests with each blend is shown in parentheses following the ignition delay values.

RFNA analyses - 81% HNO₃, 18% NO₂, 1% H₂O.

WFNA analyses - 97.6% HNO₃, 1.2% NO₂, 1.2% H₂O.

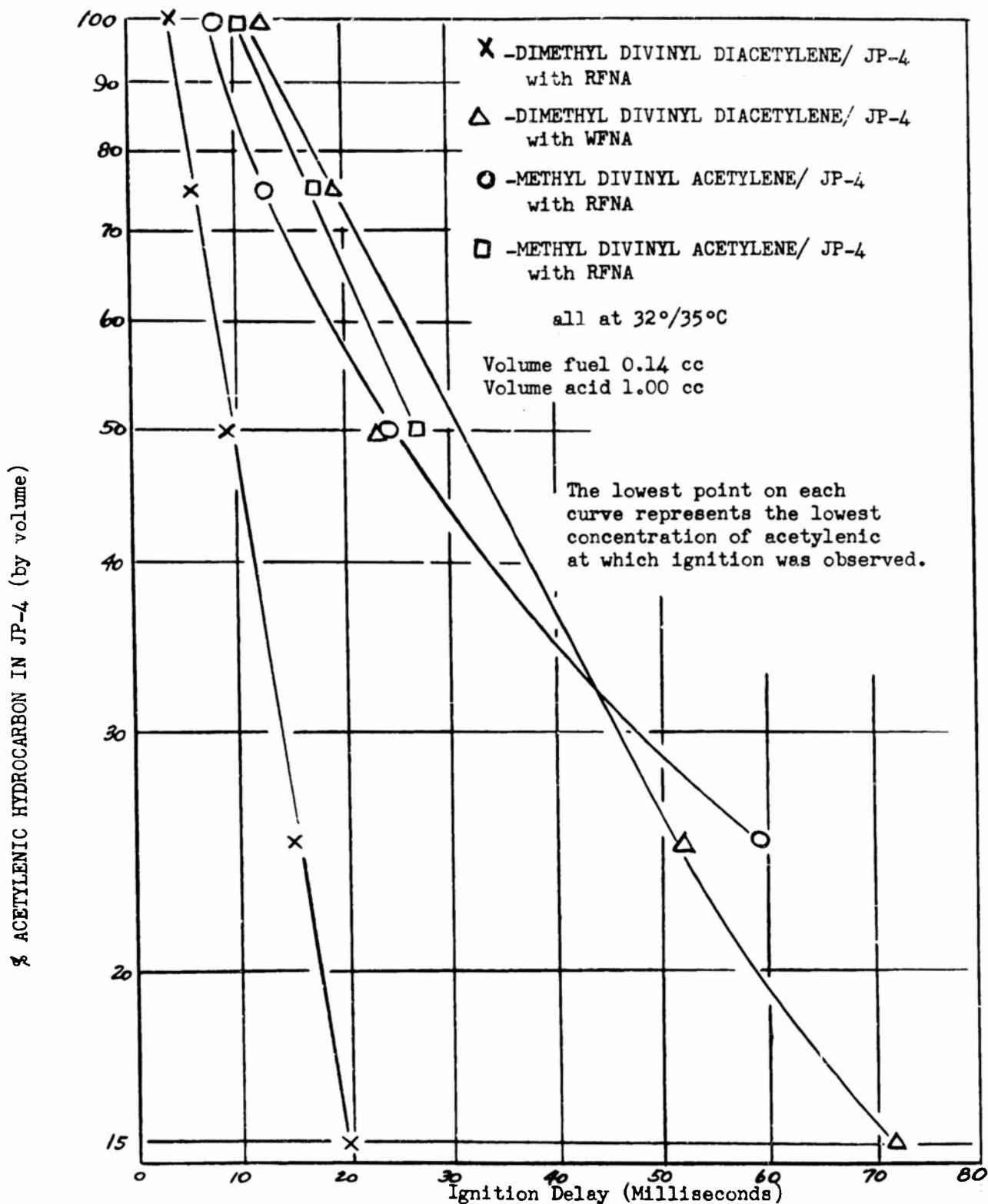


Figure 1
IGNITION DELAYS OF JP-4/
ACETYLENIC HYDROCARBON BLENDS WITH
RFNA AND WFNA

Specific Impulse Calculations

The specific impulse of the acetylenic hydrocarbons as the fuels in bipropellant mixtures were calculated by the method of Hottel et al (1). The oxidant used was dry WFNA. As a basis for comparison of the different acetylenic compounds, the stoichiometric quantity of HNO_3 , to oxidize all carbon to CO_2 and hydrogen to H_2O , was used. The combustion chamber pressure was 300 psia and the exhaust pressure was 14.7 psia. As some of the hydrocarbons had flame temperatures exceeding the range of the Hottel charts these charts had to be extended as explained in Appendix B. Although the specific impulses obtained with the extended charts may not be exact they are at least qualitatively consistent with one another.

In order to evaluate the effect of molecular structure upon the specific impulse, three series of straight chain acetylenic compounds were investigated:

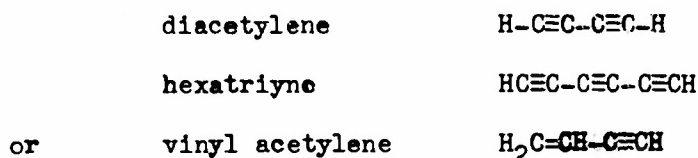
Monoyne series	C_2H_2	to	$\text{C}_{10}\text{H}_{18}$
Diyne series	C_4H_2	to	$\text{C}_{10}\text{H}_{14}$
Triyne series	C_6H_2	to	$\text{C}_{10}\text{H}_{10}$

The diyne and triyne series were subdivided into subseries according to the degree of conjugation of the triple bonds. In both series a subseries was studied with a pair of conjugated triple bonds in the 1,3 positions. In the triyne subseries the third triple bond was in the (n-1) position for hydrocarbons with n carbon atoms. In the diyne series a second subseries was studied having the triple bonds at the 1 and (n-1) positions.

(1) Hottel, H.C., Williams, G.C., Satterfield, C.N.
Thermodynamic Charts for Combustion Processes, Part One.
John Wiley & Sons, New York 1949

In the triyne series the second subseries had the triple bonds at the 1,4 and (n-1) positions. In addition, bipropellant specific impulses for a number of acetylenic compounds synthesized at New York University were also calculated.

Specific impulses were based on the heat of formation at 25°C in the liquid state either as available in the literature or as calculated. For those compounds whose heats of formation are not reported for either the liquid or gaseous state, the method of Souders et al (2) was used to compute a value. This method of estimating heat of formation, $(\Delta H_f^\circ)_g$, is for the hypothetical ideal gas at 25°C. The value of $(\Delta H_f^\circ)_g$ so obtained requires two corrections, one correction to the liquid state and the other for resonance energy not included in the method of computation. The correction for the heat of vaporization at 25°C can be estimated with sufficient accuracy by using the heat of vaporization of the corresponding paraffin at 25°C. The method of Souders et al does not have corrections for the resonance energy of conjugated triple and double-triple bonds such as occur in:



In order to evaluate the resonance energy for unsaturated bonds of the types mentioned above, heats of combustion of such compounds were experimentally determined at New York University. The experimental heats of

(2) Souders, M., Matthews, C.S., and Hurd, C. C.
Ind. Eng. Chem. 41 1048 (1949)

combustion were compared with heats of combustion calculated from the Souder's heat of formation to get the unaccounted-for resonance energy by difference. Resonance energies evaluated in this way, although consistent in sign, were not entirely satisfactory as to magnitude. The uncertainty in magnitude arose from 1) the compounds tested had a small but unknown fraction of halogenated impurities, 2) the instability of some compounds resulted in the formation of unburned carbon which could be eliminated by diluting the sample with heptane, but this increased the experimental error, 3) the experimental uncertainty was a large percentage of the value being determined.

In conjunction with the experimental evaluation of resonance energy for these types of bonds, theoretical approaches were also considered. The relation between bond length and bond energy established by Glockler (3) was found to be particularly useful, as bond lengths have been reported for the required types of conjugated unsaturated bond systems. The values obtained are in qualitative agreement with the experimental values and are considered more reliable. The resonance energy correction found to be applicable to the Souder method for computing the correct heat of formation are as follows:

<u>Structure</u>	<u>Resonance energy correction</u> <u>k cal/gm mol</u>
$-C\equiv C-C\equiv C-$	-10
$-C\equiv C-C\equiv C-C\equiv C-$	-20
$\begin{array}{c} \\ -C=C-C\equiv C- \end{array}$	- 8

(3) Glockler, G.
Discussions of the Faraday Society No. 10, 1951, "Hydrocarbons," pp.26-35
Aberdeen Univ. Press Ltd., Aberdeen 1951.

The results of the specific impulse calculations are presented in Table IV and Figure 2. Figure 2 shows the variation of specific impulse with the number of carbon atoms for the monoyne, diyne and triyne series and with conjugation. Examination of Figure 2 and Table IV shows for the compounds investigated that acetylene, C_2H_2 , has the highest specific impulse followed by diacetylene and 1,4-pentadiyne. Following acetylene, the monoynes drop abruptly in specific impulse and are below the diynes and triynes with the same number of carbon atoms. The members of the triyne series have higher calculated specific impulses than the corresponding diynes. In the diyne and triyne series the drop in specific impulse following the first member, is not as large as in the monoyne series. The unconjugated subseries have higher specific impulses than the corresponding members of the conjugated subseries for both diynes and triynes.

As a consequence of the increase in specific impulse with the increase in the number of triple bonds in the molecule there is a wide choice for selecting an optimum acetylenic fuel in the gasoline volatility range from C_5 to C_{10} . As the variation in calculated specific impulse is not great among the best of the C_5 to C_{10} hydrocarbons, other factors will determine the ultimate choice of a fuel.

In addition to the better diynes and triynes, the compounds given in Table 2 having double-triple bond conjugation also have calculated specific impulses of more than 225 up to 238 (lbs. of thrust) x (sec) per (lb. of fuel). The nitrile compound 2-butyne, 1,4-dinitrile also falls in this range.

