Executive Summary

Emissions and performance have become the dominant factors governing the acceptability of diesel fuel. The properties of the diesel-blending components and the role of alternative fuels for exhaust emissions are the subjects of this report. Correlations were made for exhaust emission components and engine performance from a very carefully prepared set of test fuels designed to reveal the relationships arising from blendstock composition and origin.

Because full-boiling diesel fuels show wide quality variations and the history of most commercial fuel is difficult to determine, a detailed study was made of three petroleum blendstocks and two alternative components in the diesel boiling range. The blendstocks were hydrogenated at two severities to make reduced sulfur (0.05 mass%) and low aromatic-content (10 vol%) products for each one. The original stocks and components and their processed products were then each distilled into six to eight narrow boiling fractions at 40°F intervals. This effort produced a set of 80 test fuel samples for the program.

Each sample was then subjected to physical and chemical analyses in the laboratory followed by combustion testing in a constant volume combustion apparatus (CVCA) and a variable compression ratio (VCR) engine. Ignition quality was measured in several ways, and exhaust emissions composition were obtained for all samples that could be run in the combustion tests (several fractions were too viscous to test). The matrix of results thus obtained was examined statistically for coverage of the variable space and for autocorrelation. This large data set was used to construct correlations for cetane number and the key emissions components.

The properties of the test fractions and the correlations were inputs to the last phase of the work — a "Clean Fuel Study". A set of fuel specifications was devised to represent a future low-emission diesel fuel. Using linear programming to calculate proportions of each component to use, several blending concepts were examined. These included:

- minimum overall emissions with and without alternative components,
- a series of varied aromatic compositions at 55 cetane number,
- a series of blends with 15 vol% aromatics having variable cetane number.

A set of 10 minimum-emissions recipes was developed, test fuels were blended, and combustion tests were made just as had been performed on the 80 fractions. The predictions compared very well with measured results and were the basis for 13 conclusions. The rest of the executive summary outlines some of the details of the project.

RATIONALE

The broad objective was to relate diesel fuel exhaust emissions to chemical composition and physical properties. The approach usually used for such a study has been to blend or analyze full boiling-range test fuels for engine studies. In the current work, the broadest region of concentrations of the various hydrocarbon types encountered in diesel fuel was preserved by working with the diesel fuel components directly, rather than specification fuels. To separate the effects of boiling range (or molecular weight), distillation was used as a probe of the test fuels, and by this means, a broad range of physical properties was also obtained.

This emphasis on stretching the boundaries of physical and chemical variables assured good coverage of the variable space for the mathematical correlation of measured performance and emissions. This course was settled upon because a study of pure compounds in the diesel range represents an impossible amount of work, and the ability to describe the multiple interactions is not developed. The more practical approach

of making narrow boiling-range cuts and using hydrocarbon type analyses gave good coverage of the variables and still allowed attribution of results to the hydrocarbon stream used for the source.

The correlations were used to design low-emission, proof-of-concept test fuels in the last phase of the work. This too required careful reasoning in the choice of general diesel specifications. While exploring the lowest emissions available from the current set of 10 diesel blendstocks, the blends were kept within specifications recognizable by contemporary engines. Also, by making several low-emission test fuels, the effect of cetane number was allowed to float and represents the options facing engine designers and regulators today.

FEEDSTOCKS

In today's refineries, diesel fuel is blended from a variety of streams in the 350° - 650°F (177°– 343°C) boiling range, but it is the materials made from boiling-range conversion processes that are most often implicated in poor performance and emissions. These problem materials include products of coking and cracking. Accordingly, feedstocks for the *Diesel Assay* were:

- light cycle oil (LCO), product of catalytic cracking
- light coker gas oil (LCGO), made by thermal cracking

Cracked materials typically come from gas oil or residuum conversion and thus represent the higher-boiling, more aromatic materials in the refinery. A typical, high quality diesel component was selected to balance the blends:

- straight-run diesel (SRD), a paraffinic basestock

An alternative fuel stock available in pilot-plant quantities and attractive to consider for future use in diesel fuel is the diesel fraction of indirect coal liquefaction such as Fischer-Tropsch (F-T) liquid.

In this study, two different F-T diesels were included:

- diesel distillate (F-T1), from Arge wax cracking
- straight-run diesel (F-T2), from the Air Products DOE pilot plant

These materials are almost all paraffins and represent a high cetane-number candidate for diesel blending.

PROCESSING

Hydrogenation was used at two severities: (1) to lower sulfur to ~0.05 mass%, and (2) to lower aromatic concentration to 10 vol%. These levels were chosen in view of current and projected pollution-control regulations, which prescribe limits on sulfur and aromatics. For all work, commercial nickel molybdenum catalyst was used with reactor temperatures in the 630° — 710°F range and pressure 600 — 2300 PSIG. The SRD was low in sulfur, so only a low aromatic, straight-run diesel was produced (LASRD). For the LCO and LCGO, both low sulfur (LSCLO and ISLCGO) and low aromatic (LALCO and LALCGO) products were produced. The F-T liquids required no processing. All the processing work was done in the U.S. Department of Energy (DOE) Alternative Fuels Utilization Program, Alternative Fuel Center at Southwest Research Institute, which was established under the DOE Alternative Fuels Utilization Program (AFUP).

This work yielded 10 materials for further study. The first step was to distill each of the 10 liquids into six to eight fractions of approximately 40°F (22°C) boiling range. The distillations were conducted with

a procedure similar to the ASTM D 2892 vacuum distillation. This gave a set of 80 samples, each approximately two liters in volume, for laboratory and combustion testing.

LABORATORY ANALYSES

The suite of laboratory analyses was applied to the 80 fractions made by vacuum distillation. These tests were selected to emphasize the properties believed to be most responsible for performance and emissions, aromatic structure and boiling range. The tests included:

- Distillation
    - D 86
    - D 2887

- Density

- Elemental
    - carbon, D 3178
    - hydrogen
    - sulfur, D 2622

- Aniline Point

- Smoke Point

- Pour Point & Cloud Point

- Refractive Index

- Hydrocarbon Type
    - D 1319, FIA
    - D 2425, GC-MS
    - NMR
    - UV Aromatics

- Viscosity
    - 40°C
    - 100°C

The multiple measures for aromatics represented by the four hydrocarbon type methods were chosen because of variation in values determined among aromatics content measurement methods. While some duplication resulted, different purposes were served including a more definitive determination in the case of the NMR analysis and more widespread availability exemplified by ASTM D 1319 Fluorescent Indicator Analysis (FIA).

COMBUSTION TESTING

CVCA

The 80 fuels in the main fuel matrix were tested at three different temperatures and pressures in a constant volume combustion apparatus. The results of these experiments, in the form of autoignition delay times, were used to develop Arrehenius expressions of the delay time as functions of temperature. These results indicated that the ignition delay times were strong functions of the boiling point distribution and the temperatures. The activation energies were also observed to be related to the boiling point distribution. Cetane numbers, determined from the delay times, also were strongly related to the boiling point of the fuel fractions and the feedstocks used to produce the fractions.

VCR Engine Tests

The 80 fuels were also tested at six different speed-load conditions in a direct-injection, variable-compression-ratio (VCR) test engine. The engine was designed specifically for fuels evaluation, and incorporated a bore-to-stroke ratio, swirl ratio, injection system characteristics, and combustion chamber geometry similar to current technology, two-valve engines. The engine was used to rate the ignition quality of the materials and to document the performance and emissions characteristics at five different speed-load test conditions.

