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INVESTIGATION OF SOURCES, PROPERTIES, AND PREPARATION OF DISTILLATE TEST FUELS

by

John N. Bowden and Jimell Erwin

SOUTHWEST RESEARCH INSTITUTE

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
NASA Contract NAS3-22783

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FOREWORD

The fuel matrix described in this report was developed under Contract NAS3-22783 for the National Aeronautics and Space Administration, Lewis Research Center. In this work, the blending correlations for viscosity, freezing point, and flash point are from the Chevron Research Company and were used with their permission. They were made available by the courtesy of Mr. R. J. O'Donnell. The many suggestions on blending and sources for basestocks from Norman R. Sefer have contributed substantially in advancing this project.

The following sources have provided hydrocracked or other kerosenes from internal streams which were central to the success of the blending work:

Sigmor Three Rivers Refinery	Mr. J. F. Olenick	Mirando kerosene
Sohio Petroleum	Mr. W. T. Wottring	HC kerosene
Tesoro-Alaska Petroleum	Mr. Mark Necessary	HC jet fuel

The NASA-Lewis Research Center Project Manager originally was Mr. Francisco Flores, and the work was completed with Mr. Roger Svehla, Fuels Research Section, Fuels Branch, Aerothermodynamics and Fuels Division, as Project Manager.

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SUMMARY

The coming of synthetic feedstocks and lower quality (heavier, sour) petroleum crudes will have effects on combustion performance. Test fuels whose properties cover the range of importance for combustion performance are needed to investigate questions of changing fuel quality. The property-controlled (PC) fuels in the current work address this need.

There has been an emerging pattern of observations which have been differentiating the effects of hydrocarbon type and simple H/C mass ratio on combustor performance. Test blends composed of controlled additions of selected aromatics to paraffinic base stocks have been developed to vary hydrocarbon-type composition while holding hydrogen content fixed. These fuels are termed composition-controlled (CC) test fuels.

The major steps in the current work were:

1. Evaluating the test fuel matrix
2. Locating suitable base stocks
3. Characterizing the acquired base stocks
4. Formulating the test fuel compositions
5. Testing the trial blends
6. Blending the test fuels
7. Inspecting and analyzing the test fuels
8. Comparison of correlation estimates with measurements

These steps were performed by iterations in which predictions were made from the known properties of available base stocks to the needed formulations to meet specified target properties. By this means inaccessible targets were identified (e.g., some boiling ranges) and requirements for new base stocks were found (e.g., high viscosity material). With trial blends for testing, successful formulations were found for all of the primary target properties. This approach to the test fuel matrices has proven sound.

The PC fuels span a boiling range from 150°C to 335°C; freezing point, -23°C to -43°C; hydrogen content, 11.8 to 14.2 mass%; aromatic content, 20 to 50 vol%; viscosity, 4 and 11 cSt; and naphthalene content, 8 and 16 vol%. In these blends, the freezing point showed the most sensitivity to changes in blend stock concentration and identity.

The CC test fuels were made in two groups: a normal and isoparaffinic base stock and a cycloparaffinic base stock. To these two base fuels were added each of three aromatic blend components to control hydrogen content. The components were alkyl benzenes, naphthene benzene, and naphthalenes. The three normal and isoparaffin blends were 13.5±0.2 mass% hydrogen, while two sets of naphthene-based blends were 12.5±0.2 and 11.5±0.2 mass% hydrogen.

In all cases, blends were made from materials which could be obtained later in larger quantities. No material had more than the limit of 0.3 mass% sulfur. Five gallons of each of the 34 test blends were produced for the NASA-Lewis Research Center. Ten gallons of each of the 17 base stocks were sent as well.

Special procedures were used to calculate five specific properties of blended fuels based on the properties of the blend components. Most properties were calculated as volumetric weighted averages of the properties of the blend stocks. Heat of combustion was calculated as a mass weighted average. The reciprocal of the smoke point was calculated as a weighted average of the reciprocals of the component smoke points. For the flash point, viscosity, and freezing point, specific blending correlations were employed. In all cases, the correlations performed well except that for some designated blends in which some cracked stocks were used, larger deviations (>5%) occurred.

INTRODUCTION

Continuing work in aviation fuels research at the NASA-Lewis Research Center has recognized the need for distillate test fuels spanning the range of properties which are important in turbine combustion and may be outside the range of those currently being used. Southwest Research Institute was selected to identify and characterize blend stocks suitable for the test fuels and then to produce sample quantities of the test fuels for laboratory analysis. This report will:

- Summarize the development of the test fuel matrix.
- Give rationale for choosing blend stocks and characterize them by chemical and physical inspections.
- Explain the formulation of the test fuels.
- Describe the properties of the resultant test fuel matrix.
- Check performance of PC property predictions.

Background

One index for describing test fuels composed of a mixture of hydrocarbon types is the H/C ratio. Predictions of combustion performance based on H/C ratio alone have not been fully successful. Test fuels with equal H/C ratios and made up of different hydrocarbon types frequently display different combustion characteristics. "It has long been recognized that the combustion behavior of a hydrocarbon is different for straight chain paraffins [both normal and iso] (which have the highest H/C ratio), cyclic paraffins (intermediate in H/C ratio) single-ring aromatics (low in H/C ratio) and condensed-ring aromatics (lowest in H/C ratio). Wide differences in the behavior of these types of hydrocarbons are clearly demonstrated with diffusion flames and measured by flame height in smoke lamps, emissivity in the luminometer test, and soot production in burners that inject atomized liquid droplets.

"Under the highly turbulent and intense mixing conditions of a gas turbine combustion, the differences noted in diffusion flame devices tend to disappear and the simple fuel quality yardsticks of hydrogen content or H/C ratio appear to adequately define the critical combustion parameters of exhaust smoke (soot production and burnup) and wall metal temperatures (due to flame emissivity or heat flux). However, combustors differ significantly in their designs for mixing fuel with air, internal recirculation patterns of flames, secondary air flows for cooling and dilution of rich burning zones, pressure and intensity of heat release, etc., leading to evidence that the actual structure of a hydrocarbon may still show an effect that is not completely predicted in terms of H/C ratio" (ref.1).

History

The impetus for developing a selection of test fuels with a wide range of properties came from observations made in laboratories engaged in combustor research. In June of 1979, the Coordinating Research Council (CRC) group on Combustion Characteristics of Aviation Turbine Fuels suggested the Test Fuel Sources and Selection Panel develop recommendations for fuels appropriate for future tests of the effect of hydrocarbon type on combustion. Consistent with goals at NASA, this matrix was linked with a larger group of fuels with specified properties which were to be met with readily available blend stocks from commercial sources. In this way NASA has approached the test fuels from two viewpoints: property control and composition control. The **property-controlled** (PC) blend stocks were selected for their specific range of properties available, while the **composition-controlled** (CC) stocks were selected for their high concentration of desired hydrocarbon types. The characteristics of the blend stocks depend upon the crude oil sources and refinery unit operations which they undergo.

The following are some of the observations which show the effects of hydrocarbon type and H/C ratio to be independent:

- Pratt and Whitney's work for NASA on the experimental vorbix combustor showed that naphthalene (condensed two-ring aromatic) added to Jet A fuel produced higher smoke than predicted by H/C ratio (ref.2).

- MIT's highly turbulent flame burner revealed that tetralin (condensed naphthene-aromatic ring structure) produced more soot than blended fuel or xylene (single-ring dimethyl benzene) at the same hydrogen level. It also showed lower soot production for decalin (condensed-ring naphthene) than mixed fuel under similar combustion conditions (ref.3).

- Southwest Research Institute's 2-inch combustor studies of fuels blended with different aromatics to the 12.8-percent H_2 level showed that an increment of wall temperature rise beyond that related to H/C ratio was associated with a condensed-ring structure. Tetralin appeared to fall outside the H/C versus temperature relationship unless both rings were assumed to be aromatic (ref.4).

- General Electric's reports to the Air Force of J79 and F101 engine combustion tests indicate that fuels containing 24 percent naphthalenes give higher smoke numbers and radiant heat flames than 1 percent naphthalene fuels of the same H/C ratio (ref.5).

With the evidence cited that hydrocarbon structure as well as H/C ratio plays a role in smoke production or liner temperatures in gas turbine combustors, the Test Fuel Sources and Selection Panel of the CRC was given the responsibility to develop a test fuel matrix related to hydrocarbon structure. They considered properties of hydrocarbon types that influence the entire combustion process. The most important physical properties that play a role are:

1. Viscosity as it affects fuel atomization and ignition.
2. Front-end volatility as it affects ignition, particularly starting.
3. End point as it affects emissions of CO and unburned hydrocarbons and also combustion efficiency.

Other important factors affecting fuel blending are the potential need to examine fuels with a broader range of properties than previously encountered for enhancement of product availability during times of feed stock shortfalls, and the possible trend toward new fuels designed to satisfy more fuel-tolerant engine systems. These changes affect freezing point, flash point, and boiling range, as well as other physical/chemical properties. Fuels such as ERBS (experimental referee broadened specification) aviation turbine fuel (ref.6), so-called broadcut fuels, and future fuels which may contain hydrocarbon and nonhydrocarbon products could alter the basic fuel properties.

The ERBS fuel was intended for use as a reference fuel for investigation into the effects of fuel property variations on the performance and durability of jet aircraft components. Two variations of the ERBS fuel were specified with the key controlled property being hydrogen content at two different levels. The test fuel blends developed in the current program have many other controlled properties in addition to hydrogen content. These are boiling range, freezing point, aromatic content, naphthalene content, viscosity, and hydrocarbon type.

Scope

The purpose of the project is to provide test fuels with a specified range of properties which have been controlled by blending selected stocks. These fuels can be used later to study the relationship of physical and chemical properties to the combustion process.

Property-Controlled (PC)

The 1970's saw the petroleum industry short of crude feedstocks, and a trend from sweet crudes to less desirable sour and heavy crudes. With this shift has come a corresponding change in refinery operations and equipment to process these crudes and conversion of crude bottoms into higher quality, more profitable products. Compounding an already complex feedstock-processing picture is the possible emergence of a synthetic fuels industry. Adjustments in governmental policies over the past months indicate an evolutionary synfuels development based on economics instead of a revolutionary, government-subsidized industry. This change in emphasis indicates that synthetic liquids from shale, coal, and tar sands may become additional feedstocks for existing refineries that have the processing capability to handle these materials.

These two factors, varying quality crudes and synthetic feedstocks, bring to the refinery hydrocarbons which will result in fuels with altered properties. With this in mind, NASA has prepared a slate of base test fuels to cover the range of variables of practical import to combustion phenomena. For these PC test fuels, the property variables were volatility (boiling range), hydrogen content, aromatic content, freezing point, kinematic viscosity at -20°C, and naphthalene content. All blends were limited to less than 0.3 mass% sulfur. Four selected test blends had to contain a cracked stock as one of the components as a test of the blending methods and correlations being used. Other properties such as surface tension and fuel atomization are not considered here; however, measurements of hydrocarbon type, mercaptan sulfur, flash point, heat of combustion, smoke point, thermal stability, and nitrogen content were made on selected blends.

Composition-Controlled (CC)

To begin the task of formulating a CC test fuel requirements matrix, the CRC Test Fuel Sources and Selection Panel studied reports of combustion performance and summarized (ref.1) it in a table which has been graphically expressed in Figure 1 (ref.7). Four summary observations (ref.1) are:

1. Straight-chain paraffins, both normal type and their isomers are excellent for combustion in all respects with minimum adverse effects.

2. With cycloparaffins, important distinction can be seen between single and double ring naphthenes in terms of viscosity, volatility, and structural effects on combustion.

3. With single-ring aromatics, important distinctions are also evident between paraffinic side chains (alkyl benzenes) and a condensed naphthenic side chain (tetralin) in terms of combustion severity.

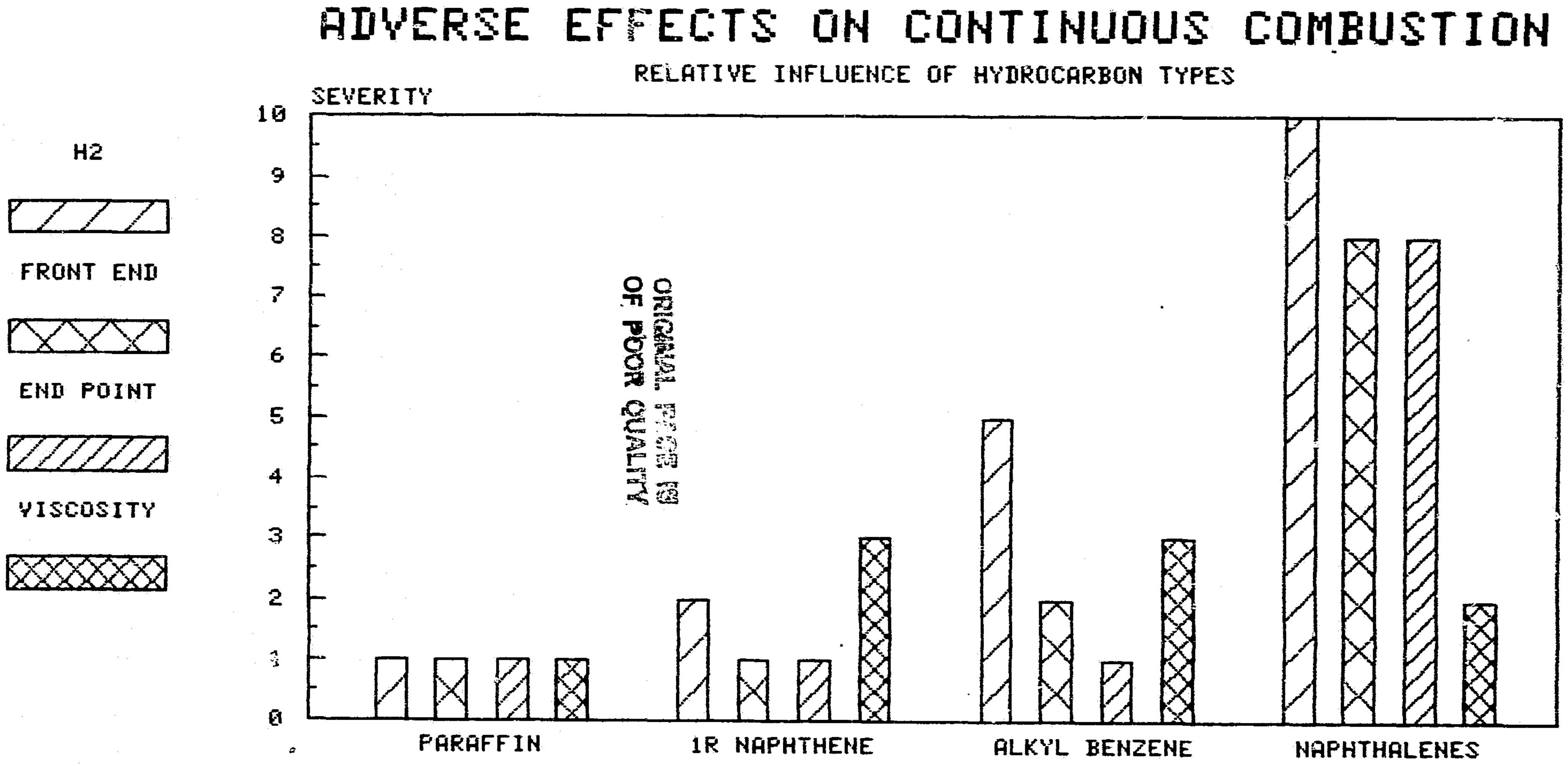


Figure 1. Adverse Effects on Combustion.

