

# 3

## Synthesis of Transit Practice

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# Diesel Fuel Quality and Effects of Fuel Additives

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# Diesel Fuel Quality and Effects of Fuel Additives

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TRANSPORTATION RESEARCH BOARD

National Research Council

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## NATIONAL COOPERATIVE TRANSIT RESEARCH & DEVELOPMENT PROGRAM

Administrators, engineers, and many others in the transit industry are faced with a multitude of complex problems that range between local, regional, and national in their prevalence. How they might be solved is open to a variety of approaches; however, it is an established fact that a highly effective approach to problems of widespread commonality is one in which operating agencies join cooperatively to support, both in financial and other participatory respects, systematic research that is well designed, practically oriented, and carried out by highly competent researchers. As problems grow rapidly in number and escalate in complexity, the value of an orderly, high-quality cooperative endeavor likewise escalates.

Recognizing this in light of the many needs of the transit industry at large, the Urban Mass Transportation Administration, U.S. Department of Transportation, got under way in 1980 the National Cooperative Transit Research & Development Program (NCTRP). This is an objective national program that provides a mechanism by which UMTA's principal client groups across the nation can join cooperatively in an attempt to solve near-term public transportation problems through applied research, development, test, and evaluation. The client groups thereby have a channel through which they can directly influence a portion of UMTA's annual activities in transit technology development and deployment. Although present funding of the NCTRP is entirely from UMTA's Section 6 funds, the planning leading to inception of the Program envisioned that UMTA's client groups would join ultimately in providing additional support, thereby enabling the Program to address a large number of problems each year.

The NCTRP operates by means of agreements between UMTA as the sponsor and (1) the National Research Council as the Primary Technical Contractor (PTC) responsible for administrative and technical services, (2) the American Public Transit Association, responsible for operation of a Technical Steering Group (TSG) comprised of representatives of transit operators, local government officials, State DOT officials, and officials from UMTA's Office of Technical Assistance, and (3) the Urban Consortium for Technology Initiatives/Public Technology, Inc., responsible for providing the local government officials for the Technical Steering Group.

Research Programs for the NCTRP are developed annually by the Technical Steering Group, which identifies key problems, ranks them in order of priority, and establishes programs of projects for UMTA approval. Once approved, they are referred to the National Research Council for acceptance and administration through the Transportation Research Board.

Research projects addressing the problems referred from UMTA are defined by panels of experts established by the Board to provide technical guidance and counsel in the problem areas. The projects are advertised widely for proposals, and qualified agencies are selected on the basis of research plans offering the greatest probabilities of success. The research is carried out by these agencies under contract to the National Research Council, and administration and surveillance of the contract work are the responsibilities of the National Research Council and Board.

The needs for transit research are many, and the National Cooperative Transit Research & Development Program is a mechanism for deriving timely solutions for transportation

problems of mutual concern to many responsible groups. In doing so, the Program operates complementary to, rather than as a substitute for or duplicate of, other transit research programs.

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The members of the technical committee selected to monitor this project and to review this report were chosen for recognized scholarly competence and with due consideration for the balance of disciplines appropriate to the project. The opinions and conclusions expressed or implied are those of the research agency that performed the research, and, while they have been accepted as appropriate by the technical committee, they are not necessarily those of the Transportation Research Board, the National Research Council, or the Urban Mass Transportation Administration, U.S. Department of Transportation.

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The Transportation Research Board evolved in 1974 from the Highway Research Board, which was established in 1920. The TRB incorporates all former HRB activities and also performs additional functions under a broader scope involving all modes of transportation and the interactions of transportation with society.

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## **PREFACE**

A vast storehouse of information exists on nearly every subject of concern to the transit industry. Much of this information has resulted from both research and the successful application of solutions to the problems faced by practitioners in their daily work. Because previously there has been no systematic means for compiling such useful information and making it available to the entire transit community, the Urban Mass Transportation Administration of the U.S. Department of Transportation has, through the mechanism of the National Cooperative Transit Research & Development Program, authorized the Transportation Research Board to undertake a series of studies to search out and synthesize useful knowledge from all available sources and to prepare documented reports on current practices in the subject areas of concern.

This synthesis series reports on various practices, making specific recommendations where appropriate but without the detailed directions usually found in handbooks or design manuals. Nonetheless, these documents can serve similar purposes, for each is a compendium of the best knowledge available on measures found to be successful in resolving specific problems. The extent to which these reports are useful will be tempered by the user's knowledge and experience in the particular problem area.

## **FOREWORD**

*By Staff  
Transportation  
Research Board*

This synthesis will be useful to administrators, engineers, and others in the transit industry concerned with evaluation of diesel fuel and fuel additives used in transit buses. Detailed information is presented on costs, benefits, and adverse effects of available fuel additives and related products.

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Administrators, engineers, and researchers are continually faced with problems on which much information exists, either in the form of reports or in terms of undocumented experience and practice. Unfortunately, this information often is scattered and unevaluated, and, as a consequence, in seeking solutions, full information on what has been learned about a problem frequently is not assembled. Costly research findings may go unused, valuable experience may be overlooked, and full consideration may not be given to the available methods of solving or alleviating the problem. In an effort to correct this situation, NCTRP Project 60-1, carried out by the Transportation Research Board as the research agency, has the objective of reporting on common transit problems and synthesizing available information. The synthesis reports from this endeavor constitute an NCTRP publication series in which various forms of relevant information are assembled into single, concise documents pertaining to specific problems or sets of closely related problems.

In recent years, environmental awareness, economic pressures, and a general decline in crude oil quality have caused transit operators to seek ways to make use of fuel

additives and less expensive blends. This report of the Transportation Research Board includes information on the evaluation of fuel additives and related products in terms of their effects on vehicle maintenance requirements, emissions control, fuel economy, fuel storage, and engine performance.

To develop this synthesis in a comprehensive manner and to ensure inclusion of significant knowledge, the Board analyzed available information assembled from numerous sources, including a large number of public transportation agencies. A topic panel of experts in the subject area was established to guide the researcher in organizing and evaluating the collected data, and to review the final synthesis report.

This synthesis is an immediately useful document that records practices that were acceptable within the limitations of the knowledge available at the time of its preparation. As the processes of advancement continue, new knowledge can be expected to be added to that now at hand.

## CONTENTS

I	SUMMARY	
	Diesel Fuel Quality Trends, 1	
	Diesel Fuel Quality, 2	
	Diesel Fuel Additives, 2	
	How to Evaluate Fuel Additives, 3	
	Alternative Fuels, 4	
5	CHAPTER ONE TRENDS IN DIESEL FUEL QUALITY	
	Historical Trends, 5	
	Future Trends, 5	
10	CHAPTER TWO MEASUREMENT OF FUEL QUALITY	
	Ignition Properties, 10	
	Engine Performance Properties, 11	
	Handling and Storage Properties, 11	
	Properties of 1-D and 2-D Fuels, 12	
	Blending 1-D and 2-D Fuels, 13	
16	CHAPTER THREE DIESEL FUEL ADDITIVES	
	Additive Types and Their Effects, 16	
	Current Practices in Additive Use, 24	
	Engine Manufacturer's Recommendations for Additives, 25	
	Summary of Additives, 25	
26	CHAPTER FOUR HOW TO EVALUATE FUEL ADDITIVES	
	Background Information, 26	
	Laboratory Tests, 27	
	Engine and Vehicle Tests, 27	
	Fleet Evaluations, 28	
	Cost-Benefit Analysis, 28	
30	CHAPTER FIVE ALTERNATIVE FUELS	
	Gaseous Fuels, 30	
	Alcohols, 30	
	Vegetable Oils, 32	
	Synthetic Fuels, 32	
34	GLOSSARY	
36	REFERENCES	
39	APPENDIX A PROPERTIES OF NO. 1-D AND NO. 2-D FUELS IN 1982 BY REGION AND MAP SHOWING REGION LOCATIONS	
42	APPENDIX B EQUATIONS AND STATISTICAL DATA RELATING TO THE CETANE NUMBER AND THE CETANE INDEX	

45	APPENDIX C	REGIONAL CETANE INDEX DISTRIBUTIONS FOR NO. 2-D FUELS, 1982
51	APPENDIX D	CALCULATIONS OF BLEND PROPERTIES AND VOLUMETRIC IMPROVEMENT COST
57	APPENDIX E	EXXON'S LOW-TEMPERATURE FLOW PROCEDURE
61	APPENDIX F	SURVEY OF FUEL AND ADDITIVES USED BY TRANSIT OPERATORS



## NCTRP TECHNICAL STEERING GROUP

Annual research programs for the NCTRP are recommended to UMTA by the NCTRP Technical Steering Group (TSG). Under contract to UMTA, the American Public Transit Association, supported by the Urban Consortium for Technology Initiatives/Public Technology, Inc., is responsible for operation of the TSG, the membership of which is as follows.

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Information on current practice was provided by many transit agencies. Their cooperation and assistance were most helpful.

# DIESEL FUEL QUALITY AND EFFECTS OF FUEL ADDITIVES

## SUMMARY

This synthesis presents information about diesel fuel and fuel additives, with emphasis on their use in transit buses. Rising fuel costs and a gradual decline in diesel fuel quality provide incentives to use fuel more efficiently. Environmental and public relations factors encourage reducing smoke and gaseous exhaust emissions. The use of additives is often proposed as a remedy for fuel-related problems but, because of their cost, additives must be shown to be effective by careful evaluation before and during their use.

The study of fuel additives necessarily involves the broader subject of fuel quality and engine performance, which additives are expected to improve. Diesel fuel quality is not a constant, and major causes of changes are identified in the study. Performance in transit buses includes concerns for emissions and efficient combustion. This synthesis describes additives in functional categories and presents a generalized approach to methods for evaluation.

Additive evaluation depends on a measurable change in fuel properties, engine performance, or both. Therefore, a background discussion of diesel fuel quality is included. This discussion covers measurement of fuel properties and how those properties relate to performance. Information on fuel quality trends and alternative fuels is also important for planning purposes. With this background, the description of fuel additive benefits should be more useful in developing evaluation methods.

## DIESEL FUEL QUALITY TRENDS

On the average, the quality of U.S. diesel fuel has decreased about four cetane numbers between 1972 and 1982. This change occurred with fuels supplied for city buses (mostly No. 1-D fuel) and for trucks and tractors (mostly No. 2-D). About one cetane number of the decline for city buses was the result of more No. 2-D being used in transit operations.

Future changes will be caused by continuing decline in crude oil quality, a steady increase in demand for distillate fuels relative to gasoline, and more conversion processing (cracking) of heavy oils to produce the needed distillates. The net effect between now and the year 2000 on diesel fuels is estimated to be:

- No. 1-D fuel will compete with jet fuel for volume of product available.
- No. 2-D fuel will increase in boiling range and density. Cetane number will

decline to minimum values allowed in specifications. Sulfur content should not change. Additives for cetane and pour point improvement will be used by more suppliers.

## **DIESEL FUEL QUALITY**

The report reviews properties important for ignition, engine performance, and for handling and storage. To ensure efficient use of fuel, it is important to obtain the quality most suitable for the engines used and the type of service. Fuel of higher quality than needed may not produce significant improvements in performance or emissions.

A survey of transit companies disclosed that some operators do not specify fuel quality other than by grade. Because the quality of fuels in recent years has decreased, it is strongly advised that complete fuel specifications be defined. The quality requirements may be patterned after ASTM to meet local requirements, with advice from the engine manufacturer and from fuel suppliers.

To ensure that fuel meets specifications, inspection results should be obtained routinely from suppliers. Information should also be requested on types of additives in the fuel. Samples should be checked on a regular basis, either in-house or by an outside laboratory.

The discussion of No. 1-D and No. 2-D grades of fuel in the report provides a basis for choice of fuel grades.

- No. 1-D fuel typically has a higher cetane number and is cleaner burning than No. 2-D.
- No. 2-D fuel generally has a lower cetane number and a higher boiling range than 1-D.
- Some No. 2-D had higher cetane numbers than some No. 1-D and may have other advantageous properties.
- Blends of No. 1-D and No. 2-D could provide adequate quality at a cost saving.
- Specifications can be developed reflecting quality of a blended fuel (i.e., the supplier would do the blending).

Implementation of the last three choices would require familiarity with the local fuel market and cooperation of fuel suppliers.

## **DIESEL FUEL ADDITIVES**

Numerous types of additives are available for use in diesel fuel, as summarized in the table on p. 3. Additives should be used only when needed to prevent or solve a problem, and when they are the most economical method of doing so. If used to modify fuel properties, the fuel response to a given additive must be measured to determine the amount of additive. Additives are fuel specific and may perform well in one fuel and poorly in another.

Most refiners use additives to protect the fuel quality or the pipelines and storage tanks. The most commonly used additives are detergents, antioxidants, corrosion inhibitors, and metal deactivators. The amounts used are usually adequate to last through normal storage periods.

Flow improvers are used by suppliers to improve pour point, most often in cold months. Ignition improvers to raise cetane number are used less frequently. With future fuel trends, the use of these types of additives by refineries is likely to increase.

Additive Type	Function	Undesirable Effects
Ignition improvers: Alkyl nitrates	Improve cetane, reduce ignition delay	None
Smoke suppressants: Barium-based	Interfere with soot formation	Emissions may be toxic
Manganese-based	Catalyze soot combustion	Deposits may harm engine
Flow improvers: Polymers	Limit wax crystals size, less filter plugging	None (does not change cloud point)
Engine performance additives: Atomizers	Combustion faster, more complete	Most do not work
	Lower fuel surface tension, smaller droplets	Droplets can be too small
Storage and handling additives: Detergents/emulsifiers/dispersants	Prevent settling or separation	None
Antioxidants/stabilizers	Prevent reactions with oxygen, which form gums	None
Corrosion inhibitors	Coat and protect metals	None
Metal deactivators	Coat metal to protect fuel from reactions catalyzed by the metal	None
Biocides	Kill slime producing bacteria/fungi	None
Demulsifiers/anti-haze	Aid separation of water	None
Antistatic additives	Increase electrical conductivity, prevent static discharge	None

It is important to know whether these additives are present if the transit operator is planning to use the same type, because the first increment of additive is most effective and additional amounts may produce little or no improvement.

Smoke suppressants and engine performance additives are not customarily used by fuel suppliers. These products are intended for the fuel user. Smoke suppressants reduce but do not eliminate smoke in the exhaust. The most successful are based on barium compounds, which leave the engine in two forms, one of which is toxic. The barium may be less toxic than the smoke, but that has not been firmly established. Test results also indicate that barium compounds increase engine deposits.

Published results on evaluation of performance additives and combustion catalyst have shown very little, if any, improvement in engine performance, fuel economy, or exhaust emissions.

Engine manufacturers have generally had good results with ignition improvers and with flow improvers. They support the use of storage and handling additives and note that their effects have been mostly beneficial. They have had bad experience with additives claimed to improve fuel economy or otherwise affect performance of well-maintained engines. They recommend against the use of performance-type additives and against the use of smoke suppressants.

One of the developers of smoke suppression additives stated that a solution should first be sought in improvements in engine operation and maintenance, in particular maintenance and adjustment of fuel injection equipment, or a change in the fuel.

## HOW TO EVALUATE FUEL ADDITIVES

Additives that modify fuel properties are evaluated by laboratory analyses of properties that may be affected at various additive concentrations. The cost can then be compared with other methods of obtaining the desired fuel property.



Additives that affect engine performance require more time and expense. The least expensive evaluation is one that has been done by someone else. However, the testing must be done in the same type of engine and vehicle, with an appropriate duty cycle and a similar fuel. For example, test results of a medium-speed railroad diesel engine at full load on heavy fuel will not be applicable to a high-speed engine in a transit bus that idles long periods using a light fuel. Such details are often lacking in testimonial letters used to support vendor claims.

The ideal basis for an informed decision about additive use is a comparison test where all conditions are controlled and the only variable is the additive. In order of increasing expense, the options are as follows:

- Engine on test stand
- Vehicle on chassis dynamometer
- Vehicle (one or two) in road test
- Fleet test in actual service

The tests would be planned to measure the desired additive effects and other factors such as performance, fuel consumption, and emissions.

## **ALTERNATIVE FUELS**

The alternative fuels likely to become available first are shale oil fuels and methanol. Good quality diesel fuel can be made from shale oil but methanol will be less expensive. The technical problems that have limited the use of fuel methanol in the past are being solved through conversions or specially designed engines and new fuel systems. Propane can make a contribution now in some areas, but is not likely to become widely available. The status of other alternative fuels is discussed further in Chapter Five.

## TRENDS IN DIESEL FUEL QUALITY

### HISTORICAL TRENDS

For several years the average cetane numbers reported in the Department of Energy (DOE) surveys have been decreasing (*1*). Figure 1 shows the average trend for type C-B (city bus) fuels, mostly No. 1-D grade. Figure 2 shows the trend for type T-T (truck and tractor) fuels, mostly No. 2-D grade. In both cases there was a drop of about four cetane numbers from 1972 to 1982, and the decrease has been most rapid in the years following the oil embargo in 1974.

In Figures 1 and 2, the fuels were classified by type of service. Type C-B for city bus service contained mostly No. 1-D and some No. 2-D fuels. Because No. 2-D fuel generally has a lower cetane number than No. 1-D, an increase in proportion of No. 2-D fuels would lower the average for Type C-B. This shift in fuel grades accounts for part of the decline in cetane number in Figure 1 and indicates that more No. 2-D fuel is being used in transit service.

The long-term decrease in cetane number is caused by a combination of factors (*2, 3*). In the past, the cetane number was largely determined by diesel fractions distilled from the crude. Cracked distillates were lower in cetane number, but the virgin stocks were high enough to allow blends that easily met specifications. Diesel fuel was a minor product relative to gasoline and normal refinery processes provided more than enough diesel fuel when gasoline demand was met.

Over the years, crudes that were high in API gravity and low in sulfur content were used preferentially because they required the least processing to make high quality products. As these sources ran out, refiners had to turn to heavier, high-sulfur crudes, which generally made lower cetane diesel fuel. They also required more cracking to meet the demand for light prod-

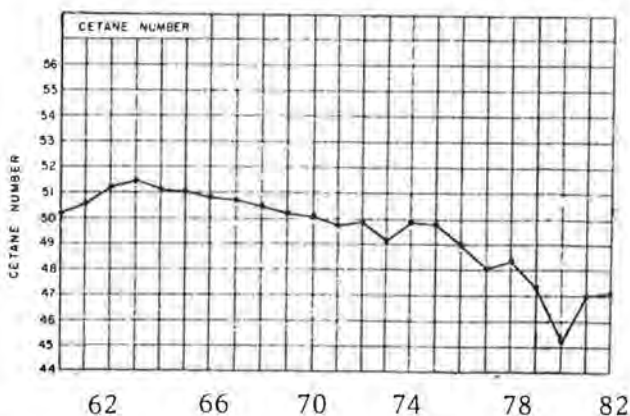


FIGURE 1 Trend of U.S. average cetane number for C-B (city bus) fuels (*1*).

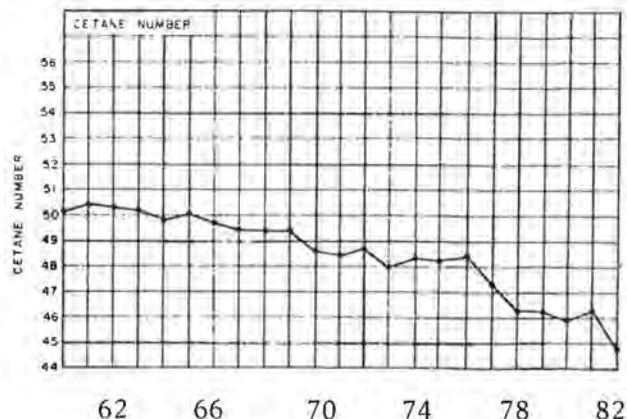


FIGURE 2 Trend of U.S. average cetane number for T-T (truck, tractor) fuels (*1*).

ucts, and diesel stock from catalytic cracking is typically 10–25 cetane numbers below the virgin stock from the same crude. Alaskan North Slope crude, which became available in 1977, provides low cetane distillates, and Canadian tar sand distillates have very low cetane numbers.

Coupled with this decline, there has been a rise in diesel fuel demand relative to gasoline demand. The proportion of automobiles using diesel engines has grown from almost zero percent in the mid 1970s to about 1 percent in 1980 and is continuing to increase. Table 1 shows the increase in diesel fuel used by transit vehicles since 1970 (*4*). The largest increase in demand has come from heavy-duty trucks, which use diesel engines almost exclusively to take advantage of higher fuel economy. These changes have made it increasingly difficult for refiners to meet diesel quality requirements simply by a judicious selection of crudes.

### FUTURE TRENDS

The consumption of petroleum in the United States has shown a remarkable reversal between 1974 and 1984. Annual growth rates of 4 to 5 percent in the early 1970s dropped to 1 to 2 percent per year in the late 1970s. Since 1980 the use of petroleum has actually declined. The cause of the major changes in petroleum use was a rapid increase in cost of crude oil in 1974 and again in 1979.

Forecasts that are discussed in this section indicate a level or slightly declining demand for the period 1985 to 2000. Projected changes in fuel-use patterns will cause shifts in the types of products needed. The combination of these major factors will require changes in refinery processing to balance crude supply

TABLE 1

ENERGY CONSUMPTION BY TRANSIT PASSENGER VEHICLES (4)

Calendar Year	Electric Power (million kWh)	Fossil Fuel (1000 gal)		
		Gasoline	Diesel	Propane
1970	2,561	37,200	270,600	31,000
1971	2,556	29,400	256,800	26,500
1972	2,428	19,647	253,250	24,400
1973	2,331	12,333	282,620	15,152
1974	2,630	7,457	316,360	3,142
1975	2,646	5,017	365,060	2,559
1976	2,576	5,203	389,187	960
1977	2,303	8,077	402,842	1,196
1978	2,223	9,318	422,017	13
1979	2,473	8,961	423,212	12
P 1980	2,446	11,400	441,300	—

NOTE: Table excludes automated guideway transit, commuter railroad, and urban ferry boat.

P = Preliminary

— = Data not available

and product demand. The effects of these changes on the future quality of diesel fuels is examined below.

### Crude Oil Supply

Recent history of crude oil supply in the United States is shown in Table 2 (5). Domestic crude production has ranged between 8.1 and 9.2 million barrels per day (bbl/d) and has remained nearly constant at about 8.6 million bbl/d for the last five years. The volume of imported crude oil increased steadily and reached about 6.5 million bbl/d from 1977 to 1979. Since 1979 imports have declined just as steadily as the previous increase to an average 3.5 million bbl/d in 1982, although the volume was down to 3.0 million bbl/d at the end of 1982. In addition to crude oil, natural gas liquids and imported products add about 3 million bbl/d to the total U.S. petroleum supply, which was about 15 million bbl/d in 1983.

Crude oil quality shows a general trend toward heavier crudes with higher sulfur contents. As an example, the National Petroleum Council in 1980 made the following comparison of sweet and sour crudes (6):

Year	Percentage of Total Supply	
	Sweet Crude	Sour Crude
1969 (actual)	64.5	35.5
1978 (actual)	54.5	45.5
1982 (forecast)	48.0	52.0
1985 (forecast)	46.3	53.7
1990 (forecast)	43.0	57.0

Sweet crude is defined as containing less than 0.5 weight percent sulfur. Sour crudes with more than that amount of sulfur made up about 50 percent of supply in 1981 and will increase further in coming years. The term "sour" refers to the odor of hydrogen sulfide that is often present in high-sulfur crudes.

TABLE 2

U.S. CRUDE OIL SUPPLY, THOUSAND BARRELS PER DAY (5)

Year	Domestic	Import	Total
1973	9,208	3,244	12,452
1974	8,774	3,477	12,251
1975	8,375	4,105	12,480
1976	8,132	5,287	13,419
1977	8,245	6,615	14,860
1978	8,707	6,356	15,063
1979	8,552	6,519	15,071
1980	8,597	5,263	13,860
1981	8,572	4,396	12,968
1982	8,671	3,461	12,132

A comparison of average crude quality can be seen in Figure 3 (7). This figure shows crude oil gravity declining from 34.7°API in 1979 to 30.8°API in 2000. (Degree API is an inverse measure of density in which lower numbers indicate heavier oils.) Sulfur content is expected to increase substantially from 0.78 to 1.14 weight percent. Another measure is the amount of residual material, such as asphalt, that boils at more than 1000°F (540°C); this residue may increase from 17.2 to 20.9 percent.

The reasons for the trend are that crude obtained from new sources is usually heavier and the production of lighter crudes from older fields is declining. For example, Prudhoe Bay crude (which has made up about 20 percent of domestic production since 1978) is fairly heavy at 27.0°API, intermediate in sulfur at 1.02 weight percent, and contains 20 percent material boiling at more than 1000°F (540°C). Mexican crude is now about 23 percent of imports and is heavy at 23 to 29°API, high in sulfur

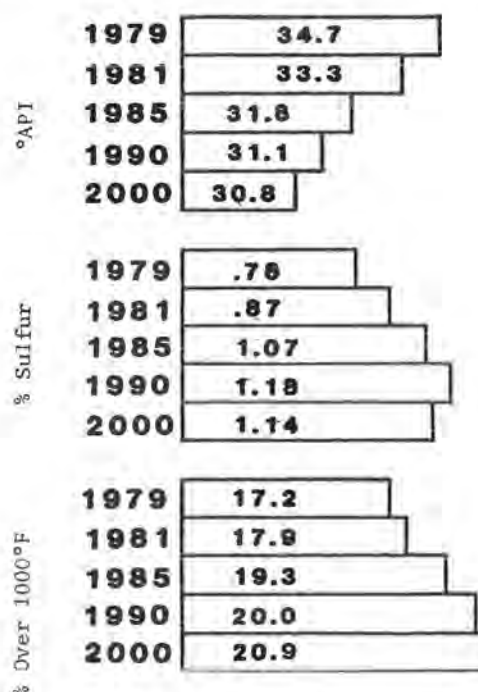


FIGURE 3 Forecast of crude oil quality by the Pace Company (7).

at 2 to 3 weight percent, and has about 24 to 32 percent residue over 1000°F.

### Product Demands

A forecast by SRI International is summarized in Table 3 (8). Gasoline demand is expected to fall about 30 percent by the year 2000. Jet fuel requirements will rise by about 35 percent and diesel fuel will increase about 64 percent. The forecast assumes that more diesel engines would be used in light vans and trucks as well as 10 percent of new cars in 1990 and 12 percent of new cars in the year 2000.

Total distillate fuel (jet fuel, heating oil, and diesel fuel) is seen as increasing steadily while gasoline declines. The gasoline-to-distillate ratio at the bottom of the table is a convenient comparison. Traditionally, gasoline production has been much higher than total distillates, indicated by the 1.65 ratio in 1982. Sometime between 1990 and 2000, demand for gasoline and distillates is predicted to be the same (ratio of 1.0).

