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DISTRIBUTION A
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ACETYLENIC COMPOUNDS
FOR
ROCKET FUELS

PREPARED FOR
OFFICE OF NAVAL RESEARCH
AND
BUREAU OF AERONAUTICS, DEPT. OF THE NAVY
CONTRACT NO. NONR-285(04)
PROJECT NO. NR 092-159
October 15, 1951

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

Dear Sir:

I should like to submit for your inspection and approval the second bimonthly report under the subject contract covering work done in the period August - September, 1951.

Very truly yours,

[Signature]

John Happel
Project Director

JH:jt
cc to: Chief, Bureau of Aeronautics
Commanding Officer
Office of Naval Research
Bimonthly Report No. 2  October 15, 1951
For the period August - September, 1951

ACETYLENIC COMPOUNDS FOR ROCKET FUELS
Prepared for the Office of Naval Research
Contract Nonr-285(04)
N. R. - 092 - 159

Chase Y. Amick
Associate Project Director

Project Director

Research Division, College of Engineering
New York University
Report No. 175.2
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SUTLJARY

Based on the program outlined in the first report a number of acetylenic compounds were selected for synthesis, using processes capable of commercial development at a reasonable cost. The proposed processes are explained. Three acetylenic alcohols and three acetylenic hydrocarbons of varied structure are being tested evaluated.

The physical properties as determined for the three acetylenic alcohols are reported. Specific impulse values for 15 representative acetylenic compounds were calculated, and the compounds are listed in order of decreasing S.I. values.
PREPARATION OF COMPOUNDS

As outlined in the first progress report, compounds of potential interest were to be made by reactions capable of reduction to an economical industrial process. Starting materials were limited in general to cheap chemicals, readily obtainable. The compounds prepared for evaluation, and the means of preparation, were as follows:

Addition of Acetylene to Ketones and Aldehydes

This reaction, the so-called ethinylation process, produces acetylenic alcohols as end products. It can be carried out either in high pressure equipment, or at low pressures using special solvent systems.

High Pressure - The high pressure synthesis works best for low molecular weight aldehydes, and General Aniline in this way makes propargyl alcohol and butynediol from acetylene and formaldehyde. Samples of both of these compounds were obtained from General Aniline; the propargyl alcohol to be evaluated as a fuel and the butynediol to be used to prepare diacetylene.

Solvent Systems - The solvent systems used to prepare acetylenic alcohols fall into two main classes:

1. Oxygenated solvents, using KOH as a catalyst.
2. Liquid ammonia, with sodium as catalyst.
Both of these techniques were used to produce acetylenic alcohols:

1. **Oxygenated solvents** - There are several variations of this process. Weizmann’s patents (1,2) describe the use of solvents as ethylene glycol dialkyl ether and other ether-type solvents. A carbonyl compound and acetylene or solid calcium carbide are the reactants. Alkali metal hydroxides are used as catalysts.

   Other solvents suggested for the reaction are dimethyl formal (3), diethyl aniline (3), and a xylene-butanol mixture (4).

   The above processes were tested, using several combinations of starting materials, in an effort to evaluate the effect of the variables. When calcium carbide was used rather than acetylene gas, the reaction proceeded very slowly, and high yields of the symmetrical acetylenic glycol (two molecules of ketone reacting) were obtained along with the acetylenic alcohol. Yields are reduced in this reaction by condensations of the ketone with itself under the influence of the alkali catalyst.

   The best yield obtained was with the xylene-toluene solvent and acetone reacting with acetylene;
a 35% yield of the acetylenic alcohol 3-methyl-1-butylene-3-ol was obtained.

Several other aldehydes used as starting materials gave little or no product. For example, furfural polymerized under these reaction conditions to a rubbery polymer.

2. Liquid ammonia - Here liquid ammonia is used as a solvent. Sodium acetylide, which is quite soluble in liquid ammonia, adds readily to aldehydes and ketones in this medium. The method is inherently more expensive than the use of organic solvents, but the reaction proceeds more rapidly and in better yields.

Three representative acetylenic alcohols obtained through the above ethynylation reaction were selected for test evaluation:

\[
\begin{align*}
\text{H=CH-CH}_2\text{OH} & \quad \text{propargyl alcohol} \\
\text{CH}_3 & \\
\text{H}_3\text{C-C=CCH} & \quad \text{3-methyl-1-butyne-3-ol} \\
\text{O} & \\
\text{CH}_3 & \\
\text{CH}_2=\text{CH-C=CCH} & \quad \text{3-methyl-4-pentene-1-yne-3-ol} \\
\text{O} & \\
\end{align*}
\]
Dehydration of Acetylenic Alcohols

Of considerable interest are the olefinic acetylene hydrocarbons obtained from the acetylenic alcohols and glycols by dehydration.

The dehydration is most easily accomplished in the laboratory by slowly feeding the alcohol into a bath of acetic anhydride kept at about 100°C; the acetylenic hydrocarbon produced is distilled continuously from the mixture. Yields are of the order of 35%, but higher yields could undoubtedly be obtained commercially by use of an improved dehydration technique.