STATISTICAL ANALYSIS

The results of the ignition quality measurements, in terms of a VCR cetane rating, compared very well with similar results obtained in the CVCA. The performance and emissions data were used to develop regression equations for the emissions and selected performance parameters in terms of the fuel composition and properties. Eighty-one different fuels and engine combustion variables were included in the statistical analysis. Preliminary analysis indicated the importance of (1) aromatic type and quantity, (2) cetane number, (3) boiling point, and (4) relationships to other hydrocarbon constituents. These relationships all appeared to be linear in the range of interest in this study.

CLEAN FUEL STUDY

The fact that the fuel properties were linearly related to the emissions justified the use of linear programming to design 10 low-emissions fuels using the same blendstocks and components that were used to develop the data base. These new fuels were tested following the same procedures that had been used in measuring the properties of the 80 test fuel samples. The results indicated that using standard linear programming techniques, where the emissions were treated as properties of the components used in the blending, that low emissions fuels can be formulated using the emissions as blending parameters of the fuel.

Introduction

Contemporary diesel fuel is a blend of several refinery streams chosen to meet specifications. The need to increase yield of transportation fuel from crude oil has resulted in converting increased proportions of residual oil to lighter products. This conversion is accomplished by thermal, catalytic, and hydrocracking of high molecular weight materials rich in aromatic compounds. The current efforts to reformulate California diesel fuel for reduced emissions from existing engines is an example of another driving force affecting refining practice: regulations designed to reduce exhaust emissions. Although derived from petroleum crude oil, reformulated diesel fuel is an alternative to current specification-grade diesel fuel, and this alternative presents opportunities and questions to be resolved by fuel and engine research.

Various concerned parties have argued that regulations for fuel reformulation have not been based on an adequate data base. Despite numerous studies (Ryan et al., 1981; and Ryan, and Erwin 1994), much ambiguity remains about the relationship of exhaust parameters to fuel composition, particularly for diesel fuel. In an effort to gather pertinent data, the automobile industry and the oil refiners have joined forces in the Air Quality Improvement Research Program (AUTO/OIL) to address this question for gasoline (Burns, et al., [1992]). The objective of that work is to define the relationship between gasoline composition and the magnitude and composition of the exhaust emissions. The results of the AUTO/OIL program will also be used, along with other data bases, to define the EPA "complex model" for reformulated gasolines. Valuable insights have been gained for compression ignition engines in the Coordinating Research Council's VE-1 program, but no program similar to AUTO/OIL has been started for diesel fuel reformulation. A more detailed understanding of the fuel/performance relationship is a readily apparent need.

The increasingly stringent restrictions on emissions from diesel fuel-powered vehicles pose a challenge for both existing petroleum fuels and proposed fuels from alternative sources. The U.S. Environmental Protection Agency (EPA) regulation limit particulates to 0.25 grams per braking horse power-hour(g/bhp-hr) in 1991 for trucks and 0.1 g/bhp-hr for city buses in 1993; in 1994, the limit will drop to 0.1 g/bhp-hr for all vehicles (Slodowske et al., [1992]). Canada is expected to adopt the same limits eventually, and Mexico will have similar standards for urban vehicles.

EPA has not prescribed the method for meeting the emissions requirements for diesel engines. Engine manufacturers have developed significantly cleaner engines without meeting the proposed standard in all cases. EPA issued regulations that limit sulfur content of diesel fuel to 0.05 weight percent (wt%) and impose a minimum 40 cetane index to cap aromatics content at present levels (Federal Register, 1989). The California Air Resources Board has also announced regulations that control diesel fuel sulfur content to less than 0.05 wt% and the aromatics content to less than 10 vol%.

Available data indicate that the control of sulfur, aromatics, and cetane number will add significantly to the cost of producing diesel fuel. Moreover, the cost will probably increase further because the legislative forces driving the quality of gasoline generally have adverse effects on the quality of diesel fuel feed and blending stocks. These factors, and the ultimately limited supply of petroleum, place continued importance on the role of alternative fuels in transportation.

This report presents the findings, of our study "Diesel Fuel Assay of Performance and Emissions". With the broad objective of relating diesel exhaust emissions and diesel performance to chemical composition and physical properties, this study also addressed the more specific concerns of the effect of hydrocarbon type. Southwest Research Institute (SwRI) chose the starting materials to provide insight about source and

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upgrading method as they affect ignition quality and emissions from different samples meeting the same limits on sulfur and aromatics, but with different processing histories.

Background Literature

Sulfur and aromatics concentrations increase with boiling point. For example, lower concentrations of aromatics and sulfur typically occur in D-1 fuel, whose boiling range of 300°– 550°F (149° – 288°C) is lower than that of D-2 fuel with a 350°– 650°F (177°– 343°C) range. What has not been shown is which of the highest boiling components are most responsible for particulate emissions or which components of refinery streams would benefit the most from processing to reduce emissions precursors (Grant et al., 1991). The approach used for determining the effects of fuel composition on engine behavior has been to blend or measure full boiling range fuels for engine tests (Tosaka et al., 1989). For instance, studies at the University of Wisconsin (Foster et al., 1987) and the Pennsylvania State University (Buzza et al., 1987) found little effect on performance and emissions attributable to fuel composition.

In contrast, Weidmann (1988) found that fuel properties have a small, measurable effect on emissions using a VW 1.67-liter, 4-cylinder engine. Hydrocarbon emissions were found to be a function of fuel cetane number, with volatility exerting a stronger influence for low cetane-number fuels. Particulate formation was a strong function of fuel density and distillation range.

Southwest Research Institute studied engine emissions for the U.S. Bureau of Mines to investigate the effect of diesel fuel composition to benefit engines used in underground mines (Ryan, 1986). Test fuels included reference diesel, JP-7 (a narrow-cut jet fuel with extremely low aromatic and sulfur contents and naturally high cetane number), alcohol/diesel mixtures, water/diesel emulsions, and methane with pilot injection. The results of these experiments indicated that the jet fuel was lower in emissions than diesel, but that the water emulsions were more effective in reducing both nitrogen oxides (NOx) and particulates. Aromatics and sulfur were also shown to affect particulate emissions. Fortnagel et al., (1983) found NOx, hydrocarbon (HC), carbon monoxide (CO), and particulate emissions to be subject to aromatic content in a Mercedes Benz prechamber-type engine. Gairing (1985) found large effects on exhaust emissions and fuel consumption attributable to fuel properties.

The work of Ullman et al., (1989,1990), in support of the CRC VE-1 Program, demonstrated that dominant fuel parameters affecting diesel engine performance and emissions are sulfur content, cetane number and aromatics content. Recently reported work by Miyamoto et al., (1992), McCarthy et al., (1992), Nikanjam (1993), and Cowley et al., (1993) all confirmed these findings, with the general consensus that sulfur content has a significant effect on the particulate emissions, and the cetane number may be the dominant factor in controlling both the particulate and the NOx emissions.

The diversity of these results is typical of the literature and emphasizes the strong influence that the engine type has on emissions from a given fuel. These studies were also performed with full-boiling fuels and made no attempt to segregate fuel properties by boiling range. Cookson et al., (1988) attempted to determine the effect of hydrocarbon-type composition on the diesel index (Method IP21) and cetane index (ASTM D 976) in 54 fuels, again using full-boiling materials.

Objective

The overall objective of this work was to determine the relationships between the fuel feedstocks and fuel processing, properties, and composition, and the resulting combustion and emissions characteristics in a diesel engine. One tool for this determination was the selection of blendstocks, rather than full-boiling

diesel fuels; therefore, a subordinate goal was to choose materials with greatest significance for performance and emissions — the cracked stocks and aromatics.

