NASA CR - 159480
EXXON/GRUS. 1KWD. 78

HIGH PERFORMANCE, HIGH DENSITY HYDROCARBON FUELS

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EXXON RESEARCH AND ENGINEERING COMPANY

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWARD

The research described in this report was performed at Exxon Research and Engineering Company, Linden, New Jersey and Contract NAS 3-20394 with Mr. J. J. Notardonato, NASA-Lewis Research Center as Project Manager.

The period of performance for the technical portion of the program was 12 April 1977 to 12 June 1978.

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I. SUMMARY

I.1 Purpose and Scope

This research was conducted for NASA's single stage to orbit transportation program (SSTO). The major objectives were to identify and evaluate new high performance, high density hydrocarbon fuels for mixed mode propulsion systems which are being considered for SSTO applications. The desirable features for such fuels are high specific impulse (I_{sp}), high density and low cost. A secondary objective was to identify potentially low cost hydrocarbon fuels with high I_{sp} regardless of density. For some applications I_{sp} alone may be the most important parameter. The initial objective was to identify a minimum of 25 potential candidates, estimate their critical properties and select the 10 best for further study.

I.2 Method of Approach

Two approaches were investigated (1) synthesis of pure compounds and (2) identification of chemical plant and refinery streams with energy dense components. Major emphasis was placed on the second of these since such sources are potentially much more cost effective. The candidates were ranked on the basis of merit index $\bar{\rho}\, I_{sp}{}^3$ (where $\bar{\rho}$ is propellant, not fuel, density). This is a strictly arbitrary ranking parameter designed to give proper weight to the two critical factors for a fuel where density is of primary importance. The merit index was estimated from the known or assumed compositions of the candidate fuels. Samples of the 10 top candidates were obtained or synthesized and evaluated by standard methods of analysis. This was done to confirm the estimated merit index and to further evaluate the top 10 fuels by means of other critical properties. RP-1 (kerosene) was employed as a basis for comparison in all tests. An evaluation of production costs was made on all 10 top candidates. For some, this amounted to no more than an estimated transport cost from production point to NASA-Lewis. For pure compounds, detailed synthesis schemes were analyzed and costed by usual methods. In addition, a literature survey was conducted to identify new areas for research in high density fuels.

I.3 Results

A total of 77 candidate fuels were identified as the original screen. These included 13 pure compounds, 52 chemical plant streams and 12 refinery streams. The top 10 candidates have densities of 0.94 - 1.02 g/cc and estimated improvements in merit index over RP-1 ranging from 4-8%.

Energy density and physical property measurements confirmed the high volumetric heat content of the top 10 candidates. These range from 400 X 10^5 kJ/m^3 (144,000 BTU/gal) to 447 X 10^5 kJ/m^3 (150,000 BTU/gal). This represents an increase of 8-19% over RP-1. Possible problem areas were indicated in low temperature properties (freezing point and viscosity) and in thermal stability.

Production cost analyses confirmed the low cost of <\$.44/kg for all of the chemical plant and refinery streams. All pure components have a projected cost >\$.44/kg.

The results of the advanced hydrocarbon fuel analysis indicate that high energy pure compounds can be synthesized either by modifying existing compounds to include high energy groups (such as cyclopropyl) or by designing new, highly strained molecules. However, costs for such new fuels would be prohibitively high for the current program. Shale liquids appear to be potential candidates for replacing RP-1 kerosene. However, high nitrogen and oxygen contents may prove troublesome. Coal liquids appear to be possible sources of pure compound candidates including acenaphthene and indenes. Coal liquids are too aromatic and have too high an oxygen content to use directly. Use of additives and carbon slurries afford fuels with high volumetric heat contents but low I_{sp} values because of poor H/C ratios. Use of such techniques may be more useful for other applications (turbine engines, for example).

Methods for improving the thermal stability of energy dense fuels were reviewed. Those showing promise included deoxygenation, control of certain trace impurities, and the use of additives.

I.3.1 High Impulse, Low Density Hydrocarbon Fuels

Several candidate fuels were found that have high I_{sp} values but low densities. These are mostly olefinic side streams from chemical plant operations. Some of these have I_{sp}'s of >300 seconds, significantly better than RP-1. These materials are readily available at costs comparable to kerosene and would have good low temperature properties. On the other hand, thermal stability of such streams could present problems.

I.4 Conclusions and Recommendations

The following conclusions were drawn from the experimental results of this program.

- Candidate high energy, high density hydrocarbon fuels can be found among existing streams and side streams of oil refineries and petrochemical plants. On the basis of cost effectiveness, further development of a fuel based upon such streams is preferred to the synthesis of pure compounds.
- Most promising streams are materials containing branched and/or naphthenic olefins, especially dicyclopentadiene derivatives.

- Possible problem areas in utilizing candidate streams are poor low temperature properties and marginal thermal stabilities.
- Potential methods for overcoming low temperature problems include blending of streams, chemical modification and use of flow improving additives.
- Thermal stability can be improved in some cases by chemical modification, deoxygenation, control of trace impurities and use of additives.

The following additional research is recommended.

- Studies of methods to improve low temperature properties of top candidate fuels.
- Studies of thermal and storage stabilities of candidate fuels (including RP-1) and of methods to improve them.
- Studies of combustion characteristics of candidate fuels.

II. INTRODUCTION

II.1 BACKGROUND AND OBJECTIVES

Mixed mode propulsion concepts are currently being studied for advanced, single stage earth orbital transportation systems for use in the post 1990 time period. These propulsion concepts are based on the sequential and/or parallel use of high density impulse and high specific impulse propellants in a single stage to increase vehicle performance and reduce vehicle dry weight. Specifically, the mixed mode concept utilizes two propulsion systems with two different fuels (Mode 1 and Mode 2) with liquid oxygen as a common oxidizer. Mode 1 engines would burn a high bulk density fuel for liftoff and early ascent to minimize performance penalties associated with carrying fuel tankage to orbit. Mode 2 engines would complete the orbital injection utilizing liquid hydrogen as the fuel. A number of potential fuels have been developed which have bulk densities significantly higher than RP-1 (kerosene). These include non-hydrocarbon fuels such as monomethylhydrazine and synthetic hydrocarbon fuels such as Shelldyne-H (RJ-5). These fuels are attractive on a performance basis but have very high projected costs.

In addition to RJ-5, there are numerous candidate fuels that are potentially attractive for use in advanced propulsion systems. As measured by density impulse, fuels of greater performance than RJ-5 are available. Moreover, fuels of slightly less performance than RJ-5 are obtainable at sufficiently lower costs to make them strong candidates for mixed mode propulsion systems. It was the major objective of this program to identify such candidates, and conduct parametric studies on them to obtain: (1) low cost synthesis processes; (2) data on production process economics; and (3) physical and thermodynamic property data critical to the design of propulsion system components. Final fuel selection would be based on vehicle sensitivity to a fuel cost/performance factor.

A secondary objective of this program was to identify cost effective fuels useful for other propulsion concepts; of particular interest were low cost fuels of high specific impulse regardless of density. This was a result of NASA's shift in emphasis to high I_{sp} fuels which occurred after the program was underway. As a result, certain candidate fuels which would otherwise have been rejected on the basis of low specific gravity were included in the evaluation phase.

II.2 GENERAL METHOD OF APPROACH

The selection and development of a hydrocarbon rocket fuel which has high density, high performance, and acceptable physical, thermodynamic, and chemical properties and, in addition, can be secured at a realistic price is a very difficult problem. There is no single, obvious, easily identified solution. There are, moreover, some very serious bounds on the problem involving raw material cost and availability, and the complexity and cost of synthesis which must be recognized in order to carry out a successful program. A petroleum based fuel such as RP-1 kerosene is inexpensive because it is prepared from a high availability, low cost raw material (crude petroleum) via a highly efficient and simplified processing sequence. Conversely, a fuel consisting of a highly purified chemical, synthesized via a complex procedure and dependent on a costly and limited availability raw material will be very expensive. As a result, the general approach employed was to search for low cost, readily available refinery and chemical plant streams and side streams whose properties indicated that they might possess the dual criteria of high density and high specific impulse. The specific methods of approach, selection criteria and evaluations of candidate fuels are described in the task statement below.

II.3 TASK STATEMENT AND DESCRIPTION

In order to accomplish the program objectives, five tasks were performed:

(1) Fuel Candidate Screening and Selection

(2) Fuel Physical Property Evaluation

(3) Fuel Production Economics

(4) Advanced Hydrocarbon Fuel Analysis

(5) Reports

II.3.1 TASK (1) FUEL CANDIDATE SCREENING AND SELECTION

The objective of this preliminary screening study was to identify a minimum of 25 potential fuels, and select the 10 most promising for additional research. Three sources were explored in the preliminary screen:

- Literature Reports

- Internal proprietary Exxon files and reports.
- Internal experts familiar with Exxon refinery fuel and chemical processes and the compositions of their associated product streams.

By NASA request, several pure compounds were included to serve as bases of comparison:

(1) RP-1 kerosene

(2) RJ-5 (Shelldyne-H)

(3) Tetrahydrotricydopentadiene

(4) Tetrahydrodicyclopentadiene (JP-10)

(5) 1,7-Octadiyne

The candidate fuels were ranked on the basis of merit index defined as

$$\text{Merit Index} = \bar{\rho} \; I_{sp}{}^{3}$$

Where $\bar{\rho}$ = propellant (not fuel) density

I_{sp} = specific impulse for propellant system

The specific impulse (I_{sp}) for each candidate fuel system was supplied by the NASA Project Manager, using the standard computer program,* from the following data:

(1) Density

(2) Heat of formation (ΔH_f; known or estimated)

(3) Molecular formula (known or estimated)

Methods for calculating or estimating ΔH_f are given in Appendix A. The propellant density $\bar{\rho}$ for each propellant system was calculated according to the formula:

$$\bar{\rho} = \gamma_v \, (62.4) \ \text{lb/ft}^3$$

---

*Gordon, S. and McBride, B. J., "Computer Porgram for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations", NASA SP-273 (1971).

Where:

$$\gamma_v = \frac{\gamma_o \gamma_f (1 + m)}{m\gamma_f + \gamma_o}$$

and:

γ_v = specific gravity of the propellant

γ_f = specific gravity of the fuel

γ_o = specific gravity of the oxidizer

m = oxidizer/fuel mixture weight ratio when $CH_r(\ell) + [(2 + r)]\ O_2(\ell) = CO(g) + r/2\ H_2O\ (g)$

It should be noted that these calculations were approximations for purposes of comparing candidate streams. No attempt was made to optimize oxygen/fuel ratios.

Although the merit index was the most important criterion, cost and availability data were also considered in selecting the 10 best fuel candidates for further study in Tasks (2) and (3).

II.3.2 TASK (2) FUEL PHYSICAL PROPERTY EVALUATION

Samples of each of the ten candidates identified were procured or synthesized and evaluated as fuels by measuring the following important properties:

(1) Heat of combustion.

(2) Viscosity at various temperatures.

(3) Freezing Points

(4) Thermal conductivity at various temperatures.

(5) Density (specific gravity) at various temperatures.

(6) Thermal stability.

(7) Distillation curves.

ASTM or ASM standard procedures were used whenever possible. Other methods are described in Appendix B.

II.3.3 TASK (3) FUEL PRODUCTION ECONOMICS

Cost effectiveness is an important criterion for final assessment of fuel value. As a result, this task was added in order to provide accurate cost figures for each of the ten top candidates identified in Task (1). The analyses were based on production rates of both 10 M and 50 M #/yr (4.5 M kg/yr) and included, where appropriate, the following details (1) synthesis routes; (2) raw material costs; (3) catalyst cost (if any); (4) power requirements; (5) transportation costs and, (6) capital expenditures. In most instances, this elaborate analysis was not necessary since the candidate fuel was a side stream or by-product stream from a process designed for another product. In these cases, the analysis included only a realistic selling price for the by-product plus transportation costs from production site to NASA-Lewis Research Center.

II.3.4 TASK (4) ADVANCED HYDROCARBON FUEL ANALYSIS

This task is aimed at identifying promising areas of research for development of new or improved hydrocarbon fuels. A literature review and analysis of reported data and data generated in this project were used. Areas of specific interest included:

1) An analysis of methods for synthesizing highly energetic hydrocarbons (high I_{sp}) and/or high density hydrocarbons (greater than 1.15 gms/cc) that would be suitable for use as fuels in rocket propulsion systems.

2) An analysis of liquid derivatives of coal and shale oil as a potential source of hydrocarbon fuels for rocket propulsion systems.

3) An analysis of fuel additives which can increase both the density and volumetric heat of combustion of the base fuels.

4) An analysis of fuel additives or modifications to improve the viscosity and thermal stability of the fuel.

II.3.5 TASK (5) REPORTS

In addition to this Final Report, a total of 11 Monthly Reports were prepared.

III. RESULTS AND DISCUSSION

III.1 TASK 1 FUEL CANDIDATE SCREENING AND SELECTION

III.1.1 METHOD OF APPROACH - SELECTION GUIDELINES

The criteria for selection of candidate fuels were

- Density (ρ)
- Specific impulse (I_{sp})
- Merit index ($\bar{\rho}\ I_{sp}{}^3$ where $\bar{\rho}$ = propellant density)
- Cost

The use of merit index ($\bar{\rho}\ I_{sp}{}^3$) is somewhat arbitrary. It represents a weighting factor which reflects the fact that single stage to orbit (SSTO) vehicles are more sensitive to specific impulse than propellant density (1). The sensitivity factors vary for different applications and, will be discussed below, I_{sp} became more important as new sensitivity analyses were made.

III.1.1.1 FACTORS AFFECTING I_{sp} VALUES (see ref. 1)

The performance of a hydrocarbon as a rocket fuel with liquid oxygen depends on its composition and heat of formation, as well as density. The molecular composition of a hydrocarbon can be represented in general as C_nH_m and its empirical composition as CH_r where r = m/n = H/C atom ratio. In general with all other factors constant, specific impulse increases with increasing r because the average molecular weight of the exhaust products decreases and the heat of formation of H_2O is more strongly negative than the heat of formation of CO. Specific impulse also increases with increasing heat of formation of the hydrocarbon fuel. Generally the specific impulse will increase with increasing heat of formation at constant r or with increasing r at constant heat of formation. For the saturated hydrocarbons in the RP-1 boiling range, the value of r is close to 2 and the heat of formation is approximately -6 K calories/gm atom. Higher (more positive) values of the heat of formation can be obtained by introducing chemical unsaturation in the form of double or triple carbon to carbon bonds into the molecule or by introducing structural strain into the molecule or by introducing structural strain into the molecule with polycyclic ring structures. (See Section IV). In each case, however, an increase in heat of formation is achieved at the expense of a decrease in r, and the increase in specific impulse is less than would have been achieved if the heat of formation had been increased at constant r. This effect is illustrated in Figure 1 (9). Thus, trade offs had to be made between heats of formation, r and density in selecting promising sources for

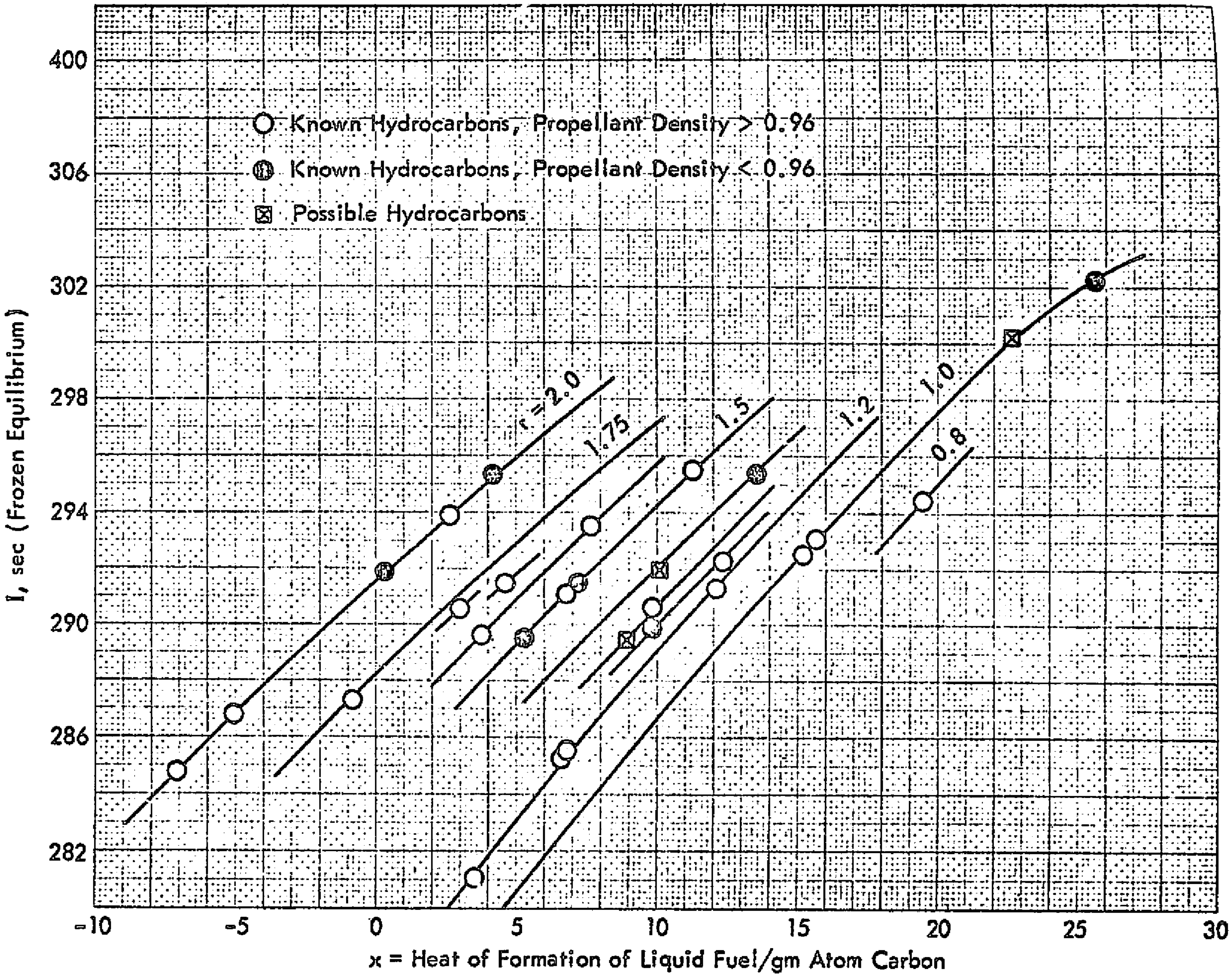


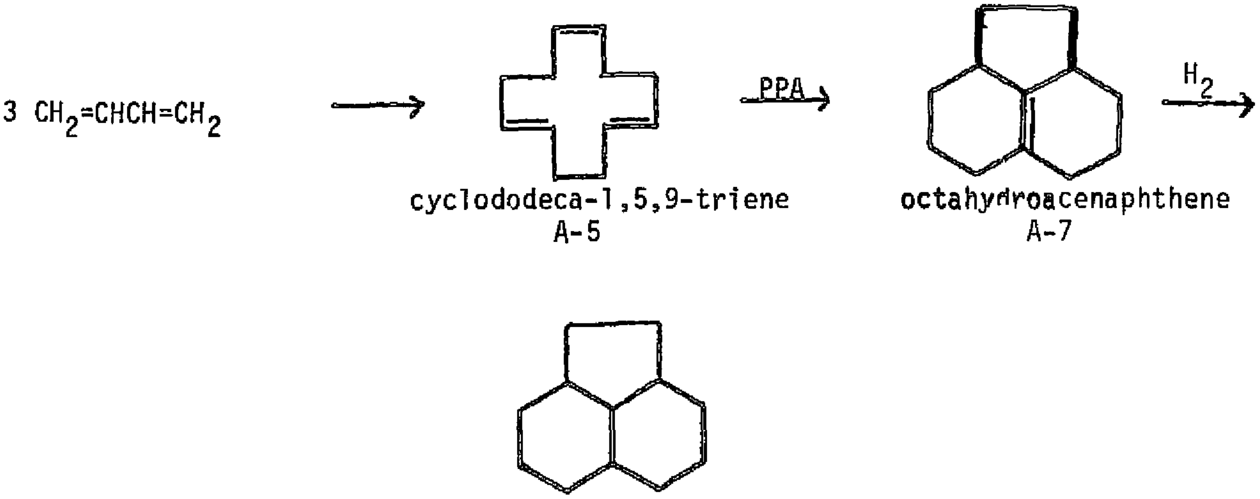
Figure 1.* SPECIFIC IMPULSE vs x AT VARIOUS VALUES OF ATOM RATIO H/C = r Stoichiometric

*Taken from reference 9.

low cost, high energy fuels. A partial list of compounds illustrating the effects of chemical structure on these critical properties is shown in Table 1. The best compromises are certain types of substituted aromatics (e.g., tetralins and indenes)certain types of naphethenes (cyclic paraffins), diolefins and especially cyclodiolefins such as dicyclopentadienes.* As a result, refinery and chemical plant streams as well as pure compound candidates were sought which would be rich in these types of structures. Both the open literature and Exxon in-house resources were searched. A total of 77 candidates were identified. These were divided into three categories: A. pure compounds, B. chemical plant streams and C. refinery streams. These are discussed separately below. Complete compositions and critical properties are given in Appendix C.

III.1.2 PURE COMPOUND CANDIDATES

A total of 13 pure compounds were identified as having potentially high energy values along with reasonably high specific gravities. Of these, six were ruled out as candidates on the basis of complex synthesis methods and extremely high cost. The remaining seven are shown in Table 2 along with certain key properties. The complete list is given in Appendix A. All compounds in Table 2 would fall into the medium to high cost category (see Section III.3). However, they were included in the preliminary screen either because they have special properties which are of potential interest to NASA or because they might serve as a basis of comparison for the less well known chemical plant and refinery streams. Compounds A-1 to A-4 have been identified previously as being promising fuels for mixed mode propulsion systems (1). Compounds A-6 and A-7 were developed by Exxon Research from cyclododecatriene (CDT, compound A-5), CDT is produced by trimerization of butadiene which, after an unusual rearrangement (2) and hydrogenation, yields compounds A-6 and A-7. Experimental details are given in Appendix F.



cyclododeca-1,5,9-triene
A-5

octahydroacenaphthene
A-7

Decahydroacenaphthene
A-6

---

* Note that data from Table 1 indicate that acetylenes would be quite promising high density fuels. However, their extreme instability and hazardous nature ruled them out as candidates for this program.

The final product, decahydroacenaphthene (DHA, Compound A-6) has attractive properties (Table 2) and may be available at modest cost. Particularly noteworthy is the H/C ratio of 1.67 and high heat of combustion (18,263 BTU/lb.). In addition, the intermediate compounds CDT (A-5) and octahydroacenaphthene (OHA, A-7) which should be obtainable at significantly lower cost also appeared to be potentially attractive. The intermediate OHA has properties very similar to DHA with a higher density.

III.1.3 CHEMICAL PLANT STREAMS

A total of 18 chemical plant streams were identified as potential candidates or precursors for high density fuels. These are shown in Table 3. They represent a wide range of compound mixtures which have either high specific gravities or the potential of possessing high energy values or both. Recent analyses for most of the streams were obtained. These are shown in Appendix C. The properties of the individual compounds and some estimated properties of these streams are given in Appendix A.

It should be noted that some of the streams, especially B-1 to B-3 are most likely useful as additives to other streams than as a raw materials source. This is because of their low density, limited availability and possible instability. B-1 is rich in potentially energetic acetylenic compounds and is extremely unstable. As a result, it was eliminated from consideration. B-2 and B-3 are of potential value as blending agents with other streams. The streams B-4 to B-7 are rich in dicyclopentadiene (DCP) methyl dicyclopentadiene (MDCP) and various co-dimers. These streams, however, are available at significantly lower cost than pure DCP or MDCP. A number of streams shown have densities exceeding 1.0. Some of these streams, especially B-15 to B-18 have not yet been thoroughly characterized and accurate data on compositions are not available. Still, enough was known for calculation of an approximate heat of formation. This information was sufficient for first phase screenings as described in Section III.1.5. The streams, B-15 to B-18, because of their aromatic character, have very high estimated heats of formations and specific gravities but low H/C (r) values. As a result of these low r values, they are less attractive than streams B-2, B-3 and B-4. The streams B-7 to B-14 all have only marginal estimated heats of formation. They were, therefore, eliminated in the preliminary screen.

III.1.3.1 MODIFIED CHEMICAL PLANT STREAMS

Three relatively inexpensive processing steps were considered as possible ways to improve the properties of chemical plant streams:

- Mild hydrogenation
- Distillation
- Blending of streams

TABLE I. EFFECTS OF STRUCTURE ON CRITICAL PROPERTIES

COMPOUNDS	DENSITY (g/cc)	H/C (r)	ΔH_f (kcal/mole)
N-Heptane	.680	2.25	-7.2
Methylcyclohexane	.773	2.0	-6.7
1-Heptane	.701	2.0	-3.65
Toluene	.872	1.1	+0.41
2-Methyl-1,5-hexadiene	.725	1.7	+0.78
Methylcyclohexadiene	.82	1.4	+0.14
1-Heptyne	.738	1.7	+2.52
Dicyclopentadiene	.985	1.2	+3.0
1,7-Octadiyne	.81	1.25	+9.8

TABLE 2. MOST PROMISING PURE COMPOUND CANDIDATES

DESIGNATION	COMPOUND	DENSITY (G/CC)	H/C RATIO	$\Delta H^{\circ}_{f,298}$ (ℓ)/n (kcal/gram atom C)
A-1	Shelldyne-H; RJ-5	1.08	1.29	+0.93(1) +2.5(2) +3.546(3)
A-2	Tetrahydrotricyclopentadiene	1.04	1.47	-2.0(2)
A-3	exo-Tetrahydrodicyclopentadiene (JP-10)	0.94	1.50	-0.9(2) -1.3(4)
A-4	1,7-Octadiyne	0.81	1.25	+9.8(2) +9.863(3)
A-5	Cyclododecatriene	0.89	1.50	+1.2(4)
A-6	Decahydroacenaphthene	0.94	1.67	-3.3(5)
A-7	Octahydroacenaphthene	0.96	1.50	-2.4(5)

---

(1) "Advanced High Pressure Engine Study for Mixed-Mode Vehicle Applications", NASA CR-135141, January, 1977.

(2) "High Density Propellants for Single Stage to Orbit Vehicles", NASA TMX-73503, December, 1976.

(3) "High Energy, Hydrocarbon Booster Fuels, A Review and Theoretical Study", Shell Development Company, NAS 7-410, September, 1966.

(4) Our estimate.*

(5) From measured heats of combustion.

*See Appendix A and S. W. Benson, et al., Chem. Reviews 69, 279 (1969).

TABLE 3. CHEMICAL PLANT STREAMS AS CANDIDATES FOR HIGH DENSITY FUELS

DESIGNATION	DENSITY G/CC (1)	H/C RATIO(2)	ΔH_{f298}(2)	MAJOR COMPONENTS
B-1	0.65 - 0.75	1.44	+8.6	Light acetylenes
B-2	0.70	1.59	+2.37	Isoprene, pentadiene; other olefins
B-3	0.65	1.49	+3.21	Cyclopentadiene, piperylene
B-4	0.99	1.20	+3.43	>85% Dicyclopentadiene (DCP)
B-5	0.96	1.33	+0.54	Methylcyclopentadiene dimer (MDCP)
B-6	0.96	1.[illegible]9	+2.33	DCP and DCP-MDCP co-dimers
B-7	0.95	1.19	+1.74	DCP, MDCP, co-dimers
B-8	1.01	1.00	+1.20	Naphthalenes and heavy aromatics
B-9	1.02	0.97	+2.41	DCP-MDCP co-dimers, naphthalenes
B-10	1.00	1.16	+1.17	Indenes and naphthalenes
B-11	0.88	1.21	+0.87	Indenes
B-12	0.90	1.23	+1.57	Indenes and xylenes
B-13	0.88	1.27	+0.25	C_8 - C_{10} Aromatics
B-14	0.96	1.32	+0.45	Heavy aromatics
B-15	1.10	0.93	+6.41	Heavy aromatics and saturates
B-16	1.10	0.60	+3.62	Heavy aromatics and saturates
B-17	1.10	0.53	+4.54	Heavy aromatics and cyclics
B-18	1.00	0.74	+2.55	Methylnaphthalenes

---

(1) Measured

(2) Estimated

Use of one or more of these techniques would be expected to result in the following desirable changes in stream characteristics.

- Increased H/C ratio
- Enhanced thermal stability
- Enhanced stability toward autoxidation and polymerization
- Improved viscosity and low temperature flow properties

Unfortunately, these advantages are usually partially offset by concomitant undesirable changes in stream characteristics such as

- Lower specific gravities
- Lower I_{sp} values (in many instances)

Thirty-four modified chemical plant streams were investigated. Properties of some of these are shown in Table 4. Others are given in Appendix A. These modified streams show improved H/C ratios but have reduced ΔH_f and specific gravities to the point that little is gained. The candidate B-22 seems to have improved energy properties compared to the parent stream, B-5. However, the improvement was not enough to render B-22 a superior candidate. Some olefinic streams may be stabilized by hydrogenation with only a minor loss in overall energy. This is particularly true for stream B-4. Streams B-19 and B-20 have similar energy properties to the parent stream, B-4, and would likely be more stable. In addition, B-20 appears to possess better low temperature properties than B-4. This is discussed further in Section III.2.

The effects of blending light, energetic streams with streams of higher density are shown in Appendix A. This process resulted in new streams of intermediate properties. However, none were significantly superior to other, unprocessed streams.

III.1.4 CANDIDATE REFINERY STREAMS

A total of 12 refinery streams were identified as promising candidates for high density fuels. These are given in Table 5. They were selected on the basis of high specific gravity and naphthene content. Naphthenes are good compromises between the high density, low H/C ratios exhibited by aromatic compounds and high H/C ratios but low densities typical of normal and branched paraffins. In addition, consideration was given to future availability in quantities (20 M kg/yr; 50 M lbs/yr) of interest to

TABLE 4

MODIFIED CHEMICAL PLANT STREAMS - EFFECTS OF HYDROGENATION AND DISTILLATION

Designation	Processing Steps	H/C Ratio	$\Delta H_f/n_{298}(\ell)/n$ (Kcal/g atm C)(1)	Density (g/cc)(1)
B-4	None	1.20	+3.43	0.99
B-19	Hydrogenate B-4	1.46	-0.09	0.97
B-20	Hydrogenate and distill B-4	1.41	+0.04	1.00
B-5	None	1.33	+0.54	0.96
B-21	Hydrogenate B-5	1.72	-3.49	0.89
B-22	Hydrogenate and distill B-5	1.55	-2.29	0.99
B-9	None	1.02	+2.41	1.02
B-23	Hydrogenate B-9	1.03	+1.50	1.01
B-24	Hydrogenate and distill B-9 (broad cut)	1.18	-0.35	0.94
B-25	Hydrogenate and distill B-9 (narrow cut)	1.26	-0.51	0.92

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1. Estimate based on calculated volumetric averages of individual components.

NASA. Refinery streams are not as well characterized as chemical plant streams. Typical inspections of the streams in Table 5 are given in Appendix C. The data were sufficient to obtain approximate heats of formation and H/C ratios. However, the discrepancies between estimated and measured properties were relatively high for some of the refinery streams.

Several of the streams in Table 5, especially C-3, C-5 and C-9 to C-12 are quite dense due to their aromatic character. Mild hydrogenation of these fuels would increase their naphthene content at the expense of aromatics, and may improve their overall characteristics especially the H/C ratio. Prior work by Exxon personnel has shown that streams C-9 to C-12 in particular, undergo partial hydrogenation under relatively mild conditions. The impact of such processing on the properties of these streams was estimated. It was found to be minor and was not considered worth pursuing further.

III.1.5 RANKING OF CANDIDATES BY ESTIMATED CRITICAL PROPERTIES

The critical properties for ranking of candidates in accordance with the objectives of the program were:

- Specific gravity
- H/C Ratio
- Heat of formation

These properties, if now known, were estimated as described in Appendix A. They were forwarded to NASA-Lewis where fuel density ($\bar{\rho}$) and specific impulse (I_{sp}) data were generated by means of a standard computer program (See Section II.3.1). The specific impulse values were calculated for an equilibrium expansion from 1000 psia to 14.7 psia, assuming combustion to CO and H_2O.

A variety of methods were used to rank the candidates. These included merit index ($\rho\ I_{sp}^3$), specific impulse (I_{sp}), $\bar{\rho}\ I_{sp}$, volumetric heat of combustion, density, cost category, quantities available and stability. Each has value in helping determine the most promising candidate for specific purposes. A complete listing of values of ρ, I_{sp}, $\bar{\rho}\ I_{sp}^3$ and volumetric heats of combustion for all candidates is given in Appendix D. Rankings by merit index, by $\bar{\rho}\ I_{sp}$ by I_{sp}, and by volumetric heat of combustion are also given in Appendix D. In each case, kerosene (RP-1) is included for purposes of comparison. Forty-seven of the 77 candidates had higher merit indices than RP-1 while 21 had higher I_{sp} values. The importance of fuel density to the rankings is apparent from a comparison of Appendix Tables D-2 and D-2. Of the top 10 candidates by $\bar{\rho}\ I_{sp}^3$ only one, A-5 is also in the top 10 by I_{sp}. Thus, quite different streams or compounds should be considered if specific impulse, I_{sp}, alone is the major criterion.

TABLE 5

REFINERY STREAMS AS CANDIDATES FOR HIGH DENSITY FUELS

Designation	Density (g/cc)$^{(1)}$	H/C Ratio$^{(2)}$	$\Delta H^{\circ}_{f,298}$ (ℓ)/n (kcal/gram atom C)$^{(2)}$	Composition (%)		
				Saturates$^{(3)}$	Aromatics	Polars$^{(4)}$
C-1	0.93	1.54	-0.4	60.3	33.7	6.0
C-2	0.91	1.82	-5.3	74.2	23.6	2.2
C-3	1.02	1.39	+0.7	12.4	69.8	17.8
C-4	0.92	1.56	-4.6	65.7	33.3	1.0
C-5	1.01	1.47	-2.0	--	--	--
C-6	0.93	1.64	-3.7	46.1	52.5	1.4
C-7	0.95	1.74	-4.6	58.3	40.6	1.1
C-8	0.97	1.61	-3.0	30.4	64.4	5.2
C-9	1.07	1.42	-1.5	16.3	77.5	6.2
C-10	1.04	1.45	-2.0	16.5	80.4	3.1
C-11	1.06	1.38	-1.2	11.2	88.3	--
C-12	0.99	1.60	-2.6	17.4	75.4	7.2

---

(1) Measured.
(2) Estimated (see Appendix A).
(3) Mostly naphthenics.
(4) Phenols and other oxygenated species plus some N and S compounds

III.1.6. TEN CANDIDATES FOR CONTINUED RESEARCH

From the 77 candidates identified, 10 were chosen for additional study. Both Exxon and NASA personnel participated in the selection process. The following criteria were used:

(1) Merit Index, $\bar{\rho} I_{sp}^3$

(2) Density

(3) Cost Category

(4) Projected Availability

(5) Other Physical Properties (viscosity, stability, etc.)

(6) Potential application to NASA projects besides SSTO.

The 10 candidates and some of their properties are given in Table 6. Also shown are two alternates. In addition, the properties of RP-1, the reference fuel, are shown. All of the first 10 have larger merit indices and greater densities than RP-1. In addition, most are in the same cost category as kerosene.

All candidates selected are in the low cost category except the pure compounds, A-3, A-5 and A-6. These are included because they serve as a basis of comparison for physical property testing. It should be noted that 1,7-octadiyne (A-4) was omitted from the list despite its high merit index ($\bar{\rho}\ I_{sp}^3 = 1.82$). This was done for the following reasons:

(1) Both experience at Exxon and literature reports indicate that acetylenes, especially diacetylenes, are among the least stable hydrocarbons, particularly at higher temperature. All are prone to chemical self-condensation and co-polymerization with other species leading to excessive deposit formation.

(2) No commercial process is available at present for the manufacture of A-4. Possible synthesis schemes, based on laboratory preparative methods would be prohibitively expensive and probably require the handling of unstable and potentially hazardous intermediates.

As a result of Exxon's recommendations A-4 was omitted in favor of the other pure compounds shown in Table 6. These candidates were investigated further as described under Task (2).

TABLE 6

TEN CANDIDATES SELECTED FOR FURTHER RESEARCH

Designation	Compound or Source	Density ρ (g/cc)	Merit Index(1) $(\bar{\rho}\, I_{sp}^{3}) \times 10^{-9}$	Cost Category(2)
C-3	Refinery stream	1.02	1.78	L
B-4	Chemical plant stream	0.99	1.76	L
A-3	*exo*-Tetrahydrodicyclopentadiene (JP-10)	0.94	1.76	H(5)
A-5	Cyclododecatriene	0.89	1.75	M
C-9	Refinery streams	1.07-1.06	1.75-1.74	L
B-20(3)	Modified chemical plant streams	0.97-1.00	1.75	L
C-1	Refinery stream	0.93	1.74	L
C-10(4)	Refinery stream	1.04	1.73	L
A-6	Decahydroacenaphthene	0.94	1.72	M
B-14	Chemical plant stream	0.96	1.71	L
Alternates				
B-2	Chemical plant stream	0.70	1.64	L
B-15	Chemical plant stream	1.10	1.69	L
RP-1	Kerosene standard	0.80	1.65	L

---

(1) $\bar{\rho}$ = propellant density; I_{sp} values calculated on equilibrium expansion from 1000 psia to 14.7 psia for stoichiometric mixture.

(2) L = "Low", <.50/kg (<$.20/#); M = "Medium", $.50-$2.50/kg ($20-$100/#); H = "High", >$2.50/kg (>$1.00/#).

(3) Modified B-4 stream selection depends on processing needed.

(4) Sample not available.

(5) Based on current selling price of $50/gal (ref. 19).

III.2 Task (2) Fuel Physical Property Evaluation

This work was undertaken to confirm the estimated properties of candidate streams by actual analytical measurement and to determine which of the 10 candidates are worthy of additional evaluation as potential fuels. The properties analyzed were:

(1) Elemental analysis (C, H, N, S)
(2) Heats of combustion
(3) Density as a function of temperature
(4) Freezing points
(5) Viscosities (at elevated temperatures)
(6) Vapor pressures
(7) Thermal stability
(8) Distillation curves(by gas chromatographic distillation)
(9) Thermal conductivities

In addition to the 10 top candidates, samples of RP-1 kerosene and a high quality JP-5 jet fuel were analyzed to serve as basis for comparison. A sample of the refinery stream C-10 was not available. Both B-2 and B-15 were evaluated as replacements.

III.2.1 Elemental Analysis of Top Candidates

The results of elemental analyses for nine candidates are shown in Table 7. Most were analyzed by standard combustion methods. Special procedures were required for the more volatile samples (B-2, B-4, and RP-1).

The measured H/C ratios for most candidates are fairly close to those estimated from assumed compositions of these streams. However, C-9 and B-14 appear significantly lower in hydrogen (more aromatic in character) than estimated and B-15 is higher (less aromatic) in hydrogen than estimated. These errors were, in turn, reflected in inaccuracies in heats of combustion measurements as compared to calculated values. This is discussed further below.

III.2.2 Heats of Combustion - ASTM D2382

This important parameter was determined for all candidates using ASTM method D2382. Results are given in Table 8. The test gives the heats of combustion in BTU/lb. These have been converted, using the measured densities to the volumetric heats of combustion, (BTU/gal) as well as to the metric units kilojoules/cubic meter(kJ/m^3). The estimated values based on assumed compositions are also given. In general, the determined values are quite close to the estimated quantities.

TABLE 7

ELEMENTAL ANALYSIS FOR TOP FUEL CANDIDATES

Fuel	% C	% H	% N	% S	H/C Ratio	
					Measured	Est. Previously(1)
A-3	88.06	11.68	---	---	1.5805	1.50
A-5	89.07	11.01	---	---	1.4729	1.50
A-6	87.89	12.01	---	---	1.6284	1.67
B-2(2)	88.05	11.42	<0.3	<0.02	1.546	1.59
B-4	90.12	9.40	<0.3	<0.02	1.2430	1.20
B-14	91.60	8.08	<0.3	0.49	1.0700	1.32
B-15(2)	92.22	7.11	<0.3	1.29	0.9170	0.65
B-20	87.71	9.63	---	---	1.3586	1.34
C-1	87.45	12.46	<0.3	0.60	1.7121(3)	1.54
C-3	87.93	10.33	<0.3	0.93	1.3980	1.39
C-9	90.10	7.49	<0.3	1.53	1.0656	1.42
RP-1(4)	85.61	14.22	---	---	1.979	---

---

(1) Based on assumed compositions
(2) Back-up candidate; not one of original top 10
(3) Average of three determinations
(4) Sample obtained from NASA-Lewis.

The highest values for volumetric heats of combustion of the top 10 candidates are C-9 (443 X 10^5 kJ/m^3; 158,903 BTU/gal), C-3 (430 X 10^5 kJ/m^3; 154, 400 BTU/gal), B-4 (430 kJ/m^3; 154,130 BTU/gal), and A-3 (419 X 10^5 kJ/m^3; 150,239 BTU/gal). C-1, a refinery stream, has a high ΔH_C (19,250 BTU/lb)and a high H/C ratio (1.7). As a result, this stream has a good merit index (see below). Samples A-5 and B-2 also have very high ΔH_C on a weight basis. B-2 is an inexpensive chem plant side stream, but is likely to be of somewhat limited availability (2 MM #/year or less). All but one of the top candidates have significantly higher volumetric heat contents than RP-1 kerosene. However, RP-1 ranks very high on a weight basis (BTU/lb).

III.2.2.1 Heats of Formation from Measured Heats of Combustion

Using the measured H/C ratios and ΔH_C given, the ΔH_f of the cadidate streams were calculated according to the relationship:

$$-CH_R- + O_2 \rightarrow CO_2 + \frac{r}{2} H_2O\ (\ell)$$

$$\frac{\Delta H_f}{n} = \frac{\Delta H_C}{n} - 94.052 - \frac{r}{2}\, 68.317$$

where r = H/C ratio, -94.052 and -68.317 are the heats of formation of CO_2 and liquid H_2O, respectively. More details on the method are given in Appendix A. The values are given in Table 9. Also shown are the estimated values which were based upon average compositions. As expected, the measured and estimated values for pure compounds and chem plant streams, whose composition was fairly accurately known are close. The values for the refinery streams, where composition had to be assumed, show greater discrepancies between measured and estimated figures.

III.2.2.2 Rankings by I_{sp} and Merit Index ($\bar{\rho}\ I_{sp}{}^3$) Using Measured Values

The ΔH_f values in Table 9 were converted to I_{sp} values by NASA-Lewis. These were, in turn, converted to merit indices. Results are summarized in Table 10. The candidates, A-6, B-20 and C-3 are not included because of low measured ΔH_f values. Of the eight candidates four, A-3, A-5, B-4 and C-1 had significantly higher merit indices than RP-1. Candidates B-14 and C-3 were penalized because of a lower I_{sp} than expected based on previous estimates. B-2 was penalized because of its low density. However, B-2 has the highest specific impulse of the group.

TABLE 8

HEATS OF COMBUSTION FOR CANDIDATE FUELS

				Volumetric Heat Content		
	ΔHc(ASTM#D2382)			Measured(1)		Est. Previously
Fuel	kJ/kg	(BTU/lb)	Density (g/cc)	kJ/m^3 (x 10^{-5})	(BTU/gal)	(BTU/gal)
A-3	44,719	(19,226)	0.9381	418.75	150,239	144,500
A-5	45,322	(19,485)	0.8863	400.95	143,855	139,700
A-6	44,573	(19,163)	0.9351	416.37	149,267	143,000
B-2(2)	46,020	(19,758)	0.7214	330.92	118,730	110,000
B-4	43,836	(18,846)	0.9818	429.59	154,130	148,700
B-14	41,482	(17,834)	0.9768	404.45	145,110	143,400
B-15(2)	40,458	(17,394)	1.1060	446.65	160,250	155,500
B-20	43,077	(18,520)	0.9620	413.64	148,409	151,100
C-1	44,775	(19,250)	0.9254	413.59	148,390	141,600
C-3	42,447	(18,249)	1.0157	430.34	154,400	155,000
C-9	41,084	(17,663)	1.0800	442.89	158,903	159,900
RP-1(3)	46,222	(19,872)	0.8057	371.73	133,370	125,000

---

(1) Based on 8.33 lb/gal for pure water
(2) Back up candidates
(3) Sample obtained from NASA-Lewis

TABLE 9

HEATS OF FORMATION OF TOP CANDIDATES FROM MEASURED HEATS OF COMBUSTION

	ΔHc		H/C	$\Delta H_{f,298}$(Kcal/gm atm C)	
Sample	kJ/kg	(BTU/#)	Ratio	Measured	Estimated
A-3 (3)	44,719	(19,226)	1.5805	-2.7316	-0.9(1),-1.3(2)
A-5	45,322	(19,485)	1.4729	+1.7274	+1.2
A-6	44,573	(19,163)	1.6284	-4.467	----
B-2	46,020	(19,758)	1.5455	+3.0972	+2.37
B-4	43,836	(18,846)	1.2430	+2.3630	+3.43
B-14	41,482	(17,834)	1.0700	-0.9125	+0.45
B-15	40,458	(17,394)	0.9170	-0.3362	----
B-20	43,077	(18,520)	1.3586	-2.8994	----
C-1	44,775	(19,250)	1.6978	-5.2906	-0.40
C-3	42,447	(18,249)	1.3980	-6.0244	+0.70
C-9	41,084	(17,663)	1.0656	-0.4365	-1.5

---

(1) "Advanced High Pressure Engine Study for Mixed-Mode Vehicle Applications", NASA C12-135141, January, 1977.