4. With condensed-ring aromatics of two or more rings and containing alkyl side chains, adverse combustion effects are reported for all properties except viscosity.

"While it would be desirable to hold all combustion-related parameters constant while only hydrocarbon structure was varied, such a test matrix might not be possible. However, the variations that would result in viscosity, front-end volatility, and end point while maintaining constant hydrogen might not be great. For example, if the JP-7 contained an average of 14.8-percent H_2, blends of three aromatic streams to a constant 13.5-percent blend level would require 21-percent methyl naphthalenes, or 29-percent tetralin or 34-percent alkyl benzene respectively. On this basis, the inevitable differences in physical properties might not prove significant and the combustion tests would be comparing aromatic streams that varied about two-fold in weight at a constant hydrogen level" (ref.8).

Thus, the three aromatic-blending components suggested were:

1. alkyl benzenes in the 150-350° boiling range
2. tetralin
3. methyl naphthalenes.

The structures of these classes of compounds are shown in Figure 2.* Each of these aromatic-blending stocks is generally available and has been utilized in prior programs. Xylene bottoms is a typical alkyl benzene stream, and tetralin is available as a commercial product as is a naphthalenic solvent. In order to examine aromatic hydrocarbon structure unambiguously, it is necessary to utilize

---

*The paraffins shown under base stocks represent normal and isoparaffins by the first structure while the second structure with the broken line parentheses suggests all three (mono, di, tri) cycloparaffins or naphthenes. Even though no substituents are drawn on the naphthene benzenes and naphthalenes, short alkyl side groups may be present.

aromatic-free base stocks. The suggested base stocks to consider are JP-7, an essentially aromatic-free special fuel made to MIL-T-38291A which is largely isoparaffinic and RJ-1, a low aromatic special fuel made to MIL-F-25558C which is largely naphthenic (ref.1).

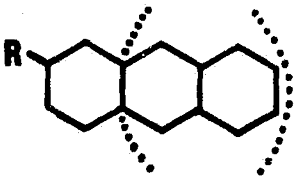
COMPOSITION-CONTROLLED

BASE STOCKS:

PARAFFINIC

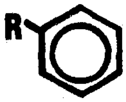
$C{-}\overset{\overset{R}{|}}{C}{-}R{-}C$

NAPHTHENIC

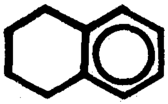


CONSTITUENTS

ALKYLBENZENES



NAPHTHENE BENZENES



NAPHTHALENES

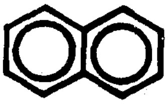


Figure 2. Hydrocarbon Types for Composition-Controlled Test Fuels.

General Approach

The governing principle in use here was meeting specifications of the test fuels as closely as possible with the available stocks and including particular hydrocarbon components when required (e.g., a cracked stock). Figure 3 shows the overall method used for conducting the project. The first task was to evaluate the prescribed test fuel requirement matrix. In order to do this, an examination was made of the test fuel requirements using the properties of candidate blend stocks and property blending correlations to see if the required blends were feasible. With many stocks and properties to consider, an automated computation was made in which all pairs of stocks were tested for controlling property (not the boiling range) for each test fuel. When the target property could be met with a given pair of blend stocks, the resulting boiling range (and other properties) was calculated and compared with the desired range for each test blend.

From these calculations, a set of candidate blend stocks was chosen from known available base stocks and those which were found with renewed searching. These base stocks were characterized and compared with the needs of the test fuel matrix. With the required test fuel properties and the available blend stocks, trial blends were prepared to test the formulations. In the period of trial blending, several candidate blend stocks were rejected and several of the test fuel matrix requirements (boiling ranges) were relaxed in order to produce practical blends. With the successful trial blend formulations, finished batches of test fuel were made for delivery to the Lewis Research Center.

There was no restriction in the program to use only binary mixtures. The two component blends were examined first and used when possible for their simplicity. There were in fact two ternary PC blends and one single component PC test fuel.

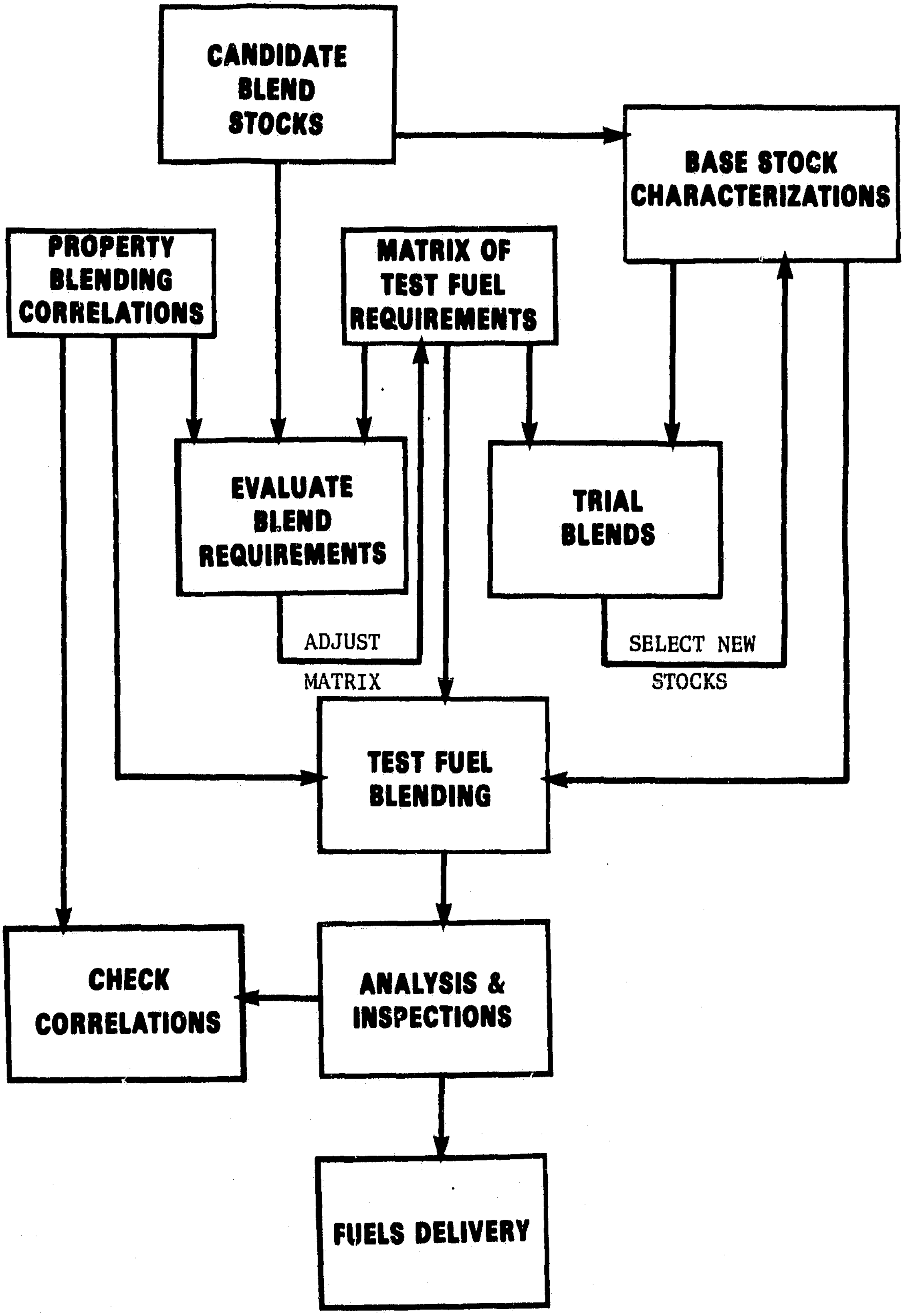


Figure 3. Organization of the Work

DESCRIPTION OF FUELS

The changes in chemical composition which lie ahead for distillate fuels will require laboratory and bench tests to track combustion performance. Such work will require a "menu" of research formulations which will meet the new property requirements. These test fuels could be used in future programs to evaluate the effect of variations in fuel properties on the combustion and other performance aspects of fuels manufactured from new crude sources and refinery processes.

General Requirements

The requirements for the properties and compositions of the test fuel matrix are presented in Table 1. These were classified into property-controlled (initially called source-controlled) and composition-controlled test fuels. The properties of interest and which were targeted for control were: volatility as indicated by initial and final boiling points, freezing point, hydrogen content, viscosity, naphthalene content, aromatic content, and hydrocarbon type.

The blending stocks used for the property-controlled fuels included finished fuels such as Jet A and No. 1 diesel fuels, refinery streams such as hydrocracked kerosene, straight run kerosene, aromatic concentrates, light cycle oil, and others. The composition-controlled blending stocks were to include a paraffinic type, a naphthenic type, alkyl benzenes, naphthene benzene, and alkyl naphthalene. These stocks were to contain a dominant fraction of the major hydrocarbon type. All of the base stocks had no more than 0.3 mass% sulfur. All must be available for later acquisition.

As shown in test fuel matrix Table 1, all fuels were to have volatility controls based on the initial and final boiling points. The property-controlled test fuels were further classified by freezing point, hydrogen content, aromatic content, viscosity, and naphthalene-content. The composition-controlled blends were controlled by hydrogen content and hydrocarbon type.

TABLE 1
TEST FUEL TARGET SPECIFICATIONS

PROPERTY-CONTROLLED FUELS

BLEND NO.	Initial Boiling point, °C	Final Boiling point, °C	Freezing point, °C	Aromatics content, vol.%	H-Cont M%	Viscosity cSt (-20 °C)	Napthalenes vol.%
1a	150± 5	298±38	-43±3	Report	Report	Report	Report
1b	↓	↓	-33±3	↓	↓	↓	↓
1c cracked	↓	↓	-23±3	↓	↓	↓	↓
2a	190± 5	↓	-43±3	↓	↓	↓	↓
2b	↓	↓	-33±3	↓	↓	↓	↓
2c	↓	↓	-23±3	↓	↓	↓	↓
3a cracked	190±10	275±15	Report	↓	11.8±0.2	↓	↓
3b	↓	↓	↓	↓	13.0±0.2	↓	↓
3c	↓	↓	↓	↓	14.2±0.2	↓	↓
4a	190±10	313±23	↓	↓	11.8±0.2	↓	↓
4b	↓	↓	↓	↓	13.0±0.2	↓	↓
4c	↓	↓	↓	↓	14.2±0.2	↓	↓
5a	150±10	↓	↓	↓	11.8±0.2	↓	↓
5b cracked	↓	↓	↓	↓	13.0±0.2	↓	↓
5c	↓	↓	↓	↓	14.2±0.2	↓	↓
6a	190±10	275±15	↓	20±5	Report	↓	↓
6b cracked	↓	↓	↓	35±5	↓	↓	↓
6c	↓	↓	↓	50±5	↓	↓	↓
7a	150±10	313±23	↓	20±5	↓	↓	↓
7b	↓	↓	↓	35±5	↓	↓	↓
7c	↓	↓	↓	50±5	↓	↓	↓
8a	180±15	298±38	↓	Report	↓	4±2	↓
8b	↓	↓	↓	↓	↓	11±2	↓
9a	↓	↓	↓	↓	↓	Report	16±2
9b	↓	↓	↓	↓	↓	↓	8±2

COMPOSITION-CONTROLLED FUELS

BLEND NO.	Initial Boiling point, °C	Final Boiling point, °C	H-Cont M%	Hydrocarbon Type	
10	150±10	300±10	13.5±0.2	P	AB
11	↓	↓	↓	↓	T
12	↓	↓	↓	↓	N
13	200±10	↓	12.5±0.2	CP	AB
14	↓	↓	↓	↓	T
15	↓	↓	↓	↓	N
16	↓	335±10	1.5±0.2	↓	AB
17	↓	↓	↓	↓	T
18	↓	↓	↓	↓	N

LEGEND
P - Normal and Isoparaffins
CP - Naphthenes
AB - Alkyl Benzene
T - Naphthene Benzene
N -.Naphthalenes
All blends: %S<0.3

When the final test fuel blends were completed and found to meet the requirements of the test fuel matrix, sufficient quantities of the blends were prepared to ship 5 gallons of each to the NASA-Lewis Research Center. Ten-gallon samples of each blending stock used in the final test fuel blends were also shipped to the NASA-Lewis Research Center. All these materials were to have been readily available in larger quantities from commercial sources.

Blending Procedure

The blend formulations (volumetric compositions) are computed from the blend stocks' properties as a linear combination (weighted average) based on volume percent of each stock. (Thermodynamic non-ideality of the resulting solutions was ignored.) The distillation range estimates were also simple volume percent weighted averages of the initial and final distillation temperatures of the blend stocks. It could be more appropriate to plot the molar average percent distilled at each temperature in the overlapping range. In recent work, this technique did not produce a better estimate than temperature averaging, so the simpler method was used. Densities were estimated by linear blending calculations.

Blends whose properties are the result of mass balances are calculated by linear averaging. For some properties the resulting value for the mixture can be calculated by use of blending coefficients or indices. Specifically for viscosity, freezing point, and flash point, the following series of general equations is used:

$$I_i = f(P_i)$$

$$I = \sum_{i=1}^{n} v_i I_i$$

$$P = f^{-1}(I)$$

where

I	blending index
P	value of property of interest
n	number of stocks
i	particular stock
v	volume fraction of a stock
f, f^{-1}	functions in Appendix A

The heat of combustion and smoke point do not blend linearly by volume, but do not require blending indices. The heat of combustion does blend linearly by mass fraction while smoke point happens to become additive as the reciprocal of the smoke point. The equations for calculating these property values for test fuel blends are given in Appendix A.