Approach

Achieving the primary objective required meeting several intermediate objectives. These intermediate objectives included producing a consistent set of performance, emission, and composition measurements on a matrix of diesel fuel components distinguished by source and processing history. To do this, we had to obtain careful physical and chemical characterizations.

The next step was the use of boiling range as a probe for the measured properties, and this goal was achieved by producing narrow distillation cuts of the test fuels much like fractions are produced in a crude oil assay. This led to the nickname for the project, the Diesel Fuel Assay.

The results obtained were evaluated for their ability to describe the influence of the measured properties on the ignition quality and exhaust composition of the test samples. These results were then mathematically fit to the property descriptions to derive predictive equations. Finally, a matrix of test fuels was prepared. In summary, the steps were:

- Feedstock selection and characterization
- Processing feedstock to controlled sulfur and aromatics compositions
- Fractionation and detailed analysis of products and fractions
- Updating combustion tests to reflect near-term technology
- Performance and emission tests of stocks, products, and fractions
- Study and correlation of analyses and combustion tests
- Demonstration and verification by low-emission fuel blends

Figure 1 shows the sequence of operations for making test fuels. Petroleum and coal-derived components were selected to represent the most difficult portions of the blending pool to conform to performance and emission goals of modern diesel engines. The petroleum components were reduced in sulfur and aromatic content by pilot-plant hydrogenation before distillation into selected boiling point ranges. The approach attempted to improve on the resolution of previous studies using full-boiling test fuels by examining the five starting materials in narrow fractions of the diesel fuel boiling range.

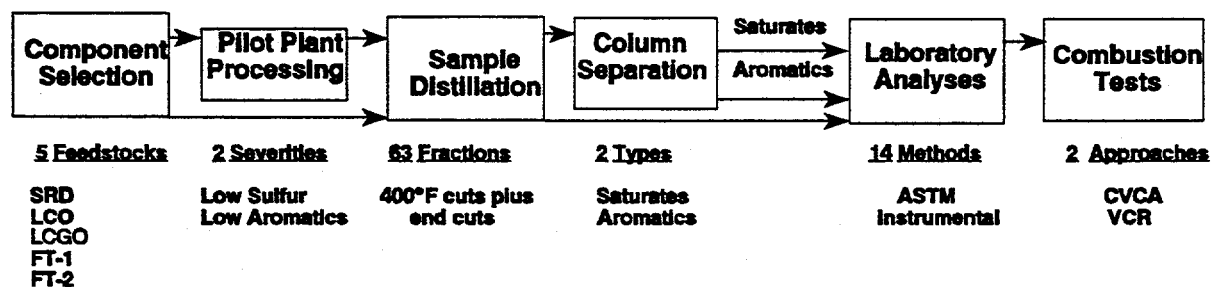| Component Selection	Pilot Plant Processing	Sample Distillation	Column Separation	Laboratory Analyses	Combustion Tests
			Saturates / Aromatics		
5 Feedstocks	**2 Severities**	**63 Fractions**	**2 Types**	**14 Methods**	**2 Approaches**
SRD	Low Sulfur	400°F cuts plus	Saturates	ASTM	CVCA
LCO	Low Aromatics	end cuts	Aromatics	Instrumental	VCR
LCGO					
FT-1					
FT-2					

Figure 1. Sequence of operations for making the test fuels

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We analyzed the resulting fractions of feedstocks and products for chemical composition and physical properties that would be most revealing for ignition quality and particulate generation. All samples were then tested for engine performance and emissions. Correlations of the emission behavior were used to guide the blending of proof-of-concept test fuels. This "Clean Fuel Study" was intended to deliver low-emission fuels while observing all other necessary (ASTM D 975-type specifications) properties. The low-emission fuels were tested in a similar manner as were the original samples. The details for each of the steps are presented in the following sections.

Materials and Processing

In modern refinery practice, diesel fuel has become a blended product composed containing a variety of streams in the 350°F – 650°F boiling range. The need to increase the yield of transportation fuel from crude oil has resulted in converting increased proportions of gas oil (>440°F or >227°C) and residual oil (resid) to lighter products. This is accomplished by thermal, catalytic, and hydrocracking of higher carbon number compounds rich in aromatics. Of the refinery streams blended into diesel fuel, the higher boiling and more aromatic ones are implicated in particulate and hydrocarbon emissions.

Products from resid conversion and gas oil cracking contribute a variety of aromatic and high molecular weight compounds to the diesel fuel blending component pool. In this study, we chose the test components to emphasize the streams which present the greatest challenge to performance and emissions.

Petroleum Stocks and Products

Efforts were made to obtain typical streams of the desired composition from willing refiners. Accordingly, we choose feedstocks for this study to include products from resid conversion and gas oil cracking. The test components ultimately chosen were:

- full-boiling straight-run diesel (SRD)
- light cycle oil from catalytic cracking (LCO)
- light coker gas oil (LCGO)

These materials, their products of pilot-plant processing (having controlled sulfur and aromatics concentration), and two Fischer-Tropsch samples were examined in laboratory and engine tests. The properties of the feedstocks appear in Table 1.

Fischer-Tropsch (F-T) Liquids

Two F-T liquids were considered in the current work to compare with the petroleum stocks. Indirect coal liquids pose opportunities for diesel fuel both as a Btu source for motive force and as a high-cetane, low-emission component for exhaust emissions control. F-T liquids are synthetic products made from coal or other sources by gasification followed by reaction over a polymerization catalyst bed. The products of this process are almost entirely normal paraffins. The DOE Office of Coal Conversion provided the first material. The production and properties of this F-T distillate are fully described by Bludis et al., 1991. An imported Arge wax was subjected to hydrocracking to produce liquid in the distillate boiling range. We have designated this material FT1.

The second F-T sample was made by Air Products under DOE Contract (Bhatt et al., 1993). The materials were supplied as hydrocarbon liquid and light wax. These samples were combined in a ratio of 1.6:1 according to their proportion in production. This material, being lower in boiling range than the

Table 1. Feedstock Properties

Test	ASTM Method	Straight-Run Diesel	Light Cycle Oil	Light Coker Gas Oil	Fischer-Tropsch1	Fischer-Tropsch2
Density Specific Gravity	D 1298	0.8458	0.9490	0.8676	0.7770	0.8081
°API		35.8	17.6	31.6	50.6	43.6
g/mL		0.8453	0.9485	0.8671	0.7767	0.8077
Distillation, °C/°F	D 86					
IBP*		353	367	385	368	363
5%		428	457	420	396	391
10		466	476	435	407	406
30		523	509	462	449	461
50		551	536	492	502	509
70		581	573	528	550	547
90		635	634	574	592	588
95		657	656	590	606	606
EP*		672	689	608	620	627
Carbon, wt%	D 3178	86.82	88.84	85.18	84.92	82.62
Hydrogen, wt%		13.31	9.84	12.58	15.12	13.76
Sulfur, wt%	D 2622	0.052	0.69	1.41	0.003	0.031
Hydrocarbon Type, vol%	D 1319					
Saturates		74.7	20.9	41.7	97.8	ND
Olefins		1.0	3.6	5.9	1.1	
Aromatics		23.6	75.5	52.4	1.1	
Viscosity @ 40°C	D 445	3.52	3.16	2.56	2.42	
@ 100°C		1.34	1.20	1.10	1.05	
Refractive Index @ 20°C	D 1218	1.4718	1.5537	1.4797	1.4342	1.4414
Cetane Index	D 976	52.6	26.1	39.3	75.4	62.2
	D 4737	54.6	23.89	38.9	81.4	64.6
UV Aromatics	Total	11.4	43.7	15.7	0.2	1.6
Analysis	Mono	4.3	6.3	8.4	0.0	0.1
Wt% Aromatic Carbon	Di	5.8	28.3	5.9	0.0	0.0
	Tri	1.3	9.1	1.4		
Cloud point, °C/°F	D2500	1/34	-10/14	Too dark	-20/-4	-5/23
Pour point, °C/°F	D 97	-1/30	-12/10	-30/-22	-20/-4	-7/19
Aniline point, °C/°F	D 611	73.0/163	9.8/50	47.6/118	92.8/199	43.2/110
Smoke point, mm	D 1322	17.2	6.2	13.3	35+	40.0

* IBP - Initial boiling point; EP - End point; ND - Not Determined

Arge wax, contained light process oils and oxygenates. From this mixture, a 350°–650°F straight-run diesel sample was distilled, designated FT2.