Two promising hydrocarbons so prepared are methyl vinyl acetylene and dimethyl divinyl acetylene, prepared from the reaction products of acetone and acetylene. These two hydrocarbons will be tested evaluated:

\[
\begin{align*}
\text{H}_2\text{C}=&\text{C}≡\text{C}≡\text{CH} & \text{3-methyl-3-butene-1-yne} \\
\text{C}_3 \\
\text{H}_2\text{C}=\text{C}=&\text{C}≡\text{C}=\text{CH}_2 & 2,5\text{-dimethyl-2,5 hexadiene-3-yne} \\
\text{CH}_3 & \text{CH}_3 & \\
\end{align*}
\]
Reaction of Sodium Acetyldes and Alkyl Halides

At present the best means of carrying out the reaction of sodium acetyldes and alkyl halides is in a medium of liquid ammonia, because of the solubility of sodium acetyldes in this solvent.

In order to become familiar with the technique, hexyne-1 was prepared from n-butyl bromide and sodium acetylide.

An attempt was made to prepare dipropargyl from ethylene dichloride and sodium acetylide. None was obtained, apparently because of the tendency of 1,2 halogen compounds as ethylene dichloride to dehydrohalogenate in the presence of sodium amide and liquid ammonia. Accordingly, several alternate routes to the synthesis of dipropargyl were attempted:

a) Preparation of diallyl from allyl chloride, formation of diallyl tetrabromide and dehydrohalogenation to dipropargyl.

b) Condensation of 1,3-dichloropropene and dehydrohalogenation of the product to give dipropargyl.

Diallyl was prepared by the above syntheses, but neither route looks promising from a commercial standpoint. However, enough will be prepared to evaluate all its characteristics.
Dehydrohalogenations

The dehydrohalogenation of dihalo compounds by means of KOH dissolved in ethanol or some other organic solvent represents another route to acetylenic compounds. To acquire some practice with the technique, methyl acetylene was prepared from propylene dibromide. The effect of the several variables involved was noted, and a yield of 52% methyl acetylene obtained.

By use of the same technique, diacetylene was prepared from 1,4-dichlorobutyn e

$$\text{ClCH}_2\text{C}≡\text{C}-\text{CH}_2\text{Cl} \xrightarrow{2 \text{KOH}} \text{HC≡C}-\text{C≡CH}$$

The dichlorobutyn e was made from butynediol obtained from the General Aniline Company.

$$\text{HOCH}_2\text{C}≡\text{C}-\text{CH}_2\text{OH} \xrightarrow{\text{SOCl}_2} \text{ClCH}_2\text{C}≡\text{C}≡\text{C}_2\text{Cl}$$

Diacetylene is a tricky compound to handle. It polymerizes very readily, and the polymer is capable of readily forming peroxides, which are explosive. So sensitive is the compound that it cannot be distilled even under vacuum without polymers forming. A considerable amount of time has been spent in developing a procedure which will yield a pure diacetylene. Vacuum sublimation was the best method for preparing a pure diacetylene, as evidenced by melting point curves run on the product.
Diacetylene itself would probably present too many handling problems to be used directly as a fuel. However, it could be used either in mixture with other fuels, or in the form of some of its derivatives.

It is stated that the Germans were able to store diacetylene by dissolving it in a 50% alcohol solution (5) and it is possible that this solution might be used as a fuel.

**Diacetylene Derivatives**

Possible derivatives of diacetylene are being investigated with a view toward commercial synthesis.
TEST EVALUATION

Physical Properties

After the preparation of an acetylenic compound, the compound was distilled and a heart cut fraction selected for the determination of physical properties.

Values were obtained for the series of three acetylenic alcohols selected for test evaluation. Freezing point, density, vapor pressure and boiling point data were obtained readily. The obtaining of viscosity and pour point data still await the arrival of a low temperature bath ordered many months ago.

The measurement of heats of combustion has been beset by certain experimental difficulties caused by the nature of the acetylenic compounds. The use of thin-walled glass bulbs, a standard procedure for volatile liquids, gave rise to erratic burning results in some cases. A consistent value was obtained for 3-pentol using this technique.

The technique now being used is that of Le Tourneau and Wattersen (6), used to report the heat of combustion of certain gasolines. The method uses a nickel steel crucible, with the sample sealed in by placing a piece of Scotch tape over the top, and then making a correction for the tape.
Values

Propargyl alcohol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 25°C</td>
<td>0.9434 grams/cc.</td>
</tr>
<tr>
<td>Boiling point</td>
<td>115°C (760 mm)</td>
</tr>
<tr>
<td>Melting point</td>
<td>-51°C</td>
</tr>
</tbody>
</table>

Methyl butynol (3-methyl-1-butyn-3-ol)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 25°C</td>
<td>0.8538 grams/cc.</td>
</tr>
<tr>
<td>Boiling point</td>
<td>104°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>1°C</td>
</tr>
</tbody>
</table>

3-Pentol (3-methyl-4-pentene-1-ylene-3-ol)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 25°C</td>
<td>0.8832 grams/cc.</td>
</tr>
<tr>
<td>Boiling point</td>
<td>118°C (750 mm)</td>
</tr>
<tr>
<td>Melting point</td>
<td>-30°C</td>
</tr>
<tr>
<td>Heat of combustion (gross)</td>
<td>15,770 BTU/lb.</td>
</tr>
</tbody>
</table>

Values for vapor pressure over a temperature range will be reported graphically in the summary report.