Since a part of this program was to investigate the availability and accuracy of blending correlations for preparing test fuels to meet certain properties, correlations found in the literature and private correlations used with permission were employed to calculate blends based on the known properties of the blending stocks. Test fuel blends were then prepared, analyzed, and the results compared to the computer-predicted values. The scheme for calculating and preparing the test fuel blends is shown in Figure 4 for binary blends. When property requirements could not be met with binary blends, the predicted properties of ternary blends were hand calculated.

In Figures 5 through 9 there are examples of the computer-generated binary blending curves. One sample for each of the five PC target properties is given. On these plots the properties of the two blend stocks are marked by triangles on the right and left ordinates. The abscissa represents the volume percent of the base stock mentioned last in the axis label. (The component mentioned first can be thought of as being at 100-percent at the "zero point" of the horizontal axis and decreasing as the concentration of its complement base stock rises.) At the composition of the named blend on each plot, the solid triangle marks the value of the subject property.

The curves for freezing point and viscosity were calculated from the corresponding blending correlations. The curvature is not noticeable for the stocks shown since their properties are not widely divergent. These examples emphasize the small departure from linearity that the correlations can make.

Analytical Requirements

In addition to the five governing properties for the PC blends and the two governing properties for the CC blends, other properties were of interest. These were the flash point, heat of combustion, smoke point, and thermal stability. These other properties were to be measured only on selected test blends as shown in Table 2. All of these other properties except thermal stability were determined for all the blend stocks.

The standard tests measured in this program are important in their own right for they are used in present day, fuel quality specifications. Changing crude sources may indicate new analytical areas of emphasis in the future. For this reason data have been gathered on the current sets of test fuels in three groups:

Composition	Physical	Chemical
Hydrogen content	Freezing point	Thermal stability
Aromatics	Distillation range	Smoke point
Naphthalenes	Density	Flash point
Sulfur content	Viscosity	Heat of combustion

With the ability to use the current fuels (and interpolations between them) in laboratory and bench tests, this broad and balanced set of analyses will make it possible to perform comparisons and measurements not included in current specifications.

TEST FUEL BLENDING

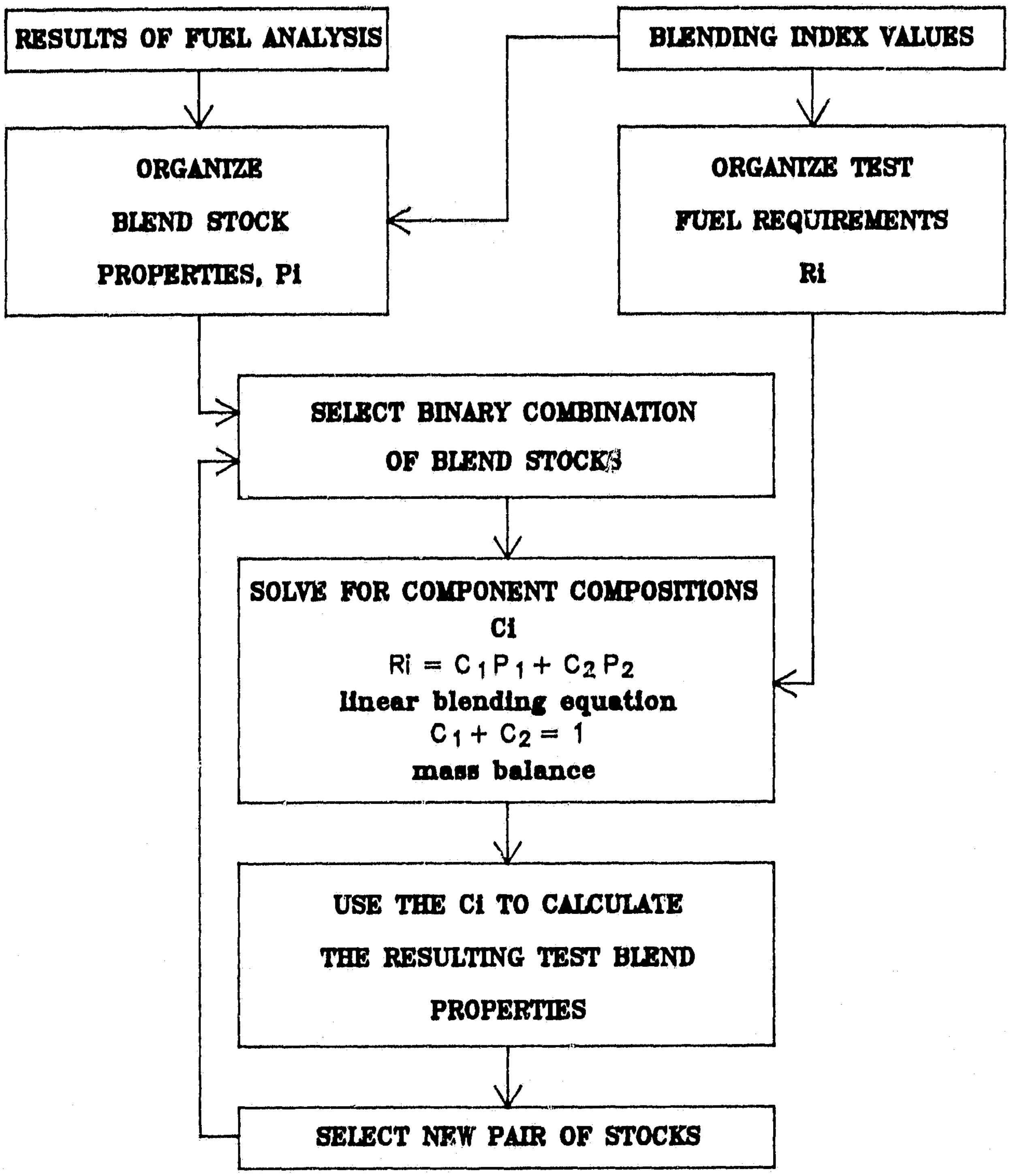


Figure 4. Procedure for Establishing Formulations of Candidate Binary Blends.

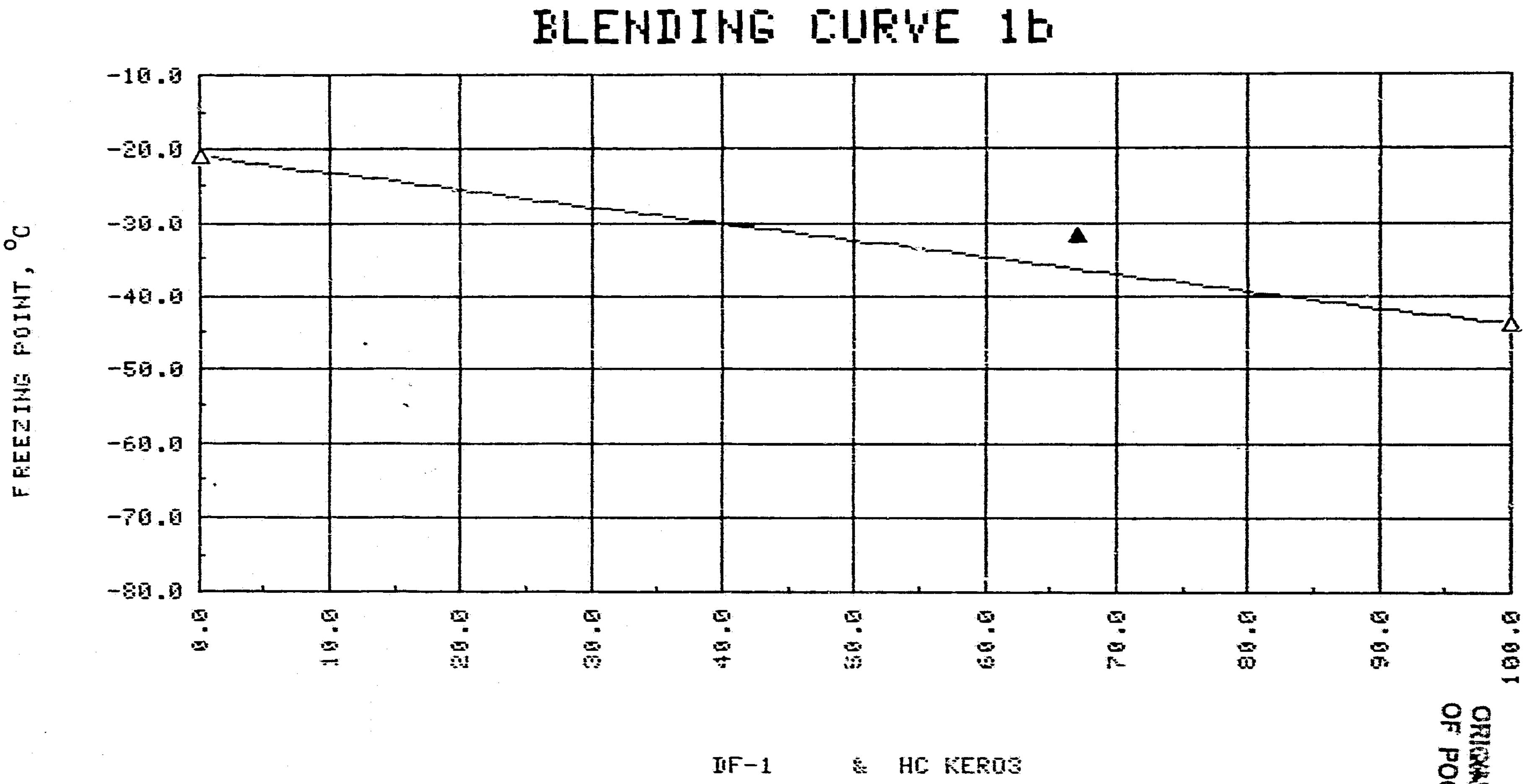


Figure 5. Example Binary Blending Curve for Freezing Point-Controlled Blend 1b.

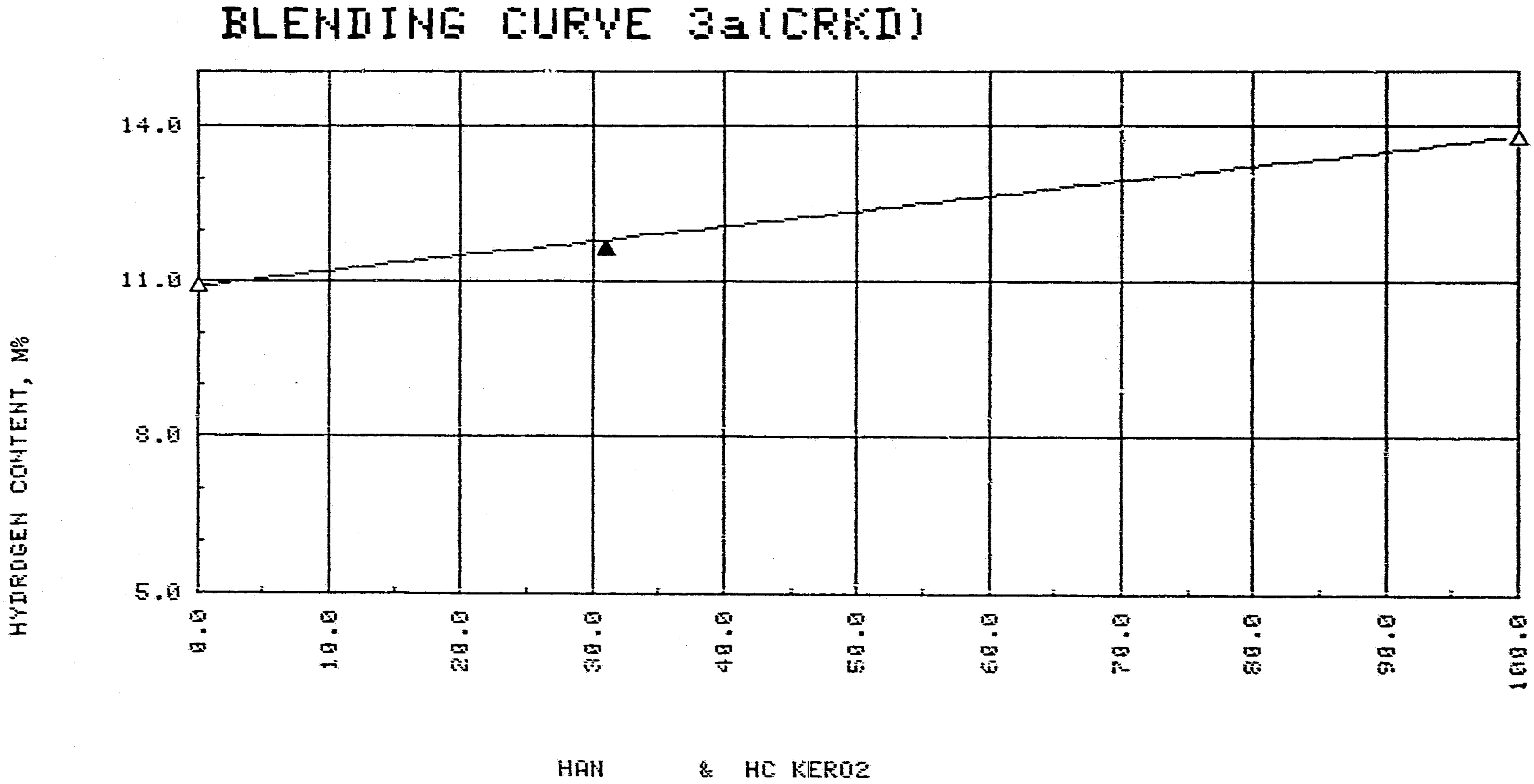


Figure 6. Example Binary Blending Curve for Hydrogen Content-Controlled Blend 3a.