Both F-T liquids were fractioned into controlled boiling-range samples. Batches of about 40 liters were distilled in a stainless steel distillation column under vacuum, and these samples were reserved for laboratory and engine testing.

Processing

The three petroleum feedstocks were processed to reduce sulfur and aromatics, then distilled into analytical samples. The processing and distillation sequence was shown in Figure 2. The LCO and LCGO were hydrogenated at two severities to reduce sulfur to 0.05 mol% and aromatic concentration to 10 vol% (per ASTM D 1319). These levels were chosen in contemplation of the limits being applied to diesel fuel in California and nationally. The straight-run diesel was naturally low in sulfur and was hydrotreated at one severity to reduce aromatics to 10 vol%. The F-T stocks required no hydrogenation.
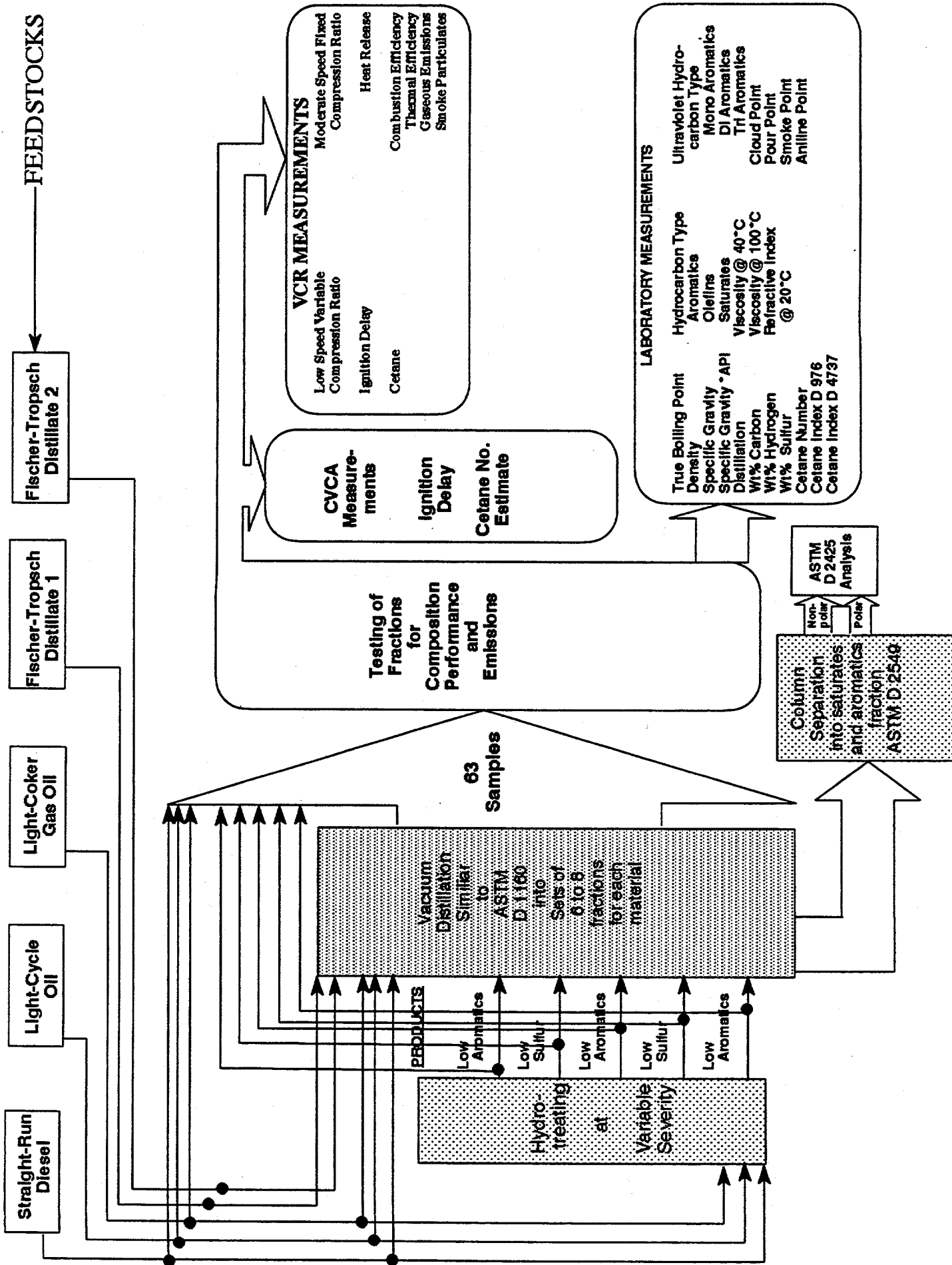
The hydrotreating was performed in the pilot plant of the U.S. DOE Alternative Fuel Center at Southwest Research Institute.[1] The reactor was a fixed bed (7.5 ft × 2 in. diameter), containing 1.56 gallons of Criterion Trilobe HDN 60 nickel-molybdenum catalyst. The feedstocks were combined with hydrogen gas preheated, and fed to the top of the reactor bed. After the reactor, two stages of pressure letdown and product separation removed unreacted hydrogen and byproduct gases. The hydrogen was cleaned and recycled, and the product was stripped to remove light ends and dissolved gases.

The process parameters for the hydrogenations are summarized in Table 2. The principal measure of processing severity is the liquid hourly space velocity (LHSV), an inverse expression of residence time in the reactor equal to the feed flowrate divided by the reactor volume expressed in consistent units.