SRI International expects the residual fuel oil demand to decrease by about 30 percent. It can be noted that the residual products amount to only 12.5 percent of total demand in 2000. At the same time, the crude oil will become heavier and contain over 20 percent residual fuel as shown in Figure 3. The net effect is that some heavy fractions in the crude oil must be converted by some form of cracking to make the added quantities of distillates needed at that time. The type of cracking selected will have important effects on the distillate quality, as discussed later.

A similar forecast of gasoline and distillates was made by the Pace Company (7) and is shown in Table 4. These estimates are slightly different from those from SRI in Table 3. The trend in gasoline-to-distillate ratio is similar and indicates the same competition for product barrels among jet fuel, heating oil, and diesel fuel.

A comprehensive forecast by Du Pont (9) estimated that diesel fuel requirements would more than double, from 900,000 bbl/d in 1981 to 1,900,000 bbl/d in 2000. Most of the increase was for medium and heavy-duty trucks. Although use of diesel engines in passenger cars and light trucks will increase, it will constitute a minor portion of the demand as indicated in Figure

TABLE 3

SRI INTERNATIONAL PROJECTIONS OF U.S. PRODUCT DEMAND (MILLION BARRELS PER DAY) (8)

Product	1980	1982	1990	2000
Gasoline	6.6	6.4	5.0	4.5
Distillates				
Jet fuel	1.1	1.1	1.3	1.5
Heating oil	1.8	1.6	1.6	1.4
Diesel fuel	1.1	1.1	1.6	1.8
Subtotal distillates	4.0	3.8	4.5	4.7
Residual fuels	2.6	1.7	2.0	1.8
Other products	3.7	2.9	2.9	3.3
Total demand	16.9	14.8	14.4	14.3
Gasoline to distillate ratio	1.65	1.68	1.11	0.96

TABLE 4

PACE COMPANY PROJECTIONS OF GASOLINE AND DISTILLATE DEMAND (MILLION BARRELS PER DAY) (7)

Product	1978	1985	1990	2000
Gasoline	7.40	5.90	6.00	6.30
Distillates				
Jet fuel	1.04	1.15	1.24	1.27
Heating oil	2.00	1.90	1.90	2.00
Diesel fuel	1.26	1.66	2.21	3.10
Subtotal distillates	4.30	4.71	5.35	6.37
Residual products	3.70	2.70	2.30	2.40
Gasoline to distillate ratio	1.72	1.25	1.12	0.99

4. The forecast allowed for improving fuel economy of all three classes of vehicles, as shown in Figure 5.

Jet fuel in the Du Pont forecast will have a slow but steady increase in demand from 1,000,000 bbl/d in 1981 to 1,300,000 bbl/d in 2000. Gasoline is expected to decline from 6,600,000 bbl/d to 5,100,000 bbl/d in the same period as a result of the shifting of trucks in all classes to diesel and continuing improved fuel economy of gasoline engines, as illustrated in Figures 6 and 7.

Although there are differences among the three forecasts selected for discussion, the trends are consistent. Gasoline demand is expected to decline, while jet fuel and diesel fuel demands will increase to levels that will require modifications to refinery processing.

A projection by Argonne National Laboratory (10) indicated future increases in fuel consumption by transit buses (Table 5). The 46 percent increase from 1980 to the year 2000 is similar to the overall trend for diesel fuel. Transit bus fuel is predominantly No. 1-D diesel fuel, which will be in competition with

Millions of Barrels  
per Day of  
Diesel Fuel

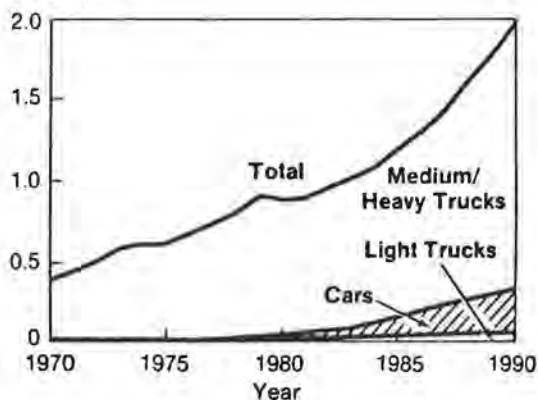


FIGURE 4 Forecast demand for highway diesel fuel by vehicle type (9).



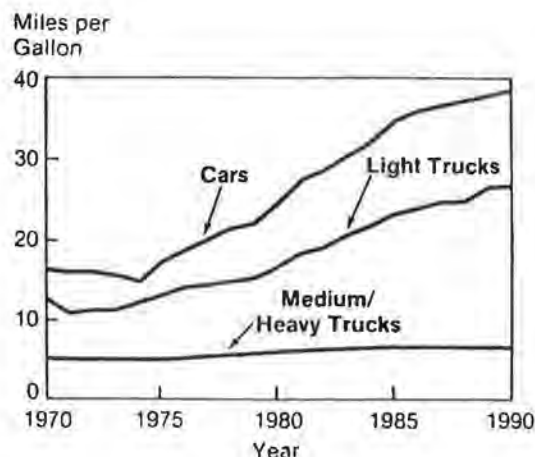


FIGURE 5 Fuel economy of diesel-powered vehicles (9).

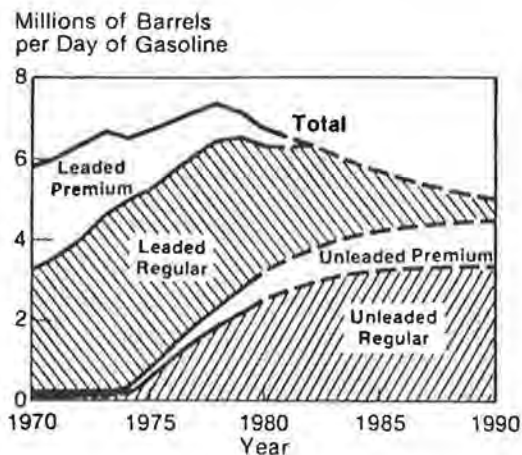


FIGURE 6 Demand for gasoline by grade (9).

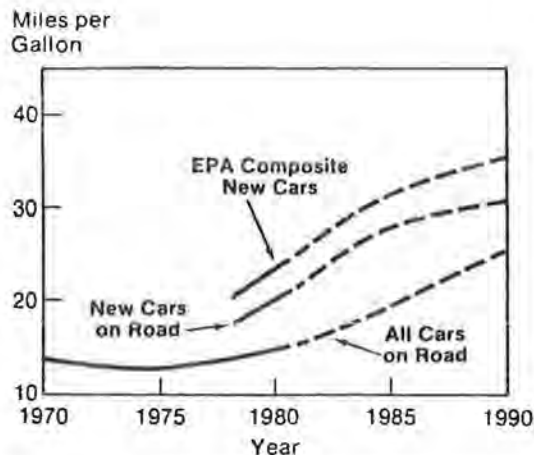


FIGURE 7 Fuel economy of gasoline-powered cars (9).

TABLE 5

ARGONNE PREDICTION OF TRANSIT BUS ANNUAL ENERGY CONSUMPTION (10)

Measure	1980	1985	1990	2000
Vehicle miles (millions)	1677.2	1955.8	2125.3	2273.2
Miles per gallon	3.6	3.3	3.3	3.3
Gallons per year (millions)	465.9	592.7	644.0	688.9
Barrels per day	30,390	38,660	42,010	44,940

jet fuel for the volumes of lower-boiling-range distillate product needed.

#### Diesel Fuel Production and Properties

If diesel fuel could be made only with straight-run stocks (distilled directly from the crude) the 400 to 650°F (230 to 340°C) fraction from most crudes would easily satisfy the minimum 40 cetane number in ASTM D 975. The straight-run diesel fraction would range from 42 cetane for an aromatic crude to 56 cetane for a paraffinic crude, with an average of about 49 to 50 cetane (11). Most No. 1-D diesel fuel is straight-run material with about 400 to 550°F (200 to 290°C) boiling range. The following discussion refers primarily to No. 2-D grade.

Most refineries produce additional stocks in the diesel boiling range by converting (cracking) higher boiling material into smaller molecules. These conversion processes fall into three groups with typical cetane number ranges for the diesel fraction as follows:

Process	Product	Cetane No.
Catalytic cracking	Light cycle oil	20-35
Thermal cracking	Visbreaker gas oil	30-40
	Coker gas oil	30-40
Hydrocracking	Hydrocracker distillate	40-60

Properties of the distillate products from catalytic or thermal cracking differ from the properties of straight run stocks. They have lower cetane numbers because they contain more aromatic compounds (unsaturated ring structures). The usual hydrotreating step to remove sulfur and improve stability adds 3 to 5 cetane numbers. These products also contribute low pour points to the final blends with straight-run stocks and they usually exhibit good response to cold-flow improvers. However, they have a lower response to cetane improvers than straight-run stocks (12).

Hydrocracking makes a high cetane product that would raise the average cetane level of the refinery diesel production. This process is costly to build and operate and will probably be used less than catalytic or thermal cracking. However, it makes excellent quality jet fuel or perhaps a premium grade of diesel fuel. The product is stable (except for a tendency toward peroxide formation, which is readily controlled with antioxidant inhibitors) and has low cloud point and pour point.

## Future Property Trends

The trends discussed previously in crude supply, product demands, and refinery processing will have certain general effects on diesel fuel properties.

### Boiling Range

Diesel fuel is expected to have a wider boiling range because of the need to obtain maximum yield. Reducing the 10 percent distillation temperature will be limited by the flash point specification. Raising the 90 percent temperature will be limited by cold-flow properties, such as cloud point or pour point. This approach applies to straight-run stocks as well as cracked products. Wider boiling range in diesel fuel tends to increase exhaust emissions, mainly unburned hydrocarbons and particulates (13).

### Density

Density of diesel fuel will tend to increase because of higher aromatics content and increased 90 percent distillation temperature.

### Cetane Number

The average cetane number of total distillate production will decrease because of the higher proportion of cracked components. However, as discussed later, refiners have various options to improve diesel fuel, such as selective blending (for example, to use the lowest cetane stocks in heating oils). Therefore, the cetane number of diesel fuels probably will not go below the minimum value allowed in local specifications.

### Sulfur Content

Higher sulfur contents would normally be expected from more sulfur in crude oils, wider boiling ranges, and more cracked components. However, with the increased use of hydrotreating of both straight-run and cracked stocks, sulfur content is likely to remain constant or rise only slightly.

### Additives

Normal use of additives by refiners will continue where needed as dispersants, antioxidants, corrosion inhibitors, and metal deactivators. Cetane improvers or pour point improvers may be beneficial at some refineries, and the trends discussed above will increase use of these additives. This fact is important to recognize if cetane or pour point additives are being considered at the fuel consumer location. If these additives are used by the supplier, the amounts added by the user will have little or no effect.

## Refinery Options

The extent of change in diesel fuel properties will vary from one refinery to another because of differences in such factors as crude oils, processing facilities, seasonal variations, and economics. A recent study by Ethyl Corporation (12) analyzed the options available to petroleum refiners to provide the increased demand for diesel fuel and to meet quality specifications at the same time. An abbreviated summary of the refinery options includes the following:

- *Selective Blending*—A refinery may have several distillate fractions with different properties. Blending these in selected proportions allows production of jet fuel, heating oil, and diesel fuels to their respective specifications. Careful planning ensures that the qualities of the several components are used most effectively. For example, more low-cetane stocks are used in heating oils, leaving higher cetane materials for diesel fuels.

- *Segregated Grades*—Providing more grades of diesel fuel is an extension of selective blending. Because railroads can use 35 cetane number fuel in their medium-speed diesel engines, segregation of that product would allow use of the higher cetane stocks in regular or premium grades. Although the addition of fuel grades will involve added costs for storage and distribution, three grades were suggested (12): Premium—over 45 cetane number, Regular—40 to 45 cetane number, and Railroad—35 to 40 cetane number.

- *Severe Hydrotreating*—By severe hydrotreating to convert aromatics compounds, cetane can be raised about 10 numbers along with other quality improvements. This operation is expensive because it requires a new process unit and uses more hydrogen than the low severity unit it replaces.

- *Other Processing*—Catalytic cracking operations can be modified to produce less gasoline and more distillate; modified catalysts can be used to improve quality of the distillate fraction. A distillate dewaxing process is available to crack paraffins selectively and improve the pour point; this would allow raising the 90 percent distillation point and increasing the yield of diesel fuel.

- *Additives*—Diesel ignition improver can be used to increase cetane number by 3 to 6 numbers, depending on the response of the fuel and concentration of additive. The cetane index will not change because it is calculated from the gravity and mid-boiling point. If specifications call for cetane index, the alternative of cetane number by engine rating would permit use of an ignition improver. Cold-flow improver may also be used as a means of meeting pour point specifications and increasing production of distillate fuels. The selection of additives and their use by the refiner will be based on the relative cost in comparison with other alternatives in blending or processing.

In summary, changes in crude supply and product demand will require use of more conversion processing to meet the increased demand for distillate fuels. The cetane number and other qualities of diesel fuel are expected to decline, but will remain within the specification limits. Fuel producers will be able to provide the increased volumes of diesel and jet fuels and maintain quality by processing and blending modifications. Some increased use of additives is expected for cetane and cold-flow improvement. There may be an increase in the number of

grades of diesel fuel in areas where cetane quality makes such segregation economical.

The main conclusions for transit operators are that the distillate product demand will be high and No. 2-D fuel will decline

in quality. No. 1-D fuel will show less change in quality because it is primarily a straight-run product. A premium grade of diesel fuel may emerge for transit use, although No. 1-D is already regarded as a premium grade in some areas.

## CHAPTER TWO

# MEASUREMENT OF FUEL QUALITY

Several tests are made on distillate fuels to measure their properties and to provide reference points for their performance. These properties can be classified into three functional areas:

- Ignition properties
- Engine performance properties
- Handling and storage properties

The fuels are produced to meet local specifications, which are normally written with reference to ASTM measurements. As an example of fuel specifications, Table 6 lists the ASTM D 975-81 requirements for the No. 1-D and No. 2-D grades of diesel fuels and the corresponding ASTM methods for property

measurements. Local specifications may include other tests and use other limiting values.

The DOE publishes an annual survey of diesel fuel property measurements supplied by the fuel manufacturers (1). The number of samples and their wide geographic distribution provide the most complete data available. Statistical analyses of the DOE data provide unweighted distributions of fuel properties based on the number of samples reported, not the actual volume of fuel sold. Table 7 gives the average properties of diesel fuels reported in the survey. Other tables based on the 1982 DOE report are included in Appendix A.

TABLE 6  
SPECIFICATION FOR DIESEL FUELS, ASTM D 975-81 (14)

Requirement	ASTM Method	No. 1-D Diesel Fuel		No. 2-D Diesel Fuel	
		Min.	Max.	Min.	Max.
Cetane number	D 613 <sup>a</sup>	40 <sup>b</sup>	-	40 <sup>b</sup>	-
Distillation, °F (°C), 90% recovery	D 86	-	550 (288)	540 (282)	640 (338)
Flash point, °F (°C)	D 93	100(38)	-	125(52)	-
Cloud point, °F (°C)	D 2500	-	c	-	c
Water & sediment, vol%	D 1796	-	0.05	-	0.05
Carbon residue on 10% bottoms, wt%	D 524	-	0.15	-	0.35
Ash, wt%	D 482	-	0.01	-	0.01
Viscosity, cSt, 40°C	D 445	1.3	2.4	1.9	4.1
Sulfur, wt%	D 129 <sup>d</sup>	-	0.5 <sup>e</sup>	-	0.5 <sup>e</sup>
Copper strip corrosion	D 130	-	No. 3	-	No. 3

<sup>a</sup>Cetane index by ASTM D 976 may be used as an approximation.

<sup>b</sup>Higher cetane ratings may be required at low temperatures or high altitudes.

<sup>c</sup>Cloud point is specified for area and season.

<sup>d</sup>ASTM D 2622 is more accurate when sulfur content is low and is frequently preferred over D 129.

<sup>e</sup>Other sulfur limits may apply in local regions or outside the U.S.A.

## IGNITION PROPERTIES

The ignition quality of diesel fuels is measured in terms of the cetane number (CN). The cetane number scale ranges between 0 and 100, although in practice cetane numbers below 25 are very difficult to measure and few ordinary fuels are higher than 60 CN. The principal effect of a low cetane number is a longer ignition delay from the start of injection to the beginning of combustion. During this longer delay more fuel is vaporized, and decomposition and oxidation reactions occur. Therefore, when the fuel-air mixture ignites, a greater fraction of the fuel is in the gas phase and at a higher temperature. These conditions cause a more rapid pressure rise in the cylinder, which shows as combustion roughness and audible knock.

Low-cetane fuel also causes misfiring and cold-start problems. Severe problems may involve incomplete combustion with excessive white smoke and low power. Fuel of higher cetane number has a shorter ignition delay with even sustained burning, which results in smooth operation and easier starting at low temperatures.

Engines vary in their cetane number requirements (15, 16). Engines designed for low-speed operation can tolerate lower cetane number fuels than engines designed for high-speed operation. With spark-ignition gasoline engines, knock begins abruptly at a particular point on the octane scale. However, with diesel engines the transition between rough, knocking operation and normal operation is more gradual. As the cetane number increases, knock severity decreases.

With compression ignition in diesel engines, use of fuel with unusually high cetane numbers is not advisable. If the cetane



TABLE 7  
AVERAGE PROPERTIES OF DIESEL FUELS (1)

Property	No. 1-D Diesel Fuel	No. 2-D Diesel Fuel
Cetane number	48.0	44.4
Cetane index	46.9	45.8
Distillation, °F (°C)		
Initial boiling point	347 (175)	383 (195)
10%	386 (197)	437 (225)
50%	428 (220)	509 (265)
90%	483 (251)	595 (313)
End point	521 (272)	644 (340)
Gravity, °API	42.5	34.5
Specific gravity	0.8132	0.8524
Density, lb/gal	6.77	7.10
Carbon residue	0.063	0.138
Flash point, °F (°C)	138 (59)	168 (76)
Ash, wt%	0.003	0.002
Sulfur, wt%	0.086	0.272
Viscosity, cSt @ 100°F	1.70	2.85
Aniline point, °F (°C)	145.8 (63.2)	143.2 (61.8)

number is too high, the engine produces less power and gets poor mileage. Each engine operates best on fuels within a range of cetane numbers. The range is bounded on the low end by fuels that cause starting problems and severe knock and on the high end by fuels that cause inefficient operation. Also, during normal operation, smoke and other pollutant emissions are minimized when using fuels within the proper range compared to either higher or lower cetane number fuels. Emissions will be discussed more fully in later sections.

The cetane number is measured by comparing the ignition delay of a fuel to that of known reference fuels in a specially constructed laboratory engine. Because of the time and cost required for the measurement of cetane number, the cetane index (CI) is often used in its place. The cetane index is calculated from the 50% boiling point and the API gravity rather than measured directly. The CI equation is given in Appendix B; results are usually similar to the cetane number ( $\pm 2$  units) especially in the range of 40 to 50 cetane. The cetane index is available for all of the samples reported in the DOE surveys, but the cetane number is available for only a small percent of the samples. It is customary to use the cetane index instead of the cetane number, but the difference in the two terms should be noted in specifications.

Collins and Unzelman have discussed the relationship between the cetane index and the cetane number using extensive Ethyl Corporation data along with European and Canadian data (2, 17). The cetane numbers in their combined data set varied from less than 30 CN to more than 60 CN. The cetane index was lower than the cetane number for high cetane numbers. The opposite occurred for low cetane numbers with the crossover point about 45 CN.

The specific gravity and aniline point are also related to the ignition properties because they vary with the fuel chemical composition.

## ENGINE PERFORMANCE PROPERTIES

Fuel properties can be related to engine performance in a laboratory where fuel consumption, power output, and exhaust emissions are measured as a function of engine speed. The generalized results are then usable as guides for actual engine and vehicle operation under widely variable conditions. The operating cycle of the vehicle determines which performance factors are important. For example, a transit bus operating cycle may include multiple stops and starts with frequent acceleration. An express bus with long periods of high-speed operation would have a different set of key properties. This section will not attempt to correlate properties and performance but will describe the properties that are important.

In the distillation test, a small sample of fuel is heated to its boiling point. The temperature of the vapor is measured and the vapor is condensed. As the amount of fuel distilled increases, the temperature increases. The result is a boiling point curve of temperature as a function of percentage of fuel distilled.

Lower boiling fuels are more volatile and vaporize more readily in the combustion chamber than the higher boiling fuels. Sulfur compounds in petroleum tend to be more concentrated in the higher boiling fractions. The higher boiling fractions also have larger molecules and the aromatic type of hydrocarbon is more common. These factors cause the higher boiling fuels to have higher viscosity, better lubricity, higher energy content, and higher specific gravity (lower API gravity). The relationship of 50 percent boiling point and specific gravity to cetane quality was noted in the previous section.

Fuels with high viscosity are more difficult to atomize than low-viscosity fuels. With a high-viscosity fuel, droplets from the injector spray tend to be larger than with low-viscosity fuel and there is greater opportunity for incomplete combustion because the larger drops take a longer time to burn. Larger droplets are more likely than small droplets to adhere to the piston or cylinder walls where they may leave a carbon deposit. However, fuels that meet ASTM specification viscosity limits for diesel fuels are easily atomized and spray pattern difficulties are mostly caused by equipment or maintenance problems.

Other properties are related to undesirable fuel components. Carbon residue is not a direct measure of the carbon formation that occurs during combustion, but it is an indicator of the potential for high rates of carbon deposition and high levels of exhaust soot. Ash is rarely high enough to cause significant problems, but when present it contributes to engine deposits and wear.

Sulfur compounds are burned to form sulfur oxides, which are acidic and cause corrosion in the engine and exhaust system, degradation of the lubricating oil, and undesirable emissions. Sulfur oxides also cause increased ring and liner wear, especially at low cooling jacket temperatures. Higher base number crankcase oils offset to a large extent the ravages of sulfur. The oil change interval needs to be carefully watched because the lubricant additive supplying the base number is depleted with use. Higher engine maintenance costs can be expected with high-sulfur fuel.

## HANDLING AND STORAGE PROPERTIES

Several property measurements are made that relate to the fuel in storage, during transfers and in the vehicle fuel system



before injection. Fuel sulfur is also important in storage and handling. Some sulfur compounds are not compatible with the elastomers that are often used as liners, glues, sealants, and diaphragms. The mercaptan class of sulfur compounds degrade elastomers and corrode copper, brass, or bronze parts in the fuel system. The copper strip corrosion test detects mercaptans and other reactive sulfur compounds. Results of the copper strip corrosion tests are reported in terms of tarnish classifications, which range from 1a (slight or no tarnish) through 4c (glossy or jet black tarnish). Any corrosion rating greater than 1a or 1b indicates a potential for causing materials problems.

The flash point is a measure of the maximum temperature at which fuel can be stored without fire or explosion hazard. The fuel volatility is a closely related property and fuels with lower 10% distillation temperatures have lower flash points.

The cloud and pour points affect the low-temperature fuel-handling characteristics. As fuel is cooled, the normal paraffin compounds solidify. At the cloud point temperature they begin to precipitate and form visible wax crystals. The crystals become large enough to plug most unheated fuel filters just below the cloud point. As the temperature is lowered further, the wax crystals grow and the fuel becomes more viscous and takes on the properties of a slurry. Eventually the wax crystals grow together and form a gel, which will not flow. The temperature just before this occurs is called the pour point.

Water and sediment are other common fuel impurities that can cause problems. Water in the fuel can freeze and form ice crystals large enough to plug fuel filters. Water also contributes to corrosion during storage and promotes the growth of algae and bacteria in storage tanks. The sediment present in fuels may contain hard, abrasive particles that cause increased wear of any moving parts and of nozzles and injectors.

Fuel lubricates several moving parts in fuel pumps and injectors, and fuel of low lubricity can increase wear rates of these components. Fuels from severe hydrogenation processing have had most of the natural lubrication compounds removed, but addition of corrosion inhibitor is a customary corrective measure. There are currently no ASTM requirements for fuel lubricity.

#### PROPERTIES OF 1-D AND 2-D FUELS

The cetane quality is the fuel property of greatest concern to most diesel fuel users. Because the cetane index (CI) is more widely available than the cetane number (CN), it is useful to see how well they correlate. The data from the 1982 DOE survey that included both CI and CN for 1-D fuels are shown in Figure 8 while data for 2-D fuels are shown in Figure 9. All of these are in the mid-range where Collins and Unzelman (2) found good correlation between the CI and the CN. The solid lines are based on a linear regression of the 1982 data. For the 1-D fuels, the equation shows that the CI is within one or two units of the CN. For the 2-D fuels, the equation obtained is almost identical to assuming that CN equals CI. The correlation equations and the statistical data are given in Appendix B.

The comparisons between the CN and CI indicate that the CI can be expected to differ from the CN by about two numbers for both 1-D and 2-D fuels. The measurement of CN by engine test is repeatable to only about two numbers. Because both CI and CN are somewhat imprecise measurements, it may be ap-

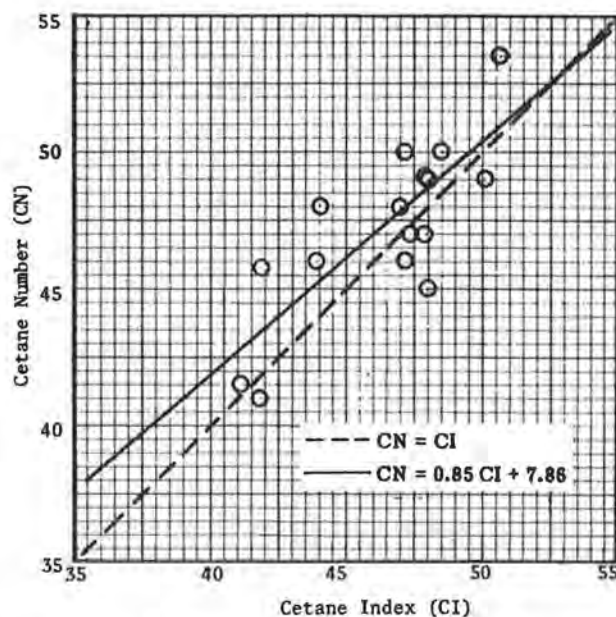


FIGURE 8 Relationship between cetane number and cetane index for grade 1-D diesel fuels, 1982 (data from ref. 1).

propriate to specify a CI value about two numbers higher than the minimum acceptable value as a safety factor. ASTM specifies 40 minimum cetane number for No. 1-D and No. 2-D diesel fuels. Most manufacturers of bus engines recommend use of 45 CN and above.

