RESEARCH MEMORANDUM

PRELIMINARY APPRAISAL OF FERROCENE AS AN IGNITING AGENT FOR JP-4 FUEL AND FUMING NITRIC ACID

By Riley O. Miller

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

WASHINGTON

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

PRELIMINARY APPRAISAL OF FERROCENE AS AN IGNITING AGENT FOR JP-4 FUEL AND FUMING NITRIC ACID

By Riley O. Miller

SUMMARY

A preliminary experimental study was made of the properties of ferrocene as a solute and as a suspension in JP-4 fuel, and of the ignition delays of ferrocene - JP-4 mixture with A.F. specification 14104 white fuming nitric acid (WFNA). The investigation covered concentrations of 4 to 10 percent by weight ferrocene, and a temperature range of -40° to 80° F.

The solubility of ferrocene in JP-4 is about 5 percent at room temperature and about 1 percent (extrapolated) at -80° F. The solubility is increased somewhat by increased aromatics content. Undissolved ferrocene particles of 100 mesh and smaller settle rapidly in JP-4.

Clear solutions of 4 and 5 percent ferrocene in JP-4 fuels containing 10 and 25 percent by volume aromatics, respectively, do not ignite with WFNA at room temperature. Mixtures containing 10 percent ferrocene (100-mesh and smaller undissolved particles in suspension) ignited with vigorous persistent flames at room temperature, but did not ignite at -38° F. The ignition delays at room temperature, however, were widely varied; the range from 85 milliseconds to over 1 second perhaps reflected differences in degree of sedimentation.

INTRODUCTION

For several years a demand has existed for an additive that will promote the ignition of hydrocarbon fuels by fuming nitric acid. Several informal reports received at this laboratory have indicated that ferrocene, $Fe(C_5H_5)_2$, may be suitable for this purpose. Ferrocene is a unique chemical in that it contains five-member carbon rings which have some of the properties of the six-member benzene ring; ferrocene thus may be considered to be an aromatic compound (ref. 1). The acid-ignitible properties of certain benzene derivatives are well known; the ignition properties of ferrocene are of speculative as well as practical interest.

An igniting agent to be of maximum usefulness in rocket application should be in a form that can be conveniently injected into the rocket chamber. Ferrocene is a solid at ordinary temperature; if it is to be used in conventional rocket equipment as an additive to hydrocarbon fuel, a study of its solubility and properties as a suspension is required.

An ideal igniting agent should function at low as well as at moderate temperatures, and should be required only in low concentration. A preliminary investigation was made of the properties of ferrocene as a solute and a suspension in JP-4 fuel, and of the ignition delays of these mixtures with A.F. specification 14104 white fuming nitric acid.

PROCEDURE

Solubility. - The solubilities of ferrocene in JP-4 containing 10 and 25 percent aromatics by volume were determined by visually observing the temperature at which ferrocene completly redissolved in a solution of known concentration.

Sedimentation. - Ferrocene was ground in a mortar and passed through a 100-mesh brass sieve. Qualitative comparisons were made of the sedimentation rate of ferrocene suspension in JP-4 (10-percent aromatics) containing no additive and small amounts of oleic acid, stearic acid, castile soap, and aerosol.

Ignition delays. - Ignition delay experiments were conducted in the modified open-cup apparatus described and discussed in references 2 to 4. Clear solutions of 4 and 5 percent by weight ferrocene in JP-4 fuels containing 10 and 25 percent by volume aromatics, respectively, and a mixture of 10 percent by weight ferrocene (100-mesh and smaller undissolved particles in suspension) were investigated with WFNA at room temperature, and 10 percent mixtures also at -40° F. A low-freezing red fuming nitric acid (RFNA) was also used at -40° F.

MATERIALS

Ferrocene. - A small sample of ferrocene received from a chemical manufacturer was used. The melting point was 174° C (345° F) and the boiling point about 240° C (464° F), according to the manufacturer.

JP-4 fuels. - The JP-4 fuel containing 10 percent by volume aromatics was NACA RF 52-288. The JP-4 fuel containing 25 percent by volume aromatics was prepared from RF 52-288 by the addition of 15 percent toluene.