(2) "High Density Propellants for Single Stage to Orbit Vehicles", NASA TMX-73503, December, 1976.

(3) Sample was RJ-10.

TABLE 10

MERIT INDICES AND I_{sp} VALUES FOR TOP CANDIDATES BASED ON MEASURED VALUES

Fuel	Fuel Density ρ (g/cc)	Propellant Density, $\bar{\rho}$ g/cc	lb/ft^3	I_{sp} (sec)(1)	Merit Index $\bar{\rho}\ I_{sp}^3$ $(lb \cdot sec^3/ft^3 \times 10^{-9})$ Measured	Estimated
A-3	0.9381	1.07	66.80	294.6	1.71	1.76
A-5	0.8863	1.05	65.55	299.3	1.76	1.75
B-2(2)	0.7214	0.96	59.93	301.3	1.64	1.64
B-4	0.9818	1.09	68.05	296.2	1.77	1.76
B-14	0.9768	1.08	67.42	285.0	1.56	1.71
B-15(2)	1.1060	1.13	70.54	281.2	1.57	1.69
C-1	0.9254	1.07	66.80	293.0	1.68	1.74
C-9	1.0800	1.12	69.92	286.2	1.64	1.75
RP-1	0.8054			296.4	1.65	

---

(1) NASA-Lewis calculation based on equilibrium expansion from 1000-14.7 psia; stoichiometric fuel ratio.

(2) Back up candidate; candidates A-6, B-20 and C-3 are not included because of low ΔH_f values.

III.2.3 Densities as a Function of Temperature

Densities for top candidates were determined at various temperatures. These are given in Table 11. Plots of density values vs. temperature for these fuels give reasonably straight lines over the range studied. The plots are given in Appendix E. These may be used to obtain density values for temperatures not given in Table 11.

III.2.4 Freezing Points

Freezing points for the top candidates are shown in Table 12. Several of the candidates exhibited high freezing points which could ultimately cause problems with low temperature flow properties. Possible ways to improve these properties are given later in the report.

III.2.5 Viscosities as a Function of Temperature

The results of viscosity measurements of nine top candidates at various temperatures are shown in Table 13. For most analyses, a Brookfield viscometer was employed. Also shown is fuel grade kerosene (RP-1) for purposes of comparison. Some of the more viscous samples, C-1, C-3 and C-9 could not be measured at temperatures below 100°F. The chem plant stream, B-2, was measured only at 100°F by routine kinematic procedure and at 50°F with the Brookfield. It was too volatile to be analyzed by the Brookfield instrument at higher temperatures.

Semi-log plots for the measured viscosities as functions of temperature are given in Appendix E. Smooth curves were obtained which can be used for extrapolations to other temperatures.

Several of the candidates, especially C-1, C-3 and C-9 were extremely viscous. Use of such streams, unmodified, below 35°C would be quite difficult.

III.2.5.1 Improving Viscosity by Blending

One method for improving viscosity is by blending viscous and non-viscous streams. Since several of the candidate streams were extremely viscous (Table 13) a short experiment was performed to determine the effects of blending a heavy stream, B-15 with less viscous ones (B-2 and B-4). The blends enployed in this experiment and the resultant densities and viscosities are shown in Table 14. It is clear that blending can significantly improve viscosity with only a relatively minor sacrifice in density. However, the merit indices of these blends (shown in Table 13) were only fair. As a result, none of these particular blends appear promising as an energy dense fuel. However, the technique of improving low temperature properties is valid and might be used in future programs.

TABLE 11

DENSITIES OF TOP CANDIDATES AS A FUNCTION OF TEMPERATURE (1)

Fuel	Density (g/cc) at °C (°F) 4.4 (40)	15.6 (60)	37.8 (100)	65.6 (150)
A-3 (4)	.9569	.9381	.9211	.8991
A-5	.8938	.8863	.8713	.8526
A-6	.9433	.9351	.9191	.8990
B-2	.7381	.7214	.7044	(2)
B-4	Solid	.9818	.9629	.9384
B-14	.9855	.9768	.9603	.9394
B-20	.9680	.9629	.9420	.9178
C-1	.9326	.9254	.9119	.8974
C-3	(3)	1.0175	--	--
C-9	(3)	1.0800	1.067	1.048
RP-1	.8134	.8054	.7895	.7695

---

(1) Values at 15.6°C (60°F) by AMS Method 20.02; other values by "Parr Method", (see O. Kratky, et. al., Z. Angew, Physique, 4, 273 (1969).

(2) To volatile to measure.

(3) To viscous to measure by Parr Method.

(4) Sample was RJ-10.

TABLE 12

FREEZING POINTS OF TOP FUEL CANDIDATES*

Fuel	Freezing PT. °C
A-3(1)	<-60
A-5	9.4
A-6	<-60
B-2	<-60
B-4	13.4
B-14	-25.7
B-20	-24.5
C-1	12.7
C-3	Too Viscous
C-9	29.8
RP-1	-62

---

*ASTM D2386

(1) Sample was RJ-10.

TABLE 13

VISCOSITIES OF TOP CANDIDATES AS FUNCTION OF TEMPERATURE (1)

Fuel	Viscosity (mm^2/s) at Temperature °C (°F) 10 (50)	25 (77)	37.8 (100)	51.7 (125)	60 (140)	65.6 (150)	98.9 (210)
A-3 (6)	4.12	3.08	2.33(2)	--	--	1.55	1.05(2)
A-5	6.92	4.18	3.39(2)	--	--	2.13	1.32(2)
A-6	7.09	4.78	3.41	--	--	2.23	1.32
B-2	0.885	(3)	0.451	--	--	--	--
B-4	(4)	3.90	2.85(2)	--	--	1.82	1.12(2)
B-14	3.31	2.42	1.76(2)	--	--	1.26	0.801(2)
B-20	--	2.87	2.35(2)	--	--	1.67	--
C-1(5)	--	--	374.7(2)	--	--	69.5	19.7(2)
C-3(5)	--	--	46,478(2)	--	--	--	86.1(2)
C-9(5)	--	--	356.3(2)	--	--	41.7	10.24(2)
RP-1 (Kerosene)	2.87	2.14	1.75	1.46	1.32	--	0.794(2)

---

(1) Brookfield viscometer with water bath, unless otherwise specified; values in C_p were converted to C_{st} and then to (mm^2/s) for comparison to Kinematic values.

(2) Kinematic values (ASTM D445).

(3) Material too volatile to be analyzed by Brookfield above 50°F.

(4) Solidifies at 50°F - value at 55.7°F = 5.15 mm^2/s (5.15 C_{st}).

(5) Sample too viscous for measurements below 100°F.

(6) Sample was RJ-10.

TABLE 14

VISCOSITIES OF SOME CANDIDATE BLENDS AS A FUNCTION OF TEMPERATURE

Blend	Density 60°/60°F (g/cc)	Viscosity (mm^2/s) At Temperature °C (°F)					Measured Merit Index ($\bar{\rho}$ I_{sp}^3)
		25(77)	37.8(100)	51.7(125)	60(140)	98.9(210)	
B-54 (10% B-2, 90% B-15	1.075	467	162.2 (1)	56.6	37.4	(2)	1.58
B-55 (25% B-2, 75% B-15)	1.023	49.5	22.14 (3)	11.4	8.70	(2)	1.58
B-2	0.7381	0.885	0.451	--	--	--	1.64
B-4	0.9818	3.90	2.85	--	--	--	1.77
B-15	1.106		1064.6			20.2	1.69
B-56 (10% B-4, 90% B-15)	1.093	--	319.5 (4)	116.9	66.5	12.2	1.59
B-57 (25% B-4, 75% B-15)	1.074	181.8	75.2 (5)	35.5	24.2	6.6	1.65
RP-1	0.8134	2.14	1.75	1.46	1.32	0.791	1.65

---

(1) Values are for Brookfield viscosities; value obtained by ASTM D445 = 111 mm^2/s.

(2) Above boiling point of B-2.

(3) ASTM D445 value = 15.3 mm^2/s.

(4) ASTM D445 value = 295 mm^2/s.

(5) ASTM D445 value = 67.9 mm^2/s.

III.2.6 Vapor Pressure Measurements

Reid vapor pressures were determined for the top ten candidates using ASTM method D323. Results are given in Table 15. Values for C-3 and C-9 were too low to measure. The measured Reid values shown in Table 15 are used to estimate "true" vapor pressure of complex mixtures such as fuels and plant streams employing the charts given in Appendix B. Instructions for their use are also given. The pure compounds and chem plant streams use Appendix Figure B-1, while the refinery streams use Figure B-2. The 10% slope in B-1 is determined by boiling distribution curves which have been measured for all candidate streams (Section II.2.6).

III.2.7 Thermal Stability Measurements

Thermal stability is an important property in determining the future usefulness of candidate fuels. As a result, considerable emphasis was placed on it. These measurements were made using the Exxon Advanced Fuel Unit. This is a unique device capable of determining, quantitatively, the rate of deposit formation over a wide range of pressures and temperatures. Details of the unit and the analytical technique are given in Appendix B. Additional details and examples of the use of this instrument may be found in Reference (3). In addition to the "base fuel", RP-1, a sample of JP-5 was available and was tested as a basis of comparison. These runs were made at 1000 psig over a temperature profile of 300-600°F.

Results are shown in Table 16. Arrhenius plots, which give the temperature profile of deposit formation are included in Appendix E. Because of their extremely high viscosity, C-1 and C-9 had to be diluted 50-50 with n-decane in order to pass through the Advanced Fuel Unit (C-3 and B-15 were too viscous at any reasonable dilution). The decane was highly purified and gives no measurable deposits by itself. RP-1 was also diluted the same way to serve as a comparison. Interestingly, the diluted RP-1 gave more carbonaceous deposits than the undiluted sample. This phenomena has been observed previously and is related to the greater insolubility of some types of deposits in decane than in the fuel itself. As a result, they tend to plate out on the tube wall rather than pass through.

As expected, the reactive,olefinic fuels, A-3, B-2, B-4 and B-20 gave moderate to large total deposits. This is consistent with previous work (3, 4) which had shown certain types of olefins to be thermally unstable. This instability is extremely high only in the case of B-2 but B-4 and B-20 might also require special treatment to minimize thermal deposits (3, 4). Surprisingly, A-5 (cyclododecatriene) was quite stable. This suggests some resonance stability conferred by the conjugated double bonds. C-1 and C-9 appear to be fairly stable to thermal decomposition, but their very high viscosities make them extremely difficult to work with. The modified chemical plant stream, B-20, produced twice as much carbonaceous deposit as RP-1 (both on an undiluted basis). However, it was somewhat more stable than B-4 from which it is derived. This implies that chemical conversion may impart thermal stability to marginal candidates.

III.2.8 Gas Chromatographic Distillation

This analysis is common in the petroleum industry and is used for a number of reasons including:

- Determining vapor pressure at various temperatures.
- Helping to determine blending curves.
- Obtaining boiling point distributions without going to tedious 15/5 distillations. These analyses were made for those candidates where they are appropriate (GC distillations have no meaning for pure compounds, for instance).
- Obtain data necessary for Reid vapor pressure interpretations.

The plots are given in Appendix E. The plots for the refinery stream (Figure E-13) are similar to crude oils and heavy distillate streams. The curves for B-2, B-4 and B-20 are very much like pure compounds indicative of the narrow boiling ranges these streams possess.

III.2.9 Thermal Conductivities of Candidate Fuels

These were measured using ASTM method C-177. Values are given in Table 17. In general, these were comparable for most candidate fuels although B-2 and B-4 gave somewhat higher values. A sample of RP-1 was tested. This material gave a slightly higher thermal conductivity than reported (present value: .1795 w/m °C; Ref. 5 reports .137).

TABLE 15

VAPOR PRESSURE MEASUREMENTS OF TOP CANDIDATES

Fuel	Reid Vapor Pressure(1) psia at 37.8°C (100°F)
A-3	0.5
A-5	0.3
A-6	<0.5
B-2	13.3
B-4	1.2
B-14	1.0
B-20	2.0
C-1	0.8
C-3	too viscous
C-9	too viscous
RP-1	0.5

---

(1) Method: ASTM D323.

TABLE 16

THERMAL STABILITY OF TOP FUEL CANDIDATES(1)

Fuel	Total Carbonaceous Deposits (μgC) (2)	As Fraction of RP-1
A-5	462	0.50
A-3	1791	1.9
A-6	1126	1.2
B-2	44000	47.5
B-4	2388	2.6
B-14	765	0.8
B-20	2014	2.2
C-1 (diluted)(3)	2032	1.2
C-9 (diluted)(3)	1256	0.8
RP-1 Standard	926	1.0
JP-5(4)	1484	1.6
RP-1 (diluted 50/50 with n-decane	1680	1.0

---

(1) Air saturated; conditions in Advanced Fuel Unit: 1000 psig; temp. zones at 300, 400, 500, and 600° F; SS 304 tube; 4 hour run; 2.5 cc/min. flow rate.

(2) In 4-hour run.

(3) Dilution 50/50 with n-decane required because of viscosity of sample; comparison was made with diluted RP-1 Fuels C-3, C-9 and B-15 could not be run even when diluted.

(4) High quality but eight years old.

TABLE 17

THERMAL CONDUCTIVITIES OF CANDIDATE FUELS(1)

Fuel	Average Temperature °C	Average Temperature °F	Thermal Conductivities, k W/m °C	Thermal Conductivities, k BTU-ft/hr-ft^2-°F
A-3	23.78	74.81	.1591	0.0919
A-5	23.34	74.02	.1623	0.0938
A-6	23.18	73.73	.1651	0.0954
B-14	23.61	74.50	.1559	0.0901
B-4	3.49	38.28	.1881	0.1087
B-4	23.10	73.59	.1847	0.1067
B-4	64.36	148.21	.1769	0.1022
RP-1	22.63	72.75	.1795(2)	0.1037(2)
B-2	.48	32.87	.2307	0.1333
C-1	1.88	35.38	.1558	0.0900
C-1	68.81	155.87	.1443	0.0834

---

(1) Method ASTM C-177

(2) Lit (refs. 5, 6) values: .137 w/m°C and 0.079 BTU-ft/hr-ft^2-°F at 77°F.

III.3 Task (3) Fuel Production Economics

Since a major objective of this program was to identify inexpensive energy dense fuels a reasonably accurate assessment of the costs of top candidates was necessary. This task was considerably simplified since most of the final 10 fuels were either chemical plant or refinery streams whose production costs were already known. All that remained in these instances was to estimate the transfer costs from the production site to NASA-Lewis. In the cases of pure compounds and modified chemical plant streams a more detailed analysis was required.

III.3.1 Costs of Chem Plant and Refinery Streams

The costs for streams B-2, B-4, B-14, C-1, C-3 and C-9 were obtained directly from Exxon personnel familiar with their production. Costs associated with loading and transfer from place of production to NASA-Lewis in Cleveland, Ohio were added to give the total costs shown in Table 18.

III.3.2 Costs of Modified Chemical Plant Streams and Pure Compounds

Estimated production costs for candidates B-20; A-3, A-5 and A-6 are shown in Table 19. Flow plans and synthesis routes are given in the following sections. The pure compound A-5 (exo-tetrahydrodicyclopentadiene, JP-10) is a commercially available material selling for ($50/gal; $6/lb) (ref. 19). Since the processing steps are not known, an economic analysis for A-3 was not attempted.

The costs shown in Table 19 included the following:

Utility Costs

- Power
- Cooling Water
- Steam

Capital Cost

(20% Return)

Fixed Costs

- Direct Operating Labor
- Direct Maintenance Labor
- Overhead
- Maintenance Materials
- Feed and Fuel Costs
- Catalysts and Chemicals
- Local Tax and Insurance

III.3.2.1 Production of B-20 (Modified Chem Plant Stream B-11)

The candidate stream B-20 is produced by mild hydrogenation of B-4 (85% dicyclopentadiene). This treatment results in partial reduction of the double bonds of B-4 (Scheme 2). The double bond in the seven membered ring hydrogenates more readily so that the partial conversion (B-4 to B-20) is readily achieved. The laboratory procedure is given in Appendix F. This increases H/C ratio and improves thermal stability somewhat. The flow plan for production of B-20 is shown in Scheme 1. The cost shown in Table 19 is based upon this flow plan.

TABLE 18

COSTS FOR CHEMICAL PLANT AND REFINERY STREAM CANDIDATES(1)

Designation	Source(2)	Cost	
		¢/Kg	¢/lb
B-2	Chem Plant	17.6	8
B-4	Chem Plant	37.5	17
B-14	Chem Plant	17.6	8
C-1	Refinery	22.0	10
C-3	Refinery	15.4	7
C-9	Refinery	15.4	7

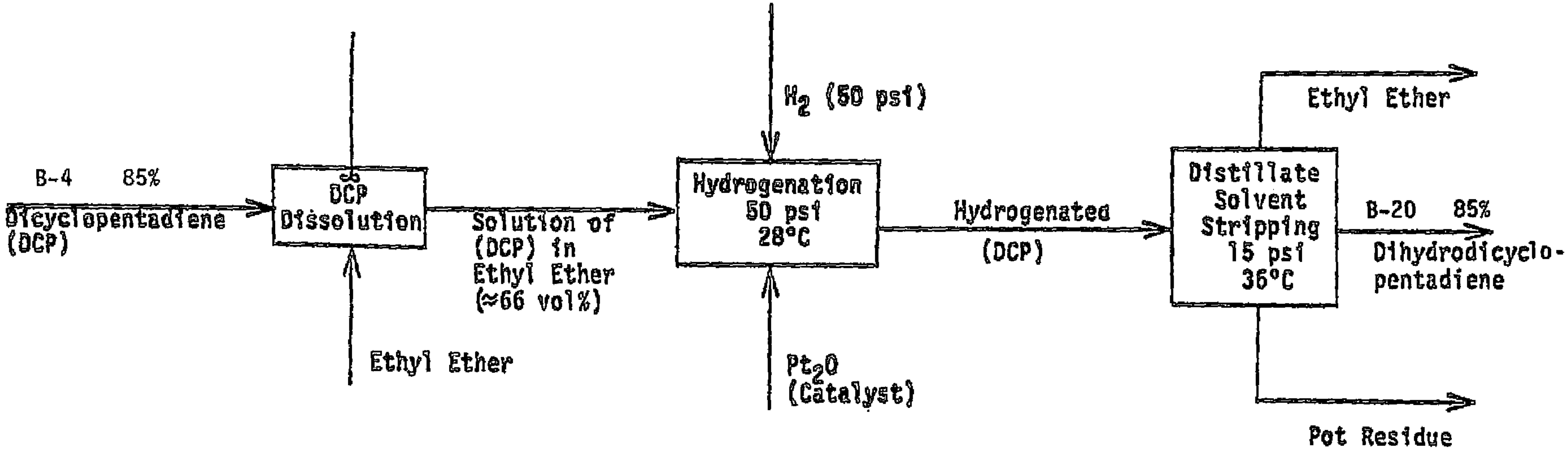
---

(1) Includes production costs plus transfer to NASA-Lewis, Cleveland, Ohio.

(2) Location of Chem Plant: Baton Rouge, LA; Refinery: Baytown, TX.

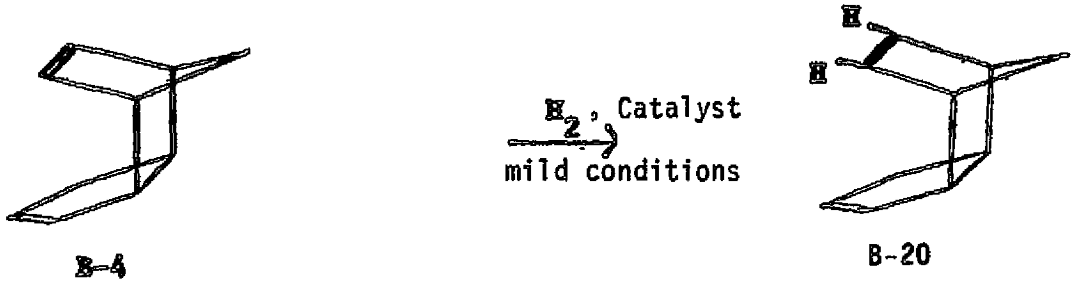
Scheme 1

Preparation of (B-20) Dihydrodicyclopentadiene



Preparation of A-3 (tetrahydroderivative of Dicyclopentadiene) uses same flow sheet as above but longer hydrogenation times.

SCHEME 2. HYDROGENATION OF B-4 (85% DICYCLOPENTADIENE)

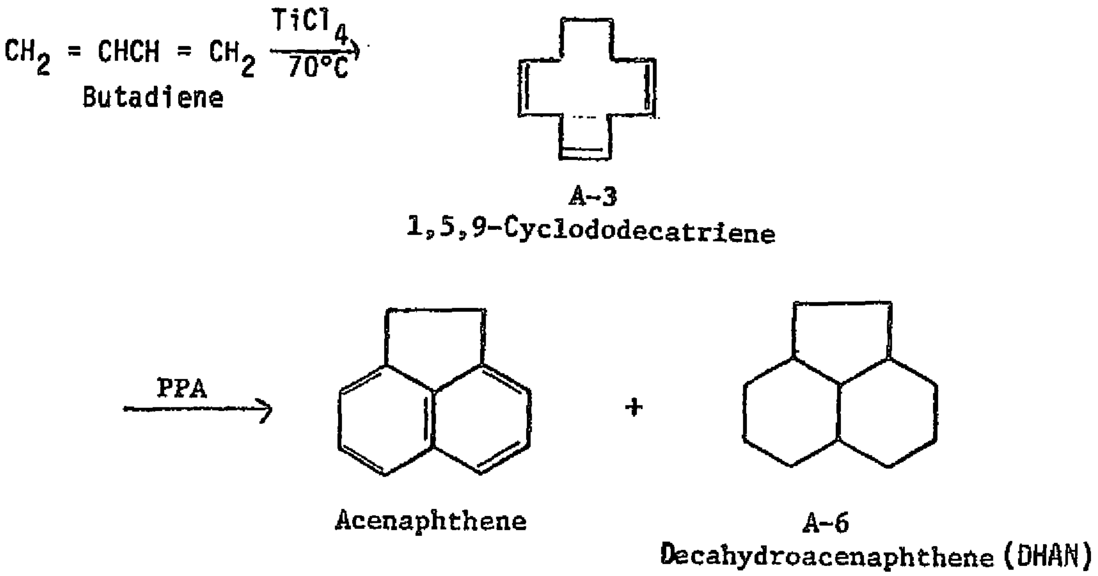


III.3.2.2 Production Costs for Cyclododecatriene (A-5) and Decahydroacenaphthene (A-6)

The candidate fuels are synthesized as shown in Scheme 3. Butadiene-1,3 is trimerized to the commercially available cyclododecatriene (A-3) over a $TiCl_4$ catalyst. This material is than readily rearranged to Decahydroacenaphthene by use of polyphosphoric acid (PPA). Details of this rearrangement are given in Appendix F. A flow plan for production of A-3 is given in Scheme 4 and that for A-6 in Scheme 5. Costs shown in Table 19 are based on these flow plans.

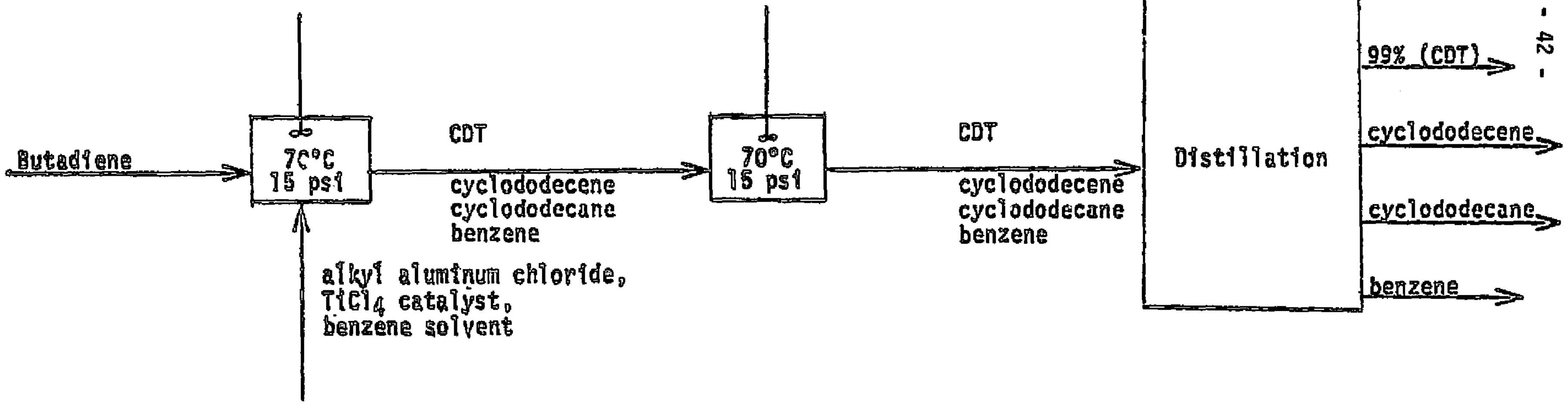
SCHEME 3

SYNTHESIS AND REARRANGEMENT OF CYCLODODECATRIENE (A-3)



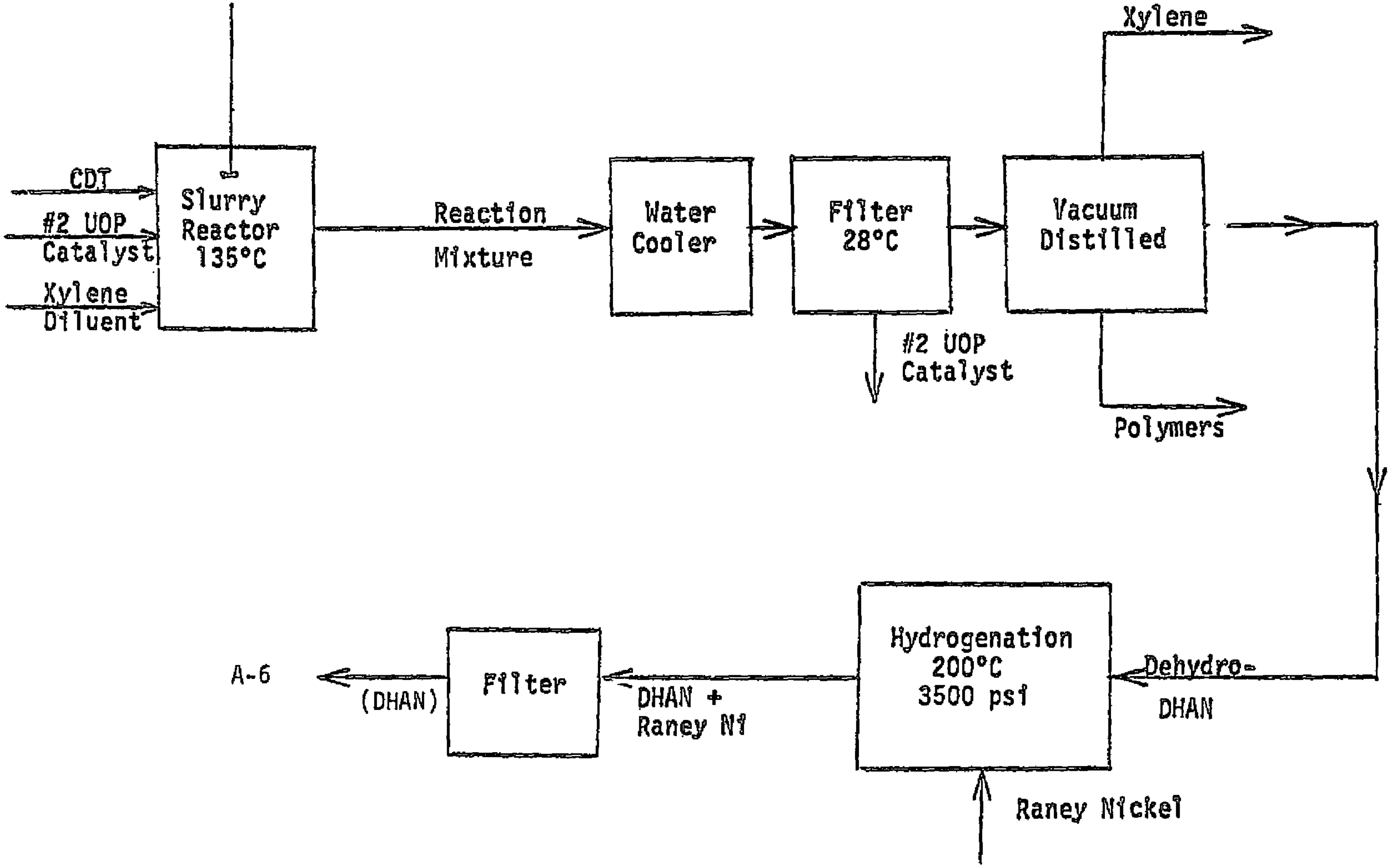
SCHEME 4

Preparation of (A-5) 1,5,9-cyclododecatriene (CDT)



Scheme 5

Preparation of A-6, Decahydroacenaphthene (DHAN)*



* CDT = 1,5,9 - Cyclodecatriene

TABLE 19

PROJECTED PRODUCTION COSTS FOR PURE COMPOUNDS AND A MODIFIED CHEMICAL PLANT STREAM (1)

Designation	Compound or Source	Cost ¢/Kg	Cost ¢/lb
A-5	Cyclododecatriene	132	60
A-6	Decahydroacenaphthene	165	75
B-20	Modified Chemical Plant Stream	41.9	19

---

(1) Cost for A-3 (JP-10) was not analyzed. Current selling price is $13/l ($50/gal; $6/lb).

These results confirm that the chemical plant and refinery streams will fall in the low cost category while pure compounds will be moderate to high cost fuels.

III.4 Task (4) Advanced Hydrocarbon Fuel Analysis

The purpose of this task is to identify areas of research which could lead to the development of new or improved hydrocarbon fuels. Four areas were investigated.

1. Synthesis of new, energetic hydrocarbons (high I_{sp}).
2. Production of liquid derivatives from shale and coal; both pure compounds and partially refined liquids.
3. Analysis of slurried fuels as potential high energy propellants.
4. An analysis of the use of additives or modifications to improve the stability and/or physical properties of candidate fuels.

III.4.1 Synthesis of Highly Energetic Hydrocarbons

The potential of hydrocarbons for supersonic propulsion has been analyzed by Conn and Dukek(8). Their conclusions are summarized in Table 20. They concluded:

". . . In short, hydrocarbons appear to be theoretically the second best fuel for either rocket or jet engines and practically are the logical fuels to fulfill the special performance needs of high Mach atmospheric vehicles and large liquid rocket boosters.

Availability, cost and ease of handling are, of course, the strongest arguments for hydrocarbon fuels. These factors loom large when some of the future estimated volume requirements are considered."

Of the various hydrocarbon types, Conn and Dukek rated cyclopentadienes and multi-ringed cycloparaffins as the most promising types (8). This conclusion is supported by others (see ref. 9 for a review) as well as our own analysis (Section III.1.1 of this report). Other compound types of potential interest are spiro-hydrocarbons and di-acetylenes such as 1,7-octadiyne (9). The theoretical performance parameters for some of these hydrocarbons have been reviewed (9). It is apparent that diacetylenes have very attractive energy properties. However, as pointed out above, difficulties in large scale synthesis and their inherent instability render acetylenes less promising than the bridged or cyclic hydrocarbons discussed below and in Appendix G.

Two approaches may be taken to the synthesis of novel, high energy fuels:

(1) Modification of existing candidate fuels.

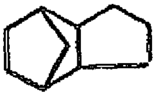
(2) Synthesis of new types of molecules.

A brief analysis of these two approaches based on a literature search follows. Details of potential new syntheses are found in Appendix G.

III.4.1.1 Modification of Existing High Energy Candidate Fuels

Two basic ring structures were identified as potentially useful as starting points for work on chemical modifications. These are perhydro-1,4,5,8-dimethano-naphthalene and the perhydro-4,7-methanoindane structures, A and B respectively.

A



B

Modifications of ring system A have been studied by Schneider et. al. at Suntech and have been reviewed (10). Some additional suggested modifications generated as part of this task are given in Appendix G. Most of these modifications deal with the introduction of the highly strained cyclopropyl groups into the basic molecule. Similar modifications of ring system B are also discussed in Appendix G.

III.4.1.2 Synthesis of New Types of Molecules

The classes of exotic fuels recommended for initial examination were selected from the recently reported advances in synthetic organic chemistry. A preliminary survey of the literature elicited several classes of exotic chemicals which may possess desirable fuel characteristics. These potential fuels are classified into the following five general categories:

- Highly strained molecules
- Dewer benzenes
- Adamantanes
- Spiro derivatives
- Clathrate derivatives

TABLE 20

COMPARISON OF KEY PROPERTIES OF HIGH PERFORMANCE LIQUID FUELS (8)

	Relative Rating (1 = Best, 5 = Worst)				
	Hydrocarbons	Metal Hydrides (e.g. B_5H_9)	Metal Slurries (e.g. Li)	H_2	Hydrazine
Thermal Stability	2	4	3	1	4
Heat Content	3	2	3	1	5
Specific Impulse (LOX)	4	3	5	1	2
Vapor Pressure	1	2	2	5	4
Combustion Characteristics	3	4	5	1	2
Viscosity-Temperature	1	2	4	5	3
Density	3	4	1	5	2
Specific Heat	2	4	2	1	4
Uniformity	4	3	5	1	2
Availability & Cost	1	4	2	4	3
Handling	1	3	4	5	2
Overall Rating:					
For Air-Breathing Engine	2	3	4	1	4
For High Thrust Rocket Engine	2	4	4	1	3

The rational for including these classes of compounds is, in general, the amount of energy given off as release of strain during combustion. Details of synthesis routes to representative compounds of all the above classes are given in Appendix G.

In summary, it seems clear that energy-dense compounds can be made using approaches outlined in Appendix G. For some applications, they may well prove useful. However, the cost associated with such syntheses is very high not only in the initial development stage but also during actual production. A more rational approach to finding new candidate fuels appears to be to search among refinery and chemical plant processes for hydrocarbon streams and side streams rich in energy-dense compounds, as described above. These low cost streams can then be modified to improve their physical and, to some extent, their energy properties as needed.

III.4.2 Liquid Derivatives from Shale and Coal

A detailed study of the potential of shale and coal as sources of high density fuels is beyond the scope of this report. However, a brief literature review revealed that these sources may have promise as potential fuel precursors.

III.4.2.1 Liquid Fuels from Oil Shale

The characteristics of shale liquids depend upon source and method of liquification. The procedures employed usually involve some form of retorting followed by distilling and hydrotreating. The quality of the final product depends upon the type of shale, boiling range of the fraction collected and severity of hydrotreating. A typical analysis of a typical kerosene fraction from both mild and severe hydrotreating of a Paraho shale is shown in Table 21 (11). These are not too dissimilar to a normal kerosene (RP-1) and one might expect somewhat similar properties. The energy properties of such liquids were estimated (see Appendix G for details). Results of such an analysis for two examples are shown in Table 22 and compared to the properties of RP-1 and chemical plant stream B-4. The severely hydrotreated sample with more hydrogen would appear to be slightly more energy rich. Additional estimated properties of shale liquids are given in Appendix G. It appears from the comparison of properties shown in Table 22 that kerosene from shale is a potential replacement for RP-1. However, shale kerosene is likely to be much more expensive to produce. In addition, the presence of various nitrogen containing impurities in shale liquids may have deleterious effects on their storage and thermal stabilities (13).

III.4.2.2 Liquids from Coal

Coal liquids are currently less well characterized than either petroleum or shale derived fuels. As a result, it is quite difficult to draw *a priori* conclusions as to the potential use of coal liquids as high density

TABLE 21

ANALYSIS OF KEROSENE FRACTIONS OF HYDROTREATED PARAHO SHALE LIQUID (11)

Compound Type	Wt.% Mild Hydrotreat	Wt.% Severe Hydrotreat
Paraffins	47.5	51.8
Monocycloparaffins	21.0	29.7
Dicycloparaffins	5.5	8.6
Tricycloparaffins	2.0	211
Total Paraffins	76.0	92.2
Alkylbenzenes	11.5	5.7
Indans	8.9	1.8
Indenes	0.2	0
Naphthalenes	2.9	0
Total Aromatics	23.5	7.5
Grand Total	99.5	99.7

TABLE 22

ENERGY PROPERTIES OF SHALE LIQUIDS COMPARED TO OTHER CANDIDATE FUELS

	Shale Liquids (1)			
	Mild Hydrotreat	Severe Hydrotreat	RP-1	B-4
Density (g/cc)	0.8124	0.7814	0.8054	0.9818
Volumetric Heat Content				
kJ/m^3 X 105	350.9	341.4	371.7	429.6
BTU/gal	125,900	122,500	133,370	154,730
I_{sp} (sec)	296.9	299.5	296.4	296.3
Merit Index ($\bar{\rho}\ I_{sp}3$)	1.66×10^9	1.68×10^9	1.65×10^9	1.77×10^9

---

(1) Estimated properties, based on reported compositions of kerosene fractions (see Appendix G for details).

fuels. It is clear, however, that coal liquids will be much more aromatic in character and contain many more polar compounds (phenols, for example) than shale. Therefore, it appears that considerable refining would be necessary to convert crude coal liquids to fuels of potential use to the space program.

One possible use of coal liquids is as a source of pure compounds (14, 15). The following have all been identified as potentially recoverable from coal (15).

- Ethylbenzene
- Pseudocumene
- Durene
- Acenaphthene
- Anthracene
- Carbazole
- Naphthalene
- Xylenes
- Phenanthrene
- Pyrene
- Pyridine bases

Of particular,interest is acenaphthene which is a precursor of octahydroarenaphthene (A-7) or decahydroacenphthene (A-6) which were identified as potentially useful fuels during this program.

III.4.3 Analysis of Fuel Slurries as Energy Dense Fuels

One way to increase the density or to improve other characteristics of fuels is to add certain high density materials which could not in themselves serve as fuels. The resultant, so called "loaded" fuels, have been the subject of considerable research. Some of the approaches to utilizing additives which are outlined in the following subsections.

III.4.3.1 Use of Light Metal Slurries

Table 20 (Section III.4.1)summarizes desirable physical and chemical properties and compares liquid hydrocarbons as a class with other fuels. An attempt was made to rank each fuel for individual properties such as thermal stability, heat content, vapor pressure, density, and cost, as well as upon its relative importance in different propulsion systems.

Light metals slurried in a hydrocarbon carrier are one means of taking advantage of the high heat content of lithium, beryllium, or boron; even slurried magnesium will demonstrate higher thrust than hydrocarbons alone for short duration flights (16). Some physical problems which impose great difficulties are the handling of slurries,the cooling of surfaces, and also the combustion of suspended metals. In addition, these metals are quite expensive. Metal slurries are considered a promising area for research for some applications.

III.4.3.2 Carbon Slurry Fuels

Many of the problems associated fuels of the light metal slurry type can be overcome by using carbon black or graphite slurries. Carbon slurries burn, give all gaseous products, and, therefore, eliminate one of the major problems with metal slurries

Carbon loading can be used to get unique high-energy fuels by using existing high-density fuels to get still higher volumetric heat contents. Thus, carbon-loaded kerosene can be formulated to have more BTU's per gallon than Shelldyne (Table 23). The flow behavior of the resultant carbon-loaded fuels will approach that of the base fuel when it is sheared.

Another important advantage of carbon loading is that high-density fuels can be formulated in existing low-cost liquid fuels. Such fuels have improved freezing point, improved low-temperature viscosity characteristics, and higher heat values relative to the existing high-density liquid fuels.

Some of the advantages over current high density fuel candidates which accrue with carbon slurries are shown in Table 23.

TABLE 23

ADVANTAGES OF CARBON SLURRY FUELS

	Est. Net Heat Value (BTU/Gal)	Viscosity, (cp)(1)		
		-65°F	-40°F	77°F
Shelldyne	163,374	20,000 (est.)	2190	17.5
T. H. Dimer	142,195	Solid	2330	5.1
60% Carbon in Kerosene	167,122	344	200	39

---

(1) At shear rate of 4285 sec^{-1}.

These data show that a 60% carbon-loaded kerosene has a net volumetric heat value somewhat greater than that of Shelldyne and significantly greater than T. H. Dimer. The viscosities of the loaded fuel at low temperatures are at considerably lower than those for the high-density liquid fuels.

The major disadvantage of carbon slurried fuels is a decrease in specific impulse (I_{sp}) as the wt.% of carbon is increased because of the lower H/C ratio. The predicted effects of carbon slurrying on some properties of RP-1 kerosene are summarized in Table 24. Details of this analysis are given in Appendix G. It is apparent from these estimates that carbon slurrying will have a significant positive effect on density and volumetric heat content but results in an offsetting decrease in I_{sp}. Thus, it appears that carbon slurry fuels may have certain distinct advantages for some applications (turbine fuels, for example) in which high heat content and good low temperature flow properties are important. However, this technique is not promising as a method for developing fuels with high I_{sp} or merit index ($\overline{\rho}\ I_{sp}^3$).

III.4.4 Analysis of Additives or Modifications to Improve Viscosity and Thermal Stability

A brief analysis of methods which might be used to improve these critical properties of candidate fuels follows. A more detailed discussion is found in Appendix G.

III.4.4.1 Viscosity Modifications

High viscosities and the associated poor low temperature flow properties are a potential problem for several of the best candidate fuels (see Sections II.2.4 and II.2.5). Several methods should be explored to circumvent this difficulty. Among the most promising are:

- Blending of Streams
- Chemical Modifications
- Use of Flow Improving Additives

The potential for blending energetic chemical plant streams to improve viscosity was discussed in Section III.2.5.1 above. It was shown that considerable reductions in viscosity can be achieved this way but usually at the expense of both density and merit index. The effects on other properties of the fuel blends must always be considered. Predicting blend viscosities is also difficult although recently, methods for doing this have been described (see Appendix G). Blending, therefore, would appear to be a useful method only if poor low temperature properties are a serious drawback.

Chemical modification is also a potentially valuable technique. For example, the increasing of branching on carbon chains, changing positions of aromatic substitution and the introduction of electron withdrawing or donating substituents all have significant effects on viscosities. Of greater interest

TABLE 24

EFFECTS OF CARBON SLURRYING ON SOME ENERGY PROPERTIES OF RP-1 (1)

Wt. % Carbon[2]	H/C Ratio	Propellant Density ρ	Estimated Heat Content (3) kJ/m^3 X 10^5	 BTU/gal	I_{sp}	Merit Index $(\bar{\rho}\ I_{sp}^3) \times 10^{-9}$
0	2.00	0.800	348.4	125,000	296.4	1.65
25	1.44	0.957	390.2	140,000	288.5	1.61
50	0.923	1.19	454.3	163,000	277.0	1.54
65	0.631	1.66	510.0	183,000	269.6	1.50
80	0.353	1.52	580.1	211,000	261.8	1.46

---

(1) See Appendix Table G-10 for complete list of properties as well as methods of estimation.

(2) As graphite.

(3) Note that measured ΔH_c for pure RP-1 was 133,370 BTU/gal (Table 8, Section III.2.2). However, estimated value of 125,000 was used in this analysis; if 133,370 BTU/gal were used, all values in this table would increase proportionally.

to this program is the effect of hydrogenation on various candidate streams. In general hydrogenation tends to lower the freezing point of olefinic streams. This is illustrated by results shown in Table 25 where the freezing points of B-4, B-20 and A-3 are compared. These materials differ largely in degree of hydrogenation (B-4 < B-20 < A-3). Once again it must be emphasized that other properties may be adversely affected by partial or complete hydrogenation.

TABLE 25

EFFECTS OF HYDROGENATION ON FREEZING POINTS

Fuel	H/C Ratio	FP (°C)
B-4	1.2	13.4
B-20	1.4	-24.5
A-3	1.6	<-60

Additives have long been used to improve the low temperature flow properties of diesel fuels and home heating oils. Most of these additives serve as wax crystal modifiers (17) and would be of limited usefulness in the case of rocket fuels. They might, however, serve as a starting point for research into appropriate low temperature flow improvers.

III.4.4.2 Thermal Stability Modifications

Based upon Exxon experience in thermal stability studies with JP-5 (18) four basic approaches to improving thermal stability which do not require chemical modifications should be explored. These are:

1. Removal and exclusion of molecular oxygen.
2. Control of trace impurities.
3. Removal of dissolved metals and control of metal surfaces.
4. Use of additives.

The most effective method was found to be deoxygenation. The improvement which can be achieved by reducing the molecular oxygen content of JP-5 to

One ppm or less is apparent from data in Table 26. However, some poor quality fuels do not respond well to deoxygenation unless certain trace impurities are removed. In general, the most deleterious impurities are peroxides, sulfides and polysulfides, although some acids, olefins and, especially acetylenic compounds can also exert a strong destabilizing effect (18).

In the present program (see Section III.2.7 above) thermal stability measurements suggested that this could be a problem with certain candidate fuels. As a result, a study of both thermal and storage stability for any candidate under serious consideration is strongly recommended.

More details on the effects of various techniques for enhancing thermal stability are given in Appendix G. A description of the Exxon thermal stability apparatus and it's usage is presented in Appendix B.