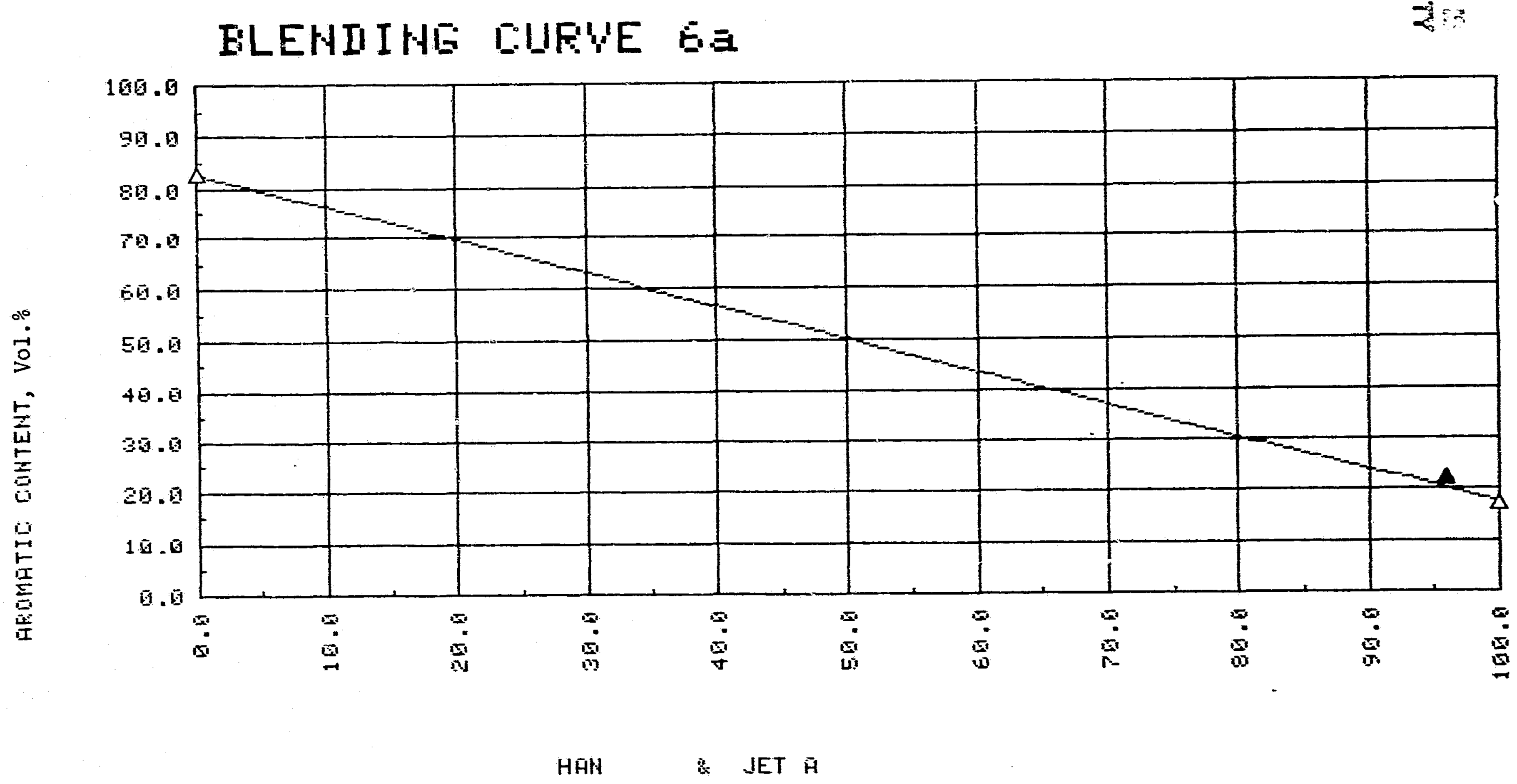


Figure 7. Example Binary Blending Curve for Aromatic Content-Controlled Blend 6a.

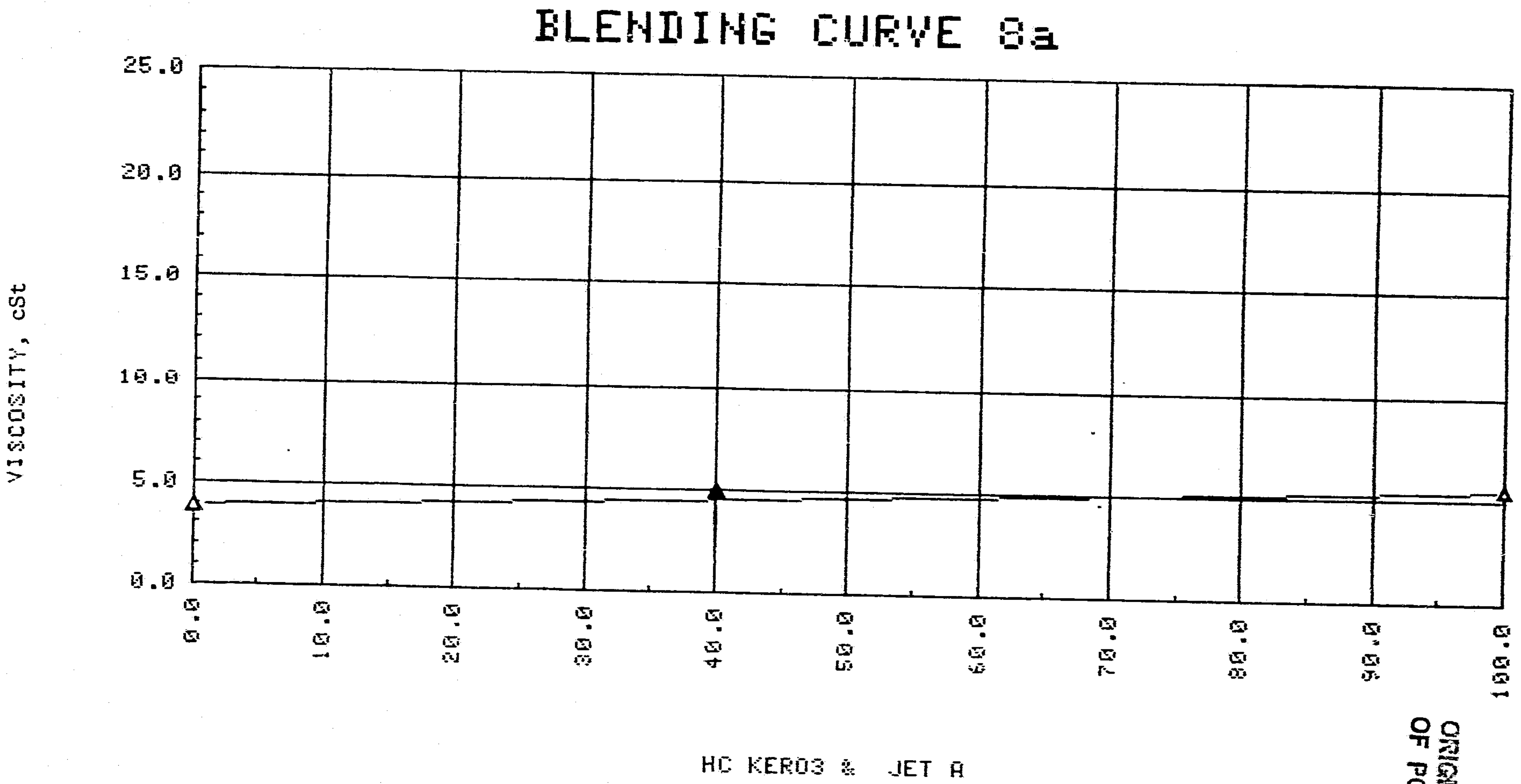


Figure 8. Example Binary Blending Curve for Viscosity-Controlled Blend 8a.

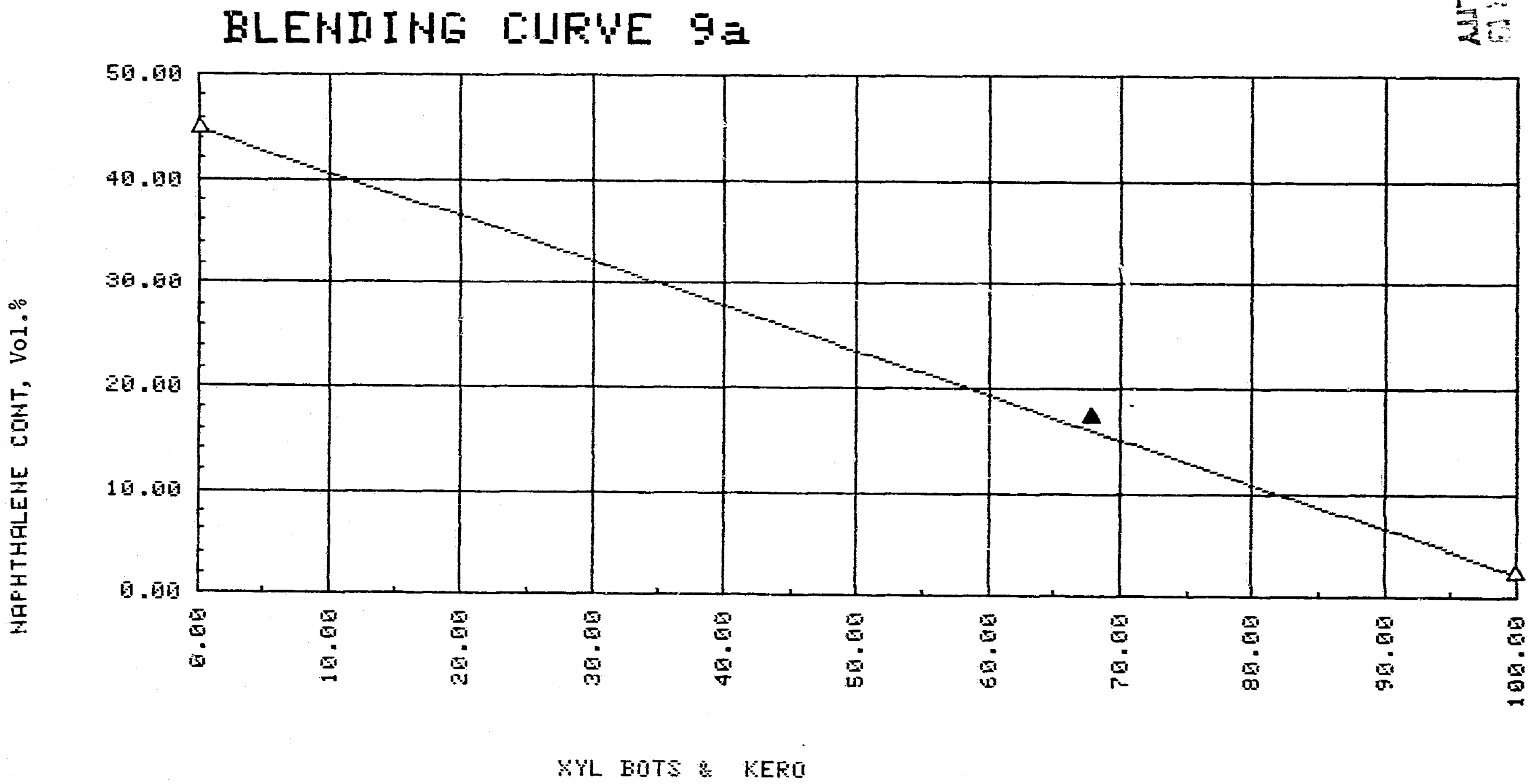


Figure 9. Example Binary Blending Curve for Naphthalene Content-Controlled Blend 9a.

TABLE 2

ANALYTICAL REQUIREMENTS

Blend No.	D1319 FIA	D2622 Total Sulfur	D3227 Mercaptans Sulfur	D86 Distillation	D56 Flash Pt.	D1268 Gravity	D2386 Frzg. Pt.	D445 Viscosity	D240 Heat of Combs.	D1322 Smoke Pt.	D1840 Naph-thalenes	D3241 JFTOT	D2425 Mass Spec.	D3431 Nitrogen	D3178 H & C
PROPERTY-CONTROLLED															
1a				*	*	*	*	*				*			
1b				*	*	*	*	*				*			
1c(cs)				*	*	*	*	*				*			
2a				*	*	*	*	*				*			
2b				*	*	*	*	*				*			
2c				*	*	*	*	*				*			
3a(cs)	*	*	*	*	*					*	*	*			
3b	*	*	*	*	*				*	*	*	*			*
3c	*	*	*	*	*				*	*	*	*			*
4a	*	*	*	*	*				*	*	*	*			*
4b	*	*	*	*	*				*	*	*	*			*
4c	*	*	*	*	*				*	*	*	*			*
5a	*	*	*	*	*				*	*	*				*
5b(cs)	*	*	*	*	*				*	*	*				*
5c	*	*	*	*	*					*	*				*
6a	*	*	*	*	*				*	*	*				*
6b(cs)	*	*	*	*	*					*	*				
6c	*	*	*	*	*				*	*	*				*
7a	*	*	*	*	*				*	*	*			*	*
7b	*	*	*	*	*				*	*	*			*	*
7c	*	*	*	*	*				*	*	*			*	*
8a	*	*	*	*	*			*		*	*			*	
8b	*	*	*	*	*			*		*	*			*	*
9a	*	*	*	*	*				*	*	*			*	*
9b	*	*	*	*	*				*	*	*			*	*
COMPOSITION-CONTROLLED															
10	*			*	*	*	*	*			*				
11	*			*	*	*	*	*			*				
12	*			*	*	*	*	*			*				
13	*			*	*	*	*	*			*				
14	*			*	*	*	*	*			*				
15	*			*	*	*	*	*			*				
16	*			*	*	*	*	*			*				
17	*			*	*	*	*	*			*				
18	*			*	*	*	*	*			*				

---

* Test Required

Property-Controlled Test Fuels

In the process of identifying blending stocks for the property-controlled test fuels, 21 samples were characterized. Eleven of these were selected for use in preparing the final test fuel blends. These stocks and their properties are shown in Table 3 and include finished fuels (Jet A, DF-1, JP-7) refinery stream (straight-run kerosene, hydrocracked kerosene, xylene tower bottoms, light cycle oil) and special products (kerosene, heavy aromatic naphtha). Table 1 indicates that certain test fuel blends require the use of cracked stocks as a component. The hydrocracked kerosenes and light cycle oil are considered to be cracked stocks.

A computer program was written to calculate the properties of binary blends made from the stocks in Table 3. In addition to the properties pertinent to the blending of the property-controlled fuels, specific gravity and sulfur content of the blends could also be calculated. Freezing point and viscosity are properties that do not blend linearly and require a special blending index for linear blend calculations. The other properties--hydrogen, aromatics, naphthalenes, sulfur, and specific gravity--blend linearly by vol% or mass%.

Freezing Point Blends

The test fuel matrix in Table 1 shows six test fuel blends controlled by freezing point. Two boiling ranges and three freezing points are represented. The computer output showed numerous calculated blends that approached the requirements. Several trial blends were prepared, analyzed for freezing point, and found to be outside the tolerance limits specified for this property. The calculation for the freezing point blends were made according to the previously described blending procedure using the equations in Appendix A made available by Chevron Research Company and based on the work of Reid and Allen (ref.8).