Other properties of RF 52-288 are:

Boiling range, °F	139 to 486
Residue, percent	1.2
Reid vapor pressure, lb/sq in.	2.7
Specific gravity at 60° F	0.776
Hydrogen-carbon ratio	0.168
Net heat, Btu/lb	18,675
Aniline point, °F	136.8
Viscosity at 100° F, centistokes	0.935

Acids. - The acid used for most of the ignition delay experiments was an A.F. specification 14104 white fuming nitric acid (WFNA). A few experiments were conducted also with a low-freezing red fuming nitric acid (RFNA) containing approximately 3 percent water and 20 percent nitrogen tetroxide. Both acids were stored in aluminum drums.

RESULTS AND DISCUSSION

Solubility of ferrocene in JP-4 fuels containing 10 and 25 percent aromatics. - Solubility data are shown as functions of temperature and aromatic content in figure 1. The curves, drawn from the experimental data and the reported melting point, are extrapolated to -80° F. The solubility of ferrocene in JP-4 is shown to be about 5 percent by weight at room temperature and about 1 percent at -80° F (approximately the maximum specified freezing temperature for JP-4). The solubility increases somewhat with aromatic content.

Sedimentation and stability. - Qualitative experiments show that the sedimentation rate of ferrocene (100-mesh and smaller particles) is quite rapid. Most of the material settles from a 1-inch column in about 2 minutes. None of the additives, oleic acid, stearic acid, castile soap, or aerosol, had an appreciable effect on the sedimentation rate.

A small amount of light-colored finely-divided precipitate was observed to form in clear solutions of ferrocene, apparently as a result of exposure to air. The additives did have some effect on this precipitate. Ferrocene which had settled out of JP-4 and had stood for over a week was found to have formed a cake that required considerable agitation to break up.

Ignition experiments. - The results of the ignition experiments are shown in table I. The clear solution of 4 and 5 percent by weight ferrocene in JP-4 fuels containing 10 and 25 percent aromatics, respectively, did not ignite at room temperature. Bubbling reactions occurred for both fuels, the more vigorous reactions occurring with the 5 percent ferrocene in the 25 percent aromatic fuel. This fuel also produced a more nearly homogeneous mixture with the acid.

Other ignition experiments showed that a 10 percent by weight partially suspended mixture of ferrocene (100 mesh or smaller) would ignite with a sustained vigorous flame at room temperature when A.F. specification WFNA was used. The delays, however, were long and variable ranging from 85 milliseconds to more than 1 second (four trials). The variation may, in part, be caused by differences in the amount of sedimentation, in spite of the fact that an attempt was made to minimize this difficulty by vigorously shaking the entire apparatus just prior to firing. Four similar experiments at -40° F did not produce ignition with WFNA, but a flame was obtained with low-freezing RFNA after a delay of about 30 seconds (1 out of 2 trials).

Appraisal. - These experiments show that ferrocene is not soluble enough in JP-4 to make the fuel self-igniting, and 10-percent mixtures containing suspended ferrocene, although hypergolic at room temperature, did not ignite at -38° F. The data indicate that, from an ignition standpoint, the use of ferrocene *per se* as an additive to JP-4 fuel is not promising. Its use to promote better combustion, however, remains unexplored. The possibility also exists that derivatives of ferrocene may have better solubility and ignition characteristics than ferrocene itself, or that ignition characteristics of small amounts of ferrocene may be augmented by other agents.

With regard to further exploitation of ferrocene with hydrocarbon fuels in rockets, the following chemical approaches should be considered:

1. Preparation and study of the properties of ferrocene derivatives. For example, if the methyl derivatives are analogous to phenyl compounds, they will have lower melting points and, consequently, higher solubilities in hydrocarbons. Amino derivatives may have even more desirable ignition characteristics than ferrocene itself.

2. Investigation of possible synergistic effects on acid ignition between small amounts of ferrocene and other additives dissolved in hydrocarbon fuels.