The 1982 DOE fuels survey reported a wide range of CI values. Figures 10 and 11 show the national distributions by

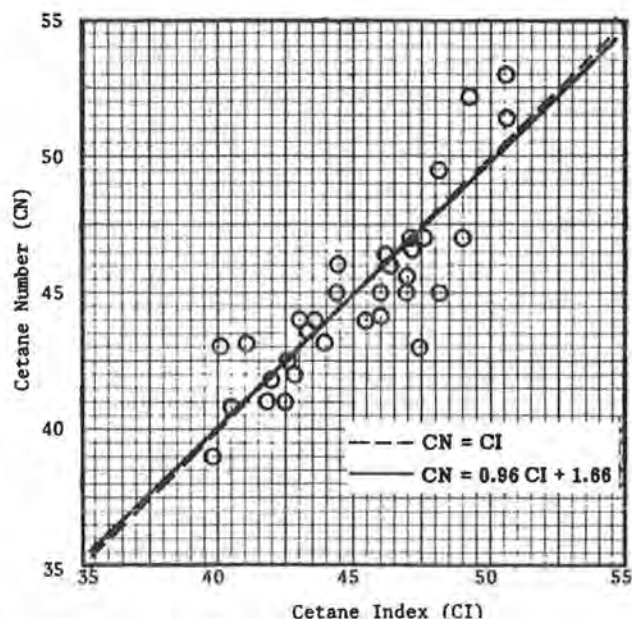


FIGURE 9 Relationship between cetane number and cetane index for grade 2-D diesel fuels, 1982 (data from ref. 1).

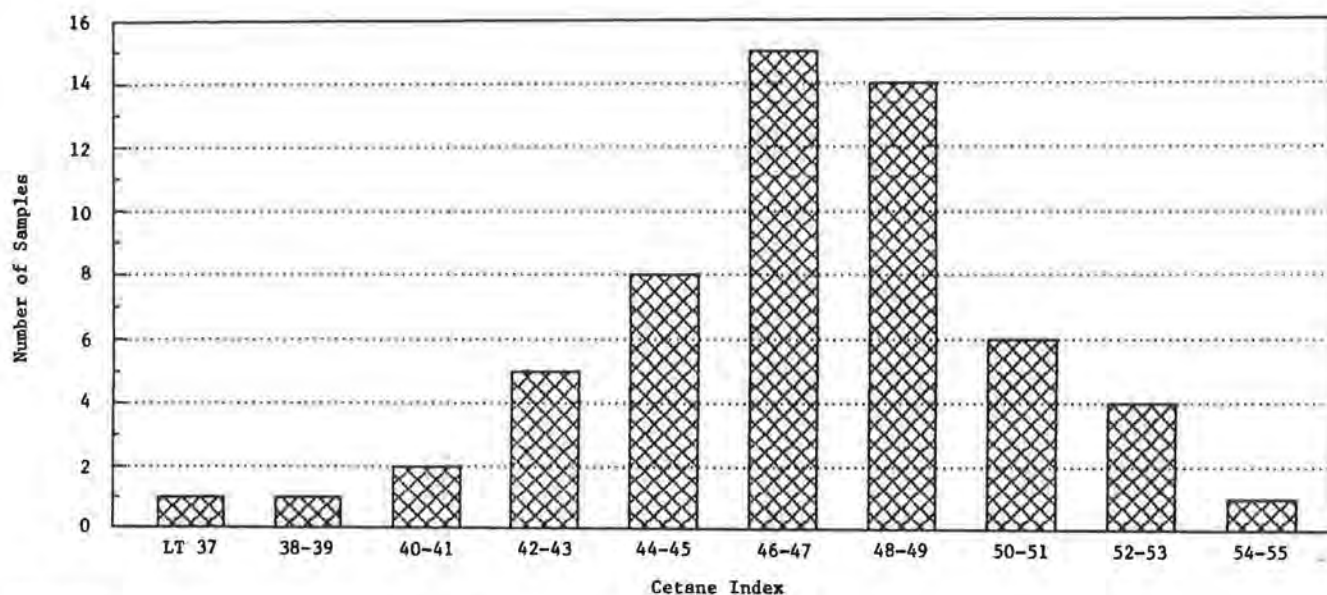


FIGURE 10 National composite of cetane index for 1-D fuels, 1982 (data from ref. 1).

number of samples for the 1-D and 2-D fuels respectively. A large fraction of the 1-D samples had 45 CI or below and no samples were reported above 55 CI. Overall, the 2-D samples had a slightly lower cetane quality than the 1-D samples.

Although cetane quality is the fuel property of greatest concern, there are also differences between other properties of the 1-D and 2-D fuels. The relative values are compared in Figure 12 and the most noticeable differences are the lower carbon residue and sulfur content for the 1-D fuel. The higher specific gravity of the 2-D fuel gives it a higher volumetric heat of combustion resulting in slightly better fuel economy. The flash point and viscosity were lower for the 1-D fuel as expected. More details are presented in Appendix C.

From the refinery point of view, the distillation curve is the major distinguishing characteristic between the 1-D and 2-D

fuels. The average distillations from the 1982 DOE fuel survey are shown graphically in Figure 13. The principal difference occurs on the high boiling point end. At about 525°F (270°C), all the 1-D fuel has evaporated, compared with only 60 percent of the 2-D fuel. This indicates that 40 percent of the 2-D fuel is higher boiling than any 1-D components. The other differences in properties between 1-D and 2-D fuels mostly reflect the properties of the added higher boiling fraction.

#### BLENDING 1-D AND 2-D FUELS

Grade 2-D diesel fuel is normally lower in cost than 1-D fuel. Locally, 2-D fuels may be available with superior properties, although smoke emissions are usually worse. Many operators

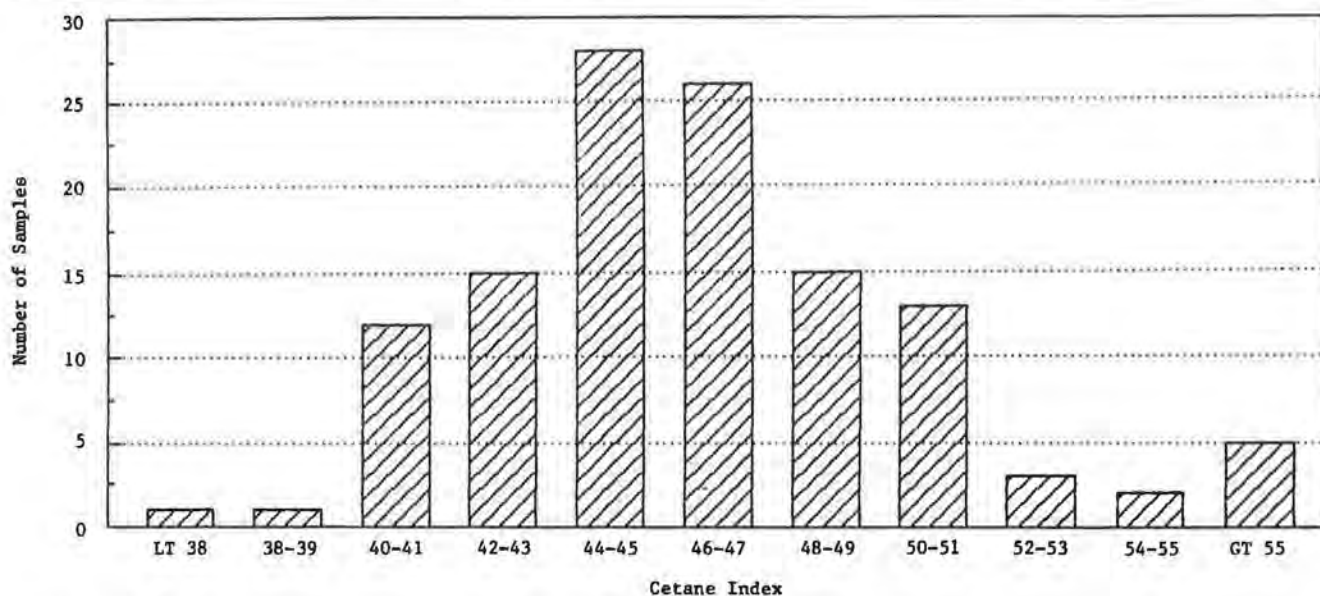


FIGURE 11 National composite of cetane index for 2-D fuels, 1982 (data from ref. 1).

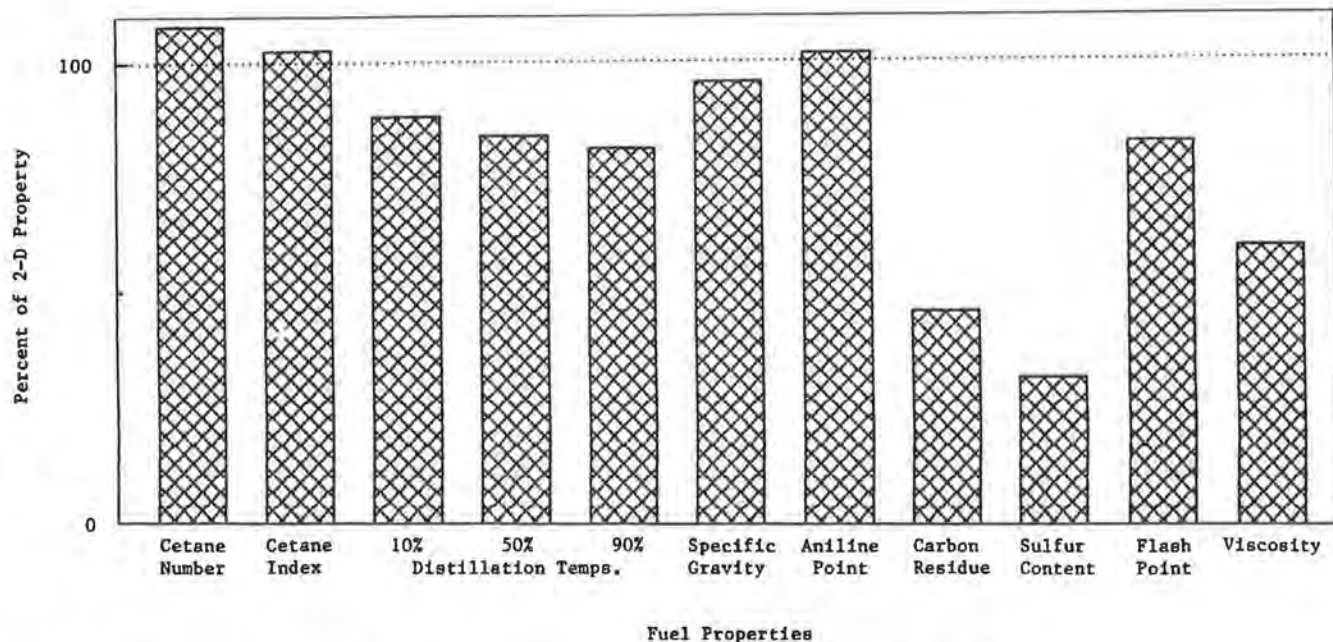


FIGURE 12 Properties of 1-D diesel fuel as a percentage of 2-D properties (data from ref. 1).

are using, or have considered, blends of the two grades. Before deciding on a blend, it is worthwhile to obtain information on the properties it will have. Several blended fuel properties can be calculated from the properties of the individual components. Other properties require laboratory measurements. The properties can be classified into three groups depending on the methods used for determining the blend properties:

1. *Linear properties*, where the final blend property lies on a straight line between the properties of the two components. Examples are specific gravity, heat of combustion, the 50% boiling point, and sulfur or other contaminants. The cetane index can be approximated by this method, but to be consistent with other blend properties it should be recalculated using the blend gravity and 50% boiling point.

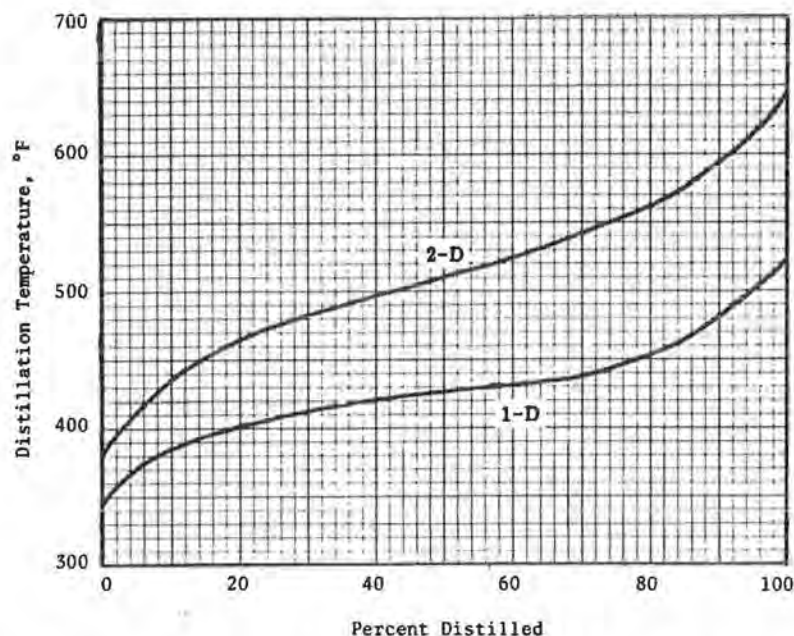


FIGURE 13 U.S. average distillation curves for 1-D and 2-D fuels, 1982 (data from ref. 1).



2. *Nonlinear properties*, where the properties between the two components lie on a curved line. One solution is to generate the curve with laboratory data. The other approach is to use a correlation or blending index to change the curve to a straight line. Examples are viscosity, flash point, cloud point, and pour point.

3. *Empirical properties*, where the result should be determined in the laboratory. This would occur when information is lacking on one or both components, or when there is no reliable correlation or method of calculation, such as corrosion. The distillation curve (except 50% point) and CN are in this group and should be measured by laboratory tests.

An example of calculated blend properties is given in Table 8. The blend stocks properties were individual samples selected from the 1982 DOE survey (1), except for the heat of combustion, which was obtained from a correlation for purposes of illustration. One blend stock was a low-cetane 1-D fuel and the other was higher cetane 2-D fuel. The blend properties were calculated for 40 percent 1-D fuel and 60 percent 2-D fuel based on volume. Details of the calculations and the necessary graphs are presented in Appendix D.

The calculated properties indicate several effects that are typical of 1-D and 2-D blends:

- Relative to the 1-D fuel, the blend has slightly higher specific gravity and heat of combustion. This is in the direction of improving fuel economy, but the difference is very small.
- If the flash points of both blend stocks are above the minimum requirement, the blend flash point will also be above the minimum, but it will be slightly lower than straight-line approximation would indicate. In this case the difference was two degrees.
- Relative to using the 1-D fuel, the blend has poor low-temperature properties. The 1-D fuel alone would allow operation down to  $-25^{\circ}\text{F}$  ( $-32^{\circ}\text{C}$ ). The blend cloud point is  $3^{\circ}\text{F}$  ( $-16^{\circ}\text{C}$ ). Temperatures of  $0^{\circ}\text{F}$  ( $-18^{\circ}\text{C}$ ) and colder could cause fuel filter plugging. The blended fuel would be usable in locations or seasons when moderate temperatures are ensured.
- The sulfur content is more than four times as high but is still an acceptable level at 0.087 weight percent.
- The carbon residue shows a slight decrease in the blend, which is unusual. In this case the carbon residue of the 2-D was lower than the 1-D; both fuels were low relative to the ASTM specification.
- The effect on smoke emissions cannot be readily predicted from the blend properties. The boiling range will be higher, which may increase smoke. The carbon residue is lower and the CI is higher, both of which tend to decrease smoke.
- The CI of the blend indicates better ignition properties than for the 1-D fuel. It should be noted that the CI of the 2-D fuel was two numbers higher than the CN. If a similar relationship holds in the blend, the actual improvement in ignition properties

may not be quite as good as indicated. A cetane engine measurement would be desirable to confirm the estimate, but even two units below the CI would be an acceptable value of 44.5.

Generally 2-D fuels cost less and are of lower quality for bus service. However, by careful selection, improvements may be made in particular properties by blending or switching from 1-D to 2-D fuels. A calculation or measurement of all the properties of concern is necessary to evaluate properly the use of blends. Gains may be made in some properties while losses occur in others. This was illustrated in the above example where improved cetane quality was obtained, but poor cold weather properties could preclude winter use in some locations, unless fuel heaters are used.

Other types of fuels can be considered for blending, such as No. 1 heating oil, kerosene, or jet fuel. Only kerosene-type jet fuel should be used (Grades Jet A, Jet A-1, or JP-5). Naphtha-type jet fuels must be avoided (Grades Jet B or JP-4) because they would reduce the flash point and cause a hazard in storage and handling; they would also reduce CN drastically.

TABLE 8

BLENDING CALCULATION EXAMPLE

Requirement	Diesel Fuel Grade		
	1-D	2-D	Blend
Composition, vol%			
No. 1-D	100	-	40
No. 2-D	-	100	60
Gravity, $^{\circ}\text{API}$	41.4	38.3	39.5
Specific gravity, $60^{\circ}\text{F}$	0.8184	0.8333	0.8273
Density, lb/gal, $60^{\circ}\text{F}$	6.816	6.940	6.890
Flash point, $^{\circ}\text{F}$	132	148	140
Cloud point, $^{\circ}\text{F}$	-26	+12	+ 3
Pour point, $^{\circ}\text{F}$	-35	-5	-14
Sulfur content, wt%	0.021	0.130	0.087
Carbon residue, wt% on 10% bottoms	0.06	0.044	0.050
Cetane number	41.5	47.0	*
Cetane index	41.2	49.0	46.5
Distillation, $^{\circ}\text{F}$			
Initial boiling point	344	372	*
10%	372	414	*
50%	410	483	454
90%	456	588	*
End point	524	632	*
Gross heat of combustion, Btu/gal	134,880	136,580	135,900

\*Laboratory measurement is required.



## DIESEL FUEL ADDITIVES

An amazing variety of substances have been promoted for use as diesel fuel additives. Some resulted from careful chemical development programs to meet specific fuel requirements. In most of these cases, test data are available and the products have received market acceptance. Other substances may be by-products or products designed for another application, but are promoted as fuel additives in an attempt to increase their market. Still others may be of more dubious origin.

For all additives, either the additive manufacturer or independent laboratories should have made adequate performance tests. Testing costs vary with the type of effects that are claimed. Major, short-term effects, such as cetane improvement, can be measured inexpensively. More subtle, long-term effects, such as reductions in wear, can be much more costly to test. In many cases, a testing program can be so expensive that some manufacturers may not be able to afford it, or may not be able to afford the capital investment required to do their own testing.

For transit companies, the additive evaluations affecting engine performance should be based on operating cycles used in the transit industry. Testing should be done in similar engines and with due consideration for emission constraints for a realistic interpretation of the results.

### ADDITIVE TYPES AND THEIR EFFECTS

At least three types of diesel fuel additives are well known and test reports have been published in the technical literature. These are ignition improvers, smoke suppressants, and flow improvers. Other additives can be classified by function in two groups: additives for combustion or engine performance; and additives for storage, handling, or fuel system compatibility. Additives for combustion or engine performance have often proved difficult to evaluate. Combustion, deposition, wear, and other processes occurring in the cylinder are complex and affected by factors other than fuel quality. Except for the smoke suppressants, additives that affect processes in the cylinder have generally not gained much market acceptance. By contrast, a number of additives for improving storage or handling have been shown to correct specific problems and are used where these problems occur.

#### Ignition Improvers

The changes in crude quality and product demand referred to in Chapter One resulted in production of fuel that lacked only sufficient CN to meet diesel fuel specifications. Several years ago, Ethyl Corporation found that small quantities of primary amyl nitrates increased the fuel CN without adverse effects on fuel storage or use. Similar compounds such as hexyl

nitrate and octyl nitrate have been found to be more effective. Other producers supply ignition improvers based on these or related nitrate compounds.

The principal effect of ignition improvers is to decrease the ignition delay, or the time between injection and the start of combustion. Ignition improvers are different from combustion catalysts, which increase the rate of combustion but do not affect ignition delay. The faster combustion should provide more heat release earlier in the cycle to give slightly greater power. The fuel should also be burned more completely so that exhaust emissions would contain less soot and hydrocarbons. By shortening the ignition delay, ignition improvers cause some of the effects that are attributed to combustion catalysts. Heat release occurs earlier because ignition is earlier. Combustion is more complete because the earlier ignition allows more time for completion.

How much CN improvement can be obtained by using ignition improvers? Several factors are involved. High CN in the untreated fuel, low specific gravity (high API gravity), high mid-range boiling temperature, and straight-run distillate all correlate with higher cetane gains. Typical CN improvement that can be obtained with fuels of varying CN (before treatment) and API gravity is shown in Table 9 (17). At 34°API gravity and 0.10 volume percent ignition improver, the CN gain varies from 4.6 to 5.9 as the clear, or untreated, fuel CN varies from 35 to 55. Comparing gravities at 55 clear CN, fuel with 40°API gravity gains 6.5 cetane numbers at 0.10 percent ignition improver while fuel with 34°API gravity gains only 5.9 cetane numbers when using 0.10 percent ignition improver. In general, the lower cetane fuels do not respond as much as the higher cetane fuels.

Another aspect of the CN gain can be shown with the data in Table 9. The first increment of ignition improver is more effective than subsequent increments. For example, the 34°API gravity and 40 CN combination improves 3.1 cetane numbers with the first 0.05 percent additive, then 1.9 additional numbers with the second 0.05 percent and only 1.3 additional numbers with the third 0.05 percent. This means that the cost per CN gain increases at higher additive concentration.

The way that fuel responds to ignition improver additive is important to fuel manufacturers and to the transit operators. In Chapter One it was noted that the cost per CN gained by processing also increased with increasing cetane improvement. In the future, fuel manufacturers may use both processing and ignition improver additive to take best advantage of the lower cost, first increments of both approaches. If a transit operator tries to further boost the CN of fuel that already contains additive from the manufacturer, much more additive will be required than normal for a given cetane gain. If there are questions about the additive content of a fuel, the fuel supplier should be contacted. Samples can also be analyzed for the general class

TABLE 9  
TYPICAL CETANE NUMBER IMPROVEMENT (17)

Gravity (°API)	Mid-Boiling Temp. (°F)	Clear CN	CN Improvement @ Volume % Ignition Improver		
			0.05	0.10	0.15
30.3	490	35.0	2.7	4.3	5.5
33.2	490	40.0	3.1	4.9	6.3
36.1	490	45.0	3.5	5.5	7.0
37.9	490	50.0	3.7	6.0	7.6
40.0	490	55.0	4.0	6.5	8.2
34.0	443	35.0	2.9	4.6	5.9
34.0	479	40.0	3.1	5.0	6.3
34.0	511	45.0	3.3	5.3	6.8
34.0	540	50.0	3.5	5.6	7.2
34.0	566	55.0	3.7	5.9	7.5

of nitrates used in ignition improvers. A standard analytical procedure, ASTM Method D 4046, is available to measure concentrations between 0.03 and 0.30 volume percent (18).

The difference in additive response between straight-run distillates and light cycle oils, which are cracked stocks, is shown in Figure 14. The cetane gain is much better for the straight-run distillates. The cracked stocks, noted previously, are lower in cetane quality than straight-run material. Equations for calculating a predicted cetane gain and a graphical procedure for interpolating are given in Appendix B.

#### Smoke Suppressants

The problem of black smoke and other pollutants in diesel exhaust has received much attention from additive manufacturers. White or blue smoke is caused by unburned fuel droplets and is a temporary condition that occurs during cold starts (19). Black smoke is caused by soot formed during the combustion process. Several studies have shown relationships between soot and fuel properties (20, 27). Other pollutants include nitrogen

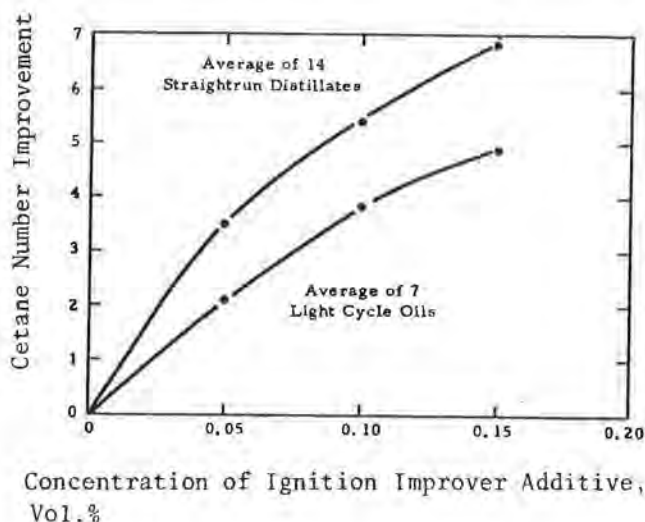


FIGURE 14 Response of straight-run distillates and cracked stocks (light cycle oils) to ignition improver additive (25).

oxides (NOx), carbon monoxide (CO), sulfur oxides (SOx), polyaromatic hydrocarbons, and odor, which is usually attributed to aldehydes or other partially oxygenated hydrocarbons. The pollutants most noticeable to the public are black smoke and odor. Most additive developers have concentrated their efforts on oxidizing the black smoke with hope that the polyaromatic hydrocarbons and odor would be oxidized along with it.

Soot particles are formed from the gas phase at high temperatures. They have a complex structure suggesting different mechanisms at different stages of growth. In regions of a flame that are locally or temporarily oxygen deficient, some of the fuel undergoes pyrolysis producing short hydrogen-deficient carbon chains, often resembling acetylene or butadiene. These fragments condense to form interconnected six-membered rings with aromatic structures. The individual soot crystallites contain several layers of these rings and are nearly spherical in shape. These agglomerate to form chain-like structures, reminiscent of strings of beads with occasional branches. The soot particles that are collected from the exhaust are generally extensive chains of similarly sized crystallites rather than individual crystallites (28, 29). Excellent photographs and more details of the soot-forming processes are given in references 30 through 33.

The cetane number of the fuel has a significant effect on soot production. El Nesr et al. (34) using a Witte, four-stroke engine, were able to relate smoke, carbon monoxide, formaldehyde, and nitrogen oxides emissions to the CN of the fuel (with additive). They noted that the optimum CN in all cases was in the range of 50 to 70. Cyclohexane was an exception in that it reduced emissions when used in concentrations of up to 3.0 percent, but had no effect on the CN of a 40 cetane fuel. Their results are shown in Figure 15. The increase in emissions at low cetane numbers was explained as being due mainly to the shorter combustion time left after the longer ignition delays, which caused incomplete combustion. The engines were run at the same speed during the tests. There is a slight evidence for increases in emissions at high cetane numbers, which El Nesr et al. believed were caused by the injection period extending past ignition with short ignition delays. Fuel at the end of the injection was pyrolyzed as it entered the flame. These results are highly dependent on engine type. Golothan (26) found that smoke increased with increasing CN between 31 and 45, but this trend is not normal in direct injection engines unless the CN grossly exceeds the engine requirements.