III.5 High Impulse, Low Density Fuel Candidates*

As described above, the primary screening criteria for fuel candidates were I_{sp}, density and low cost. As a result, the majority of candidates were selected largely because they had densities of close to 1.0 g/cc. The few exceptions (B-1, B-2, B-3, for example) were included mainly as potential blending agents. The final selection was made on the basis of an arbitrary merit index, $\bar{\rho}\ I_{sp}^3$, where density is quite heavily weighted. However, sensitivity to various fuel properties change as vehicle design is modified. As a result, recent sensitivity analyses (7) indicate that for some of NASA's programs including SSTO, a different ranking parameter might be employed. This is the reduction in gross liftoff weight (Δ % GLOW) as compared to base fuel RP-1 and is estimated by (7):

$$\Delta\ \%\ \text{GLOW} = \Delta\ \%\ I_{sp}\ (-2.4) + \Delta\ \%\ \rho\ (-0.10)$$

Reductions in GLOW were estimated this way by NASA for some of the top fuel candidates. These results are shown in Table 27. All candidate fuels would give some reduction in GLOW over the base fuel, RP-1, although in some instances, the difference is small. Significantly, the best top 10 fuel using this type of ranking would be B-2 a light, olefinic chemical plant stream. This material would give about a 4% reduction in GLOW. The best candidate from the merit index standpoint, B-4, is less attractive with this type of analysis. Also shown in Table 27 is B-60, a light olefin stream that was excluded in the original screen. This material has an estimated reduction in GLOW over RP-1 of nearly 5%.

As a result, some fuels and fuel blends which had previously been ruled out on the basis of low density were reexamined to identify those with potentially high I_{sp} ratings. The best ones are given in Table 28. Those shown are all of the low cost category (<$.44/kg). Most have greater I_{sp}'s than RP-1. However, most also have other problems (see "Comments" - Table 28). Nevertheless, B-2, B-37, B-46, B-4 and especially, B-60, may have promise as low cost, high impulse fuels

---

* This section was not part of original work plan but was added later at NASA's request.

TABLE 26

COMPARISON OF THE EFFECT OF DEOXYGENATION ON FRESH AND AGED JP-5

Fuel	O_2 Content PPM	Total Carbonaceous Deposits(1) Micrograms of Carbon	Total Carbonaceous Deposits(1) As PPM Based as Total Fuel	Average Apparent Activation Energy for the Rate of Deposit Formation kcal/mole
Fresh JP-5	64	2,404	1.24	15.3 (450-550°F)
	<0.1	315	0.16	2.1 (300-600°F)
Ashland JP-5 (4 years old) AFFB-9-67	58	3,992	2.05	6.1 (350-500°F) 16.3 (500-600°F)
	<0.1	655	0.34	2.7 (300-600°F)

(1) Cumulative carbonaceous deposits produced in 4 hours in the Esso Advanced Fuel Unit. Conditions: 1,000 psig; S. S. 304 tube, Zone 1-300°F, Zone 2-400°F, Zone 3-500°F, Zone 4-600°F.

TABLE 27

PROJECTED REDUCTION IN GROSS LIFT OFF WEIGHT (GLOW) USING TOP FUEL CANDIDATES(1)

Fuel	Δ % I_{sp}(2)	Δ % $\bar{\rho}$(2)	Δ % GLOW(2)
A-3	-0.506	16.77	-0.46
A-5	0.945	10.55	-3.33
A-6	- .270	16.77	-1.03
B-2	2.13	-13.04	-3.82
B-4	-0.340	22.980	-2.21
B-14	-0.708	19.25	-0.22
B-20	-0.101	20.49	-1.81
C-1	0.337	15.52	-2.36
C-3	-0.135	26.72	-2.35
B-60(3)	2.50	-10.00	-4.80(4)

---

(1) Calculated by J. Notardonato, NASA-Lewis from: Δ % GLOW = Δ % I_{sp} (-2.4) + Δ % $\bar{\rho}$ (-.10); $\bar{\rho}$ = propellant density (See ref. 7).

(2) Variation from RP-1.

(3) Chemical plant olefin stream; properties estimated, not included in original top 10.

(4) Exxon estimate.

TABLE 28

POTENTIAL HIGH IMPULSE FUELS

Code	Sp. Gr. (g/cc)	I_{sp} (sec)	ΔHc kJ/kg	BTU/lb	Comments
B-60	0.75 (2)	303.4 (2)	46,201	19,863	Available - stability unknown
B-28	0.76 (1)	303.0 (2)	------	------	Blend of B-1 and B-4 - unstable
B-2	0.72	302.7	46,020	19,758	Limited availability
B-3	0.65	302.2 (2)	------	------	Limited availability
B-37	0.78 (2)	299.7 (2)	------	------	Blend of B-2 and B-4
B-58	0.65 (2)	299.5 (2)	------	------	Large volume but likely unstable
B-46	0.78 (2)	299.1 (2)	------	------	Blend of B-3 and B-4
B-59	0.65 (2)	296.9 (2)	------	------	Low volume - somewhat unstable
RP-1	0.81	296.4	46,222	19,872	Kerosene
B-4	0.98	296.3	43,836	18,846	Medium - large volume, possible poor low temperature properties.

---

(1) Olefin stream from chemical plant.

(2) Estimated.

The high energy value of B-60 was confirmed by BTU analysis making this material a potentially attractive fuel. It is an inexpensive, readily available chemical plant stream rich in olefins and branched olefins similar to isoprene.

IV. CONCLUSIONS AND RECOMMENDATIONS

IV.1 Conclusions

The conclusions concerning the feasibility of each of the top 10 candidates as high energy, high density fuels for SSTO applications are summarized in Table 29. In addition, the following general conclusions were drawn from the results described in the previous sections of this report.

- Low cost, high energy, high density hydrocarbon fuels can be found among the many streams and side streams of oil refineries and petrochemical plants. The search described above by no means exhausted potential sources and yet 77 candidates were identified, many of which had one or more superior properties when compared to RP-1 kerosene. On the basis of cost effectiveness this type of approach is preferred to a synthesis program aimed at producing pure compound candidates.
- The best overall candidates were chemical plant olefin streams especially those rich in cyclic (naphthenic) olefins.
- Stability and handling characteristics are important considerations in selecting high energy hydrocarbon fuels. Paraffins are the most stable class with acetylenes the least stable. Olefins, particularly cyclic olefins, appear to be good compromises between high energy, high density and stability.
- Other important properties to be considered in selecting fuel candidates are
  - \+ Thermal and storage stability
  - \+ Freezing point
  - \+ Low temperature viscosity
- Improvements in low temperature properties can be achieved by the following techniques:
  - \+ Chemical modification (e.g. partial hydrogenation of olefins)
  - \+ Blending streams
  - \+ Use of additives (e.g. low temperature flow improvers)

However, some of these modifications result in somewhat lower I_{sp} values; tradeoffs may be required.

- Improvements in thermal and/or storage stability can be achieved by:

  - Deoxygenation
  - Control of trace impurities and dissolved metals
  - Chemical modification (e.g. partial hydrogenation)
  - Use of additives

- Chemical synthesis of high energy, high density fuels is a potentially fertile area for research. Introduction of high strained rings such as cyclopropyl groups confers significant energy to some existing structures. In addition, entirely new molecules may be constructed. Promising areas include adamantanes. Dewar benzenes and spiro compounds. However, synthesis of such materials would be complicated and very costly.

- Shale liquids are a potential replacement for RP-1 kerosene. Difficulties may be encountered with the high nitrogen levels and large amounts of polar compounds. Unrefined coal liquids, because of their aromatic character and large amounts of polar compounds are not attractive as energy dense fuels. However, they may provide a source of useful pure compounds such as acenaphthenes and indenes.

- Carbon slurried fuels may be useful for some applications (e.g. turbine fuels). However, the low H/C ratio that results on addition of carbon reduces the I_{sp} values excessively for use in this program.

- Low cost, high I_{sp} but low density fuels can also be identified among chemical plant olefin streams. Some of these show potential improvements in gross lift-off weight (GLOW) over RP-1 of nearly 5%.

IV.2 Recommendations for Additional Research

Further research in several areas is required before any of the candidate fuels can be evaluated fully. This additional research should include:

A. Studies of methods to improve low temperature properties. These studies should include:

- Partial hydrogenation or other chemical modifications where appropriate.
- Use of additives to improve low temperature flow properties.
- Blending studies of high energy streams.

B. Thermal and storage stability research. This work should be extended to existing fuels such as RP-1 and would include:

- Determination of stability characteristics of each candidate fuel over a range of temperatures.
- Investigation of the effect of deoxygenation.
- Studies of trace impurity effects (except for pure compounds).
- Chemical modifications (such as partial hydrogenation) and their effects on both storage and thermal stability.
- Studies of effects of fuel additives.
- Studies of effects of dissolved metals and metal surfaces.

C. Studies of combustion characteristics of candidate fuels. Actual combustion of the top candidate fuels is needed to determine their burning characteristics, stability, emissions, etc., before any final assessment as to their usefullness can be made.

TABLE 29

CONCLUSIONS AND RECOMMENDATIONS FOR FEASIBILITY OF TOP 10 CANDIDATES AS HIGH ENERGY FUELS

Candidate	Description (Compound or Source)	Merit Index ρI_{sp}^3	Conclusions[1]
B-4	Chemical plant stream rich in dicyclopentadiene	1.77	● BEST CANDIDATE; possible low temperature problems, marginal thermal stability
A-5	Pure Cyclododecatriene	1.76	● FEASIBLE; moderate cost; marginal freezing point
A-3	Pure Tetrahydrodicyclopentadiene	1.71	● FEASIBLE; moderate to high cost; marginal thermal stability
C-1	Refinery stream	1.68	● FEASIBLE; viscous; marginal freezing point
B-2[2]	Chemical Plant Stream rich in Olefins	1.64	● NOT FEASIBLE; marginal merit index because of low density; high I_{sp}; possible blending agent
C-9	Refinery Stream	1.64	● NOT FEASIBLE; marginal merit index, high viscosity, high freezing point
B-14	Chemical Plant Stream rich in Aromatics	1.54	● NOT FEASIBLE; low energy, good low temperature properties
B-20	Modified B-4 Stream	ND[3]	● NOT FEASIBLE; no advantages over parent B-4 stream
C-3	Refinery Stream	ND[2]	● NOT FEASIBLE; low energy
A-6	Pure Dihydroacenaphthene	ND[3]	● NOT FEASIBLE; lower energy than parent A-5; high cost; good low temperature properties

---

(1) "NOT FEASIBLE" = not recommended as possible replacement for RP-1 in SSTO applications.

(2) Replaces B-10 in original top 10 list.

(3) ND = not determined because of low ΔH_f values.

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APPENDIX A.

ESTIMATED PHYSICAL PROPERTIES OF CANDIDATE FUELS AND METHODS OF ESTIMATION

A-1. Introduction - Stoichrometric Combustion - General Properties of Hydrocarbon Types

A-2. Estimates of Heat of Formation and Combustion for Pure Liquid Compounds

- (a) Benson Method
- (b) Franklin Method
- (c) Estimating Heats of Vaporization
  - (1) Vapor Pressure Plot - Clausius Clapeyron
  - (2) Trouton's Rule
- (d) Kharasch Method

A-3. Estimating Properties for Streams of Known Composition

- (a) General concepts
  - (1) Conservation of mass
  - (2) Additivity of Heats of Combustion
  - (3) Data worksheet with example
- (b) Blends of Streams of Known Composition
  - (1) H/C ratio
  - (2) ΔH_f
  - (3) Fuel Density

A-4. Effects of Hydrogenation and Distillation on Estimated Stream Properties

- (a) Hydrogenation
- (b) Distillation

A-5. Specific Impulse and Merit Index Estimations of Streams

- (a) Discussion and Definitions
- (b) Tables of Results
- (c) Comparison of ΔH_f additivity method and I_{sp} additivity methods

A-6. References to Appendix A

ESTIMATION OF PHYSICAL PROPERTIES OF CANDIDATE FUELS

A-1 Introduction

In this study, the estimation and determination of physical properties of the candidate fuels played an important role in choosing the best candidates. The most important properties include the density of the liquid hydrocarbon fuel, the hydrogen to carbon number ratio, and the heat of formation of the liquid fuel in its standard state. The standard state is taken as 25°C and 1 atm. pressure. These properties are used to evaluate the specific impulse and the merit index for each candidate. The merit index is defined as $\overline{\rho}\, I_{sp}{}^{3}$, and this index was used to determine the relative worth of each fuel on a comparative basis. The higher the merit index, the better are the properties of a given fuel. Of course, this is external to other factors which must be studied in any fuel evaluation, including items such as cost, future availability, pumping properties and thermal properties.

Since the estimation of the heat of formation is critical to the evaluation of the merit index when literature values are not available, it is useful to examine more closely what is meant by this term. The heat of formation may be defined as the enthalpy change of the following reaction for one mole of a liquid hydrocarbon, with all compounds in their standard state;

$$nC\ (s) + \frac{m}{2} H_2\ (g) \longrightarrow CnHm\ (\ell)$$

and is denoted by $\Delta H^\circ_{f,298}(\ell)$. For convenience, the absolute enthalpy of every element in its stable state of aggregation at 1 atm pressure and 25°C is conventionally assigned the value zero.

Two estimation methods were used to find the heat of formation of hydrocarbons in the gaseous phase. These are the methods of Franklin (1, 2) and of Benson and co-workers (3). These methods will subsequently be described in more detail. However, it must be pointed out that once the heats of formation have been estimated for the gaseous hydrocarbon, it is necessary to determine the value of the heat of vaporization in order to obtain the heat of formation of the liquid hydrocarbon. These three quantities are related by the following relationship, which is based upon Hess' law of constant heat summation:

$$\Delta H^\circ_{f,298}(\ell) + \Delta H^\circ_{VAP,298} = \Delta H^\circ_{f,298}(g)$$

The heat of vaporization may be found in the open literature, or it may be predicted from Trouton's rule or from a vapor pressure plot according to the Clausius-Clapeyron equation. These methods will be elaborated more fully in the following sections.

It is desirable to carry out the formation reaction directly in a calorimetric vessel; however, the majority of formation reactions are unsuitable for calorimetric measurement. There is an indirect method which is generally applicable if the hydrocarbon burns easily to form definite products. The heat of formation can be calculated from a measured or estimated value of the heat of combustion of the compound. The standard heat of combustion for a liquid hydrocarbon is defined for this study as the negative of the enthalpy change of the following reaction;

$$CnHm(\ell) + (n + \frac{m}{4})\ O_2(g) \longrightarrow n\ CO_2(g) + \frac{m}{2} H_2O(g)$$

where all compounds are in the standard state of 1 atm pressure and 25°C in the physical state of aggregation given in the equation. The standard heat of combustion is given the symbol $- \Delta H^\circ_{f,298}(\ell)$. In terms of the hydrogen to carbon number ratio, r, which is defined as

$$r = m/n,$$

the above equation may be rewritten more compactly as:

$$CH_r(\ell) + (1 + \frac{r}{4})\ O_2(g) \longrightarrow CO_2(g) + \frac{r}{2} H_2O(g)$$

Measured values of the heat of combustion must take into account any side reactions which take place, including the condensation of water vapor and the reaction of impurities in the fuel containing oxygen, nitrogen, sulfur, and other elements. However, estimates of the heat of combustion are quite useful for predicting heats of formation. The method of Khurasch (4) is a group contribution method of this type, and will be detailed in a later section.

Other methods for the direct estimation of the standard heat of formation are available. These include procedures based on additive bond energies such as those due to Klages (2, 5), Pauling (6), and others (7). These schemes are not more accurate than the methods mentioned earlier, and are somewhat more cumbersome to employ.

To put the values of the standard heat of formation on an even basis, it is useful to rewrite the formation reaction in terms of the H/C ratio:

$$C(s) + \frac{r}{2} H_2(g) \longrightarrow C\ H_r(\ell)$$

The reactants and products are at 1 atm pressure and 25°C, and the enthalpy change of the reaction is denoted by $\Delta H^\circ_{f,298}(\ell)/n$. This is expressed typically in units of kcal per gram atom carbon, and is especially suited to describing the average properties of a mixture of compounds. The chemical plant streams and refinery streams can thus be described in the same manner as individual pure compounds when this notation is used.

It is also quite instructive to point out several general trends among families of hydrocarbons. In general, paraffins and naphthenic compounds are the least dense hydrocarbons. They have the highest heat of combustion per unit weight, but the lowest heat of combustion per unit volume. They are stable, non-corrosive, and clean-burning. Aromatics, on the other hand, represent the hydrocarbons with the greatest density. They have low heats of combustion per unit weight and high heats of combustion per unit volume. Aromatics are stable compounds, but they are smoky-burning. Olefins exhibit properties which are intermediate to those of the paraffins and the aromatics. The olefins burn cleanly, but they are very reactive and sometimes unstable. These general properties are summarized in the table below:

Compound Type	Paraffins	Olefins	Aromatics
Density	Lowest	Intermediate	Highest
$-\Delta H_c$ per Weight	Highest	Intermediate	Lowest
$-\Delta H_c$ per Volume	Lowest	Intermediate	Highest
Reactivity	Stable	Reactive	Stable
Combustion Quality	Clean-Burn	Clean-Burn	Smoky-Burn

From these general considerations, it is seen that the best fuels for high density, high performance applications are likely to contain aromatics and olefins. This is not all-inclusive, since many other types of compounds could be considered, including acetylenes, highly strained ringed compounds, diolefins, etc. However, the general trends seen here can easily be extended to encompass these types of hydrocarbons.

A-2. Estimates of Heats of Formation and Combustion for Pure Compounds

(a) Franklin Method for Estimating $H^\circ_{f,298}(g)$

Franklin has presented a simple technique for predicting the heat of formation of pure gaseous compounds (1, 2). He found that the heat of formation of various hydrocarbons could be estimated with a high degree of accuracy by adding the empirically determined values for the substituent groups. This is the so-called "group additivity" theory. Thus, from measured heats of formation (or heats of combustion) for known compounds, one can determine the group contributions for each substituent group. These values are then used as a basis for calculating the heats of formation of other, unknown, materials.

Franklin's values for the various group contributions, as well as certain correction factors, are shown in Table A-1. The procedure for carrying out the computations is shown for a simple molecule in Example 1.

TABLE A-1

FRANKLIN'S GROUP CONTRIBUTIONS AND CORRELATIONS FOR ESTIMATING HEATS OF FORMATION OF GASES

Group	K-cal/mole (298°K)	Group	K-cal/mole (298°K)
CH_3	-10.12	-OH (primary)	-41.9
CH_2	-4.926	-OH (sec.)	-44.9
CH	-1.09	-OH (tert.)	-49.2
C	0.80	-OH (phenol)	-46.9
$H_2C = CH_2$	15.00	$\begin{smallmatrix}H\diagdown\\ \diagup\end{smallmatrix}C = O$	-33.9
CH = CH (trans.)	17.83		
CH = CH (cis)	18.88	$\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}C = O$	-31.6
$-\overset{\shortmid}{C} = CH_2$	16.89		
$\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}C = C\begin{smallmatrix}\diagup H\\ \diagdown\end{smallmatrix}$	20.19	$-C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$	-94.6
$\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}C = C\begin{smallmatrix}\diagup\\ \diagdown\end{smallmatrix}$	24.57	$-C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ (ester)	-79.8
≡CH	27.10	-O- (ether)	-27.2
		$-NH_2$	2.8
≡C-	27.34	$\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}NH$	12.0
-CN	29.5	-SH	5.7
Aromatic C-H	3.30	-S-	11.6
Aromatic C-R	5.57	Condensed Aromatic	4.28
C_6 cycloparaffin	-0.45	Adj. Quaternary C's	5.0
C_5 cycloparaffin	5.68	Adj. CH and C	2.5
C_5 cycloparaffin	18.4		
C_3 cycloparaffin	24.22		
C_2H_5 side chain	1.5		
3 adj. CH groups	1.6		

EXAMPLE 1: Estimation of $\Delta H_f(g)$ for Cyclopentane

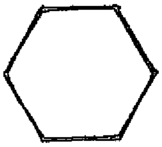
Molecular Model:

The molecule consists of five CH_2 groups arranged in a cycloparaffin ring.

Group Type	Number	Contribution Per Group (Kcal/mole)	Total Contribution
CH_2	5	-4.926	-24.63
C_5 cycloparaffin ring	1	+5.68	+ 5.68
			= -18.95 Kcal/mole

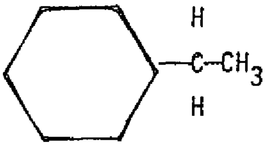
Franklin's method can also be used to make predictions on the effect of structural modifications to the heat of formation of a given compound. This is illustrated in Example 2 below, where we consider the alkylation of a double bond in cyclohexene to form a new molecule, ethyl cyclohexane. This reaction would be carried out in the presence of a strong acid.

EXAMPLE 2: Alkylation of a Cycloolefin



Old Molecule

$\Delta H_f(g)$ = -1.28 kcal/mole



New Molecule

$\Delta H_f(g)$ = ?

Group Type	Loss or Gain in No. of Groups	Contribution Per Group (kcal/mole)	Total Contribution
cyclohexene	Start	---	-1.28
$H_2C = CH_2$	-1	+15.00	-15.00
CH_2	+3	-4.926	-14.78
CH_3	+1	-10.12	-10.12

$\Delta H_f(g)$ = -41.18 kcal/mole

(b) Benson Method for Estimating $\Delta H^{\circ}_{f,298}(g)$

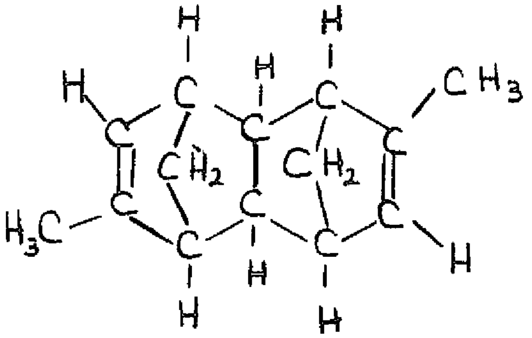
Benson, et. al. (3) have presented a method for the calculation of the standard heat of formation of gaseous hydrocarbons. This scheme is, like Franklin's work, based on the group additivity principle. Benson's correlations and corrections, which are shown in Table A-3, are accurate to within ±1 kcal/mole. Values are not shown for functional groups containing nitrogen, oxygen, or sulfur, although they are available in reference (3). Arbitrarily assigned group values are indicated in Table A-3 by square brackets around the group name.

Before giving an example of the application of Benson's method, the reasons for applying corrections to the estimates is discussed. The underlying assumption of group additivity does not allow for the interactions of next-nearest neighbors, although in some molecules these interactions considerably influence the molecular properties. These effects are accounted for by applying the various conformational corrections.

An example of the value of Benson's method for predicting the heat of formation of a new fuel molecule is illustrated by Example 3 below. In this illustrative example, we follow Benson's nomenclature by first denoting the central polyvalent atom and placing its ligands in parentheses. For example, CX_3-CX_3 can be represented as 2 [C-(C) $(X)_3$] and CX_3 - CY_3 is [C-(C) $(X)_3$] + [C-(C) $(Y)_3$].

EXAMPLE 3: High Density Jet Fuel

SHELLDYNE FUEL
MOLECULAR MODEL



Bond Type	Number	ΔH_f (kcal/mole) per bond	Total Contribution
C-(C)$(H)_3$	2	-10.08	-20.16
C_d-$(C)_2$	2	10.34	20.68
C_d-(C)(H)	2	8.59	17.18
C-$(C)_3$(H)	2	-1.90	-11.40
C-$(C)_2(H)_2$	2	-4.95	- 9.90

$\Delta H^{\circ}_{f,298}(g)$= - 3.60 kcal/mole

The actual value for ethyl cyclohexane is -41.05 kcal/mole (API value, ref. 15).

Some typical heat of formation values estimated by Franklin's method are compared with actual values in Table A-2. The estimated values are quite good for paraffins, but are slightly less accurate for aromatic compounds or compounds containing other functional groups.

TABLE A-2

ESTIMATED VS. ACTUAL HEATS OF FORMATION USING FRANKLIN METHOD

	$\Delta H^{\circ}_{f,298}(g)$, kcal/mole	
	Estimated	Actual
Ethane	-20.24	-20.24(1)
n-Decane	-59.65	-59.67(2)
Cyclopentane	-18.95	-18.46(2)
trans-3-Hexene	-11.8	-12.6(1)
Isoprene	18.9	18.1(1)
Diphenyl	44.1	43.2(1)
Acetone	-51.84	-51.7(2)
n-Butylamine	-22.10	-22.8

---

(1) API values - ref. 1.

(2) Ref. (3).

TABLE A-3

BENSON'S GROUP CONTRIBUTIONS AND CORRELATIONS FOR ESTIMATING HEATS OF FORMATION OF GASES

Group	Kcal/mole (298°K)	Group	Kcal/mole (298°K)
$C-(H)_3(C)$	-10.08	$C_t-(H)$	26.93
$C-(H)_2(C)_2$	-4.95	$C_t-(C)$	27.55
$C-(H)(C)_3$	-1.90	$C_t-(C_d)$	29.20
$C-(C)_4$	0.50		
$C_d-(H)_2$	6.26	$C_b-(H)$	3.30
$C_d-(H)(C)$	8.59	$C_b-(C)$	5.51
$C_d-(C)_2$	10.34	$C_b-(C_d)$	5.68
$C_d-(C_d)(H)$	6.78	$[C_b-(C_t)]$	5.7
$C_d-(C_d)(C)$	8.88	$C_b-(C_b)$	4.96
$[C_d-(C_b)(H)]$	6.78	Alkene gauche	0.80
$[C_d-(C_t)(H)]$	6.78	Alkene gauche	0.50
		cis correction	1.00
		ortho correction	0.57
$C-(C_d)(C)(H)$	-4.76	C_3 cycloparaffin	27.6
$C-(C_d)_2(H)_2$	-4.29	C_4 cycloparaffin	26.2
$C-(C_d)(C_b)(H)_2$	-4.29	C_5 cycloparaffin	6.3
$C-(C_t)(C)(H)_2$	-4.73	C_6 cycloparaffin	0.0
$C-(C_b)(C)(H)_2$	-4.86	C_3 cycloolefin	53.7
$C-(C_d)(C)_2(H)$	-1.48	C_4 cycloolefin	29.8
$C-(C_t)(C)_2(H)$	-1.72	C_5 cycloolefin	5.9
$C-(C_b)(C)_2(H)$	-0.98	C_6 cycloolefin	1.4
		C_5 cyclodiolefin	6.0
$C-(C_d)(C)_3$	1.68	C_6 cyclodiolefin-1,3	4.8

BENSON'S GROUP CONTRIBUTIONS AND CORRELATIONS FOR ESTIMATING HEATS OF FORMATION OF GASES

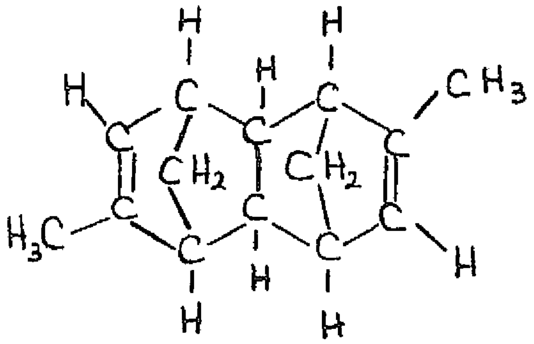
Group	Kcal/mole (298°K)	Group	Kcal/mole (298°K)
$C-(C_b)(C)_3$	2.81	C_6 cyclodiolefin-1,4	0.5

Subscript Notation:

d - double bonded carbon
t - triple bonded
b - aromatic carbon

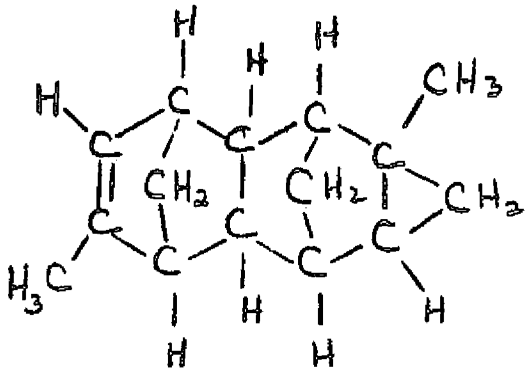
This method of synthesizing molecules thermodynamically was used to predict the heats of formation of high density fuel molecules, as well as the technique of applying corrections to the heat of formation of a compound of known structure which can be modified structurally to produce an estimate for a new compound. In the following predictive example, we show how this technique can be used to predict before synthesis the heat content of a new fuel molecule. We proceed by noting the structural modification, the addition of a methylene group, CH_2, across one double bond, and the changes in the group contributions which this produces.

EXAMPLE 4: <u>Modification of High Density Jet Fuel</u>



SHELLDYNE MOLECULE

ΔH_f = 3.60 kcal/mole



MODIFIED SHELLDYNE STRUCTURE

Loss	Total ΔH_f	Gain	Total ΔH_f
2 $[C-(C_d)(C)_2(H)]$	-2.96	4 $[C-(C)_3(H)]$	-7.60
$C_d-(H)_2$	+6.26	$C-(C)_2(H)_2$	-4.95
	+3.30	C_3 cycloparaffin	+27.60
			+15.05

New ΔH_f = old ΔH_f - loss contribution + gain contribution

$= -3.60 - 3.30 + 15.05$

$\Delta H^\circ_{f,298}(g) = +8.15$ kcal/mole

The effect of structural modifications is evidenced by a change in the value of the heat of formation which, as in the above example, can be quite large in magnitude. The estimates obtained using Benson's method are in excellent agreement with literature values, as shown by Table A-4. Comparison with Table A-2 shows that Benson's estimates agree closely with Franklin's values. Thus, either method is satisfactory for predicting heats of formation of gaseous hydrocarbons.

TABLE A-4

ESTIMATED VS. ACTUAL HEATS OF FORMATION USING BENSON'S METHOD

	$\Delta H^\circ_{f,298}(g)$, kcal/mole	
	Estimated	Actual
Ethane	-20.16	-20.24(1)
n-Decane	-59.76	-59.67(2)
Cyclopentane	-18.46	-18.46(2)
trans-3-Hexene	-12.49	-12.6(1)
Isoprene	18.09	18.1(1)
Diphenyl	42.92	43.2(1)
Acetone	-51.7	-51.7(2)

---

(1) API values - ref. 1.

(2) Ref. (3).

To convert values obtained for the vapor phase into heats of formation for the liquid phase, it is necessary to know the heat of vaporization of the substance. The following section delineates some of the methods which can be used to estimate ΔH_{VAP}, if literature values are not available.

(c) Heats of Vaporization

1. Clausius-Clapeyron Vapor Pressure Plot

In the absence of tabulated values of the heat of vaporization, this quantity can be estimated from known vapor pressure data as a function of temperature. The general method is described by Castellan (8), who also points out that the existence of vapor pressure and its increase with temperature are consequences of the Maxwell-Boltzmann energy distribution of the liquid molecules.

The Clausius-Clapeyron equation may be written as

$$\frac{dp}{dT} = \frac{-\Delta H_{VAP}}{RT}$$

If it is assumed that ΔH_{VAP} is independent of temperature, this equation can be integrated to obtain:

$$\ell n \frac{P_1}{P_2} = \frac{-\Delta H_{VAP}}{R} \quad \frac{1}{T_1} - \frac{1}{T_2}$$

This equation suggests that a plot of the natural logarithm of vapor pressure vs. the reciprocal of absolute temperature should yield a straight line whose slope is equal to $-\Delta H_{VAP}/R$. It is seen that the data fall on a straight line, with the result that the heat of vaporization is calculated to be 11.92 kcal/mole according to the relation given above.

This is a powerful method, and it allows for the subsequent calculation of the liquid heat of formation from an estimate for the vapor obtained by the methods of Benson or Franklin. For example, the heat of formation for gaseous indene can be estimated by Benson's method to be $\Delta H_f(g) = +41.48$ kcal/mole. Therefore, the liquid heat of formation is:

$$\begin{aligned}\Delta H_f(\ell) &= \Delta H_f(g) - \Delta H_{VAP}\\ &= 41.48 - 11.92\\ &= 29.56 \text{ kcal/mole}\end{aligned}$$

This can also be converted to the heat of formation per gram atom carbon by simply dividing through by the carbon number for indene, C_9H_8, as follows:

$$\frac{\Delta H_f(\ell)}{n} = \frac{29.56}{9} = +3.28 \text{ kcal/gram atom C}$$

The utility of this method is only limited by the availability of the vapor pressure data for a given compound. If such data is unavailable, other methods for determining the heat of vaporization must be used. One well-known technique is described in the next section. Other methods are available for calculating the latent heat of vaporization, which are based on vapor pressure plots of reference substances. These are due to Othmer (10, 11) and Gordon (12). They are useful in determining the latent heat at various temperatures, but they are generally harder to apply than the Clausius-Clapeyron technique and require more data, which typically cannot be found.

2. Trouton's Rule

An empirical rule called Trouton's rule is described in reference (8) which can be used for a rough estimate of the heat of vaporization. It is based upon the observation that for many liquids, the entropy of vaporization at the normal boiling point has approximately the same value:

$$\Delta S_{VAP} \approx 21 \frac{\text{cal}}{^\circ\text{k}\cdot\text{mole}}$$

This relation is called Trouton's rule, and it follows immediately that for liquids which obey it,

$$\Delta H_{VAP} = 21\ T_b\ (\text{cal/mole})$$

where T_b is the normal boiling point of the liquid in degrees Kelvin. This is useful for obtaining an approximate heat of vaporization from a knowledge of the liquid's boiling point.

Trouton's rule is not valid for associated liquids such as water, alcohols, and amines. For substances with boiling points below 150°K it also fails. If Trouton's rule is applied to indene, whose boiling point is 182.44°C, it is found that ΔH_{VAP} is equal to 9.57 kcal/mole. This is less accurate than the value obtained by a Clausius-Clapeyron vapor pressure plot, but it represents a very good estimate of the actual value.

Other variations of the basic idea behind Trouton's rule can be found in the literature, Hildebrand's rule, which uses a temperature T_H instead of the boiling temperature in the following relation;

$$\Delta H_{VAP} = 22.1\ T_H\ (\text{cal/mole})$$

is based on the Hildebrand entropy, $\Delta S_H = 22.1$ cal/°k·mole. The Hildebrand temperature, T_H, is defined as that temperature at which the vapor concentration is 1/22.4 moles/liter; it can be tabulated as a function of T_b for a known value of ΔS_H. The Hildebrand entropy is found to remain more constant than the Trouton entropy, with a resultant increase in the accuracy of the estimate. Hildebrand's rule includes low-boiling substances but cannot be used to predict the heat of vaporization of associated liquids.

As an example, we can again consider indene, whose boiling point is 182.44°C = 455.6°K. The Hildebrand temperature is 460°K. Therefore, the heat of vaporization is estimated to be (22.1)(460) = 10,170 cal/mole or 10.17 kcal/mole. It is immediately seen that this result is more accurate than that based on a Trouton estimate, although it is still too small.

The third and final method which is based on the Trouton rule is an empirical correlation presented by Benson et. al. (<u>3</u>). The formula used gave satisfactory results, and is presented below:

$$\Delta H_{VAP} = S_T\ [(1.76 \times 10^{-3})\ t_b + 0.253]\ (\text{kcal/mole})$$

where S_T is the Trouton constant (taken by Benson as 22 cal/°K·mole), and t_b is the boiling temperature in degrees Centigrade. When used for indene, this method yields a heat of vaporization of 12.63 kcal/mole if S_T is taken as 22, and 12.06 is S_T is taken as 21. These are both very good estimates of the actual number, and Benson's correlation is therefore quite useful.

It is important to note that of the three methods based on Trouton's idea, only Benson's yields ΔH_{VAP} at 25°C directly. The other two methods yield a value of ΔH_{VAP} from the boiling point which is then assumed to be constant over the entire temperature range of interest. In some cases this is not exactly true, but in making estimates this assumption can be taken as valid for all pratical purposes.

(d) <u>Kharasch Method for Estimating $\Delta H^\circ_{f,298}(\ell)$</u>

It would be desirable to estimate the heat of formation of a liquid compound directly, without having to make two individual estimates to reach the same destination. A method presented by Kharasch (<u>13</u>) and used extensively to supplement values appearing in ICT (<u>14</u>) allows us to make a such a direct estimate. The method is simple and accurate to within one or two percent.

Actually, the method gives an estimate of the heat of combustion of the liquid, which is directly convertible to a value of the heat of formation by using known heats of formation for the other compounds appearing in the stoichiometric combustion equation. Kharasch based his method on combustion of the liquid hydrocarbon with gaseous oxygen to form liquid water and gaseous oxygen to form liquid water and gaseous carbon dioxide. It is assumed that the heat generated during burning in oxygen is due to the interdisplacement of the electrons between the carbon and oxygen atoms. It is further assumed that the net amount of energy interchanges in the form of heat is equal to 26.05 kcal per electron per mole, if the initial and final states of the electron correspond to that around the carbon nucleus in methane and in carbon dioxide, respectively. Correction factors are applied to those electrons that are displaced from the reference position.

The correction factors for various structural factors are shown in Table A-5, along with a condensed summary of the technique. As an example of this predictive method, we consider a cholanthrene molecule in Example 5.

EXAMPLE 5: Heat of Combustion of Cholanthrene

Cholanthrene Molecule

$C_{19}H_{12}$

$N = 19 \times 4 + 12 = 88$

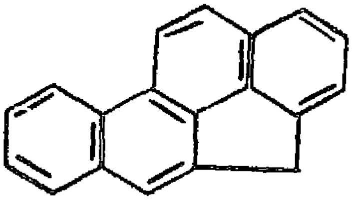


TABLE A-5

SUMMARY OF HEAT OF COMBUSTION ESTIMATES BY METHOD OF KHARASCH

$-\Delta H_c(\ell) = (26.05)\ N + \text{Corrections (kcal/mole)}$

where N = total number of electrons in molecule, and the corrections are as tabulated below

ATOM	N
Carbon	4
Hydrogen	1
Oxygen	-2

TABLE A-5 (Continued)

Pair of Electrons Held Between	Correction Per Group
Aromatic radical: Aromatic radical	-6.5
Aromatic radical: Aliphatic radical	-3.5
Ethylene bond	+13.0
Aromatic radical: Vinyl radical	-6.5
Ethylene bond in ring system	+6.5
Acetylene bond, 1 or more replaceable H	+46.1
Acetylene, no replaceable H, R-C≡C-R	+33.1
Aromatic radical carbon: Acetylene radical	-6.5
Primary Alcohol	+13.0
Secondary Alcohol	+6.5
Tertiary Alcohol	+3.5
Aromatic radical: Hydroxyl group	+3.5

Structural Group	Number	Correction Per Group	Total Correction
Aromatic - Aromatic	6	-6.5	-39.0 - 7.0
Aromatic - Aliphatic	2	-3.5	- 7.0
			-46.0

$-\Delta H_c(\ell) = (88)(26.05)\ -46.0 = 2246.4$ kcal/mole

The method of Khurasch is quite useful for predicting the heat of combustion of polynuclear compounds, as shown in the above example. The reduction of this figure to a heat of formation value is accomplished by considering the stoichiometry:

$$CnHm(\ell) + (n + \frac{m}{4})\ O_2(g) \rightarrow \frac{m}{2}\ H_2O(\ell)\ n\ CO_2(g)$$

The heat of formation is found by noting that

$$\Delta H_c(\ell) = \frac{m}{2} \cdot \Delta H_f[H_2O(\ell)] + n \cdot \Delta H_f\ [CO_2(g)] - \Delta H_f(\ell)$$

The heat of formation of oxygen gas is zero, so it does not enter into the calculation. Solving for the heat of formation

$$\Delta H_f(\ell) = \Delta H_c(\ell) + \frac{m}{2} \cdot \Delta H_f\ [H_2O(\ell)] + n \cdot \Delta H_f\ [CO_2(g)]$$

The heats of formation at standard conditions are given below from reference (8):

Compound	Phase	$\Delta H^\circ_{f,298}$ (kcal/mole)
H_2O	liquid	-68.3174
H_2O	vapor	-57.7979
CO_2	vapor	-94.0518
O_2	vapor	0.0

Thus, we can find the heat of formation of cholanthrene, for example, as

$$\Delta H^\circ_{f,298}(\ell) = (2246.4) + (12/2)\ (-68.3174) + (19)\ (-94.0518)$$

$$= 49.51 \text{ kcal/mole}$$

Also, $\frac{\Delta H^\circ_{f,298}(\ell)}{n} = \frac{49.51}{19} = +2.61$ kcal/gram atom C

We can also point out at this time that the heat of combustion obtained by the method of Kharasch is not the same as the standard heat of combustion referred to earlier. The standard heat of combustion is for gaseous combustion products, both H_2O and CO_2, while in the Kharasch technique, the reference is to a liquid water product. This can be accounted for by applying the heats of formation of the liquid and gaseous H_2O given above to the estimated value as shown in Example 6.

EXAMPLE 6: Correction to Standard Heat of Combustion

For Cholanthrene, $C_{19}H_{12}$, it is desired to find the standard heat of combustion from a Kharasch estimate.

Estimate: $-\Delta H_c(\ell) = 2246.4$ kcal/mole

(From Example 5, with liquid H_2O product)

Correction (according to stoichiometry, for $H_2O(g)$ product)

$$=\left(\frac{12}{2}\right)(68.3174 - 57.7979) = -63.1$$

Therefore, $-\Delta H^\circ_{c,298}(\ell) = 2246.4 - 63.1 = 2183.3$ kcal/mole

---

The fact that only one estimate is used to find the standard heat of formation makes the Kharasch technique the method of choice for many compounds whose heats of vaporization cannot be found or predicted. When enough data is available to use Benson's or Franklin's method, they should be used, because they are generally more accurate. This can be seen by comparing the accuracy of the Kharasch estimates in Table A-6 with those in Tables A-2 and A-3.

TABLE A-6

ESTIMATED VS. ACTUAL HEATS OF FORMATION USING METHOD OF KHARASCH

	$\Delta H^\circ_{f,298}(\ell)$, kcal/mole	
	Estimated	Actual
Ethane	-28.36	-22.50(1)
n-Decane	-76.91	-79.95(1)
Cyclopentane	-30.35	-25.30(1)
trans-3-Hexene	-23.42	-20.57(1)
Isoprene	+11.87	+11.80)1)
Diphenyl	+27.69	+23.39(2)

---

(1) API values - ref. 15.

(2) Ref. (13).

(e) Estimates of Standards $\Delta H_f(\ell)/n$ for Hydrocarbons

The standard heats of formation for various liquid hydrocarbons have been estimated by the methods described on the preceding sections. Literature values were used when they were available. The values of the standard heat of formation for the pure hydrocarbon candidates are given in Table A-7, along with the appropriate source or estimation techniques used. The values for the individual components which appear in the chemical plant streams are given in Table A-8.

TABLE A-7

VALUES OF STANDARD HEAT OF FORMATION FOR PURE LIQUID HYDROCARBON CANDIDATE FUELS

Compound Code	Compound Name	$\frac{\Delta H^\circ_{f,298}(\ell)}{n}$ $\frac{\text{kcal}}{\text{gram atom C}}$	Source or Method
A-1	Shelldyne	0.93 2.5 3.546	1 2 3
A-2	Tetrahydrotricyclopentadiene	-2.0	2
A-3	Tetrahydrodicyclopentadiene	-0.9	2
A-4	1,7-Octadiyne	9.8 9.863	2 3
A-5	Cyclododecatriene	1.2	4
A-6	Decahydroacenaphthene	-3.3	5
A-7	Octahydroacenaphthene	-2.4	5
A-8	Spiro (5.5) undec-2-ene	-1.94	6
A-9	Spiro (5.6) dodec-7-ene	-2.28	6
A-10	Spiro (5.6) dodecane	-4.72	6
A-11	Tetrahydrofluorene	1.88	6
A-12	Dodecahydrofluorene	-3.57	6
A-13	Tricyclopropanated Cyclodecatriene	-0.05	6

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1. Reference (17).
2. Reference (18).
3. Reference (19).
4. Benson method with Trouton estimate.
5. Based on measured heats of combustion.
6. Khurasch method.