3. Stabilization of ferrocene suspensions in hydrocarbon fuels by means of gelling agents.

A fair appraisal of suspended ferrocene as an igniting agent is difficult because of a lack of ignition data on other suspensions in hydrocarbons. There is some evidence for the supposition that igniting agents that are relatively insoluble in hydrocarbons and occur as suspensions may produce ignition more readily than those agents that are totally dissolved. An objective approach, therefore, would be to investigate suspensions of other agents, as well as ferrocene; examples of agents of this type are hydrazine and the alkali metals.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 25, 1953

REFERENCES

1. Woodward, R. B., Rosenblum, M., and Whiting, M. C.: A New Aromatic System. Jour. Am. Chem. Soc., vol. 74, no. 13, July 10, 1952, pp. 3458-3459.

2. Miller, Riley O.: Low-Temperature Ignition-Delay Characteristics of Several Rocket Fuels with Mixed Acid in Modified Open-Cup-Type Apparatus. NACA RM E50H16, 1950.

3. Miller, Riley O.: Ignition-Delay Characteristics in Modified Open-Cup Apparatus of Several Fuels with Nitric Acid Oxidants within Temperature Range 70° to -105° F. NACA RM E51J11, 1951.

4. Ladanyi, Dezso J., and Miller, Riley O.: Comparison of Ignition Delays of Several Propellant Combinations Obtained with Modified Open-Cup and Small-Scale Rocket Engine Apparatus. NACA RM E53D03, 1953.

TABLE I. - IGNITION CHARACTERISTICS OF FERROCENE - JP-4 MIXTURES

WITH A.F. SPECIFICATION 14104 WHITE FUMING NITRIC ACID

Fuel mixture	Temperature, °F	Ignition delay, milliseconds	Qualitative observations
Clear solutions			
4 Percent by weight ferrocene in JP-4 containing 10 percent by volume aromatics	72 72	[a]NI NI	Bubbling reactions, red fumes; acid and fuel in two layers
5 Percent by weight ferrocene in JP-4 containing 25 percent by volume aromatics	72 72	NI NI	Bubbling reactions more vigorous; less separation of acid and fuel
Suspensions			
10 Percent by weight ferrocene in JP-4 containing 10 percent by volume aromatics (100-mesh and smaller particles in suspension)	77 77 77 77	85 160 $\approx$85 $>$1000	Vigorous prolonged flames. Liquid residue remaining formed a suspension in water
	-38 -38 -38 -38	NI NI NI NI	No bubbling noticed, no noticeable separation of fuel and acid
	[b]-38 [b]-38	$\approx$30 sec NI	Sustained bright flame No ignition

[a]No ignition.

[b]Data obtained with low-freezing red fuming nitric acid.