Different types of hydrocarbons have different sooting tendencies. In general, paraffinic molecules require quite fuel-rich conditions to form soot, whereas aromatics form soot under leaner conditions. Aromatics also have a much lower hydrogen content than paraffins and the sooting tendency increases with decreasing hydrogen saturation of the molecule. Voorhies et al. (20) found the fuel hydrogen content to be better than other properties as a predictor of sooting tendency in a laboratory test engine. Using fuels that were blended to isolate the effects of CN, fuel volatility, and hydrogen content, they found that smoke correlated only with the weight percent hydrogen in the fuel. These results are shown in Figure 16. Other factors that affect smoke, such as boiling range, were not investigated. These findings conflict with El Nesr's results, and the difference may be due to the fuels. Voorhies et al. used special blends to obtain variations in both the cetane quality and hydrogen content while holding the other property constant. El Nesr et al. used mostly

commercial fuels where the percent hydrogen is normally higher in fuels with high CN, so their results with untreated fuels could also have been due to the hydrogen content. Their results with cyclohexane also show that this particular hydrocarbon type lowers the sooting tendency considerably without altering the CN. Unfortunately, cyclohexane is quite expensive and the required concentration was fairly high.

Most of the soot control additives that have been used are metal salts and metal organic compounds. The alkali metals (usually lithium, sodium, or potassium) are known combustion and gasification catalysts, but they are also quite corrosive. Iron and manganese compounds, such as ferrocene or methylcyclopentadienylmanganese tricarbonyl (MMT), are popular in boilers and turbine engines, although other compounds containing

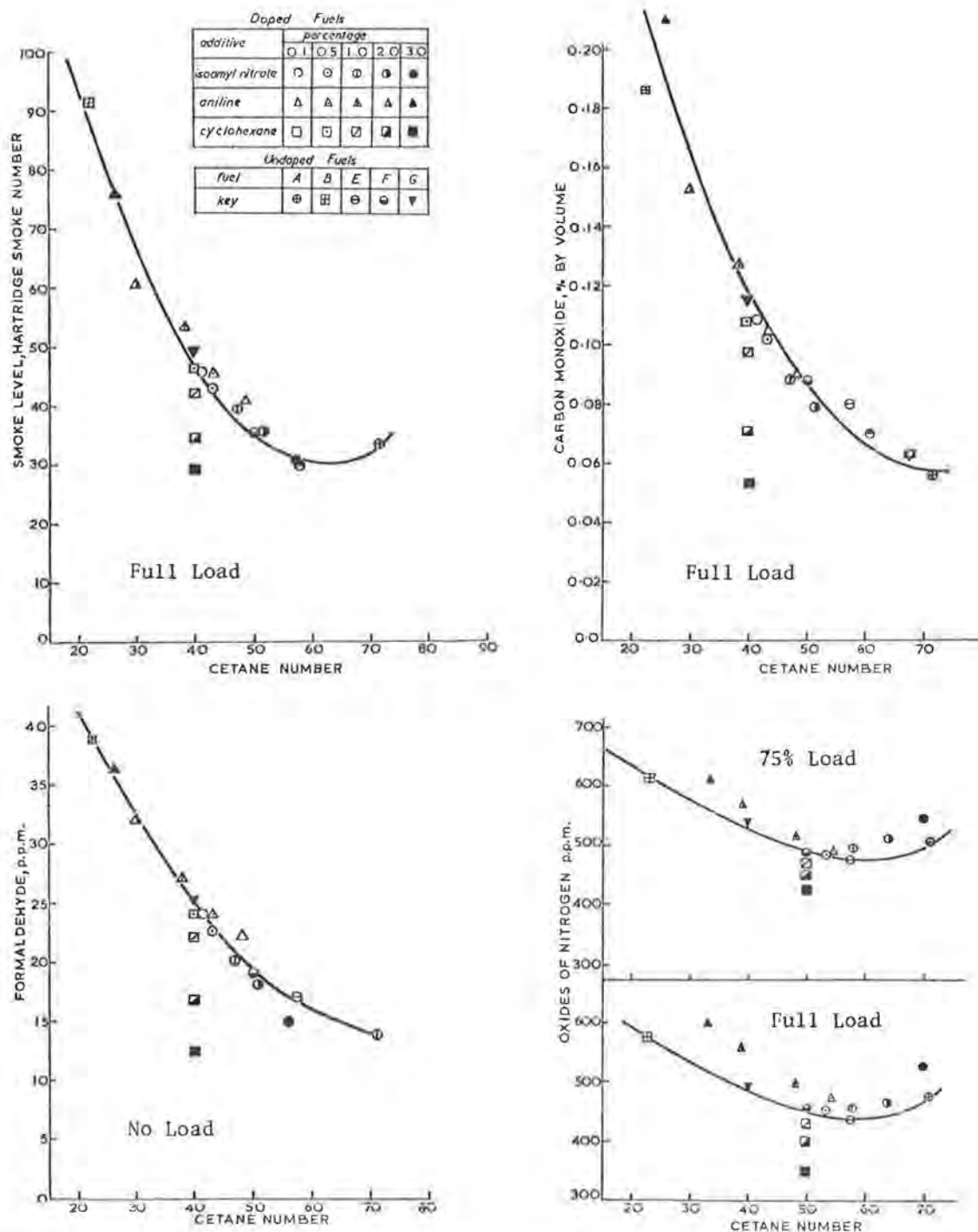


FIGURE 15 Emissions versus cetane number for doped (containing ignition improver additive) and undoped (additive free) fuels with a Witte engine at 720 RPM (35).



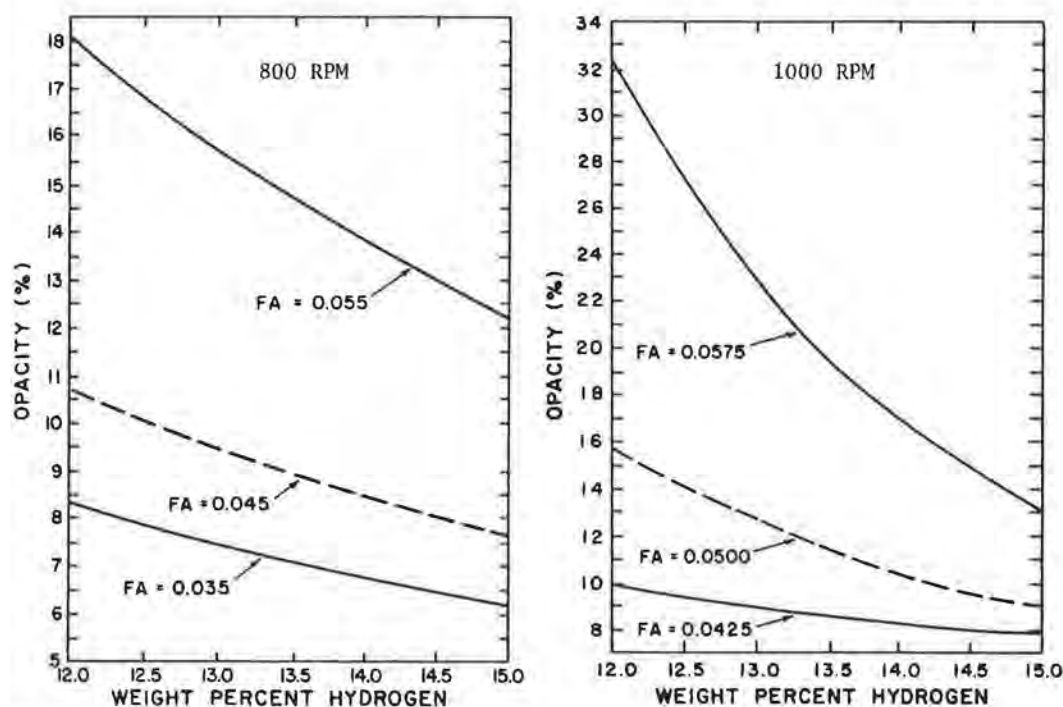


FIGURE 16 The effect of fuel percent hydrogen on opacity that is due to exhaust smoke. Laboratory test engine at compression ratio of 32:1, injection advance 13 degrees BTDC, fuel to air ratios (FA) and speeds indicated (27).

calcium or cobalt are sometimes used (35). For diesel engines, barium-based compounds give generally superior performance (28, 36) and are the additive of choice for most operators, although occasional success is reported with manganese compounds (37).

Barium and manganese compounds apparently act chemically to reduce soot (28). In the flame, the organometallic molecules decompose to form ions, which are the active agents in soot reduction. Barium ions apparently interfere directly with the condensation reaction that starts the soot particle growing. In addition, they react with water molecules in the flame to produce hydroxyl radicals, highly reactive molecular fragments that in turn react rapidly with both the soot and the soot precursors. Much more soot is formed in flames than is emitted from them. The fate of almost all soot particles is oxidation later in leaner portions of the flame, a process aided by the MMT additive. Manganese ions, formed from decomposition of the MMT, catalyze oxidation of the soot particles causing them to burn faster. The particles should also burn for a longer time as the combustion gases are cooled by expansion during the power stroke, because soot containing small amounts of manganese burns at a lower temperature than manganese-free soot. Because the mechanisms are quite different, Howard and Kausch (28) have suggested that carefully formulated mixtures of barium and manganese compounds might perform better than compounds containing either metal by itself. However, other investigators (38) have found evidence that the barium also acts as a soot combustion catalyst.

In developing an improved barium-based antismoke additive, Golothan of Shell International performed extensive laboratory and engine tests, including 40,000-mile (64,000-km) road tests.

In the laboratory, the additives consistently reduced the smoke at all engine operating conditions, but never eliminated it. Smoke reductions were typically 40 to 50 percent, but at high load conditions 60 to 70 percent reductions were achieved. In the extended mileage vehicle tests, smoke reductions were typically 35 percent but varied from 10 to 60 percent. The variation, it was explained, was caused by injector deposits forming, then flaking off. The injectors were not serviced during the 40,000-mile test run. The problem of injector deposits was apparently corrected later during the additive development program by incorporating a dispersant (unspecified) in the additive (26).

These smoke reduction findings were confirmed by Apostollescu et al. (38) using a 350 in.<sup>3</sup> (5.7 L), six-cylinder, direct injection, Perkins 6.354 diesel engine. The additive contained 22.5 percent barium by weight and was added to the diesel fuel at 0.25% concentration by volume. Results are shown in Figures 17 and 18. The percent reduction varied with engine load and speed and the smallest reductions occurred under medium speed and medium loads, similar to trends reported by Golothan.

Smoke suppressing additives that contain metals cause other changes in the exhaust emissions besides smoke reduction. The exhaust contains soot, carbon monoxide, nitrogen oxides, sulfur oxides, unburned hydrocarbons, polynuclear aromatics, soluble barium compounds (chiefly barium carbonate), and the insoluble barium sulfate. Golothan (26) found no significant change in carbon monoxide, nitrogen oxides, and polynuclear aromatics when using the barium-based additive. The mechanisms of soot inhibition discussed previously (28) imply a possible reduction in unburned hydrocarbons, but there are not sufficient data to support the implication. Hare et al. (39) found decreases in the carbon emissions and in the exhaust opacity when using a bar-



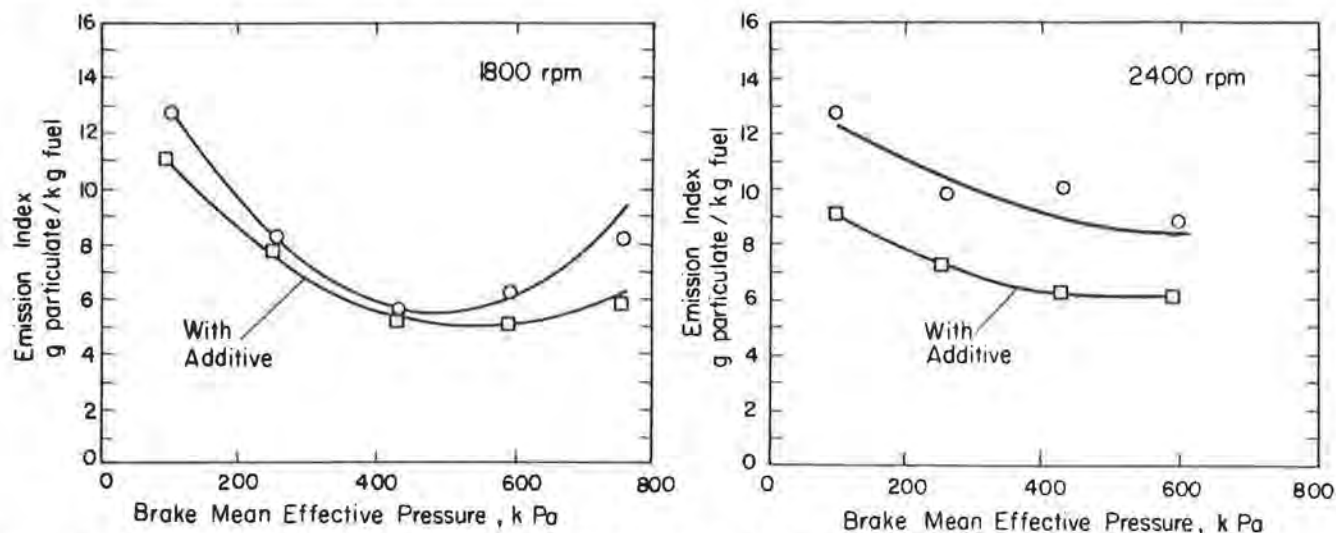


FIGURE 17 Variation of particulate emissions with load for fuels with and without barium-containing additives (39).

ium-based additive, but the total mass of particulate emissions was about the same, the loss of carbon being made up by barium sulfate. This observation was confirmed by the work of Truex et al. (40). Although most of the barium goes out in the exhaust, the proportion that is soluble varies with the additive level and fuel sulfur content. The barium increases the conversion of fuel sulfur to sulfate and it appears in the exhaust as particulate barium sulfate, which is stable, insoluble, and nontoxic. This uses some of the sulfur and reduces the emission of sulfur oxides. When there is insufficient sulfur for the barium, the excess barium is emitted in soluble forms, which are toxic.

Is the cure worse than the ailment? Does the use of barium-based additives just replace carbon particulates with toxic barium? The toxicity of soot is often misunderstood. Carbon is relatively nontoxic, but many substances that are toxic adhere

strongly to the carbon particles. The danger caused by ingesting carbon depends on what the carbon has picked up along the way. The polynuclear aromatic hydrocarbons formed during combustion are part of a large class of substances, many of which cause cancer. They are formed with the soot, adhere to it, and will be ingested if the soot is ingested. By comparison, the soluble barium compounds may pose less danger, and Golothan (26) has argued that worst-case exposures are minuscule compared to natural exposure in drinking water, food, and air. However, arguments of this type must be backed by extensive, unequivocal data to have much influence with environmental regulatory agencies. The toxicity of the manganese oxides produced from MMT additives is also controversial, but appears to be worse than the barium emissions (28).

The barium-based additives are alkaline and may neutralize

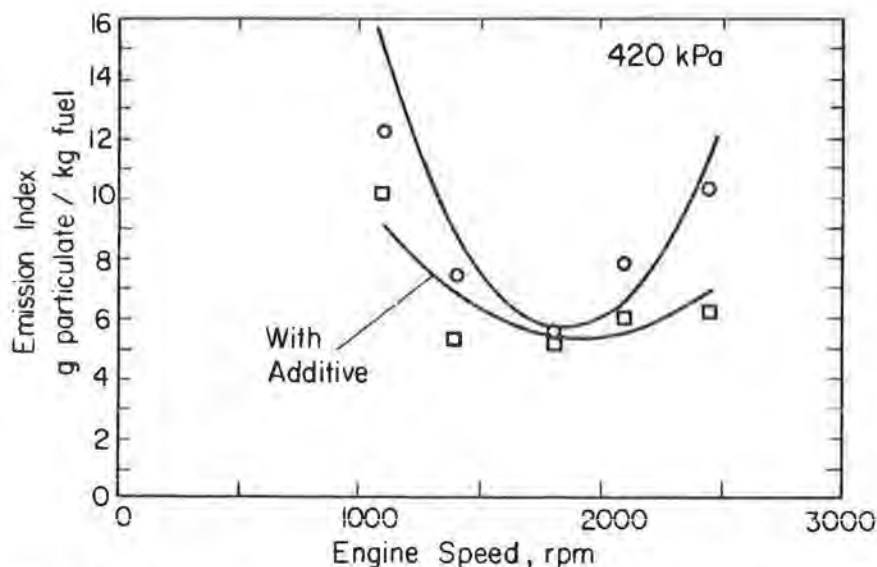


FIGURE 18 Variation of particulate emissions with speed for fuels with and without barium-containing additives (39).

acidic fuel components or combustion products that cause corrosion and contribute to engine wear. Glover (41) reported that wear of the top compression ring in a Caterpillar L-1 engine burning 1 percent sulfur fuel with additive was only about  $\frac{1}{3}$  as much as expected in the 720-hour test. A GM 6V-71 test engine was run 270 hours each on treated and untreated 0.4 percent sulfur fuel and the top compression ring wear was measured by weight loss. The wear while using the treated fuel was only about half as much as it was while using the fuel without additive. However, Golothan (26) was unable to find consistent evidence of wear reduction in either his 40,000-mile road test or the extensive laboratory engine tests, and concluded that the benefit must be dependent on operating conditions or engine type. There was also no evidence of increased wear despite the flaking deposits he observed. Others (37, 40) have also noted that while using barium additives, there were increased engine deposits that were light in color and occasionally flaked off and went out with the exhaust without increasing the wear rates.

In summary, metal-based antismoke additives can provide a significant reduction in black smoke emission and in some cases a reduction in sulfur oxides emissions. The amount of smoke reduction varies with load, speed, engine type, and many other design and operating factors. The best results are typically 30 to 50 percent reductions, but under some conditions there is almost no effect. The additive causes an increase in engine deposits but does not appear to cause increased wear, and in some cases may reduce wear. There is no discernible effect on other emissions except those resulting from the metal. Barium-based additives cause emissions in two forms: barium sulfate, which is insoluble and non-toxic; and other barium compounds, which are soluble and toxic. The small quantities of toxic compounds appear to cause less environmental harm than the combustion products adhering to smoke particles, but that result has not been unequivocally established. Manganese-based additives cause emissions that may be more toxic than those caused by barium.

Occasionally, nonmetal additives are mentioned with respect to smoke suppression, or other exhaust emissions. These are of two types, both of which act indirectly to influence the combustion process. One contains dispersing agents that help keep injectors clean and thus promote proper fuel atomization, which is necessary for complete combustion. The other type involves compounds such as isoamyl alcohol, isoamyl nitrate, nitromethane, or di-tert-butyl peroxide, that act to increase or decrease the ignition delay, so they affect the CN. McCreath (42) reported no significant effect of these compounds on soot formation, but found that those that reduced ignition delay reduced nitrogen oxides and increased carbon monoxide emissions. On the other hand, those that increased ignition delay caused slight increases in both nitrogen oxides and carbon monoxide emissions. Murayama and Tsukahara (43) reported lower NO<sub>x</sub> emissions using ignition improvers in fuels that were initially very low in cetane quality.

Interesting experimental results have been obtained using water or alcohols in conjunction with diesel fuel. Success in reducing both nitrogen oxides and diesel smoke by use of emulsions of diesel fuel and water has been reported with four-stroke engines. Results with two-stroke engines have been mixed (44-49). Experimental emulsions of methanol or ethanol in diesel fuel have also shown a reduction in smoke (50-52) but more development and testing should be done before general mar-

keting of emulsion fuels takes place. Mine diesel engines may provide a pioneering application (53) because emissions control is more critical in an underground mine than on the surface.

Golothan was one of the scientists who developed the barium-based, smoke suppression additives that are now available. Better additives remain a distant prospect and in view of the highly variable response to today's barium-based additives, his 1967 comments remain applicable:

[I]t is still true in general that a solution should first be sought in improvements in engine operation and maintenance, in particular maintenance and adjustment of the fuel injection equipment. It is also evident, however, that the fuel can play an important part in the formation of smoke and a change in the fuel, where this is practical, could provide a remedy in many instances. The use of antismoke additives is still in its infancy, but so far the main objection to using them is their cost. . . . In response to public pressure, the operator will not only have to improve the maintenance of his engines, but he is also likely to give more consideration to the use of alternative fuels and antismoke additives (26).

### Flow Improvers

Additives that lower the fuel pour point and the temperature at which the fuel would cause a filter to plug are called flow improvers. The cloud point is the highest temperature at which the normal paraffins are insoluble and will form wax crystals. Flow improvers are used in small concentrations and do not lower the cloud point. Substances that do lower the cloud point would be classed as solvents and higher concentrations are required for the solvent function than for the flow-improver function.

Flow improvers work by changing the way wax crystals grow. Using the flow improver, the wax crystals are smaller but more numerous. They have less tendency to coalesce, or grow together. For this reason, flow improvers are also referred to as pour depressants or wax crystal modifiers. A suspension of small particles usually flows better than a suspension containing the same weight of larger particles. If the particles are small enough, they can pass through the pores of a filter without plugging it.

Several factors affect flow-improver function. The wax crystal modification apparently occurs when molecules of the flow improver co-crystallize with the paraffin and are incorporated into the structure. The flow improvers are long-chain polymers that contain segments resembling paraffin molecules. Frankenfeld and Taylor (54, 55) believe that flow improvement of different additives depends on their ability to co-crystallize with the particular paraffins in the fuel. Fuels with different distributions of paraffins give different responses to the same flow improver. It appears that the optimum flow improver is fuel specific (56). A flow improver may gain or lose effectiveness if the fuel is produced from a different crude source or with significantly different processing.

Filters plug just below the cloud point when untreated fuel is used, but neither the cloud point nor the pour point tests adequately represent the filter plugging temperature when fuel containing a flow improver is being used. Steere and Marino (57) describe Exxon's Low Temperature Flow Test (Appendix E) in which the fuel is cooled and periodically filtered through a screen with 40- $\mu$ m openings. The minimum operability temperature occurs when 160 mL cannot be filtered in 60 seconds.

Results of the test correlated well with road test results using four tractors, one pickup truck, and one passenger car. Because flow improvers tend to be fuel specific, field tests of this type may be worthwhile for evaluations.

Like many other additives, the first increment of flow improver is more effective than successive increments and a concentration is eventually reached where almost no further improvement can be made. This is illustrated in Figure 19, which shows the pour point response of two different distillate fuels, both high in paraffins, which were derived from shale oil (55). Little improvement was made beyond that obtained with 0.20 weight percent. Reddy and McMillan (57) found the same effect using three different flow improvers in several grade No. 2-D diesel fuels. Their criteria were the temperature difference between the cloud point and the temperature of filter plugging. With no additive, the filters plugged at the cloud point. The maximum improvement for a 37- $\mu\text{m}$  screen filter was 14°F (8°C). For a 130- $\mu\text{m}$  Saran sock filter it was 22°F (12°C). Both maximum improvements occurred at about 0.20% concentration of active ingredient. For all three additives, the manufacturers' recommended concentrations ranged between about 0.015 and

0.028 percent, which provided only about  $\frac{1}{3}$  to  $\frac{1}{2}$  the maximum improvement available.

Some of the alternatives to using flow improvers are not practical in many situations. Arctic grade diesel fuels with exceptionally low cloud points represent an ideal solution, but they may be expensive or unavailable in some locations. Dewaxing is a refinery process that could lower the cloud point, but it is expensive, and may lower the cetane number. Therefore, it is rarely used in making diesel fuels. Diluting the diesel fuel with a lightweight fuel, such as kerosene, works and has been popular in some areas, but it is also quite expensive. The use of flow improvers is gaining increased acceptance as an economical solution for cold-flow problems. Another solution is the use of fuel heaters, and several types have provided good service.

#### Performance Additives

A number of processes occur in the combustion chamber. Many additives are marketed with claims to affect those proc-

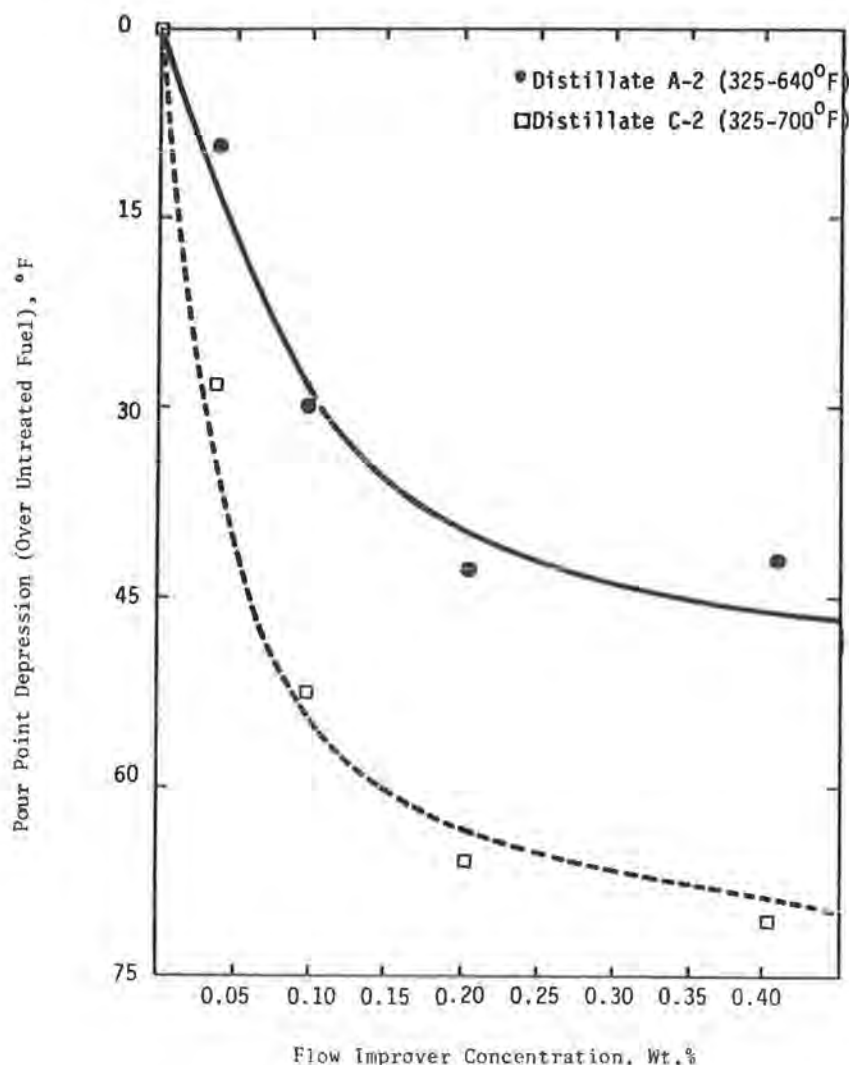


FIGURE 19 Response of two different fuels to a flow improver (56).



esses and improve performance in some way. Ignition, soot formation, and additives that affect them have already been discussed. Other processes include fuel pyrolysis, fuel-air mixing, the combustion process after ignition, formation of gaseous pollutants, and carbon deposition. These processes are complex and interrelated and it is often not clear how changes in one of them may affect others. Little data have been published in the technical literature that show significant performance improvement by using additives that are supposed to affect these processes.