TABLE A-8

VALUES OF STANDARD HEAT OF FORMATION FOR INDIVIDUAL COMPOUNDS IN CHEMICAL PLANT STREAMS

Compound	H/C Ratio	$\Delta H^\circ_{f,298}(\ell)/n$ (kcal/gram atom C)	Source or Method
Methane	4.0	-21.0	2
Ethane	3.0	-11.25	1
1-Butene-3-yne	1.0	+15.7	3
1,2-Butadiene	1.5	+8.57	1
1,3-Butadiene	1.5	+5.30	1
1-Butyne	1.5	+8.62	1
2-Butyne	1.5	+7.27	1
Cyclopentadiene	1.2	+5.4	3
2-Methyl-1,3-Butadiene	1.6	+2.36	1
1,3-Pentadiene	1.6	+2.60	1
1,4-Pentadiene	1.6	+3.95	1
Cyclopentane		-5.06	1
2-Methyl-1-Butene	2.0	-2.97	1
3-Methyl-1-Butene	2.0	-2.52	1
2-Methyl-2-Butene	2.0	-3.33	1
1-Pentene	2.0	-2.22	1
cis-2-Pentene	2.0	-2.58	1
trans-2-Pentene	2.0	-2.79	1
2-Methylpentane		-8.59	3
Methylcyclopentane	1.333	+3.2	1
1,5-Hexadiene	1.667	+2.35	1
Methyl cyclopentane		-5.51	1
Toluene	1.142	+0.41	1
1-Heptyne	1.714	+2.52	1
2-Methyl-1,5-Hexadiene	1.714	+0.78	1

TABLE A-8 (Continued)

VALUES OF STANDARD HEAT OF FORMATION FOR INDIVIDUAL COMPOUNDS IN CHEMICAL PLANT STREAMS

Compound	H/C Ratio	$\Delta H^\circ_{f,298}(\ell)/n$ (kcal/gram atom C)	Source or Method
Styrene	1.0	+3.104	1
Ethylbenzene	1.25	-0.372	1
Xylenes	1.25	-0.74	1
2,5-Dimethyl-1,5-Hexadiene	1.75	-1.07	1
Indene	0.889	+3.44	4
Methyl Styrenes	1.111	+1.94	1
Cumene	1.333	-1.09	1
2,6-Dimethyl-1,5-Heptadiene	1.778	-1.07	1
Naphthalene	0.8	+2.3	1
Methyl Indene	1.0	+2.3	3
Dicyclopentadiene	1.2	+3.0	5
Dihydro-Dicyclopentadiene		+0.49	5
Butylbenzene	1.4	-1.53	1
Methyl Naphthalene	0.9091	+1.23	6
Dimethyl Indene	1.091	_1.3	3
Dimethyl Indane		-0.83	7
Cyclopentadiene-Methylcyclopentadiene Codimer		+2.1	5
		-0.63	5
Dimethyl Naphthalene	1.0		
		+0.33	7
Methylcyclopentadiene Dimer	1.33		
		+0.3	5
Dihydro-Methylcyclopentadiene Dimer		-1.98	5
Trimethyl Naphthalene	1.077	-0.4	7
Chrysene	0.667	+6.1	7
Pentacene	0.6364	+6.0	7
Fused Dibenzpyrene	0.5455	+0.26	7
Hexacene	0.6154	+5.9	7

TABLE A-8 (Continued)

VALUES OF STANDARD HEAT OF FORMATION FOR INDIVIDUAL COMPOUNDS IN CHEMICAL PLANT STREAMS

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1. Reference (15).
2. Reference (18).
3. Benson with Trouton estimate.
4. Average of Franklin and Benson with vapor pressure plot.
5. From measured heats of combustion.
6. Reference (20).
7. Khurasch estimate.

SAMPLE CALCULATIONS FOR MIXTURES

For a single component, e.g. isoprene in Table A-7, whose molecular formula, molecular weight, weight fraction, and heat of combustion are known, we can calculate the remaining four columns in the Table with the following relations:

$$\text{Wt. Percent Carbon} = \frac{n\ M_C\ (100)}{n\ M_C \div m\ M_H} = \frac{(5)\ (12.01115)\ (100)}{(5)\ (12.01115) + (8)\ (1.00797)} = 88.16\%$$

$$\text{Wt. Fraction Carbon in Stream from Component} = \frac{(\%\ C)\ (\text{Wt. Fraction})}{100} = \frac{(88.16)\ (530.0\ g/kg)}{100} = 467.25\ g/$$

$$\text{Moles of Component} = \frac{\text{Wt. Fraction}}{\text{Molecular Weight}} = \frac{(530.0\ g/kg)}{(68.114\ g/mole)} = 7.78\ \text{moles/kg}$$

$$\text{Contribution of Total Heat of Combustion} = (\text{Moles})\ (-\Delta H_c) = (7.78\ \text{moles/kg})\ (713.25\ \text{kcal/mole}) = 5549.8\ \text{kcal/kg}$$

Adding up the columns as shown in Table A-7, we obtain the following summary for the stream:

Total Wt. Fraction (identified compounds) = 987.0 g/kg
Total Wt. Fraction Carbon = 870.60 g/kg
Total Heat of Combustion = 10.325.8 kcal/kg

ANALYSIS OF WORKSHEET DATA FOR STREAM B-2

$$r = \begin{matrix}\text{H/C}\\ \text{Ratio}\end{matrix} = \frac{(\text{Wt. H})/M_H}{(\text{Wt. C})/M_C} = \frac{(987-870.6\ \text{gH})/(1.00797\ \text{gH/mole H})}{(870.6\ \text{gC})/(12.01115\ \text{gC/mole C})} = 1.593$$

$$\text{Empirical Molecular Wt.} = M_C + r\,M_H = 12.01115 + (1.593)\ (1.00797)$$

$$= 13.617\ \text{g/gram atom C}$$

$$\begin{matrix}\text{Heat of}\\ \text{Combustion}\end{matrix} = \frac{-\Delta H^{\circ}_{f,298}(\ell)}{n} = \frac{(10{,}325.8\ \text{kcal/kg})}{(987.0\ \text{g/kg})} \times \left(\frac{13.617\ \text{g}}{\text{gram atom C}}\right)$$

$$= 142.46\ \text{kcal/gram atom C}$$

$$\begin{matrix}\text{Heat of}\\ \text{Formation}\end{matrix} = \frac{\Delta H^{\circ}_{f,298}(\ell)}{n} = 142.42 - 94.0518 - \frac{(1.593)}{2}(57.7979) = +2.37\ \text{kcal/gram atom C}$$

$$\begin{matrix}\text{Heat of}\\ \text{Combustion}\end{matrix} = \left(\frac{10{,}325.8\ \text{kcal/kg}}{987.0\ \text{g/kg}}\right) \times \left(\frac{1.8\ \text{BTU/lb}}{\text{kcal/g}}\right) = 18{,}830\ \text{BTU/lb}$$

$$\begin{matrix}\text{Heat of}\\ \text{Combustion}\end{matrix} = (18{,}830\ \text{BTU/lb})(0.70\ \text{g/cc})\left(\frac{62.48\ \text{lb/ft}^3}{\text{g/cc}}\right)\left(\frac{0.13368\ \text{ft}^3}{\text{gal}}\right)$$

$$= 110{,}000\ \text{BTU/gal}$$

3. Physical Property Estimates for Defined Streams and Blends

The properties of chemical plant streams and refinery streams of known composition can be calculated on the basis of the properties of the individual components of each stream. For the hydrogen to carbon number ratio and the heats of formation and combustion, this is most easily done in a worksheet form as shown in Table A-9 for one of the chemical plant streams. This is followed by sample calculations in Figure 3 and an analysis of the calculated data in Figure 4 for the same stream. In Figure 4, the calculations are based on the assumption that the weight of unidentifiable components in the stream is negligible.

It was further implied in the worksheet that the contributions to the heats of combustion for the individual components were additive. This is only exactly true if there are no enthalpy changes associated with the mixing process, in which all of the pure compounds are taken at 1 atm pressure and 25°C and are mixed together to form the stream at the same temperature and pressure. This is closely approximated by the chemical plant streams, which do not contain appreciable amounts of any polar or associated substances, and thus, the impact of this assumption on the refinery streams is unknown. The deviations in the heat of formation and combustion calculations caused by this assumption can be positive or negative, and are of unknown magnitude.

Sometimes it is desirable to blend two streams together to obtain improved performance qualities. In such cases, it is necessary to estimate the new properties of the blend, including the hydrogen to carbon number ratio, the heat of formation, the heat of combustion, and the density. The equations for these estimates are given in Table A-10, and Example 7 below illustrates their use. The equation for the H/C ratio is based on the conservation of mass. The equations for the combustion properties are based on the additivity of the heats of combustion. The estimated blend density is calculated by a volumetric average method.

EXAMPLE 7: Blend Properties

Consider a blend of streams with the following properties:

	Wt.% of Blend	H/C Ratio	$\frac{\Delta H^\circ_{f,298}(\ell)}{n}$	$-\Delta H_C$ (BTU/lb)	$-\Delta H_C$ BTU/gal	Density (g/cc)
Stream X	30	1.60	+4.50	19,130	127,700	0.80
Stream Y	70	1.20	+3.20	17,960	157,400	1.05

TABLE A-9

WORKSHEET FOR CHEMICAL PLANT STREAM B-2

Name of Compound	Molecular Formula	Molecular Weight	Weight Fraction of Stream (g per Kg)	Wt. % Carbon in Component	Wt. Fraction Carbon in Stream from Component	Moles of Component	$-\Delta H^\circ_{c,298}(\ell)$ of Component (kcal/mole)	Contribution to heat of Combustion
2-Butyne	C_4H_6	54.088	0.1	88.82	0.09	0.002	579.1	1.1
3-Methyl-1-Butene	C_5H_{10}	70.130	0.1	85.63	0.09	0.001	742.61	1.1
1,4-Pentadiene	C_5H_8	68.114	0.1	88.16	0.09	0.001	721.2	1.0
1-Pentene	C_5H	70.130	0.1	85.63	0.08	0.001	748.16	1.1
2-Methyl-1-Butene	C_5H	70.130	0.3	85.63	0.26	0.004	744.39	3.2
trans-2-Pentene	C_5H	70.130	0.3	85.63	0.26	0.004	745.28	3.2
Isoprene	C_5H	68.114	530.0	88.16	467.25	7.78	713.25	5549.8
cis-2-Pentene	C_5H_{10}	70.130	3.6	85.63	3.08	0.05	746.33	36.6
2-Methyl-2-Butene	C_5H_{10}	70.130	40.0	85.63	34.25	0.57	742.61	423.5
Cyclopentadiene	C_5H_6	66.104	58.4	90.85	53.06	0.883	670.0	591.9
trans-1,3-Pentadiene	C_5H_8	68.114	319.0	88.16	281.23	4.68	714.5	3346.2
cis-1,3-Pentadiene	C_5H_8	68.114	35.0	88.16	30.86	0.51	714.4	367.1
		Total Weight =	987.0 g	Total Wt. Carbon =	870.60 g		Total Heat of Combustion =	10,325.8

TABLE A-10

ESTIMATING PROPERTIES OF BLENDS

A. H/C Ratio

$$\text{Wt. Fraction C} = C = \frac{W_{f1}\,M_C}{M_C + r_1 M_H} + \frac{W_{f2}\,M_C}{M_C + r_2 M_H}$$

$$r_B = \frac{(1-C)/M_H}{C/M_C}$$

B. Density

$$\rho_B = \frac{1}{\dfrac{W_{f1}}{\rho_1} + \dfrac{W_{f2}}{\rho_2}}$$

C. Heat of Combustion

$$-\Delta H_{C,B} = W_{f1}\,(-\Delta H_{C,1}) + W_{f2}\,(-\Delta H_{C,2})$$

$$\frac{-\Delta H_{C,B}}{n} = (-\Delta H_{C,B})(M_C + r_B M_H)$$

D. Heat of Formation

$$\Delta H^\circ_{f,298}(\ell) = \frac{-\Delta H_{C,B}}{n} + [\Delta H^\circ_{f,298}\,(CO_2(g))] + [\Delta H^\circ_{f,298}(H_2O\,(g))]$$

EXAMPLE 7: Blend Properties (continued)

The blend properties are then calculated as:

$$\text{Wt. Fraction Carbon} = \frac{(0.3)(12.01115)}{(12.01115) + (1.6)(1.00797)} + \frac{(0.7)(12.0115)}{(12.0115)+(1.2)(1.00797)}$$

$$= 0.900$$

$$r_B = \text{H/C Ratio} = \frac{(1-0.9)/1.00797}{0.9/12.01115} = 1.317$$

$$\rho_B = \frac{1}{\frac{0.3\ \text{gX/g}}{0.80\ \text{gX/cc}} + \frac{0.7\ \text{gY/g}}{.05\ \text{gY/cc}}} = 0.960\ \text{g/cc}$$

$$-\Delta H_{C,B} = (0.3)(19{,}130) + (0.7)(17{,}960) = 13{,}210\ \text{BTU/lb}$$

$$-\Delta H_{C,B} = (18{,}310)(0.96)(62.48)(0.13368) = 146{,}800\ \text{BTU/lb}$$

$$-\Delta H_{C,B} = \frac{18{,}311}{1800} = 10.17\ \text{kcal/g}$$

$$\frac{-\Delta H_{C,B}}{n} = (10.17\ [(12.01115 + (1.317)(1.00797)] = 135.69\ \text{kcal/gram atom C}$$

$$\frac{\Delta H^\circ_{f,298}}{n} = 135.69 + (-94.0518) + \frac{(1.317)}{2}(-57.7979) = +3.58\ \text{kcal/gram atom C}$$

From the example, it is seen that the properties of a blend are intermediate between those of the streams it is composed of. These ideas can easily be extended to blends of three or more streams. This makes the estimation of the properties of a candidate blend a straightforward procedure.

A-4. Effects of Simple Processing on Stream Properties

There are many processing alternatives which can be taken on a stream to improve its properties. Most of the more difficult procedures are used for the purification and separation operations, which are aimed at removing unstable or unwanted compounds and leaving one or more desired components in a concentrated form. However, simple distillation into rough cuts can be used to remove the majority of unwanted material without incurring a large cost. If the increase in the resulting product's utility as a fuel is increased, and if the cost which is incurred in this simple processing is small, then the processing should be used.

Distillation is aimed at removing a cut or cuts from a stream in a specified boiling range. It is obviously carried out for purification, and the results depend to a small degree on the individual molecular weights as well as the boiling properties of a stream's constituents. In general, the removal of saturated (paraffinic or napthenic) compounds from a stream will increase both the density and heat of formation of the stream, but will lower the hydrogen to carbon number ratio. The removal of condensed polynuclear aromatics and other lighter aromatics will have the opposite affect, lowering the stream's density and heat of formation while increasing its H/C ratio. The removal of olefins, diolefins, cyclic compounds, alkyl-substituted aromatics, and other compounds affect the stream's properties in a manner that is dependent on the remaining constituents of the stream, in a fashion that parallels the relative effects of removing paraffins and condensed aromatics.

Another simple process is hydrogenation, which can be carried out by any number of techniques. Typically, all use a finely divided metal catalyst at moderate pressures and temperatures. The hydrogenation can be carried out selectively to hydrogenate olefins while leaving aromatic rings intact, or it can be used to vigorously hydrogenate everything to saturated compounds. The difference in these methods is accomplished by using different catalysts and by changing operating conditions, or by a combination of these parameters.

The general effects of hydrogenation on a stream's properties is to increase the saturate content and thereby lower the density and the heat of formation, while at the same time the H/C ratio is obviously increased. In some cases, this will give improved fuel performance, but in any case, it will be likely to enhance the thermal stability of the fuel and to decrease the formation of deposits and gum.

In any processing method, be it distillation, hydrogenation, or some other technique, there must be an increase in the usefulness of the fuel from one or more of a number of possible standpoints before the processing cost is justified. This increased usefulness can come in any of the following forms: increased performance, enhanced thermal stability, better pumping and handling characteristics, fewer safety risks, better boiling and freezing properties, or better thermal properties. Of course, the effects on many of these parameters cannot be estimated beforehand, although the important performance criteria can be predicted with a fair amount of accuracy, as was discussed in earlier sections.

A-5. Specific Impulse and Merit Index

The candidate fuels were screened on the basis of their specific impulse and, more particularly, their merit index. The specific impulse may be defined as the thrust developed per unit weight rate of consumption of propellant when the liquid fuel and oxidizer are combusted stoichiometrically to form gaseous carbon monoxide and water vapor for an equilibrium expansion from 1000 psia to 14.7 psia. The propellant merit index is defined for the purposes of this study as the product of the specific impulse raised to the third power multiplied by the propellant bulk density. The stoichiometry and equations for calculating the propellant bulk density are shown in Figure 3. The calculation of the specific impulse is based on the H/C number ratio of a candidate fuel and upon the standard heat of formation per gram atom carbon of the fuel, and was carried out by the NASA-LeRC Project Manager from a standard computer program for all of the candidate fuels. This calculation is an approximation and is based on an assumed combustion to CO and H_2O.

FIGURE 3

STOICHIOMETRY AND CALCULATION OF PROPELLANT BULK DENSITY

A. Stoichiometry

$$CH_r(\ell) + [(2 + r)/4]\ O_2(\ell) = CO(g) + (r/2)\ H_2O(g)$$

where r = H/C number ratio of fuel

B. Stoichiometric Mixture Ratio, m

$$m = \frac{\text{Wt. Oxygen}}{\text{Wt. Fuel}} = \frac{[(2 + r)/4]\ (31.9988)}{12.01115 + (1.00797)(r)}$$

C. Propellant Bulk Density, $\overline{\rho}$

$$\overline{\rho} = 62.4\ \gamma_{AV}\ (\#/ft^3)$$

$$\text{where } \gamma_{AV} = \frac{\gamma_o\ \gamma_f\ (1 + m)}{m\gamma_f + \gamma_o}$$

and where γ_{AV} = specific gravity of the propellant

γ_f = specific gravity of the fuel

γ_o = specific gravity of the oxidizer (1.4 for LOX)

D. Example: Compound A-5

Given $r = 1.5$, $\gamma_f = 0.89$ and $\gamma_o = 1.14$, we can calculate

$$m = \frac{[(2 + 1.5)/4]\ (31.9988}{12.01115 + (1.00797)(1.5)} = 2.070$$

$$\gamma_{AV} = \frac{(1.14)(0.89)(1 + 2.07)}{(2.07)(0.89) + 1.14} = 1.044$$

$$\overline{\rho} = (62.4)(1.044) = 65.17\ \#/\text{ft}^3$$

(b). Tabulated Results

The estimation of the physical properties of each candidate fuel enables us to obtain values for the specific impulse and the merit index. These were provided to us by NASA-LeRC, who ran a computer program to calculate these figures using our estimates of the average properties of each stream. The results are shown in Table A-11 for the pure compound candidates, in Table A-12 for the chemical plant streams and blends, and in Table A-13 for the refinery streams. The physical and thermodynamic properties of interest are also listed. The relative rank of each of the candidate fuels is shown in Table A-14. In addition, the twenty candidates with the highest values for the merit index are listed in Table A-15.

(c). Comparison of Methods

The specific impulse and the merit index of a stream can actually be calculated by either of two methods. The first method uses an average value of the heat of formation and the H/C ratio of the stream, based on the assumption that the heats of combustion of the individual compounds in the stream are additive in proportion to their weight fractions. This method was used to calculate the values appearing in Tables A-11 through A-13. The second method uses calculated I_{sp} values for each of the individual compounds in the stream, based upon the heat of formation and H/C ratio for each individual compound. These I_{sp} values are then combined according to the weight fraction of each component of the stream.

It turns out that the two methods are entirely equivalent. For example, the average properties of chemical plant stream B-2 (including the H/C ratio and the standard heat of formation) result in a calculated specific impulse of 302.7 seconds. This result is based on the additivity of the heats of combustion of the stream's components. Utilizing the second approach, if the specific impulse is calculated for each compound in the stream, and summed in proportion to the weight fraction of each compound, the result should approximately be the same as above. The tabulation in Table A-14 shows that this is indeed the case for stream B-2, where the method based on the additivity of the specific impulses results in a net specific impulse of 302.67 seconds for the stream.

This agreement also held for all of the other streams, and is due to the nature of the calculation methods. The heat of combustion is directly related to the heat of formation. The heat of formation, in turn, is related to the specific impulse when the H/C ratio is employed. Effectively, the heat of combustion and the specific impulse are related to each other. Therefore, it is reasonable that the two methods outlined above give the same result when either heats of combustion or specific impulse values of individual compounds are added in proportion to their weight fraction in a given stream. Since heat of combustion data are frequently available in the literature, whereas specific impulse values for individual compounds are normally calculated from heats of formation (which are found from combustion experiments), it is much easier to employ the method based on the additivity of heats of combustion. This results in the necessity of calculating only one specific impulse value for the entire stream, instead of ten or twenty values for all of the components in the stream, which saves valuable computer time.

TABLE A-11

CHARACTERISTICS OF PURE COMPOUND CANDIDATES

Code Number	Compound Name	Molecular Formula	Density (g/ml)	H/C Ratio	$\Delta H^{\circ}_{f,298}(\ell)$ n (kcal/gram atom C)	I_{sp} (a) (sec)	$\bar{\rho}$ Isp X 10-4 (lb·sec/ft^3)	$\bar{\rho}$ Isp^3 X 10-9 (lb·sec^3/ft^3)
A-1	Shelldyne	$C_{14}H_{18}$	1.08	1.286	+2.5	296.7	2.07	1.82
A-2	Tetrahydro tricyclopentadiene	$C_{15}H_{22}$	1.04	1.467	-2.0	293.2	2.02	1.74
A-3	Tetrahydro dicyclopentadiene	$C_{10}H_{16}$	0.94	1.6	-0.9	297.9	1.98	1.76
A-4	1,7-Octadiyne	C_8H_{10}	0.81	1.25	+9.9	30 .5	1.92	1.82
A-5	Cyclododecatriene	$C_{12}H_{18}$	0.89	1.5	+1.2	299.2	1.95	1.75
A-6	Decahydroacenaphthene	$C_{12}H_{20}$	0.94	1.667	-3.3	295.6	1.97	1.72
A-7	Octahydroacenaphthene	$H_{12}H_{18}$	0.96	1.5	-2.4	293.4	1.97	1.69
A-8	Spiro (5.5) undec-2-ene	$C_{11}H_{18}$	1.0	1.636	-1.94	296.7	2.02	1.78
A-9	Spiro (5.6) dodec-7-ene	$C_{12}H_{20}$	1.0	1.667	-2.28	296.7	2.02	1.78
A-10	Spiro (5.6) dodecane	$C_{12}H_{22}$	1.0	1.833	-4.72	296.7	2.02	1.78
A-11	Tetrahydrofluorene	$C_{13}H_{14}$	1.02	1.077	+1.88	290.4	1.98	1.67
A-12	Dodecahydrofluorene	$C_{13}H_{22}$	0.95	1.692	-3.57	295.7	1.98	1.73
A-13	Tricyclopropanated Cyclododecatriene	$C_{15}H_{24}$	1.0	1.600	-0.05	299.2	2.04	1.82

(a) At stoichiometric oxygen to fuel mixture ratio.

(b) $\bar{\rho}$ denotes the propellant density (as distinguished from the fuel density listed).

(c) Merit index - quantitative characteristic for screening of fuel candidates.

TABLE A-12

CHARACTERISTICS OF CHEMICAL PLANT STREAM CANDIDATES

Code Number	Density (g/ml)	H/C Ratio	$\Delta H^\circ_{f,298}(\ell)/n$ (kcal/gram atom C)	I_{sp} (sec)	$\bar{\rho}\, I_{sp} \times 10^{-4}$ (lb·sec/ft^3)	$\bar{\rho}\, I_{sp}^3 \times 10^{-9}$ (lb·sec^3/ft^3)
B-1	0.70	1.44	+8.6	309.1	1.82	1.74
B-2	0.70	1.59	+2.37	302.7	1.79	1.64
B-3	0.65	1.49	+3.21	302.2	1.72	1.57
B-4	0.99	1.20	+3.43	296.3	2.00	1.76
B-5	0.96	1.33	+0.54	294.4	1.97	1.71
B-6	0.96	1.19	+2.33	294.3	1.97	1.70
B-7	0.95	1.19	+1.74	293.3	1.95	1.68
B-8	1.01	1.0	+1.2	287.2	1.95	1.61
B-9	1.02	0.97	+2.41	288.6	1.97	1.64
B-10	1.00	1.16	+1.17	291.6	1.98	1.68
B-11	0.88	1.21	+0.87	291.9	1.89	1.61
B-12	0.90	1.23	+1.57	293.7	1.92	1.65
B-13	0.88	1.27	+0.25	292.6	1.89	1.62
B-14	0.96	1.32	+0.45	294.3	1.97	1.71
B-15	1.10	0.65	+6.41	289.0	2.03	1.69
B-16	1.10	0.60	+3.62	282.0	1.98	1.57
B-17	1.10	0.53	+4.54	282.0	1.98	1.57
B-18	1.00	0.74	+2.55	284.0	1.92	1.55
B-19	0.97	1.46	-0.09	296.1	1.99	1.75
B-20	1.00	1.41	+0.04	295.2	2.01	1.75
B-21	0.89	1.72	-3.49	296.3	1.94	1.70
B-22	0.99	1.55	-2.29	294.7	2.00	1.74
B-23	1.01	1.03	+1.50	288.5	1.99	1.66
B-24	0.94	1.18	-0.35	289.3	1.92	1.61
B-25	0.92	1.26	-0.51	290.8	1.91	1.62
B-26	0.90	1.226	+3.94	297.7	1.94	1.72
B-27	0.82	1.262	+4.71	299.8	1.88	1.69
B-28	0.76	1.321	+6.01	303.0	1.85	1.70
B-29	0.92	1.013	+2.99	291.1	1.91	1.62
B-30	0.83	1.083	+3.90	294.5	1.85	1.61
B-31	0.76	1.200	+5.46	299.7	1.82	1.64
B-32	0.90	1.187	+1.90	293.2	1.91	1.64

TABLE A-12 (Continued)

CHARACTERISTICS OF CHEMICAL PLANT STREAM CANDIDATES

Code Number	Density (g/ml)	H/C Ratio	$\Delta H^\circ_{f,298}(\ell)/n$ (kcal/gram atom·C)	I_{sp} (sec)	$\bar{\rho}\, I_{sp} \times 10^{-4}$ (lb·sec/ft^3)	$\bar{\rho}\, I_{sp}^{3} \times 10^{-9}$ (lb·sec^3/ft^3)
B-33	0.82	1.229	+3.01	296.2	1.86	1.63
B-34	0.76	1.299	+4.87	300.7	1.83	1.66
B-35	0.90	1.241	+3.32	296.9	1.94	1.71
B-36	0.82	1.298	+3.16	297.9	1.87	1.66
B-37	0.76	1.395	+2.90	299.7	1.83	1.64
B-38	0.92	1.027	+2.38	290.2	1.90	1.60
B-39	0.83	1.118	+2.37	292.4	1.84	1.58
B-40	0.76	1.273	+2.37	294.4	1.80	1.58
B-41	0.90	1.201	+1.28	297.3	1.91	1.63
B-42	0.82	1.265	+1.46	296.9	1.85	1.60
B-43	0.76	1.373	+1.75	297.6	1.81	1.60
B-44	0.94	1.231	+3.40	299.1	1.97	1.74
B-45	0.88	1.273	+3.36	290.2	1.93	1.71
B-46	0.78	1.343	+3.31	291.4	1.84	1.65
B-47	0.97	1.017	+2.46	295.7	1.94	1.64
B-48	0.89	1.093	+2.58	292.6	1.89	1.60
B-49	0.79	1.222	+2.78	295.7	1.83	1.60
B-50	0.95	1.191	+1.37	292.6	1.95	1.67
B-51	0.88	1.240	+1.66	294.0	1.90	1.64
B-52	0.79	1.321	+2.17	296.9	1.84	1.62
B-53	0.955	1.641	-2.54	296.1	1.98	1.74

TABLE A-13

CHARACTERISTICS OF REFINERY STREAM CANDIDATES

Code Number	Density (g/ml)	H/C Ratio	$\Delta H^{o}_{f,298}(\ell)/n$ (kcal/gram atom·C)	I_{sp} (sec)	$\bar{\rho}\ I_{sp} \times 10^{-4}$ (lb·sec/ft^3)	$\bar{\rho}\ I_{sp}^{3} \times 10^{-9}$ (lb·sec^3/ft^3)
C-1	0.930	1.54	-0.4	297.4	1.97	1.74
C-2	0.912	1.82	-5.3	296.6	1.95	1.70
C-3	1.023	1.39	+0.7	296.0	2.03	1.78
C-4	0.923	1.56	-4.6	291.0	1.92	1.63
C-5	1.009	1.47	-2.0	293.0	2.00	1.72
C-6	0.948	1.64	-3.7	294.0	1.96	1.70
C-7	0.934	1.74	-4.6	295.1	1.96	1.71
C-8	0.967	1.61	-3.0	294.7	1.98	1.72
C-9	1.07	1.42	-1.5	293.0	2.04	1.75
C-10	1.04	1.45	-1.20	292.8	2.02	1.73
C-11	1.064	1.38	-1.2	292.8	2.03	1.74
C-12	1.985	1.60	-2.6	295.2	2.00	1.74

TABLE A-14

SPECIFIC IMPULSE OF STREAM FROM I_{sp} OF INDIVIDUAL COMPONENTS

(Example using compounds present in chemical plant stream B-2)

Name of Compound	Wt. Fraction (lb/lb_{mix})	I_{sp} of Compound ($lb \cdot sec/lb$)	Contribution to Net I_{sp} ($lb \cdot sec/lb_{mix}$)
2-Butyne	0.0001	308.2	0.03
3-Methyl-1-Butene	0.0001	302.8	0.03
1,4-Pentadiene	0.0001	305.1	0.03
1-Pentene	0.0001	302.7	0.03
2-Methyl-1-Butene	0.0003	302.3	0.09
trans-2-Pentene	0.0003	302.5	0.09
2-Methyl-1,3-Butadiene	0.5300	302.8	160.48
cis-2-Pentene	0.0036	302.5	1.09
2-Methyl-2-Butene	0.0400	301.7	12.07
Cyclopentadiene	0.0584	299.6	17.50
trans-1,3-Pentadiene	0.3190	303.1	96.69
cis-1,3-Pentadiene	0.0350	303.1	10.61
Totals	0.9870 lb/lb_{mix}		298.74 $lb \cdot sec/lb_{mix}$

Therefore, the net specific impulse is

$$I_{sp} = \frac{298.74\ lb \cdot sec/lb_{mix}}{0.9870\ lb/lb_{mix}} = 302.67\ sec$$

A-6. References for Appendix A.

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APPENDIX B.

METHODS OF ANALYSIS AND TABLES FOR DATA EXTRAPOLATION

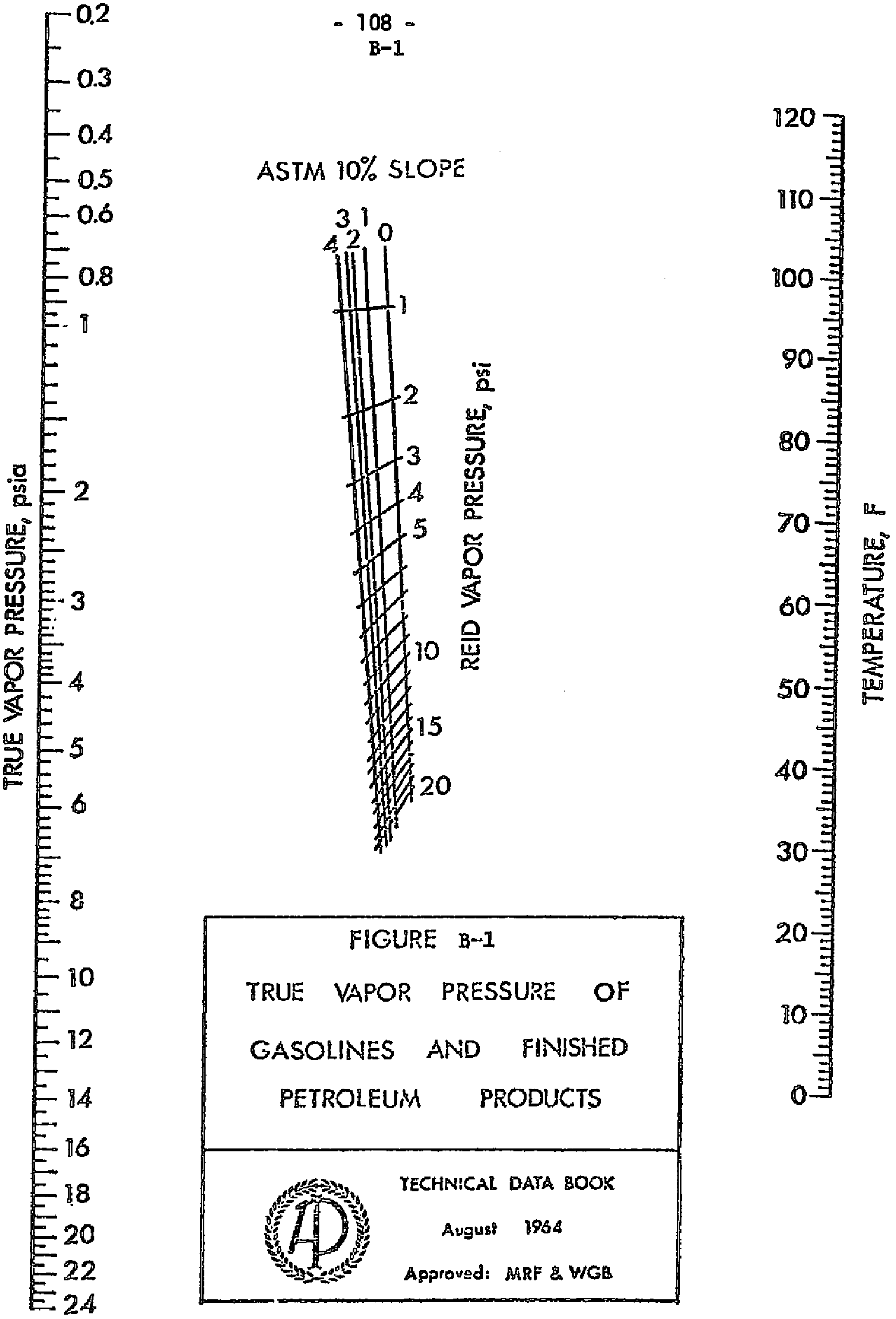

FIGURE B-1

TRUE VAPOR PRESSURE OF GASOLINES AND FINISHED PETROLEUM PRODUCTS

TECHNICAL DATA BOOK
August 1964
Approved: MRF & WGB

B-2

Comments on Figure B-1

Purpose

Figure A-1 is useful for estimating the true vapor pressure of a gasoline or finished petroleum products, including chem plant streams, at normal storage temperatures. Crude oils and refinery streams are treated similarly in Figure A-2.

Reliability

No estimate of the reliability of this figure is available.

Notation

Slope = slope of the ASTM D 86 distillation curve at 10% by volume distilled = $\frac{T_{15} - T_5}{10}$, in °F per percent distilled.

Special Comments

In the absence of distillation data, the following approximate values of the ASTM 1% slope may be used:

Motor gasoline	3	Light naphtha (9 to 14 psi Rvp)	3.5
Aviation gasoline	2	Naphtha (2 to 8 psi Rvp)	2.5

Literature Source

The figure is given in API Bull. 2513: Evaporation Loss in the Petroleum Industry - Causes and Control, American Petroleum Institute, New York (1959).

Example

Estimate the tvp at 70°F of a naphtha having a 10% ASTM slope of 3.5 and a Reid vapor pressure (Rvp) of 11 psi.

Locate the point on the grid of Figure A-1 corresponding to a slope of 3.5 and Rvp of 11. A straight line extended from the 70°F point on the temperature scale through this grid point intersects the tvp scale of 6.9 psia.

B-2

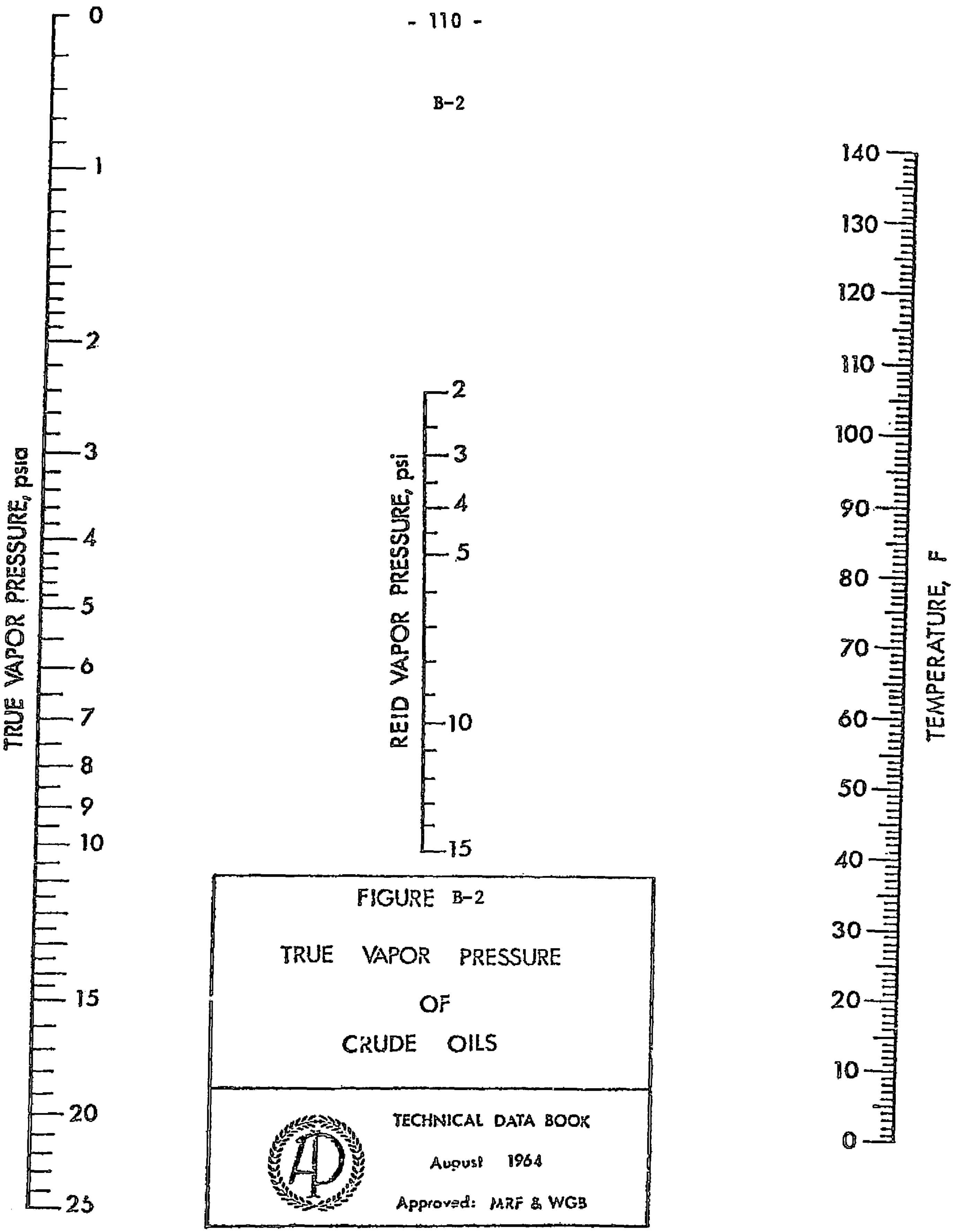

FIGURE B-2

TRUE VAPOR PRESSURE
OF
CRUDE OILS

TECHNICAL DATA BOOK
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Approved: MRF & WGB

Comments on Figure B-2

Purpose

Figure A-2 is useful for estimating the true vapor pressure (tvp) of crude oils and refinery streams at normal storage temperatures. Gasolines and finished products are treated similarly in Figure A-1.

Reliability

No estimate of the reliability of this figure is available.

Literature Source

The figure was given in API Bull. 2513: Evaporation Loss in the Petroleum Industry - Causes and Control, American Petroleum Institute, New York (1959).

Example

Estimate the tvp at 70°F of a crude oil having an Rvp of 6 psi.

A straight line on Figure A-2 connecting the 70°F point on the temperature scale and the 6 psi Rvp point intersects the tvp scale at 4.2 psia.

APPENDIX B-3

EXPERIMENTAL EQUIPMENT USED IN THE MEASUREMENT OF JET FUEL STABILITY

B.1 Design and Construction of the Exxon Advanced Fuel Unit

B.1.1 General Design Features

The Exxon Advanced Fuel Unit is unique in being able to measure fuel stabilities over a wide temperature range. Present fuel stability units are limited to the relatively low pressures and temperatures characteristic of present day aircraft. As a result, we designed and constructed an Advanced Fuel Unit specifically to simulate the extreme temperature and pressure environment anticipated for high speed aircraft. The Advanced Fuel Unit was designed to operate at pressures up to 1500 psig and metal temperatures up to 1500°F. Because of the possibility of employing regenerative cooling, the capability for high heat flux operation was also felt to be important. As a result, the unit was designed to have two separate electrical systems, one for the low heat fluxes encountered in normal operations and a second electrical system to produce the high heat fluxes characteristic of regenerative cooling circuits. A comparison of the capabilities of the Advanced Fuel unit with standard fuel stability units is shown in Table B.1.

B.1.2 Details of the Unit

A schematic of the Advanced Fuel Unit is shown in Figure B.1 and a detailed drawing of the low power unit is shown in Figure B.2. The fuel to be tested in the unit is first placed in a sparge tank where its dissolved molecular oxygen content is adjusted by means of bubbling a gas such as air, oxygen-free helium, or a specific oxygen-nitrogen gas blend through the liquid. The dissolved oxygen content of the tested fuel can be measured by an in-line polarographic type oxygen analyzer or by means of small samples injected into a modified thermal conductivity gas chromatograph.

The quantity of molecular oxygen dissolved in a fuel at equilibrium at a given temperature is a function of the partial pressure in the gas contacting the fuel. Since the partial pressure is a function of both the oxygen concentration in the gas and the total gas pressure, low oxygen contents in a jet fuel are achieved by sparging the liquid with a low oxygen concentration gas at a low total pressure. In our system, the fuel is sparged at atmospheric pressure.

The treated fuel must be delivered to the reaction section of the Advanced Fuel Unit at pressures up to 1500 psig (∿100 atmospheres). If the sparge gas were also used to pressure the treated fuel and deliver it to the reaction section, the dissolved oxygen content in the fuel would rise to a level dictated by the new oxygen partial pressure in the gas, which at 1500 psig would be approximately 100 times greater than at the spargin conditions. To eliminate the problem, the treated fuel from the sparge tank is transferred to a movable double-piston fuel delivery system.

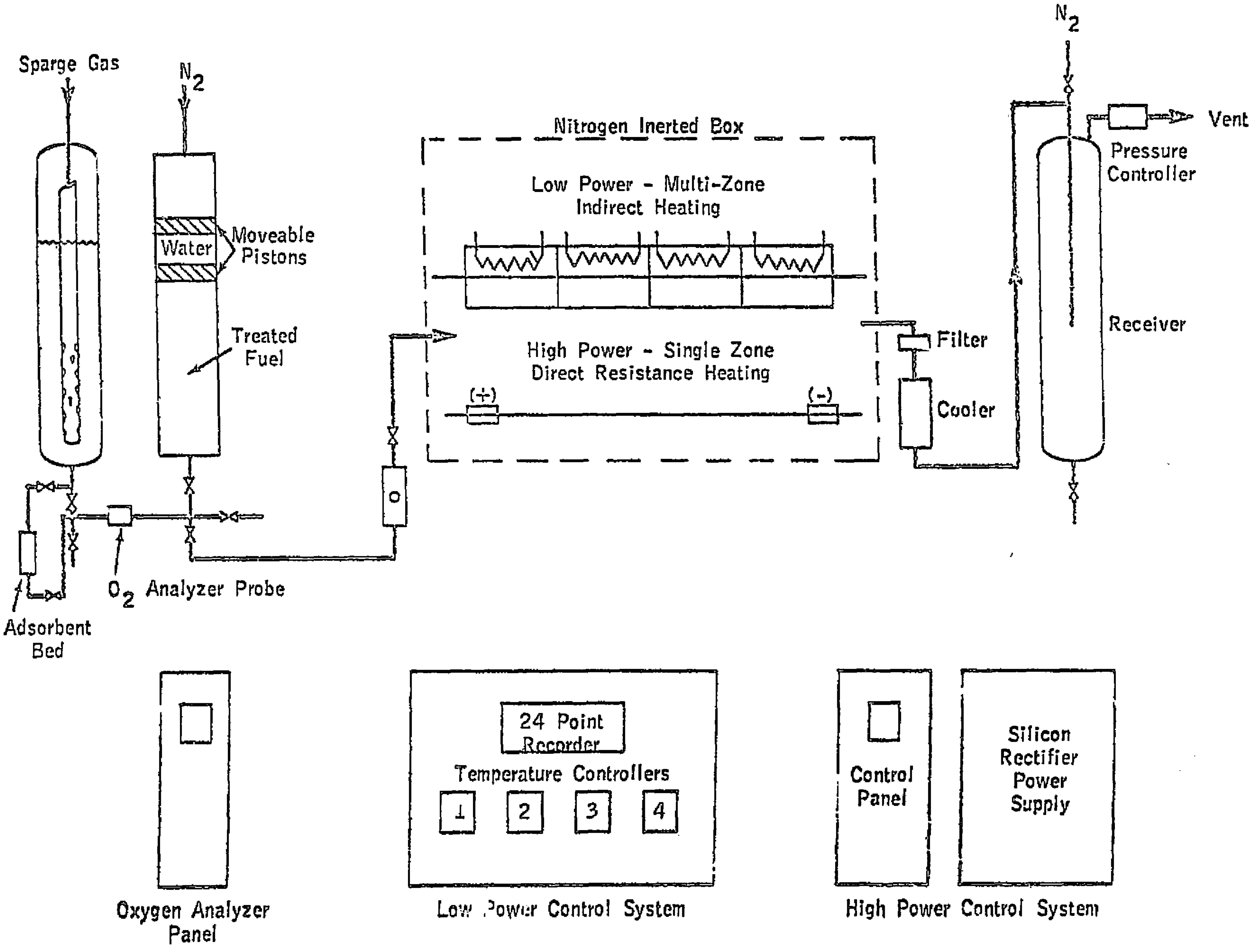
TABLE B.1

Comparison of Fuel Stability Units

	Standard Units	Esso Advanced Fuel Unit
Maximum Temperature	600-800°F	1500°F
Maximum Pressure	150-250 psig	1500 psig
Heat Flux	Low (e.g. 10,000 BTU/hr-ft^2)	Low or High (e.g. 2,000,000 BTU/hr-ft^2)
Measuring Technique	Indirect (Visual)	Direct (Gravimetric)
Metal Type	Aluminum	S.S. 304 S.S. 316 Ni-Co Super alloys titanium alloys aluminum

FIGURE B-3

EXXON ADVANCED FUEL UNIT SCHEMATIC



This system is shown in detail in Figure B-5. The treated fuel is separated from the high pressure nitrogen used to drive the fuel by a double-piston arrangement. In this arrangement, the two pistons enclose a water containing barrier zone. Water, which is essentially insoluble in jet fuel range hydrocarbons, was chosen for this barrier zone in order to provide a quick means of detecting any leakage across the piston seals into the treated fuel.