Table 2. Processing Parameters

	Avg Temp, °F/°C	Total Press, psig	Feed Rate, gal/hr	Total H₂, SCFH	LHSV, hr⁻¹
STRAIGHT-RUN DIESEL					
High severity — low aromatics	630/332	1500	1.6	60	1.03
LIGHT-CYCLE OIL					
Low severity — low sulfur	710/377	650	1.9	110	1.05
High severity — low aromatics	686/363	2300	0.74	130	0.41
LIGHT COKER GAS OIL					
Low severity — low sulfur	650/343	600	2.2	140	1.22
High severity — low aromatics	676/358	2200	0.98	117	0.56

FEEDSTOCKS

Straight-Run Diesel

Light-Cycle Oil

Light-Coker Gas Oil

Fischer-Tropsch Distillate 1

Fischer-Tropsch Distillate 2

VCR MEASUREMENTS

Low Speed Variable Compression Ratio

Ignition Delay

Cetane

Moderate Speed Fixed Compression Ratio

Heat Release

Combustion Efficiency
Thermal Efficiency
Gaseous Emissions
Smoke Particulates

CVCA Measurements

Ignition Delay

Cetane No. Estimate

LABORATORY MEASUREMENTS

True Boiling Point
Density
Specific Gravity
Specific Gravity °API
Distillation
Wt% Carbon
Wt% Hydrogen
Wt% Sulfur
Cetane Number
Cetane Index D 976
Cetane Index D 4737

Hydrocarbon Type
Aromatics
Olefins
Saturates
Viscosity @ 40°C
Viscosity @ 100°C
Refractive Index @ 20°C

Ultraviolet Hydrocarbon Type
Mono Aromatics
Di Aromatics
Tri Aromatics
Cloud Point
Pour Point
Smoke Point
Aniline Point

Testing of Fractions for Composition Performance and Emissions

ASTM D 2425 Analysis

Column Separation into saturates and aromatics fraction ASTM D 2549

Non-polar

Polar

63 Samples

Vacuum Distillation Similar to ASTM D 1160 into Sets of 6 to 8 fractions for each material

PRODUCTS

Low Aromatics
Low Sulfur
Low Aromatics
Low Sulfur
Low Aromatics

Hydro-treating at Variable Severity

Distillation

Efforts to separate fuels such as these into the individual compounds have been partially successful in the laboratory. However, the number of compounds is extremely large, and therefore, it is, not possible to study the combustion of each individual compound and all the possible interactions among the various compounds. A more practical approach — and the one used in this project — is to separate the fuels into a reasonable number of fractions that can be studied in detail.

Each of the five feedstocks and the five hydrotreated products were distilled under vacuum into congruent (corresponding cut point) boiling-range fractions. The following boiling point ranges were selected for the cuts:

Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7
Initial Boiling Point - 440°F	440° - 480°F	480° - 520°F	520° - 560°F	560° - 600°F	600° - 640°F	640° - End Point
<227°C	227°- 249°C	249°- 271°C	271°- 293°C	293°- 315°C	315°- 338°C	>338°C

Approximately 40 liters of each material were charged to a stainless steel kettle and column, which was operated along the lines of a ASTM D 1160 distillation. The actual ranges of the sample fractions differed from these ideal cuts, and boiling range comparisons should be made among the cuts of closest temperature range rather than fraction number. The number of fractions distilled from each feedstock and product vary in number depending on the boiling range of the starting material. The most even alignment of fractions is presented in Table 3. With the original five materials, the processed products, and all their fractions, 80 samples comprised the test fuel matrix for the Diesel Assay.

LABORATORY EVALUATION

The five basestocks, five hydrotreated products, and their distillation fractions were characterized by physical and chemical tests and by combustion experiments as shown in Figure 2. The results appear in Appendix A as Tables A-1 through A-10 and were the subject of an American Chemical Society paper (Erwin, 1992). The laboratory measurements listed in the tables were applied to each of the 80 fractions made by vacuum distillation. The list includes two measures of aromatic content: D 1319 and the ultraviolet (UV) method (Kohl et al., 1991). Similar information can be inferred from the nuclear magnetic resonance (NMR) measurements. The fluorescent indicator analysis (ASTM D 1319) is widely used and is included in emissions regulations. This analysis is regularly applied to diesel fuel samples, although the method is designed for depentanized gasoline and relies on measurements of column length taken up by saturates, aromatics, and olefins, made visible by fluorescent dye, hence the name FIA (fluorescent indicator analysis). The vol% aromatics determined this way can be affected by cycloparaffins or polar materials. The low aromatic content and high cycloparaffin content of FT1, as well as the oxygenates in FT2, made the results of D 1319 unworkable for these samples.

The UV method compares sample absorbance at selected wavelengths with reference spectra of solutions of aromatics composed of representative compounds in the diesel boiling range. Because the absorbance is proportional to the aromatic rings, wt% aromatic carbon is reported without regard to substituents. Both methods are indirect, so instrumental analysis by gas chromatography/mass spectrometer (GC/MS) and NMR were indicated.

The hydrocarbon-type determinations by ASTM D 2425 are presented in Appendix A, Tables A-11 through A-15. This method requires a separation of each sample into polar and nonpolar fractions, which

Table 3. Corresponding Boiling Ranges of Fractions

	Feed	#1	#2	#3	#4	#5	#6	#7	#8
°F °C	Selected. Temp. Ranges	<400 <204	400-440 204-227	440-480 227-249	480-520 249-271	520-560 271-293	560-600 293-316	600-640 316-338	640+ 338+

IBP-EP and 5%-95% shown (°F)

STRAIGHT-RUN DIESEL

	FL-1627	FL-1793	FL-1794	FL-1795	FL-1796	FL-1797	FL-1798	FL-1799	FL-1800
°F	353-672	282-475	452-515	476-529	502-556	536-576	570-610	610-643	657-698
°C	178-356	139-246	233-268	247-276	261-291	280-302	299-321	321-339	347-370
°F	428-657	324-462	464-506	484-521	509-550	542-568	576-602	616-638	663-691
°C	220-347	162-219	240-263	251-272	265-288	283-298	302-317	324-337	351-366
Vol%	11.5	9.0	8.0	16.5	16.5	14.0	11.0	13.5

LOW-AROMATIC STRAIGHT-RUN DIESEL

	FL-1873	FL-1876	FL-1877	FL-1878	FL-1879	FL-1880	FL-1881	FL-1882	FL-1883
°F	262-664	201-351	361-455	427-488	474-526	520-562	559-597	605-641	659-715
°C	128-351	94-177	183-235	219-253	246-274	271-294	293-314	318-338	348-379
°F	380-644	212-334	381-447	438-480	480-515	528-557	567-591	613-635	670-705
°C	193-340	100-168	194-231	226-249	249-268	276-292	297-311	323-335	354-374
Vol%	5.0	10.0	9.5	15.0	16.5	17.5	13.5	13.0

LIGHT-CYCLE OIL

	FL-1538	FL-1555	FL-1556	FL-1557	FL-1558	FL-1559	FL-1560	FL-1561	-
°F	367-689	382-460	442-492	477-518	508-544	542-575	578-614	616-734	-
°C	186-365	194-238	228-256	247-270	264-284	283-302	303-323	324-390	-
°F	457-656	384-449	444-479	481-503	514-534	546-566	582-601	636-709	-
°C	236-347	196-232	229-248	249-262	268-279	286-297	306-316	336-376	-
Vol%	8.9	9.2	19.9	15.0	14.3	11.7	21.0	-

LOW-SULFUR LIGHT-CYCLE OIL

	FL-1615	FL-1850	FL-1851	FL-1852	FL-1853	FL-1854	FL-1855	FL-1856	-
°F	392-682	317-510	422-544	458-548	495-572	533-595	593-630	641-738	-
°C	200-361	158-266	217-284	237-281	257-300	278-312	312-332	324-390	-
°F	436-642	356-481	440-516	469-533	502-559	541-585	593-622	645-727	-
°C	224-339	180-249	227-269	243-278	261-293	283-307	312-328	341-386	-
Vol%	12.3	15.7	20.5	16.5	14.1	10.0	10.9	-

LOW-AROMATIC LIGHT CYCLE OIL

	Lo-Arom LCO	(#0)*	(#1)*	(#2)*	(#3)*	(#4)*	(#5)*	(#6)*	-
	FL-1562	FL-1566	FL-1567	FL-1568	FL-1569	FL-1570	FL-1571	FL-1572	-
°F	390-657	340-419	402-453	439-488	472-514	511-544	543-574	599-715	-
°C	199-347	171-215	206-234	226-253	244-268	266-284	284-301	315-379	-
°F	354-694	354-411	411-439	444-474	476-501	513-534	546-565	603-694	-
°C	179-368	179-210	211-226	229-246	247-261	267-279	286-296	317-368	-
Vol%	11.3	13.9	17.8	18.3	15.1	10.0	13.6	