Fuel pyrolysis refers to the breaking of large fuel molecules into reactive fragments. It occurs at high temperatures and is affected by additives only to the extent that they alter the temperature in the cylinder. Pyrolysis has been suggested as one of the causes of polyaromatic hydrocarbons. Ray and Long (58) found that when a diesel engine was operated improperly (by overfueling or using incorrect injection timing) the exhaust contained increased amounts of polyaromatic hydrocarbons, but when an ignition improver was used they were reduced. They found that the ignition improver did not affect the pyrolysis reaction, but with better ignition the pollutants were oxidized during combustion. This suggests that, in terms of emissions, ignition-improver additives may partially compensate for insufficient maintenance.

The mixing of fuel and air is determined mostly by equipment, and additives seem to have little application. Some additives are advertised as altering viscosity or surface tension to give better atomization, or smaller droplets. Any injector will produce a range of droplet sizes with a given fuel. In particular, droplets coming at the end of injection may be significantly oversized because of equipment factors.

Obtaining droplets small enough is the most common atomization problem, but they can be made too small. Droplets that are too small are quickly stopped by friction and penetrate only a short distance into the air so that the overall fuel-air mixing is poor. Droplets that are too large travel too far and may land on the piston or cylinder walls. Any success with additives designed to modify droplet size most likely occurs when some injector malfunction is causing improper droplet sizes. Good injector maintenance is normally a better solution to the problem.

Another mechanism has recently been discovered, which relates to fuel-air mixing, called "microexplosions." It has been observed with single, fairly large droplets in laboratory studies, but the occurrence in diesel fuel sprays has not been confirmed. Microexplosions occur when the fuel contains an unusually low boiling component. In an emulsion fuel, for example, water can be a low-boiling component and droplets from emulsions of this type are prone to microexplosions. The microexplosion is not a combustion or chemical reaction phenomenon, but occurs when the low-boiling component suddenly vaporizes forming gas or steam that blows the droplet apart (59). This mechanism may be part of the reason for reduced emissions observed when using emulsion fuels.

The microexplosion mechanism requires that the fuel contain a fairly large percentage of the low-boiling component and is not restricted to emulsion fuels. The use of a hydrocarbon for a low-boiling component would probably cause an unacceptably low flash point. Emulsions may be formulated in the future to take advantage of microexplosions, but it is unlikely that any additive used in low concentrations could cause them.

Many substances have been added to fuels as combustion

catalysts (60,61). Most data published in the technical literature indicate that only the barium and manganese compounds can be used effectively in diesel engines. Other substances are good combustion catalysts, but cannot be used in diesel engines for other reasons. For example, the metals sodium, lithium, and potassium increase combustion rates and decrease smoke emissions from an open flame, but they are very corrosive and cause engine damage when they are present in the fuel. Vanadium oxides are in a similar category. As a solid in contact with hot gases, they increase the oxidation rate of both hydrocarbons and sulfur compounds. Iron and chromium compounds are effective catalysts at the very high temperatures that occur in rocket motors, but do not seem to work at the temperatures that occur in a diesel engine.

Combustion catalysts may be the most vigorously promoted additives in the diesel fuel aftermarket. However, with the exception of the limited success with the barium and manganese smoke suppressants, tests have generally indicated failure or, at best, a marginal success. In typical evaluations by testing laboratories, untreated and treated fuel are run successively in the same instrumented engine for comparison. Results have usually indicated almost no change in either the fuel economy or in the exhaust soot levels. Slight reductions in other emissions have occurred under some load conditions, but even that benefit has not always been repeatable.

In the combustion chamber, carbon deposits occur from mechanisms similar to those that produce soot. Additives that are supposed to prevent carbon deposition through a detergent or dispersant action mostly are burned along with the rest of the fuel and have little effect. Their function is in the liquid and they do not affect the combustion process significantly. The smoke suppressants, as discussed previously, cause deposits that are more easily removed and they may reduce the volume of carbon deposits. However, the metals in smoke suppressants or combustion catalysts form ash, which adds to the deposits and may be abrasive. Performance additives, particularly the combustion catalysts, should be avoided until products that work become available and the results can be verified by scientific testing procedures.

#### Additives for Storage and Handling

In contrast to performance additives, many effective additives are available for preventing problems that occur in transportation and storage, or in the vehicle fuel system. Although they go by a variety of names, the additives of most interest can be described as detergents, antioxidants, corrosion inhibitors, and metal deactivators. Refiners routinely use these additives in fuels to ensure that fuel quality will not deteriorate in storage. Pipeline companies require that products contain specified amounts of detergents and antioxidants before accepting the material for shipment. Corrosion inhibitors are commonly used to protect storage tanks and pipelines. Some additive suppliers market mixtures described as multifunctional, which will fit manufacturers' requirements in several areas.

Detergents are a broad class of chemical compounds that have different solubility characteristics in different parts of the molecule. This allows them to bridge between dissimilar materials, keeping small particles of substances, such as gums,



suspended in the fuel. Depending on the application, they are also referred to as dispersants, emulsifiers, or stabilizers in reference to preventing particle settling or phase separation (62).

Many detergents will emulsify water. This may be desirable to prevent small amounts of water in the fuel from separating in the bottom of a fuel tank. It also may be undesirable if there is already some water in the bottom of a storage tank that should not be incorporated into the fuel. Water can increase corrosion, which provides an incentive for additive suppliers to market products containing corrosion inhibitors along with detergents.

Antioxidants are used to improve storage stability. In the presence of air, portions of the fuel can react with oxygen to form gums. The antioxidant interferes with that reaction and prevents gum formation.

Metal deactivators also improve storage stability. Copper is a catalyst for oxidation reactions. Fuels that contact copper, brass, or other copper alloys are subject to rapid gum formation. Metal deactivators coat the metal surface to stop the reactions and are sometimes called copper deactivators.

Corrosion inhibitors function in a manner similar to metal deactivators, by depositing a thin film on the surface of the metal. The film prevents corrosion by water or reactive compounds in the fuel. A small concentration in the fuel is necessary to maintain the film presence on the metal surface.

Other additives are available for special purposes, such as deicers, demulsifiers, biocides, and conductivity improvers. Deicing additives dissolve preferentially in water where they lower the freezing point. They are used most commonly in gasolines to prevent ice in carburetors or fuel lines. They are sometimes used in diesel fuels to prevent traces of water from forming ice crystals, which could plug the fuel lines or filter. Propanol and similar alcohols are commonly used, but many deicers contain esters, amines, or ethers. Most chemicals, other than the alcohols, that are deicers are also detergents and are sometimes advertised as multipurpose additives for both functions.

Demulsifier additives can be used to destabilize small amounts of water that have been emulsified into the fuel. They are also called antidetergents or emulsion breakers, and cause the water to settle out of fuel in storage. Putting antidetergents in the storage tank to separate water is another method of preventing ice crystals from plugging filters and keeping water-related corrosion out of the vehicle fuel tank.

Slime is an additional problem that occurs when the fuel contains traces of water or is in contact with water on the tank bottom. The slime forms as a result of bacteria, fungus, or yeast action and can plug fuel filters. Biocides that are soluble in both fuel and water are added to kill the bacteria and prevent the slime formation. Du Pont (63) has published a procedure for sampling and testing water from the storage tank bottoms to measure biological activity and determine whether biocides are needed. The best preventive is frequent checking of tanks for the presence of water and prompt draining of any water found.

Additives used in other fuels are sometimes advertised for diesel fuel use. For example, electrical conductivity additives are used in jet fuels to prevent static discharge during aircraft refueling. However, diesel fuels have adequate electrical conductivity from polar compounds normally present; the exception might be diesel fuel from high severity hydrogen processing, which removes polar compounds.

## CURRENT PRACTICES IN ADDITIVE USE

Fuel and additive use by transit operators was surveyed in December 1982. A survey form was mailed to 25 transit operators in the United States and Canada. Their locations include climatic extremes of temperature, humidity, and altitude. The survey questions covered the grades of fuel used, fuel quality control, and the additives used. Nineteen replies were received. Follow-up telephone calls were made to operators who indicated experience with additives. Results of the survey are shown in Table 10 and a copy of the survey form is included in Appendix F.

The first question related to the fuel grades used. Six operators used only grade No. 1-D, five operators used only No. 2-D, and the remaining eight were using both grades subject to some limitations. One of the eight initiated a test program with 2-D, and two used only 1-D during the winter, then switched to blends or straight 2-D for the other seasons. Five operators were using blends that contained between 50 and 70 percent No. 2-D fuel. Two operators also indicated testing alternative fuels, which were Jet A fuel and methanol. The methanol will be used neat (not in a fuel blend) with custom-designed spark-ignition engines.

Quality control generally seems to be accomplished indirectly with occasional inspections rather than by demanding specified inspection results from the suppliers. Ten operators indicated

TABLE 10  
RESULTS OF FUEL AND ADDITIVE USE SURVEY

Item	Responses (% of replies)
Grades of fuel in use	
Use 1-D only	32
Use 2-D only	26
Use both grades seasonally	16
Use blends	26
Fuel inspection results from supplier	
Obtained routinely	26
Obtained on request	21
Not obtained	53
Other fuel inspection results	
Tests made by outside laboratory	74
Tests made in-house	58
Check for appearance and odor only	42
Fuel related problems	
Excessive smoke	32
Injector sticking	11
Water in fuel	11
Other	32
Filtering of fuel	
To remove particulates	84
To remove water	74
Additives used by fuel supplier	
None or unknown	100
Additives used by transit operator	
Additives used routinely	16
Additives being tested	21
Users who rely on supplier for concentration	86
Mixing	
Users of additives or blends who make no special provision for mixing	71

that their fuel supplier provided no inspection results. Four received them only on request, or at extra cost. Five received inspection results routinely, and in phone conversations two of these indicated that they did not specify values for any properties. Eight operators indicated that they routinely inspected fuel samples for appearance and odor, 11 performed some laboratory tests in-house, and 14 sent out samples for testing. Some commented that the lab tests were done randomly or occasionally rather than routinely. Two people commented orally that shipments had recently been turned down because of poor quality.

Fuel specifications were not requested on the survey, but none of the operators who were phoned indicated using any. Only one commented that they had a specified requirement, and that was a minimum 44°API gravity for smoke control. The general pattern seems to be that fuel properties are not specified, but they are watched and fuel shipments are turned down if they are unusable. In view of the variations in diesel fuel quality and the general trends toward lower quality, operators should be encouraged to specify fuel properties and to make more frequent fuel inspections.

Smoke is the main fuel-related problem that operators have experienced but several other problems are of concern. Six operators reported excess smoke, two reported injector sticking, and two reported water in the fuel. Each of the following problems was reported by one operator: storage stability (biological), starting, carbon deposits in the combustion chamber, high sulfur, dirt, and low API gravity (high specific gravity). Sixteen operators use filtration systems for particulates and 14 use filtration systems for water.

Three operators used additives routinely. Four others had tested or were planning to test additives. The three additives used routinely were a biocide, a flow improver, and an additive designed to increase fuel economy through improved lubrication. Another operator, not part of the survey, used a combustion catalyst additive claimed to reduce and soften deposits and suppress smoke. It contains an iron compound, a magnesium sulfonate to inhibit corrosion, and a biocide. The additives that are being tested include a smoke suppressant described as a combustion catalyst and three different fuel economy improvers.

The operators using additives have followed the suppliers' recommendations for concentration. One indicated using both in-house tests and the suppliers' recommendations for flow-improver dosage. All others used the suppliers' recommendations only.

Mixing may be inadequate for much of the additive use. One operator used an air bubbler to stir the additive into the fuel. Although air agitation provided mixing, it has a high hazard potential with the presence of air, fuel, and the possibility of ignition from static electricity. Another operator had experimented with a venturi pump, which metered the additive into the fuel during delivery. These two systems probably provided good mixing, but five others made no provision for mixing. The additive was put into the fuel storage tank before fuel delivery and the only mixing was incidental to the fuel entering the tank.

A wide variety of mixers are available. Their cost is generally small compared to the overall expense of an additive evaluation. In many cases the fuel pump can be used for economical mixing. The outlet line is returned to the tank inlet so that the fuel can be pumped around a loop and returned to the same tank. Circulation of this type for enough time to pump three tank volumes

will generally give good mixing. The method does not work well if the tank inlet and outlet are located very close to each other. Provision for adequate mixing is recommended for both additive use and for using blends of 1-D and 2-D fuels.

## ENGINE MANUFACTURER'S RECOMMENDATIONS FOR ADDITIVES

Most of the engines used in transit buses were made by the Detroit Diesel Allison (DDA) Division of General Motors Corporation. Their published specifications prohibit adding any fuel substance that contains either gasoline or alcohol to diesel fuel for safety reasons (64). One exception is the use of isopropyl alcohol to prevent fuel-line freezing. The maximum concentration is one pint isopropyl alcohol per 125 gallons (0.1 percent) of diesel fuel. DDA also does not recommend the use of drained lubricating oil in diesel fuel, and states that its use could void warranties.

One of DDA's fuel specialists was contacted by phone. Detroit Diesel Allison has many years of experience in fuel and additive studies that confirm the main findings of this report. Ignition improvers have better reputations with engine manufacturers than most other additives. DDA's experience has been that ignition improvers are effective.

DDA has also had good experience with a number of flow improvers. However, they are fuel specific and a change in fuel generally requires a change in flow improver. Some flow improvers on the market are not very effective. Others may not be economic because they require a high concentration, or because of high price. A laboratory testing program is essential for evaluating flow improvers.

DDA's experience with the barium-based smoke suppressants has been negative. In their engines, smoke was reduced, but engine deposits were significantly increased. The location and nature of the deposits led them to expect engine damage from continued use (65).

Results with other performance additives have been negative. Most additives simply did not do what they were claimed to do. A few worked temporarily or under very limited conditions. Careful examination of the engines and fuel systems after testing revealed that most performance additives were causing harmful side effects, which would increase the long-term operating, maintenance, or replacement costs. Most engine manufacturers do not honor warranties if it can be determined that damage was caused by user-supplied additives.

Additives for storage and handling were found to be effective when used properly. The fuel user is often unaware of them because these additives are added at the refinery. In general, additive manufacturers who can supply beneficial test results sell their products at the refinery level.

## SUMMARY OF ADDITIVES

Transit operators need more information about their fuels and the additives used in them than has been available. Fuel inspection data and information on additives in the delivered fuel should be sought from the fuel supplier. This should be supplemented or checked with more testing done in-house or by outside testing laboratories as this would make it easy to identify and solve fuel-related problems.

Ignition improvers and flow improvers are usually worthwhile if they are needed, but economical use requires knowledge of the additive concentration (if any) in the fuel as delivered. Smoke suppressants help, but good maintenance is a better solution to the problem of smoke. Additives for fuel handling and storage are often effective and are commonly used by suppliers. They

should be used by transit agencies only to correct specific problems when they occur. Performance additives, particularly combustion catalysts, generally should be avoided. Good ones may exist, or may be developed in the future, but most evaluations have produced few positive results and there have been indications that some could be harmful.

## CHAPTER FOUR

# HOW TO EVALUATE FUEL ADDITIVES

Transit operators are frequently asked to evaluate fuel additives but thorough technical evaluations that measure the benefits and liabilities are expensive and time-consuming. The following outline is intended as a guide to help improve the usefulness of additive evaluations.

## BACKGROUND INFORMATION

The most important background information is a specific statement of the additive effects. Many additives are marketed as multifunctional. These usually contain mixtures, although in a few cases a single substance performs more than one function. Whatever the reason, an attempt to evaluate more than one function in a single testing program adds considerably to the difficulty. If an additive is claimed to reduce smoke, improve mileage, and reduce wear, decide on one major function and set up the testing program to measure that effect. Observations of the other effects can be made as incidental information for detailed testing later.

The manufacturer's test results relating to the additive effects should be available. The testing procedures should either follow well-known methods, such as those published by ASTM or engine manufacturers, or the procedures should be described in detail. The information should be adequate to allow someone else to repeat the tests and achieve the same results. This allows others to review these methods to determine if the claimed effect was actually measured, if test conditions were realistic, and if the effects were due only to the additive. The results should be examined to see if they support the statement of additive effect. If the manufacturer's testing appears to be inadequate, unscientific, or nonexistent, the supplier has no basis for the claimed effects. Testimonials from users without adequate test results are of little value. The testing program should be designed to avoid any problems or questionable areas that may be apparent in the manufacturer's test results.

The statement of additive effect should include a specific dose rate, the size of effect to be expected, and the time required to observe the effect. It should also include any limitations or qualifications relating to the fuel or operation conditions. For example, the statement "using 0.25 wt percent additive reduces smoke by 40 percent at the rated load and speed within the first hour of operation" is specific and the cost can be determined.

When a specific statement of additive effect has been estab-

lished, examine it for testability. The best kind of statement can be tested with current record-keeping practices; others will require a considerable amount of extra work in-house or require outside testing services. For example, if the statement of effect claims a 15 percent improvement in fuel economy, it should be testable with careful controls and reasonable length of time using regular fuel and driving records. A two percent improvement in fuel economy may be worth the additive cost, but so many factors can influence fuel economy by a few percent that fleet measurement would be impractical. An improvement that small can be measured in laboratory test engines, but only with considerable difficulty. Additional information on fuel economy testing is available in SAE J 1264, "Joint RCCC/SAE Fuel Consumption Test Procedure (Short-Term In-Service Vehicle) Type 1"; SAE J 1321, "Joint TMC/SAE Fuel Consumption Test Procedure Type 2"; SAE J 1376, "Fuel Economy Measurement Test (Engineering Type) for Trucks and Buses"; and reference 66.

For good additive evaluations the additive effect must be isolated. This means that two sets of data are required: one obtained with the test group using the additive, and the other with a control group using identical conditions without the additive. In many cases, tests have been conducted that showed a difference in performance, but other changes were made beside the additive. Different maintenance procedures, such as a change in tire pressure, or equipment modifications, such as different replacement parts, that affect performance could cast doubt on the validity of additive evaluations. The extra time and effort to standardize procedures, keep accurate, detailed records, and manage the control group can be costly. The payoff comes when the study is completed and the additive cost is known, the change in performance is known, and the change in performance can only be attributed to the additive.

Delayed action effects should be avoided if they can be identified. A rare example of a real delayed action effect occurs in gasoline engines when lead compounds deposited on the walls of the combustion chamber continue to provide some anti-knock protection for a short time after switching from leaded to unleaded gasoline.

Evaluations of fuels and fuel additives generally involve three levels of testing: fuel properties tests, engine or vehicle tests, and fleet tests. Most additive evaluations by transit operators have concentrated on fleet tests, but worthwhile information can be obtained at lower cost from the others. Some evaluations



by additive manufacturers have included fuel properties and engine tests. However, in many cases inadequate or nonstandard test methods were used. The most reliable evaluations are those made by independent testing laboratories that have no vested interests relating to the test results. Standard test procedures should be used wherever possible.

## LABORATORY TESTS

Fuel property measurements should be made on fuel containing the additive at the recommended dose rate and on the same fuel with no additive for comparison. Particular attention should be paid to tests designed to show problems such as the stability, flash point, or particulate contamination tests. Table 6 in Chapter Two gives regular fuel specifications and ASTM test methods and Table 11 lists some additional tests that are recommended for additive evaluations.

The regular fuel inspections were discussed in Chapter Two. The additional tests measure properties of particular interest for using additives. In most cases these tests cannot be correlated precisely with a condition that the additive may correct (or cause), but they provide useful indicators and they may also serve as a basis for comparing additives. They may bring problems to light early in the evaluation program before damage occurs or before all the evaluation funds have been committed.

The accelerated stability test measures the tendency of the fuel to form insoluble deposits resulting from exposure to oxygen or heat. Test conditions are not likely to match field conditions, but the results may correlate in a general way with injector deposits and injector sticking problems. The test is particularly recommended for detergent or antioxidant additives. A related test for deposition tendency, ASTM D 3711, may also be useful.

The neutralization number measures the acidity or basicity of the fuel and is related to the fuel's tendency to cause corrosion. The least corrosion occurs when neither acids nor bases are present. The rate of corrosion cannot be correlated exactly with the results of the test because the rates vary with chemical components of the fuel that are not identified in the test. However, it is a useful indicator of the corrosion potential of the fuel. This test is recommended for any additive.

The particulate contamination test is a sensitive indicator of

particles that could plug fuel filters or cause increased injector and piston ring wear (67). It was designed for aviation fuels but can be useful for diesel fuels. Additives might also cause removal of scale or sediments from storage tanks and in that case the testing should be made on a sample obtained after mixing and storage.

In evaluating flow improvers it may be useful to develop a test with the actual filters used in the fleet or to use Exxon's test procedures. The ASTM tests for cloud point and pour point do not predict the filter plugging temperature when flow improvers are used (57). A local test procedure may be particularly useful if the same type of fuel filter is used throughout the fleet. Use a new, clean filter for the untreated fuel and for each fuel-additive combination to be tested. Start just above the cloud point and periodically filter each sample while slowly lowering the temperature. Record the low temperature limit when the filter plugs or the filtration rate slows significantly. The rate of cooling should be kept within limits so that it is approximately the same for every sample. Exxon's Low Temperature Flow Test procedure (54) provides results that have been shown to correlate with field experience. Details are presented in Appendix E.

The water emulsion characteristics test measures the ability of the fuel to emulsify water. Water and fuel are mixed in a specified high-speed mixer then allowed to settle. Time for separation is reported if separation occurs in less than an hour. If not, relative amounts of fuel, water, and emulsion at the end of the hour are reported. This test would be most useful when the water dispersion tendency of a detergent additive is in question or is being compared.

## ENGINE AND VEHICLE TESTS

Engine and vehicle tests provide an opportunity to measure the effects of an additive under carefully controlled conditions. Many variables that cannot be controlled during routine operation can be eliminated on the engine test stand. The usual engine test procedure requires a newly rebuilt engine, instrumented for measuring and recording performance factors. After a break-in period, engine speed, power output, and fuel consumption rates are recorded periodically. Data usually include both pressure and temperature in the intake air, exhaust, cooling, and lubricating systems. Exhaust instrumentation normally includes measurements of unburned hydrocarbons, carbon monoxide, and nitrogen oxides. Others, such as aldehydes, visible smoke, odor, and particulates, can be included. Particulates can be collected for analyses including total mass, particle size distribution, and chemical constituents.

An operating cycle is specified for the engine test. It may be selected to conform to an established procedure, to simulate a normal driving cycle, or it may be a special cycle designed to show the additive's effect. The operating cycle specifies a time period for idle and for several conditions of engine speed and load. Special procedures, such as lubricant sampling, or unusual equipment items would be specified. When the cycle is completed and the measurements are recorded, the results are compared to those obtained with an identical engine using the same base fuel, without the additive. Alternatively, the results may be compared with baseline conditions for the same engine operated previously with a similar fuel with no additive.

The vehicle tests are similar to the engine tests. A vehicle is

TABLE 11

### ADDITIONAL FUEL PROPERTY MEASUREMENTS RECOMMENDED FOR ADDITIVE EVALUATIONS

Fuel Property	ASTM Procedure
Pour point, °F	D 97
Cold filter plugging temp., °F	*
Accelerated stability	D 2274
Neutralization number	D 974 or D 664
Gravity, API @ 60°F	D 1298
Heat of combustion, Btu/lb	D 240
Water emulsion characteristics	D 1401
Particulate contamination	D 2276

\*No ASTM procedure is available. An approach to developing a local procedure is outlined in the text, and Exxon's Low-Temperature Flow Test procedure (54) is given in Appendix E.



instrumented to measure similar parameters as those measured in the engine tests. The vehicle is then driven on a chassis dynamometer or over a prescribed route while the measurements are recorded. Instrumentation is more difficult for the vehicle tests, but the operating conditions are more realistic.

Engine and vehicle tests present an opportunity to verify claims and to perform a thorough check for side effects. This can prevent costly surprises that may occur if testing is initiated on a larger scale. The engine and vehicle tests may also indicate any special equipment or maintenance procedures that may be required when using the additive.

## FLEET EVALUATIONS

The two most overlooked factors in fleet evaluations are record keeping and control groups. A precise statement of additive effect will provide the first requirements for record keeping. The fuel property measurements with and without the additive should be carefully examined for indications of other effects, which could make a difference in the economics. For example, if an additive caused a significant increase in the acid or base neutralization number, it may be desirable to look for evidence of corrosion by analyzing samples of fuel for metals that may have come from storage tanks or fuel systems and to keep those records. They can be used later to measure the effect on tank or component life. Similarly, the engine and vehicle tests may indicate other areas for further record keeping.

Accurate records may have another benefit. In the fuel additive survey, one transit operator indicated that a fleet evaluation had been made of an additive guaranteed to improve fuel economy. Records of the evaluation showed a slight decrease in fuel economy relative to a control group. On the basis of their records the transit authority succeeded in getting a complete refund of the money spent on the additive.

To be certain that an additive produces a particular effect, a control group must be used. The base fuel and the vehicles

should be the same in both the test and the control group. Maintenance, routes, and operating conditions should be the same, or as similar as possible, and the same records must be kept. Any other factors that could affect performance, such as passenger loading or weather conditions, should be balanced between the test and control groups as closely as possible.

Past operating data have been used instead of a control group. Many changes occur with time that the transit operator may not be able to prevent. An improvement in maintenance procedures, for example, or a change in available replacement parts could invalidate the test. Operators have initiated fleet tests of additives designed to improve wintertime performance only to find that the following winter was unusually mild or severe. Better control groups can be obtained by dividing the fleet.

In selling aftermarket additives (that is, additives sold to fuel users rather than fuel manufacturers) suppliers have generally relied on testimonials. Accurate data can be obtained from fuel properties tests, engine and vehicle tests, and from fleet tests. To avoid misrepresentation, most test laboratories will require that their reports be quoted in full nor not at all. Customers should demand better data on fuel additives than the testimonials they have been provided in the past.

## COST-BENEFIT ANALYSIS

The performance evaluation should provide the necessary data for a cost-benefit analysis. When the evaluation is completed, the amount of benefit should be known for various concentrations of additive. This is often shown graphically as a response curve. Any additional cost factors, besides the additive cost, should have become apparent during the testing. These cost factors might include storage, handling, or mixing. The costs or benefits resulting from changes or additions to the maintenance and operating procedures should be included if they are required as a result of using the additive.

A useful statistic for cost analysis is the cost per unit im-

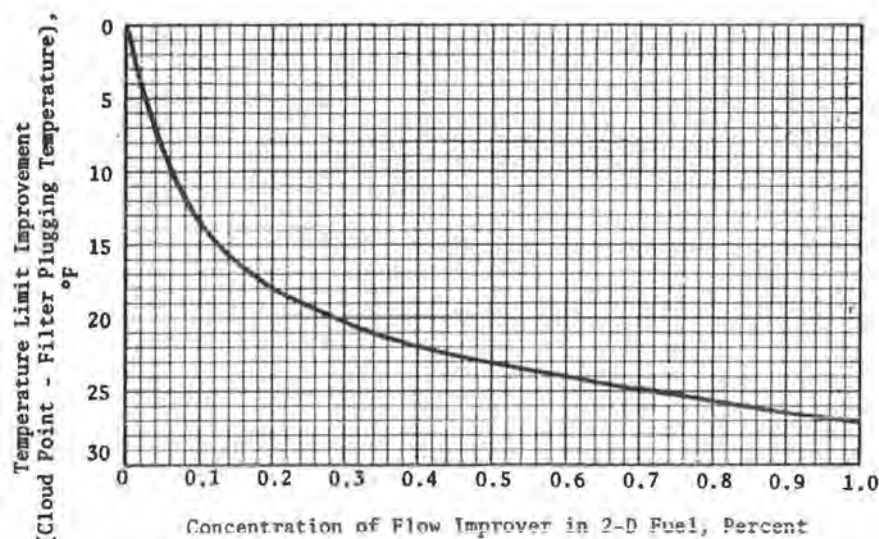


FIGURE 20 Typical response curve for extending the fuel low temperature limit with a flow improver additive. (For illustration only; actual response varies with both fuel properties and additive properties.)