Table IV
Specific Impulse for Acetylenic Compounds
as Bipropellants with WFNA

<u>Series</u>	<u>Compound</u>	<u>Flame Temp.</u> <u>deg.F</u>	<u>Isp=(lb.thrust)(sec.)</u> <u>lb.fuel</u>
Monoyne	Acetylene C_2H_2	5460**	237.6
	*Propyne C_3H_4	5300	229.6
	1-Butyne C_4H_6	5210	228.7
	1-Pentyne C_5H_8	5160	227.7
	1-Hexyne C_6H_{10}	5120	226.7
	1-Heptyne C_7H_{12}	5110	225.6
	1-Octyne C_8H_{14}	5100	224.6
	1-Decyne $C_{10}H_{18}$	5070	224.2
Diyne	*Diacetylene C_4H_2	5520**	237.6
	*1,4-Pentadiyne C_5H_4	5420**	234.5
	*1,5-Hexadiyne C_6H_6	5340**	231.8
	*1,6-Heptadiyne C_7H_8	5280	230.8
	*1,7-Octadiyne C_8H_{10}	5240	228.4
	1,8-Nonadiyne C_9H_{12}	5210	227.0
	1,9-Decadiyne $C_{10}H_{14}$	5190	226.0
	1,3-Pentadiyne C_5H_4	5370**	231.7
	*1,3-Hexadiyne C_6H_6	5310**	229.9
	1,3-Heptadiyne C_7H_8	5260	227.7
	1,3-Octadiyne C_8H_{10}	5210	226.8

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<u>Series</u>	<u>Compound</u>	<u>Flame Temp.</u> <u>deg.F</u>	<u>Isp=</u> (lb.thrust)(sec.)
			<u>lb.fuel</u>
Triyne	Hexatriyne C_6H_2	5620**	234.1
	1,3,6-Heptatriyne C_7H_4	5540**	233.0
	1,3,7-Octatriyne C_8H_6	5470**	231.1
	1,3,8-Nonatriyne C_9H_8	5420**	229.7
	1,3,9-Decatriyne $C_{10}H_{10}$	5370**	229.9
	1,4,7-Octatriyne C_8H_6	5490**	231.9
	1,4,8-Nonatriyne C_9H_8	5440**	231.0
	1,4,9-Decatriyne $C_{10}H_{10}$	5390**	230.8
Olefinic	*Methyl vinyl acetylene C_5H_6	5660**	233.6
	*Methyl divinyl acetylene C_7H_8	5300	227.8
	*Dimethyl divinyl diacetylene $C_{10}H_{10}$	5120	225.9
Nitrile	*2-Butyne 1,4-dinitrile C_4N_2	5840**	225.0

*Compounds synthesized at New York University

**Results for compounds with flame temperatures above 5300°F
(the limit on the charts of Hottel et al (1)) were calculated
using charts of extended range obtained by extrapolating the
charts of Hottel et al.

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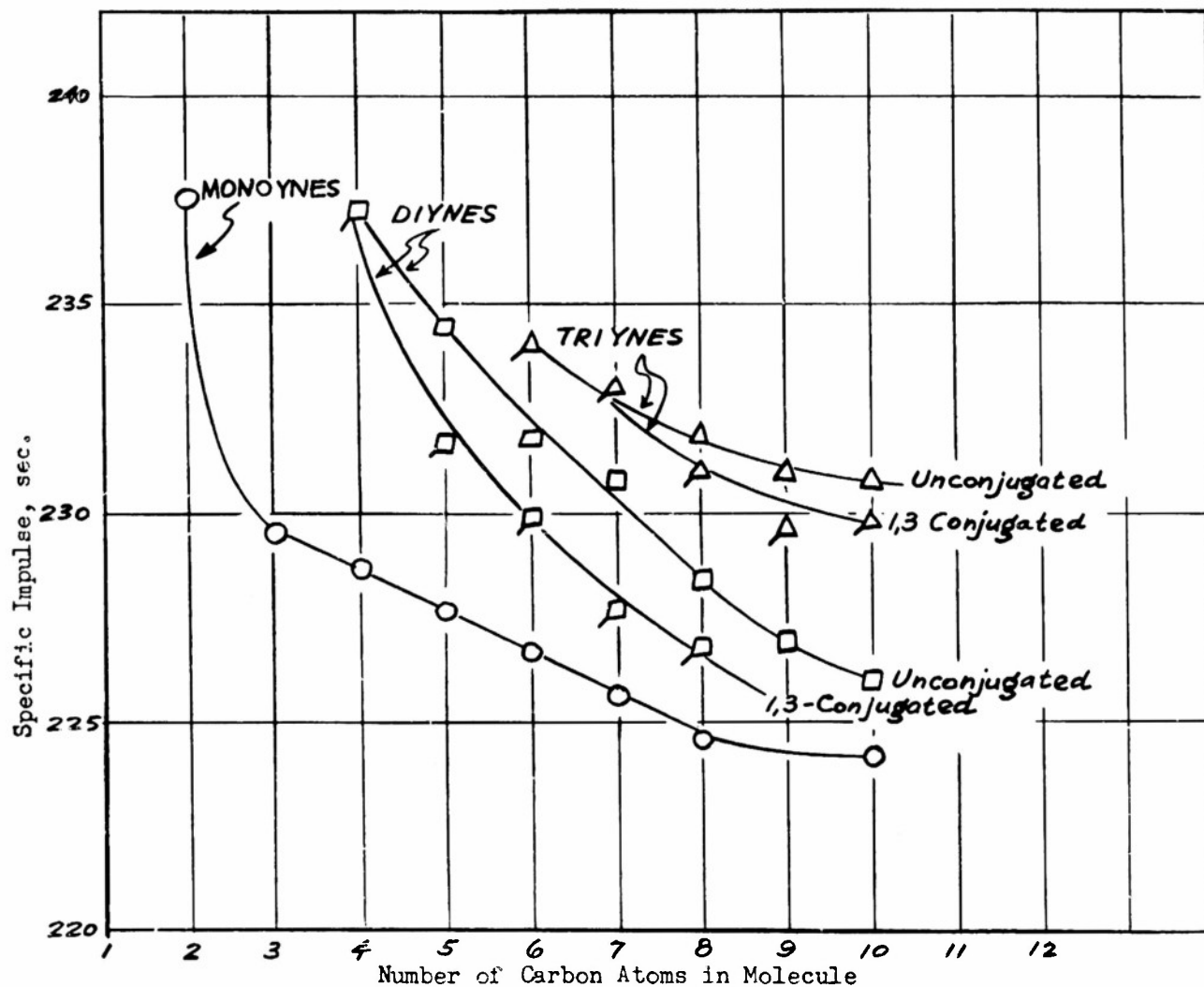


Figure 2

SPECIFIC IMPULSE OF ACETYLENIC HYDROCARBONS
AS BI-PROPELLANTS WITH WFNA
(SPECIFIC IMPULSE VS NO. OF C ATOMS)

Rocket Testing by Reaction Motors, Inc.

Reaction Motors, Inc. has evaluated methyl vinyl acetylene and methyl divinyl acetylene as potential rocket propellants, in an 80 lb. thrust motor. The operating conditions for determining the experimental points were as follows:

- a) Thrust level - approximately 80 lbs.
- b) RFNA (18% NO_2) temperature approximately 24 to 20°C.
- c) Fuel temperature approximately 0°C.
- d) L^* - 50 inches.
- e) Chamber pressure - approximately 300 psia.
- f) Injector - four sets of 2 on 1 impinging jets.
- g) Thrust chamber was water cooled.

A comparison of calculated and experimental specific impulse for several bipropellant mixtures is presented on Figures 3 and 4. The calculated results are for both WFNA and RFNA while the experimental data are for RFNA only. The calculation for WFNA covered a broader range of oxidant to fuel ratio with more intermediate points than the calculations for RFNA. As the calculations for WFNA gave a curve consistently higher for methyl vinyl acetylene than for methyl divinyl acetylene, the curves through the three points using RFNA were drawn in the same way even though the mid-point for methyl vinyl acetylene fell on the curve for methyl divinyl acetylene.

Legend:

Calc. = Calculated
MeVA = Methyl Vinyl Acetylene
MDVA = Methyl Divinyl Acetylene
WFNA = White Fuming Nitric Acid

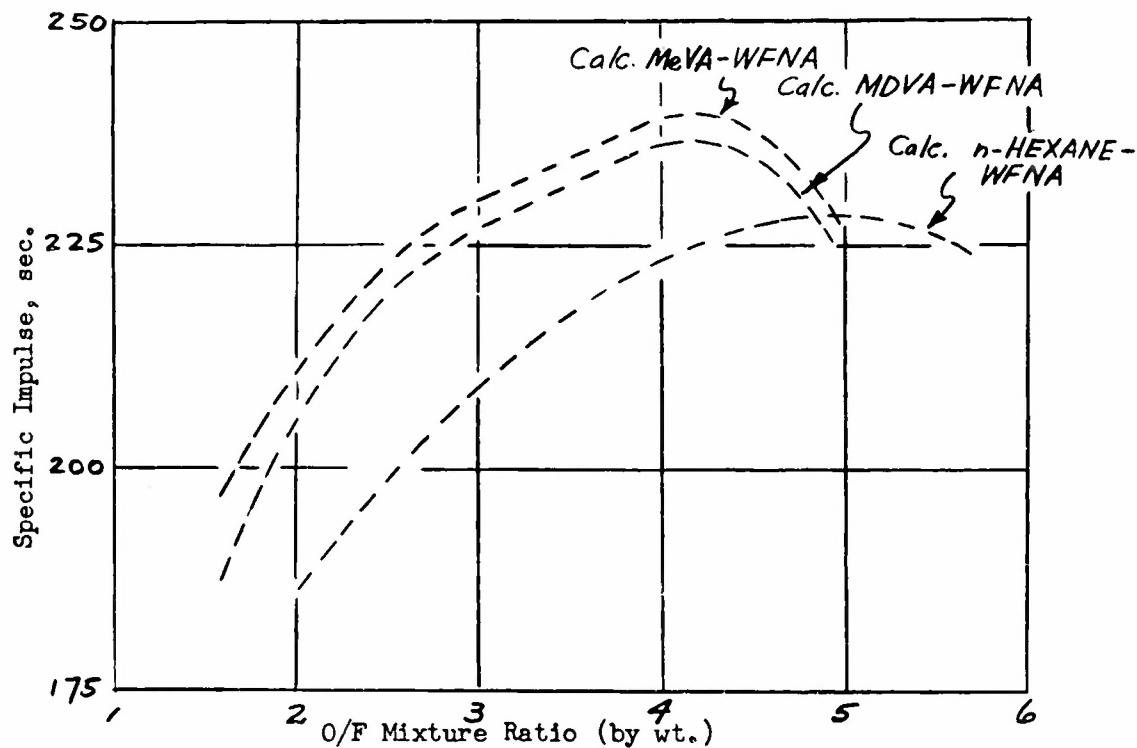


Figure 3

CALCULATED SPECIFIC IMPULSES VS O/F RATIO
FOR WFNA AND ACETYLENIC HYDROCARBONS

Legend:

Calc. = Calculated
Exp. = Experimental
MeVA = Methyl Vinyl Acetylene $\square$
MDVA = Methyl Divinyl Acetylene $\circ$
RFNA = Red Fuming Nitric Acid