Table 3. Corresponding Boiling Ranges of Fractions
(Continued)

	Feed	#1	#2	#3	#4	#5	#6	#7	#8
LIGHT-COKER GAS OIL									
	FL-1440	FL-1546	FL-1547	FL-1548	FL-1549	FL-1550	FL-1551	-	-
°F	385-608	379-461	440-491	480-526	521-565	559-595	599-645	-	-
°C	196-320	193-238	227-255	249-274	272-296	293-313	315-341	-	-
°F	420-590	391-436	445-478	485-512	529-551	564-583	601-635	-	-
°C	216-310	199-224	229-248	252-267	276-288	296-306	316-335	-	-
	Vol%	25.0	17.0	17.0	16.0	13.0	18.0	-	-
LOW-SULFUR LIGHT-CYCLE GAS OIL									
	FL-1442	FL-1862	FL-1863	FL-1864	FL-1865	FL-1866	FL-1867	-	-
°F	380-599	337-457	379-453	421-492	462-526	500-550	558-607	-	-
°C	193-315	169-236	193-234	216-256	239-274	260-288	292-319	-	-
°F	416-572	354-441	395-467	430-481	472-512	510-543	565-624	-	-
°C	213-300	179-227	202-242	221-249	244-267	266-284	296-329	-	-
	Vol%	13.5	15.5	19.5	18.0	15.5	18.0	-	-
LOW-AROMATIC LIGHT-CYCLE GAS OIL									
	FL-1443	FL-1597	FL-1598	FL-1599	FL-1600	FL-1601	FL-1602	FL-1603	-
°F	412-612	358-430	394-466	429-485	466-520	498-546	537-574	585-644	-
°C	211-322	181-221	201-241	221-252	241-271	259-286	281-301	307-340	-
°F	429-597	371-421	401-449	442-477	472-509	506-536	547-570	594-632	-
°C	221-314	188-216	205-232	228-247	244-265	263-280	286-299	312-333	-
	Vol%	8.5	15.5	18.3	16.1	15.0	12.5	14.0	-
FISCHER-TROPSCH 1									
	FL-1840	FL-1898	FL-1899	FL-1900	FL-1901	FL-1902	FL-1903	FL-1904	-
°F	368-620	336-456	386-474	424-488	467-521	511-557	547-589	595-638	-
°C	187-327	169-236	197-246	218-253	242-272	266-292	286-309	313-337	-
°F	396-606	352-438	395-463	436-482	477-511	519-549	555-583	605-633	-
°C	202-319	178-226	202-239	224-250	247-266	271-287	291-306	318-334	-
	Vol%	20.0	11.5	11.0	11.5	13.0	15.5	15.7	-
FISCHER-TROPSCH 2									
	FL-2095	FL-2115	FL-2116	FL-2117	FL-2118	FL-2119	FL-2120	FL-2121	-
°F	363-627	216-392	316-428	358-537	392-522	442-526	482-565	529-603	-
°C	184-331	102-200	158-220	181-281	200-272	228-274	250-296	276-317	-
°F	391-606	266-372	326-408	377-459	418-482	462-516	506-558	549-591	-
°C	199-319	130-189	163-209	192-237	214-250	239-269	263-292	287-311	-
	Vol%	16.3	10.1	12.0	10.5	18.2	17.3	15.7	-

* LA-LCO fractions were numbered differently as shown.

is a laborious process. To remain within budget, groups of samples were mixed to represent the middle portion of the boiling range in some cases, as noted on the tables. We believed that little information would be lost by combining similar samples in this way. This presumption was verified by measuring the whole set of samples for the low-aromatic straight-run diesel. In these tables, the usual D 2425 report for saturates and aromatics was simplified into a unified listing of hydrocarbon types for each sample.

This characterization of the test fuel and fuel fractions was aimed at identifying the components in fuel that contribute to differences in engine performance in terms of both power and emissions. A comprehensive analysis of the diesel fuel would entail identifying each compound present in the fuel (if such level of detail were possible). This approach would create more data than could be reasonably handled and is extremely time-consuming and expensive, requiring two-dimensional GC analysis and laborious interpretation of the resulting data.

The next set of results concern the nuclear magnetic resonance spectroscopic examination of the samples. The work was performed at the University of Utah Chemistry Department. Table A-16 lists the regions of chemical shift into which the responses for the samples were divided. The instrumental procedures for the integration of these samples included:

1.   Long acquisition time (AT) is used to guarantee the necessary digital resolution.
2.   Wide spectral width (SW = 20000 → 40 ppm) is used to guarantee that all protons are equally excited.
3.   Long d1 delay used to let protons fully recover between pulses.

The procedure for making the quantitative integration of the NMR spectra was as follows: Each spectrum was first phased manually to have as flat a baseline as possible. Next, the spectrum was individually referenced to the observed TMS line. The spectrum was then accurately divided into five chemical-shift regions (Table A-16). This division of shifts has been used for correlation of fuel properties in the past (Bailey et al., 1986). The baseline was again corrected with the TMS line also covered by a segment of the integration line; integration was taken after the segment has been removed.

The results for all samples are reported in Table A-17. Variability (uncertainty) with each value is reported in the table because the reproducibility of manual phasing could not be guaranteed. By repeated integration on selected spectra the variability was estimated as around ± 1.0%. For example, 30.5 should be read as 30.5 ± 1.0%.

COMBUSTION EXPERIMENTS

SwRI has developed two different apparatus and procedures specifically for determining the effects of fuel composition on performance and emissions. Several different pure compounds, fuel blends, and fuel components have already been evaluated in these devices in previous DOE-sponsored projects at SwRI (Ryan, 1987).

Ignition Quality

Ignition quality was determined in a constant volume combustion apparatus (CVCA). A small quantity of sample is injected into a volume of hot air to simulate the conditions in a compression ignition engine cylinder for estimation of cetane number. The CVCA, described in detail by Ryan (1985) and Ryan et al, (1987, 1988) is shown schematically in Figure 3. The equipment consists of the constant volume combustion bomb, a single-shot fuel injection system, and a data acquisition system to monitor the various temperatures and pressures as the fuel is injected into the bomb, ignites, and burns. The pressure in the bomb is measured and used to determine the ignition delay and the combustion rates. The ignition delay

times, measured at various initial temperatures, have been used to develop Arrhenius expressions for the delay time as functions of temperature. In addition, the ignition delay time has been used to determine the cetane number using a procedure described below.

The CVCA has been used to determine the cetane number of unknown fuels by comparing the ignition delay time of the unknown fuels to a calibration of cetane number versus the ignition delay time. The calibration is developed using several different blends of the primary reference fuels — hexadecane and heptamethylnonane. Researchers have observed in previous studies that the calibrations shift periodically. They have found, however, that the calibrations can be checked and adjusted using the results of measurements of the 100 cetane number (CN) reference fuels. In the work reported here, the calibrations were checked daily, and the calibrations did not shift appreciably over the duration of the measurements. The CVCA measurements were studied by Ryan et al, (1992), who measured the ignition and basic combustion characteristics at three different initial temperatures in the CVCA.