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TABLE 3
PROPERTY CONTROLLED BLENDING STOCKS

SAMPLE CODE	AL-10582-T	AL-11275-F	AL-9749-F	AL-9998-F	AL-11310-F	AL-11286-A	AL-10724-F	AL-10735-A	AL-11311-T	AL-11276-F	AL-11381-F
FUEL TYPE	Jet A	DF-1 Diesel Fuel	Straight Run Kerosene	Hydro-Cracked Kerosene	Hydro-Cracked Kerosene	Xylene Twr. Btms. Stream	Kerosene	Heavy Aromatic Naptha	JP-7	Light Cycle Oil	Hydro-Cracked Kerosene
SOURCE	Ashland	Howell	Howell	Sohio HC kero 01	Tesoro HC kero 03	Suntech	Howell	Exxon	Ashland	Howell	Sohio HC kero 02
PROPERTIES											
Hydrogen, Mass %	13.81	13.99	13.17	14.08	14.06	9.78	14.17	10.91	14.47	10.65	13.79
Carbon, Mass %	86.35	85.86	86.71	85.40	85.28	90.25	85.93	88.71	85.49	88.83	86.48
Distillation, D86, °C											
IBP	183	203	192	147	150	143	164	174	197	198	181
10% Recovered	195	211	221	187	166	147	186	194	207	247	198
50% Recovered	213	220	238	226	192	151	199	218	214	272	219
90% Recovered	241	255	251	269	244	163	216	253	237	314	253
EP	264	317	282	317	281	198	241	281	262	345	273
Freezing Point, °C	-48	-21	-28	-17	-44	-72	-45	-66	-41	-13	-40
Aromatic Content, Vol%	17.3	14.4	24.0	11.0	11.7	99.6	12.4	82.8	3.1	66	20.5
Viscosity @ -20°C, cSt	5.36	7.35	8.19	Froze	3.90	1.59	4.23	5.86	6.32	22.2*	6.39
Flash Point, D56,°C	60	76	65	48	47	34	52	59	72	63	66
Net Heat of Combustion,											
MJ/kg	43.271	43.803	43.215	43.171	43.848	40.119	43.825	41.416	44.040	41.683	42.896
BTU/lb	18,603	18,832	18,579	18,560	18,851	17,248	18,841	17,805	18,934	17,920	18,442
Smoke Point, mm	22.2	25.1	16.5	22.0	24.7	7.3	26.5	7.0	30.9	6.9	20.8
Sulfur, Mass %	0.008	0.01	0.01	0.01	0.01	0	0.01	0.20	0.01	0.22	0.01
Specific Gravity, 16/16°C	0.8146	0.8044	0.8338	0.8081	0.7976	0.8740	0.7949	0.8922	0.8025	0.9194	0.8174
Naphthalenes, Mass %	0.7	4.2	9.25	0.4	0.1	0.2	2.3	10.8	0.04	44.9	0.6

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* Extrapolated from measurements at 40° and 0°C

After many trial blends, the test fuels listed in Table 4 were blended and evaluated. Blend 1c required the use of a cracked blending stock and one such stock originally available did not give consistent freezing point results either alone or in blends. A recent report by Affens, et al. (ref.9) shows that certain normal paraffins that may be present in fuels tend to raise the freezing point, but not necessarily in proportion to their carbon numbers. It was shown that the presence of normal paraffins C-16, C-15, and C-14 raised the freezing point of a hydrocarbon solution. In the order shown, C-16 raised the freezing point the most, C-14 the least. However, C-12 and C-13 paraffins in combination with C-16, and at certain concentrations, may lower the freezing point of a solution. This kind of behavior among normal alkanes makes it difficult to predict freezing points based on the mid-percent boiling temperature, especially since the n-alkanes in the aircraft turbine fuel generally have the highest melting point temperatures of the various hydrocarbon types for a given molecular weight. The melting points of individual hydrocarbons and their solubility in the other hydrocarbon fuel components, have a definite influence on the freezing point of the overall fuel. In spite of these factors, the Chevron freezing point index predicted freezing points reasonably close to the measured values as shown in Table 5. The initial boiling point (IBP) target limits for blends 1a and 2b were met, while the target limits for blends 1b, 1c, 2a, and 2c were off by one or two degrees Celsius. The target final boiling point (FBP) limits for blends 1a, 1b, 2a, 2b, and 2c were all met. The FBP for blend 1c was 4°C high. It should be noted that the precision of ASTM D 86, Standard Method for Distillation of Petroleum Products, is as high as 2.5°C for repeatability and 7.0°C for reproducibility at the IBP, and 2.5°C for repeatability and 5.0°C for reproducibility at the FBP. The precision for the automatic distillation method described in Annex A1 of ASTM Method D 86 states that repeatability for IBP is 3.5°C and reproducibility is 8.5°C. For FBP it is 3.5°C for repeatability and 10.5°C for reproducibility. Therefore, the required IBP range of ±5°C for blends 1a, 1b, 1c, 2a, 2b, and 2c may have been unduly restrictive.

TABLE 4. FREEZING POINT BLENDS
COMPOSITION, VOL%

Blends	1a	1b	1c	2a	2b	2c
Sample Code	AL-11310-F	AL-11407-F	AL-11537-F Cracked	AL-11338-F	AL-11339-F	AL-11361-F
Blend Stocks						
Kerosene - Alaska AL-11310-F	100	67.3	38.0	---	---	---
DF-1 AL-11275-F	---	32.7	---	7.4	38.0	89.0
Light Cycle Oil AL-11267-F	---	---	62.0	---	---	---
Jet A AL-10582-F	---	---	---	92.6	62.0	---
Kerosene - Howell AL-10724-F	---	---	---	---	---	11.0

TABLE 5
FREEZING POINT BLEND PROPERTIES

Blends Sample Code		1a AL-11310-F	1b AL-11407-F	1c Crkd AL-11537-F	2a AL-11338-F	2b AL-11339-F	2c AI-11361-F
PROPERTY							
Distillation, °C							
IBP	Target	145 - 155			185 - 195		
IBP	Meas.	150	157	156	184	188	197
IBP	Calc.	150*	167	180	184	191	194
10% recovered	Meas.	166	177	188	197	201	208
50% recovered	Meas.	192	206	252	213	216	219
90% recovered	Meas.	244	249	303	240	244	250
FBP	Meas.	281	293	339	278	294	308
FBP	Calc.	281*	292	320	268	285	317
FBP		260 - 335					
Flash Point, °C	Meas.	47	46	48	59	64	71
Freeze Point, °C	Target	-43±3	-33±3	-23±3	-43±3	-33±3	-23±3
	Meas.	-44	-32	-20	-46	-30	-23
	Calc.	-44*	-33	-23	-43	-33	-23
Specific Gravity, 16/16°C	Meas.	0.7976	0.8012	0.8735	0.8132	0.8123	0.8081
	Calc.	0.7976*	0.8001	0.8733	0.8138	0.8107	0.8037
Viscosity at -20°C,cSt	Meas.	3.90	4.72	9.69	5.68	6.12	6.36
	Calc.	3.90*	4.8	10.0	5.5	6.0	6.9
Thermal Stability, JFTOT							
ΔP, mm Hg	Meas.	65	0	115	0	72	0
Visual Deposit Rating	Meas.	3	3	4+	2	4	4
TDR spun	Meas.	8	8	29	13	47	34
TDR spot	Meas.	11	9	33	15	48	41
Hydrogen, Mass %	Calc.	14.06*	14.0	11.9	13.8	13.9	13.9
Aromatics, Vol%	Calc.	11.7*	12.6	45.5	17.1	16.2	14.1
Sulfur, Mass %	Calc.	0*	0.003	0.14	0.008	0.008	0.009

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* As received fuel (one component)

Hydrogen-Content Blends

The first computer calculations for the hydrogen content blends yielded estimated blends for all the required test fuels except for blends 3a and 5b, which required cracked stocks and for blend 5a. Although the properties of three cracked blending stocks were in the data base, the target IBP and FBP for blend 3a could not be met. Introduction of a new hydrocracked kerosene as a blending stock produced calculated blends that met the targets for blend 3a. Blend 5a required the use of three components to meet the target values for %H, IBP, and FBP, so the formulation was hand-calculated.

The final formulations for the hydrogen-content blends are shown in Table 6, and the properties determined for blends 3a, 3b, 3c, 4a, 4b, 4c, 5a, 5b, and 5c are given in Table 7. The target values for hydrogen content, IBP, and FBP for these blends were all met with the exception of the IBP for blend 3a and FBP for blend 5a. The combined requirement in blend 3a for cracked stocks and low hydrogen content limited the available blend stocks to the heavy aromatic naphtha which had a low IBP and the hydrocracked kerosene. The amount of heavy aromatic naphtha required to meet the hydrogen content target, influenced the IBP of the final blend so that it was 6°C below the target limit. After eight trial blends, blend 3a still failed to meet the IBP target, and the final blend was prepared with this deviation. The FBP for final blend 5a was 2°C below the target limit even though a trial blend with virtually the same formulation was within the limit.

Aromatic-Content Blends

The computer calculations provided four aromatic-content-controlled blends (6a, 6c, 7a, and 7b) that were well within the target limits for aromatics, IBP, and FBP, and two blends (6b and 7c) that were just outside limits for IBP. Blend 6b, which required a cracked blending stock, was 2°C below the target for IBP, and blend 7c was 2°C above the target. The formulations for the aromatic-content blends are given in Table 8, and the properties for the same blends are in Table 9. Coincidentally, the hydrogen-content blend 5b also met the aromatic content, IBP, and FBP targets for blend 7b; therefore, they have the same composition.

TABLE 6. HYDROGEN-CONTENT BLENDS

COMPOSITION, VOL%

Blends Sample Code, AL-	3a 11538-F Cracked	3b 11277-F	3c 11345-F	4a 11329-F	4b 11331-F	4c 11346-F	5a 11337-F	5b 11278-F Cracked	5c 11409-F
Blend Stocks									
Heavy aromatic naphtha AL-10734-A	69.0	7.5	---	71.1	32.1	---	36.0	34.0	69.4
Hydrocracked kerosene AL-11381-F	31.0	---	---	---	---	---	---	---	---
Straight run kerosene AL-9749-F	---	92.5	---	---	---	---	---	---	---
Jet A AL-10582-T	---	---	40.9	---	---	---	---	---	
JP-7 AL-11311-T	---	---	59.1	---	---	43.8	---	---	30.6
DF-1 AL-11275-F	---	---	---	28.9	67.9	56.2	---	---	---
Hydrocracked kerosene AL-9998-F	---	---	---	---	---	---	39.9	66.0	---
Xylene tower bottoms AL-11286-F	---	---	---	---	---	---	24.1	---	---

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TABLE 7
HYDROGEN-CONTENT BLEND PROPERTIES

Blends Sample Code		3a Crkd AL-11538-F	3b AL-11277-F	3c AL-11345-F	4a AL-11329-F	4b AL-11331-F	4c AL-11346-F	5a AL-11337-F	5b Crkd AL-11278-F	5c AL-11409-F
PROPERTY										
Aromatics , Vol%	Meas.	63.9	30.1	9.7	62.6	36.2	10.1	59.0	35.5	9.5
	Calc.	62.7	28.4	8.9	63.0	36.4	9.4	58.2	36.0	8.6
Sulfur Total, Mass %	Meas.	0.13	0.02	0	0.14	0.07	0	0.07	0.07	0
	Calc.	0.14	0.02	0.006	0.14	0.07	0.008	0.08	0.07	0.008
Sulfur, Mercaptans, M%	Meas.	0.0007	0.0003	Trace	0.0013	0.0007	Trace	0.0005	0.0006	0
Distillation, °C										
IBP	Target	180 – 200						140 – 160		
IBP	Meas.	174	183	191	181	193	200	146	156	151
IBP	Calc.	176	190	191	182	194	200	156	156	162
10% recovered	Meas.	197	218	202	202	207	210	162	191	193
50% recovered	Meas.	219	237	214	220	221	218	203	222	219
90% recovered	Meas.	254	250	238	256	257	247	253	262	251
FBP	Meas.	281	277	262	296	309	295	288	306	281
FBP	Calc.	275	282	263	291	305	293	276	305	300
FBP	Target	260 – 290			290 – 335					
Flash Point, °C	Meas.	61	67	64	65	72	73	39	52	48
Smoke Point, mm	Meas.	8.9	14.5	27.2	9.9	14.4	28.1	9.5	14.1	27.1
Naphthalenes, Mass %	Meas.	8.0	10.2	0.4	9.1	6.3	2.4	4.5	4.4	0.3
	Calc.	7.7	9.4	0.3	8.9	6.3	2.4	4.1	3.9	0.3
Hydrogen, Mass %	Target	11.8±0.2	13.0±0.2	14.2±0.2	11.8±0.2	13.0±0.2	14.2±0.2	11.8±0.2	13.0±0.2	14.2±0.2
	Meas.	11.62	13.05	14.08	11.79	12.97	14.25	11.83	12.86	14.23
	Calc.	11.8	13.0	14.2	11.8	13.0	14.2	11.8	13.0	14.2
Carbon, Mass %	Meas.	87.78	87.04	85.52	88.22	86.91	85.87	87.89	86.78	85.63
Net Heat of Combustion										
MJ/kg	Meas.	41.451	43.568	43.939	42.576	43.384	44.247	42.779	43.294	N.D.*
BTU/lb	Meas.	17821	18731	18890	18304	18652	19023	18392	18613	N.D.
Thermal Stability, JFTOT										
ΔP, mm Hg	Meas.	125	0	0	0	0	0	N.D.	N.D.	N.D.
Visual Deposit Rating	Meas.	4+	4	1	3	3	3	N.D.	N.D.	N.D.
TDR Spun	Meas.	50+	20	4	50+	50+	17	N.D.	N.D.	N.D.
TDR Spot	Meas.	50+	22	13	50+	50+	17	N.D.	N.D.	N.D.
Viscosity at -20°C, cSt	Calc.	5.8	8.1	5.9	6.3	6.8	6.9	5.0	8.2	8.6
Specific Gravity	Calc.	0.8524	0.8382	0.8075	0.8668	0.8326	0.8036	0.8530	0.8368	0.8064
Freezing Point, °C	Calc.	-52	-30	-41	-34	-22	-23	-44	-43	-34

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*N.D. Not Determined

TABLE 8. AROMATIC-CONTENT BLENDS

COMPOSITION, VOL%

Blend Sample Code	6a AL-11279-F	6b AL-11568-F Cracked	6c AL-11280-F	7a AL-11281-F	7b AL-11278-F	7c AL-11282-F
Blend Stocks						
Jet A AL-10582-T	96.0	---	---	---	---	---
Heavy aromatic naphtha AL-10735-A	4.0	22.0	44.2	12.5	34.0	54.3
Straight run kerosene AL-9749-F	---	---	55.8	---	---	---
Hydrocracked kerosene AL-11381-F	---	78.0	---	---	---	---
Hydrocracked kerosene AL-9998-F	---	---	---	87.5	66.0	45.7