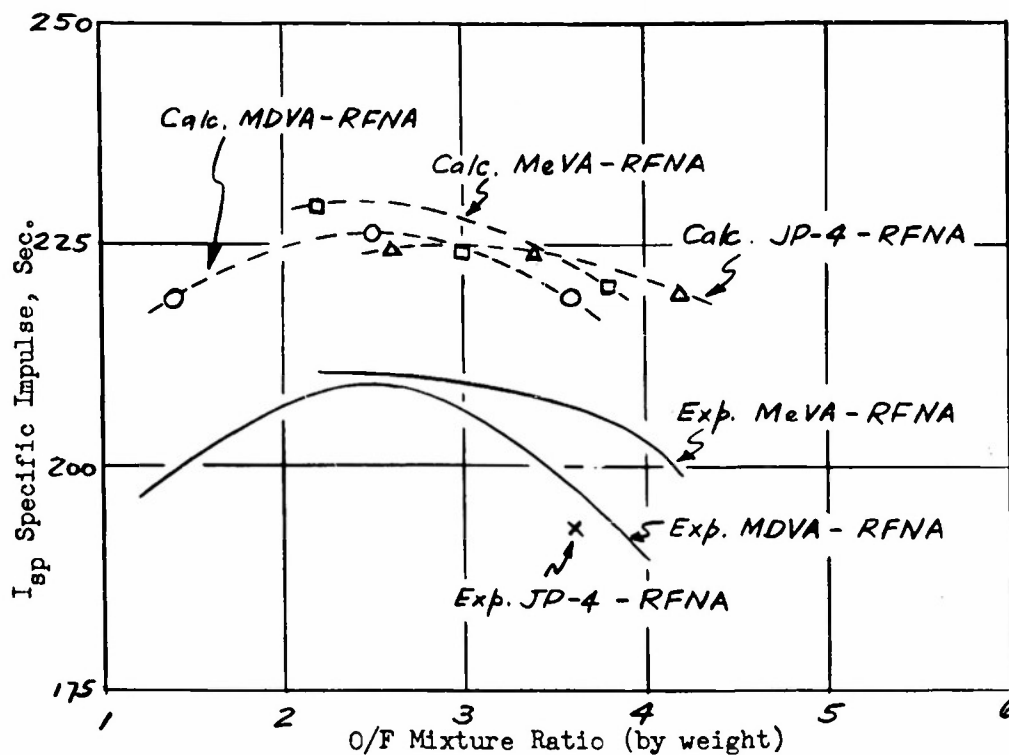


Figure 4

CALCULATED AND EXPERIMENTAL
SPECIFIC IMPULSES VS O/F RATIO
FOR RFNA AND ACETYLENIC HYDROCARBONS

On Figures 3 and 4 the calculated and experimental curves for specific impulse of methyl vinyl acetylene and methyl divinyl acetylene both indicate a slight superiority for the former. On the experimental curves the difference between the maximum impulses of 210 and 209 (lb. thrust) x (sec.) per (lb.fuel) is within the experimental uncertainty of the curves.

A similar comparison can be made between the calculated curve for n-hexane with WFNA, JP-4 as $C_{9.66}H_{19}$ with RFNA and an experimental point (at O/F ratio of 4.6) for JP-4 with RFNA. Both calculated curves have maxima below the corresponding maxima for methyl divinyl acetylene. The experimental point for JP-4 lies below the experimental curve for methyl divinyl acetylene at this O/F ratio even though the calculated curve with RFNA lies above at this O/F ratio.

In summary the two acetylenic hydrocarbons studied have a higher possible theoretical I_{sp} than heptane or JP-4 as $C_{9.66}H_{19}$ and on motor testing gave higher I_{sp} than a corresponding point for JP-4.

It is pertinent to present the comments of Reaction Motors on the operating characteristics of these acetylenic hydrocarbons

"Operating Characteristics

- a) Starting - smooth hypergolic starts on all tests.
- b) Combustion - smooth combustion except at extreme O/F ratio wherein combustion was somewhat rough.

c) Shutdown -- smooth; however, care must be taken to prevent reignition of small quantities of propellants which may have been trapped in the lines between the propellant valve and injector during shutdown.

d) Performance:

Methyl vinyl acetylene - maximum specific impulse 210 seconds at an O/F ratio of 3.4, with a corresponding characteristic velocity of 5050 ft./sec.

Methyl divinyl acetylene - maximum specific impulse of approximately 209 seconds at an O/F ratio of approximately 3.5, with a corresponding characteristic velocity of 4925 ft./sec. It is evident from these data that the performance of methyl vinyl acetylene and methyl divinyl acetylene with RFNA are equivalent. The difference between the optimum values is well within experimental error".

Detonation Sensitivity Testing

In order to determine the susceptibility to detonation of several acetylenic hydrocarbons, and to compare detonation sensitivity to mechanical impact sensitivity,* a series of tests were performed at Picatinny Arsenal, Dover, New Jersey. The following compounds were tested:

2,2-bis (tert-butyl peroxy) butane**
hexane
divinyl diacetylene
1,6-heptadiyne
dimethyl divinyl acetylene
divinyl acetylene
dimethyl divinyl diacetylene
divinyl acetylene
dimethyl divinyl diacetylene
1,3-hexadiyne
methyl divinyl acetylene
methyl vinyl acetylene

The testing procedure, which was suggested in an article; Shanley & Greenspan, "Highly Concentrated Hydrogen Peroxide", IEC, 39, 1536 (1947) is as follows:

10 ml of the fuel to be tested is
measured into a 15 x 150 mm Pyrex
test tube. A Number "4" electric
blasting cap is lowered into the
test tube so that it is half

*This test is described in detail in Appendix C, "Mechanical Impact Test".

**The compound referred to as 2,2-bis(tert-butylperoxy)butane, or

just "peroxy-butane" is actually technical
2,2-bis(tert-butylperoxy)butane supplied by
Shell Development Co., who gave the analysis
as

approx. 70% 2,2-bis(tert-butylperoxy)butane
approx. 30% di-tert-butyl peroxide.

immersed in the fuel. The test tube is then placed in a 7" section of 3/4" lead pipe having 1/4" wall thickness (AA grade). This pipe is supported upright on a mandrel in a 1" thick steel plate. The blasting cap is then detonated.

When the aforementioned testing procedure was utilized, several distinct categories of results were observed.

Hexane was used as the inert control. It was felt that hexane was sufficiently stable so as to undergo absolutely no decomposition when subjected to the shock of a detonating blasting cap.

1. No Detonation - For example: see Figure 5, detonation #1, for hexane. The lead pipe was broken, but not in two separate pieces. The shattering effect was probably due to the transmittal of the shock of the blasting cap by the inert liquid. Excess liquid remained after the blast.
2. Detonation - For example: see Figure 5, detonation #2, for peroxy butane. The lower half of the lead pipe was shattered into many small fragments, and the upper half was recovered as a single distorted piece.

In this case, the shattering effect was caused by the more or less complete detonation of the liquid under test. No excess liquid was recovered.

3. Partial Detonation* - For example: see Figure 5, detonation #15 for a 90% peroxy butane/10% hexane mixture. In these cases, the lead pipe was broken into two separate pieces, and each half recovered as a distorted section. The shattering effect is postulated to be caused by the detonation of the liquid in the immediate vicinity of the blasting cap; however, the liquid does not sustain a propagated detonation wave, and therefore will not detonate completely. In nearly all cases of this type, excess liquid was noted.

When a pure liquid achieved complete detonation, or partial detonation, it was diluted with hexane (in 10% increments) until the no detonation level was reached. In this manner, a measure of relative instability was sought.

When a pure liquid produced no detonation, it was diluted with peroxy butane until the partial detonation level was reached. In this manner, a measure of relative stability was sought.

All runs were made at a sample temperature of 20°C.

*This term, and accompanying explanation, per conversation with Mr. G.D. Clift of High Explosives Section, Picatinny Arsenal.



NO DETONATION
100% Hexane



DETONATION
100% Peroxybutane



PARTIAL DETONATION
90% Peroxybutane
10% Hexane

Figure 5 DETONATION STUDIES

It should be noted with respect to any conclusions which may be drawn from the results that, with the exception of pure hexane, only one detonation was performed on each specific fuel concentration. No duplicates were run. Perhaps more conclusive data would result if duplicates of the runs were made, and also more acetylenic compounds run.

Consulting the Table V, it will be seen that the only pure liquids which detonated are those which have an impact rating of >100%. Therefore, that correlation may be made between the impact sensitivity and detonation sensitivity.

The compounds are listed in decreasing order of impact sensitivity; inspecting the data, the following tentative correlation may be postulated for pure compounds:

<u>IMPACT RATING</u>	<u>DETONATION RATING</u>
>100%	Detonation
From 50% to 100%	Partial Detonation
up to 50%	No Detonation

The overlap in the region of the 50% impact rating may be due to the fact that the impact tests are run in 10% dilution increments. Perhaps a finer line could be drawn if the impact tests were run in smaller increments in the 50% range.

The results of the tests made on diluted compounds are slightly more nebulous.

Dilution with Hexane to produce No Detonation:

From the Table V, it would seem that of the three neat compounds which detonated, the peroxy butane is the least powerful. This is borne out by the photographic evidence qualitatively: The detonation of peroxy butane produced the largest fragments.

Among the three compounds which produced partial detonation when pure, the order of increasing sensitivity correlate with the impact ratings. However, dimethyl divinyl diacetylene shows a greater sensitivity than peroxy butane, which does detonate. This apparent paradox may be due to any of the following reasons:

- a. Inaccurate data. Duplicates should be run.
- b. Dimethyl divinyl diacetylene may possess exceptionally wide partial detonation limits, and peroxy butane narrow partial detonation limits.
- c. Dimethyl divinyl diacetylene's No detonation point is between 50% and 60% hexane dilution; the 50% figure for peroxy butane is a very marginal No detonation. (The lead pipe was in one piece, but was literally joined by a "thread" which later broke). It is plausible then that the data for these two as listed is not sufficiently precise, and peroxy butane has a higher (more sensitive) No detonation rating than does dimethyl divinyl diacetylene.

d. Differences in the thickness of the lead pipe.

Dilution with Peroxy butane to produce Partial Detonation:

These data give good qualitative correlation with the impact ratings; perhaps even better correlation would be attained if smaller dilution increments were used.

ACETYLENIC HYDROCARBONS AS MONOPROPELLANTS

Many acetylenic compounds are thermodynamically unstable and under the proper conditions will decompose spontaneously to form carbon and hydrogen with the simultaneous liberation of large quantities of heat. This behavior suggests their use as monopropellants in rocket engines. The exhaust products from such fuels would consist of a completely combustible mixture of carbon and hydrogen. By contrast, partially oxidized exhaust products are produced by most monopropellants such as nitro-methane, CH_3NO_2 . This leads to the expectation that the acetylenic hydrocarbons may also be of considerable importance in rocket-ram jet applications.

Minimum Spark Ignition Energy Data
from Experiment, Inc.

As a means of obtaining a kinetic parameter for possible monopropellants, Experiment, Inc. has developed a test involving study of ignition characteristics of a fuel with small fuse wires. The method is somewhat similar to their minimum spark ignition test with oxidant-fuel mixtures, but uses small wires, electrically exploded, as approximating a point source of ignition. Although time has not yet permitted a full evaluation of the factors involved, the method has been employed to characterize the ignition of monopropellants in the vapor phase. The monopropellant pressure at the minimum energy for ignition has been employed as a means of comparing fuels. Details of the test procedure are described in a recent Experiment, Inc. report (4).

(4) Experiment, Inc. "Second Annual Report on Monofuel Rocket and Ram-Rocket Development", April 1, 1953, Contract Nord 11473. (CONFIDENTIAL)

A number of samples of acetylenic compounds were furnished by this laboratory to Experiment, Inc. for evaluation by the above test. The results are shown in Table VI.