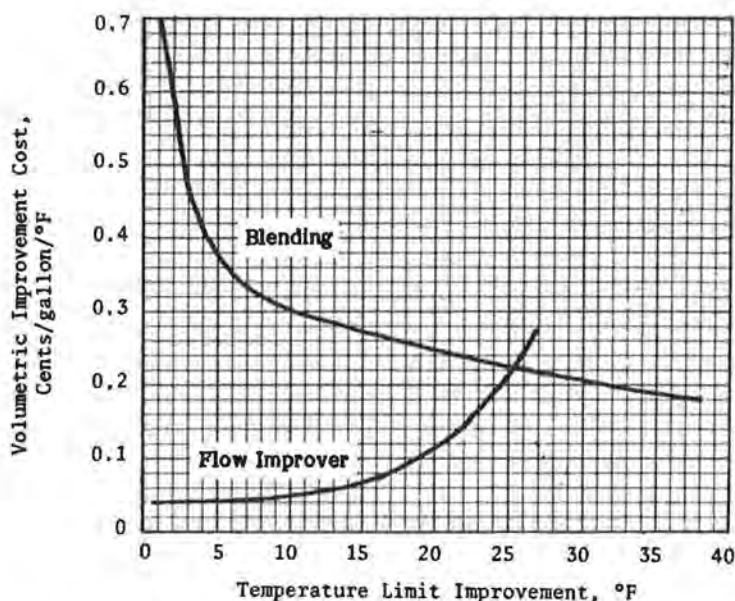


FIGURE 21 Example graphs of volumetric improvement cost for extending the fuels' low temperature limits. (Based on Figure 19 and Table 12.) (For illustration only; actual improvement cost will vary with fuel, additive, and prices.)

provement on a volume basis. For example, refiners have long used the cost per octane number improvement for a barrel of gasoline as a basis for comparing additives or processes. This volumetric improvement cost usually varies with additive concentration, so a graphic representation is quite helpful. This can be made from the additive costs and the response curve.

A response curve is illustrated in Figure 20 for a flow improver in 2-D fuel. To illustrate an improvement cost graph, the total costs are assumed to be a typical \$7.73 per gallon of additive (\$425 per drum). The cost per gallon of treated fuel can be calculated for various additive concentrations. For the same concentrations, the number of °F improvement can be found from the response curve. Dividing the cost per gallon of treated fuel by the number of °F improvement provides an improvement cost in terms of cents per gallon per °F. This cost is obtained for various concentrations for making the improvement cost graph.

The same procedure can be repeated for other additives or for other ways of accomplishing the same goal. For example, the cloud point of 2-D fuel can be lowered by blending it with 1-D fuel. Let us assume that the 2-D fuel cloud point is +12°F and the 1-D fuel cloud point is -26°F. The calculation methods of Appendix D can be used to find blend cloud points at various blending ratios. The fuel cost increase that results from using each blend is calculated and divided by the number of °F improvement. This provides a volumetric improvement cost for the blend in terms of cents per gallon per °F, which can be compared with the volumetric improvement cost for the additive. Table 12 lists the improvement costs for the blend, based on the assumption that the 1-D fuel costs 7¢ per gallon more than the 2-D fuel.

The blend cost and the additive cost are shown graphically in Figure 21. For this case, the additive is the more economic

method of reducing the temperature limit up to about 25°F reduction; then blending becomes more economic up to the 38°F reduction available when 1-D is completely substituted for the 2-D fuel. Beyond that, the additive could be used with straight 1-D fuel to extend the temperature limit further. It should be noted that flow improvers are fuel specific and the 1-D fuel will not respond in the same way as the 2-D fuel. The improvement in temperature limit will have to be calculated with its own response curve. An example of the numerical calculations is given in Appendix D.

Deciding whether to use the flow improver also depends on

TABLE 12

EXAMPLE VOLUMETRIC IMPROVEMENT COST FOR EXTENDING A FUEL'S LOW-TEMPERATURE LIMIT BY BLENDING<sup>a</sup>

2-D in Blend (%)	Cloud Point (°F)	Cloud Pt. Reduction (°F)	Increased Cost (¢/gal)	Increased Cost (¢/gal/°F)
100	+12	0	0	0
90	+11	1	0.7	0.70
80	+9	3	1.4	0.47
70	+6	6	2.1	0.35
60	+3	9	2.8	0.31
50	0	12	3.5	0.29
40	-3	15	4.2	0.28
30	-8	20	4.9	0.25
20	-13	25	5.6	0.22
10	-19	31	6.3	0.20
0	-26	38	7.0	0.18

<sup>a</sup> For illustration only; actual costs will depend on fuel properties and prices.

how cold it will get. Reasonable estimates of temperature extremes can be made from a statistical analysis of past weather records. Consultants are available for services of this type. In addition, some states have climatological offices that may provide the necessary information. Some guidance can also be ob-

tained from ASTM specification D 975, which gives 10th percentile minimum temperatures (the temperature was below that number 10 percent of the time). Maps are provided showing the statistic by state or smaller region for each winter month (14).

## CHAPTER FIVE

# ALTERNATIVE FUELS

Alternative sources of energy have received nationwide attention since the 1974 interruption of crude oil imports, which was accompanied by a substantial increase in crude prices. At that time, the incentives were to develop reliable domestic sources of energy and to extend available supplies for protection of the nation and its economy. In 1979, the prices of imported crude oil rose abruptly when political events in Iran diminished crude oil supply. Since that occurrence, energy conservation has received increased emphasis. Recent reductions in crude prices, although small, have caused a slowdown in development of synthetic crudes, but not in the overall search for more economical fuels. This section summarizes the current status of several alternative fuels for potential application in diesel engines.

Although much research has been done on production and utilization of alternative fuels, there are still problems to be solved with application of several fuels. The products most likely to be commercialized in the near term are methanol and fuels derived from shale oil, as discussed in the following sections.

## GASEOUS FUELS

Natural gas or its major component, methane, has been used commercially in modified diesel engines to drive electric generators or gas pipeline compressors. Spark plugs may be installed in each cylinder to ensure ignition, or the engine may be set up for dual-fuel operation where a small amount of diesel fuel is injected to take the place of a spark plug (68, 69). These engines are usually four-stroke design that are readily adapted to gaseous fuels. Gas is admitted to the engine by carburetion or continuous port injection. For two-stroke engines with continuous air flow, too much fuel would be lost with the exhaust. In these engines, fuel would be admitted by timed port injection (low pressure) or timed cylinder injection (high pressure).

The stationary application with an assured source of natural gas fuel eliminates the need for providing fuel storage. Methane has also been used for vehicles with gasoline engines, but the compressed gas at 2400 psig (17,000 kPa) pressure requires heavy storage tanks. Current research programs are aimed at fuel storage systems for CNG (compressed natural gas) or LNG [liquefied natural gas at  $-260^{\circ}\text{F}$  ( $-160^{\circ}\text{C}$ ) and atmospheric

pressure] (70). Both CNG and LNG are being used by several fleets of trucks and a few automobiles.

Propane has a high octane number (about 130 research octane) that encourages its use in gasoline engines. It may also be used in modified diesel engines with fuel systems similar to the natural gas systems just discussed. A moderate pressure fuel tank is required for about 200 psig (1400 kPa) at ambient temperature. The energy content of propane is about 72 percent of gasoline or 63 percent of diesel fuel on a volume basis, which makes propane economical when the price per gallon has the same or lower ratio to the other fuels. The city of Vienna, Austria uses propane for its bus fleet with modified gasoline engines.

Hydrogen can also be burned in spark-ignited engines when special precautions are taken to avoid both backfiring in the fuel induction system and pre-ignition in the combustion chamber (71). Fuel storage is an important technological factor that will probably delay hydrogen use for several years. High pressure tanks are currently less economical than liquid hydrogen vessels with elaborate insulation. Research is continuing on metal hydrides for hydrogen storage, where hydrogen is combined with metals at low temperatures and is heated to release the hydrogen to the engine. Although a few experimental vehicles have been converted to hydrogen, a significant technical breakthrough is necessary to reduce fuel tank weight.

## ALCOHOLS

The two alcohols that are the main candidates for fuel use are methanol and ethanol. Heavier alcohols, such as propanol and butanol, have been studied but find limited use because of their less favorable cost or engine performance, except as co-solvents to improve water tolerance of methanol in blends with gasoline. Selected chemical and physical properties of the two alcohols are presented in Table 13 for comparison with gasoline or diesel fuel (72).

Methanol is one of the most promising candidates for replacing petroleum-derived fuels (73). It is made from carbon monoxide and hydrogen, which in turn can be made by gasifying coal or biomass, although most present production comes from natural gas. The processes are well-known and commercially available. The Btu cost of fuel-grade methanol is close to gasoline



TABLE 13  
PROPERTIES OF ALCOHOLS AND HYDROCARBON FUELS<sup>a</sup>

Property	Methanol	Ethanol	Typical Gasoline	Typical 2-D Diesel Fuel
Formula	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	-	-
Composition, wt%				
Carbon	37.5	52.2	85-88	87-88
Hydrogen	12.6	13.1	12-15	12-13
Oxygen	49.9	34.7	-	-
Sulfur	-	-	ab. 0.03	ab. 0.1
Density, lb/gal	6.63	6.63	5.8-6.5	7.1-7.3
Specific gravity	0.796	0.794	0.70-0.78	0.85-0.87
Boiling point, °F	149	172	80-437	360-600
Net heat of comb. <sup>b</sup>				
Btu/lb	8,570	11,500	18,900	18,300
Btu/gal	56,560	75,670	115,400	131,100

<sup>a</sup> Data on methanol, ethanol, and gasoline from reference 72.

<sup>b</sup> The net heat of combustion was used to provide a more valid basis for comparison. It does not include heat from condensing the water vapor; thus it more accurately represents processes in the engine than does the gross heat of combustion.

and much less than synthetic fuels from other sources. There is currently a world-wide methanol surplus and some plants have been shut down for lack of a market.

Recent studies indicate that the problems that, in the past, limited the fuel uses of neat methanol (not blended with other fuels) can be solved. In spark-ignited engines, its high octane rating allows the use of high compression ratios with a high efficiency that partially compensates for its low heat of combustion. Additives have been used successfully to solve the cold-start problems. The use of different materials in the construction of the fuel tank and fuel system prevents corrosion and compatibility problems while new lubricating oils show promise for preventing rapid engine wear.

The use of neat methanol requires completely redesigned engines, fuel systems, and lubricants, but there are adequate incentives for making these changes. Although the cost of converting present spark-ignited or diesel vehicles would be high, the cost of producing a new methanol-fueled vehicle is projected to be about the same as standard vehicles. The exhaust contains no visible smoke and relatively low levels of other pollutants. There is evidence that the exhaust could be cleaned up with catalytic converters containing relatively inexpensive domestic metals instead of the more expensive imported metals currently required. Methanol's availability, its environmental benefits, and solution of its technical problems may bring it into rapidly expanding use. The limiting factors may be the time required to set up a complete, new fuel-distribution system and to gain public acceptance.

Methanol normally would not be considered a good diesel fuel. It has a long ignition delay in a diesel engine so its cetane number is low (as opposed to a high value of about 109 research octane). The lubricating effect is low and fuel injectors tend to stick. It has an energy content of about 43 percent of diesel fuel. Also, methanol is not soluble in diesel fuel except with the use of emulsifiers. However, methanol has been tested in diesel engines.

In one series of tests, a medium-speed, two-stroke diesel engine was modified to dual-fuel configuration (74). A small amount of diesel fuel was injected at each cylinder as pilot fuel. This served as an ignition source for the methanol injected through the main injector later in each cycle. The main injectors were replaced with larger ones because the volume of methanol required for equivalent energy input is 2.3 times the volume of diesel fuel. Finally, a small amount of diesel fuel was mixed with the methanol to prevent injector sticking. The results showed that 80 percent of the fuel energy could be furnished by methanol with horsepower and thermal efficiency equal to or slightly better than the baseline diesel fuel.

Recent field tests in Germany used straight methanol in buses powered by diesel engines (75). The direct-injection engines were modified by adding a spark plug or staged injection at each cylinder. Acceptance was generally good, and methanol provided improved starting torque. Problems reported were deposits in the fuel system (methanol is corrosive to several metals) and emulsions in the lubricating oil and injector pumps. Also, for comparable range, larger fuel tanks are needed.

Testing of methanol-fueled buses has been recommended by Booz-Allen & Hamilton for the Florida Department of Transportation and the Port Authority of Allegheny County, Pennsylvania (76). The modification kit for a DDA 6V-71 engine, developed through an UMTA grant, is estimated to cost \$5,000 per bus. Dynamometer testing of one bus will provide the basis for modifying three additional buses in both studies for track testing. Also, the California Energy Commission will test a different General Motors engine in 1984, modified to operate on methanol.

Ethanol is similar to methanol in having a high octane number (about 105 research) and therefore low CN. It also has low lubricity. Its energy content is higher than methanol at about 58 percent of diesel fuel on a volume basis. Also, ethanol will form solutions with diesel fuel, although they may not be stable and can separate in the presence of very small amounts of water.

Using ethanol in diesel engines has been studied by numerous investigators with a variety of approaches for introducing the alcohol into the engine (68). These methods and their limitations are as follows:

- *Solutions* of anhydrous ethanol in diesel fuel are limited to about 20 percent ethanol by solubility. This proportion can be increased to about 30 percent by inclusion of heavier alcohols (propanol to hexanol) as co-solvents. Power output decreases unless injection pump capacity is increased to offset the lower fuel energy content. Materials compatibility problems also were found.

- *Emulsions* of ethanol in diesel fuel have been used to accept varying amounts of water in the ethanol. The amount of emulsifier chemical approaches the amount of alcohol in the mixture, increases the fuel cost, and affects engine emissions adversely. Emulsions have high viscosity at low temperatures and may separate on freezing. Ethanol content of the emulsions is limited to about 25 percent.

- *Fumigation* is a dual-fuel technique to introduce ethanol into the intake air by a vaporizer or carburetor. Up to 50 percent of the fuel energy can be supplied by the alcohol in the mid-load range, but controls are needed to reduce the ethanol at high or low loads. Two fuel tanks and pumps are required.

- *Pilot ignition* can be used as with methanol and gaseous



TABLE 14

SELECTED PROPERTIES OF VEGETABLE OILS AND DIESEL FUEL (77,78)

Property	Vegetable Oils				Baseline Diesel Fuel
	Peanut	Corn	Sunflower	Soybean	
Gravity, °API	22.7	21.8	21.8	21.9	35.0
Flash point, °F	622	608	608	597	165
Pour point, °F	28	-2	16	16	-8
Viscosity, cSt @ 100°F	39.5	33.5	33.5	32.3	2.4
Cetane number	39.0	34.4	33.4	41.5	48
Net heat of comb., Btu/lb	15,950	-	16,130	15,900	18,480

fuels described earlier to increase the alcohol energy contribution to 90 percent of the total. Two fuel systems including injection pumps are required, with oversize injectors for the ethanol to achieve full power.

- *Neat ethanol* (100 percent alcohol) can be used with spark-ignition systems similar to those described earlier for gaseous fuels. The same result can be reached by use of cetane improver in ethanol so that it will ignite by compression without a spark plug. This approach is not significantly better than pilot ignition because 10 to 20 percent additive is required, at a substantial cost.

These several techniques were investigated as a means of extending fuel supplies. Because ethanol currently costs more per gallon than diesel fuel (and much more per Btu content) there is no economic incentive for using ethanol at present. A captive supply or lower cost ethanol could reverse this conclusion.

In summary, alcohols require engine modifications or a specially designed engine for use in transit vehicles. Currently, only methanol offers the economic incentive to develop the necessary engines and the supply system.

## VEGETABLE OILS

Replacing diesel fuel with vegetable oil of various types has been evaluated by numerous investigators since the 1930s. Blends with diesel fuel have been used, but most vegetable oils can perform reasonably well as straight fuels. Table 14 shows properties of four selected oils compared with diesel fuel (77, 78). Oils from peanuts, corn, sunflowers, and soybeans are similar to each other and quite different from diesel fuel. They have higher flash points and lower cetane numbers than diesel fuels. The major differences are in the flow properties of density, pour point, and viscosity of the oils, which affect spray characteristics in fuel injection systems. Engine tests on these fuels in blends with diesel fuel showed that thermal efficiency was higher, reaching a peak of about 7 to 9 percent above the baseline diesel fuel at about 60 percent vegetable oil in the blends. At higher concentrations, performance declined because of degrading atomization of the fuel with higher viscosity. The neat vegetable oils would not run in the test engine.

In a more recent study (78) four types of vegetable oils (cottonseed oil replaced corn oil) with three or four levels of processing made a total of 14 oils for testing. Complete analyses of the oils and a systematic investigation of injection and atomization characteristics preceded the engine testing. Heating the oils to 290°F (140°C) improved their spray characteristics to the equivalent of diesel fuel. The neat oils were compared with No. 2 diesel in both direct-injection (DI) and indirect-injection (IDI) engines for performance and 100-hour durability runs. Fuel consumption for all oils was similar to the base fuel in both engines. The DI engine showed some deposits on the injection nozzle and lubricating oil contamination, while the IDI engine did not show these results.

The main conclusion was that heating the oils to improve spray patterns avoided the nozzle deposits and lubricating oil problems reported in the literature. The DI configuration has less favorable results because of fuel impingement and showed more effect of fuel composition variables. A proposed specification was developed for vegetable oils for use in diesel engines, with a provision to minimize unsaturation for DI engine use. The conclusions apply only to four-stroke engines, which were used in testing.

## SYNTHETIC FUELS

Oil shale is a type of porous rock containing organic material called kerogen. Retorting at about 900°F (480°C) will convert the kerogen to a synthetic crude oil, yielding about 20 to 30 gallons per ton (80 to 120 L/Mg) of rock. Coal can be converted to a liquid by reaction with hydrogen at high pressure and temperature, usually with catalysts. The resulting yield of synthetic liquid products may amount to 80 to 120 gallons per ton (330 to 500 L/Mg) of coal processed. These materials are called synthetic crudes because they have been manufactured from the natural raw materials.

Properties of the synthetic crude oils are different from petroleum crudes. Table 15 shows a brief list of items for comparison with Arabian Light Crude as a representative crude oil (79). This natural crude mostly consists of hydrocarbons with a small amount of sulfur bound into molecules with the carbon and hydrogen. Only minor amounts of oxygen and nitrogen are present in petroleum.

TABLE 15

ANALYSES OF CRUDE OIL AND UNTREATED SYNTHETIC CRUDES (79)

Property	Arabian Light Crude	Paraho Shale Oil	Solvent Refined Coal
Gravity, °API	33.4	20.2	18.6
Sulfur, wt%	1.7	0.7	0.3
Carbon, wt%	85.0	84.3	84.6
Hydrogen, wt%	13.1	11.3	10.5
Oxygen, wt%	0.1	1.2	3.8
Nitrogen, wt%	0.1	2.2	0.9
Hydrogen to carbon atom ratio	1.84	1.60	1.48

The shale oil and coal liquid in Table 15 examples are typical products of the initial conversion step. Both are higher density (lower API gravity) than petroleum because they contain more aromatic ring structures, especially the coal liquid. The synthetics are lower in sulfur, but much higher in oxygen and nitrogen, which are present in ring-shaped molecules called heterocyclic compounds. The nitrogen compounds are unstable and react with other compounds or with oxygen to form organic sediment (sludge). The oxygen compounds are also reactive, have strong odors, and are "non-fuel" contaminants. The low ratios of hydrogen to carbon at the bottom of the table indicate that the synthetics are deficient in hydrogen compared to higher quality crude oils.

The usual upgrading process for synthetic crudes is severe hydrogenation. Catalytic reactions with hydrogen at high pressure and temperature accomplish two major improvements. First, they convert the heterocyclic compounds to hydrocarbons and remove most of the sulfur, oxygen, and nitrogen. Second, they add hydrogen to the molecules and raise the hydrogen-to-carbon ratio to levels approaching petroleum. Conversion reactions at the same time increase the yield of naphtha (gasoline blend stocks) and diesel fractions. The upgraded crude then is ready for further processing in a modern refinery with hydrotreating and hydrocracking operations. Adequate refining will make products that meet current specifications (80). Although there may be some variation in properties or composition of the synthetic products, their performance in engines has been found to be similar to conventional petroleum products. Research is continuing to demonstrate whether the small differences from petroleum will affect materials compatibility, thermal stability, long-term storage stability, emissions, or other performance factors that show up only in actual use of the products.

Two important shale oil developments were scheduled to occur in 1983. In the first operation, Geokinetics was to refine 82,000 barrels of shale oil at the Caribou Four Corners Refinery in Salt Lake City. The objective was to produce quantities of jet fuel, diesel fuel, and gasoline for the Department of Defense. The Air Force, Army, and Navy will use the fuels in testing programs (81).

The second development was scheduled completion of Union Oil Company's first commercial shale oil retort at Parachute Creek, Colorado (82). The shale oil will be upgraded and a portion of it will be delivered to the Gary Refining Company at Fruita, Colorado (near Grand Junction). Gary Refining will process the upgraded shale oil along with other crudes to make commercial products on a continuing basis. They also have a

contract to produce over 300 million gallons of JP-4 jet fuel from 100 percent shale oil for testing and full-scale use at two western Air Force bases (83).

Another approach to the use of coal is indirect liquefaction. The first step is the same as for methanol production where the coal is gasified. The gases are purified to remove contaminants leaving carbon monoxide and hydrogen. These gases are reassembled in this case to make hydrocarbons. One version of the process was used in Germany during World War II. The more modern Sasol process is used in three plants in South Africa to produce a major portion of the gasoline, diesel fuel, and chemicals needed in that country. Plans for commercializing direct coal liquefaction processes, where hydrogen is added directly to coal, have been shelved or delayed because the economics are currently unfavorable.

Tar sands have potential for development in the United States because small-scale plants to separate the bitumen (tar) from the sand or rock may be feasible. The hydrocarbon recovered is similar to the heavy, high boiling residue from crude oil. Processing to make lighter products will involve the conversion processes discussed earlier. Thermal conversion, such as coking, followed by hydrotreating has been done in Alberta, Canada since the 1960s. The diesel fuel product accounts for about 10 percent of the Canadian supply and has a CN of about 32 (12). The quality can be upgraded by blending or other processing, or a superior product could be made by hydrocracking.

The commercialization of alternative fuels in the United States has been slowed by diminished demand for products and the resulting lower cost of crude oil. However, development has not stopped entirely, and both government and energy companies are continuing research on fuel production, product quality, and utilization. There is a continuing need to be prepared to use alternative sources of energy in an emergency situation, or when crude supply and cost make them economical.

The alternative fuels that are expected to become available first are shale oil fuels and methanol. Methanol will be less expensive, but it requires specially designed vehicles and a distribution system. Tar-sand production is commercial in Canada and some pilot plants are operating in this country. Propane is often available in some areas and may be an economic alternative. In terms of the overall national requirement for transportation fuels, propane and tar-sand fuels represent a relatively small resource. Propane production is less than two percent of the total refinery and natural gas liquids output. Shale oil and methanol made from coal could be developed to provide a significant portion of the liquid fuel demand.