TABLE 9
AROMATIC-CONTENT BLEND PROPERTIES

Blends Sample Code		6a AL-11279-F	6b Crkd AL-11568-F	6c AL-11280-F	7a AL-11281-F	7b AL-11278-F	7c AL-11282-F
PROPERTY							
Aromatics, Vol%	Target	205	35±5	50±5	20±5	35±5	50±5
	Meas.	21.4	34.8	50.5	20.9	35.5	50.5
	Calc.	20	35	50	20	35	50
Sulfur Total, Mass %	Meas.	0.01	0.04	0.09	0.02	0.07	0.02
	Calc.	0.016	0.04	0.09	0.03	0.07	0.11
Sulfur, Mercaptans, Mass %		0.0001	0.0002	0.0009	0.0003	0.0006	0.0010
Distillation, °C							
IBP	Target	←	180 – 200	→	←	140 – 160	→
IBP	Meas.	183	178	181	152	156	162
IBP	Calc.	183	179	184	150	156	162
10% recovered	Meas.	198	197	206	186	194	192
50% recovered	Meas.	213	219	231	223	222	219
90% recovered	Meas.	252	253	252	263	262	257
FBP	Meas.	271	285	270	308	306	297
FBP	Calc.	264	274	282	312	305	297
FBP	Target	←	260 – 290	→	←	290 – 335	→
Flash Point, °C	Meas.	65	63	65	47	52	54
Smoke Point, mm	Meas.	18.9	14.0	11.3	18.9	14.1	10.1
Napthalenes, Mass %	Meas.	1.2	3.0	11.4	1.9	4.4	6.7
	Calc.	1.2	3.0	9.9	1.7	3.9	6.0
Hydrogen, Mass %	Meas.	13.70	N.D.*	12.11	13.53	12.86	12.30
	Calc.	13.7	13.2	12.1	13.7	13.0	12.4
Carbon, Mass %	Meas.	86.18	N.D.	87.81	85.93	86.78	87.47
Net Heat of Combustion							
MJ/kg	Meas.	43.627	N.D.	45.091	43.645	43.294	42.540
BTU/lb	Meas.	18756	N.D.	18386	18764	18613	18285
Nitrogen, ppm	Meas.	N.D.	N.D.	N.D.	10	7	13
Freezing Point, °C	Calc.	-46	-43	-37	-37	-38	-43
Viscosity at -20°C, cSt	Calc.	5.4	5.6	7.1	8.3	8.2	7.4
Specific Gravity	Calc.	0.8178	0.8339	0.8596	0.8186	0.8368	0.8538

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*N.D. Not Determined

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Viscosity and Naphthalene-Content Blends

The formulation for the viscosity and naphthalene-content blends are shown in Table 10 and their properties in Table 11. The computer calculations provided blends meeting target values for viscosity IBP and FBP for the viscosity-controlled blend 8b, but not for blend 8a. The computer calculation was based on a target viscosity value of 4 cSt at -20°C; however, the tolerance was ± 2 which did not enter into the computer calculation. Using a viscosity blending chart, the viscosities of the blending stocks Jet A (AL-10582-T) and kerosene from Alaska (AL-11310-F) were used to calculate a blend with a viscosity of 5 cSt, which is still within the ±2cSt tolerance range of the target value.

The final blend 8a, then, was prepared based on the above calculation; however, the IBP was 2°C below the target limit. One component of blend 8b, light cycle oil (AL-11276-F), has a freezing point of -13°C, which is above the -20°C temperature for viscosity measurement, hence the viscosity could not be measured directly. Therefore, measurements were made at 0 and 40°C, the values were plotted on an ASTM standard viscosity versus temperature chart and extrapolated to -20°C. The value at this temperature was entered into the computer data base for calculation of blend 8b. The FBP for this blend was 4°C above the target value.

The naphthalene-content final blends, 9a and 9b, were prepared according to computer calculated formulations as shown in Table 10. The properties for these blends appear in Table 11.

Composition-Controlled Test Fuels

The composition-controlled test fuels were designed to be controlled by hydrogen content and hydrocarbon type in addition to IBP and FBP. Two base blending stocks were to be essentially free of aromatic components, one composed of normal and isoparaffins only and the other with single and double ring naphthenes. The aromatic blending components would be of three types: alkyl benzenes, naphthene-benzenes (tetralin), and alkyl naphthalenes. The base paraffinic fuels originally

TABLE 10. VISCOSITY AND NAPHTHALENE-CONTENT BLENDS COMPOSITION, VOL%

Blends Sample Code	8a AL-11408-F	8b AL-11328-F	9a AL-11317-F	9b AL-11318-F
Blending Stocks				
Jet A AL-10582-T	60	---	---	---
Kerosene - Alaska AL-11310-F	40	---	---	---
Light Cycle Oil AL-11276-F	---	62.8	32.3	---
Kerosene AL-10724-F	---	37.2	67.7	18.0
Straight run Kerosene AL-9749-F	---	---	---	82.0

TABLE 11
VISCOSITY AND NAPHTHALENE-CONTENT BLEND PROPERTIES

Blends		8a	8b	9a	9b
Sample Code		AL-11408-F	AI-11328-F	AL-11317-F	AL-11318-F
PROPERTY					
Aromatics, Vol%	Meas.	15.8	45.4	29.2	22.8
	Calc.	15.1	46.1	29.7	21.9
Sulfur Total, Mass %	Meas.	0	0.15	0.08	0.01
	Calc.	0.005	0.14	0.07	0.008
Sulfur, Mercaptans, Mass %	Meas.	0	0.0032	0.0012	0.0002
Distillation, °C					
IBP	Target	← 165 - 195 →			
IBP	Meas.	163	172	169	173
	Calc.	170	185	175	187
10% recovered	Meas.	182	203	192	211
50% recovered	Meas.	207	246	218	232
90% recovered	Meas.	242	304	284	248
FBP	Meas.	274	339	325	267
	Calc.	271	305	274	274
	Target	← 260 - 335 →			
Flash Point, °C	Meas.	48	59	53	61
Viscosity at -20°C, cSt	Target	4±2	11±2	-	-
	Meas.	4.81	10.10	N.D.	N.D.
	Calc.	4.7	11.0	6.7	7.2
Nitrogen, ppm	Meas.	10	47	21	10
Hydrogen, Mass %	Meas.	N.D.*	11.92	12.89	13.30
	Calc.	13.9	11.9	13.0	13.3
Carbon, Mass %	Meas.	N.D.	87.75	86.79	86.44
Smoke Point, mm	Meas.	23.8	9.6	14.3	15.1
Naphthalenes, Mass %	Target	-	-	16±2	8±2
	Meas.	0.5	29.0	17.45	8.66
	Calc.	0.5	29.0	16	8
Net Heat of Combustion					
MJ/kg	Meas.	N.D.	N.D.	43.048	43.433
BTU/lb	Meas.	N.D.	N.D.	18531	18673
Specific Gravity	Calc.	0.8078	0.8730	0.8350	0.8268
Freezing Point, °C	Calc.	-45	-19	-26	-29

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*N.D. Not Determined

recommended were JP-7 for normal and isoparaffins, RJ-1 for the cycloparaffin or naphthenic fuel. The JP-7 available to this program was manufactured by Ashland Oil Company and their mass spectrometry analyses of the saturate fraction gave the following results:

Normal and Branched Alkanes	68.0%
1-ring Naphthenes	18.5%
2-ring Condensed Naphthenes	9.7%
3-ring Condensed Naphthenes	2.3%
4-ring Condensed Naphthenes	0.7%
5-ring Condensed Naphthenes	0.8%
6-ring Condensed Naphthenes	0.0%

The fuel had about 3 percent aromatic content; however, the high (32%) naphthene concentration was not acceptable and no other source of JP-7 was found. Therefore, a search for other paraffinic base stocks resulted in the selection of two solvents available from Exxon: Isopar G and Isopar M (the predominant component in Exxon's JP-7). The hydrocarbon type analyses by mass spectroscopy for these two samples in Table 12 show 8.6 and 16.3 mass% naphthenes, respectively. A blend of 50 percent of each component was determined to give smooth boiling curve. The blend was used as the paraffinic base stock for the composition-controlled test fuels and was estimated to contain 12.4 mass% naphthenes. A one-quart sample of Isopar M received earlier in the program and analyzed by a different laboratory according to the mass spectrometry method D 2425, gave the following results:

Normal and isoparaffins	80.3 mass %
Monocycloparaffins	16.8 mass %
Dicycloparaffins	2.4 mass %
Tricycloparaffins	0.2 mass %
Alkyl benzenes	0.3 mass %

From this analysis, the solvent showed a moderate amount of monocycloparaffins, but was virtually free of aromatics, and was sufficiently high in normal and

TABLE 12
BLENDING STOCKS FOR COMPOSITION-CONTROLLED BLENDS

SAMPLE CODE	FL-0265-F	FL-0266-F	FL-0283-F	AL-11286-A	AL-9762-A	FL-0268-S
Description	Isopar G	Isopar M	Dearomatized Mirando Kerosene	Xylene Tower Bottoms	Tetralin Solvent	Naphthalene Solvent
Source	EXXON	EXXON	SIGMOR/SwRI	SUNTECH	DUPONT	MARATHON
Properties						
Hydrogen Content, Mass %	15.28	15.02	13.43	9.78	9.16	7.77
Carbon Content, Mass %	84.05	84.82	86.33	90.25	90.84	92.25
Boiling Range, °C						
IBP	159	203	152	143	-	238
10% Recovered	163	209	207	147	-	243
50% Recovered	166	219	239	151	207(BP)	248
90% Recovered	171	243	261	163	-	264
EP	207	269	285	198	-	301
Smoke Point, mm	44.4	36.6	17.5	7.3	6.6	5.3
Heat of Combustion, net. MJ/kg	43.73	43.98	42.80	40.12	40.89	39.71
Sulfur Content, Mass %	0.01	0.01	0.01	0	0.01	0.01
Specific Gravity, 15/15°C	0.7805	0.7487	0.8670	0.8740	0.9738	1.0014
Viscosity @ -20°C	3.22	11.85	13.48	1.59	6.57	Froze
Aromatics, FIA, v%	0.4	2.5	4.1	99.6	98	100
Olefins, FIA, v%	0.8	1.4	3.8	0.4	0	0
Saturates, FIA, v%	98.6	96.1	92.1	0	2	0
Freezing Point, °C	-70	-73	-70	-72	-35	-7
Flash Point, °C	38	72	50	34	74	105
Naphthalenes Content, v%	0.001	0.004	0.01	0.20	0.68	73.4
Hydrocarbon Types, D2425, Mass %						
Paraffins	91.4	83.7	16.32	1.2	0.3	1.2
Noncondensed Cycloparaffins	8.6	14.7	0.88	-	-	-
Condensed Dicyloparaffins	-	1.6	59.64	-	-	-
Condensed Tricycloparaffins	-	-	17.81	-	-	-
Total Naphthenes	8.6	16.3	78.82	2.2	0.9	-
Alkylbenzenes	-	-	3.88	96.5	18.1	3.2
Indanes/Tetralins	-	-	0.67	-	80.4	4.3
Indenes/$C_n H_{2n-10}$	-	-	0.14	-	-	2.2
Alkylnaphthalenes	-	-	0.12	0.1	-	89.1
Acenaphthenes	-	-	0.02	-	0.2	0.1
Fluorenes	-	-	0.02	-	0.1	-
Triaromatics	-	-	0.02	-	-	-

isoparaffins to be suitable as a basestock. Based on these analyses, the 50/50 mixture of Isopar G and M represents the best possible basestock which could be found for normal and isoparaffins.

The RJ-1 fuel recommended as a potential naphthene base fuel was not available, and an exhaustive search failed to locate a fuel, solvent, or refinery stream with a high percentage of cycloparaffins. A kerosene refined from a Mirando crude known to be highly naphthenic was obtained from the Sigmor Three Rivers Refinery and processed at SwRI for removal of aromatics by silica gel adsorption. (Mirando crude was the source of RJ-1.) The process employed is described in Appendix B. The properties for the dearomatized Mirando kerosene used as the naphthene base fuel are shown also in Table 12. Based on the mass spectrometry analysis for hydrocarbon type, this fuel contained 16 mass percent of normal and isoparaffins and the naphthene fraction was composed primarily of dicyclo- and tricycloparaffins. This fact may be beneficial to combustion testing since monocycloparaffins behave more like normal paraffins. Other aromatic-free naphthenic solvents investigated as candidates for the naphthenic base fuel contained a maximum of 58 vol% naphthenes.

The aromatic components selected for the composition-controlled blends are shown in Table 12. The xylene tower bottoms from Sun Tech was composed of 96.5 mass percent alkyl benzenes. The tetralin solvent from du Pont is reported by the supplier to contain 97 mass percent tetrahydronaphthalene. The mass spectrometry analysis by D 2425 gave 80.4 mass percent as shown in Table 12; however, since this is a relatively pure compound and D 2425 is intended for hydrocarbon mixtures, the tetralin concentration resulting from this test method was considered suspect. A gas chromatography analysis of the Tetralin solvent confirmed the 97 mass percent given by the supplier. Therefore, the du Pont analysis of

Tetrahydronaphthalene	97% (mass)
Decahydronaphthalene	2%
Naphthalene	1%

was used to calculate the composition of the blends that included tetralin solvent shown in Table 13.