Since the minimum energy of all the fuels previously tested had occurred at a time of approximately four milliseconds, it was decided to fix the time and vary the pressure in order to obtain a basis for comparing these fuels. Experiment, Inc. feels that the data presented in Table VI, while not as good as might be desired, does give an indication of the ignition characteristics of this series of monopropellants; the lower the minimum pressure at ignition, the greater the ease of ignition of the fuel. It is seen that certain of the acetylenic compounds tested, and in particular 1,5-hexadiyne, would appear to be capable of ignition with ease, and also possess a favorable specific impulse (190 sec.).

Calculation of Specific Impulse

The method of Maxwell, Dickinson, and Caldin (5) was used to calculate monopropellant specific impulse values. Their method is based upon the following assumptions:

- (a) Thermal equilibrium is maintained between the solid particles and the gas phase in the exhaust stream from the rocket.
- (b) The solid particles have the same velocity as the gas at all stages of the expansion.
- (c) The volume of solid particles is negligible compared with that of the gas, and their vapor pressure can be neglected.

(5) Maxwell, Dickinson, & Caldin, Aircraft Engineering, 18, 350 (1946).

Table VI

Fuse Wire Ignition Characteristics

<u>Fuel</u>	<u>Temp- erature °C</u>	<u>Fusion Time, Milli- seconds</u>	<u>Ign. Energy Joules</u>	<u>Min. Pres. at</u>	
				<u>Ign. Energy Atm.</u>	<u>Abs.</u>
2,5-Dimethyl,1,5-hexadiene, 3-yne*	220		No ign. #		
Ethylene	100		No ign. §		>35
Propyne**	100	4.0	0.065		7.1
Propyne	150	4.0	0.055		6.4
Nitromethane	175	4.1	0.046		4.5
Acetylene**	100	4.0	0.070		3.5
1,7-Octadiyne*	220	4.0	0.060	3.3-3.6	
3-Methyl 3-butyne 1-yne*	100	3.6	0.055	2.7-2.9	
Ethylene Oxide**	100	4.0	0.064		2.16
Diacetylene*	25	4.0	0.036		0.34
1,5-Hexadiyne*	100	4.0	0.030		0.050

*Furnished by Marsel and Happel of New York University.

#No ignition was obtained at 3.9 atmospheres absolute at 220°C at a fusion time of 4.6 milliseconds. It is believed that the sample used had gone bad since the fuel had turned a pale green color.

§No ignition was obtained at pressures up to 35 atmospheres absolute at 100°C at fusion times up to 44 milliseconds and energies up to 0.5 joules.

**Values picked from energy-pressure and energy-time curves.

(d) The pressure due to the thermal motion of the solid particles can be neglected.

(e) The gas obeys the perfect gas laws.

The equation as finally derived for the calculation of the specific impulse of a gaseous stream containing solid particles is:

$$I_{sp} = \left[\frac{2K}{K-1} \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{K-1}{K}} \right] \frac{J A_1 R T_1}{M g_c} \right]^{\frac{1}{2}}$$

where $K = \frac{A_1 R + A_1 C_v + A_2 s M}{A_1 C_v + A_2 s M}$

C_v = specific heat of gas, BTU/(lb-mol)(°R)

J = mechanical equivalent of heat, 778 ft-lb/BTU

M = molecular weight of gas

s = specific heat of solid, BTU/(lb-mol)(°R)

A_1, A_2 = weight fraction of gas and solid, respectively

P_1, P_2 = pressure in rocket motor and external pressure, respectively

R = 1.99 BTU/(lb-mol)(°R)

T_1 = adiabatic flame temperature, °R

g_c = 32.2 (lb.mass)(ft)/(lb. force)(sec²)

For purposes of comparison, it is permissible to set P_1 and P_2 arbitrarily at 300 psia and 14.7 psia, respectively. The adiabatic flame temperature was estimated from a knowledge of the heat of formation and by the use of the assumption that the compound has completely decomposed to carbon and hydrogen. In order to evaluate the effect of molecular structure upon the specific impulse, three series of acetylenic compounds were investigated:

Monoyne series;	C_2H_2	to	C_5H_8
Diyne series;	C_4H_2	to	C_8H_{10}
Triyne series;	C_6H_2	to	$C_{11}H_{12}$

The diyne and triyne series were subdivided into subseries according to the degree of conjugation of the triple bonds. In both series a subseries was studied with a pair of conjugated triple bonds in the 1,3 positions. In the triyne subseries the third triple bond was in the (n-1) position for hydrocarbons with n carbon atoms. In the diyne series a second subseries was studied having the triple bonds at the 1 and (n-1) positions. In the triyne series the second subseries had the triple bonds at the 1,4 and (n-1) positions. In addition, the monopropellant specific impulse for a number of acetylenic compounds synthesized at New York University was also calculated.

Specific impulses were based on the heat of formation data described in the Section on acetylenic hydrocarbons as bipropellants.

The results of the specific impulse calculation are given in Table VII and Figure 6. Figure 6 shows the variation of specific impulse with the number of carbon atoms, for the monoyne, diyne, triyne and tetrayne series and with type of conjugation. Examination of Figure 6 shows that acetylene C_2H_2 , gives the highest specific impulse of all the hydrocarbons investigated. This is generally found to be the case, both for monopropellant and mixed fuel-oxidant propellant specific impulses. The monopropellant specific impulse falls off very rapidly for the monoyne series, however, as shown by the plot and it is apparent that for hydrocarbons having a volatility in the range of gasoline, that is

C_5-C_9 , the specific impulse is appreciably below that for diyne and triyne series.

The diyne and triyne series both display a maximum. For the diyne series, the optimum fuel is 1,4-pentadiyne, C_5H_4 , with a specific impulse value of 196 seconds. As in the monoyne series the specific impulse falls off with number of carbon atoms per molecule above the maximum but not as sharply as for the monoyne series. In the triyne series the optimum fuel is 1,4,7-octatriyne with a specific impulse of 186 seconds. For this series, the decrease in specific impulse with number of carbon atoms is comparatively small, so that the choice of a triyne monopropellant would probably depend more strongly on other factors. It is noteworthy that in the unconjugated diyne series higher specific impulses are obtained for the C_5 and C_6 members than for any triyne. This is of practical concern as the diynes should be simpler to prepare and should cost much less than the triynes.

In comparing the optimum compounds acetylene C_2H_2 , hexadiyne C_6H_6 , and octatriyne C_8H_6 , it is observed that the hydrogen to carbon atom ratio is either equal to one or just less than one.

For the tetrayne series, the calculation of the specific impulse was limited to the first member of the series octatetrayne, C_8H_2 , because of the relatively low specific impulse obtained for this compound as compared with the previous series. It was reasoned that if the optimum value occurred at a hydrogen to carbon ratio of approximately one as in the previous cases, it would be necessary to go to $C_{12}H_{10}$ or $C_{13}H_{12}$ before the maximum was reached, and these high molecular weight

Table VII
Specific Impulse For Acetylenic Compounds
as Monopropellants

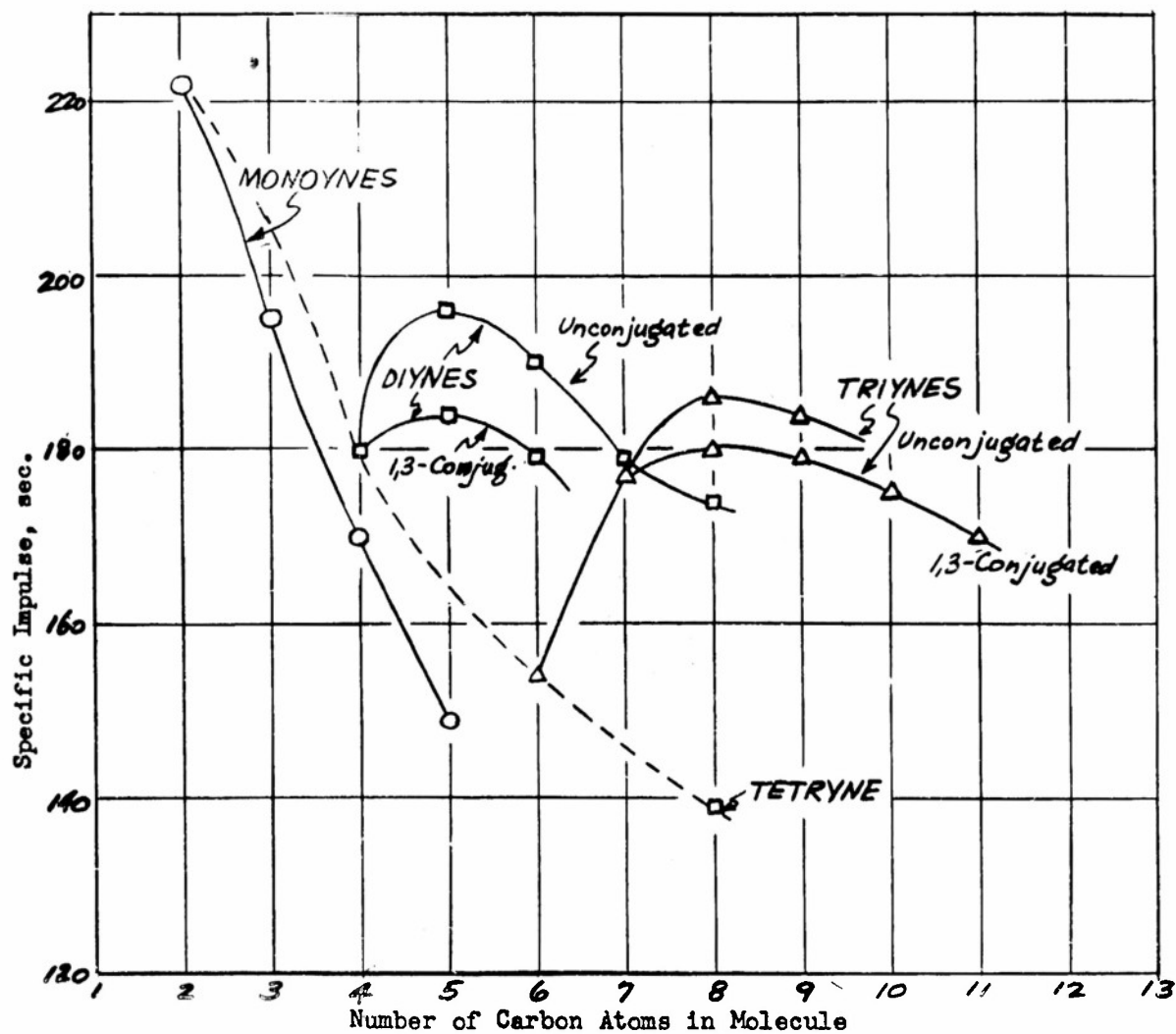
<u>Series</u>	<u>Compound</u>	<u>Flame Temp.</u> <u>deg.F</u>	<u>I_{sp}=(lb.thrust)(sec.)</u> <u>lb.fuel</u>
Monyne	Acetylene C ₂ H ₂	4640	222
	*Propyne C ₃ H ₄	2620	195
	1-Butyne C ₄ H ₆	1710	170
	1-Pentyne C ₅ H ₈	1175	149
Diyne	*Diacetylene C ₄ H ₂	5390	180
	*1,4-Pentadiyne C ₅ H ₄	4280	196
	*1,5-Hexadiyne C ₆ H ₆	3240	190
	*1,6-Heptadiyne C ₇ H ₈	2550	179
	*1,7-Octadiyne C ₈ H ₁₀	2150	174
	1,3-Pentadiyne C ₅ H ₄	3720	184
	*1,3-Hexadiyne C ₆ H ₆	2820	179
Triyne	Hexatriyne C ₆ H ₂	5680	154
	1,3,6-Heptatriyne C ₇ H ₄	4820	177
	1,3,7-Octatriyne C ₈ H ₆	3790	180
	1,3,8-Nonatriyne C ₉ H ₈	3180	179
	1,3,9-Decatriyne C ₁₀ H ₁₀	2700	175
	1,3,10-Undecatriyne C ₁₁ H ₁₂	2300	170
	1,4,7-Octatriyne C ₈ H ₆	4060	186
	1,4,8-Nonatriyne C ₉ H ₈	3370	184