The fuel then passes through a heated tubular reactor section, which is contained inside of four, independently controlled heaters. A tubular reactor was used rather than an annular reactor area so as to more closely simulate a heat exchanger or an engine manifold environment. A series of isothermal temperature zones were employed so that a given rate of deposit formation can be related as closely as possible to a given temperature, rather than to a constantly increasing, changing temperature environment. Each heater zone is approximately 12 inches in length and contains both a control thermocouple and a readout thermocouple, both of which sense the metal tube surface temperature. Bulk fuel temperature is measured at the exit. Each heated section contains a thickwalled stainless steel pipe, designed to provide as nearly a constant temperature in each zone as possible. This thickwalled pipe also serves to prevent any direct radiant energy transfer from the glowing electrical heater elements to the thermocouples which would result in erroneous readings. The rate of deposit formation occurring inside the tube is measured after the run by cutting the tubular reactor in each zone into a number of lengths (e.g., four sections three inches long per heated zone) and analyzing four carbonaceous deposits using the modified LECO carbon analyzer described in Section B.2.

After the fuel leaves the heated reactor tube section, it is partially cooled, passes through a filter and then is cooled to ambient temperature. The fuel then enters a high pressure receiver tank where it is kept under nitrogen pressure. As the fuel level rises, the excess nitrogen is released through a MITY-MITE type of pressure controller to vent. The reaction temperature is controlled by a series of zone heaters. Each zone heater is individually controlled by a proportional temperature controller (West Instrument Corp. digital set point unit Model JYSCR) used in conjunction with a zero crossover firing Power Unit (West Instrument Corp. Model PZSCR-25-240). A strip chart recorder is also contained in the low power unit which has the capability to record up to 24 temperature points.

FIGURE B-4

Exxon Advanced Fuel Unit - Detailed Flow Plan

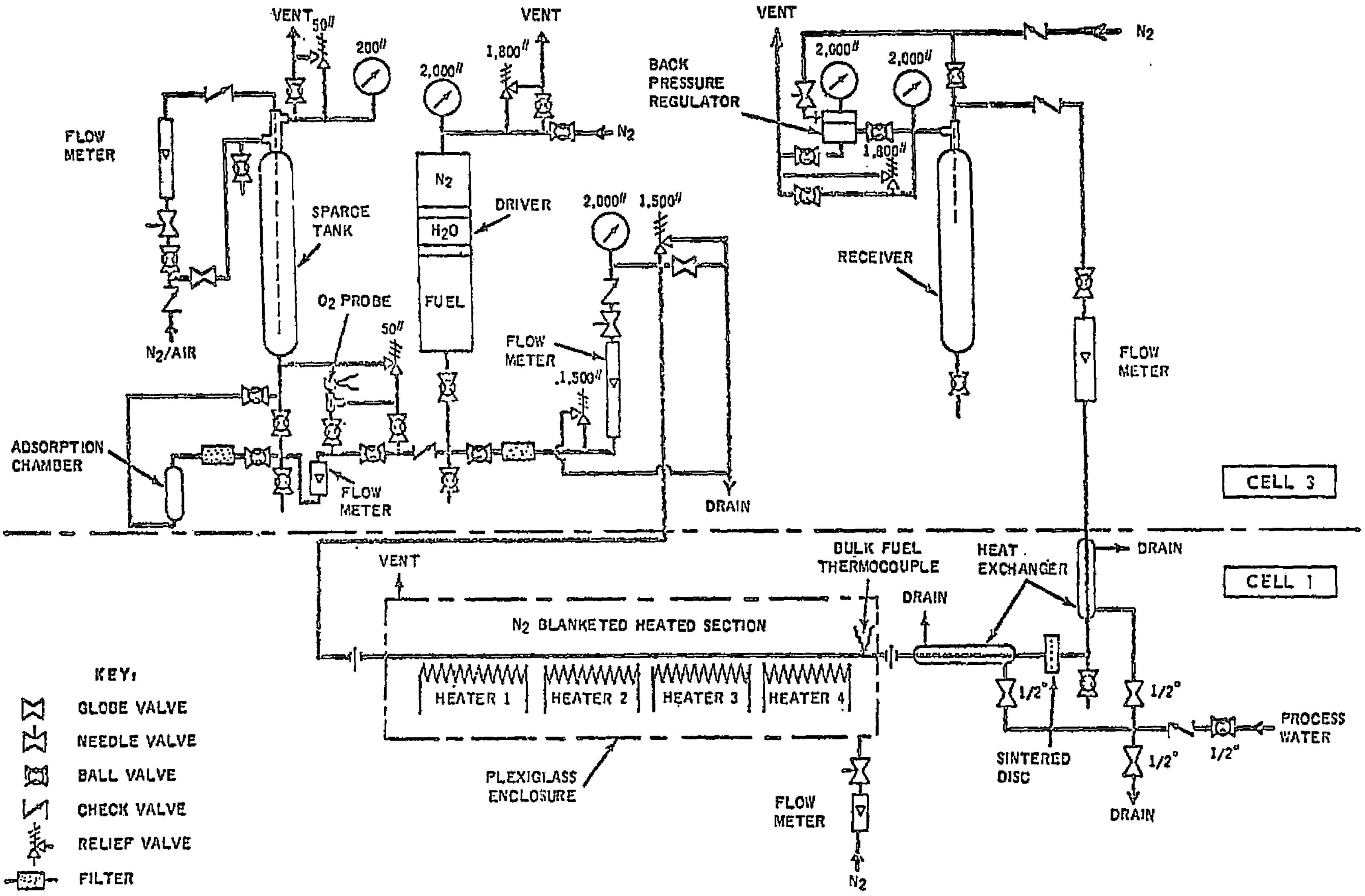
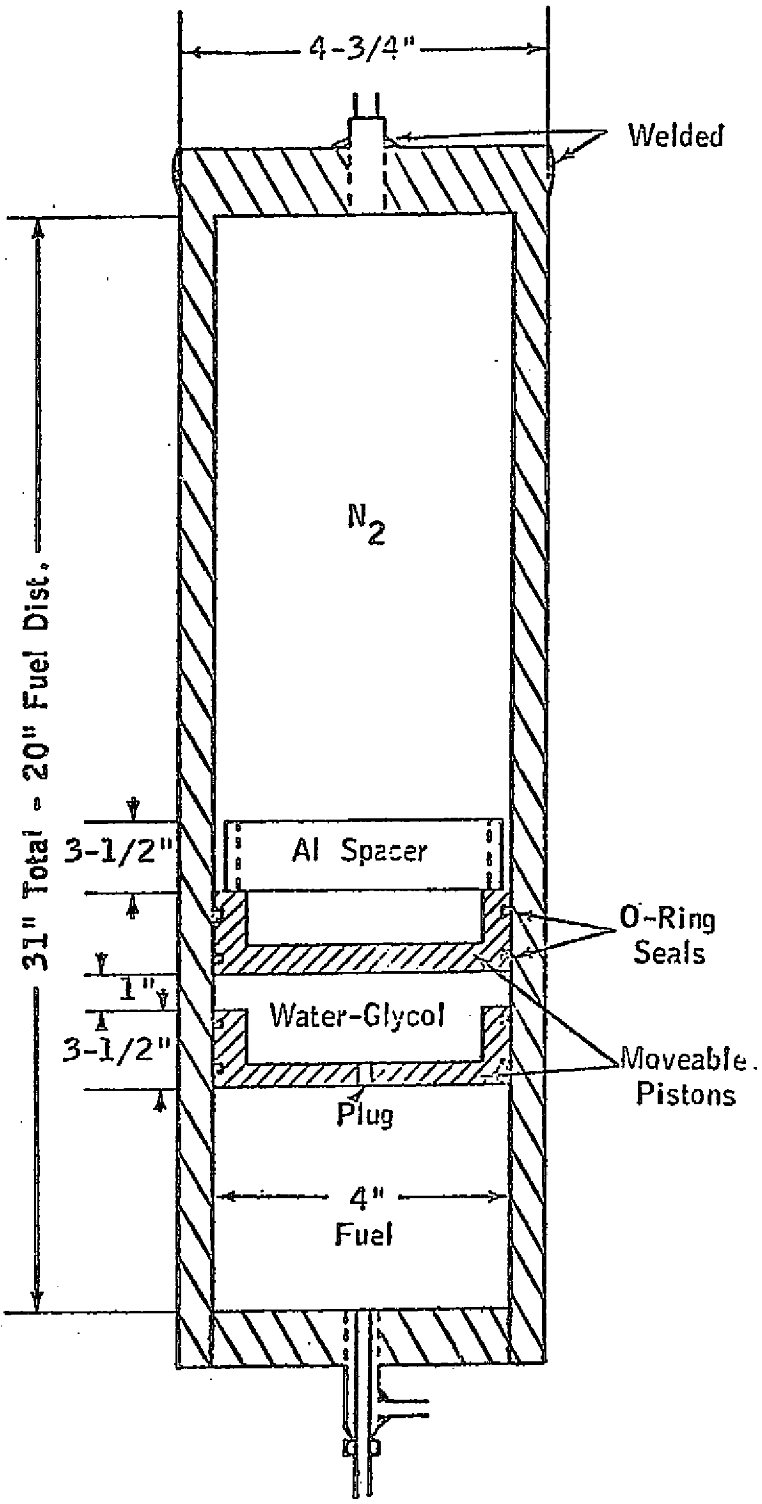


FIGURE B-5

DETAILS OF DOUBLE-PISTON FUEL DELIVERY STYSEM



B-4 SYSTEM FOR THE GRAVIMETRIC MEASUREMENT OF CARBONACEOUS DEPOSITS

C.1 Apparatus and Operation Procedure

The analytical system used for the measurement of carbonaceous deposits is shown in Figure C.1. The system employs a LECO No. 589-600 Low Carbon Analyzer (Laboratory Equipment Company, St. Joseph, Michigan) which is normally used for extremely accurate measurement of the carbon contained inside of metal specimens, after a high frequency induction furnace combustion of the total specimen at 3000°F. In our system, this procedure has been modified so that only the carbonaceous deposits on the metal specimen surfaces are oxidized. As shown in the schematic in Figure C.1, the tube specimen is placed in a pyrex tube inside a laboratory tube furnace controlled by a Gardsman Controller, using a thermocouple positioned just above the test specimen. Pure oxygen is first scrubbed with H_2SO_4 to remove any residual hydrocarbons and then passed through a purification chamber for water and carbon dioxide removal. Initially, the carbonaceous deposits were oxidized from the test specimens at 1200°F for eight minutes (5 minutes static plus 170 seconds with flowing oxygen during the instrument collect mode of operation). Subsequent tests with specimens of deposits formed in the 700-1200°F range indicated that a 1500°F oxidation temperature was necessary to insure complete deposit removal; and this temperature was adopted as the standard oxidation temperature. The effluent gas passes through a dust trap, a sulfur trap and then into a heated catalytic furnace where any carbon monoxide formed is oxidized, e.g.,

$$CO + 1/2\ O_2 \rightarrow CO_2$$

Any water present is removed in a trap before the sample gases enter the analyzer itself. In the Low Carbon Analyzer, the carbon dioxide formed is swept by the oxygen into a collection trap. After a pre-determined collection time (170 seconds), the trap is automatically heated to desorb the carbon dioxide and an inert gas (helium) drives the carbon dioxide into a selective filter. The gas then passes through a thermal conductivity cell. The output of the cell is amplified, integrated and the integral value recorded on a digital voltmeter. The detailed run procedure is shown in the appendix.

C.1.1 Calibration of the Analytical System

C.1.1.1 Initial Calibration

The analytical system for the measurement of carbonaceous deposit was calibrated using two separate sets of standards. The first set of standards were carbon samples prepared at Exxon Research using a precise microgram range analytical balance. The second set of standards were obtained from the instrument manufacturer (i.e., LECO). The standard carbon analyzer procedure shown in the appendix was employed. Results of these calibration runs are shown in Table C.1. As can be seen, the analytical system is both accurate and reproducible. As an added check against the accuracy of the system, LECO standard samples are run each day the analyzer is used for the measurement of carbonaceous deposits.

FIGURE B-6

ANALYTICAL SYSTEM FOR MEASUREMENT OF CARBONACEOUS DEPOSITS

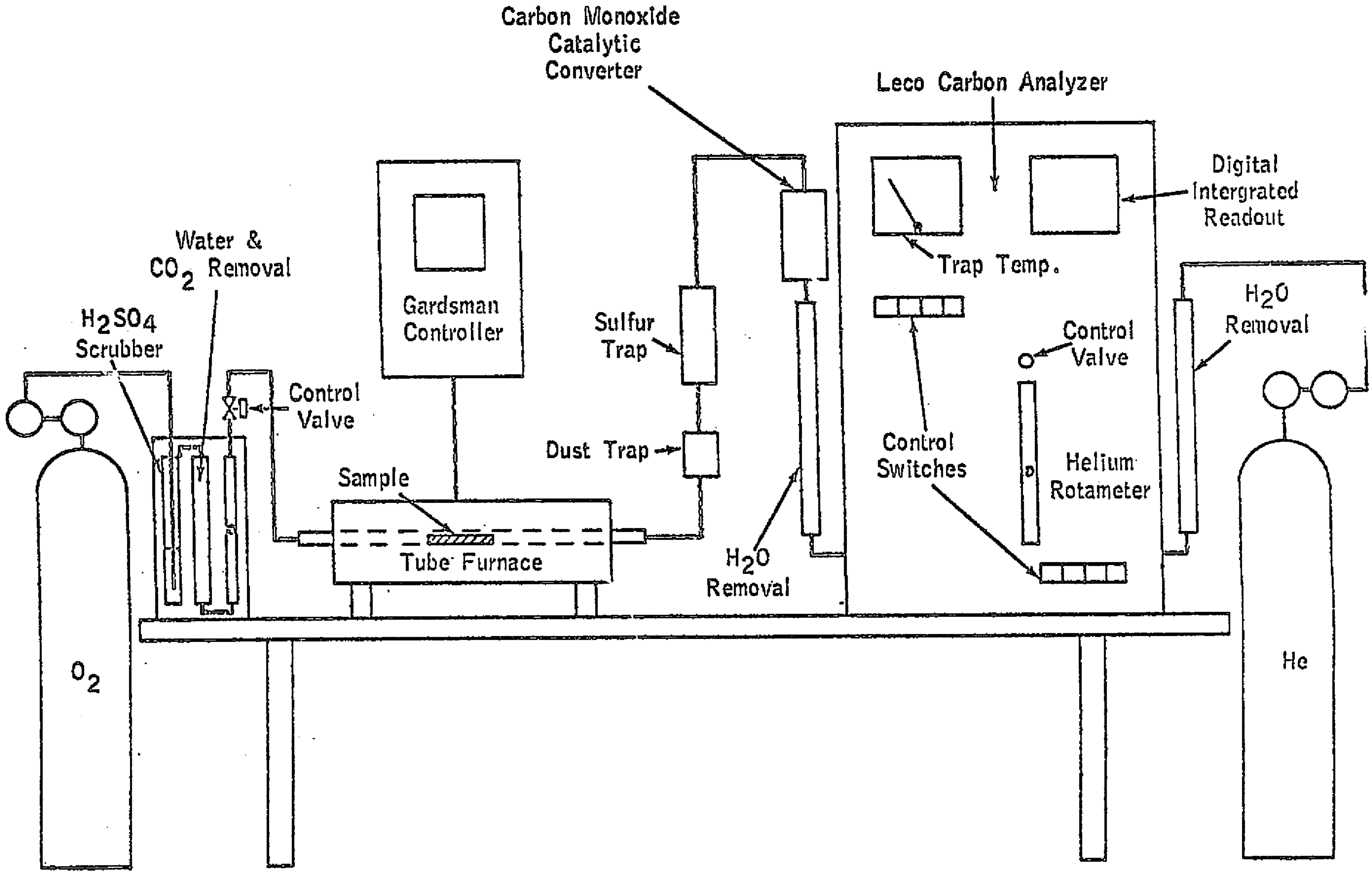


TABLE B-2

CALIBRATION RESULTS FOR MODIFIED LECO CARBON ANALYZER SYSTEM

Type of Standard	Micrograms of Carbon Actual	 Analyzer Reading
Activated Carbon	139	178
	1,180	1,050
	164	189
	998	910
	1,010	1,060
	574	610
LECO	450	445
	450	459
	31	54
	450	447
	450	446
	450	383
	450	451
	465	465
	465	462
	465	469

B.1.1.2 Day-to-Day Operating Calibration

The modified LECO system is also calibrated each day it is operated using the LECO supplied carbon standards. A standard is run initially to insure that the analytical system is operating correctly. Additional standards are also run on the same day along with the test specimens to check on the accuracy and reproducibility of the analytical data.

APPENDIX C.

COMPOSITION AND ESTIMATED CRITICAL PROPERTIES OF CANDIDATE FUELS

APPENDIX TABLE C-1

COMPOSITION OF CHEMICAL PLANT STREAM B-1*

Component	Wt. %
Methane	5.48
Ethane	0.57
1,3-Butadiene	33.19
1,2 Butadiene	4.31
Methyl Acetylene	—
Ethyl Acetylene	11.16
Vinyl Acetylene	21.05
Dimethyl Acetylene	2.39
C_5+	21.85

Density (g/cc) = 0.65-0.75

*By gas chromatography (except density).

APPENDIX TABLE C-2

COMPOSITION OF
CHEMICAL PLANT STREAMS B-2 AND B-3*

Component	Wt. % in Streams	
	B-2	B-3
C_4's and lighter, Pentanes	<.01	<.01
Dimethylacetylene	<.01	.04
3-Methylbutene-1	<.01	<.01
Pentadiene-1,4	<.01	<.01
Pentene-1	<.01	<.01
2-Methylbutene-1, Trans-Pentene-2	.06	<.01
ISOPRENE	53.0	62.0
Cis-Pentene-2	.36	<.01
2-Methylbutene-2	4.0	.03
Cyclopentadiene	5.84	27.7
Trans-Pentadiene-1, 3	31.9	7.6
Cis-Pentadiene-1, 3	3.5	1.9
	0.70	0.65

*By Gas Chromatography

APPENDIX TABLE C-3

COMPOSITION OF STREAMS B-4 - B-7*

Component	Wt. % in Streams			
	B-6	B-4	B-5	B-7
C_2				
C_3				
Butadiene				
Isoprene		0.6		
Tr-Pentadiene 1,3				
Cyclopentadiene (Monomer)		8.8		
Methylcyclopentadiene (Monomer)				4.0
C_6 Other			0.4	0.1
Toluene	tr		0.9	0.2
C_7 Cyclodiene				
C_8 Aromatic	1.0		0.1	4.8
C_8 Other				tr
C_4 - CPD Codimer	1.9			
C_5 Acyclic-CPD Codimer	5.5	0.4		1.9
Dicyclopentadiene	37.3	88.9	0.4	24.5
CPD-MCPD Codimer	35.8	0.9	0.9	22.4
Methylcyclopentadiene Dimer	6.7		53.2	24.7
C_9 or C_{10} Aromatic or Other Codimer	11.5	0.3	0.6	15.9
	0.96	0.99	0.96	0.95

*By Gas Chromatography

APPENDIX TABLE C-4

COMPOSITION OF STREAMS B-8 AND B-9

Component	Wt. % in Streams	
	B-8	B-9
Isoprene	0.1	
Cyclopentadiene (Monomer)		0.9
Methylcyclopentadiene (Monomer)		0.8
C_6 Other		0.7
Toluene	0.7	
C_7 Cyclodiene		
C_8 Aromatic	0.2	
C_8 Other		
C_4 - CPD Codimer		21.9
C_5 Acyclic-CPD Codimer		
Dicyclopentadiene		
CPD-MCPD Codimer		
Methylcyclopentadiene Dimer		
C_9 or C_{10} Aromatic or Other Codimer	3.3	
Naphthalene	2.0	13.6
Dimethylindene	2.1	
Methylnaphthalene	30.3	
Dimethylnaphthalene	31.1	33.7
Trimethylnaphthalene	19.0	
Cyclic Trimers		
Cyclic Tetramers		18.7
Cyclic Pentamers		9.4
Heavier	11.8	
	1.01	1.02

APPENDIX TABLE C-5

COMPOSITION OF STREAMS B-10 - B-14

	Wt. % in Streams				
Component	B-11	B-13	B-12	B-10	B-14
C_6*	1.06	.37	—	—	20.4
Toluene	23.70	.25	—	.13	20.5
C_7*	3.23	.42	—	.08	2.52
Ethyl Benzene	3.44	8.94	1.21	2.86	2.56
M,P-Xylenes	9.61	28.30	4.57	9.54	15.98
C_8*	.74	.62	.09	.23	1.23
Styrene	6.44	20.96	4.20	6.79	—
O-Xylene	5.34	14.15	3.54	6.06	—
C_8*	8.14	17.20	11.29	8.43	—
Vinyl Toluene	8.84	6.38	21.73	9.90	—
C_9*	2.16	.94	5.92	2.54	16.52
DCP**	.30	.22	.37	.21	.15
C_9*	.55	.20	1.48	.64	6.68
Indene	4.82	.61	13.91	6.19	—
C_{10}*	9.37	.20	22.98	14.82	—
Methyl Indene	5.47	—	6.06	12.43	4.80
C_{10}*	.38	.03	.47	.30	—
MCPDD**	.08	—	.08	.69	—
C_{10}*	.16	—	.14	.50	—
Naphthalene	3.47	—	1.44	10.09	4.37
C_{11}*	2.73	.17	.40	7.58	4.36
Density (g/cc)	0.88	0.88	0.90	1.00	0.96

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* Denotes unidentified aromatics and olefins including piperylenes.

** DCP = Dicyclopentadiene **MCPDD = Methylcyclopentadienedimer.

TABLE C-6

STREAM BLENDS

Designation	Wt. Percent B-1	Blended Into Stream	H/C Ratio	$\frac{\Delta H_f(\ell)}{n}$	Density
	0	B-4	1.203	+3.43	0.99
B-26	10	B-4	1.226	+3.94	0.90
B-27	25	B-4	1.262	+4.71	0.82
B-28	50	B-4	1.321	+6.01	0.76
	100	B-4	1.442	+8.6	0.70
	0	B-9	0.967	+2.41	1.02
B-29	10	B-9	1.013	+2.99	0.92
B-30	25	B-9	1.083	+3.90	0.83
B-31	50	B-9	1.200	+5.46	0.76
	100	B-9	1.442	+8.6	0.70
	0	B-10	1.159	+1.17	1.00
B-32	10	B-10	1.187	+1.90	0.90
B-33	25	B-10	1.229	+3.01	0.82
B-34	50	B-10	1.299	+4.87	0.76
	100	B-10	1.442	+8.6	0.70

Designation	Wt. Percent B-2	Blended Into Stream	H/C Ratio	$\frac{\Delta H_f(\ell)}{n}$	Density
	0	B-4	1.203	+3.43	0.99
B-35	10	B-4	1.241	+3.32	0.90
B-36	25	B-4	1.298	+3.16	0.82
B-37	50	B-4	1.395	+2.90	0.76
	100	B-4	1.593	+2.37	0.70
	0	B-9	0.967	+2.41	1.02
B-38	10	B-9	1.027	+2.38	0.92
B-39	25	B-9	1.118	+2.37	0.83
B-40	50	B-9	1.273	+2.37	0.76
	100	B-9	1.593	+2.37	0.70
	0	B-10	1.159	+1.17	1.00
B-41	10	B-10	1.201	+1.28	0.90
B-42	25	B-10	1.265	+1.46	0.82
B-43	50	B-10	1.373	+1.75	0.76
	100	B-10	1.593	+2.37	0.70

TABLE C-6 (Cont.)

STREAM BLENDS

Density	Wt. Percent B-3	Blended Into Stream	H/C Ratio	$\frac{\Delta H_f(\ell)}{n}$	Density
	0	B-4	1.203	+3.43	0.99
B-44	10	B-4	1.231	+3.40	0.94
B-45	25	B-4	1.273	+3.36	0.88
B-46	50	B-4	1.343	+3.31	0.78
	100	B-4	1.487	+3.21	0.65
	0	B-9	0.967	+2.41	1.02
B-47	10	B-9	1.017	+2.46	0.97
B-48	25	B-9	1.093	+2.58	0.89
B-49	50	B-9	1.222	+2.78	0.79
	100	B-9	1.487	+3.21	0.65
	0	B-10	1.159	+1.17	1.00
B-50	10	B-10	1.191	+1.37	0.95
B-51	25	B-10	1.240	+1.66	0.88
B-52	50	B-10	1.321	+2.17	0.79
	100	B-10	1.487	+3.21	0.65

TABLE C-7

CALCULATED AVERAGE PROPERTIES OF BLENDS OF B-2 IN B-15 (1)

Wt. Percent B-2 in B-15	I_{SP} (sec)	Density	H/C Ratio	$\bar{\rho}$	$\bar{\rho}\ I_{SP}$ x 10^{-4}	$\bar{\rho}\ I_{SP}{}^3$ x 10^{-9}
0	289.0	1.10	0.65	1.125	2.028	1.694
10	290.37	1.041	0.738	1.101	1.996	1.683
25	292.43	0.963	0.873	1.069	1.951	1.669
50	295.85	0.856	1.103	1.023	1.888	1.652
100	302.7	0.70	1.59	0.9483	1.791	1.641

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(1) These blends were not given a designation or code number.

APPENDIX TABLE C-8

INSPECTIONS ON STREAMS C-1 - C-4

Stream	C-1	C-2	C-3	C-4
Gravity, °API	20.6	23.6	6.8	21.8
Sp. Gravity	0.9303	0.9123	1.0231	0.9230
Viscosity, @ 100°F, cs (SSU)	452(2092)	244(1130)	50,600(234,390)	169(784)
@ 210°F, cs (SSU)	20.2(99.3)	16.1(81.7)	87.3(407)	11.4(64.1)
V.G.C.	0.857	0.839	0.960	0.861
Aniline Point, °C (°F)	94(202)	100(213)	24(75)	196
Pour Point, °C (°F)	-12(10)	2(35)	35(95)	(-10)
Clay Gel Saturates, %	60.3	74.2	12.4	65.7
Aromatics	33.7	23.6	69.8	33.3
Polar	6.0	2.2	17.8	1.0
Flash, °C (°F)	268(505)	240(465)		(455)
U.V. Absorbativity @ 260 nm				
Viscosity Index	36	67		37
Inspections on Fractions from Clay Gel				
Saturates: Pour Point, °C (°F)	-21(-5)	-15(+5)		-35(-30)
Sp. Gravity	.8735	.8725	.8926	.8725
Viscosity @ 100°F, cs (SSU)	150(693)	145(673)	--	934(437)
@ 210°F, cs (SSU)	13.5(72.1)	13.3(71.2)	--	9.09(56.1)
V.G.C.	0.793	0.792	--	0.802
V.I.	92	92	--	74
Aromatics: Sp. Gravity	.9739	.9488	1.0126	.9714
Viscosity @ 100°F, cs	--	--	--	1090(5053)
@ 210°F, cs	40.8(190.4)	29.3(136.8)	49.7(232)	20.5(95.5)
V.G.C.	0.902	0.874	0.953	0.913
V.I.	--	--	--	-2

APPENDIX TABLE C-9

INSPECTIONS ON STREAMS C-5 - C-7

Stream	C-5	C-7		C-6	
Gravity, °API	8.7	20.0		17.8	
Viscosity, SSU @ 100°F	35,700	1,250		1,840	
@ 210°F	16.5	69.1		77.5	
Viscosity Gravity Constant	.95	.87		.89	
Viscosity Index		-20		-43	
Color, ASTM		1.0		1.5-	
Aniline Point, °F		162		160	
Sulfur, % by X-ray	0.19	0.060		0.080	
Nitrogen, ppm		180		230	
Clay Gel Analysis					
Saturates		58.3		46.1	
Aromatics		40.6		52.5	
Polar		1.1		1.4	
Inspections on Clay Gel Cuts		Sat.	Arom.	Sat.	Arom.
Special Gravity		.8992	.9469	.9038	.9884
Vis., SSU @ 110		510	4640	481	8370
@ 210		57.2	92.0	56.9	108.4

APPENDIX TABLE C-10

INSPECTIONS ON STREAMS C-8 - C-12

Stream	C-8	C-9	C-10	C-11	C-12
°API Gravity 60°F	25.0	0.7	4.6	1.5	12.1
Viscosity - SSU 100°F	189.1	1081	1470	---	--
210°F	45.2	55.1	61.9	58.9	95.4
Aniline Point °F	188	91	91	---	--
Color ASTM	5-	8+	8-	---	--
Flash Point, O.C. °F	420	410	390	395	--
Pour Point °F	40	70	65	---	--
Clay Gel Analysis					
Saturates %	59.4	212	16.5	11.7	17.4
Aromatics %	38.3	70.8	80.4	88.3	75.4
Polars %	2.3	8.9	3.1	---	7.2
Asphaltenes	0	0	0	0	0

APPENDIX TABLE C-11

COMPOUND TYPE ANALYSIS FOR SATURATE FRACTION OF STREAM C-3

Compound Type	Total Sats[1] Wt. %
Iso-Paraffins	0.0
Normal Paraffins	4.583
1-Ring Napthenes	16.202
2-Ring Naphthenes	17.302
3-Ring Naphthenes	23.522
4-Ring Naphthenes	18.047
5-Ring Naphthenes	9.655
6-Ring Naphthenes	5.060
Mono-Aromatics	5.630
Totals	100.000

MS Residue on Saturate Fraction

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1. n-Paraffins not determined analytically - n-paraffin row reflects total paraffins

APPENDIX TABLE C-12

MISCELLANEOUS AVERAGES AND SUMMARIES ON VOLATILE AROMATICS

Elemental Analysis by MS, Wt. %	
Atomic Carbon:	89.47
Atomic Hydrogen:	10.05
Atomic Sulfur:	0.23
Atomic Oxygen:	0.25
Total:	100.01
Atomic H/C Ratio:	1.339

Characteristic Averages on Sample	
Molecular Weight:	360.614
Carbon Number:	27.481
Z Number (CNH2N-Z):	17.452
C Atoms in Sidechains:	13.411

DISTRIBUTION OF AROMATIC RINGS

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Non-Aromatics	0.0	0.0	0.0	0.0
1 Ring Aroms	7.875	0.0	0.022	7.897
2 Ring Aroms	36.212	2.263	1.214	39.688
3 Ring Aroms	28.934	0.280	2.455	31.669
4 Ring Aroms	16.351	0.0	1.794	18.145
5 Ring Aroms	2.000	0.0	0.203	2.204
6 Ring Aroms	0.395		0.0	0.395
7+ Ring Aroms	0.007			0.007
Totals:	91.775	2.543	5.688	100.006

APPENDIX TABLE C-13

TYPE ANALYSIS ON AROMATIC FRACTION OF STREAM C-3

Compound Type	Wt. % on Volatiles	Wt. % on Stream	Wt. % on Fresh Feed	Wt. % on Total Feed	Average MW	Average Carbon No.	Avg. Carb. Sidechains
CNH$_2$N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH$_2$N- 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH$_2$N- 4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH$_2$N- 6	0.660	0.660	0.660	0.660	371.87	26.99	20.99
CNH$_2$N- 8	3.181	3.181	3.181	3.181	380.79	27.77	18.77
CNH$_2$N-10	4.035	4.035	4.035	4.035	386.27	28.30	19.30
CNH$_2$N-12	8.155	8.155	8.155	8.155	367.17	27.08	17.08
CNH$_2$N-14	10.694	10.694	10.694	10.694	367.04	27.22	15.22
CNH$_2$N-16	17.363	17.363	17.363	17.363	356.65	26.62	14.62
CNH$_2$N-18	15.895	15.895	15.895	15.895	354.92	26.64	12.64
CNH$_2$N-20	13.039	13.039	13.039	13.039	353.62	26.69	11.69
CNH$_2$N-22	9.786	9.786	9.786	9.786	352.02	26.72	10.72
CNH$_2$N-24	4.853	4.853	4.853	4.853	359.54	27.40	9.40
CNH$_2$N-26	1.711	1.711	1.711	1.711	369.41	28.24	9.24
CNH$_2$N-28	1.327	1.327	1.327	1.327	369.58	28.40	8.40
CNH$_2$N-30	0.673	0.673	0.673	0.673	380.58	29.33	7.33
CNH$_2$N-32	0.179	0.179	0.179	0.179	401.48	30.96	8.96
CNH$_2$N-34	0.163	0.163	0.163	0.163	384.68	29.91	5.91
CNH$_2$N-36	0.053	0.053	0.053	0.053	369.84	28.99	4.99
CNH$_2$N-38	0.007	0.007	0.007	0.007	382.00	30.00	4.00
CNH$_2$N-40	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH$_2$N-42	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH$_2$N-44	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX TABLE C-13

(Continued)

Compound Type	Wt. % on Volatiles	Wt. % on Stream	Wt. % on Fresh Feed	Wt. % on Total Feed	Average MW	Average Carbon No.	Avg. Carb. Sidechains
CNH_2N- 2S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N- 4S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N- 6S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N- 8S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N-10S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N-12S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N-14S	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N-16S	2.263	2.263	2.263	2.263	359.52	24.54	12.54
CNH_2N-18S	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX TABLE C-14

COMPOUND TYPE ANALYSIS FOR SATURATE FRACTION OF STREAM C-6

Compound Type	Total Sats[1] Wt. %
Iso-Paraffins	0.0
Normal Paraffins	5.833
1-Ring Naphthenes	16.701
2-Ring Naphthenes	15.570
3-Ring Naphthenes	18.569
4-Ring Naphthenes	17.967
5-Ring Naphthenes	9.709
6-Ring Naphthenes	7.167
Mono-Aromatics	8.485
Totals	100.00

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[1] N-Paraffins not determined analytically - N-paraffin row reflects total paraffins

APPENDIX TABLE C-15

MISCELLANEOUS AVERAGES AND SUMMARIES ON VOLATILE STREAMS IN STREAM C-6

Elemental Analysis by MS, Wt. %	
Atomic Carbon:	89.15
Atomic Hydrogen:	10.67
Atomic Sulfur:	0.0
Atomic Oxygen:	0.18
Total:	100.01

Characteristic Averages on Sample	
Molecular Weight:	404.212
Carbon Number:	30.871
Z Number (CNH$_2$N-Z):	17.082
C Atoms in Sidechains:	16.748

DISTRIBUTION OF AROMATIC RINGS*

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Non-Aromatics	0.0	0.0	0.0	0.0
1-Ring Aroms	11.621	0.0	0.0	11.621
2-Ring Aroms	39.322	0.0	0.840	40.162
3-Ring Aroms	25.596	0.0	2.013	27.609
4-Ring Aroms	15.529	0.0	1.682	17.212
5-Ring Aroms	2.424	0.0	0.166	2.590
6-Ring Aroms	0.813		0.0	0.813
7+ Ring Aroms	0.0			0.0
Totals	95.304	0.0	4.702	100.006

MISCELLANEOUS AVERAGES AND SUMMARIES ON STREAM

DISTRIBUTION OF AROMATIC RINGS*

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Non-Aromatics	0.0	0.0	0.0	0.0
1-Ring Aroms	11.621	0.0	0.0	11.621
2-Ring Aroms	39.322	0.0	0.840	40.162
3-Ring Aroms	25.596	0.0	2.013	27.609
4-Ring Aroms	15.529	0.0	1.682	17.212
5-Ring Aroms	2.424	0.0	0.166	2.590
6-Ring Aroms	0.813		0.0	0.813
7+ Ring Aroms	0.0			0.0
Totals:	95.304	0.0	4.702	100.006

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*Note: Naphthenic and heterocyclic rings are not considered as aromatics. For example, tetralins, benzothiophenes and octahydroanthracenes are listed as 1-ring aromatics.

APPENDIX TABLE C-16

TYPE ANALYSIS ON AROMATIC FRACTION OF STREAM

Compound Type	Wt. % on Volatiles	Wt. % on Stream	Wt. % on Fresh Feed	Wt. % on Total Feed	Average MW	Average Carbon No.	Avg. Car. Sidechains
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.752	0.752	0.752	0.752	389.65	28.26	22.26
CNH_2N	4.205	4.205	4.205	4.205	395.69	28.83	19.83
CNH_2N	6.664	6.664	6.664	6.664	391.82	28.70	19.70
CNH_2N	10.125	10.125	10.125	10.125	385.97	28.43	18.43
CNH_2N	12.243	12.243	12.243	12.243	395.54	29.25	17.25
CNH_2N	16.954	16.954	16.954	16.954	398.40	29.60	17.60
CNH_2N	13.837	13.837	13.837	13.837	398.90	29.78	15.78
CNH_2N	11.759	11.759	11.759	11.759	412.03	30.86	15.86
CNH_2N	8.046	8.046	8.046	8.046	416.83	31.35	15.35
CNH_2N	4.506	4.506	4.506	4.506	423.60	31.97	13.97
CNH_2N	2.978	2.978	2.978	2.978	439.82	33.27	14.27
CNH_2N	1.543	1.543	1.543	1.543	444.95	33.78	13.78
CNH_2N	0.881	0.881	0.881	0.881	453.61	34.54	12.54
CNH_2N	0.499	0.499	0.499	0.499	465.39	35.53	13.53
CNH_2N	0.219	0.219	0.219	0.219	476.75	36.48	12.48
CNH_2N	0.094	0.094	0.094	0.094	485.59	37.26	13.26
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX TABLE C-17

COMPOUND TYPE ANALYSIS FOR SATURATE FRACTION OF STREAM C-7

Compound Type	Total Sats[1] Wt. %
Iso-Paraffins	0.0
Normal Paraffins	6.646
1-Ring Naphthenes	18.226
2-Ring Naphthenes	16.175
3-Ring Naphthenes	17.813
4-Ring Naphthenes	16.095
5-Ring Naphthenes	11.681
6-Ring Naphthenes	8.196
Mono-Aromatics	5.167
Total	100.000

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1. N-Paraffins not determined analytically - n-paraffin row reflects total paraffins

APPENDIX TABLE C-18

MISCELLANEOUS AVERAGES AND SUMMARIES ON VOLATILE AROMATICS ON STREAM C-7

Elemental Analysis by MS, Wt. %	
Atomic Carbon:	88.80
Atomic Hydrogen:	11.04
Atomic Sulfur:	0.0
Atomic Oxygen:	0.16
Total:	100.00

Characteristic Averages on Sample	
Molecular Weight:	415.604
Carbon Number	31.690
Z Number (C_NH_{2N-Z}):	15.695
C Atoms in Sidechains:	18.269

DISTRIBUTION OF AROMATIC RINGS*

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Non-Aromatics	0.0	0.0	0.0	0.0
1-Ring Aroms	19.223	0.0	0.082	19.305
2-Ring Aroms	42.130	0.0	1.371	43.501
3-Ring Aroms	21.005	0.0	1.602	22.607
4-Ring Aroms	10.963	0.0	1.183	12.146
5-Ring Aroms	1.661	0.0	0.160	1.821
6-Ring Aroms	0.587		0.018	0.605
7+ Ring Aroms	0.017			0.017
Totals:	95.586	0.0	4.417	100.003

MISCELLANEOUS AVERAGES AND SUMMARIES ON STREAM

DISTRIBUTION OF AROMATIC RINGS*

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Non-Aromatics	0.0	0.0	0.0	0.0
1-Ring Aroms	19.223	0.0	0.082	19.305
2-Ring Aroms	42.130	0.0	1.371	43.501
3-Ring Aroms	21.005	0.0	1.602	22.607
4-Ring Aroms	10.963	0.0	1.183	12.146
5-Ring Aroms	1.661	0.0	0.160	1.821
6-Ring Aroms	0.587		0.018	0.605
7+ Ring Aroms	0.017			0.017
Totals:	95.586	0.0	4.417	100.003

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*Note: Naphthenic and heterocyclic rings are not considered as aromatics. For example, tetralins, benzothiophenes and octahydroanthracenes are listed as 1-ring aromatics.

APPENDIX TABLE C-19

COMPOUND TYPE ANALYSIS FOR AROMATIC FRACTION OF STREAM C-7

Compound Type	Wt. % on Volatiles	Wt. % on Stream	Wt. % on Fresh Feed	Wt. % on Total Feed	Average MW	Average Carbon No.	Avg. Carb. Sidechains
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	2.089	2.089	2.089	2.089	427.64	30.97	24.97
CNH_2N	7.665	7.665	7.665	7.665	416.44	30.32	21.32
CNH_2N	9.468	9.468	9.468	9.468	416.26	30.45	21.45
CNH_2N	12.449	12.449	12.449	12.449	401.32	29.52	19.52
CNH_2N	13.817	13.817	13.817	13.817	408.47	30.18	18.18
CNH_2N	15.865	15.865	15.865	15.865	411.94	30.57	18.57
CNH_2N	11.951	11.951	11.951	11.951	413.07	30.79	16.79
CNH_2N	9.054	9.054	9.054	9.054	417.81	31.27	16.27
CNH_2N	5.872	5.872	5.872	5.872	422.96	31.78	15.78
CNH_2N	3.103	3.103	3.103	3.103	433.36	32.67	14.67
CNH_2N	1.988	1.988	1.988	1.988	441.41	33.35	14.39
CNH_2N	1.068	1.068	1.068	1.068	451.52	34.25	14.25
CNH_2N	0.593	0.593	0.593	0.593	456.83	34.77	12.77
CNH_2N	0.339	0.339	0.339	0.339	462.34	35.31	13.31
CNH_2N	0.152	0.152	0.152	0.152	472.98	36.21	12.21
CNH_2N	0.096	0.096	0.096	0.096	469.40	36.10	12.10
CNH_2N	0.014	0.014	0.014	0.014	450.13	34.87	8.87
CNH_2N	0.003	0.003	0.003	0.003	387.00	30.50	2.50
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNH_2N	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX D

RANKING OF FUEL CANDIDATES

TABLE D-1

ESTIMATED PROPERTIES FOR EVALUATION OF FUEL CANDIDATES*

Code Name	Fuel Density, ρ (g/cc)	I_{SP} (sec)	$\bar{\rho}\ I_{SP} \times 10^{-4}$ $(lb \cdot sec/ft^3)^{(1)}$	Merit Index $\bar{\rho}\ I_{SP}^3 \times 10^{-9}$ $(lb \cdot sec^3/ft^3)$	Volumetric Heat of Combustion (BTU/gal)
A-1	1.08	296.7	2.07	1.82	163,000
A-2	1.04	293.2	2.02	1.74	139,700
A-3	0.94	297.9	1.98	1.76	144,500
A-4	0.81	307.5	1.92	1.82	128,300
A-5	0.89	299.2	1.95	1.75	139,700
A-6	0.94	295.6	1.97	1.72	143,000
A-7	0.96	293.4	1.97	1.69	143,500
A-8	1.0	296.7	2.02	1.78	153,300
A-9	1.0	296.7	2.02	1.78	153,500
A-10	1.0	296.7	2.02	1.78	154,200
A-11	1.02	290.4	1.98	1.67	148,600
A-12	0.95	295.7	1.98	1.73	145,000
A-13	1.0	299.2	2.04	1.82	154,200
B-1	0.70	209.1	1.82	1.74	161,000
B-2	0.70	302.7	1.79	1.64	110,000
B-3	0.65	302.2	1.72	1.57	101,400
B-4	0.99	296.3	2.00	1.76	148,700
B-5	0.96	294.4	1.97	1.71	143,700
B-6	0.96	294.3	1.97	1.70	142,800
B-7	0.95	293.3	1.95	1.68	140,700
B-8	1.01	287.2	1.95	1.61	143,300
B-9	1.02	288.6	1.97	1.64	146,800

*$\bar{\rho}$ = propellant density; I_{sp} values calculated for equilibrium expansion from 1,000 psia to 14.7 psia on stoichiometric fuel mixture.