Engine Tests

The results obtained to measure combustion quality and emissions were from a single-cylinder research engine designed at SwRI for studying fuel effects on combustion. The engine, described in detail by Ryan (1987), was modified for this work to be representative of current-technology, two-valve per cylinder engines. The engine was used to perform two types of experiments. Each fuel was rated for ignition quality in one procedure and tested for emissions and performance in another procedure involving five speed-load test conditions (termed Modes 1 through 5). Details of the engine design and configuration are presented in this section, as are the test conditions and test procedures.
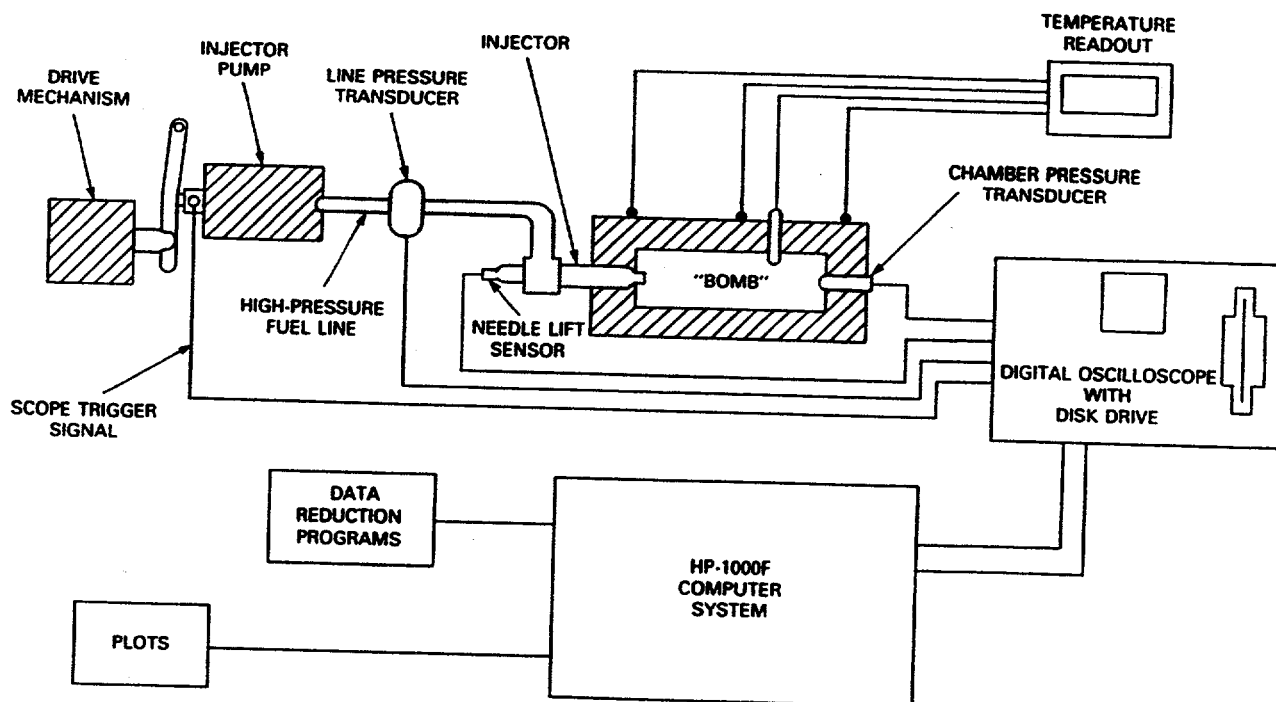

Figure 3. Constant volume combustion apparatus

Test Engine

The test engine is a single-cylinder research engine designed at SwRI for fuel-combustion research. The general configuration is a two-valve, direct-injection, variable compression ratio (VCR) engine. The design is based on a CLR-type crankcase and a head and cylinder liner assembly designed and built at SwRI. Variable compression ratio is achieved by moving the head and cylinder liner assembly relative to the centerline of the crankshaft. A variation from 12:1 to 20:1 compression ratio was possible in the configuration used for these experiments.

The engine was modified to be geometrically similar to current, two-valve engines. The modifications, as compared to the previously reported configuration Ryan et al., 1988) , included a new connecting rod length and stroke length to achieve the desired bore-to-stroke ratio, and a modified intake port and valve to achieve a swirl ratio of 2.7. The analysis used to arrive at this head design is presented in Appendix B. The head and cylinder liner assembly are shown schematically in Figure 4, and details of the engine configuration are presented in Table 4.

Instrumentation

The amounts of test fuel available for testing were generally limited; therefore, efforts were made to minimize the quantity of fuel required for flushing and filling the fuel system. Fuel flow was measured volumetrically using a calibrated burette that was connected to both the fill and return ports of the injection pump. The intake air was supplied using a large compressor. The air temperature, pressure, and humidity were all controlled, and air flow rate was measured and controlled using a metering control valve.
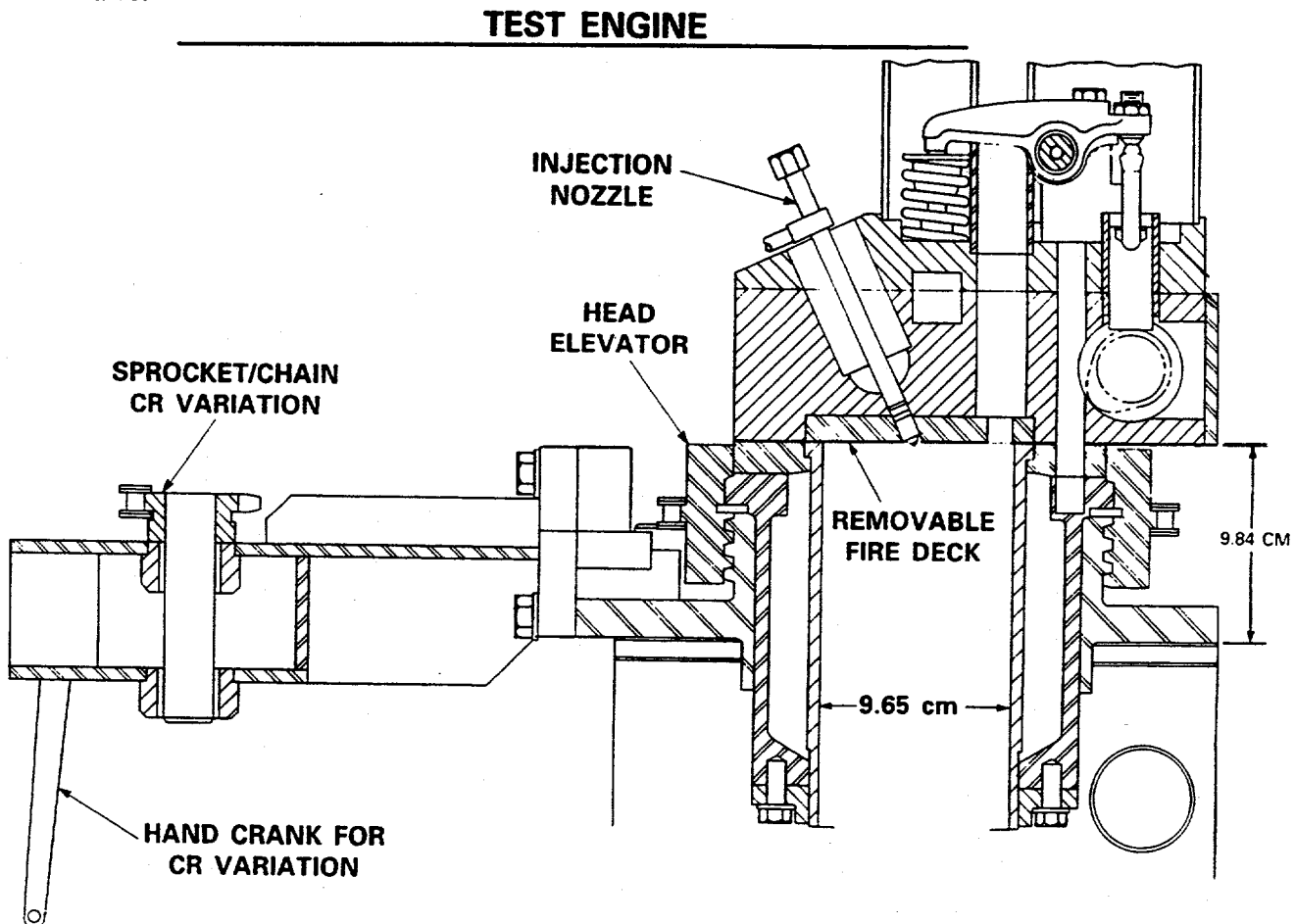