TABLE 13
FINAL COMPOSITION-CONTROLLED BLENDS

Code Number Blend Number	FL-0279-F 10	FL-0280-F 11	FL-0281-F 12	FL-0284-F 13	FL-0285-F 14	FL-0286-F 15	FL-0287-F 16	FL-0288-F 17	FL-0289-F 18
Components, Mass %									
Isopar G, FL-0265-F	34.85	36.4	37.65	---	---	---	---	---	---
Isopar M, FL-0266-F	34.85	36.4	37.65	---	---	---	---	---	---
Mirando Kerosene, Dearomatized, FL-0283-F	---	---	---	74.52	78.22	83.57	47.12	54.8	65.9
Xylene Tower Bottoms, AL-11286-A	30.30	---	---	25.48	---	---	52.88	---	---
Tetralin Solvent, AL-9762-A	---	27.2	---	---	21.78	---	---	45.2	----
Naphthalene Solvent, FL-0268-S	---	---	24.70	---	---	16.43	---	---	34.1
Properties									
Hydrogen, Mass %									
Required	13.5±0.2	13.5±0.2	13.5±0.2	12.5±0.2	12.5±0.2	12.5±0.2	11.5±0.2	11.5±0.2	11.5±0.2
Measured	13.56	13.54	13.44	12.51	12.45	12.48	11.49	11.50	11.47
Carbon, Mass %	85.97	86.16	86.11	87.39	87.28	87.43	88.10	88.45	88.40
Distillation, °C									
IBP, Required	150±10	150±10	150±10	200±10	200±10	200±10	200±10	200±10	200±10
Measured	150	167	166	146	170	165	143	174	172
50% Recovered	174	194	199	228	229	242	177	216	242
EP, Required	300±10	300±10	300±10	300±10	300±10	300±10	335±10	335±10	335±10
Measured	262	260	278	286	285	294	291	283	287
Aromatics, vol% (FIA)	28.4	24.4	20.0	31.7	23.4	20.4	67.9	45.5	36.1
Olefins, vol% (FIA)	1.3	0.9	0.5	3.2	3.0	2.8	4.5	3.1	2.5
Saturates, vol% (FIA)	70.3	74.7	79.5	65.1	73.6	76.8	27.6	51.4	61.4
Flash Point, °C	38	50	48	44	55	58	38	63	66
Specific Gravity, 15/15°C	0.7941	0.8132	0.8081	0.8676	0.8883	0.8860	0.8697	0.9129	0.9082
Freezing Point, °C	<-71	<-68	-31	<-71	<-67	-48	<-68	<-68	-30
Viscosity @ -20°C, cSt	3.03	5.36	5.57	5.58	10.20	11.82	2.98	8.35	10.98
Naphthalenes, vol%	0.04	0.20	16.4	0.04	0.16	12.18	0.08	0.32	24.50
Hydrocarbon Types, D2425, Mass %									
Paraffins	61.4	63.7	66.2	12.5	12.8	13.8	8.3	9.0	11.2
Noncondensed Cycloparaffins	8.8	8.5	8.8	1.6	1.1	1.2	1.8	0.8	0.9
Condensed Dicycloparaffins	0.6	1.1	0.6	44.4	47.1	49.8	28.1	33.6	39.3
Condensed Tricycloparaffins	—	—	—	13.3	13.9	14.9	8.4	9.8	11.7
Total Naphthenes	(9.4)	(9.6)	(9.4)	(59.3)	(62.1)	(65.9)	(38.3)	(44.2)	(51.9)
Alkylbenzenes	29.2	—	0.8	27.5	3.0	3.8	52.9	2.1	3.6
Indanes/Tetralins	—	26.4	1.1	0.5	21.6	1.3	0.3	44.2	1.9
Indenes/C_nH_{2n-10}	—	---	0.5	0.1	0.1	0.5	0.1	0.1	0.9
Naphthalene	—	0.3	—	—	0.2	—	—	0.4	—
Alkylnaphthalenes	0.03	—	22.0	0.1	0.1	14.7	0.1	0.1	30.5
Acenaphthenes	—	—	—	0.01	0.02	0.02	0.01	0.01	0.01
Fluorenes	—	—	—	0.01	0.02	0.02	0.01	0.01	0.01
Triaromatics	—	—	—	0.01	0.02	0.02	0.01	0.01	0.01

Several sources of naphthalene blend stock were investigated for this program as follows:

Stock	Source	Range °C	Naphthalenes Vol %	% A, vol
Mixed naphthalenes	Koppers	142-303	73	99.96
AN-3N	Amoco	210-287	70	90
Aromatic 400	Getty	213-330	40	100
LG-3	Crowley	229-260	5-83	---
4555	Marathon	225-286	73	100

The final selection was the Marathon product based mainly on the fact that it was derived from petroleum. The Koppers material, the initial choice, is a coal-derived product. The analysis for naphthalene was performed by ASTM method D 1840 which is intended for analysis of straight-run jet fuels containing no more than 5 percent naphthalenes; therefore, the values shown may be in error. The mass spectrometer analyses of the Marathon naphthalene solvent (FL-0268-S) gave a value of 89.1 mass percent alkylnaphthalene as shown in Table 12.

The blending stocks shown in Table 12 permitted blending of nine composition-controlled fuels (blends 10 through 18) that met target values for hydrogen content, approached the desired hydrocarbon type composition, but failed to meet the target IBP and FBP values for 16 out of 18 data points. To meet the target boiling range values, additional paraffinic and naphthenic base fuels with broader boiling ranges would be needed to permit adjustment of the IBP and FBP of the composition-controlled test fuels. If such materials were found, thorough characterizations would be needed for hydrocarbons present. Specifically lengthening side chains on cycloparaffins would increase the end point of the boiling range, but would simultaneously increase the paraffinic combustion behavior. Cycloparaffins of increased ring size would also contribute to higher boiling ranges, but are not normally high in concentration in fuel sources.

Table 13 contains the formulation and analytical results for the nine composition-controlled test fuel blends. The hydrocarbon type analyses were calculated from the mass spectrometry analysis conducted on the components of each blend. One exception was the tetralin solvent in which the value given by the supplier was used in the calculation as explained earlier.

DISCUSSION OF RESULTS

The main result of the current work was developing a workable technique, or approach, to produce the PC and CC test fuels. In so doing, suitable blend stocks were identified and characterized. The tangible product, 68 five-gallon cans of test fuels and base stocks, will be important in laboratory and bench test work on combustion performance.

These materials meet the objectives set out in the two test fuel matrices. In some cases, the specific boiling range requirement of a fuel was relaxed, but all of the primary target properties were met. While it is true some of the base stocks are refinery streams--not articles of commerce, this aspect of the family of stocks makes it more general. The goal has been to find the source which would allow the test fuel targets to be met as closely as possible with readily obtainable intermediate refinery streams or final products, but not specialty chemicals.

Additional considerations concerning fuel sources include: the compositions of products and process streams change with time (depending on refinery objectives and the crudes available), samples drawn and analyzed may not agree in composition and properties with drums of product shipped, speciality materials may fit fuel needs, but may not be economic for larger-scale combustor testing. The last consideration emerged in searching for the CC naphthenic blend stock.

Of all the blending stocks used, only one, the light cycle oil (AL-11276-F), was suspect of not having adequate storage stability. A sample was evaluated by ASTM D 2274, Oxidation Stability of Distillate Fuel Oil (Accelerated Method) and gave a value of 4.8 mg/100 mL, well above the maximum permitted for some military diesel fuels (1.5 mg/100 mL). Therefore, those blends which had the light cycle oil as a component, and one can of this blending stock, were treated with antioxidant at 24 mg/L, composed of 72-percent 2,4-dimethyl 6-tertiary butyl phenol plus other alkylated phenols, prior to shipment to NASA-Lewis. Cans containing antioxidant were so marked.

There is no large-scale commercial use for a stock with an artificially high concentration of naphthenes such as was required as a CC base stock. Eventually, a kerosene made from Mirando crude was found. (Mirando is one of the Texas Gulf Coast crude segregations high in naphthenes.) This material is produced in conjunction with a higher-boiling fraction which is used in "low cold test" (low pour point) lubricants. The Mirando kerosene has had its aromatic content reduced by silica gel adsorption (Appendix B) before use in the fuel blends. Although this processing was an extra step in acquiring the naphthenic blend stock, it is a unit operation which is available at certain refineries that produce aromatic concentrates.

There were trade-offs in attempting to find a high percentage normal and isoparaffin stock for the CC fuels, and the cracked stocks for the PC blends. For instance, the intended paraffinic base stock, JP-7, was found to contain 32 vol% naphthenes. Improvement was made by selecting higher concentration paraffinic solvents of the correct boiling range. The upper end of the paraffinic boiling range (not covered by Isopar G or M) might be covered by a straight-run fraction from a paraffinic crude.

The property targets of the test fuels were achieved in most all cases. It was frequently difficult to meet the boiling range with the available stocks at the same time the main governing property was met. A contributing cause of this circumstance was the use of end point and initial point to mark the boiling range. The experimental measurement of these terminal points is much more erratic than interior points, say the 5 percent and 90 percent distilled temperatures. In addition the prediction of these extreme points is less accurate than previous estimates have shown averaging interior points to be.

In general, it took 4.2 trial blends per PC test fuel to achieve the target properties. As shown in Table 14, the blends using cracked stocks required 7.3 trial blends for completion. This higher number was in part due to the restricted selection of cracked stocks; however, the candidates were as numerous as most other base stock types. One contributing factor was the ability to estimate blend formulations involving cracked stocks (see below).

TABLE 14
BLENDING STATISTICS PROPERTY-CONTROLLED

Base stocks tried: 21
Base stocks selected: 11

Blend No.	# Components	# Trials	# Stocks Tried
1a	1	5	7
1b	2	8	8
1c crkd	2	10	8
2a	2	6	3
2b	2	5	3
2c	2	5	4
3a crkd	2	9	10
3b	2	2	2
3c	2	2	3
4a	3	2	3
4b	2	2	3
4c	2	2	4
5a	2	3	4
5b crkd	2	2	2
5c	2	5	4
6a	2	2	2
6b crkd	3	8	10
6c	2	3	2
7a	2	2	2
7b	2	2	2
7c	2	2	2
8a	2	5	6
8b	2	4	6
9a	2	4	5
9b	2	4	4

The smaller number of CC trial blends indicates the more direct approach apparent in Table 15. This is mostly because each base stock was uniquely chosen for its composition in an attempt to maximize the concentration of the various hydrocarbon types. This led to an attempt to achieve desired concentration of HC type, IBP, FBP, and mass%H with two or at most three components. This number of stocks did not permit adequate "degrees of freedom" to meet four independently chosen specifications. In this case, after HC type was maximized in the base stocks, the hydrogen content target was fulfilled allowing the boiling range to vary.

Most of the correlations in use today were developed in 1930-1950's when cracked materials were less common. The changing quality of crude stocks available and the emergence of synthetic crudes both work together to call into question the continuing accuracy of the standard blending and property correlations in use for aviation and other high-quality distillate fuels. Part of the current work is a brief examination of the effectiveness of the correlations used.

Some unusual materials (pure solvents, narrow cuts) used as base stocks for the CC test fuels were never part of the data sets from which blending correlations were derived. For this reason, the examination of the performance of the correlations is limited here to the PC blends.

First, the set of target properties was examined for the success in predicting property values of the blends from the measured values of the base stocks and the blend composition. Table 16 shows the results of this examination. The base stock properties in Table 3 were used with the compositions in Tables 4, 6, 8, and 10 to obtain the predictions in the third column. The predictions were made with the linear equations in Figure 4 or with the equations in Appendix A by the method described under the heading Blending Procedure. In keeping with the simplicity of composition-determined properties, mass% hydrogen and vol% aromatics, these blends showed low average deviations. The larger deviation shown by naphthalene content reflects uncertainty in the measuring method more than any peculiarity of the base stocks which were kerosenes and light cycle oil.

TABLE 15

BLENDING STATISTICS COMPOSITION-CONTROLLED

Base stocks tried: 24
Base stocks selected: 6

Blend No.	# Components	# Trials	Originally # Stocks Tried Base	Originally # Stocks Tried Arom.
10	3	2	5	7
11	3	2	5	1
12	3	4	5	2
13	2	2	9	7
14	2	2	9	1
15	2	2	9	2
16	2	2	9	7
17	2	2	9	1
18	2	2	9	2

TABLE 16
DEVIATION OF MEASURED & PREDICTED TARGET PROPERTIES OF PC BLENDS

All Target Properties by Blend

Blend No.	Required	Predicted	Measured	Difference
1a	Not a binary blend		-44.0	---
1b	-33.00 °C	-32.45	-32.00	0.45
1c crkd	-23.00 Freezing	-19.74	-20.00	-0.26
2a	-43.00 Point	-43.25	-46.00	-2.75
2b	-33.00	-31.87	-30.00	1.87
2c	-23.00	-22.36	-23.00	-0.64
3a crkd	11.80 M% H	11.80	11.62	-0.18
3b	13.00	13.00	13.05	0.05
3c	14.20	14.20	14.08	-0.12
4a	11.80	11.80	11.79	-0.01
4b	13.00	13.00	12.97	-0.03
4c	14.20	14.20	14.25	0.05
5a	11.80	11.80	11.79	-0.01
5b crkd	13.00	13.00	12.86	-0.14
5c	14.20	14.20	14.23	0.03
6a	20.00 V% A	19.99	21.40	1.41
6b crkd	35.00	35.00	34.80	-0.20
6c	50.00	49.99	50.50	0.51
7a	20.00	19.98	20.90	0.92
7b	35.00	35.42	35.50	0.08
7c	50.00	49.99	50.50	0.51
8a	4.00 mm^2/sec	4.71	4.81	0.10
8b	11.00 (=cSt)	11.24	10.10	-1.14
9a	16.00 V% Naph	16.05	17.45	1.40
9b	8.00	8.00	8.66	0.66

Averages by Property

Property	ASTM Method	# Averaged	Avg. Deviation
Freezing Point	D2386	5	1.19 °C
Hydrogen Content	D3178	9	0.06 M%
Aromatic Content	D1319	6	0.60 V%
Viscosity	D445	2	0.62 mm^2/sec
Naphthalene Content	D1840	2	1.03 V%

The freezing point and viscosity values for the test fuels were predicted with blending indices. The average freezing point deviation, 1.19°C, was a significant fraction of the range of deviations, -2.75° to 1.87°C or 4.62°C. The deviation for freezing point arises in part from the errors in the measurement method and the complicated behavior of the interactions of the hydrocarbon components with respect to the freezing of their solutions. The average deviation for viscosity in the target blends is uncharacteristically high due to the performance of blend 8b which suffered from the attempt to adhere to the boiling range and still possess a high viscosity.

When the results of the entire set of PC blends are considered, Table 17 can be made. In this table the differences for eight properties are shown. In the cases of freezing point, viscosity, smoke point, flash point, and heat of combustion, two values are given. The left columns are the differences between the measured values and the blend values predicted by volumetric averaging of blend stock properties. The differences in the right columns were formed from the measured values and blend values predicted by specific calculation, either blending correlations or other calculations. The last two rows, respectively, list the number of points considered by property for each property and average deviation. The deviation is the absolute value of the difference.

In each case, the deviations were less for the special calculation procedure than for linear blending calculation. (No comparison is possible for heat of combustion since the values for the blend stocks were determined on a mass-percent basis.) The blend properties which were determined by mass balances (mass% hydrogen, vol% aromatics, and vol% naphthalenes) showed lower average deviations in the entire set of blends than the target sets. Deviation for freezing point was smaller than in the target set. In the target set more selectivity was exercised with respect to the choice of base stocks appropriate to establishing the freezing point. These stocks were more like the materials originally used to derive the correlations. Of all blends, 1c showed the poorest performance as may be noted by its deviations being consistently high above average in all properties. While the use of a cracked base stock in blend 1c may be one cause, not all blends containing a cracked stock were poorly predicted. The best predicted blend was blend 2b.