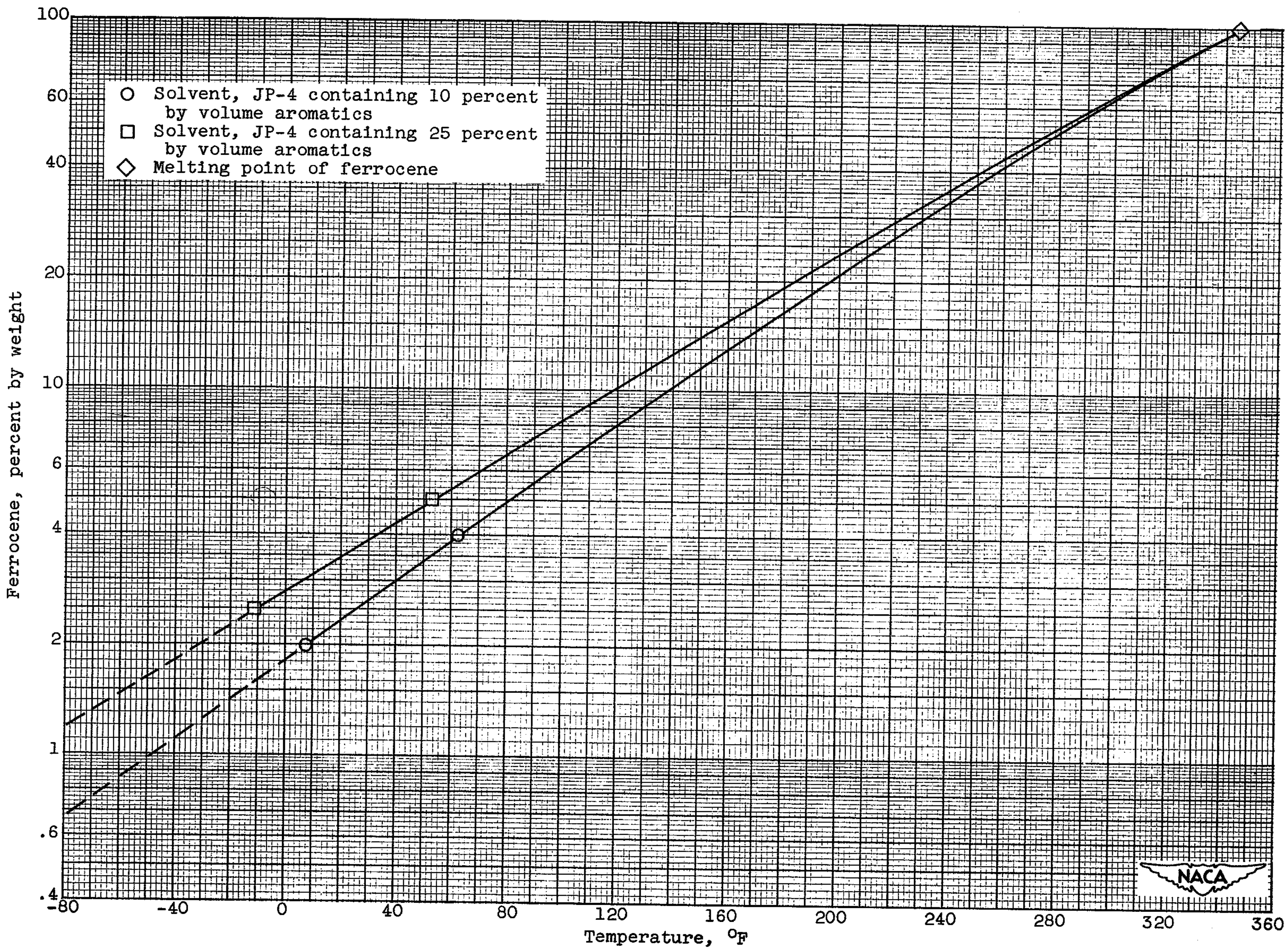

Figure 1. - Solubility of ferrocene in JP-4 fuels containing 10 and 25 percent by volume aromatics.

CONFIDENTIAL

RESEARCH MEMORANDUM

PRELIMINARY APPRAISAL OF FERROCENE AS AN IGNITING AGENT

FOR JP-4 FUEL AND FUMING NITRIC ACID

Riley O. Miller

Riley O. Miller
Aeronautical Research Scientist
Propulsion Systems

Approved:

John L. Sloop

John L. Sloop
Aeronautical Research Scientist
Propulsion Systems

for L. C. Gibbons

Walter T. Olson
Chief, Fuels and Combustion
Research Division

sks-8/25/53

Fuels - Properties, Physical and Chemical 3.4.2

Fuels - Rockets (Includes Fuel and Oxidant) 3.4.3.3

Combustion Research - General 3.5.1

Miller, Riley O.

Abstract

A preliminary experimental study was made of the properties of ferrocene as a solute and as a suspension in JP-4 fuel, and of the ignition delays of ferrocene - JP-4 mixture with A.F. specification 14104 white fuming nitric acid (WFNA). The investigation covered concentrations of 4 to 10 percent by weight ferrocene, and a temperature range of -40° to 80° F.

The solubility of ferrocene in JP-4 is about 5 percent at room temperature and about 1 percent (extrapolated) at -80° F. The solubility is increased somewhat by increased aromatics content. Undissolved ferrocene particles of 100 mesh and smaller settle rapidly in JP-4.

Clear solutions of 4 and 5 percent ferrocene in JP-4 fuels containing 10 and 25 percent by volume aromatics, respectively, do not ignite with WFNA at room temperature. Mixtures containing 10 percent ferrocene (100-mesh and smaller undissolved particles in suspension) ignited with vigorous persistent flames at room temperature, but did not ignite at -38° F. The ignition delays at room temperature, however, were widely varied; the range from 85 milliseconds to over 1 second perhaps reflected differences in degree of sedimentation.