<u>Series</u>	<u>Compound</u>	<u>Flame Temp.</u> <u>deg.F</u>	<u>I_{sp}=(lb.thrust)(sec.)</u> <u>lb.fuel</u>
Tetrayne	Octatetrayne C_8H_2	5860	139
Olefenic	*Methyl vinyl acetylene C_5H_6	2070	168
	*Methyl divinyl acetylene C_7H_8	1600	149
	*Dimethyl divinyl diacetylene $C_{10}H_{10}$	1980	153
Nitrile	*2-Butyne 1,4-dinitrile C_4N_2	6500	156

*Compounds synthesized at New York University

Figure 6

SPECIFIC IMPULSE OF ACETYLENIC COMPOUNDS
AS MONOPROPELLANTS
(SPECIFIC IMPULSE VS NO. OF C ATOMS)



substances might be solids at atmospheric conditions. Since the tetraynes show no indication of superiority as monopropellants and, in addition, would be so much more difficult to prepare than the diynes for example, it was decided not to proceed beyond the first member at this time.

The specific impulse values for several compounds having double-triple bond conjugation are also presented in Table VII. These compounds have appreciably lower specific impulse values than the diynes or triynes with the same number of carbon atoms. In conclusion, 1,4-pentadiyne has the highest monopropellant specific impulse of any of the normally liquid acetylenic compounds.

The specific impulse for other monopropellants currently being considered (6) are listed in Table VIII. With the exception of nitro methane none of the compounds is superior to the best of the diynes or triynes listed in Table VII. The acetylenic compounds have the advantage over all the compounds listed in Table VIII in that the exit gases are completely combustible consisting of only hydrogen and carbon, consequently the acetylenic compounds can be used very effectively in ducted jets. The monopropellants containing oxygen produce exit gases which are partly burned and thus are not as effective in a ducted jet. A monopropellant such as hydrazine has nitrogen as diluent in the exit gas so that it too is not as effective as an acetylenic compound in a ducted jet.

(6) Report on "Symposium on Liquid Monofuels" held at Wyandotte Chemical Corp. on Sept. 22 and 23, 1953.

Table VIII
Specific Impulse for Miscellaneous Compounds
as Monopropellants(6)

<u>Compound</u>	<u>Flame Temp.</u> <u>deg.F</u>	<u>I_{sp}=lb. thrust</u> <u>lb.Fuel per sec.</u>
90%-Hydrogen Peroxide H_2O_2	1360	132
Nitro Methane CH_3NO_2	3990	227
Ethylene Oxide $\text{C}_2\text{H}_4\text{O}$	1790	160
n-Propyl Nitrate $\text{C}_3\text{H}_7\text{NO}_3$	1840	170
60-40 Ethyl and Propyl Nitrates	-	184
Hydrazine N_2H_4	1125	171

Outside Testing

The Wyandotte Chemical Co., after a study of the acetylenic compounds prepared on this project, were recently furnished at their request with small samples of 1,6-heptadiyne and 3-butyne-1-ol, for testing as monopropellants.

ACETYLENIC HYDROCARBONS AS RAM JET FUELS

Several acetylenic hydrocarbons were analyzed for use as possible ram jet fuels. The analysis included a consideration of their applicability as straight ram jet fuels and as rocket-ram fuels. Two factors were evaluated; the total theoretical thrust developed, and the impulse efficiency or combustion efficiency.

The total theoretical thrust is computed from the specific impulse. This specific impulse calculation is outlined in the next paragraph. The computation of the total thrust developed is detailed in the section on the ram-rocket. The impulse efficiency is related to the minimum spark ignition energy by an empirical relationship, shown in Figure 8.

Calculation of Specific Impulse and Impulse Efficiency

Theoretical air and fuel specific impulses were calculated for various acetylenic hydrocarbons, all of which had been synthesized at New York University. These values were computed at 14.7 psia using the stoichiometric air-fuel ratio. The air specific impulse was calculated from the following formula:

$$(1) \quad S_a = \sqrt{\frac{2(k_e + 1) R_e T_s}{k_e g}} \left(1 + \frac{m_f}{m_a} \right)$$

The fuel specific impulse is given as:

$$(2) \quad S_f = \frac{m_a}{m_f} S_a, \quad \text{where}$$

T_s = adiabatic stagnation temperature

k_e = ratio of average specific heat of exit gases at constant pressure and constant volume

$$R_e = \frac{1544}{\text{Molecular Weight of exit gases}}$$

m_f = 1.0 lb. fuel per sec.

m_a = stoichiometric lbs. of air per sec. corresponding to 1.0 lb. fuel per sec.

The results for selected acetylenic hydrocarbons, together with the physical properties of these materials, are shown in Tables IX and X.

It is apparent from these calculated specific impulses that none of the acetylenic hydrocarbons show a marked improvement over JP-4. This is not surprising, since the heat of combustion per pound for hydrocarbons varies only by a slight amount. Increments in the heating value with increasing unsaturation are offset by the absence of the hydrogen atoms. Consequently, from the viewpoint of theoretical specific impulses, none of the acetylenic hydrocarbons can be looked upon as an improvement upon JP-4. However, from the impulse efficiency aspect, the acetylenic hydrocarbons may possess a marked advantage over JP-4.

Table IX
Physical Properties of Acetylenic Hydrocarbons

NYU No.	Compound	Density g/cc at 20°C	M.Pt. °F	B.Pt. °F	Impact Sens.*	H.C. Net BTU/lb
JP-4	(Kerosene fraction) $C_{12}H_{26}$				20%	18,400
16	3,6-DIMETHYL 2,6-OCTADIENE 4-YNE	0.807	-76	343	30%	18,205
19	1,6-HEPTADIYNE	0.805	-121	237	50%	18,550
26	2-METHYL 1-BUTENE 3-YNE	0.680 at 11°C	<-112	93	40%	18,820
41	2-METHYL 1,5-HEXADIENE 3-YNE	0.781	<-85	226	50%	18,276
47	2,7-DIMETHYL 1,7-OCTADIENE 3,5-DIYNE	0.843	22	106 at 1.5 mm	80%	18,000
50	1,3-HEXADIYNE	0.796	<-85	117.5 at 113 mm	>100%	18,833

*See Appendix C

Table X
Air-Fuel Specific Impulses for Acetylenic Hydrocarbons

Compound Number	Name	Specific Impulses		$\frac{\text{lbs. air}}{\text{lb. fuel}}$
		$\frac{\text{Air-Fuel}}{\text{Air}}$	$\frac{\text{Fuel}}{\text{Fuel}}$	
JP-4	(Kerosene fraction) $\text{C}_{12}\text{H}_{26}$	174.1	185.5	14.89
NYU-16	3,6-DIMETHYL 2,6-OCTADIENE 3-YNE	172.3	185.2	13.83
NYU-19	1,6-HEPTADIYNE	175.5	188.7	13.43
NYU-26	2-METHYL 1-BUTENE 3-YNE	174.2	189.2	13.52
NYU-41	2-METHYL 1,5-HEXADIENE 3-YNE	173.8	186.7	13.43
NYU-47	2,7-DIMETHYL 1,7-OCTADIENE 3,5-DIYNE	174.0	187.1	13.20
NYU-50	1,3-HEXADIYNE	175.8	189.0	13.19

Impulse Efficiency of Acetylenic Hydrocarbons

The correlation of ram jet performance with the minimum spark ignition energy has been studied by Calcote, et al (7). Their studies revealed a definite relationship between the minimum spark ignition energy for a given fuel and the experimentally determined impulse efficiency. The impulse efficiency is defined by equation (3) as:

$$(3) \quad \eta_i = \frac{S_a}{S_a(th)} \times 100 \quad \text{where}$$

S_a = experimental air specific impulse

$S_a(th)$ = theoretical air specific impulse

η_i = impulse efficiency

The experimental air specific impulse is computed from measured variables, using the method of Rudnick (8).

A plot of Calcote's (7) data relating impulse efficiency to minimum spark ignition energy is shown in Figure 7. The minimum spark ignition energy was measured by the method of Calcote (7,9). The most important point to be observed from the plotted data is the fact that the various measurements can be related by a single straight line.

(7) Calcote, et al, "Minimum Spark Ignition Energy" Experiment, Inc., TP-36, (March 1950) (Confidential).

(8) Rudnick, J. Aero. Sci., 14, 540 (1947)

(9) Calcote, et al, IEC-44, 2656 (1952).