TABLE 17
DEVIATION OF MEASURED AND PREDICTED PROPERTIES FOR ALL PC BLENDS

Blend No.	% Hydrogen	% Aromatic	% Naphthalene	Freezing Point		Viscosity		Smoke Point		Flash Point		Heat of Combustion
				Volume Linear	By Correlation	Volume Linear	By Correlation	Volume Linear	By Correlation	Volume Linear	By Correlation	
1a	-	-	-	-	-	-	-	-	-	-	-	-
1b	-0.04	+0.02	-	+ 4.48	+0.45	-0.31	-0.03	-	-	-10.48	-8.02	-
1c (Crkd)	-0.95	+0.07	-	+ 4.78	-0.26	-5.74	-0.97	-	-	-8.92	-7.99	-
2a	-0.02	+0.01	-	+ 0.00	-2.75	+0.17	+0.20	-	-	-2.18	-1.95	-
2b	+0.02	+0.00	-	+ 7.74	+1.87	+0.00	+0.09	-	-	-2.08	-1.22	-
2c	-0.11	-0.08	-	+ 0.64	-0.64	-0.15	-0.03	-	-	-2.36	-1.34	-
3a (Crkd)	-0.18	+0.41	+0.38	+ 5.94	+0.23	-1.41	-1.15	-2.38	+0.09	-0.17	-0.02	-169.74
3b	+0.05	+1.69	+0.84	+ 0.85	-0.91	+0.08	+0.12	-1.29	-0.48	+2.45	+2.49	+213.79
3c	-0.12	+0.79	+0.07	+ 2.86	+2.42	-0.03	-0.00	-0.14	+0.57	-3.09	-2.56	+ 92.57
4a	-0.01	-0.43	+0.22	+18.99	+3.13	+0.01	+0.05	-2.33	+1.06	+1.09	+1.91	+223.57
4b	-0.03	-0.16	-0.04	+13.44	+4.08	-0.07	-0.03	-4.89	+0.68	+1.46	+2.45	+173.27
4c	+0.05	+0.65	-0.00	+ 6.76	+3.78	+0.00	+0.02	+0.46	+0.75	-1.25	-1.19	+146.38
5a	-	-	-	-	-	-	-	-	-	-	-	-
5b (Crkd)	-0.14	+0.08	+0.48	- 9.34	-20.02	-0.39	-0.07	-2.80	+1.37	+0.26	+0.65	+326.73
5c	+0.03	+0.91	+0.02	- 9.66	-12.39	-0.27	-0.04	+2.38	+2.97	-7.34	-5.70	-
6a	+0.01	+1.41	+0.05	+ 2.74	+2.43	+0.02	+0.02	-2.58	-1.49	+5.04	+5.04	+188.70
6b (Crkd)	-	-	-	-	-	-	-	-	-	-	-	-
6c	-0.06	+0.51	+1.48	+ 7.80	-0.98	-0.06	+0.06	-1.00	+0.99	+2.65	+2.79	+162.08
7a	-0.15	+0.92	+0.21	-13.87	-17.92	-1.17	-1.01	-1.22	+1.55	-2.37	-2.19	+306.86
7b	-0.14	+0.08	+0.48	- 4.34	-15.02	-0.39	-0.07	-2.80	+1.37	+0.26	+0.65	+326.73
7c	-0.06	+0.51	+0.67	+ 0.61	-14.84	-0.35	-0.02	-3.76	-0.07	+0.03	+0.48	+157.42
8a	-0.01	+0.74	+0.00	+ 1.40	+0.77	+0.03	+0.10	+0.60	+0.66	-6.80	-6.18	-
8b	-0.06	-0.72	-0.05	+ 5.90	+1.37	-5.60	-1.14	-4.59	+0.08	+0.09	+0.53	-
9a	-0.14	-0.55	+1.40	+ 8.66	+3.51	-	-	-5.87	+0.48	-2.55	-2.17	+ 17.51
9b	-0.05	+0.89	+0.66	+ 2.06	+1.19	-	-	-3.20	-2.60	-1.66	-1.25	+ 48.66
No. Averaged	22	22	17	22		20		17		22		14
Avg. Deviations	0.11	0.53	0.41	6.04	5.04	0.81	0.26	2.49	1.02	2.94	2.67	182.43

CONCLUSIONS

The aims of both of the test fuel matrices have been fulfilled although boiling range requirements had to be relaxed in some cases. In this way some of the specific requirements have changed to accommodate the base stocks which exist. In the case of high concentration naphthenes, no stock exists in commerce, so one was made. It can be replicated at larger scale in a small refinery. All the other stocks came from commercial sources either as specification, commercial products or as usually encountered intermediate streams.

By searching among available base stocks, the PC fuels were produced. The approach of a computer-prediction plus blending iteration was successful both at producing trial formulations and winnowing the candidate base stocks. This calculate-and-blend method also quickly revealed which aspects of the matrix of requirements were more challenging to meet.

The CC fuels all have compositions resembling the ideals encompassed in the original matrix. The key is the very low aromatic content of the base stocks coupled with specific HC type aromatic blending components. By using a straight-run kerosene and commercial solvent, the types of major hydrocarbon and lesser constituents show a more typical composition which would not be possible if coal liquids or pure compounds alone were used. The exception is the tetralin which is nearly a pure material.

In all cases of PC and CC, new test blends can be made by interpolating between the 34 existing test fuels. Particular care should be given to freezing point blends and volatility ranges. Consideration might be given to using D-86 5 percent and 90 percent recovered temperatures as volatility range delimiters. If large quantities are to be produced, analyses must be made on samples of the candidate stocks during selection and repeated upon delivery.

The operation of the blending correlations is very good for all properties and all stocks except <u>some</u> cracked stocks. When the percent deviation rises about 5 percent, questions should be raised about why the deviations are occurring and what treatment they warrant. In the current matrix, a family of blends of the cracked base stocks distributed about the target point spanning the full range of compositions would help resolve their behavior. If only some cracked stocks are anomalous, a larger selection of cracked materials could be explored to seek the reasons.

The irregular behavior of the deviations for naphthalene blends should be noted. The materials used in the naphthalene target blends also produced high deviations.

APPENDIX A
BLENDING CORRELATIONS

Nonlinear Blending Relations

Correlations

Viscosity, (VIS)

Chevron Viscosity Blending Index Function 2

$$VI_i = \frac{\mathrm{Log}\ (VIS_i)}{\mathrm{Log}\ (VIS_i)+3} \qquad VIS = 10^{\left(\frac{3 * VI}{1 - VI}\right)}$$

(mm^2/sec or cSt)

Freezing Point, (FP)

Chevron Freezing Point Blending Index

$$FPI_i = \exp\left(\frac{54\ (FP_i - 125)}{1800 - T50_i}\right) \qquad FP(°F) = \frac{(1800 - T50)\ \ell n\ FPI}{54} + 125$$

To convert to °C

$$FP(°C) = \frac{5}{9}\ (FP(°F)-32)$$

Flash Point (FLP)

Chevron Flash Point Blending Index

$$FLPI_i = e^{(-0.03\ FLP_i)} \qquad FLP(°C) = -\frac{\ell n\ FLPI}{0.03}$$

Calculations

Heat of Combustion - Blended by Mass (ΔH)

$$\Delta H(MJ/Kg) = \sum_{i=1}^{n} v_i\ \frac{SG_i}{SG}\ \Delta H_i$$

Smoke Point (SP)

$$SP(mm) = \left[\sum_{i=1}^{n} \frac{v_i}{SP_i}\right]^{-1}$$

APPENDIX B
PROCESSING THE NAPHTHENIC BASE STOCK

The aromatic concentration of the naphthene-rich Mirando kerosene had to be reduced to control interferences with the intentionally added aromatic components. Several approaches were attempted. Adsorption on alumina and solvent extraction proved unworkable. The method which showed most promise and which was finally developed for processing was column elution chromatography on a large-scale using silica gel. The new and unique features of the process are in the adsorbent regeneration step.

A first attempt at adsorption of aromatics from neat kerosene on silica gel was unsuccessful. The initial effluent was aromatic-free, but the aromatic front moved rapidly through the column indicating an apparently low capacity. Next, elution chromatography modeled after ASTM D 2549 was tried.

A glass column 1000 mm in length with an I.D. of 12 mm was packed with 83.7 g of 100-200 mesh silica gel. A 50-g quantity of Mirando kerosene was diluted with 40 mL of n-pentane and added to the column which was pre-wetted with 45 mL of n-pentane. The flask that contained the kerosene and n-pentane was rinsed with three 5 mL portions of n-pentane which were added to the column. An additional 70 mL of n-pentane were added after which a slight pressure was applied.

N-pentane containing most saturated hydrocarbons was collected. When the top of the n-pentane layer reached about 1/3 of the way down the column, ethyl ether was added, followed by chloroform and ethyl alcohol. These three solvents removed the aromatics from the column. The n-pentane containing the saturate fraction was evaporated on a rotary vaporizer (Rotovapor) after which the ether and chloroform-ethanol fractions were evaporated to recover the aromatics.

To determine the feasibility of reusing the silica gel, the packing was removed from the column, dried in an oven, and recharged to the column. A fresh 50 g sample of

Mirando kerosene was separated (chromatographed) following the same procedure outlined above.

A third separation was performed using fresh silica gel, but only 25 g of Mirando kerosene with the same volumes of n-pentane and the other solvents. The results of these three chromatographic separations were as follows:

Separation:	1st	2nd	3rd
Silica gel condition	Fresh	Re-used	Fresh
Sample size, g	50	50	25
Recovered, g			
Non-aromatics	40.735	38.661	20.403
Aromatics	8.792	10.936	4.493
Total	49.527	49.597	24.896
FIA analysis on non-aromatic fraction			
Aromatics, V%	8.3	8.9	3.4
Olefins, V%	3.8	2.9	2.9
Saturates, V%	87.9	88.2	93.7
FIA analysis on aromatic fraction			
Aromatics, V%	---	---	99.8
Olefins, V%	--	---	0.2
Saturates, V%		---	None

The FIA analyses for the neat Mirando kerosene was 24.7% aromatics, 1.8 % olefins, and 73.5% saturates. The olefin analyses by the FIA procedure was indicated by a yellow fluorescense of added indicator dye in the silica gel column. It is known, however, that some hydrocarbons other than olefins do contribute to the yellow fluorescense; therefore, the level of olefins present as indicated by this method may be high.

These experiments show that:

1. The aromatics in the Mirando kerosene can be removed by elution chromatography. The requirements to scale up this process to enable the practical treatment of Mirando kerosene can now be evaluated.
2. The silica gel could be re-used without apparent loss in adsorption effectiveness.
3. The higher ratio of n-pentane to kerosene in the feed to the column provided much better separation of the aromatics and non-aromatics.

The most complicated part of the procedure was the regeneration. For this reason, simplification was sought. Two techniques seemed promising. In the first method (A) after the saturates have been eluted with n-pentane, toluene is used to elute the aromatics adsorbed on the silica gel. Afterwards, n-pentane is again used, but this time to free the column of toluene. A second method (B) sought to achieve regeneration with ethyl alcohol followed by heating of the column and drying by a current of nitrogen.

The percent by volume of aromatics obtained in these trials were as follows:

Cycle	0	1	2	3
Method A	19.1	11.3	2.1	3.7
Method B		10.6	21.7	---

The first cycle of Method A showed higher aromatic percentages than were later obtained at least in part, because the flowrate from the column was higher than desired. In subsequent runs the flow was reduced to between three and four mL/min. Method B was not pursued since full regeneration was not achieved.

A sample of bulk-grade silica gel was tested for fitness in the column. All runs were made at between 3 and 4 mL/min. The first attempt followed the sequence of method A above, while the second try began directly with the toluene addition to see whether preconditioning could lower the high aromatic concentration evident in the first series and in the trials on reagent-grade silica gel. The results (percent aromatics by volume) were:

Cycle	0	1	2
First instance	19.1	12.6	2.3
Second instance		6.6	2.0

The pre-conditioning with toluene improved the effectiveness of the silica gel separtion during the first cycle.

With a method worked out, scaleup began in a four-inch ID column. The commercial grade Grace silica gel was activated overnight at 200°C before charging. The kerosene and pentane were preblended before pumping to the top of the column. Rotary evaporation was replaced by fractional distillation.

The product from the first batch showed <u>no</u> aromatics at a flowrate of about 100 mL/min. The second run contained 1.3 percent aromatics by volume, having been eluted at about three times the flow rate of the first run. With the flow parameters worked out, measuring aromatic content of each batch was discontinued.

Additional column space was set up as were two other small stills. The aromatic content of the first batch from the larger column was 1.1 percent by volume. The overall through-put of columns and stills ranged from 9 to 12 liters/day. Distillation and collection of pentane required ice-water cooling and was the bottleneck in the operation. Considering labor costs, it was more economical to distill only the pentane from the collected saturates. The pentane used to regenerate the column was left with the toluene when it was clear that it was three times as expensive to reclaim it as to procure fresh pentane.

Approximately 38 gallons of dearomatized kerosene were obtained from the processing of Mirando kerosene through the 4" and 6" columns. The final composite dearomatized kerosene had an aromatic content of about 4.1 volume percent, which was higher than the first few batches of processed material. This is attributed tentatively to loss of adsorption efficiency of the silica gel columns, although this has not been confirmed. Adsorption of water and other polar materials can contribute to the decline. This value is very similar to that for fuel RJ-1 originally suggested as the naphthenic blending stock for this program.

APPENDIX C

ABBREVIATIONS AND SYMBOLS

ASTM	American Society for Testing and Materials
CC	Composition-controlled
C_n	Carbon number n (n is a numeral)
CO	Carbon monoxide
CRC	Coordinating Research Council
Crkd	Cracked
EP	End point
ERBS	Experimental referee broadened specification fuel
FBP	Final boiling point
FIA	Fluorescent indicator analysis
FLP	Flash point
FLPI	Flash point blending index
FP	Freezing point
FPBI	Freezing point blending index
HC	Hydrocracked or hydrocarbon
H/C	Ratio of hydrogen to carbon by mass
IBP	Initial boiling point
I.D.	Inner diameter
JFTOT	Jet fuel thermal oxidation test
M%	Mass percent
M%A	Mass percent aromatics
M%H	Mass percent hydrogen
MIT	Massachusetts Institute of Technology
n	Number of components
Naph	Naphthalenes
NASA	National Aeronautics and Space Administration
ND	Not determined
PC	Property-controlled
PPM	Parts per million

SG	Specific gravity
SP	Smoke Point
SwRI	Southwest Research Institute
T50	ASTM D 86 50% temperature
TDR	Tube deposit rating
v	Volume fraction
VI	Viscosity blending index
VIS	Viscosity
vol%, V%	Volume percent
vs	Versus
ΔH	Heat of Combustion

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