Ignition Characteristics

Firm plans have been approved by the Bureau of Aeronautics for Reaction Motors to test the ignition characteristics of the acetylenic compounds synthesized at New York University. However, it will take approximately 300 ml. of liquid to run the test, and in the case of certain of the compounds, stability tests must first be run before this amount of material is prepared.

Specific Impulse

In calculating values of specific impulse of a liquid fuel for the ideal case of isentropic flow through
the rocket exhaust nozzle, a tedious and time consuming trial and error procedure must be used for the determination of the adiabatic flame temperature, and the composition of the product gases, as affected by dissociation. In order to avoid this procedure, various methods have been devised to eliminate part or all of the trial and error procedure.

One method, described by Huff and Calvert (7) permits the determination of the product gas equilibrium composition (in the C-H-O systems) for temperatures from 2000-5000°K, in two trials by means of specially prepared charts. Since the flame temperature of a propellant is not ordinarily known, several determinations of equilibrium compositions at assumed flame temperatures are required.

A second method by Hottel, Williams and Satterfield (8) permits calculation of the specific impulse of any system containing the four above-mentioned elements without any trial and error calculations. This is made possible by use of fictitious gas compositions and appropriate charts. Unfortunately, however, the charts extend only up to 3200°K while the flame temperatures for acetylenic compounds using O₂ as a fuel are in the range of 3500-4200°K. This means that extrapolation of the Hottel Charts would be required for use in this work.

- 10 -
It was decided that because of the simplicity of the method, it would be used to indicate which of a number of acetylenic compounds might be interesting because of high values of specific impulse. Although the values as calculated early in the program were based on liquid $O_2$ as the oxidizer, they are now being calculated using white fuming nitric acid, at the suggestion of the ONR.
**RESTRICTED**

**ACETYLENIC COMPOUNDS, LISTED IN ORDER OF DECREASING VALUES OF SPECIFIC IMPULSE**

Chamber Pressure, 300 psia  
Exhaust Pressure, 14.7 psia  
O₂/Fuel Ratio in Stoichiometric Proportions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Acetylene</td>
<td>HC=CH</td>
</tr>
<tr>
<td>Methyl acetylene</td>
<td>H₃C=C=CH</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>HC≡C=C≡CH</td>
</tr>
<tr>
<td>Hexatriene</td>
<td>HC≡C=C≡C≡C≡CH</td>
</tr>
<tr>
<td>Hexadiene (diallyl)</td>
<td>HC≡C-CH₂-CH₂-C≡CH</td>
</tr>
<tr>
<td>Cyanoacetylene</td>
<td>HC≡C-CH=CH=CH=N</td>
</tr>
<tr>
<td>Divinyl acetylene</td>
<td>CH₂=CH-C≡C-CH=CH₂</td>
</tr>
<tr>
<td>Hydroxypentadiene</td>
<td>HC≡C=C≡C-CH₂OH</td>
</tr>
<tr>
<td>Phenyl acetylene</td>
<td>C₆H₅C≡CH</td>
</tr>
<tr>
<td>Hexyne</td>
<td>CH₃-(CH₂)₃C≡CH</td>
</tr>
<tr>
<td>Dimethylaminopentadiyne</td>
<td>HC≡C-C≡C-CH₂-N(CH₃)₂</td>
</tr>
<tr>
<td>3-pentol</td>
<td>HC≡C-C≡C-CH=CH₂</td>
</tr>
<tr>
<td></td>
<td>CH₃ \ CH</td>
</tr>
<tr>
<td>Diethylaminopropyne</td>
<td>(C₂H₅)₂NCH₂C≡CH</td>
</tr>
<tr>
<td>Propargyl alcohol</td>
<td>HC≡C-CH₂OH</td>
</tr>
<tr>
<td>Dimethylaminopropyne</td>
<td>(CH₃)₂NCH₂C≡CH</td>
</tr>
<tr>
<td>Methyl butynol</td>
<td>CH₃-C≡C≡CH</td>
</tr>
<tr>
<td></td>
<td>CH₃ \ OH</td>
</tr>
<tr>
<td>Propargyl amine</td>
<td>NC≡C-CH₂NH₂</td>
</tr>
</tbody>
</table>

Compounds at the head of the list will be given preference in the synthesis program.
BIBLIOGRAPHY

(1) Weizmann, Brit. Pat. 580,921 (1946)
(2) Weizmann, Brit. Pat. 573,527 (1945)
(3) Brit. Pat. 544,221 (1942)
(4) U. S. Pat. 2,385,547 (1945)