Reference (7): CALCOTE, et al; "MINIMUM SPARK IGNITION," EXPERIMENT, INC., TP-36

CORRELATION OF BURNER EFFICIENCY WITH IGNITION ENERGY
EFFECT OF PRESSURE AND FUEL TYPE

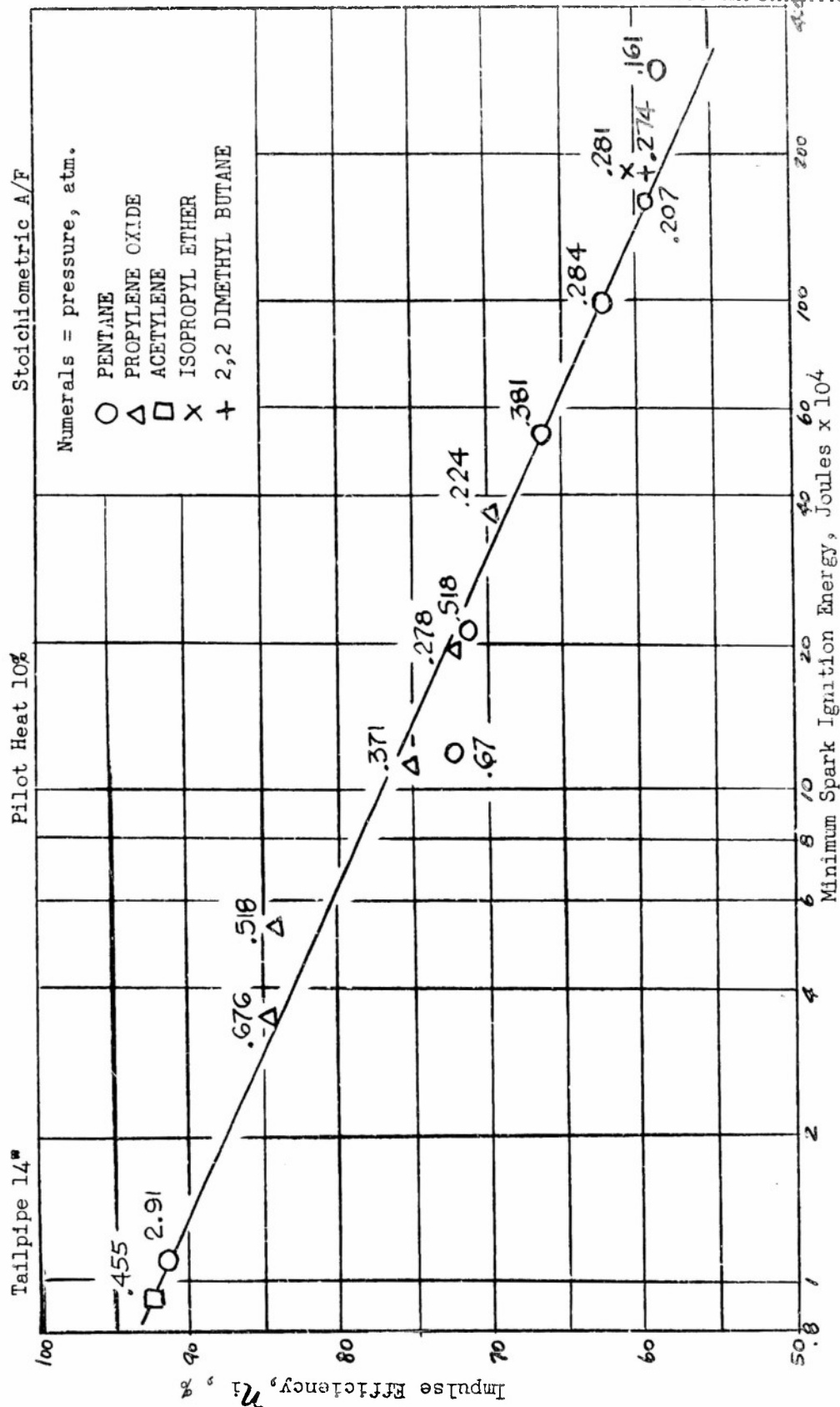


Figure 7

IMPULSE EFFICIENCY VS. MINIMUM SPARK IGNITION ENERGY FOR VARIOUS COMPOUNDS

CONFIDENTIAL
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This straight line correlates the burner efficiency with minimum spark ignition energy for widely different fuel species over a considerable range of pressures. Thus, it may be concluded that if the value of the spark ignition energy were known for a given compound, the burner efficiency for that particular fuel could be estimated from Figure 7.

The minimum spark ignition energies for five acetylenic hydrocarbons prepared by New York University were measured by Experiment, Incorporated. The results are shown in Table XI.

Table XI

Minimum Spark Ignition Energy for Acetylenic Hydrocarbons at 0.5 atm.

<u>Compound No.</u>	<u>Compound</u>	<u>Minimum Spark Ignition energy, Joules</u>
19	1,6-heptadiyne	17.5×10^{-4}
13	Dimethyl divinyl acetylene	15.5×10^{-4}
26	Methyl vinyl acetylene	11.2×10^{-4}
50	1,3-hexadiyne	8.0×10^{-4}
41	Methyl divinyl acetylene	7.5×10^{-4}

It should be noted that these measurements were made at 0.5 atm.

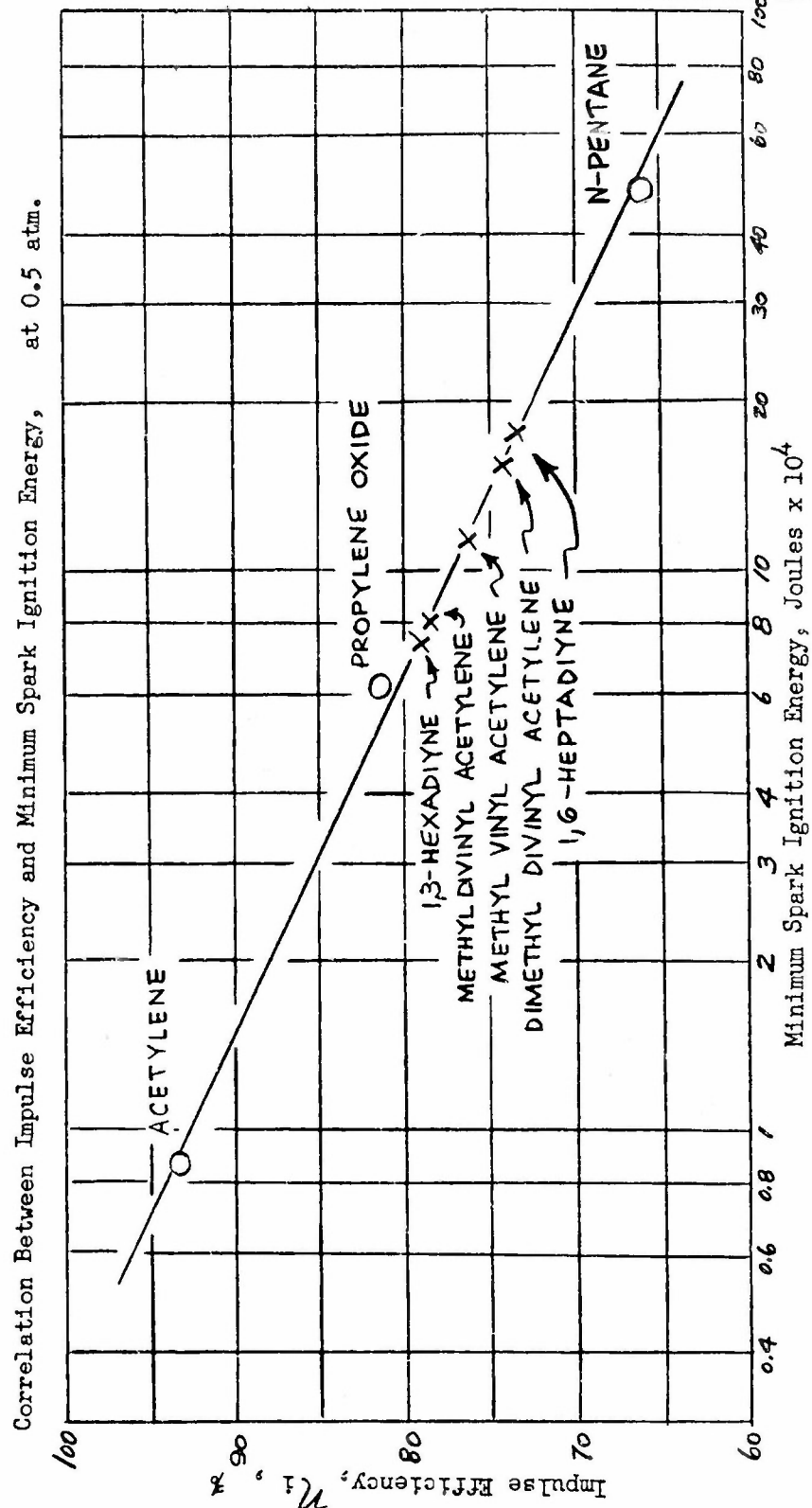


Figure 8
IMPULSE EFFICIENCY VS. MINIMUM SPARK
IGNITION ENERGY FOR ACETYLENIC HYDROCARBONS

Figure (8) has been prepared in order to show more clearly a comparison between the burner efficiencies of these acetylenic compounds and those of the compounds shown on Figure 7. The data for pentane, acetylene, and propylene oxide at 0.5 atm have been estimated from Figure 7, and these three values plotted on Figure 8. The minimum spark ignition energies for the five acetylenic compounds (Table XI) have been plotted on the straight line which these three points fixed. Thus a direct comparison can be made between the impulse efficiency of the acetylenics and that of the other compounds. This comparison, of course, depends on the validity of the straight line relationship between minimum spark ignition energy and impulse efficiency.

The acetylenic hydrocarbons show a considerably higher impulse efficiency than the paraffins as typified by n-pentane. This increment, in the case of N.Y.U. 41, methyl divinyl acetylene, amounts to about 12%. The impulse efficiency for higher molecular weight paraffins is probably lower than that of n-pentane, because the minimum spark ignition energy uniformly increases with molecular weight in a given homologues series (9), thus producing a reduction in the impulse efficiency. Therefore, the impulse efficiency of methyl divinyl acetylene is probably 20 to 25 per cent greater than that of JP-4. This should result in a larger experimental fuel specific impulse for methyl divinyl acetylene than for JP-4, even though JP-4 has a higher theoretical fuel specific impulse than methyl divinyl acetylene.

It should be observed that methyl divinyl acetylene has a higher impulse efficiency, 78.5 per cent, than methyl vinyl acetylene,

76 per cent, or 1,6-heptadiyne, 73 per cent. This result agrees with the observation of Calcote (9) as to the apparent effect of conjugation upon the minimum spark energy. Calcote pointed out that the minimum spark energy is apparently reduced by the presence of a resonating structure in the molecule.

Therefore, the acetylenic hydrocarbons show definite promise for use as ram jet fuels, because of their probable higher impulse efficiency in combustion compared to JP-4. It is also suggested that a blend of JP-4 and one of the more promising acetylenic hydrocarbons such as methyl divinyl acetylene, would also have superior combustion characteristics.

The Ram Rocket

After the monopropellant specific impulse was calculated, it was now possible to proceed with a computation of the gross thrust for a straight tailed rocket ram jet using a given fuel. This was done by the following method. It was assumed that the rocket ram jet is operating at 40,000 feet altitude and at Mach 1. In order to simplify the computation, swallowed shock at the inlet and a choked exhaust were postulated. Under these conditions with a feed rate of 1 lb. fuel per second and a diffuser inlet area fixed by the stoichiometric amount of air required for the fuel; the gross thrust of the rocket ram jet could be expressed by the following general equation:

$$(4) \quad F_g = F_e - F_i - p_o (A_e - A_i)$$

Where F_g = gross thrust, lbs.
 F_e = stream thrust at exit.
 F_i = stream thrust at inlet.
 p_o = 2.72 psia at 40,000 ft.
 A = area, in.²

From a momentum balance, the exit stream thrust may be expressed as:

$$(5) \quad F_e = F_r + \eta_d \left(\frac{p_t}{p_o} \right) p_o A_2$$

Where F_r = monopropellant specific impulse of the rocket.

η_d = subsonic diffuser recovery factor = 0.96 for Mach 1.

σ_o = normal shock recovery factor = 1.0 for swallowed shock.

p_t = stagnation pressure.