Figure 4. volume combustion ratio profile schematic

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Table 4. Engine Specifications

Bore × Stroke (mm)	96.5 × 104.9
Rod Length (mm)	166.5
Corrosion	12:1 to 20:1
Displacement (cm³)	767.2
Deck Height (mm)	7.9 to 0.4
Injection Pump (mm × mm)	11 × 11
Injection Pressure (MPa)	100
Combustion Chamber	Mexican Hat
Re-entrant	
Re-entrant Angle	25°
Bowl Opening (mm)	43.3
Bowl Depth (mm)	19.3
Swirl Ratio	2.7

The engine temperatures and pressures were monitored using a PC-based data acquisition system that logged the data every 30 seconds. A water-cooled piezoelectric pressure transducer was installed in the combustion chamber to measure the cylinder pressure. These data, as well as the corresponding injection pressure and nozzle needle lift data, were logged every 0.5 degree of crankshaft rotation, using a Preston Scientific A/D and Hewlett Packard A900 computer system. We used a First Law Analysis of the cylinder pressure data to compute heat release rates, which were used as an indication of combustion quality.

The exhaust emissions were sampled downstream of a mixing tank located in the exhaust of the engine. The gases were analyzed for CO_2 and CO using nondispersive infrared spectroscopy. Hydrocarbons were measured using a flame ionization detector. Nitrogen oxides (NOx) were measured using a chemiluminescence instrument, and smoke was determined using a Bosch smoke meter.

Test Procedures

Each of the test fuels was examined in two different types of experiments in the engine. First, each fuel was rated for ignition quality following a procedure very similar to that used in the standard cetane rating procedure (ASTM D 613).

The procedure developed for ignition quality rating was based on operating the engine at a selected "standard condition" for both the test fuels and selected blends of the primary reference fuels for cetane rating (Hexadecane with a CN of 100, and Heptamethylnonane with a CN of 15). Table 5 lists the conditions that were selected for this work. The injection timing was fixed at 12° Before Top Dead Center (BTDC). The engine was operated on each reference fuel blend, and the compression ratio varied until ignition occurred at Top Dead Center (TDC). A calibration curve was then developed in which the cetane number was presented as a function of the compression ratio. The test fuels were then operated at the "standard condition," and the compression ratio was varied to give ignition at TDC. This compression ratio was then used in the calibration curve to determine the cetane number.

Table 5. Test Condition for Ignition Quality Rating

Speed	900 rpm
Air/Fuel Ratio	50:1
Injection Timing	12° BTDC
Intake Temperature	38°C
Intake Pressure	115 kPa
Coolant Temperature	66°C

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The calibration curve used in this work is presented in Figure 5, along with the regression equation for the data. The test conditions were selected to give the broadest possible variation of compression ratio for the range of cetane number used in the reference fuel blends.
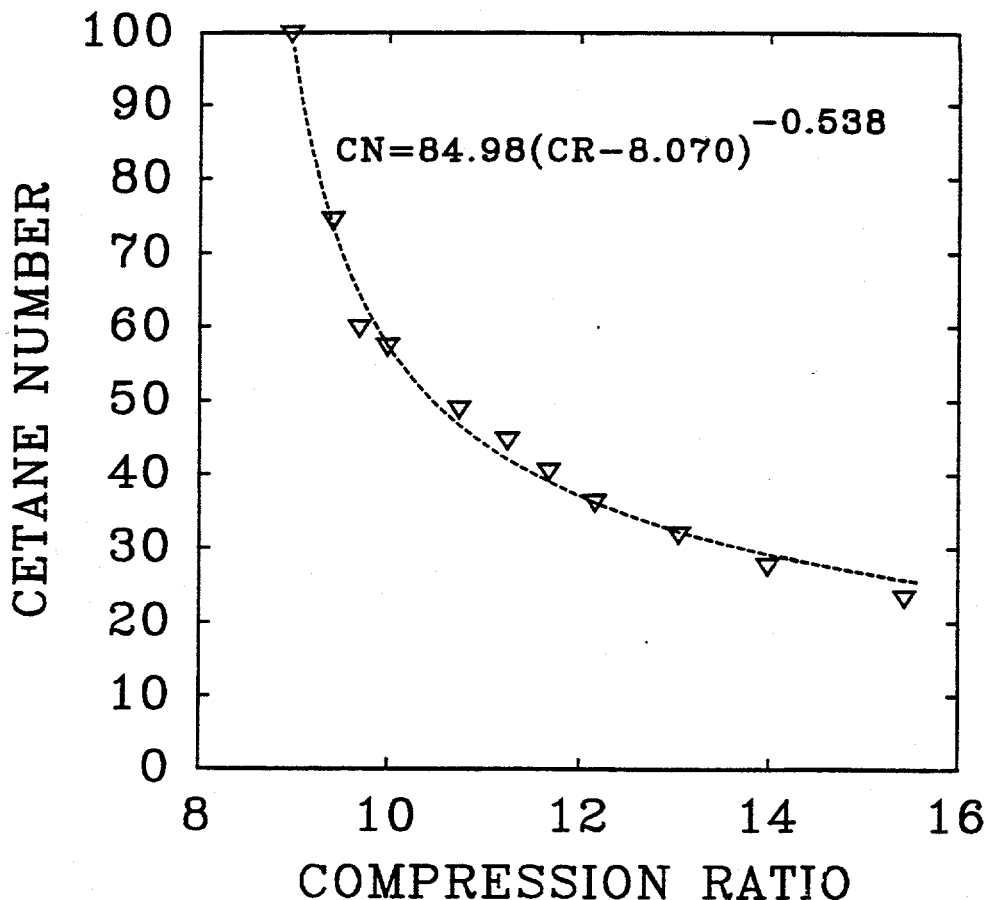

$$CN = 84.98(CR-8.070)^{-0.538}$$

Figure 5. Cetane number calibration curve

Performance and emissions data were obtained at five different test conditions or modes. These data consisted of the normal power and efficiency measurements, as well as engine heat-release analysis and gaseous emissions and smoke. The test conditions included rated torque at fixed timing, rated torque using the best torque timing for each fuel, the rated power condition, and two part-load conditions at the rated power speed. Details of the modes are presented in Table 6.

Table 6. Test Condition for Performance and Emissions.

Mode	Speed (rpm)	Air Fuel Ratio	Injection Timing
1	1200	28:1	3° BTDC
2	1200	28:1	Variable
3	1500	28:1	3° BTDC
4	1500	40:1	3° BTDC
5	1500	50:1	3° BTDC