TABLE D-1 (Continued)

Code Name	Fuel Density, ρ (g/cc)	I_{SP} (sec)	$\bar{\rho}\, I_{SP} \times 10^{-4}$ $(\mathrm{lb \cdot sec/ft^3})^{(1)}$	Merit Index $\bar{\rho}\, I_{SP}{}^3 \times 10^{-9}$ $(\mathrm{lb \cdot sec^3/ft^3})$	Volumetric Heat of Combustion (BTU/gal)
B-10	1.00	291.6	1.98	1.68	146,700
B-11	0.88	291.9	1.89	1.61	129,900
B-12	0.90	293.7	1.92	1.65	133,900
B-13	0.88	292.6	1.89	1.62	130,400
B-14	0.96	294.3	1.97	1.71	143,400
B-15	1.10	289.0	2.03	1.69	155,500
B-16	1.10	282.0	1.98	1.57	150,500
B-17	1.10	282.0	1.98	1.57	150,000
B-18	1.00	284.0	1.92	1.55	138,800
B-19	0.97	296.1	1.99	1.75	147,100
B-20	1.00	295.2	2.01	1.75	151,100
B-21	0.89	296.3	1.94	1.70	136,400
B-22	0.99	294.7	2.00	1.74	149,600
B-23	1.01	288.5	1.99	1.66	145,600
B-24	0.94	289.3	1.92	1.61	136,700
B-25	0.92	290.8	1.91	1.62	135,300
B-26	0.90	297.7	1.94	1.72	---
B-27	0.82	299.8	1.88	1.69	---
B-28	0.76	303.0	1.85	1.70	---
B-29	0.92	291.1	1.91	1.62	---
B-30	0.83	294.5	1.85	1.61	---
B-31	0.76	299.7	1.82	1.64	---
B-32	0.90	293.2	1.91	1.64	---

TABLE D-1 (Continued)

Code Name	Fuel Density, ρ (g/cc)	I_{SP} (sec)	$\bar{\rho}\, I_{SP} \times 10^{-4}$ $(\mathrm{lb \cdot sec/ft^3})(1)$	Merit Index $\bar{\rho}\, I_{SP}^3 \times 10^{-9}$ $(\mathrm{lb \cdot sec^3/ft^3})$	Volumetric Heat of Combustion (BTU/gal)
B-33	0.82	296.2	1.86	1.63	——
B-34	0.76	300.7	1.83	1.66	——
B-35	0.90	296.9	1.94	1.71	——
B-36	0.82	297.9	1.87	1.66	——
B-37	0.76	299.7	1.83	1.64	——
B-38	0.92	290.2	1.90	1.60	——
B-39	0.83	292.4	1.84	1.58	——
B-40	0.76	296.1	1.80	1.58	——
B-41	0.90	292.6	1.91	1.63	——
B-42	0.82	294.4	1.85	1.60	——
B-43	0.76	297.3	1.81	1.60	——
B-44	0.94	296.9	1.97	1.74	——
B-45	0.88	297.6	1.93	1.71	——
B-46	0.78	299.1	1.84	1.65	——
B-47	0.97	290.2	1.94	1.64	——
B-48	0.89	291.4	1.89	1.60	——
B-49	0.79	295.7	1.83	1.60	——
B-50	0.95	292.6	1.95	1.67	——
B-51	0.88	294.0	1.90	1.64	——
B-52	0.79	296.9	1.84	1.62	——
B-53	0.95	296.1	1.98	1.74	——
C-1	0.930	297.4	1.97	1.74	141,600
C-2	0.912	295.6	1.95	1.70	140,300

TABLE D-1 (Continued)

Code Name	Fuel Density, ρ (g/cc)	I_{SP} (sec)	$\bar{\rho}\ I_{SP} \times 10^{-4}$ (lb·sec/ft^3)(1)	Merit Index $\bar{\rho}\ I_{SP}^3 \times 10^{-9}$ (lb·sec^3/ft^3)	Volumetric Heat of Combustion (BTU/gal)
C-3	1.023	296.0	2.03	1.78	155,000
C-4	0.923	291.0	1.92	1.63	137,600
C-5	1.009	293.0	2.00	1.72	151,300
C-6	0.948	294.0	1.96	1.70	143,800
C-7	0.934	295.1	1.96	1.71	142,600
C-8	0.967	294.7	1.98	1.72	146,800
C-9	1.07	293.0	2.04	1.75	159,900
C-10	1.04	292.8	2.02	1.73	155,300
C-11	1.064	292.8	2.03	1.74	158,700
C-12	0.985	295.2	2.00	1.74	149,900

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(1) $\bar{\rho}$ = propellant density, not fuel density, which is designated as ρ

TABLE D-2

OVERALL RANKING OF CANDIDATE FUELS BY MERIT INDEX*

Merit Index x 10^{-9} (lb. sec^3/ft^3)	Pure Compounds	Chemical Plant Streams	Refinery Streams
1.82	A-1,4,13		
1.78	A-8,9,10		C-3
1.76	A-3	B-4	
1.75	A-5	B-19,20	C-9
1.74	A-2	B-1,22,44,53	C-1,11,12
1.73	A-12		C-10
1.72	A-6	B-26	C-5,8
1.71		B-5,14,35,45	C-7
1.70		B-6,21,28	C-2,6
1.69	A-7	B-15,27	
1.68		B-7,10	
1.67	A-11	B-50	
1.66		B-23,34,36	
1.65	RP-1	B-12,46	RP-1 (Kerosene)
1.64		B-2,9,31,32,37,47,51	
1.63		B-33,41	C-4
1.62		B-13,25,29,52	
1.61		B-8,11,24,30	
1.60		B-38,42,43,48,49	
1.58		B-39,40	
1.57		B-3,16,17	
1.55		B-18	

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*Merit Index = $\bar{\rho}\ I_{SP}^{3}$

TABLE D-3

OVERALL RANKING OF CANDIDATES BY $\bar{\rho}\ I_{SP}$

$\bar{\rho}\ I_{SP} \times 10^{-4}$ (lb. sec/ft^3)	Pure Compounds	Chemical Plant Streams	Refinery Streams
2.07	A-1		
2.04	A-13		C-9
2.03		B-15	C-3,11
2.02	A-2,8,9,10		C-10
2.01		B-20	
2.00		B-4,22	C-5,12
1.99		B-19,23	
1.98	A-3,11,12	B-10,16,17,53	C-8
1.97	A-6,7	B-5,6,9,14,44	C-1
1.96			C-6,7
1.95	A-5	B-7,8,50	C-2
1.94		B-21,26,35,47	
1.93		B-45	
1.92	A-4	B-12,18,24	C-4
1.91		B-25,29,32,41	
1.90		B-38,51	
1.89		B-11,13,48	
1.88	RP-1	B-27	RP-1
1.87		B-36	
1.86		B-33	
1.85		B-28,30,42	
1.84		B-39,46,52	

TABLE D-3

OVERALL RANKING OF CANDIDATES BY $\bar{\rho}\ I_{SP}$

(Continued)

$\bar{\rho}\ I_{SP} \times 10^{-4}$ (lb. sec/ft^3)	Pure Compounds	Chemical Plant Streams	Refinery Streams
1.83		B-34,37,49	
1.82		B-1,31	
1.81		B-43	
1.80		B-40	
1.79		B-2	
1.72		B-3	

TABLE D-4

OVERALL RANKING OF CANDIDATES BY SPECIFIC IMPULSE

I_{SP} (sec)	Pure Compounds	Chemical Plant Streams	Refinery Streams
309.1		B-1	
307.5	A-4		
303.0		B-28	
302.7		B-2	
302.2		B-3	
300.7		B-34	
299.8		B-27	
299.7		B-31,37	
299.2	A-5,13		
299.1		B-46	
297.9	A-3	B-36	
297.7		B-26	
297.6		B-45	
207.4			C-1
207.3		B-43	
296.9		B-35,44,52	
296.7	A-1,8,9,10		
296.4	RP-1		RP-1
296.3		B-4,21	
296.2		B-33	
296.1		B-19,40,53	
296.0			C-3
295.7	A-12	B-49	

TABLE D-4 (Continued)

I_{SP} (sec)	Pure Compounds	Chemical Plant Streams	Refinery Streams
295.6	A-6		C-12
295.2		B-20	C-12
295.1			C-7
294.7		B-22	C-8
294.5		B-30	
294.4		B-5,42	
294.3		B-6,14	
294.0		B-51	C-6
293.7		B-12	
293.4	A-7		
293.3		B-7	
293.2	A-2	B-32	
293.0			C-5,9
292.8			C-10,11
292.6		B-13,41,50	
292.4		B-39	
291.9		B-11	
291.6		B-10	
291.4		B-48	
291.1		B-29	
291.0			C-4
290.8		B-25	
290.4	A-11		
290.2		B-38,47	

TABLE D-4 (Continued)

I_{SP} (sec)	Pure Compounds	Chemical Plant Streams	Refinery Streams
289.3		B-24	
289.0		B-15	
288.6		B-9	
288.5		B-23	
287.2		B-8	
284.0		B-18	
282.0		B-16,17	

TABLE D-5

OVERALL RANKING OF CANDIDATES BY ESTIMATED VOLUMETRIC HEAT OF COMBUSTION

Heat of Combustion (BTU/gal)	Pure Compounds	Chemical Plant Streams	Refinery Streams
163,000	A-1		
161,000		B-1	
159,900			C-9
158,700			C-11
155,500		B-15	
155,300			C-10
155,000			C-3
154,600	A-13		
154,200	A-10		
153,500	A-9		
153,300	A-8		
151,300			C-5
151,100		B-20	
150,500		B-16	
150,000		B-17	
149,900			C-12
149,600		B-22	
148,700		B-4	
148,600	A-11		
147,100		B-19	
146,800		B-9	C-8
146,700		B-10	

TABLE D-5 (Continued)

Heat of Combustion (BTU/gal)	Pure Compounds	Chemical Plant Streams	Refinery Streams
145,800		B-53	
145,600		B-23	
145,000	A-12		
144,500	A-3		
143,800			C-6
143,700		B-5	
143,500	A-7		
143,400		B-14	
143,300		B-8	
143,000	A-6		
142,800		B-6	
142,600			C-7
141,600			C-1
140,700		B-7	
140,300			C-2
139,700	A-2		
138,800		B-18	
136,700		B-24	
136,400		B-21	
135,300		B-25	
133,900		B-12	
130,400		B-13	
129,900		B-11	

TABLE D-5 (Continued)

Heat of Combustion (BTU/gal)	Pure Compounds	Chemical Plant Streams	Refinery Streams
128,300	A-4		
125,000	RP-1		RP-1
110,000			
101,400			

APPENDIX E.

TABLES AND PLOTS OF SOME PHYSICAL PROPERTIES FOR TOP FUEL CANDIDATES

FIG. E-1 EFFECTS OF TEMPERATURE ON DENSITY FOR SOME PURE COMPOUNDS

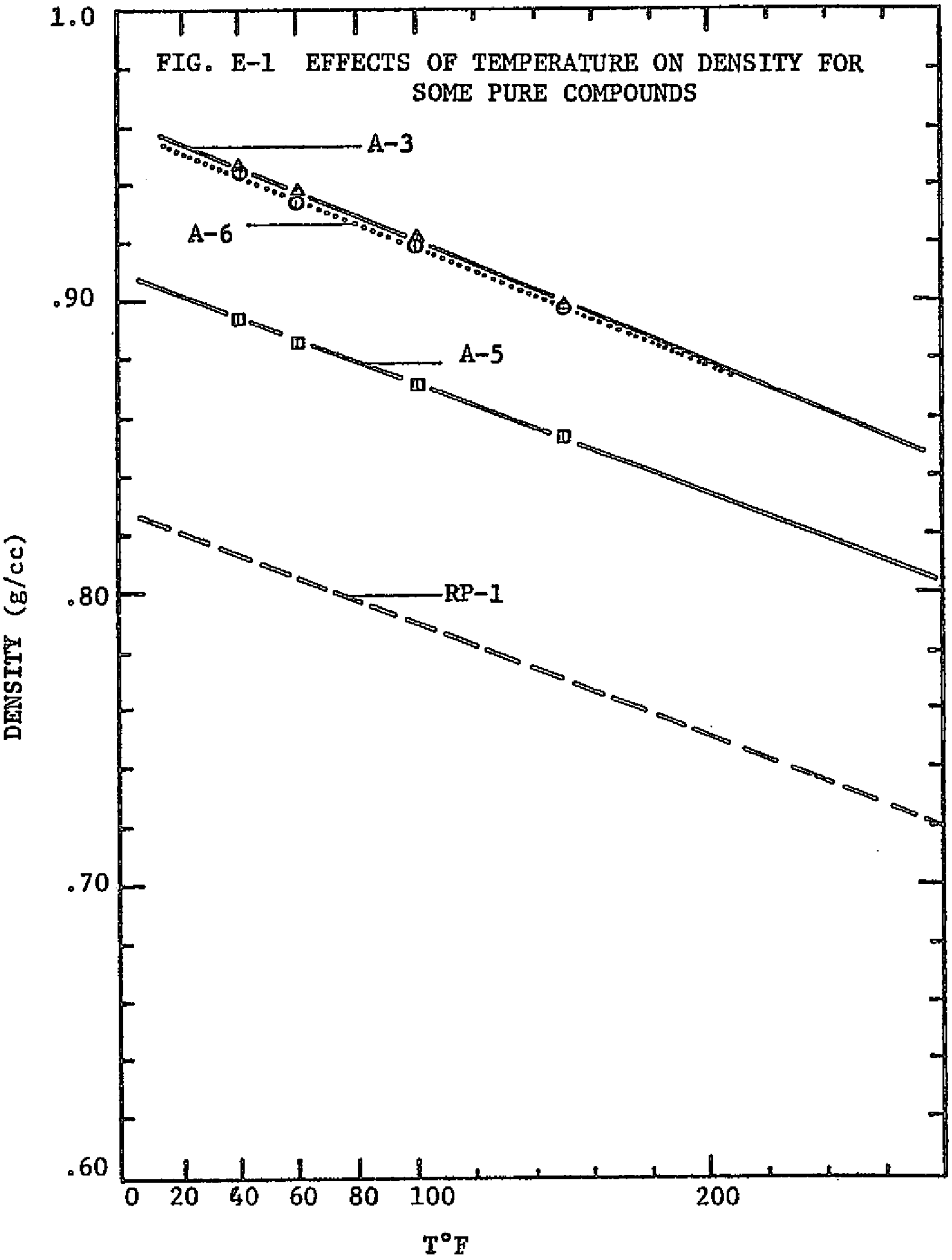


FIG. 2 EFFECTS OF TEMPERATURE ON DENSITY FOR CHEM. PLANT SYSTEMS

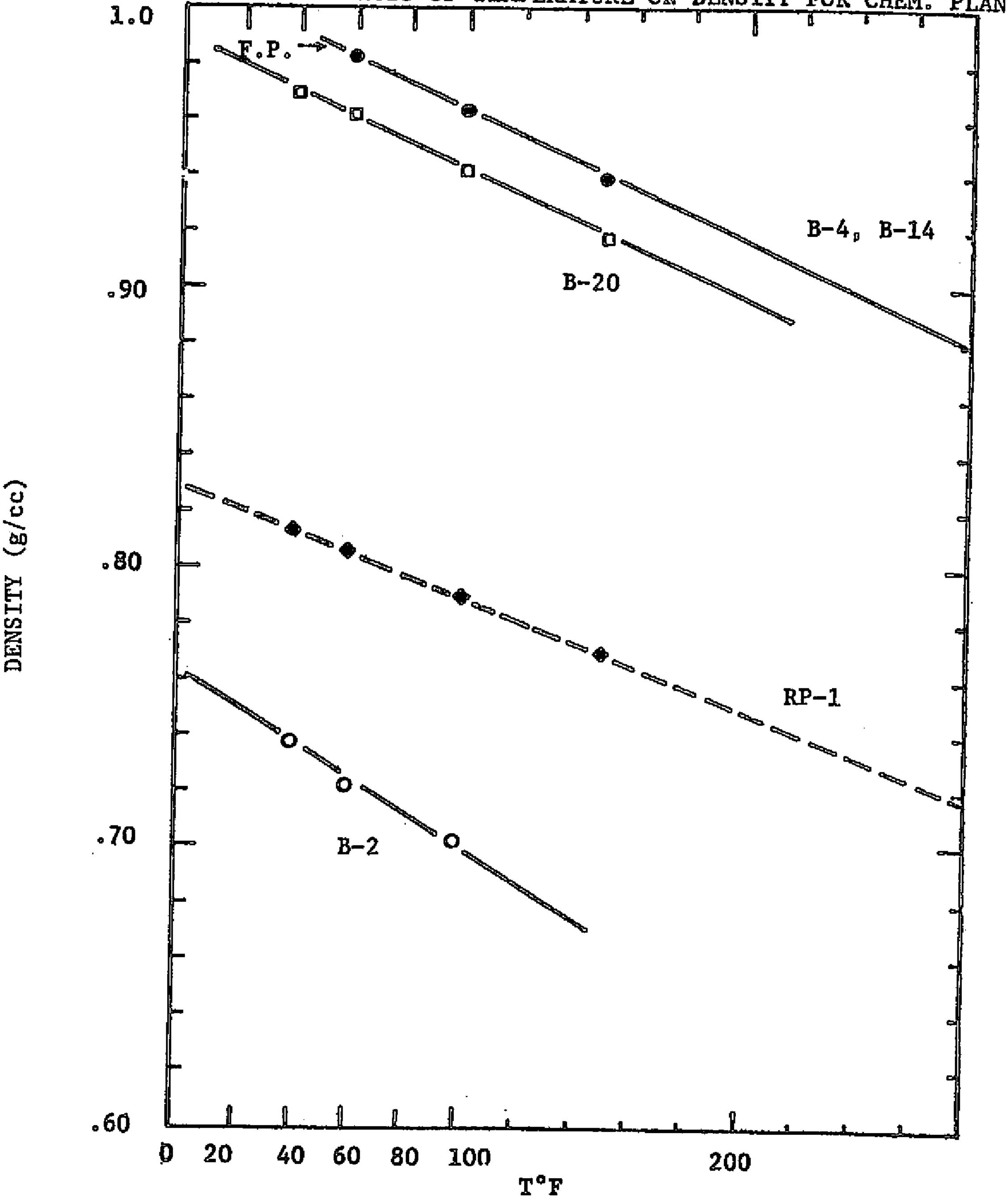


FIG. 3 EFFECTS OF TEMPERATURE ON DENSITIES OF SOME REFINERY STREAMS

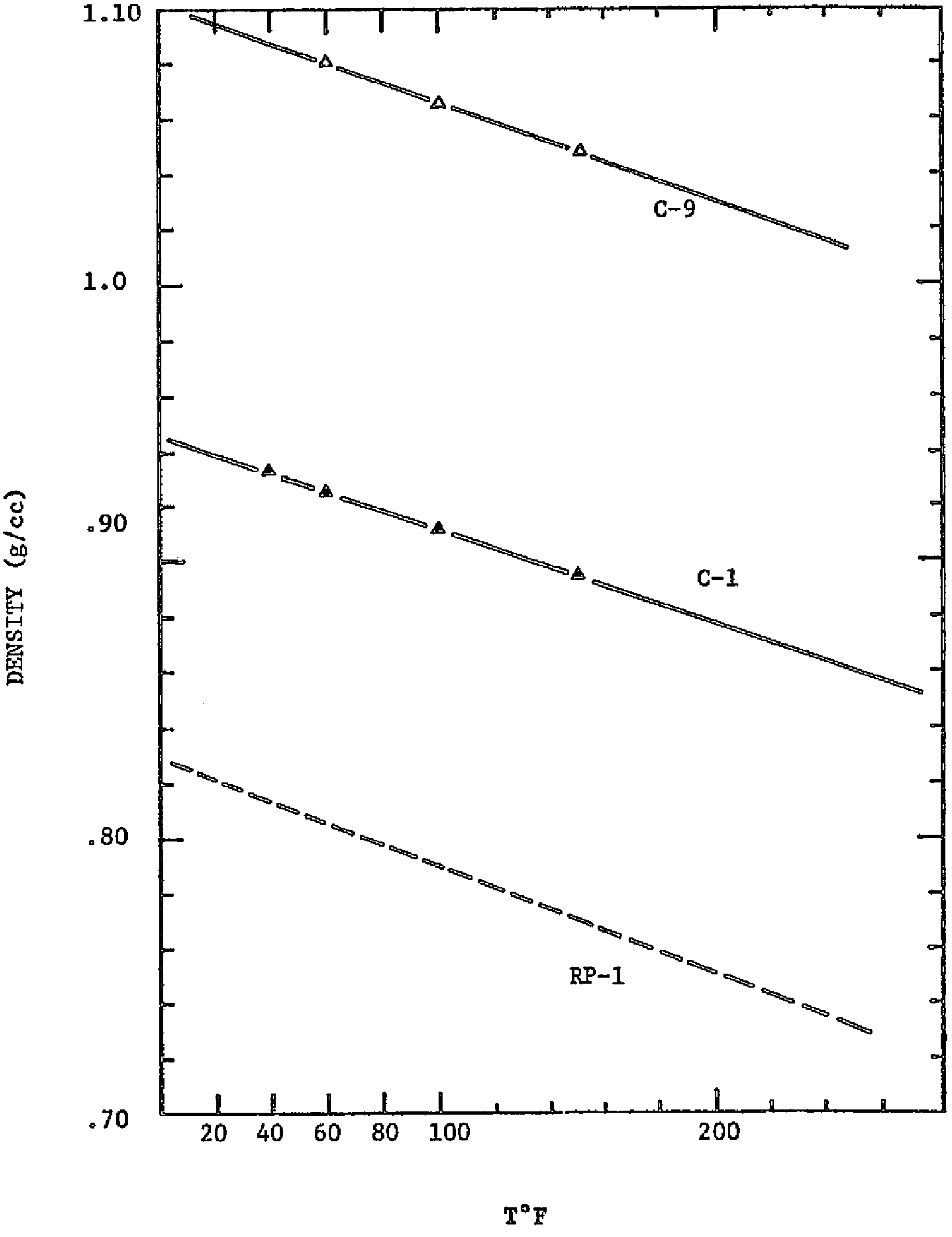


FIG. E-4 VISCOSITES VS. TEMPERATURE FOR PURE COMPOUND CANDIDATES

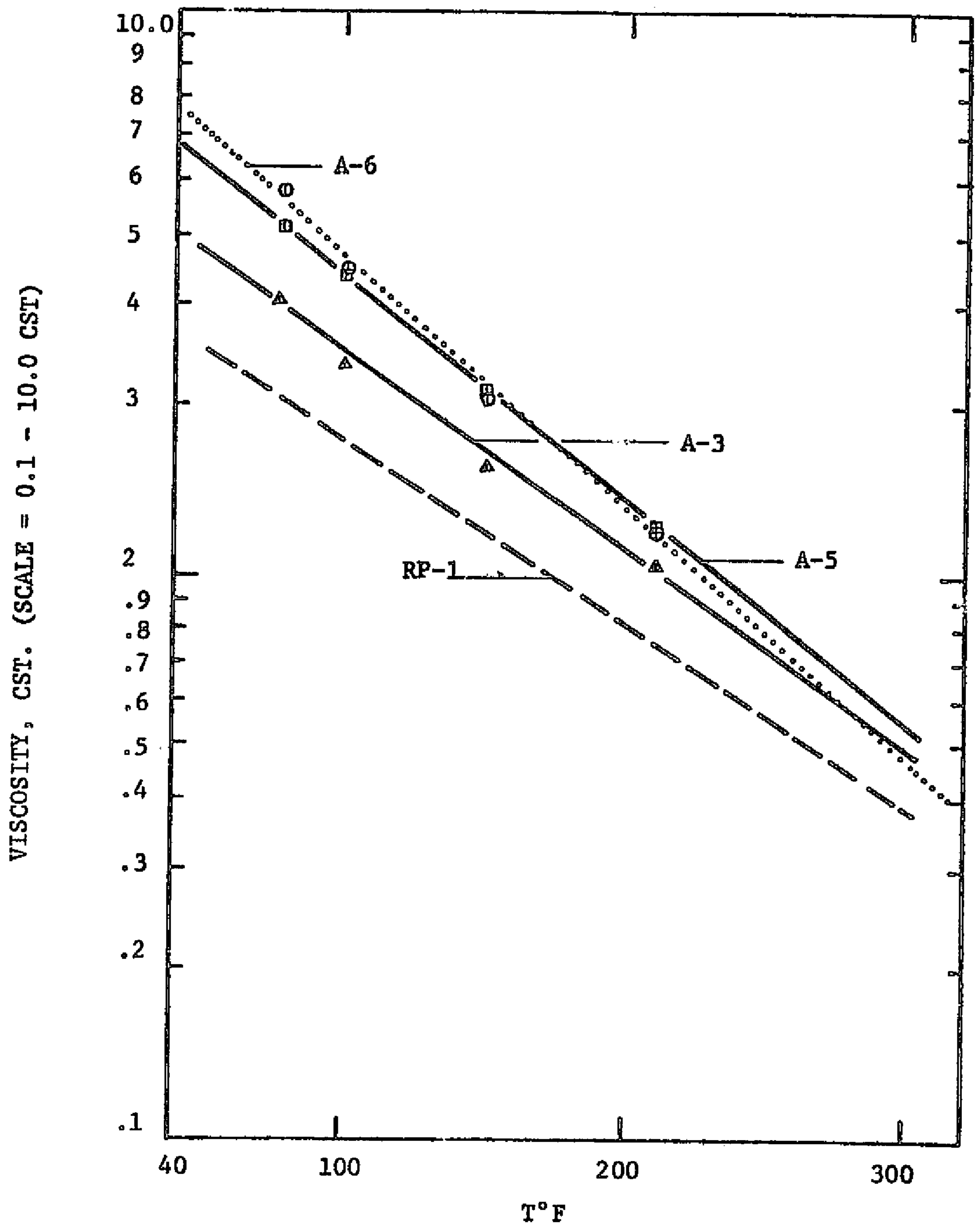


FIG. E-5 VISCOSITIES FOR CHEM. PLANT STREAMS AS FUNCTION OF TEMPERATURE

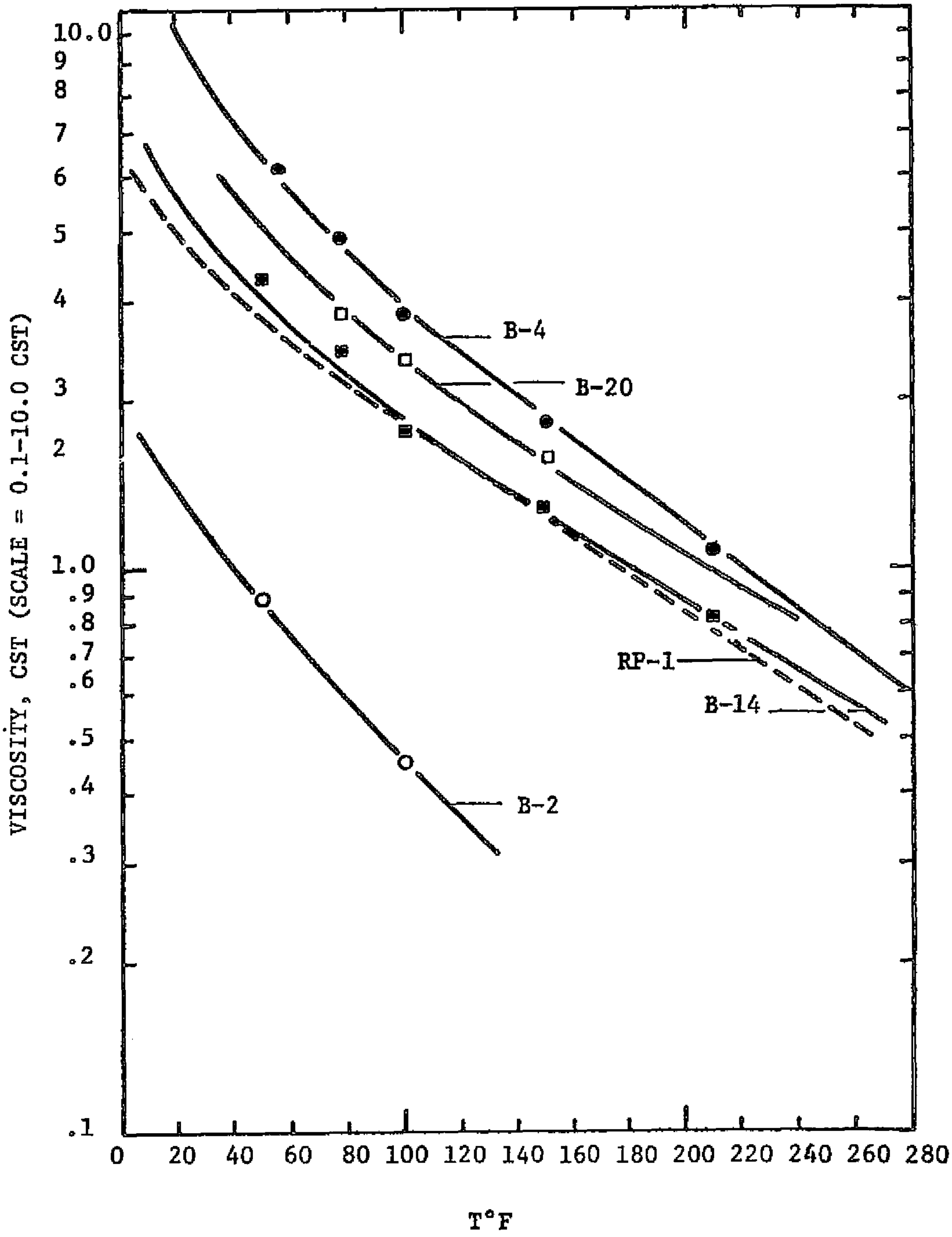


FIG. E-6 VISCOSITIES FOR REFINERY STREAMS AS A FUNCTION OF TEMPERATURE

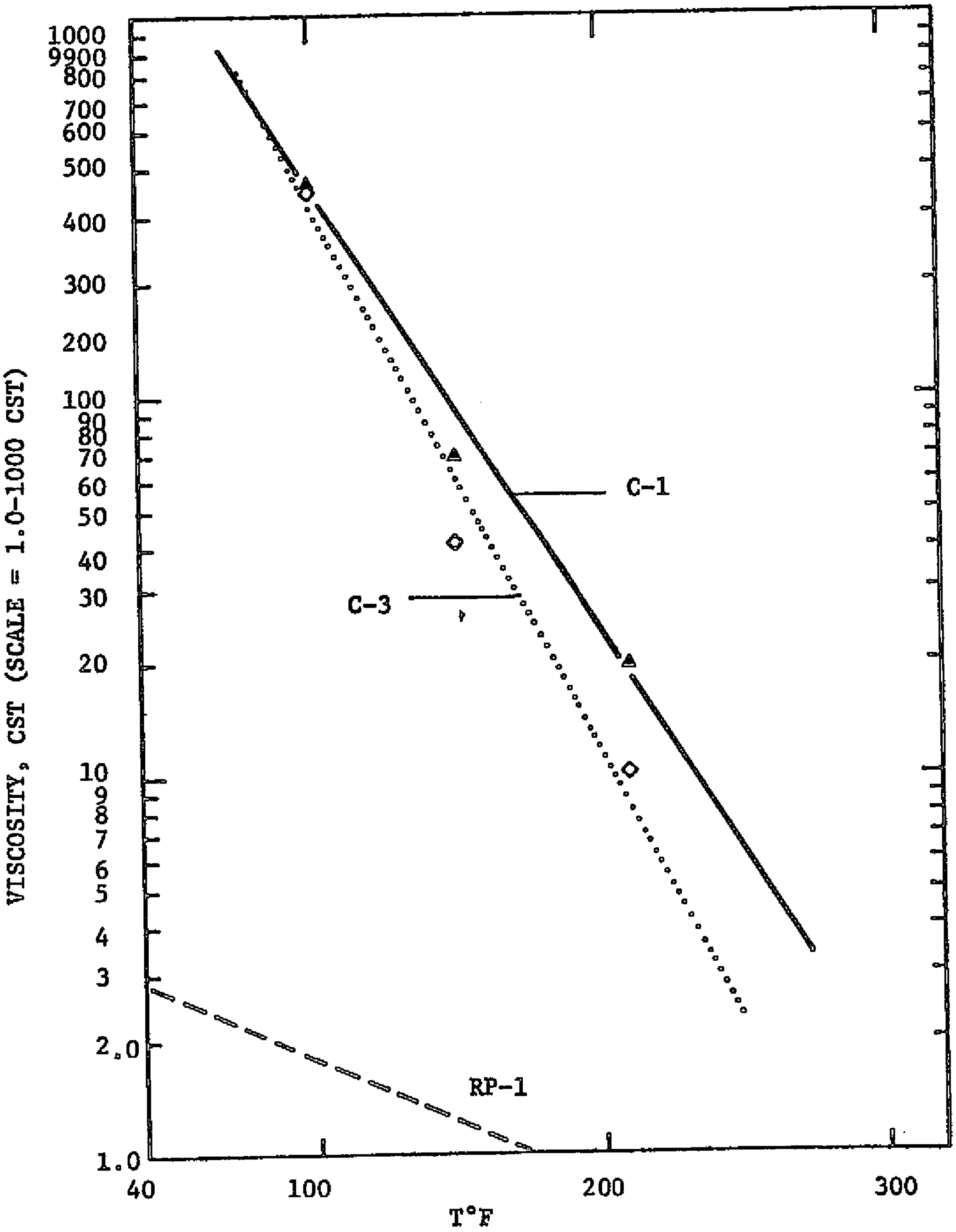


FIG. E-7 VISCOSITIES OF SOME BLENDS OF B-2 AND B-15

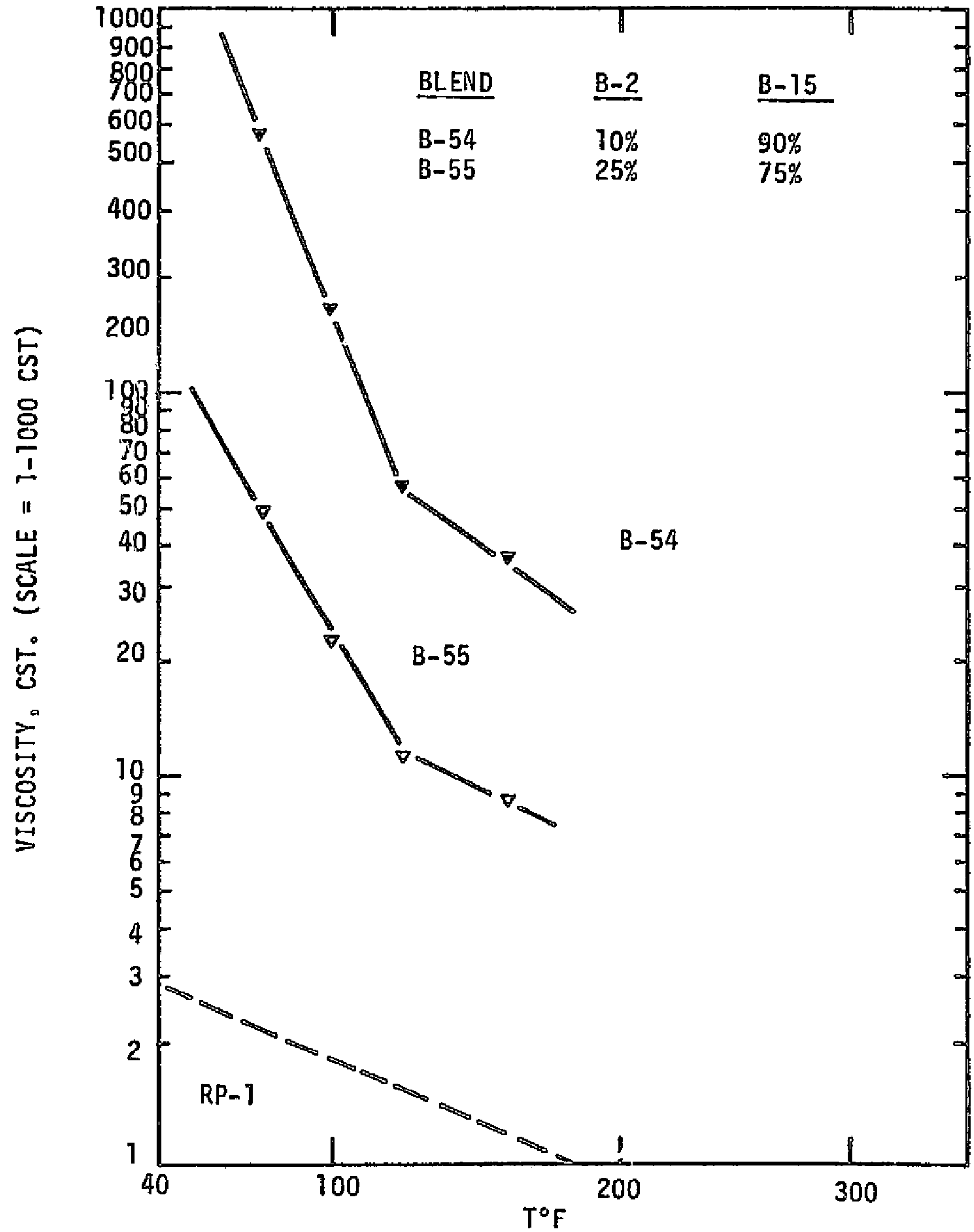


FIG. E-8 VISCOSITIES OF SOME BLENDS OF B-4 and B-15

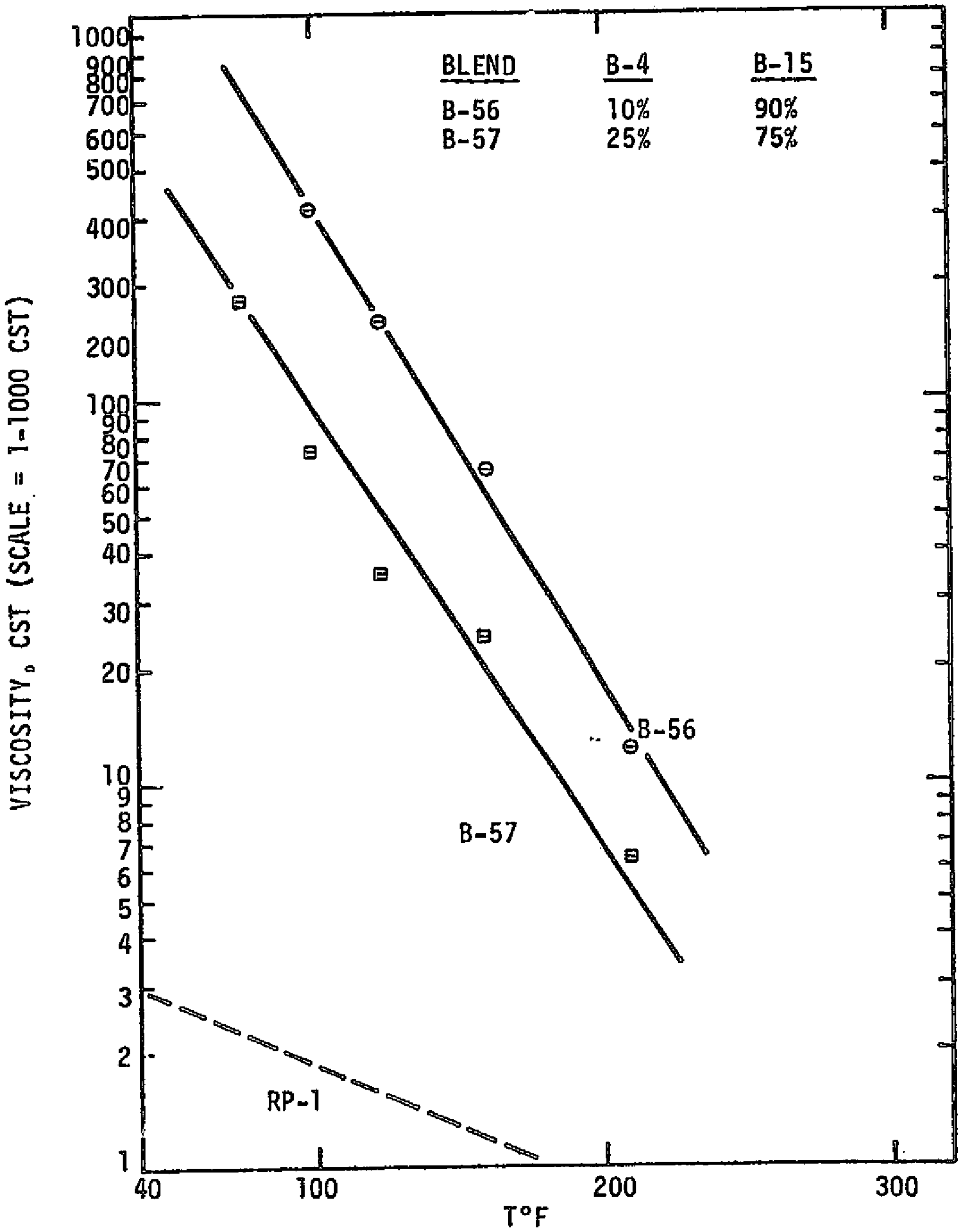


FIGURE E-9 ARRHENIUS PLOTS FOR SOME PURE COMPOUND CANDIDATES

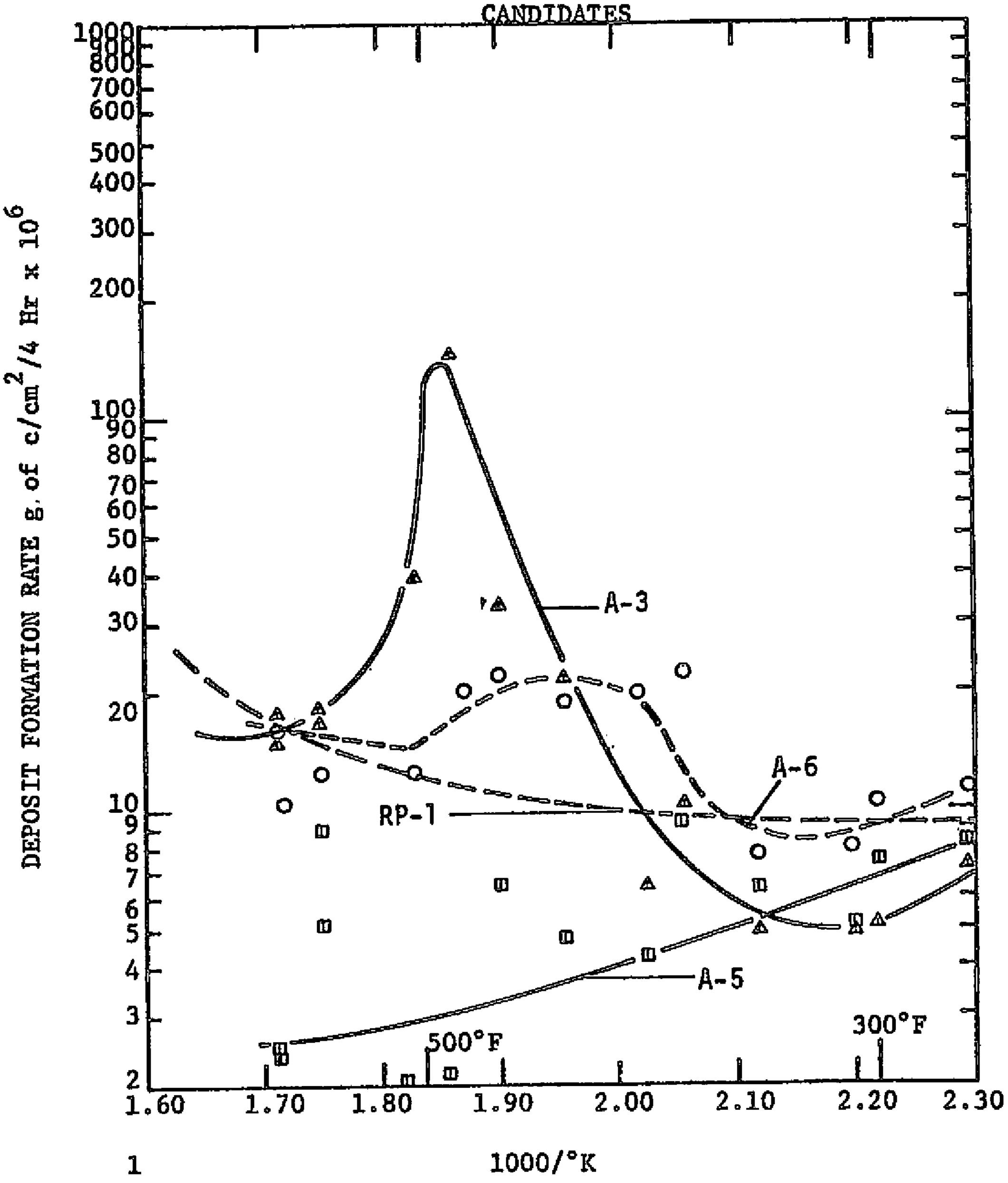


FIGURE E-10 ARRHENIUS PLOTS FOR SOME CHEM PLANT STREAMS

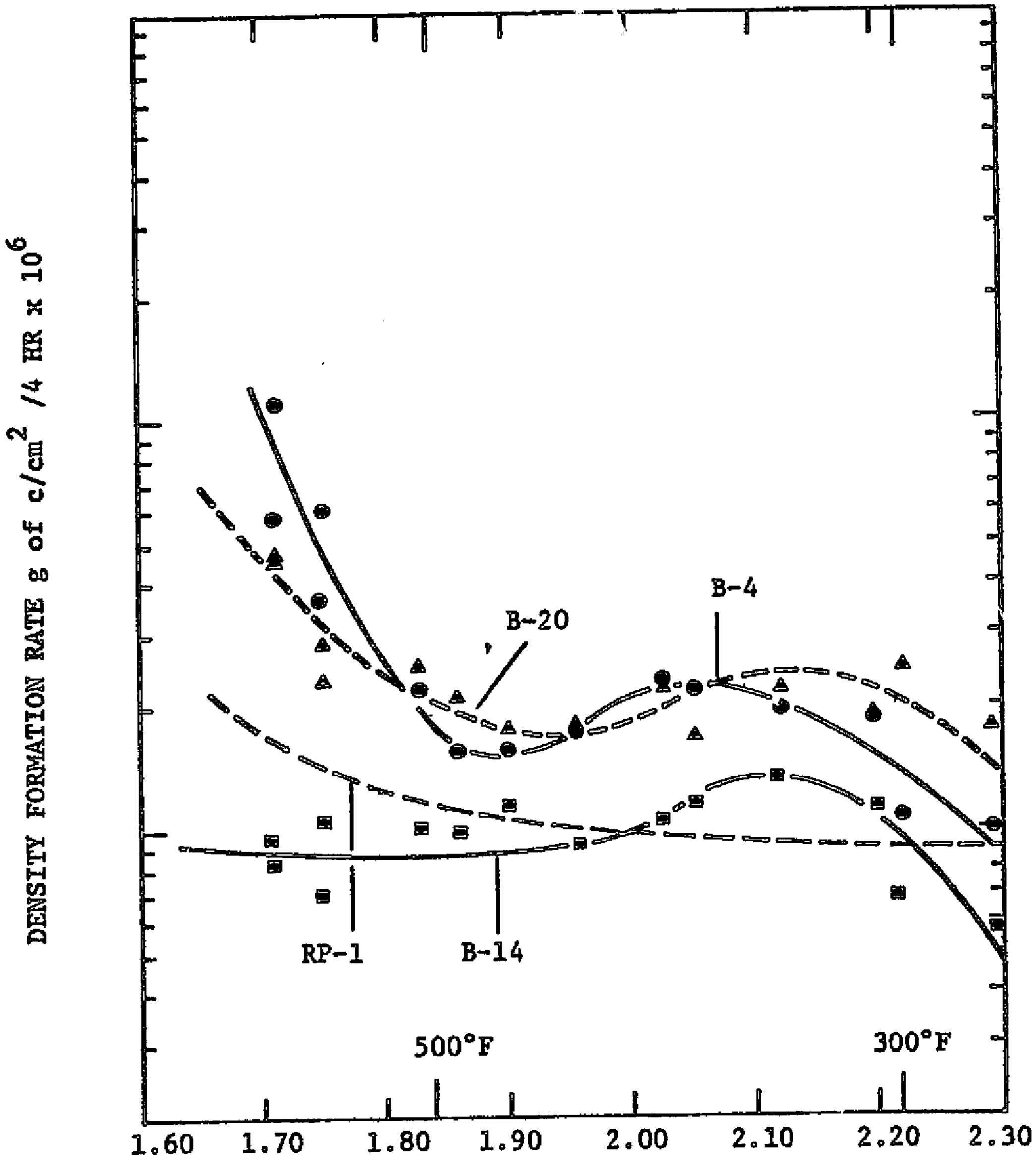


FIGURE E-11
ARRHENIUS PLOTS FOR SOME REFINERY STREAMS (DILUTED 50/50 WITH n-DECANE)