The inlet stream thrust can be expressed as:

$$(6) \quad F_i = p_i A_i (1 + k M_i^2)$$

For swallowed shock, Mach. No: $M_i = M_o = 1.0$, $p_i = p_o = 2.72$ psia.

$$(7) \quad F_i = (2.72 \text{ psia}) A_i (1 + k)$$

Also for operation under conditions of choked exhaust;

$$(8) \quad F_e = m_a s_a, \text{ where}$$

m_a = stoichiometric air flow rate corresponding to 1 lb. fuel per sec.

s_a = air specific impulse for the given fuel as calculated from equation (1).

If equations (4), (7), and (8) are combined, F_g becomes

$$(9) \quad F_g = m_a s_a + p_o A_i (1 + k) - p_o (A_2 - A_i)$$

For any given fuel, A_2 may be calculated from equation (4) using

$\eta_d = 0.96$, $\sigma_o = 1.0$ and $\left(\frac{p_t}{p_o}\right) = 1.893$. A_i was fixed as soon as

the assumption of stoichiometric air-fuel proportions was made, and

can be calculated by the use of equation (10).

$$(10) \quad A_1 = \frac{m \cdot a_o}{kgp \cdot M_o} \quad , \text{ where}$$

$$a_o = \text{local velocity of sound} = 974 \text{ fps}$$

$$p_o = 2.72 \text{ psia}$$

$$M_o = 1.0$$

$$g = 32.2 \text{ ft. per sec.}^2$$

Equation (9) was used to calculate the gross thrust for a rocket ram jet using various acetylenic fuels. In order to evaluate the incremental effect of the rocket ram jet with respect to the ram jet alone, it is necessary that the gross thrust for a ram jet also be computed under the same conditions of flight. Equation (9) can be used for this purpose, using a value of A_2 calculated from equation (5) with F_r missing. Table XII shows the results of these computations. The incremental thrust represents the improvement in gross thrust to be obtained by the use of the rocket ram jet over the ram jet alone. It is apparent that the incremental thrust amounts to an increase of approximately 10 to 15 percent. As far as the hydrocarbons are concerned, the incremental thrust is almost a constant figure, roughly 85 to 105 lb., with 1,4-pentadiyne showing the largest value, 106. This is not surprising when it is recalled that 1,4-pentadiyne showed the highest monopropellant specific impulse of any of the acetylenic compounds investigated. However, it should be noted that the fuel specific impulse of 1,4-pentadiyne is lower than that of any of the other hydrocarbons listed.

The highest total thrust for the rocket ram jet is shown by the 1,6-heptadiyne. Even so, this value for the rocket ram jet,

Table XII

Ram Rocket Performance Characteristics for Some Acetylenic Compounds at Mach 1

Compound Number	Compound	Specific Impulses lb/lb/sec			Total Thrust lb.			Stoich- iometric $\frac{m_{air}}{m_{fuel}}$
		Monopro- pellant	Air	Fuel	Rocket Ramjet	Ramjet	Incremental Thrust	
NYU-19	1,6-Heptadiyne	179.	188.7	2535	837.	737.	100.	13.43
" 26	Methyl Vinyl Acetylene	168.	189.2	2560	834.	744.	90.	13.52
" 41	Methyl Divinyl Acetylene	149.	186.7	2510	805.	720.5	84.5	13.43
" 50	1,3-Hexadiyne	179.	189.0	2490	824.	723.	101.	13.19
	1,4-Pentadiyne	196.	190.2	2445	820.	714.	106.	12.85
JP-4	Kerosene cut	-	185.5	2770	-	783.	-	14.89

837 lbs., is only 55 lbs. higher than that of JP-4 for the ram jet alone. Consequently, it is doubtful if any net advantage would be derived by the use of the acetylenic hydrocarbon after the weight of the rocket is taken into account. However, there is another feature as to the operation of a ram jet that might put the acetylenic hydrocarbons in a more advantageous position. In order to operate a ram jet, the propulsive duct must already be flying at a sufficiently high Mach number to draw in the required air for combustion. The rocket-ram jet might offer the means for designing a self-accelerating ram jet. This possibility has been explored in the next portion of this report.

Performance of A Rocket-Ram Jet for the Launching Condition:

The same conditions of flight were assumed in this analysis as in the section on Monopropellant Specific Impulse. The inlet and exit cross sectional areas for a straight tailed rocket-ram jet were calculated from equations (5) and (10) for each particular fuel. Conditions at launching were then analyzed using these fixed values for the diffuser cross sectional areas.

The gross thrust of the rocket-ram jet will be equal to the sum of the monopropellant rocket thrust of the fuel and the gross thrust of the ram jet itself. The gross thrust of the ram jet on launching will, of course, be negative and can be calculated from equation (11).

$$(11) \quad F_g = \frac{\dot{m}_a}{g} (V_3 - V_1) \quad \text{where}$$

$\dot{m}_a$ = air flow rate

V_3 = exit velocity, ft. per sec.

V_1 = inlet velocity, ft. per sec., or

973 ft. per sec., at 40,000 ft.
altitude.

The exit velocity may be determined by solving an energy balance equation (12) simultaneously with

$$(12) \quad V_3^2 = 2gJ(h_1 - h_3)$$

the gas law relationship at the exit of the duct.

Calculated results for several acetylenic derivatives are shown in Table XIII.

Table XIII
Ram Rocket Performance Characteristics for Some Acetylenic Compounds at Mach 1

Compound Number	Compound	Specific Impulses lb/lb/sec			Total Thrust lb.			Stoich- iometric $\frac{M_{air}}{M_{fuel}}$
		Monopro- pellant	Air	Fuel	Rocket Ramjet	Ramjet	Incremental Thrust	
NYU-19	1,6-Heptadiyne	179.	183.9	2535	837.	737.	100.	13.43
" 26	Methyl Vinyl Acetylene	168.	189.2	2560	834.	744.	90.	13.52
" 37	2-Butyne 1,4-Dinitrile	157.	203.	1470	527.	441.	86.	7.21
" 41	Methyl Divinyl Acetylene	149.	186.7	2510	805.	720.5	84.5	13.43
" 50	1,3-Hexadiyne	179.	189.0	2490	824.	723.	101.	13.19
	1,4-Pentadiyne	196.	190.2	2445	820.	714.	106.	12.85
JP-4	Kerosene cut	-	185.5	2770	-	783.	-	14.89

The results shown in Table XIII indicate that none of the fuels analyzed will produce a positive thrust on launching. However, NYU-37, 2-butyne, 1,4-dinitrile, had a negative thrust of only 8 lbs. Thus by designing the ram jet on the fuel rich side, it would be possible to burn this fuel in such a way as to achieve an initial positive thrust. However, this particular compound has a very low fuel specific impulse, 1470 lb./lb./sec., although the air specific impulse, 203 lb./lb./sec., is satisfactorily high. In general it can be said that those fuels which have a low $\frac{m_{air}}{m_{fuel}}$ stoichiometric ratio may give rise to positive thrusts on launching. However, these fuels will ordinarily contain nitrogen and consequently have low fuel specific impulses. Thus, a consideration of the calculated results seems to indicate that it is highly improbable that any fuel with a high specific impulse will produce an accelerating thrust on launching.

On the other hand, it should be recalled that these calculations and remarks are all based in stoichiometric air fuel proportions. By designing the ram jet on the fuel rich side, the resultant thrust for non-burning conditions must increase in value. An alternative procedure might involve variation of the air-fuel ratio during the flight. This might make it possible to achieve an initial positive thrust on launching.

RECOMMENDATIONS

The following recommendations are made concerning future work:

1. In view of the proven interest in acetylenic hydrocarbons, synthesis work should be continued on a moderate scale in an effort to produce compounds with the optimum values for specific impulse and ignition delay, as well as favorable physical properties such as melting point. The analysis as presented in this report points up the most favorable types of structures to be synthesized.
2. More complete evaluation studies should be made on methyl divinyl acetylene, in view of its favorable properties. This evaluation program would include testing of stability on storage, means of improving stability, corrosion studies, and the like.
3. Pilot plant quantities of more desirable fuels should be made for evaluation purposes. This should include development work on continuous processes for preparing the desired compounds.
4. Evaluation studies should be made on the economics of larger scale commercial production of the more favorable compounds.

5. Further testing should be done on the use of acetylenic compounds, and in particular the acetylenic hydrocarbons, as additives to improve ignition characteristics of less reactive fuels, such as JP-4.

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APPENDICES

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APPENDIX A

A Study of Some Factors Affecting Ignition Delay Measurements

Investigations into the factors that affect the measurements of ignition delay have brought to light some of the reasons why ignition delay values reported by this laboratory were not in agreement with results obtained by other laboratories which used essentially the same apparatus. As reported in our previous technical report, (footnote 10) we have been using the cylindrical tester developed by the California Research Corporation (footnote 11). The alterations in the electrical system that we found necessary to make are fully described in our June 15, 1953 report (footnote 10) on pages 13-20 and 45-50.

In conducting the following investigations, it was decided to use the fuels supplied to us by the various reporting laboratories as outlined at the Bartlesville meeting of the Petroleum Derivable Fuels conference. This set of fuels was chosen so that results of our investigation could be compared with values obtained from other laboratories. The fuels in question are:

(10) N. Y. U. Research Division Report No. 175.12
dated June 15, 1953.

(11) California Research Corporation "Liquid Rocket
Fuels" Summary Report October 31, 1950 (Confidential)

Dioxaphospholane Blend RF 311
Ethyl Mercaptal of Acetaldehyde
N,N,N',N' Tetramethyl propane 1,3 diamine
Methyl Disulfide
Triethylamine
Methyl divinyl acetylene

The effect of the resistance level, at which the transducer is set to fire, upon the recorded value of ignition delay is discussed in the aforementioned N. Y. U. Report. The procedure for setting the resistance level is described on pp 47-50 of that report. The ignition delay times for the six fuels in question at 75°F, using RFNA as the oxidizer, are given in Table XIV for varying resistances. The other conditions for the values given in this table are the use of a drop height of 6.0 millimeters and the "stop" probe 2-3/4 inches above the point of the fuel cup. (See discussion following). Times are in milliseconds.

Table XIV
Ignition Delay as a Function of Firing Resistance Level

	Firing Resistance Level of Transducer (ohms)				
	2000	5000	10,000	100,000	200,000
Shell Dioxaphospholane	∞	∞	∞	∞	3.2
Methyl divinyl acetylene	9.3	7.5	9.6	9.0	9.8
Phillips fuel N,N,N',N'	∞	∞	∞	27.6	6.2
Methyl disulfide	∞	10.7	24.4	6.2	6.0
Ethyl Mercaptal of Acetaldehyde	∞	∞	∞	∞	3.2
Triethylamine	∞	∞	∞	∞	27.1

A value of infinity means that the "stop channel" did not trip which indicates that the resistance of the ionized gases did not fall below the setting of the transducer. The reason that some of the values do not seem to fall in line (such as for methyl disulfide) is that only a single run was made at each resistance and since values tend to be erratic at low resistances, too much reliance cannot be placed on any single value. The trend of the values in Table XIV is evident, however. It is clear that the resistance level of the ionized gases of combustion is different for different fuels and that the recorded ignition delays are longer when the transducer is set at low resistance levels. As discussed in the previous N.Y.U. Report No. 175.12 (10) on pages 16-18, the recorded ignition delays will asymptotically approach a constant value at high settings of transducer resistance. This constant value seemed to have been reached by a 200,000 ohm setting. It is interesting to note that the methyl divinyl acetylene gave constant values of ignition delay at all resistance levels. This indicates that the rate of combustion for this fuel is very rapid, resulting in a high concentration of ionized gases. With the fuels that did not trip the timer at resistances below 200,000 ohms, the rate of combustion may be much slower, resulting in a smaller concentration of ionized gases in the flame front.