## GLOSSARY

- aniline point** The highest temperature at which a test fuel will not mix with aniline. Fuels with high aromatic contents tend to have low aniline points.
- antioxidants** Substances that interfere with slow oxidation reactions in fuel storage.
- API gravity** A density measurement commonly used for petroleum and petroleum products. Water is 10°API; higher numbers indicate lower density.
- aromatic** Compounds containing an unsaturated ring structure of six carbon atoms, such as benzene. The name was applied because of their pungent odor.
- atomize** To produce a fine spray by pressurizing through a nozzle, sometimes assisted by air or gas.
- barrel** Forty-two U.S. gallons. Common unit of measurement for petroleum and petroleum products.
- base number** A measure of a lubricant's ability to neutralize acids that may be formed during combustion.
- biocide** A substance that is toxic to bacteria and fungi.
- bitumen** Tar or pitch; the hydrocarbon in tar sand.
- blend** A fuel mixture in which more than one component is used. The components must be miscible and form a single phase. (See also *emulsion*; *neat*.)
- boiling range** The temperature span from when boiling begins to the temperature at which the last fraction is vaporized in a specified batch distillation.
- catalytic cracking** Cracking in the presence of a catalyst that causes the reaction to proceed at a higher rate than thermal cracking. Often called *cat cracking*.
- catalyst** A substance that increases the rate of a chemical reaction, but is not consumed as one of the reactants.
- cetane** A saturated hydrocarbon having 16 carbon atoms used as a high quality diesel reference fuel.
- cetane improver** Same as *ignition improver*.
- cetane index** An approximation of the cetane number calculated from the API gravity and the mid-boiling point. (See Appendix B.)
- cetane number** For a fuel, it is the percentage of pure cetane in a mixture with heptamethylnonane that has an ignition delay equal to the fuel being tested.
- cloud point** The temperature at which wax crystals begin to form in the fuel. Also called *wax appearance point*.
- combustion catalysts** Substances that, at a given temperature, increase the rate of combustion. They do not generally affect the ignition delay.
- condensed aromatic** Describes compounds containing two or more connected unsaturated ring structures. Also called *polynuclear aromatic*.
- corrosion inhibitors** Substances that prevent corrosion by forming a thin temporary coating over the protected metal.
- cracking** A chemical reaction in which hydrocarbon molecules are broken (cracked) into smaller molecules.
- crude** Petroleum before processing. (See also *heavy crude*; *sour crude*; *sweet crude*.)
- degrees API (or °API)** A unit of density measurement commonly used for petroleum and petroleum products. (See *API gravity*.)
- detergent** A soluble substance that holds insoluble foreign matter in fluid suspension. Typically, one end of the molecule is soluble in the fluid and the other end in the foreign matter.
- dispersant** A substance that tends to prevent the settling of small particles or droplets of an immiscible liquid.
- distillation curve** The relationship between boiling point and the percent evaporated in a specified batch distillation. Also called *boiling point temperatures*.
- elastomer** An elastic, rubber-like polymer.
- emulsion** A fuel composition containing immiscible components with one component dispersed as tiny droplets within the other. (See also *blend*; *neat*.)
- flow improver** An additive that allows the fuel to remain fluid and free flowing at lower temperatures by inhibiting the formation of large wax crystals. Also called *pour point improver*.
- heavy crude** Crudes with high specific gravity. The API gravity is usually 25 or less. Heavy crudes tend to be higher in aromatics and have higher viscosity than normal crudes.
- heteroatoms** Describes compounds containing oxygen, nitrogen, or sulfur in addition to carbon and hydrogen, usually in a ring structure.
- hydrocracking** Cracking in the presence of high pressure hydrogen and catalyst with significant conversion of large molecules to smaller molecules.
- hydrogenation** A class of chemical reactions, including hydrocracking and hydrotreating reactions, in which hydrogen is added to molecules. It is commonly characterized in terms of reaction conditions, with severe hydrogenation implying use of higher than normal temperature, use of pressure, and long reaction times. Less extreme reaction conditions may be termed moderate or mild hydrogenation. Higher severity conditions result in higher hydrogen consumption per barrel of feedstock.
- hydrotreating** A catalytic oil hydrogenation process that causes little or no cracking. The hydrogen content of the oil is increased and some of the sulfur, oxygen, and nitrogen atoms are removed.
- ignition improver** An additive that reduces the ignition delay of a fuel, thereby increasing its cetane number.
- ion** An atom or a molecular fragment that carries an electric charge, as a result of gaining or losing one or more electrons.
- isoparaffins** Paraffins in which the carbon chain is branched. (See *normal paraffins*.)
- kerogen** The hydrocarbon contained in oil shale. Usually used in reference to western, rather than eastern, oil shales.
- mercaptan** Compounds in which a hydrocarbon is attached to one bond of a sulfur atom and the other sulfur bond is attached to a hydrogen atom. Mercaptans typically have strong, unpleasant odors.
- metal deactivator** Same as *corrosion inhibitors*, but with specific affinity for copper and its alloys.
- naphthenes** Hydrocarbons containing saturated ring structures.
- neat** In reference to fuel, a composition in which one com-



- ponent is used alone. Also means without additives. (*See also blend; emulsion.*)
- normal paraffins** Paraffins in which the carbon chain contains no branches. Sometimes called *straight-chain paraffins*. (*See isoparaffins.*)
- octane number** A measure of the anti-knock tendency of a fuel in a spark-ignition engine at prescribed conditions. Fuels with a high octane number typically have a low cetane number and vice versa.
- oil shale** A fine-grained rock containing hydrocarbons.
- olefins** Hydrocarbons containing unsaturated bonds.
- organometallic** An organic molecule containing a metal atom.
- paraffins** Saturated hydrocarbons that do not contain ring structures.
- polyaromatic hydrocarbons** Same as **condensed aromatic**, with two or more aromatic rings.
- polymer** A compound made up of small molecules joined together to form large molecules. They are characterized by repeating structural units.
- polynuclear aromatic** Same as **condensed aromatic**.
- pour point** In a specified test, the lowest temperature at which an oil will flow.
- pour point improver (or pour point depressant)** Same as **flow improver**.
- pyrolysis** The breaking of any molecule into smaller molecules by heating, similar to thermal cracking. In pyrolysis, some small molecules recombine to form tars or coke.
- radical** A reactive molecular fragment.
- residual oil** A high boiling fraction of crude oil, usually boiling higher than 850°F (450°C). Also called *resid*, *residuum*, or *residue oil*.
- response** With reference to an additive, the change in fuel property with increasing additive concentration.
- retorting** With reference to oil shale, the process of heating the rock to provide a shale oil vapor, which is condensed.
- saturated** In reference to hydrocarbons, it indicates that each carbon atom is singly bonded to adjacent carbon or hydrogen atoms. Multiple bonds are removed by adding hydrogen. When all the multiple bonds have been hydrogenated, no more hydrogen can be added to the molecule, hence the term saturation.
- shale oil** Oil derived from the processing of oil shale by retorting, extraction, or other means.
- slurry** A mixture of a liquid and a particulate solid.
- sour crude** Crude that contains more than 0.5 weight percent sulfur. Sour refers to the hydrogen sulfide odor often associated with high-sulfur crudes. (*See sweet crude.*)
- specific gravity** The ratio of the mass of a material to the mass of an equal volume of water, at a given temperature for each. For example, Sp. Gr. 60°F/60°F = 0.850 means a given volume of product at 60°F weighs 85% as much as water at 60°F.
- straight run** Petroleum products obtained by crude distillation only, sometimes called *virgin stocks*.
- sweet crude** Crude that contains less than 0.5 weight percent sulfur. (*See sour crude.*)
- tar sand** Sand or sandstone that contains a heavy hydrocarbon in the space between the grains.
- thermal cracking** Cracking induced by heat. Pyrolysis of saturated hydrocarbons.
- virgin stock** *See straight run.*
- viscosity** The resistance of a fluid to a shearing or stirring motion. There are several different methods of measurement, but most assign higher numbers to fluids that flow slowly.
- volumetric improvement cost** The cost of making a specified improvement in some fuel property expressed on a volume basis. (*See Appendix D.*)
- wax appearance point** *See cloud point.*



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## APPENDIX A

### PROPERTIES OF NO. 1-D AND NO. 2-D FUELS IN 1982 BY REGION AND MAP SHOWING REGION LOCATIONS

TABLE A-1

SUMMARY OF NO. 2 DIESEL FUELS, 1982 (INFORMATION FROM REF. 1)

Region	Eastern			Southern			Central			Rocky Mountain			Western			U.S. Average		
Number of Samples	75			43			68			35			37			120		
	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.
Gravity, °API	29.4	34.4	43.6	29.4	33.5	39.6	29.4	34.9	39.5	30.9	34.7	39.5	30.9	34.0	39.5	29.4	34.5	43.6
Flash Point, °F	136	158	236	136	172	202	128	168	208	146	174	216	146	172	216	128	168	236
Viscosity, cSt at 100°F	2.10	2.85	4.34	2.30	2.91	3.98	2.12	2.70	4.11	2.21	2.86	4.11	2.10	3.17	4.11	2.10	2.85	4.34
Cloud point, °F	-20	-	30	-16	-	20	-10	-	20	-8	-	28	-18	-	42	-20	-	42
Pour point, °F	-30	-	25	-20	-	10	-30	-	10	-10	-	20	-40	-	35	-40	-	35
Sulfur content, wt%	0.020	0.222	0.550	0.070	0.252	0.970	0.050	0.289	0.550	0.096	0.345	0.540	0.020	0.301	0.540	0.020	0.272	0.970
Aniline point, °F	116.0	144.4	193.0	118.4	139.1	157.0	116.0	139.7	157.0	128.0	142.7	157.6	130.0	144.4	152.0	116.0	143.2	193.0
Carbon Residue:																		
on 10%, wt%	0.000	0.145	0.450	0.000	0.164	0.450	0.000	0.131	0.250	0.050	0.136	0.200	0.010	0.128	0.200	0.000	0.138	0.450
Ash, Wt%	0.000	0.002	0.016	0.000	0.001	0.007	0.000	0.002	0.016	0.000	0.001	0.006	0.000	0.002	0.020	0.000	0.002	0.020
Cetane number	39.0	44.3	53.0	40.0	43.7	47.1	39.0	43.9	52.2	39.5	44.1	49.5	40.3	44.1	47.0	39.0	44.4	53.0
Cetane index	35.1	45.8	60.0	35.1	44.5	57.7	37.9	45.8	55.4	37.9	47.2	59.0	39.8	47.0	59.0	35.1	45.8	60.0
Distillation temp, °F																		
volume recovered:																		
IBP	298	381	480	298	388	435	298	380	430	315	385	452	315	387	460	298	383	480
10%	379	436	520	379	438	469	379	432	492	391	444	492	398	459	518	379	437	520
50%	451	509	568	451	510	536	451	502	546	473	517	551	462	526	564	451	509	568
90%	520	595	643	554	600	643	551	588	622	567	604	640	546	607	632	520	595	643
End Point	684	646	715	588	649	715	588	636	690	605	647	695	593	650	710	584	644	715



TABLE A-2

SUMMARY OF NO. 1 DIESEL FUELS, 1982 (INFORMATION FROM REF. 1)

Region	Eastern			Southern			Central			Rocky Mountain			Western			U.S. Average		
Number of Samples	33			11			34			19			10			57		
	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.
Gravity, °API	39.8	42.8	47.0	41.1	42.7	44.1	39.8	42.7	45.0	37.4	41.8	45.0	38.1	42.0	48.8	37.4	42.5	48.8
Flash point, °F	114	139	172	114	140	154	114	138	172	108	137	172	102	136	158	102	138	172
Viscosity, cSt at 100°F	1.45	1.69	2.00	1.45	1.60	1.70	1.52	1.75	2.41	1.50	1.76	2.60	1.40	1.62	2.10	1.40	1.70	2.60
Cloud point, °F	-50	-	20	-50	-	20	-48	-	20	-56	-	23	-56	-	-4	-56	-	20
Pour point, °F	-55	-	-20	-55	-	-25	-55	-	-5	-60	-	0	-60	-	-10	-60	-	0
Sulfur content, wt%	0.001	0.064	0.280	0.001	0.051	0.110	0.010	0.131	0.390	0.000	0.146	0.390	0.000	0.062	0.210	0.000	0.086	0.390
Aniline point, °F	137.5	147.2	167.0	142.5	146.7	151.0	140.9	146.6	160.0	135.3	143.5	151.0	133.0	140.2	151.0	133.0	145.8	167.0
Carbon residue:																		
on 10%, wt%	0.000	0.055	0.092	0.050	0.067	0.090	0.060	0.079	0.110	0.020	0.073	0.100	0.010	0.069	0.110	0.000	0.063	0.110
Ash, wt%	0.000	0.004	0.026	0.001	0.002	0.006	0.000	0.002	0.026	0.000	0.001	0.006	0.000	0.001	0.001	0.000	0.003	0.026
Cetane number	46.0	49.7	56.4	47.0	48.2	50.0	46.0	48.1	50.0	45.0	46.1	47.0	43.0	44.6	45.8	43.0	48.0	56.4
Cetane index	32.0	47.6	53.3	32.0	44.8	50.1	43.3	47.5	53.8	39.0	45.8	53.8	39.0	43.9	49.0	32.0	46.9	53.8
Distillation temp, °F																		
volume recovered:																		
18P	258	348	394	258	331	366	258	347	394	276	341	364	276	340	372	258	347	394
10%	352	388	418	352	375	388	352	384	410	296	378	419	296	365	406	206	386	530
50%	374	428	462	374	416	438	392	429	499	392	430	505	382	418	443	384	428	505
90%	428	479	530	428	476	501	451	486	589	451	492	593	459	476	519	428	483	593
End point	475	516	569	492	522	542	486	526	641	473	528	641	473	510	565	473	521	641

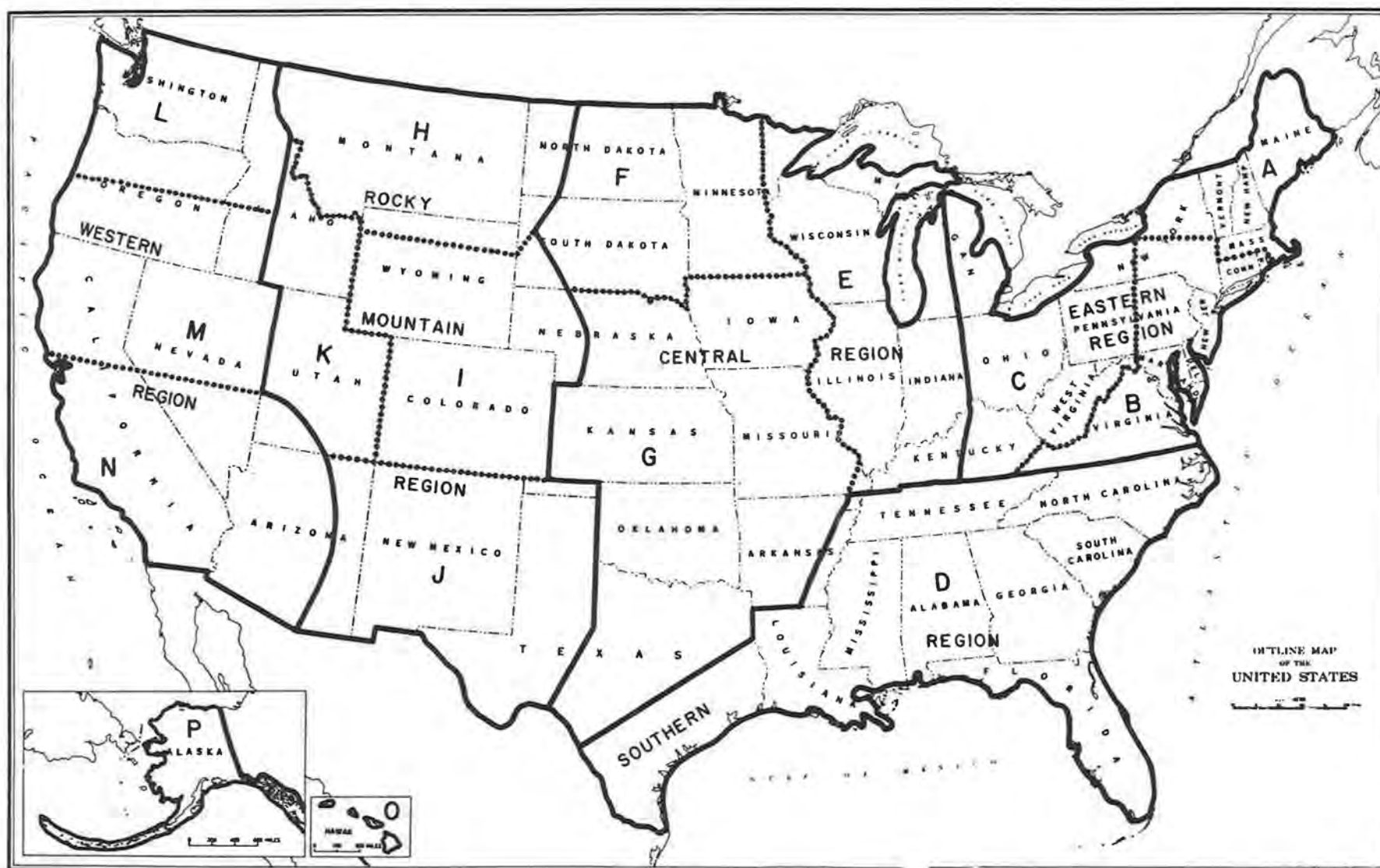


FIGURE A-1 Map showing the regions used in the national survey of diesel fuels (information from ref. 1).

## APPENDIX B

### EQUATIONS AND STATISTICAL DATA RELATING TO THE CETANE NUMBER AND THE CETANE INDEX

EQUATIONS FOR CETANE INDEX (CI) AND ESTIMATED CETANE NUMBER (CN)

Equation for cetane index per ASTM method D 976-80:

$$CI = -420.34 + 0.016G^2 + 0.192 G \log M + 65.01 (\log M)^2 - 0.0001809 M^2 \quad (\text{Eq. B-1})$$

Equation based on 1-D data, 1982 DOE survey, correlation coefficient = 80%:

$$CN_1 = 0.85 CI + 7.86 \quad (\text{Eq. B-2})$$

Equation based on 2-D data, 1982 DOE survey, correlation coefficient = 89%:

$$CN_2 = 0.96 CI + 1.66 \quad (\text{Eq. B-3})$$

where:

G = API gravity

M = Temperature in degrees Fahrenheit of the 50% boiling point per ASTM D 86

AP = Aniline point in degrees Fahrenheit per ASTM D 611

CI = Cetane index

CN<sub>1</sub> = Estimated cetane number based on 1-D data 1982

CN<sub>2</sub> = Estimated cetane number based on 2-D data 1982,

TABLE B-1

COMPARISONS OF CETANE INDEX AND ESTIMATED CETANE NUMBERS WITH OBSERVED CETANE NUMBERS IN 1982 DOE FUEL SURVEY

Comparison	Average Deviation (X)	Standard Deviation (σ)	Number of Data Points
<u>Diesel Fuel Grade 1-D</u>			
CN-CI (Eq. B-1)	0.88	1.93	16
CN-CN <sub>1</sub> (Eq. B-2)	-0.05	1.83	16
<u>Diesel Fuel Grade 2-D</u>			
CN-CI (Eq. B-1)	-0.14	1.49	32

Improvement in cetane quality with ignition improver additives can be calculated by either of the two methods:

1. If the cetane number is known for an untreated fuel and for a fuel with one or more additive concentrations, the Ethyl Ignition Improver Susceptibility Chart is used (2). This is a special graph on which the cetane number



normally plots as a straight line with additive concentration. To find the additive concentration to yield a desired cetane number, plot the available data and draw the straight line that fits best. The required concentration is read where the line crosses the desired cetane number.

2. If cetane number measurements are not available, the cetane improvement for a given volume of ignition improver can be calculated with Eq. B-4:

$$\text{CNI} = 0.169 (G/10)^{1.444} (M/100) \ln (1 + 17.6 D) \quad (\text{Eq. B-4})$$

where:

CNI = Cetane number improvement

G = API Gravity

M = Temperature in degrees fahrenheit of the 50 percent boiling point

D = Volume percent of the ignition improver

ln = Natural logarithm (base e).

To calculate the additive concentration required for a particular cetane number improvement, use Eq. B-5, which is Eq. B-4 rearranged to solve for the volume percent of ignition improver:

$$D = 0.057 (e^a - 1) \quad (\text{Eq. B-5})$$

where:

$$a = \frac{16,400 (\text{CNI})}{(M)(G^{1.444})}$$

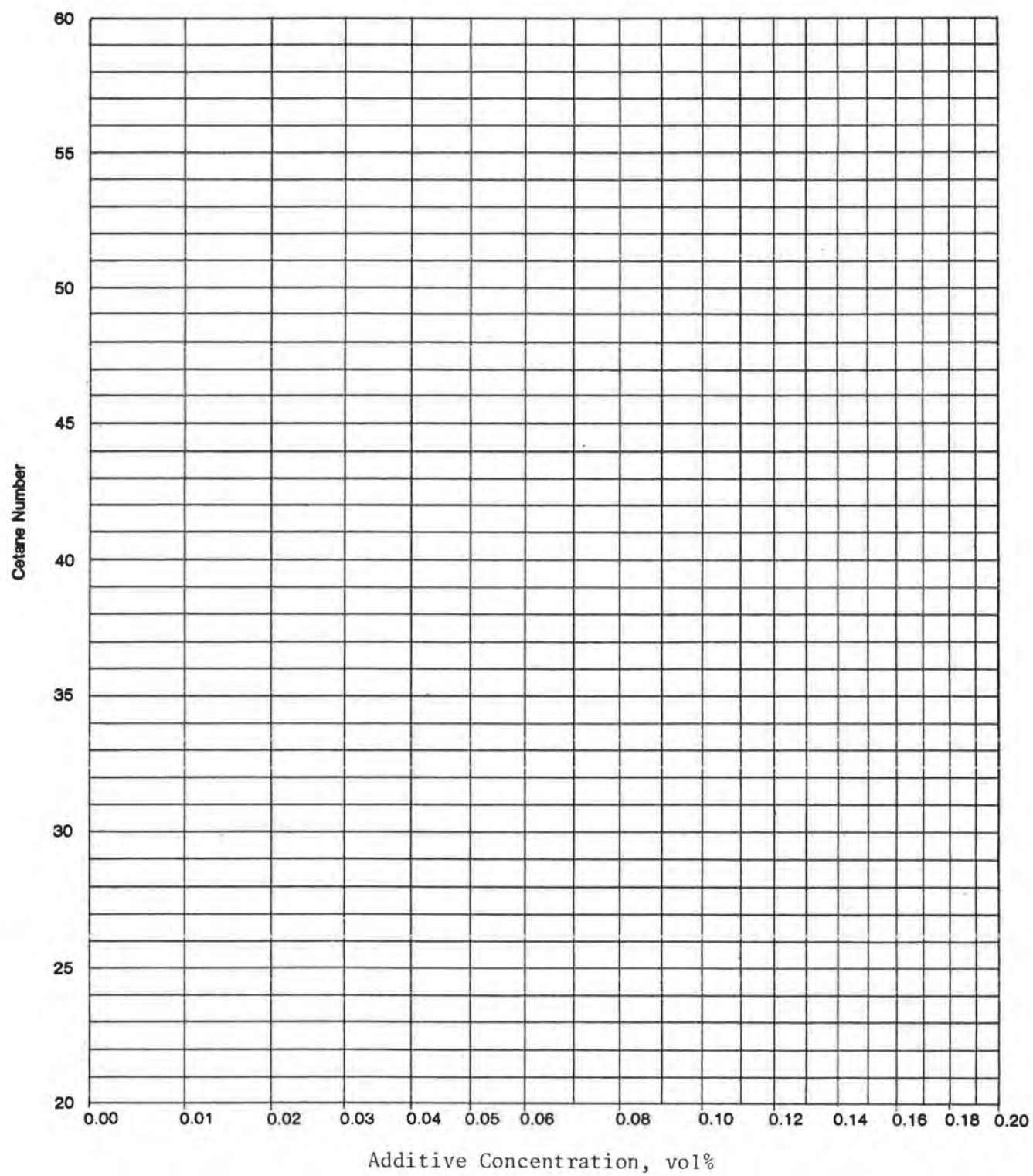


FIGURE B-1 Ethyl ignition improver susceptibility chart.

## APPENDIX C

### REGIONAL CETANE INDEX DISTRIBUTIONS FOR NO. 2-D FUELS, 1982

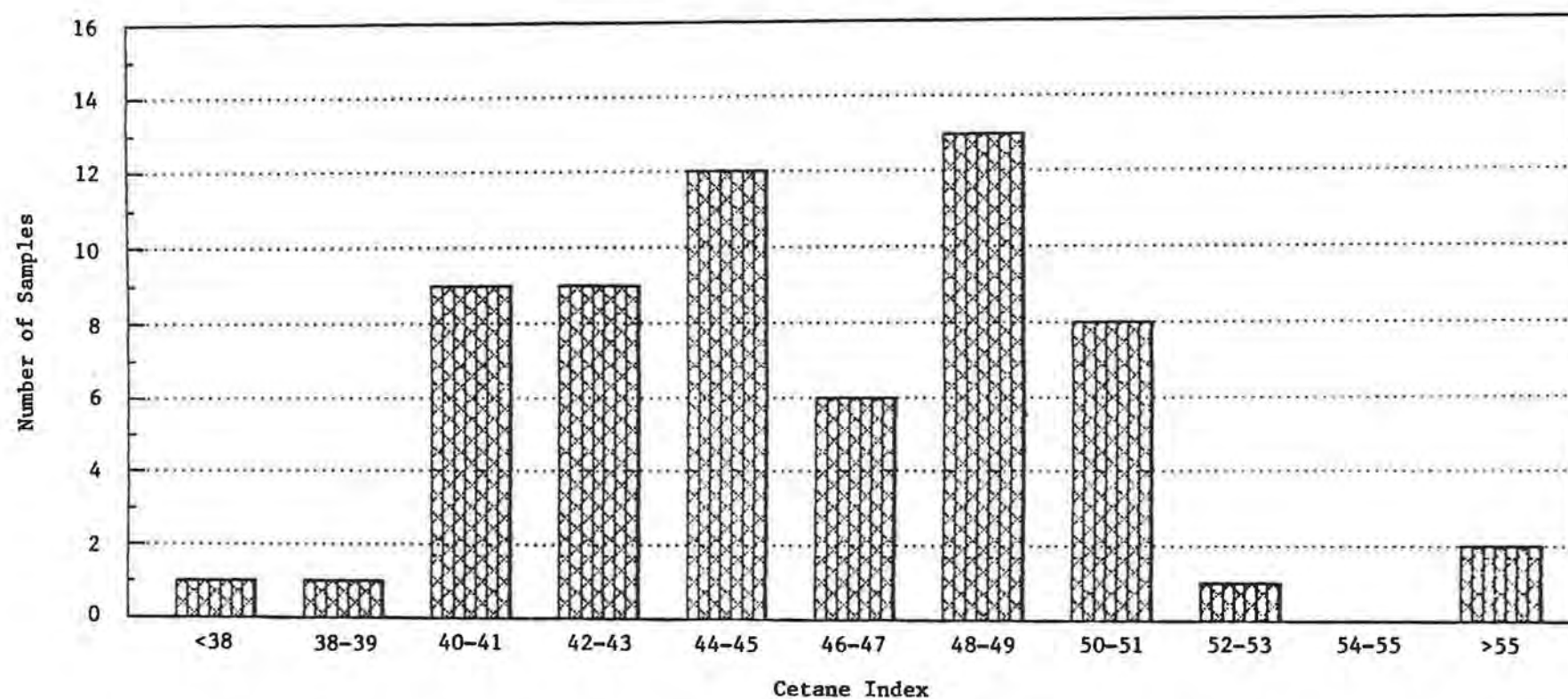


FIGURE C-1 Eastern region distribution of cetane index for No. 2-D fuels, 1982.



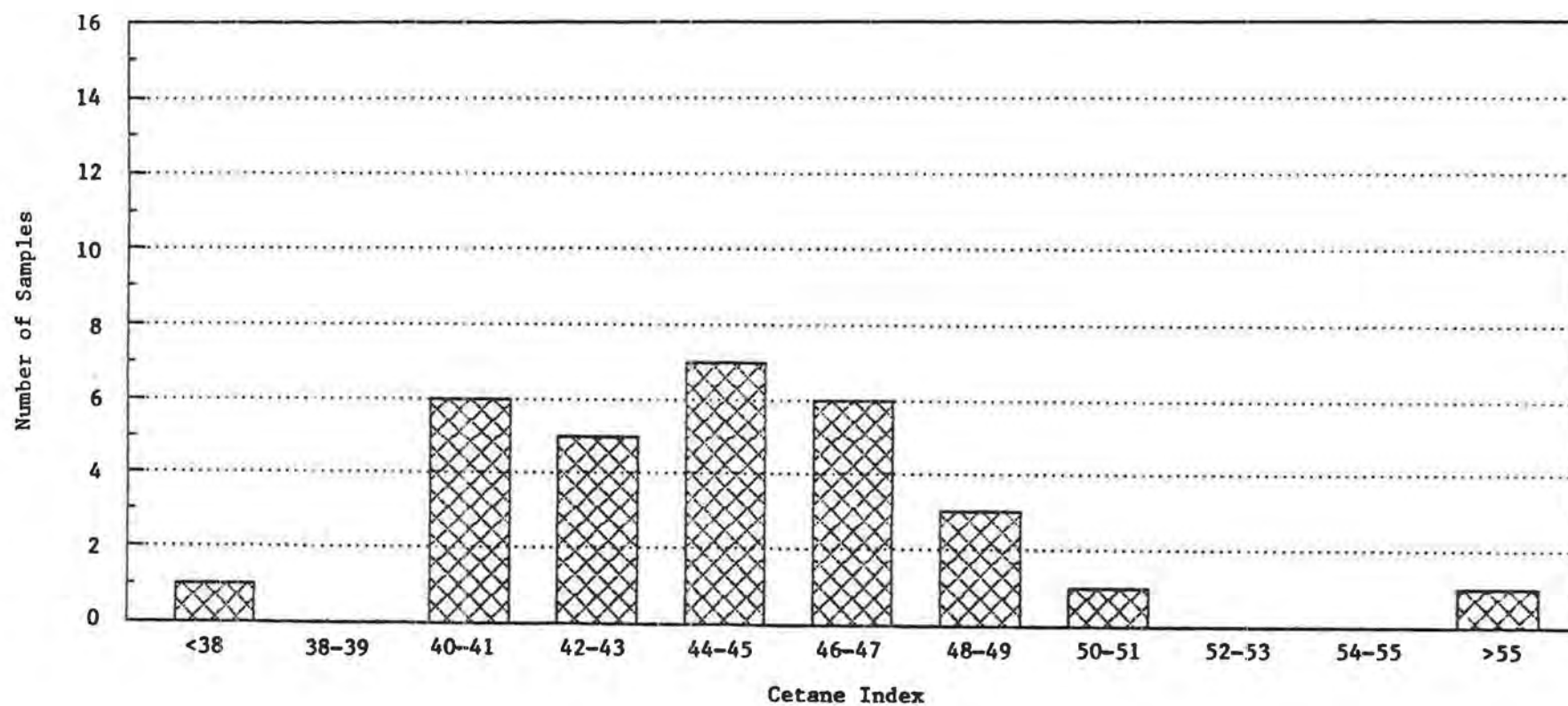


FIGURE C-2 Southern region distribution of cetane index for No. 2-D fuels, 1982.