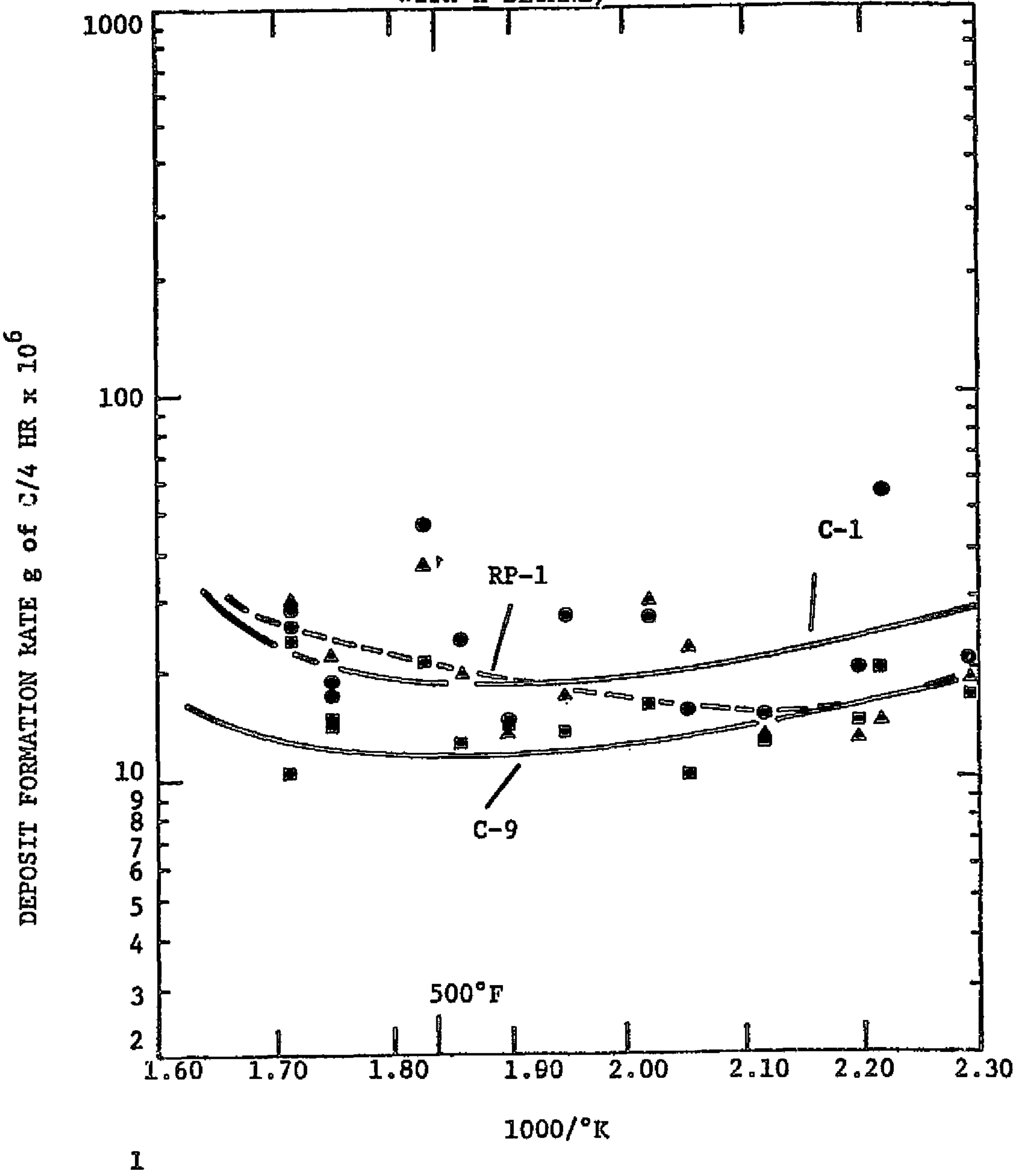


FIGURE E-12

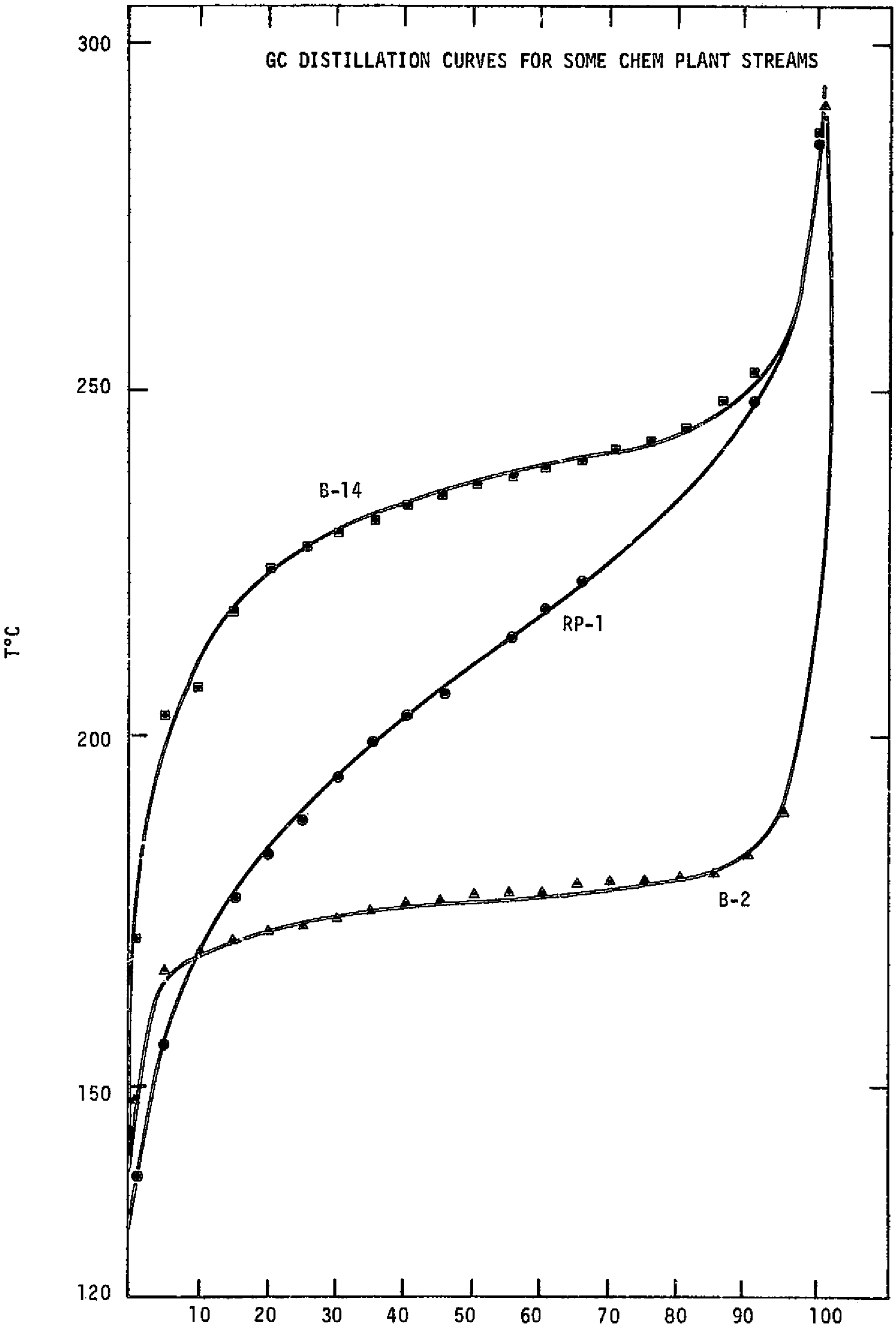

GC DISTILLATION CURVES FOR SOME CHEM PLANT STREAMS
T°C
300
250
200
150
120
10
20
30
40
50
60
70
80
90
100
B-14
RP-1
B-2

FIGURE E-13

DISTILLATION CURVES FOR B-4 AND B-20

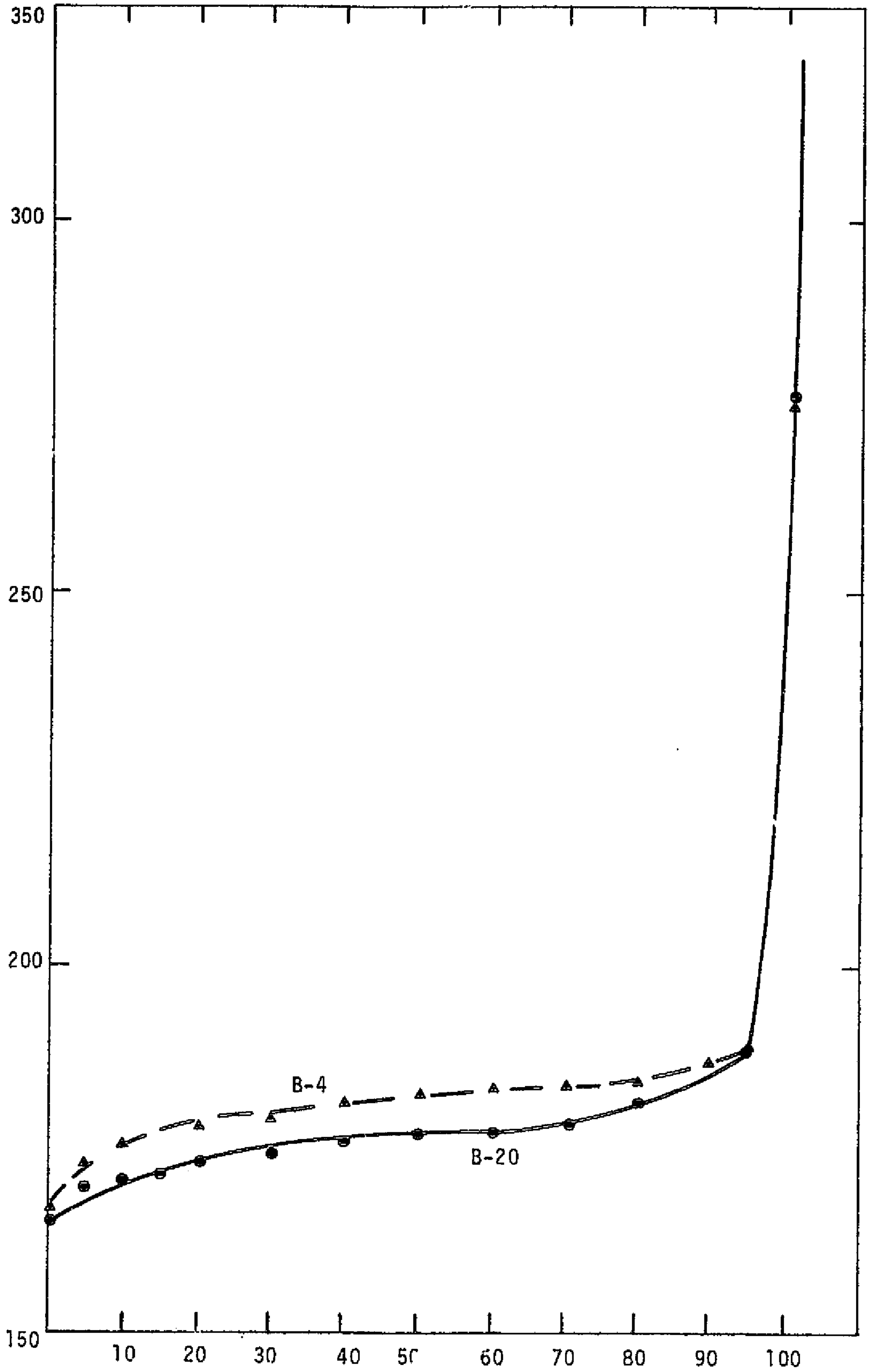
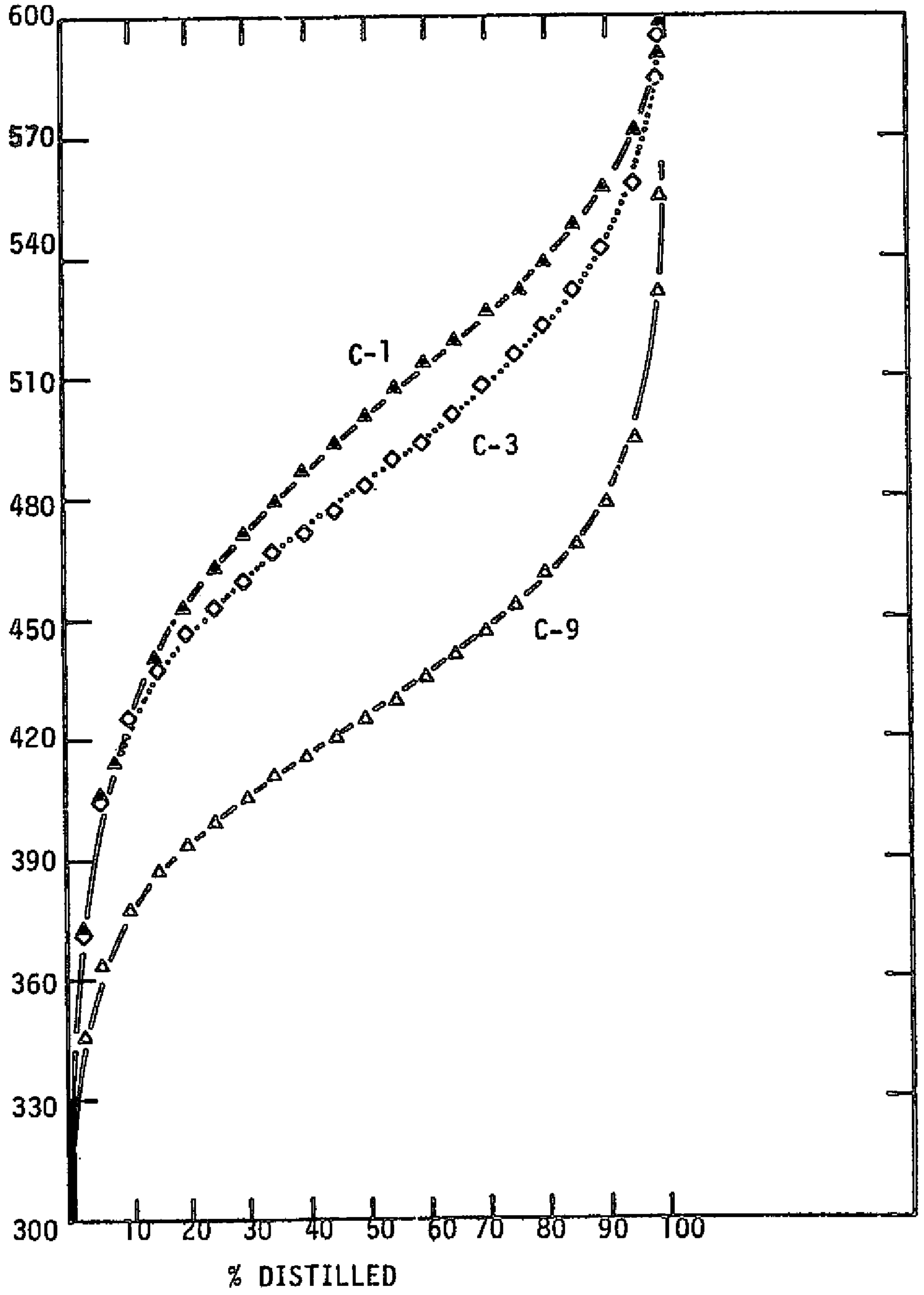


FIG. E-14 DISTILLATION CURVES FOR SOME REFINERY STREAMS



APPENDIX F.

SYNTHESIS OF PURE COMPOUND CANDIDATES AND MODIFIED CHEMICAL PLANT STREAMS

F.1 Synthesis of Decahydroacenaphthene (A-6)

F.2 Conversion of B-4 to B-20

F.1 Synthesis of Decahydroacenaphthene (A-6) by Rearrangement of 1,5,9-Cyclododecatriene (CDT).

A 3-l, 4-necked flask equipped with a condenser, thermometer, stirrer, and dropping funnel was charged with 1800 g of polyphosphoric acid. The acid was heated to 150°, and 500 g. (3.6 moles) of CDT was added over a l-hr. period. The reaction mixture was stirred vigorously while the temperaturewas maintained at 140-160° for 3 hr. after the addition was completed. The mixture was cooled to 100° and poured onto 2 kg. of ice. The mixture was allowed to warm to room temperature and was filtered to remove a small amount of green gum which was suspended. The aqueous layer was separated from the organic layer and extracted with six successive 150-ml. portions of hexane. The hexane fractions were added to the organic layer, and this solution was washed three times with 150 ml. of water, once with 150 ml. of 10% NaOH solution, three times with 150 ml. of water, and once with 150 ml. of saturated NaCl solution. The ether solution was then dried over anhydrous $MgSO_4$ and filtered, and the petroleum either was removed on a rotary evaporator. The liquid residue was distilled in vacuo, yielding 288 g. (48%) of A-6 as a light yellow liquid (b.p. 98-106° at 6 mm), 24 g (4%) of a pale yellow solid (b.p. 150° at 9 mm), and 174 g (29%) of a dark green, low-melting resin.

Anal: C = 87.89; H = 12.01

Calculated for $C_{12}H_{20}$:

C = 87.71; H = 12.27

F.2 Conversion of B-4 to B-20 by Partial Hydrogenation

B-20 (200 g.) dissolved in 100 cc of anhydrous ether was charged to a 500 cc Parr pressure reactor. One g of platinum oxide catalyst was added and the reactor was pressured with hydrogen to 50 psi. After several hours shaking , the pressure fell to 13 psi indicating about 80% of theoretical hydrogen uptake (one mole) assuming B-4 is 100% dicyclopentadiene. The catalyst was filtered and the ether was removed at atmospheric pressure leaving a clear yellow liquid.

Anal: C = 89.95; H = 9.40

Calculated for $C_{10}H_{14}$:

C = 89.55; H = 10.45

APPENDIX G.

ADVANCED HYDROCARBON FUEL ANALYSIS

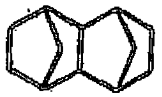
G.1 Analysis of Synthesis Methods

This section is a paper chemistry study of methods for synthesizing highly energetic and/or high density hydrocarbons using two approaches:

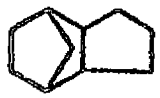
- Modification of Existing Candidate Fuels
- Synthesis of New Types of Molecules

G.I.1 - Molecular Modification of Existing Candidate Fuels

Two basic ring structures are the perhydro-1,4,5,8-dimethanonaphthalene and the perhydro-4,7-methanoindane structures, A and B respectively.



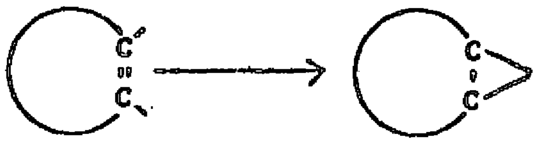
A



B

Both these molecules, and their non-methano bridged counterparts, may be used as templates, which upon suitable molecular modification may afford candidate fuels with improved characteristics. The structures and physical properties of these template molecules are summarized in Table G.1.

One synthetic approach to the formation of the target fuels could involve the interaction of suitable reagents with olefinic derivatives of the template molecules. Both mono- and bis-olefinic derivatives will be employed. A generalized formulation of the modification to be effected would be:



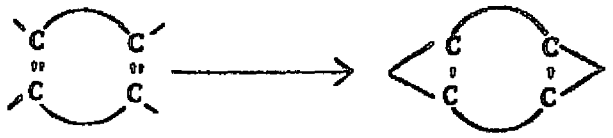
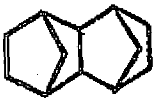
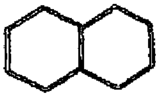
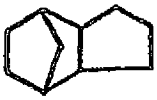
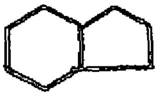


Table G.1

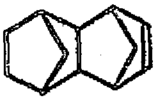
Substrates Proposed for Molecular Modification

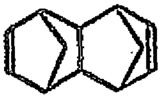
Shelldyne-H Variants	Specific Gravity	BTU per Gal (net)
	1.0065	152,000
	0.8965 0.8699	137,500 (cis) 133,300 (trans)
Dicyclopentadiene Variants		
	0.879	139,000
	0.8844 0.8627	137,500 (cis) 132,300 (trans)

In the sections immediately below are illustrated, in detail, (1) the procedures we could use for the formation of olefinic derivatives of the compounds in Table G.1, and (2) the preferred methods for formation of cyclopropyl groups.

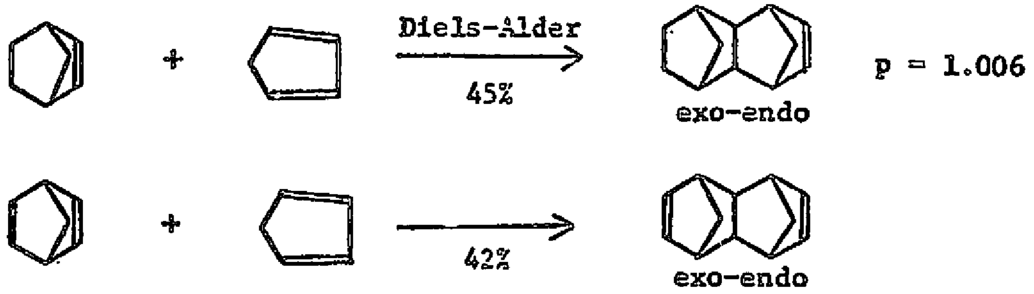
Task G.1.1.1- Tetracyclo-$[4.4.0.1^{2,5}1.^{7,10}]$-Dodecane Olefinic Analogs

The title ring system is representative of the basic molecular framework of Shelldyne-H. The specific olefinic substrates of this class which seem most promising would incorporate one and two double bonds in the positions as indicated in the structural formula below.



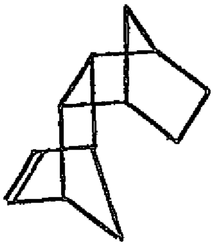


Derivatives of this general class are conveniently prepared via the Diels-Alder reaction between cyclopentadiene and either norbornene and norbornadiene (3, 4)

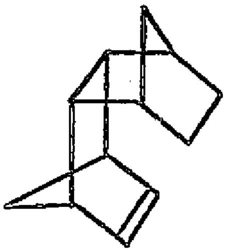


As noted in the equation above, the products of these reactions are the exo-endo isomers (5). In view of their comparative ease of preparation, these stereoisomers are quite promising. However, we also feel that it is imperative to study the changes imparted to the density and volumetric heat of combustion produced by variation of the stereochemical configuration of the target ring system. For example, in the simple bicyclic ring system, decalin, the cis isomer is both more dense and also exhibits a higher heat of combustion than the trans isomer. The effect of stereoisomerism on the density, volumetric heat of combustion, and low temperature viscosity of the perhydro-1,4,5,8-dimethanonaphthalenes cannot be predicted a priori and would have to be experimentally examined.

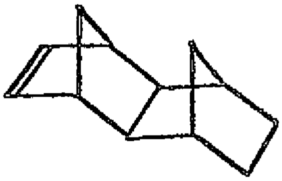
Of the remaining three possible steroisomers of the 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene ring system,



endo-exo



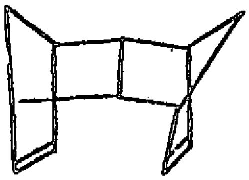
endo-endo



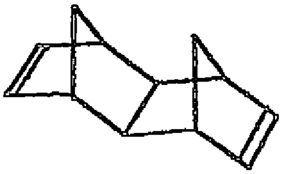
exo-exo

detailed syntheses have been recently recorded in the literature for the formation of endo-exo (6) and endo-endo analogs (7).

Analogously, of the remaining two stereoisomeric forms of the 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene ring system



endo-endo



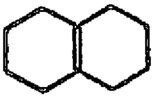
exo-exo

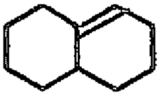
the preparation of the endo-endo isomer has recently been described (8).

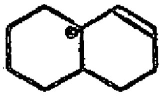
G.1.1.2 - Bicyclo-[4.4.0]-Decane Ring System

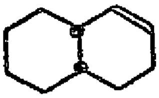
The exclusion of the methano bridges from the basic Shelldyne-H molecule leads to derivatives of decalin.

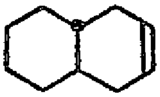
Of the six possible isomeric forms of octalin,

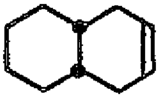

9,10-octalin


1,9-octalin

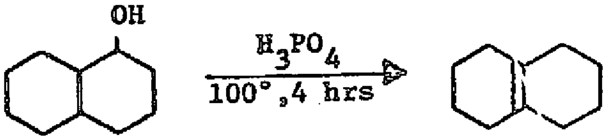

trans-1,2-octalin


cis-1,2-octalin


trans-2,3-octalin

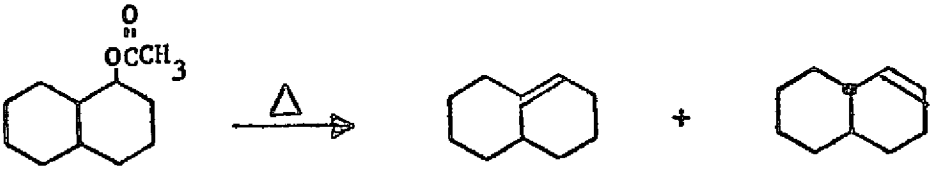

cis-2,3-octalin

each has been obtained (9) in various enrichment ratios as a result of reactions performed on the differing 1-decalol isomers. In the transformations illustrated below, the percent yield for each isomer refers to the isolable amount of the specific olefin in relation to the other isomers produced in the reaction (9).



(Mixture of isomers; Ref. 10)

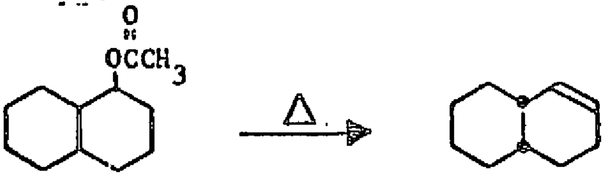
94%



(trans-trans; Ref. 28)

58%

41%



(cis-cis; Ref. (11)

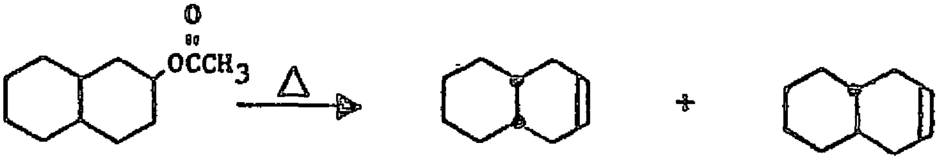
91%

One major modification which could be effected upon the template ring systems shown is the inclusion of three-membered carbocyclic bridges. This change should impart both a large increase to the volumetric heat of combustion of the template molecules as well as impart a lowering of their melting points (and hopefully, their viscosities). This supposition is supported by the physical properties of model compounds:

Density Effect of Ring Formation

Structure	Specific Gravity	M.P., °C
	0.909	-19
	0.991	-50

The data presented above are representative and illustrates the increase in density which accompany the inclusion or formation of a cyclopropyl grouping. It should also be noted that the melting points decreased drastically.

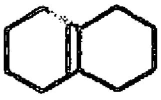


(Mixtures of isomers; Comm. Avail.)

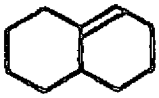
37%

10%

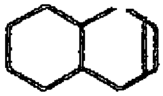
The densities have been reported for three of these isomers as shown below (12-14). It is to be expected that the candidate fuels to be produced by the inclusion of cyclopropyl groups will have comparably greater densities.



$\rho = 0.9160$



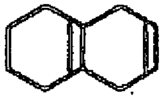
$\rho = 0.9009$



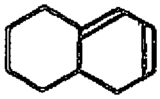
$\rho = 0.8941$.

Alternative preparations of the target olefins could be considered. A considerable body of literature has been published in this area. As an example, pure 9,10-octalin has recently been prepared by reduction of naphthalene by lithium metal in mixed amine solvents (15). Separation from the 1,9-octalin by-product was conveniently effected owing to the greater reactivity of the less sterically crowded 1,9-isomer toward bis-3-methyl-2-butylborane (16).

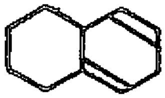
The various bis-olefinic derivatives (hexahydronaphthalenes) which are worthy of consideration are shown below. Also noted are the densities where available.



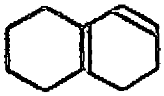
$\rho = 0.9446$
(Ref. 17)



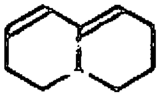
$\rho = 0.9369$
(Ref. 18)



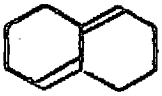
$\rho = 0.9726$
(Ref. 19)



(Ref. 20,21)



(Ref. 22)



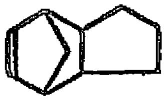
$\rho = 0.9701$
(Ref. 17)

G.1.1.3 - Tricyclo-[4.2.1.0^{2},5]-decane Olefinic Analogs

The title class of olefins could be utilized for the formation of cyclopropyl derivatives of the basic dicyclopentadiene structure B. In general, the preferred synthetic route to this class of compounds involves the Diels-Alder dimerization of cyclopentadienes.

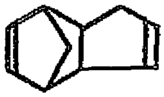
Other olefins of possible interest include:

Dicyclopentadiene Olefinic Substrates

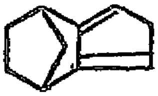


(Ref. 23; ρ = 0.9571)

(Ref. 24)



(Comm. Avail.; ρ = 0.9772)



(Ref. 25; ρ = 0.9918)

The molecules listed above exist predominantly in the endo configuration.

G.1.1.4- Bicyclo-[4.3.0]-nonane Olefinic Analogs

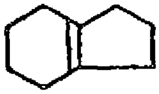
Included in Table 3-4 are the structures and reported literature preparations of a variety of olefins of this class.

G.1.14 - Formation of New Cyclopropyl Derivatives

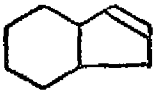
Olefins whose syntheses were discussed in the preceeding section could be utilized as substrates for the inclusion of both cyclopropyl and aziridine groups. A generalized formulation of the transformations to be effected is illustrated below:

TABLE G.2

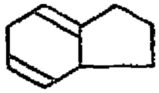
Indene Olefinic Analogs



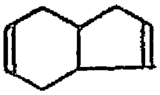
(Ref. 26; ρ = 0.9032)



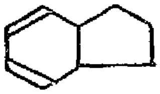
(Ref. 27)



(Ref. 28; ρ = 0.9340)

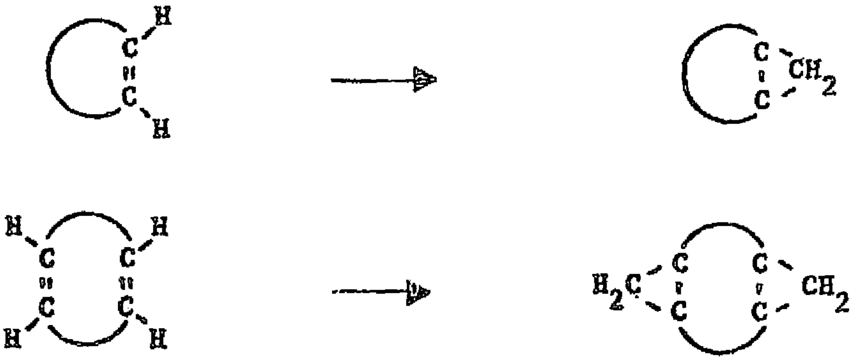


(Comm. Avail;
ρ = 0.9227)



(Ref. 29; ρ = 0.9274)

(Comm. Avail.)



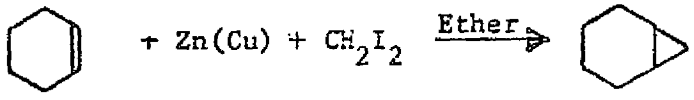
In the sections below, are discussed the preferred synthetic routes to effect these transformations.

It is generally conceeded that the most useful method for the generation of cyclopropyl groups from olefins involves the use of the versatile Simmons-Smith reagent (30). The reagent is conveniently prepared by the reaction of methylene iodide in ether solution with an activated zinc-copper couple prepared as described by Shank and Shechter (31).

$$CH_2I_2 + Zn(Cu) \longrightarrow (CH_2I)ZnI \text{ or } (CH_2I)_2Zn, ZnI_2$$

Simmons-Smith Reagent

A typical reaction in which the Simmons-Smith reagent is used to generate a cyclopropyl group from an olefin is illustrated below (32).



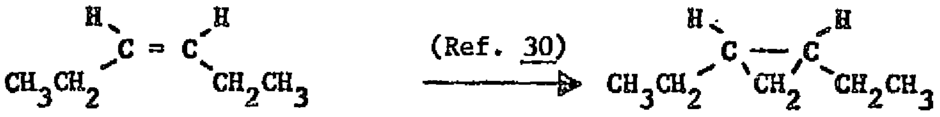
55-60%

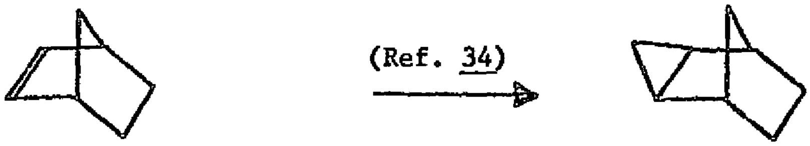
The reaction is general, and if either the olefin or the cyclopropane is sensitive to zinc iodide (a Lewis Acid), the procedure may be modified by the use of diethyl ether containing one-equivalent of 1,2-dimethoxyethane, glyme. Zinc iodide is quantitatively removed from solution as its crystalline and insoluble 1:1 complex with glyme (33).

It was initially proposed that free carbene ($:CH_2$) was generated in the Simmons-Smith reaction. This has been discounted, however, and it is now conceeded that the active species is the reagent itself as formulated above. It is interesting to note that the Simmons-Smith reaction is stereospecific in that the products are those produced exclusively via cis-

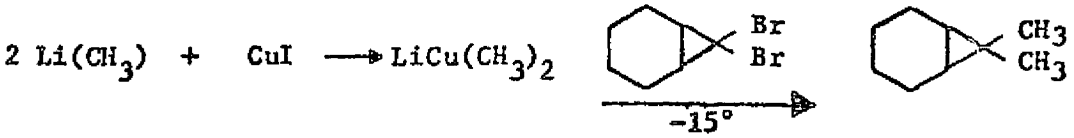
C-3

addition. Thus, cis- and trans-3-hexene afford pure cis- and pure trans-1,2-diethylcyclopropane. The examples shown below illustrate this point.

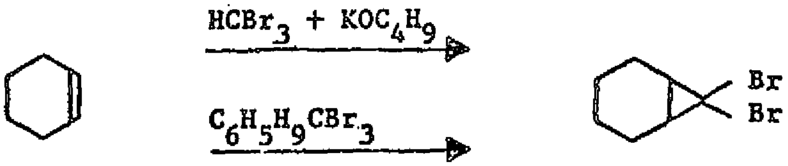




The Simmons-Smith reaction could be used for the generation of cyclopropyl bridges on each of the olefins whose syntheses were discussed in the section above. The reaction appears to be quite general. The variety of conditions under which the reaction will proceed allows several approaches to the same target structure. For example, a highly reactive zinc-copper couple has been prepared recently by treating either zinc dust or grannules with a hot solution of cupric acetate in acetic acid, followed by washing with acetic and then ether (35). The formation of norcarane or bicyclo-[6.1.0]-nonane from either cyclohexene or cyclooxtene led to increased yields of from 61 to 82%. Also, it has been recently reported that zinc dust itself works quite well in dimethoxyethane solvent (36). In addition, a simulated but highly reactive Simmons-Smith reagent can be prepared from diethyl zinc (37). If, as determined in Phase 1 of our proposed research (Section 4), it is deemed more advantageous to utilize dialkyl-substituted cyclopropyl functionality, a synthetic route to these derivatives has also been reported (38). It involves the coupling of lithium dialkylcopper with alkyl geminal dihalides.



The geminal-dibromo cyclopropane precursor are conveniently prepared by the addition of dibromocarbene into the double bond of an olefin (39,40).



G.1.2 - Promising Types of New Molecules

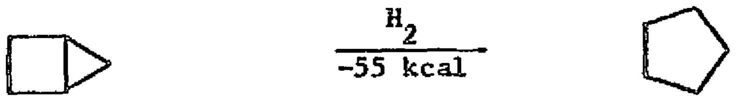
The classes of exotic fuels recommended for initial examination have been selected from the more recently reported advances in synthetic organic chemistry. We have made a preliminary survey of the literature and have outlined below several classes of exotic chemicals which may possess the desired fuel characteristics. These potential fuels are classified into the following five general categories:

- Highly strained molecules
- Dewer benzenes
- Adamantanes
- Spiro derivatives
- Clathrate derivatives

It is to be emphasized that the compounds whose syntheses are described below are only illustrative examples of the types of molecules of each of the five classes listed above. The list of compounds cited is not intended to be either all inclusive or exclusive. The specific compounds listed, however, would provide the starting point for the preliminary evaluation of the most suitable derivative of each class.

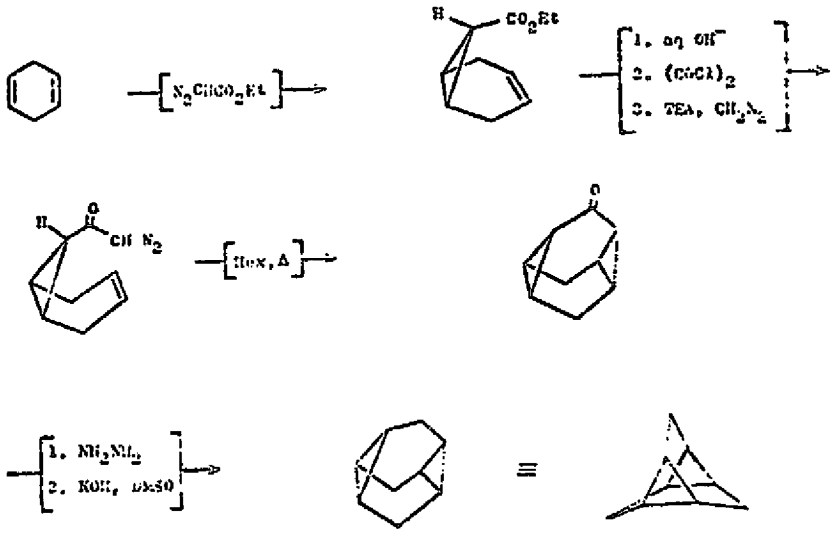
G.1.2.1 - Highly Strained Molecules

The rational for including members of the title class for consideration rests upon the large amount of energy released when they are combusted. For example, when the highly strained molecule, bicyclopentane, was first prepared, its hydrogenation to cyclopentane resulted in the liberation of 55 kcal per mole of H_2. This represented the highest heat of hydrogenation measured until that time (41).



Recent advances in synthetic organic chemistry have led to the formation of other, and more highly strained molecules. Listed in Table G.3. are twelve candidate fuels which we feel show promise.

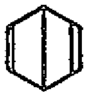
Asteranes are systems in which the cyclohexane rings are rigidly held in their boat conformational forms in a three-dimensional network. The high strain energy of this system is therefore attributable to two factors, (1) the higher energy of the boat form as compared to the chair form of cyclohexane, and (2) the strain of the ring system over which the cyclohexane rings are bound. The synthesis of the simplest member of this series, tri-asterane, has been described (42) and is summarized below.



Tri-Asterane

G.1.2.2 - Dewer-Benzenes

It is interesting to note that the planar Dewer structure for benzene, A, was postulated nearly one-hundred years ago. Until ten years ago, however, no compound of this general class had ever been isolated. Recently, the advances in synthetic organic chemistry have indeed led to the formation of isolable derivatives of bicyclo-[2.2.0]-hexa-2,5-diene, B (53).

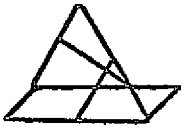


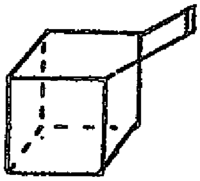
A

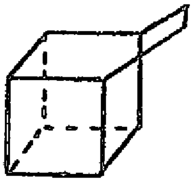
B

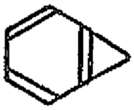
Table C.3

Strained Hydrocarbons


Ref. 42


Ref. 43

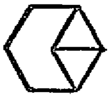

Ref. 43

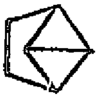

Ref. 44

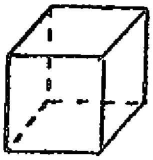

Ref. 45

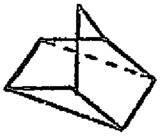

Ref. 46

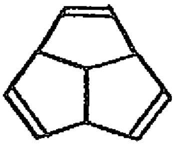

Ref. 47


Ref. 48


Ref. 49

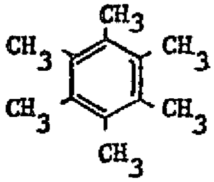

Ref. 50


Ref. 51


Ref. 52

Interest in this general class of compounds is dictated by two considerations. First, the bicyclo- 2.2.0 -hexa-2,5-diene molecule is very highly strained (54), and may therefore possess a high heat of combustion. Secondly, in lieu of corroborative literature data, it is to be expected that poly-alkyl substituted derivatives of B (most are liquids) should exhibit high densities by consideration of the reported densities of analogous benzene derivatives.

$\rho = 0.8787$



$\rho = 1.072$

While Dewer benzene itself has recently been prepared (54), it is unstable with a half-life of 2 days at room temperature. Included in Table G.4 are the specific derivatives of Dewer benzene proposed for evaluation. The references for their preparation have been noted.

G.1.2.3 - Adamantanes

The covalent linking of carbon atoms in a tetrahedral fashion in space leads to the most compact allotropic form of carbon, the diamond. The simplest hydrocarbon based on the diamonoid structure is adamantane, which accordingly exhibits a high density, $\rho = 1.07$. However, adamantane itself is strain free (58).

The most promising adamantane derivatives are shown in Table G.5. A typical synthesis, only one of those we would evaluate, is shown below.

Diamantane (Congressane)

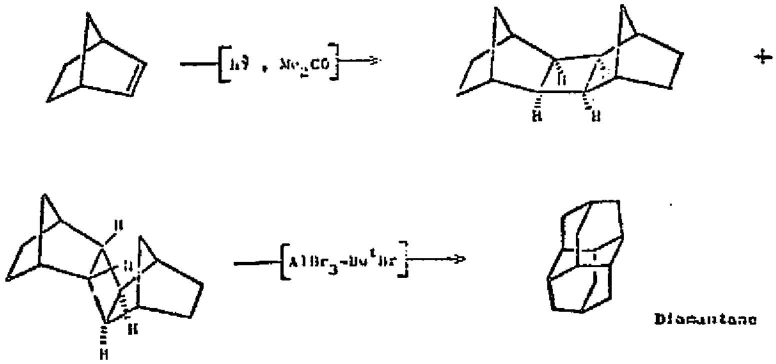
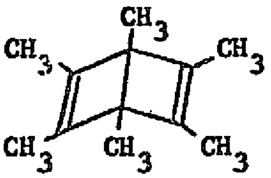


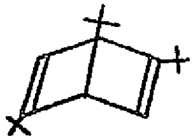
Table G.4

Dewer Benzenes

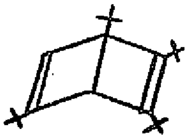


(Comm. Avail.)

(Ref. 56)



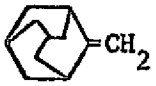
(Ref. 55)



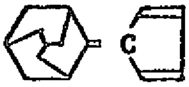
(Ref. 57)

Table G.5

Novel Adamantane Analogs



(Ref. 59)

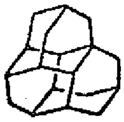


(Ref. 60)

(Ref. 60)

(Ref. 61)

(Ref. 62)



(Ref. 63)

(Ref. 64)

(Ref. 65)

(Ref. 66)

(Ref. 67)

(Ref. 68)

(Ref. 69)

G.1.3.4 - Spiro Derivatives

The inclusion of a spiro carbon atom into hydrocarbons leads to an increase in strain energy. For example, Kozina has experimentally determined a value of 97.2 kcal/mole as the incremental heat of combustion per mole for the introduction of the quaternary carbon atom (70). In addition, the density of spiro hydrocarbons is greater than their open chain homologous as illustrated below (C_{10-12} hydrocarbons). In general, the fewer members to the ring, the better for the energetics (i.e., 3 membered rings are better than 4 membered).