The next variable affecting the recorded values of ignition delay (using the cylindrical tester) that was investigated was the distance between the surface of the fuel and the lowest level of the

"stop" probe. The "stop" probe is a 1/4 inch O.D. stainless steel tube that extends down the center of the cylindrical tester. It was found that when the "stop" probe is close to the surface of the fuel, very low values are recorded on the timer. The cause of this was attributed to mechanical splashing of the fuel onto the probe, resulting in tripping of the timer before the explosion takes place. The results obtained with four fuels with a varying probe height are shown in Table XV. The transducer used in these tests was an instrument supplied by the Berkeley Scientific Corporation. Our tests with a known resistance showed that this transducer fired at a level above two million ohms. As mentioned above, constant ignition delay values are attained at resistance levels of above 200,000 ohms so that the Berkeley transducer fires well into this constant value region. The values in Table II are for RFNA as the oxidizer, a temperature of 75°F, and a drop height of 6.0 millimeters. (See following discussion).

Table XV
Ignition Delay as a Function of Probe Height

	<u>Height of Probe Above the</u> <u>Point of the Conical Fuel Cup (inches)</u>							
	<u>1</u>	<u>1-3/4</u>	<u>2-3/4</u>	<u>3-3/4</u>	<u>4-3/4</u>	<u>5-3/4</u>	<u>6-3/4</u>	<u>7-3/4</u>
Methyl Disulfide	2.7	3.5	5.7	20.4	28.4	31.4	31.7	105
Triethylamine	4.2	9.7	24.1	-	23.6	-	-	34
Shell-Dioxaphosphalane	1.8	2.0	1.9	-	2.3	-	2.9	-
Methyl divinyl acetylene	2.3	2.4	10.4	-	11.6	-	10.5	-

The triethylamine and the methyl divinyl acetylene seemed to attain constant values above heights of 2-3/4 inches. The low time values below this level is probably due to splashing of the probe. The Shell Dioxaphosphalane remained essentially constant at all heights, while the methyl disulfide gradually increased in value as the probe was raised. This latter result indicates that either the rate of oxidation or the velocity of the combustion gases up the cylinder, or both, might be important factors in the recorded ignition delay values. The values in Table XV for the 7-3/4 inch level can not be relied upon since this is near the top of the cylinder and end effects might come into play.

The distance through which the cylindrical tester falls after the trigger block has been pulled out has been found to affect the ignition delay values. As this distance is increased, the ignition delay values have been found to decrease. The cause of this has been attributed to the cylindrical tester attaining a higher velocity as it is dropped through a greater distance. As it hits the oxidizer in the bottom of the tester block, the oxidizer is forced through the ports at a greater velocity than if the cylindrical tester had fallen through a shorter distance. As a result of the oxidizer hitting the fuel with a greater velocity, a more intimate and quicker mixing of the two liquids is obtained and a shorter ignition delay results. When the cylindrical tester is dropped through a short distance, the velocity of the oxidizer hitting the fuel is reduced, and it takes longer for the fuel and oxidizer to mix thoroughly enough to react.

A measure of the oxidizer velocity is the instrument factor. This factor is the time required for the oxidizer to travel from the "start" probe to the center of the fuel cup. Figure 9 is a plot of the instrument factor as a function of the distance through which the cylindrical tester falls after the trigger has been released. This distance has been called the "drop height." As can be seen, the factor attains close to a constant value at drop heights greater than about 10 millimeters. This indicates that the velocity of the cylindrical tester, at the time it hits the oxidizer, has attained approximately a constant value at this drop height.

It was found that when ignition delay values were run at high drop heights, the "stop" probe had to be raised in order to prevent the splashing of fuel onto the probe from tripping the stop channel prematurely.

Table XVI shows the effect of the drop height on two different fuels. The Berkeley transducer was used, the "stop" probe was 2-1/4 inches above the point of the fuel cup. The ignition delay values, in milliseconds, are the average of at least two runs in each case. Two drop heights were used.

The values of ignition delay that we consider to be most significant were obtained using a drop height of 6.0 millimeters. A series of runs that were made on the six compounds in question at 75°F, with a drop height of 10.5 millimeters and the "stop" probe at 3 inches above the point of the fuel cup gave ignition delay values essentially the same as those obtained at the 6.0 mm drop height.

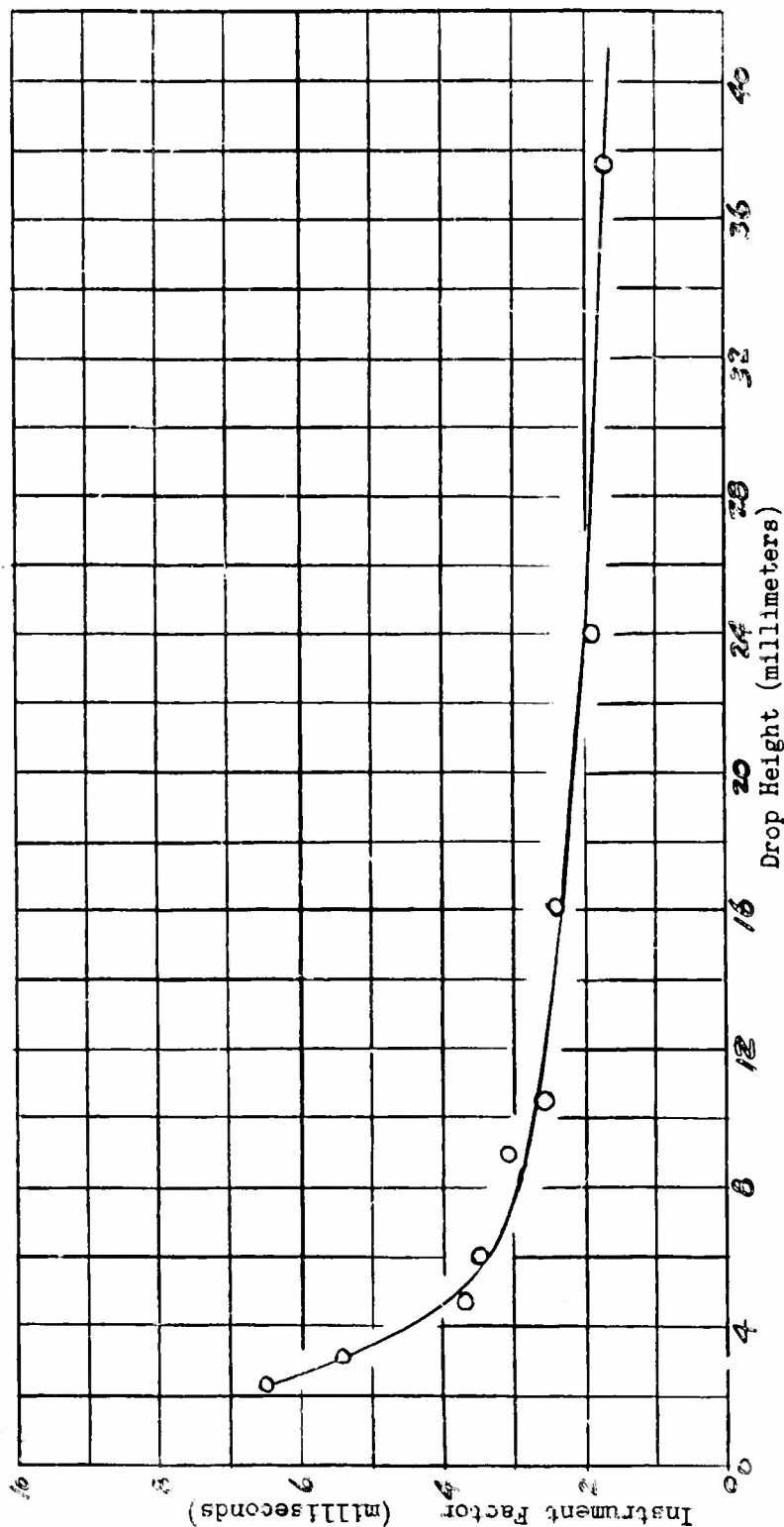


Figure 9
EFFECT OF DROP HEIGHT ON IGNITION DELAY
(INSTRUMENT FACTOR VS. DROP HEIGHT)

Table XVI

Effect of Drop Height on Ignition Delay

<u>Methyl Disulfide</u>			<u>Triethylamine</u>		
	<u>Drop Height</u>			<u>Drop Height</u>	
<u>Temp.</u>	<u>6.0 mm</u>	<u>2.3 mm</u>	<u>Temp.</u>	<u>6.0 mm</u>	<u>2.3 mm</u>
-65°F	13.5 ms	22.1 ms	-65°F	38.6 ms	∞ ms
-40°F	4.6	7.6	-40°F	26.4	156.9
32°F	6.8	13.4	32°F	23.4	32.0
75°F	5.2	8.7	75°F	23.6	30.8

APPENDIX B

Method of Extending Charts of Hottel, et al (1)

About half of the acetylenic compounds considered as bipropellents have flame and exhaust temperatures above the range given on the charts by Hottel, et al (of Table IV). This is true particularly of the charts given in Figures 29, 31 and 32 of Hottel; consequently a reliable and rapid method for extrapolating these charts was required. The graphical method of smoothing and extrapolating data of T. R. Running is such a method. (12)

Running's procedure consists of first getting the curve of the first derivative as a series of connected straight line segments. In smoothing data it is only necessary to integrate the derived curve over the desired range and add the result to initial value, appropriately determined. In extrapolating data by Running's method the derived curve is extrapolated as a straight line and then proceed as for smoothing data. In the present application the extrapolation was very simple as in every case the derived curve was a single straight line vs. temperature and the extrapolation for an additional 400 degrees

- (1) Hottel, H.C., Williams, G.C., Satterfield, C.N.
Thermodynamic Charts for Combustion Processes, Part One.
John Wiley and Sons, New York 1949
- (12) Perry-Chem.Eng. Handbook 3rd Ed. P. 90-92
McGraw Hill, New York 1950

Kelvin was very simple and accurate. Before extrapolating any of the charts they were cross smoothed against the interpolation parameter at constant temperature for a number of temperatures. These smoothed values were then smoothed and extrapolated vs. temperature at constant parameter values. The original chart of Figure 30 given by Hottel et al covers a broad enough range so that it can be used directly with the charts of extended temperature range.

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