Structure	Specific Gravity
	0.9193
n-$C_{10}H_{22}$	0.7300
	0.9285
n-$C_{11}H_{24}$	0.7402
	0.9278
n-$C_{12}H_{26}$	0.7487

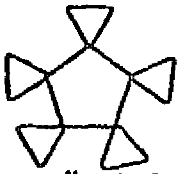
A selected list of interesting and novel spiro analogs reported in the recent literature are included in Table G.6.

G.1.2.5 - Clathrate Type Compounds

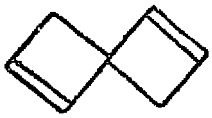
The intriguing possibility that an increase in density and volumetric heat of combustion may be observed by the inclusion of small molecules into the cage structure of a larger molecule has led us to propose an investigation directed at this approach. A preliminary review of the literature has turned up one example of the "bird-cage" inclusion type. This is cyclohexane sandwiched between bridged aromatic rings (78). Three areas are promising:

Table G.6

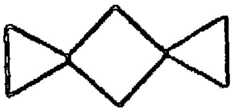
Novel Spiro Analogs


("Rotane"; Ref. 71)

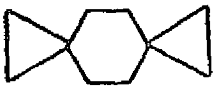

(Ref. 76)


(Ref. 72)


(Ref. 77)

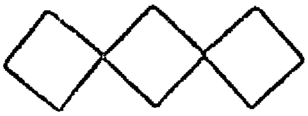

(Ref. 73)


(Ref. 75b)


(Ref. 74)

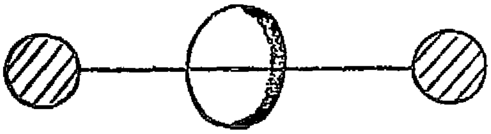

(Ref. 77a,b)


(Ref. 75)


(Ref. 75b)

- "Catenanes"

- "Hooplanes"



- "Bird-Cage" Inclusion Compounds

It is to be understood that while derivatives of the first two classes above have been formed, they are of a very complex natura and are not suitable as candidate missile fuels. Also, derivatives of the third class listed above are not known. Synthesis routes and structural proofs would have to be developed.

G.2 Shale Rock is an Alternate Source of a Hydrocarbon Fuel

The world's largest deposits of oil shale which are sufficiently rich in organic matter to warrant development are located in the United States. The oil shale strata of the Green River Formation in Colorado, Utah, and Wyoming covers about 16,000 square miles. More than 1.5 trillion barrels of oil could be obtained from the shale by destructive distillation of those deposits holding fifteen gallons of oil per ton of shale rock (79 - 81). This ultimate potential must be distinguished from the current capability or that capability which will be available in the next few decades. The capability of the United States has been estimated as being 54 G (billion) barrels in one study (82), and 77 G barrels in an Exxon study (83).

The largest potential usage in the United States is for gasoline and jet fuels, as pointed out in two separate Exxon studies (83, 84). Some of these jet fuels are alternatives to the kerosene fuel being used as the reference fuel for this study, as will be shown presently. By-products from shale oil production include ammonia, sulfur, and coke, while asphalts, waxes, and detergents will also be available from refining operations. Organic chemicals are also possibilities (85).

The destructive distillation processes used to prepare synthetic crude oil from shale rock include direct above-ground retorting, indirect above-ground retorting, and in-situ retorting of the shale in place. The technical feasibility of the underground retorting of shale rock by in-situ methods has not been proven, because of the shale's low porosity, low permeability, and toughness. Above-ground retorting methods have been successfully demonstrated in numerous retorts, including commercial apparatus in other countries.

The oil yield varies from formation to formation and within the same deposit. A representative sample of Colorado shale oil might contain 1.6 to 2.2 percent nitrogen, 0.7 to 0.8 percent sulfur, and 1.5 to 2.0 percent oxygen by weight. The crude oil typically has an atomic H/C ratio of 1.6 to 1.65, an API gravity of 20 (spec. grav. = 0.93), and a pour point between 80 and 90°F (79). A typical crude shale oil composition is shown in Table G-7 as function of boiling range. The nonhydrocarbon compounds could be extracted with acid to reduce the nitrogen and sulfur content, but this would represent an unacceptable yield loss because of their large number. Upgrading of the crude oil or its distillation fractions is therefore carried out by hydrodenitrogenation and other secondary (refining) processing techniques to avoid losses.

In one of the Exxon studies mentioned earlier (84), an intensive investigation into refinery operations resulted in a preference for the processing sequence shown in Figures G.1 and G.3. It features mild thermal cracking of long-chain normal paraffins at the mine site to reduce the pour point, and fractionation combined with recycling to eliminate a portion of the heavy ends. The major products are gasoline, jet fuel, diesel fuel, and heating oil, which

TABLE G.7

COMPOSITION OF CRUDE COLORADO SHALE OIL (86)

Boiling Range, °C	0-10 190-270	10-20 270-310	20-30 310-350	30-40 350-380	40-50 380-410	0-50 190-410	50-100 410-Residue	0-100 Whole Crude
Hydrocarbons, wt.%								
Straight chain paraffins	8	8	8	8	10	8	3	6
Isoparaffins and naphthenes	7	6	4	3	3	5	5	5
Straight chain olefins	10	9	11	11	9	10	3	6
Branched olefins any cycloolefins	31	25	19	14	12	20	5	12
Monocyclic aromatics	6	8	6	8	5	6	2	4
Polycyclic aromatics	9	9	9	10	7	9	2	6
Total Hydrocarbons	71	65	57	52	46	58	20	39
Nonhydrocarbons, wt.%								
Nitrogen compounds	12	14	21	26	33	21	51	36
Sulfur compounds	5	4	4	5	5	5	7	6
Oxygen compounds	12	17	18	17	16	16	22	19
Total heteroatom compounds	29	35	43	48	54	42	80	61

will probably be used initially as blends with conventional petroleum products. The conceptual design was based on a number of factors, the most important of which were availability of technology, business considerations including economics, and transportation and distribution.

Further work in the above-mentioned Exxon analysis dealt with experimental aspects of developing jet fuels from crude shale oil (87). The effects of hydroprocessing were noted on a number of shale oil properties. Some of hydrogenating shale oil from both paraho and Tosco retorts is shown in Table G.8, including the effects on the nitrogen and sulfur content as well as a distribution of compound types from mass spectrometry. These hydrogenation products were analyzed in the present study to determine their performance in and applicability to SSTO vehicles. Certain assumptions were made as to the physical properties of the various compound types, based on information from reference (88). The assumptions and the results of the analysis are given in Table G.9, along with the properties of the reference fuel, kerosene.

It is readily seen that the shale-oil derived jet fuels are similar in most respects to kerosene; note, especially that the values for density-impulse and for merit index are approximately equal. This suggests that shale oil can be refined to products which can serve as substitutes for the base fuel, kerosene. However, since the nitrogen content of the hydroprocessed shale oil is still above the level found in ordinary petroleum-based fuels, it will be important to study the effect of different nitrogen compound types upon the thermal stability and upon the storage stability of shale derived fuels. Especially important are the pyridine and pyrrole types of nitrogen compounds which have been shown to cause rapid gum formation under oxidizing conditions in crude shale oil (89).

FIGURE G-1

Route Selected to Process Shale Oil at the Mine Site (84)

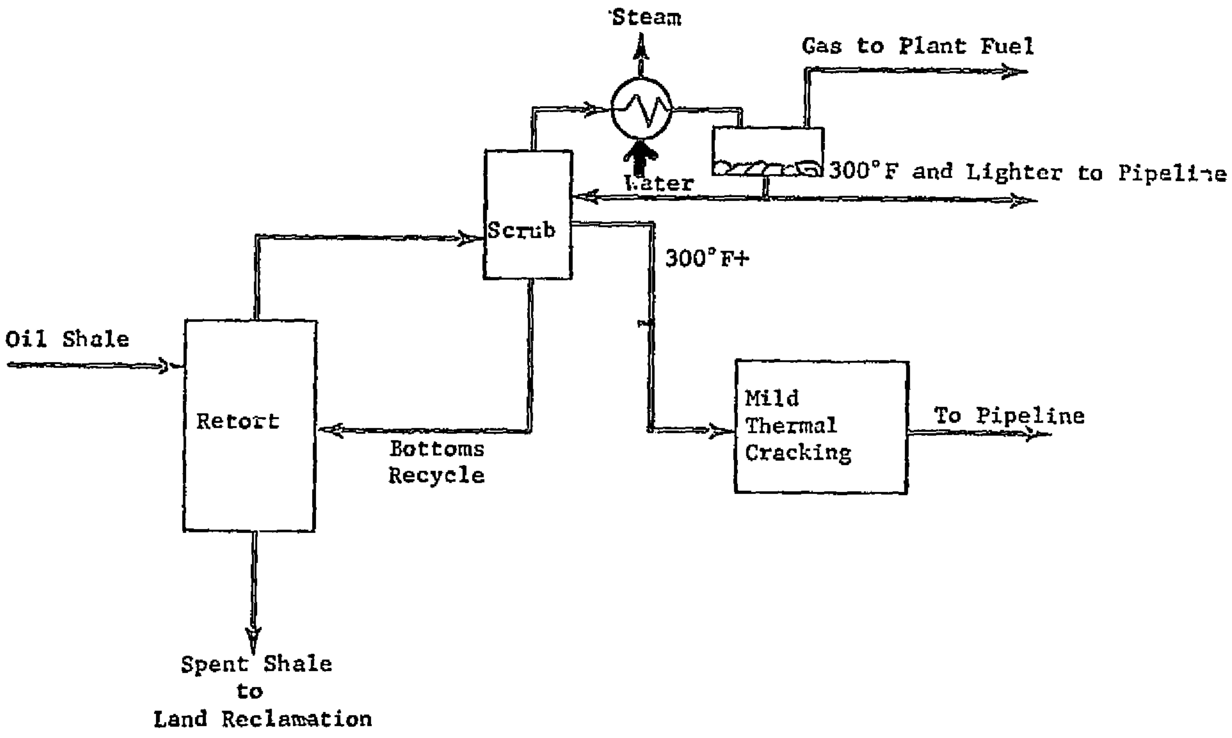


FIGURE G-2

Refining of Shale Oil to Finished Products at Conventional Refinery (84)

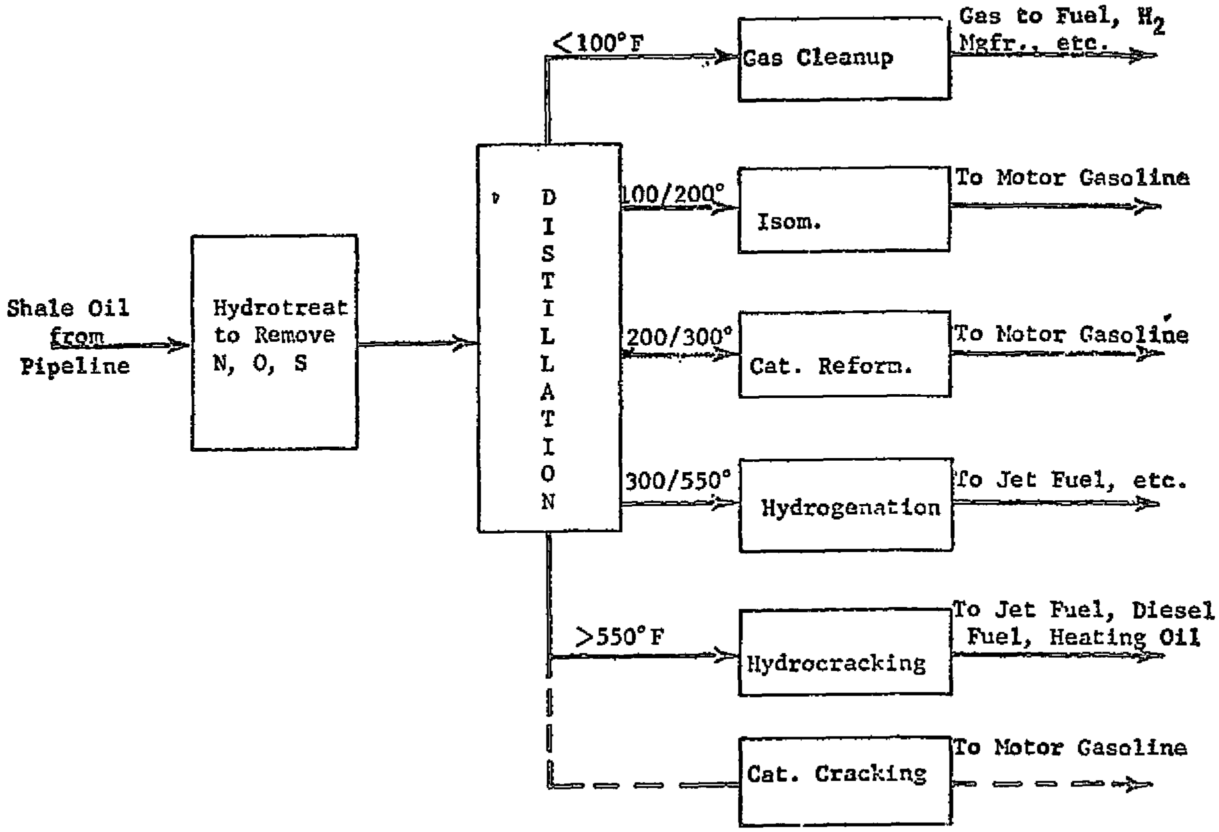


TABLE G-8

PROPERTIES OF HYDROTREATED SHALE OILS (87)

	TOSCO SHALE OIL			PARAHO SHALE OIL		
	Whole Shale Oil	Kerosene Fraction	Normal-Severity Hydrogenation Product (b)	Whole Shale Oil	Kerosene Fraction	Low-Severity Hydrogenation Product (b)
Density (g/cc)	0.9279	0.8247	0.7814	0.9383	0.8241	0.8124
Paraffins	3.7	25.8	51.8	---	25.8	51.8
Monocycloparaffins	0.0	28.3	29.7	---	28.3	29.7
Dicycloparaffins	34.7	9.3	8.6	---	9.3	8.6
Tricycloparaffins	19.7	6.4	2.1	---	6.4	2.1
Total Saturates	58.1	69.8	92.2	---	69.8	92.2
Alkylbenzenes	11.0	17.0	5.7	---	17.0	5.7
Indans	10.5	7.9	1.8	---	7.9	1.8
Indenes	7.7	2.7	0.0	---	2.7	0.0
Naphthalenes	12.2	2.3	0.0	---	2.3	0.0
Total Aromatics	41.4	29.9	7.5	---	29.9	7.5
Sulfur, wt. percent	0.6700	0.7600	0.0036	0.71	0.8200	0.0002
Nitrogen, wt. percent	1.8500	0.8700	0.0020	2.00	0.3700	0.1700

(a) Normal severity hydrotreatment of kerosene fraction at 700°F (271°C), 1500 psig, and 1.0 liquid hourly space velocity (LHSV).

(b) Low severity hydrotreatment of kerosene fraction at 700°F, 800 psig, and 1.0 LHSV.

TABLE G-9

PERFORMANCE PROPERTIES OF HYDROTREATED SHALE OIL FRACTIONS

	Tosco Shale Oil Fraction (a)	Paraho Shale Oil Fraction (a)	Kerosene (RP-1)
Fuel Density (g/cc)	0.7814	0.8124	0.80
Atomic H/C Ratio	2.07	1.91	2.0
Heat of Combustion			
(BTU/lb)	18,800	18,600	18,700
(BTU/gal)	122,500	126,000	125,000
Heat of Formation (kcal/gram atom Carbon)	-6.66	-5.48	-6.0
Stoichiometric (O/F)w	2.31	2.24	2.28
Propellent Density (g/cc)	1.001	1.014	1.009
Specific Impulse (sec)	$\approx$ 299.5	$\approx$296.9	296.4
Density Impulse, $\bar{\rho}\ I_{sp}{}^{3}$ (lb·sec/ft^3)	$(62.4)(1.001)(I_{sp})$ $\approx 1.87 \times 10^4$	$(1.014)(62.4)(I_{sp})$ $\approx 1.88 \times 10^4$	1.88×10^4
Merit Index, $\bar{\rho}\ I_{sp}{}^{3}$ (lb·sec^3/ft^3)	$(\bar{\rho}\ I_{sp}) \times I_{sp}{}^2$ $\approx 1.68 \times 10^9$	$(\bar{\rho}\ I_{sp}) \times I_{sp}{}^2$ $\approx 1.66 \times 10^9$	1.65×10^9

(a) Refer to hydrogenated products shown in Table G-8.

Assumptions:

1) Average paraffin molecular wt. = 230
2) Average no. alkyl chains/aromatic molecule = 4.0
3) Average no. carbons/alkyl chain for aromatics = 3.5
4) Average no. alkyl/carbons/aromatic molecule = 14.0

Analysis of a Hydrotreated Kerosene Fractions from Paraho & Tosco Shale Oil

I. Mild H_2 of Paraho

Table 4-2 in "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Cruce Oils," Phase 2, AFAPL-TR-75-10, Volume II, ER&E, May, 1976, page 70 - gives composition by mass spec. as:

	Product 111 (wt.%)
Paraffins	47.5
Monocycloparaffins	21.0
Pi	5.5
Tri	2.0
Total Paraffins	76.0
Alkylbenzenes	11.5
Indans	8.9
Indenes	0.2
Naphthalenes	2.9
Total Aromatics	23.5
Grand Total	99.5

ASSUMPTIONS

Alkyl Subst./Arom. Molecule = 4.1
Carbons/Alkyl Subst. = 2.4
Alkyl Carbons/Arom. Molecule = 13.94

This information is useful in making Khurasch estimate of the ΔH_c of each group (aromatics):

Alkylbenzenes:

Analysis of a Hydrotreated Kerosene Fractions from Paraho and Tosco Shale Oil

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This information is useful in making a Khurasch estimate of the ΔH_c of each group (aromatics):

Alkylbenzenes:

$(CH_2)_{13}$ $C_{20}H_{34}$

#el. = 20.4 + 34 = 114

4 arom - alkyl

$\Delta H_c = (26.05)(114) + (4)(-3.5) = 2955.7$

Corrected to gas H_2O product = 2776.9

ESTIMATE OF ΔH_C (SEE APPENDIX A)

TABLE 6-10 SHALE OIL-DERIVIED FUEL (LOW-SEVERITY H_2 OF KEROSENE)

Compound Type	Wt. %	Mol. Forms	Mol. Wt.	% C	Contr. to C.	ΔH_C/mole	Moles	Contr. of ΔH_C
Sat. & Paraffins	76.0	$C_{16.4}H_{32.6}$	230.000	85.71	65.140	2388.0	0.33	789.08
Alkylbenzenes	11.5	$C_{20}H_{34}$	274.494	87.51	10.064	2776.9	0.04	116.34
Indanes	8.9	$C_{23}H_{38}$	314.559	87.82	7.816	3172.6	0.02	89.76
Indenes	0.2	$C_{23}H_{36}$	312.543	88.39	0.177	3131.0	0.006	2.00
Naphthalenes	2.9	$C_{24}H_{36}$	324.554	88.82	2.576	3235.2	0.009	28.91
Totals	99.5				85.773			1026.09

$$r = \frac{(99.5 - 85.773)/1.00797}{85.793/12.01115} = 1.907$$

$CH_{1.91}$
Emp. MW = 13.933

$$\frac{\Delta H_C}{n} = \left(\frac{1026.09}{99.5}\right)(13.933) = 143.688$$

$$\frac{\Delta H_f}{n} = 143.688 - 94.0518 - \frac{1.907}{2}(57.7979) = 5.48$$

$$\Delta H_c \ \frac{(1026.90)(1.8)}{(0.0995)} = 18{,}560 \text{ BTU/lb}$$

$\rho = 0.8124$

Then, $\Delta H_c = (0.8124)(8.345375)(18562.43) = 125{,}900$ BTU/gal

Indanes:

$C_nH_{2n}-8$ Nuclear C = 9

$C_{23}H_{38}$

$\Delta H_c = (26.05)(23.4 + 38) + (4)(-3.5) = 3372.5$

Corrected = 3172.6

Indenes:

$C_nH_{2n}-10$ Nuclear C = 9 $C_{23}H_{36}$

$\Delta H_c = (26.05)(23.4 + 36) + (4)(-3.5) - 3320.4$

Corrected = 313.05

Naphthalenes:

$C_nH_{2n}-12$ $C_{24}H_{36}$

$\Delta H_c = (26.05)(24.4 + 36) + (4)(-3.5) = 3424.6$

Corrected = 3235.2

For specific impulse; $r = 1.907$

$\Delta H_{f/n} = 5.48$

$I_{sp} = 296.9$ sec

Assume:

$m - 2.243$

$\bar{\rho} = 1.014$

$\bar{\rho}\, I_{sp} = 1.88 \times 10^4$

$\bar{\rho}\, I_{sp}{}^3 = 1.66 \times 10^9$

Conclusions:

A mild hydrogenation of a kerosene range distillate from shale oil yields an acceptable fuel which is quite similar in performance to kerosene. Therefore, shale rock provides us with an alternate source of supplies of fuels having performance similar to kerosene. (But probably more Nitrogen). (0.17 wt.%).

A similar analysis of severely hydrotreated fuel was made to give the data shown in the main body of the report.

G Carbon-Slurried Fuels

Carbon black and graphite slurries can be used to get unique high-energy fuels by using existing high-density fuels to obtain high volumetric heat contents. These slurries have improved freezing point, improved low-temperature viscosity characteristics, and can be formulated in existing low-cost liquid fuels. The major disadvantage to slurring with carbon is a decrease in the specific impulse as the weight percent carbon is increased, in spite of increased propellant density. This effect is large enough to result in decreases in the merit index from the value for the base fuel as the carbon loading is increased.

As an example, Table G-11 shows the effects of slurrying the reference fuel kerosene (RP-1) with carbon. Both a high and a low estimate are included, corresponding to the addition of graphite and carbon black, respectively.

A similar analysis for the addition of carbon to candidate fuel B-4 is shown in Table G-12.

TABLE G-11

ESTIMATED PARAMETERS FOR EVALUATING SLURRIES OF KEROSENE WITH CARBON

Weight Percent Carbon	Form of Carbon	Atomic H/C Ratio	$\Delta H^{\circ}_{f,298}/n$ $\frac{kcal}{gram\ atom\ C}$	Fuel Density (g/cc)	$(O/F)_w$	Propellant Density, $\bar{\rho}$ (g/cc)	Estimated* Specific Impulse, I_{sp} (sec)	Merit Index* $\bar{\rho}\ I_{sp}^3 \times 10^{-9}$ $\frac{lb \cdot sec^3}{ft^3}$
0	---	2.00	-6.0	0.80	2.28	1.01	296.4	1.65
25	Graphite	1.44	-4.29	0.957	2.04	1.07	288.5	1.61
25	Carbon Black	1.44	-5.04	0.922	2.04	1.06	287.1	1.56
50	Graphite	0.923	-2.73	1.19	1.81	1.16	277.0	1.54
50	Carbon Black	0.923	-4.17	1.09	1.81	1.12	274.0	1.44
65	Graphite	0.631	-1.86	1.39	1.66	1.22	269.6	1.50
65	Carbon Black	0.631	-3.68	1.22	1.66	1.17	265.3	1.36
80	Graphite	0.353	-1.02	1.68	1.52	1.31	261.8	1.46
80	Carbon Black	0.353	-3.22	1.39	1.52	1.23	256.1	1.29

---

(1) Specific impulse values were calculated using an equation presented in reference (92) which do not agree exactly with similar values calculated by NASA-LeRC. They should be used only to observe general trend in the data.

TABLE G-12

CARBON SLURRIED WITH B-4 (1)

Wt. % Carbon	$-\Delta H_c$ (BTU/gal)	H/C Ratio	$\frac{\Delta H_f}{n}$	Estimated I_{sp}	Propellant Density	$\bar{\rho}\, I_{sp}^3$ X 10^{-9}
0	148,700	1.20	+3.43	296.3 (296.11)	1.08	1.76 (1.75)
25	164,200	0.8779	+2.44	(286.52)	1.146	(1.68)
50	185,900	0.5712	+1.67	(275.72)	1.223	(1.60)
65	203,700	0.3942	+1.17	(268.77)	1.280	(1.55)
80	227,100	0.2221	+0.67	(261.44)	1.347	(1.50)

---

(1) All values are highest estimates with $\rho_c = 2.32$

$-\Delta H_{clc} = 14,100$ B/#

G.4 - Analysis of Additives or Modifications to Improve Viscosity and Thermal Stability

G.4 - Viscosity Modifications

Many of the factors affecting the viscosity of certain types of liquids are not understood. This resistance to flow arises because the liquid molecules exert attractive and repulsive short range forces on one another (93). Indeed, the viscosities of several monatomic liquids can be calculated quite accurately simply by knowing the size of the atom. Unfortunately, the application of this procedure to more complex liquid species such as high density jet fuels is presently out of the question. (94).

However, considerable progress has been made in understanding the factors that affect the viscosity of liquids as well as viscosity blending techniques which can reduce the viscosity of existing and potential fuels. Recently, there has been a rekindling of interest in the macromolecular structure of liquids. The high density of Shelldyne-H can be attributed in part to the fact that its molecules exhibit a degree of regularity and order in their liquid molecular arrangement.

A number of workers have made observations and developed predictive relations for the variation of viscosity with molecular composition. It is well known for example that the viscosities of various isomeric organic molecules can be substantially different when measured at the same temperature. (95) Normal esters possess a greater viscosity than those with branched carbon chains. Viscosity can be increased by the substution of an electron attracting atom or group such as a halogen or NO_2. In aromatic compounds, viscosity is influenced by the nature and position of the substituent with the trans isomer generally possessing a higher viscosity than the cis.

Molecular association of liquids has been correlated with viscosity. The fluidity, $\phi = 1/\eta$, is almost a linear function of temperature for many molecules. The ϕ-t lines are parallel for nonassociated homologous series. For associated liquids, the ϕ-t graphs are curved. Thus, $d\phi/dt$ is characteristic of a given homologous series of normal liquids, the length of the intercept of ϕ on the t axis giving the effect of one CH_2 group.

At temperatures of equal fluidities, the temperature increments for CH_2 and for various other atoms and groups have the same value in a given series. This does not hold for associated liquids.

A number of predictive viscosity/structure relationships have been proposed. (95)

The relation of Dunston and Thole is

$$\log \eta = aM + b, \qquad (1)$$

where M is the molecular weight, a is a general constant and b is a constant characteristic of the given homologous series. The values of $\Delta \log (\eta \times 10^5)$ between successive CH_2 groups for a class of compounds are practically constant at a given temperature. The increments are approximately additive.

Souders (96) developed a similar relationship,

$$\log (\log \eta) = m\rho - 2.9$$

where η = viscosity in millipoises
ρ = density in g/ml
M = a constant, characteristic of each liquid.

The product of M and the molecular weight is termed the viscosity constitutional constant. This may be found by summing general atomic and structural constants, some of which are presented below

CH_3	55.6
H	2.7
C	50.2
N	37.0
five carbon ring	-24.0
six carbon ring	-21.0

Other generalizations have been established. Some of these are

- In a homologous series, the addition of CH_2 increases the viscosity, but at a diminishing rate.
- In two simply related series of corresponding compounds, the one with the higher molecular weight has the greater viscosity.
- The viscosity of an iso compound is less than that of the normal compound.
- Ring closure increases the viscosity.
- Formation of a double bond linkage from a single one slightly decreases the viscosity.

The problem of predicting a blended viscosity in liquid hydrocarbon systems has existed for many years, yet there is at present no "universally" accepted method for calculating mixture viscosities. A number of different methods have been described (97-99), none of these have been completely satisfactory for predicting the viscosity of a blended fuel.

One of the major difficulties in developing a viscosity blending method is that the specific factors which influence viscosity blending have not been clearly defined for most systems. Consequently, most of the methods are simply viscosity averaging methods, which require the viscosities of the components at the desired temperature and weighting factors (volume, weight or mole fractions). Only a few of the methods take into account differences in the behavior of different components. For example, the Wright method incorporates the slope of the viscosity--temperature curve, which is characteristic of the nature of the component, in the averaging procedure. A further difficulty is that binary systems of defined hydrocarbons, e.g., toluene/n-octane, benzene/cyclohexane, frequently show maxima or minima in the viscosity higher (or lower) than the viscosity of either of the components. None of the common methods can predict these types of behavior. A series of several of the most common viscosity blending approaches is presented below.

The most common viscosity averaging methods are of the form

$$f(\nu_{blend}) = \sum_{i} F_i f(\nu_i) \qquad (1)$$

where $f(\nu)$ is some function of the viscosity and F_i is a weighting factor (volume, weight or mole fraction). The various methods generally differ in the specific form of the viscosity function.

- ASTM Method - One of the earliest methods was suggested by the ASTM(100). This method utilizes the standard ASTM viscosity-temperature chart ordinate for $f(\nu)$; and takes the form:

$$\log \log \; (\nu_{blend} + k) = \sum_{i} V_i \; \log \log \; (\nu_i + k) \qquad (2)$$

where V_i is the volume fraction and k is a variable whose value depends on the magnitude of the viscosity, decreasing in a stepwise fashion from 0.75 at $\nu = 0.5$cs to 0.6 at $\nu \geq 1.5$cs.

The ASTM method is generally quite satisfactory for predicting the viscosity of blends of similar molecules. However, large deviations between calculated and observed viscosities have been noted for systems formulated when light molecular weight components are mixed with heavy molecular weight fractions. Generally, the calculated blend viscosity is considerably lower than the observed blend viscosity.

- Sparks - La Mantia Method - In order to overcome the short comings noted above, experimental data were taken on a series of low molecular weight/high molecular weight hydrocarbon components. A rather specific correlation was developed based on the results obtained.

$$\log(\log \nu_{blend} + 1.3) = \sum_i V_i \log(\log \nu_i + 1.3) \qquad (3)$$

- Kendall - Monroe Method - An entirely different form of the viscosity function and averaging method was found to be highly satisfactory by the API for mixtures of specific hydrocarbons. In this method, the "log-log" function is replaced by a cube-root function. A further difference is the use of absolute rather than kinematic viscosities.

$$\mu_{blend} = (\sum_i x_i \mu_i^{1/3})^3 \qquad (4)$$

where x_i is the mole fraction.

The above methods do not take into account the character of the components which is most commonly manifested by differing slopes of the viscosity - temperature curves. Discussed below are two methods which have attempted to overcome this deficiency.

- Wilson Method - In the method proposed by Wilson(101), the blend viscosity is determined from specialized blending charts. Differences in component types are taken into account by using different charts, e.g., the first chart recommended by Wilson is for blends of heavy paraffinic oils with light naphthenic oils. Since charts are available for only a small number of combinations, the method is of very limited usefulness.

- Wright Method - The method developed by Wright (10), requires viscosities of the components at two temperatures. From these data, the viscosity-temperature curves of the components are plotted on ASTM paper and extrapolated to 100 and 2 cs. Two viscosity-temperature points for the blend are located on the 100 and 2 cs ordinates respectively by volume averaging the corresponding component values, and connection of these two points yields the viscosity-temperature curve for the blend. This procedure differs from the ASTM blending procedure in which the blend viscosity is obtained by volume averaging along the abscissa (at the single desired temperature).

As described above, the Wright method requires a rather cumbersome graphical solution using ASTM viscosity charts.

As a result of analyzing physical property corrections, one can make a series of broad generalizations, which should be used to guide the choice of a blending agent. The key factors are summarized below:

Favoring High Heat of Combustion (Per unit weight)

- High Hydrogen to Carbon Ratio
- Rings, especially small rings
- Strain energy, ring, and otherwise

Favoring High Density

- Condensed rings
- Double bonds
- Molecular symmetry
- Liquid crystal-like packing

Favoring Low Viscosity

- No hydrogen bonding
- Disorder, as by alkyl substitution
- Cis versus trans
- Lower molecular weight
- Iso-paraffin vs normal
- Disruption of packing - by swelling "liquid holes"

Most of the factors favor low viscosity will also help reduce melting point. While all of these factors could not be included in the same molecule, they are trend factors which should be considered.

G.4.2 - Thermal Stability Modifications

Modifications to improve the thermal stability of hydrocarbon fuels were analyzee based on Exxon Research's extensive, first hand knowledge in this area.

For a number of years, Exxon has conducted a program for the U.S. Navy to study and evaluate methods for enhancing the thermal stability of fuels of the JP-5 type. Four basic approaches were investigated:

- Removal and exclusion of molecular oxygen.
- Control of trace impurities of various types.
- Reduction of dissolved metals and control of metal surfaces.
- Use of additives.

The results and conclusions from this study are generally applicable to the thermal stability of hydrocarbon fuels and are summarized below.

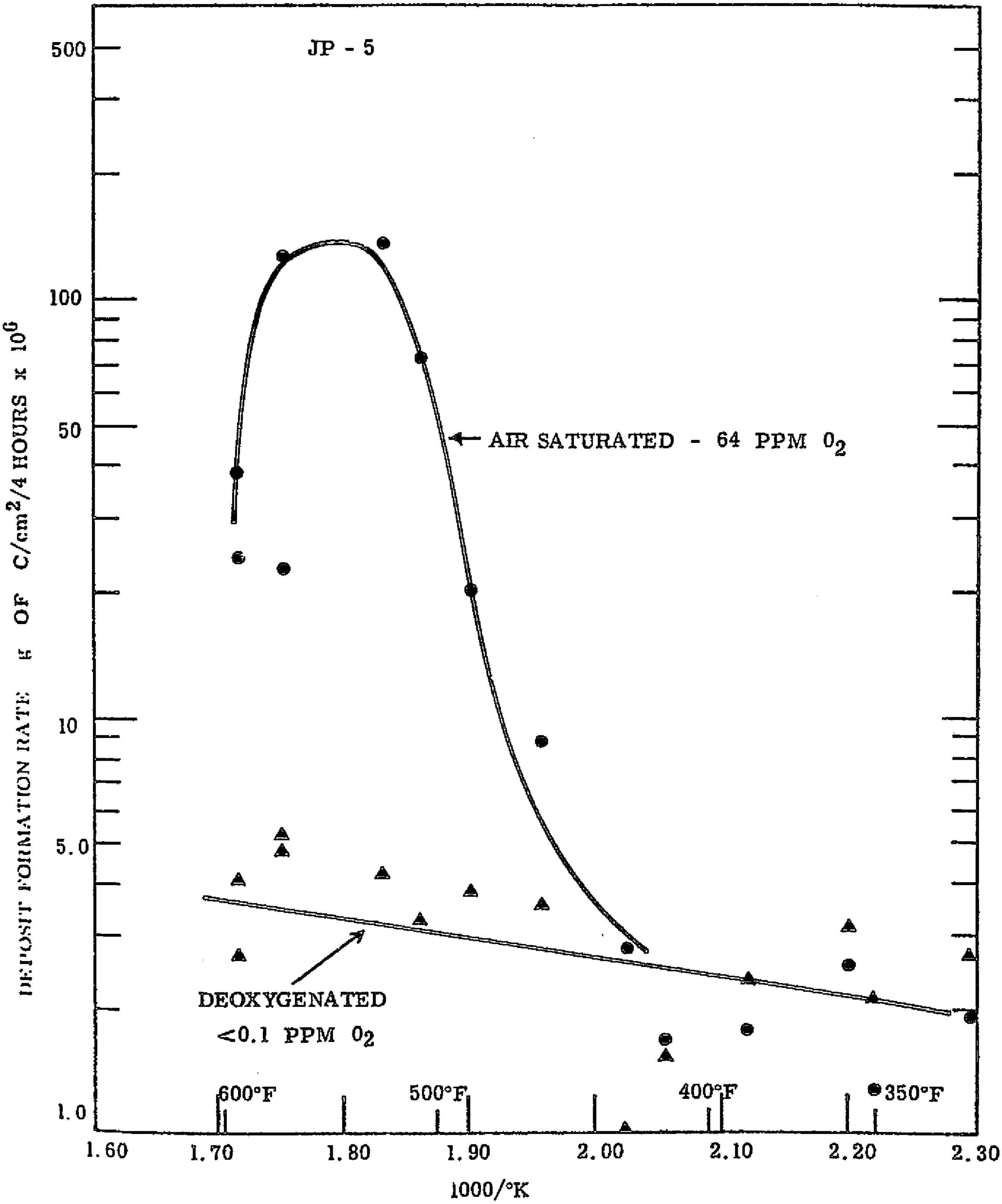
The removal of dissolved oxygen was found to be the most effective modification for enhancing fuel stability. Deposit formation under high temperature conditions, a measure of instability, was significantly reduced by removing molecular oxygen for most fuels studied (Table 26 Section II.4.4.2, Figure G-12). Both the total deposits formed and the deposit formation rates as shown by Arrhenius plots are much lower in the deoxygenated fuels.

This effect was found to be operative for most fuels studied. However, there were a few exceptions. These were fuels which contained relatively large quantities of trace impurities, especially sulfur-containing compounds. This led to a study of the effects of such trace impurities on high temperature stability of hydrocarbon fuels which is described in the following sections.

It was found that the effects of impurities varied greatly from type to type. Results indicated that trace levels of sulfur compounds can have a very strong effect on stability even in a rigorously deoxygenated fuel (i.e., less than 1 PPM). Moreover, the different classes of sulfur compounds which can be present in JP-5 fuel were found to have a markedly different effect on stability. Of the three major classes of sulfur compounds found in the parent crude oil, condensed thiophenes had no deleterious effect on stability, whereas a thiol and various sulfides markedly decreased fuel stability. Thiols are currently restricted in JP-5 (10 PPM S maximum) and if sweetening processes are used to achieve this level, then two additional classes of sulfur compounds, i.e., disulfides and possibly polysulfides, could be introduced into the fuel. Both disulfides and polysulfides were found to be extremely deleterious

Figure G-12

Arrhenius Plot - JP-5



in a deoxygenated fuel. Thus, sweetening processes will have to banned in the production of high stability fuels and hydro-catalytic processes, in all probability, used in their place. An analysis of trends in refinery jet fuel processing indicates that hydro-catalytic processes should increase in importance with time. Thus, the anticipated future trend in refinery processes is quite compatible with these results.

The effect of trace impurity nitrogen compounds was also investigated in a deoxygenated fuel at the 100 PPM N level. A wide spectrum of nitrogen compound types which are representative of those potentially present in jet fuels were evaluated. These nitrogen compound types included pyrroles, pyridines, amines, non-aromatic heterocyclics and an amide. The effect of nitrogen compound level was also investigated with both a pyrrole and a pyridine type compound. In general, nitrogen compounds were found not to be highly deleterious in a deoxygenated fuel. This lack of a strong adverse effect on stability of nitrogen compounds in a deoxygenated fuel is in contrast to their highly deleterious nature in air saturated systems. The effects of oxygen compounds were also evaluated at the 100 PPM level. Classes of organic oxygen compounds investigated included peroxides, carboxylic acids, phenols, furans, esters, alcohols and ketones.

The presence of peroxides resulted in extremely high rates of deposit formation, producing deposit formation levels equivalent to highly deleterious species such as disulfides even though present at much lower concentrations. For a given level, peroxides are among the most deleterious trace impurity compounds evaluated to date. Thus, hydrocarbon hydroperoxide formation (for example, during long periods of storage) must be prevented if the fuel is to exhibit high stability when it is deoxygenated and exposed to high temperature stress.

The effect of the presence of carboxylic acids on deposit formation varied widely with the acid employed. At the 100 PPM O level two carboxylic acids increased deposits, whereas other carboxylic acids did not. At the 10 PPM O level, which is representative of a level required to meet the present military total acidity specification, the presence of decanoic acid was still deleterious. The results indicate that the carboxylic acid content of a high stability fuel may have to be controlled.

The presence of phenolic compounds at the 100 PPM O level had relatively little effect on total deposit formation, although some increase in local deposit formation rate was observed. Even at the 1000 PPM O level the presence of dimethylphenol had little effect on total deposits. This lack of an inhibiting effect on a deoxygenated system at high temperatures is in contrast to the behavior of phenolic compounds in air saturated fuels at ambient conditions where they are employed as an additive to enhance storage stability.

The effect of furan compounds was evaluated using benzofuran and dibenzofuran, which are typical of furan compounds potentially present in jet fuel. The presence of these furan compounds in deoxygenated fuel did not increase the level of deposits which were formed. Thus, the removal of furan-type compounds will not be required for the production of high stability fuel.

Some representative esters, alcohols and ketones, were also studied at the 100 PPM O level. The naphthenic compounds, cyclohexylformate, methylcyclohexanol and methylcyclohexanone did not increase deposit formation. The aromatic and straight chain aliphatic analogs, however, were somewhat more deleterious. Thus, methylbenzoate, phenylformate, dodecyl alcohol and 5-nonanone all contributed to moderately higher deposit formation rates.

The effects of representative olefins on deposit formation were investigated using a deoxygenated pure compound blend which simulates jet fuel compositions. It was necessary to use the pure compound blend to avoid interference from other olefins, naturally occurring in the fuel. The blend consisted of 24% of n-dodecane, 24% of 2,2,5-trimethylhexane, 30% of isopropylcyclohexane and 20% of sec-butylbenzene (all percentages by weight). The olefins were added at the 2 wt. % level.

The influence of olefins on deposit formation varies with chemical structure. Aliphatic monoolefins such as 1-dodecene have little or no effect on deposit formation in deoxygenated fuel while certain alicyclic (naphthenic) and aromatic monoolefins were deleterious. Diolefins also showed varying influences depending on their structure. Aliphatic diolefins with conjugated double bonds were relatively harmless while, in the aromatic series, those with double bonds conjugated with the ring proved to be the most deleterious. Most olefins studied promoted deposit formation at temperatures below 700°F, a range where deoxygenated fuels are normally quite stable. A represenative acetylenic hydrocarbon, 1-decyne, was evaluated, also at the 2 wt. % level in the 4-compound blend. This compound was the most deleterious material studied.

Work with deoxygenated pure compound blends has been extended to determining the effect of condensed ring compounds of the type normally present in fuels. Naphthalene was chosen as being represenative of aromatic compounds with condensed six membered rings and decalin was chosen as being representative of a condensed ring naphthene. Both compounds were evaluated at the 5 wt. % level in a synthetic fuel blend whose overall composition was held at 50% total paraffins, 30% total naphthenes and 20% total aromatics. The presence of either decalin or naphthalene reduced deposits relative to the blend containing no condensed ring compound. However, the simultaneous presence of decalin and naphthalene increased deposits relative to the blends containing either decalin or naphthalene alone. This work was extended to indan and tetralin, two other condensed ring-systems common in jet fuels. In this case, no deleterious interactions were observed. Indan and tetralin, alone or in conjunction, showed no tendency to promote deposit formation. In a rigorously deoxygenated system, the major compound classes found in jet fuel (normal paraffins, branched paraffins, naphthenes and aromatics) are all quite stable at temperatures below 1,000°F.

The effect of pressure, an important design parameter, has also been studied. Results show that the effect of total pressure on the deposit formation process is complex. However, results have shown that deposit formation rates at 1000 psig are equivalent to, or less than, rates at 250 psig with deoxygenated fuels (both fresh and aged) at temperatures up to 1000°F. Thus, the higher pressures required by an advanced fuel system are not deleterious toward fuel stability in a deoxygenated system.

Dissolved Metals

The effects of metal surfaces on deposit formation in deoxygenated JP-5 was investigated. Tubes made of Inconel, titanium, copper-nickel, aluminum and a titanium-aluminum-vanadium alloy were substituted for the stainless steel 304 tube which was employed in all previous runs in the Advanced Fuel Unit. The usual temperature zones from 700-1000°F were employed in all cases except with aluminum where lower temperatures were used. Significantly higher deposits were found with all the new materials except the Ti-3Al-2.5 V alloy. Use of this material resulted in about 10% lower deposits than with the SS-304 tube (104). These effects are quite different from those obtained in oxygenated systems (105). In oxygenated systems, copper was found to be quite deleterious while titanium, aluminum and the Ti-3Al-2.5 V alloy were all equivalent in their tendencies to promote deposit formation.

It has been widely shown in the literature that soluble metals can catalyze reactions involved in autoxidation (107-109). Soluble transition metals compounds such as metal phthalocyanines, stearates, and naphthenates catalyze autoxidation reactions in kerosine. Insoluble metal oxides such as CuO, MnO_2, Cr_2O_3 and NiO catalyze the liquid phase oxidation of olefins such as cyclohexene. The mechanism of metal catalysis is complex. It may play a primary role by initiating autoxidation reactions or it may play a role in secondary processes by decomposing hydroperoxides formed from other initiators (107-109). The theory has been advanced that all hydrocarbon autoxidations are trace metal catalyzed (108) In our studies with deoxygenated systems, it appears that dissolved metals have much less effect (111). Some additional deposits are encountered with dissolved copper and iron, but not nearly to the extent of that encountered in air saturated systems.

Additives

Fuel additives of the antioxidant type are often added to stabilize fuels. It might be expected that such addition, while effective in oxygen saturated systems, would be of little or no value in promoting fuel stability in systems where the oxygen has been removed. Our work (12) not only established this, but also showed that some additives are actually deleterious at high temperatures (104). The effects varied greatly with the chemical structure of the antioxidant. In addition to antioxidants, other additives are employed (for example, benzotriazole as a metal deactivator) to enhance thermal stability.

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