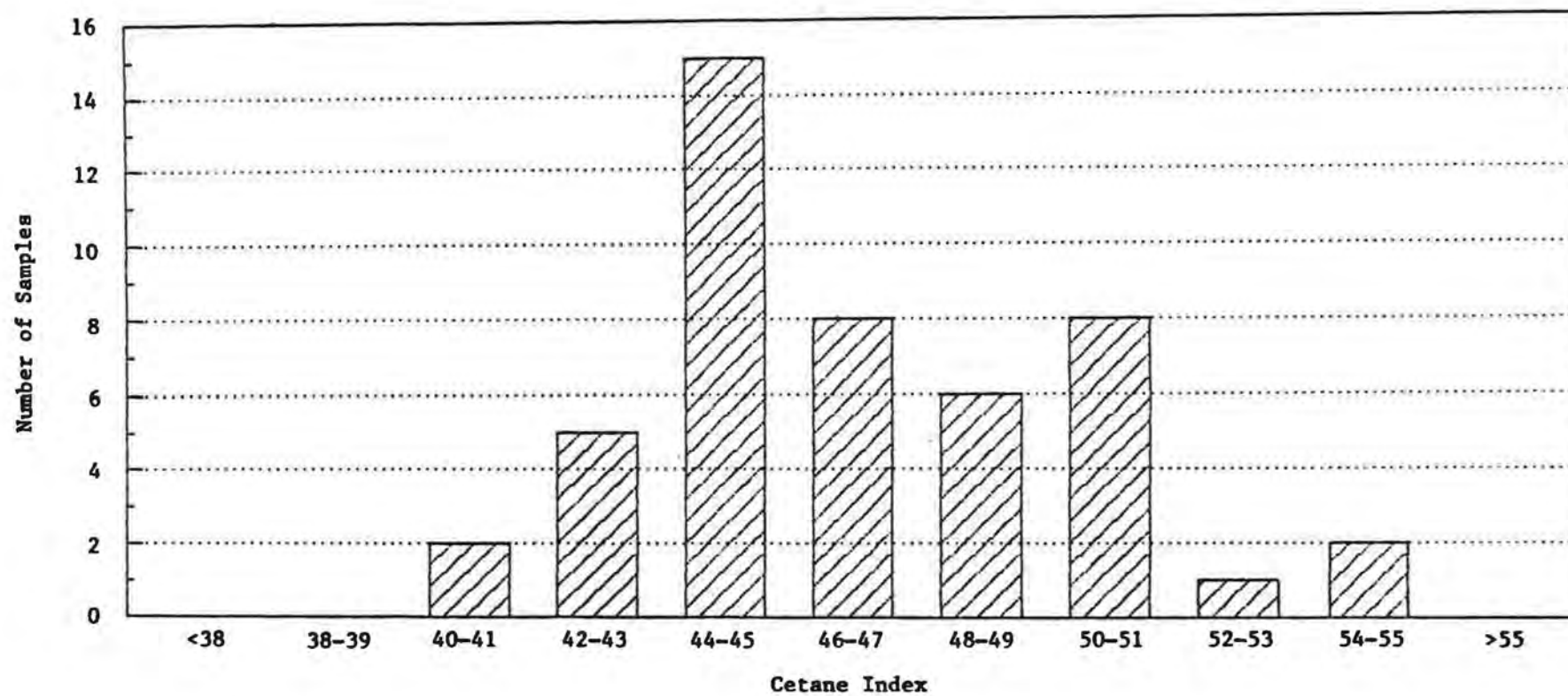


FIGURE C-3 Central region distribution of cetane index for No. 2-D fuels, 1982.

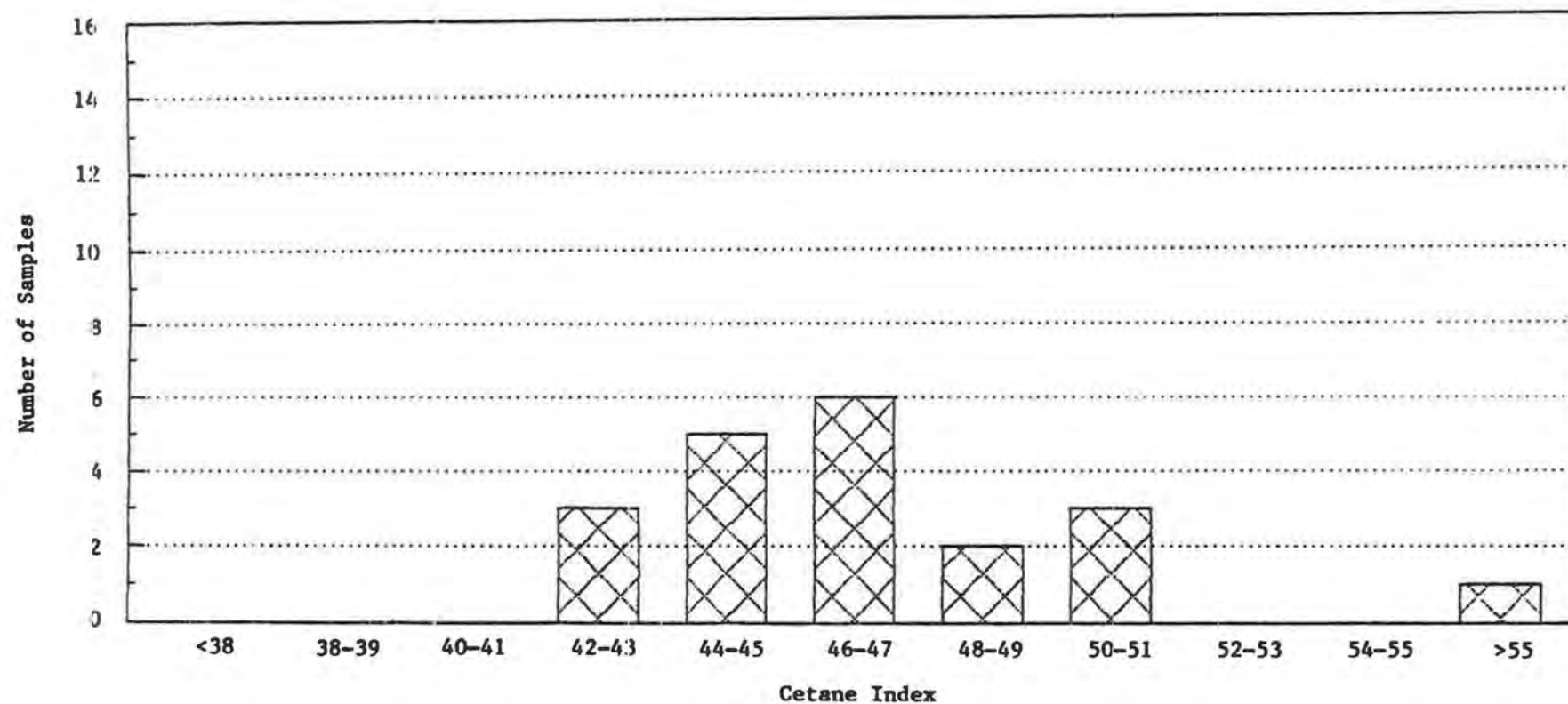


FIGURE C-4 Rocky Mountain region distribution of cetane index for No. 2-D fuels, 1982.



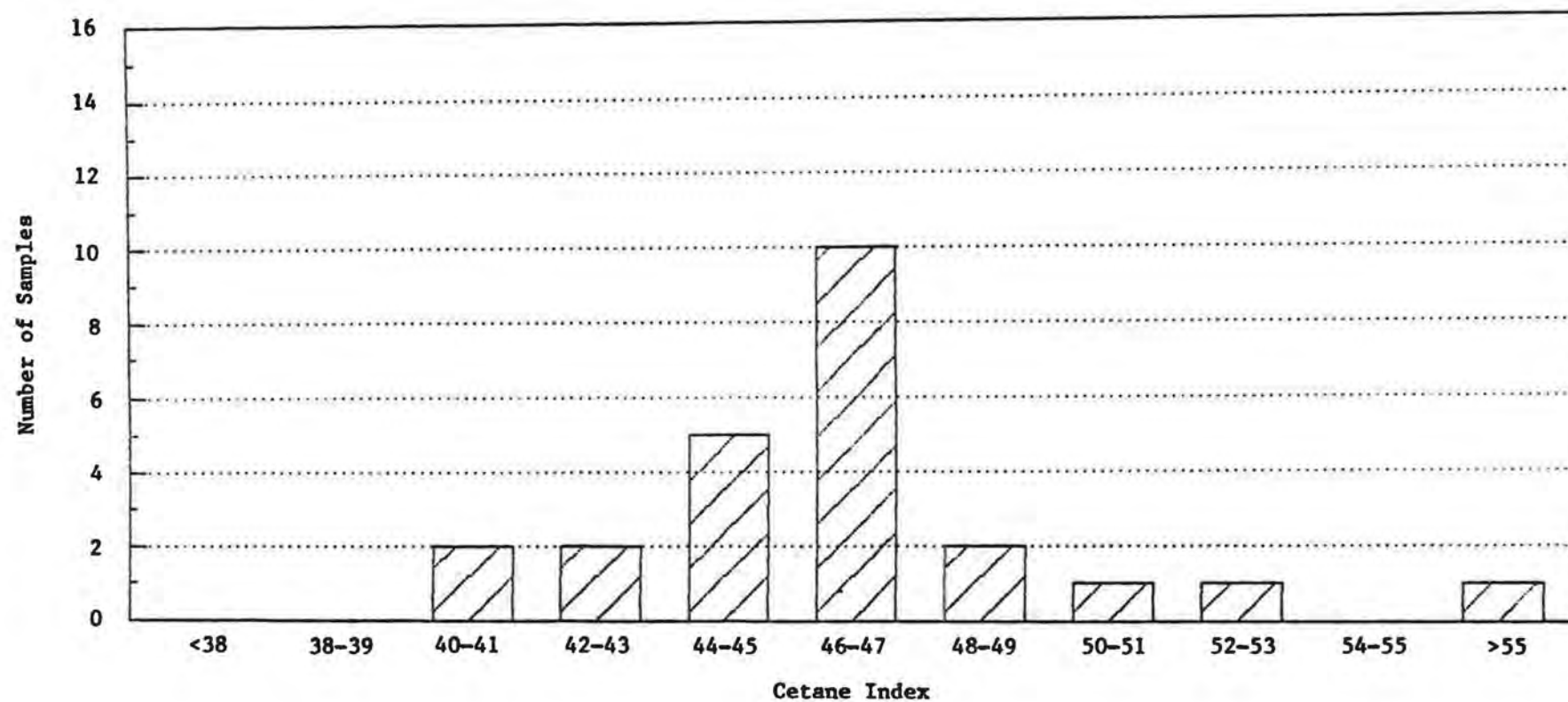


FIGURE C-5 Western region distribution of cetane index for No. 2-D fuels, 1982.

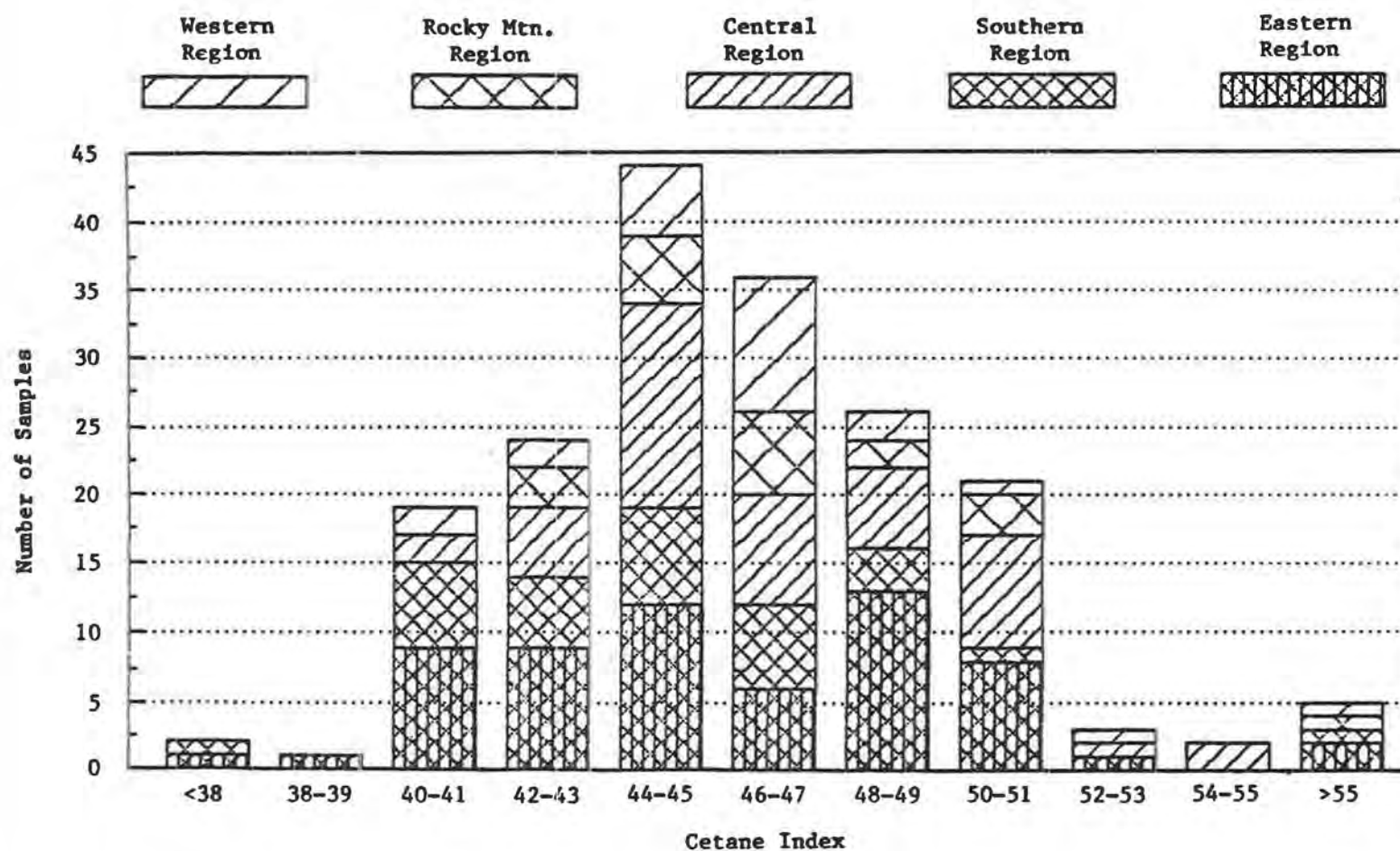


FIGURE C-6 USA regional distribution of cetane index for No. 2-D fuels, 1982.

## APPENDIX D

### CALCULATIONS OF BLEND PROPERTIES AND VOLUMETRIC IMPROVEMENT COST

Some blend properties are calculated on a weight basis, whereas others are calculated on a volume basis. In the example used in Table 8 of this synthesis, the blend was specified as 40 percent 1-D and 60 percent 2-D by volume, so it was necessary to calculate the weight fractions.

The specific gravity at 60°F is calculated from the API gravity with Eq. D-1:

$$SG = 141.5 / (131.5 + G) \quad (\text{Eq. D-1})$$

where:

SG = specific gravity at 60°F (g/mL)

G = API gravity.

For the 1-D fuel the specific gravity is:  $SG = 141.5 / (131.5 + 41.4) = 0.8184$  g/mL. Similarly, the 2-D fuel specific gravity is 0.8333 g/mL.

The blend specific gravity is calculated on a volume basis using Eq. D-2:

$$(V_1) (P_1) + (V_2) (P_2) = P_B \quad (\text{Eq. D-2})$$

where:

V = Volume fraction

P = Property

Subscripts 1 and 2 refer to the components and B refers to the blend. The blend specific gravity using Eq. D-2 is:  
 $SG_B = (0.4) (0.8184) + (0.6) (0.8333) = 0.8273$ .

The weight fraction is given by Eq. D-3:

$$W = (V) (SG/SG_B) \quad (\text{Eq. D-3})$$

Using Eq. D-3 the weight fraction of 1-D fuel is:  $W = (0.4)(0.8184/0.8273) = 0.3957$ . Similarly, the weight fraction of the 2-D fuel is 0.6043.

The blend properties, which are calculated on a weight basis, can now be obtained with Eq. D-4:

$$W_1 P_1 + W_2 P_2 = P_B \quad (\text{Eq. D-4})$$

where:

W = Weight fraction

P = Property

The subscripts have the same meaning as in Eq. D-2. For example, the sulfur content is calculated as follows:  $(0.3957)(0.021) + (0.6043)(0.130) = 0.087\%$ .

To calculate the blend cetane index it is necessary to calculate the blend API gravity and the blend 50 percent distillation point. The API gravity is given by Eq. D-5:

$$G = (141.5 - 131.5 SG)/SG \quad (\text{Eq. D-5})$$

Using Eq. D-5, the API gravity is:  $G = (141.5 - 131.5 \times 0.8273)/0.8273 = 39.5^\circ\text{API}$ . The 50% boiling point is calculated volumetrically, so Eq. D-2 is used:  $50\% \text{ pt.} = (0.4)(410) + (0.6)(483) = 453.8^\circ\text{F}$ . The cetane index can now be calculated using Eq. B-1:

$$\begin{aligned} \text{CI} &= -420.34 + 0.016(39.5)^2 + 0.192(39.5) \log 453.8 + 65.01(\log 453.8)^2 - 0.0001809(453.8)^2 \\ &= -420.34 + 25.01 + 20.15 + 458.90 - 37.25 \\ &= 46.5 \end{aligned}$$

The heat of combustion and some other properties are sometimes given on either weight or volume basis. They can be converted from one to the other using the density in pounds per gallon, which is 8.328 times the specific gravity.

The cloud point, pour point, and flash points do not blend linearly. A graph is used to obtain index values, which do blend linearly on a volume basis. Eq. D-2 is then used to obtain the blend index; then the graph is used again to obtain the blend value. Figures D-1, D-2, and D-3, which are based on the work of Hu and Burns (84), give blend index curves for the cloud point, pour point, and flash point.

The cloud point of the 1-D fuel in the blending examples was  $-26^\circ\text{F}$ . Using Figure D-1 gives the index value 1.5. Similarly, the 2-D, which has a cloud point of  $+12^\circ\text{F}$ , has a cloud point index value of 8.2. Eq. D-2 yields a blend cloud point index  $= (0.4)(1.5) + (0.6)(8.2) = 5.5$ . This index value is now used with Figure D-1 to find the corresponding cloud point, which is  $+3.0^\circ\text{F}$  for the blend.

The same procedure is used for the pour point and the flash point. Table D-1 gives example index values obtained using Figures D-2 and D-3 respectively along with Eq. D-2.

TABLE D-1  
EXAMPLE INTERMEDIATE RESULTS IN CALCULATING  
A BLEND POUR POINT AND FLASH POINT USING INDEXES

	1-D Fuel	2-D Fuel	Blend
Composition, vol%			
1-D fuel	100	0	40
2-D fuel	0	100	60
Component pour points, $^\circ\text{F}$	-35	-5	-
Pour point index	1.3	3.1	2.4
Blend pour point, $^\circ\text{F}$	-	-	-14
Component flash points, $^\circ\text{F}$	132	148	-
Flash point index	15.0	9.5	11.7
Blend flash point, $^\circ\text{F}$	-	-	140



In the event that a blend contains more than two components, both Eq. D-2 and Eq. D-4 can be generalized to include all the components. The general form of Eq. D-2 is:

$$V_1 P_1 + V_2 P_2 + \dots + V_n P_n = P_B$$

The general form of Eq. D-4 is:

$$W_1 P_1 + W_2 P_2 + \dots + W_n P_n = P_B$$

The subscript  $n$  is the number of components in the blend.

A useful statistic for economic comparisons is the volumetric improvement cost. It can be used for comparing the cost of improving fuel properties by blending or by the use of additives. Assuming the 1-D fuel costs \$0.07 per gallon more than 2-D fuel, the blend containing 40 percent 1-D fuel costs  $(0.4)(7\text{¢}) = 2.8\text{¢}$  per gallon more than straight 2-D fuel. The cloud point of the blend is  $+3^\circ\text{F}$ , which is a  $9^\circ\text{F}$  improvement over the 2-D fuel. The volumetric improvement cost is then  $2.8\text{¢}$  per gal/ $9^\circ\text{F}$ , which yields  $0.31\text{¢}$  per gal/ $^\circ\text{F}$ . The improvement in sulfur content was  $0.130\% - 0.087\% = 0.043\%$ , and the volumetric improvement cost was  $2.8\text{¢}$  per gal/ $0.043\% = 65.1\text{¢}$  per gal/sulfur percent. The cetane index for the 2-D fuel was greater than for the blend, so the volumetric improvement cost would be negative for cetane index.

The volumetric improvement cost for additive effects are obtained in a similar way. The total costs associated with using the additive are calculated. For the example case, the cost was assumed to be \$425.00 per drum of flow improver, or \$7.73 per gallon. The response curve, Figure 20, indicates that a  $9^\circ\text{F}$  improvement can be obtained at about 0.055% additive. The additive cost per gallon of fuel is  $(0.00055)(\$7.73/\text{gal}) = \$0.00425/\text{gal}$  or  $0.425\text{¢}/\text{gal}$ . Dividing this by the  $9^\circ\text{F}$  improvement yields  $0.047\text{¢}$  per gal/ $^\circ\text{F}$ . The calculations are repeated at several blend compositions or additive levels to construct the curve of volumetric improvement cost versus the amount of improvement. The curves are useful for economic comparisons.

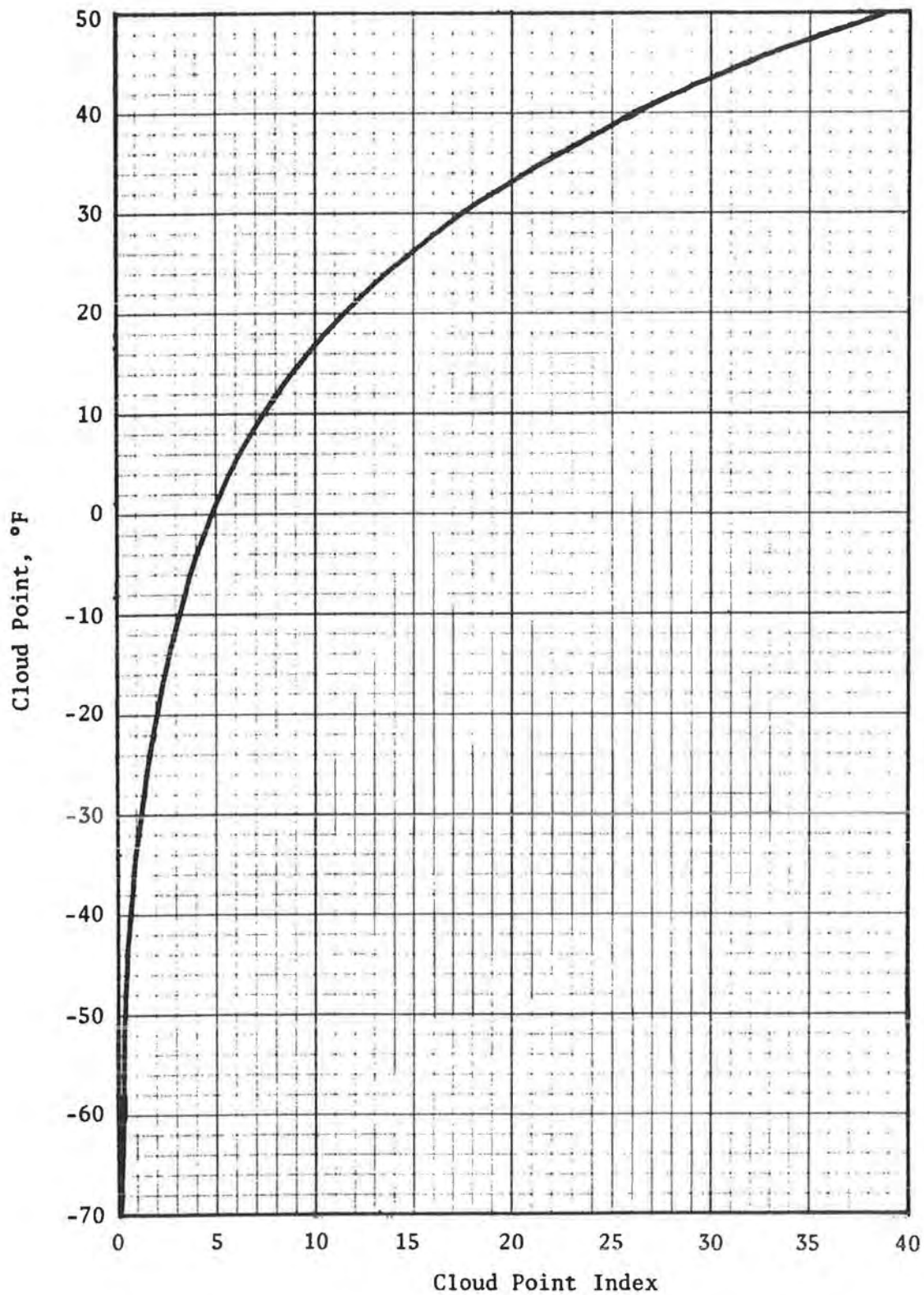


FIGURE D-1 Graph of cloud point index for blend calculations (data from ref. 84).

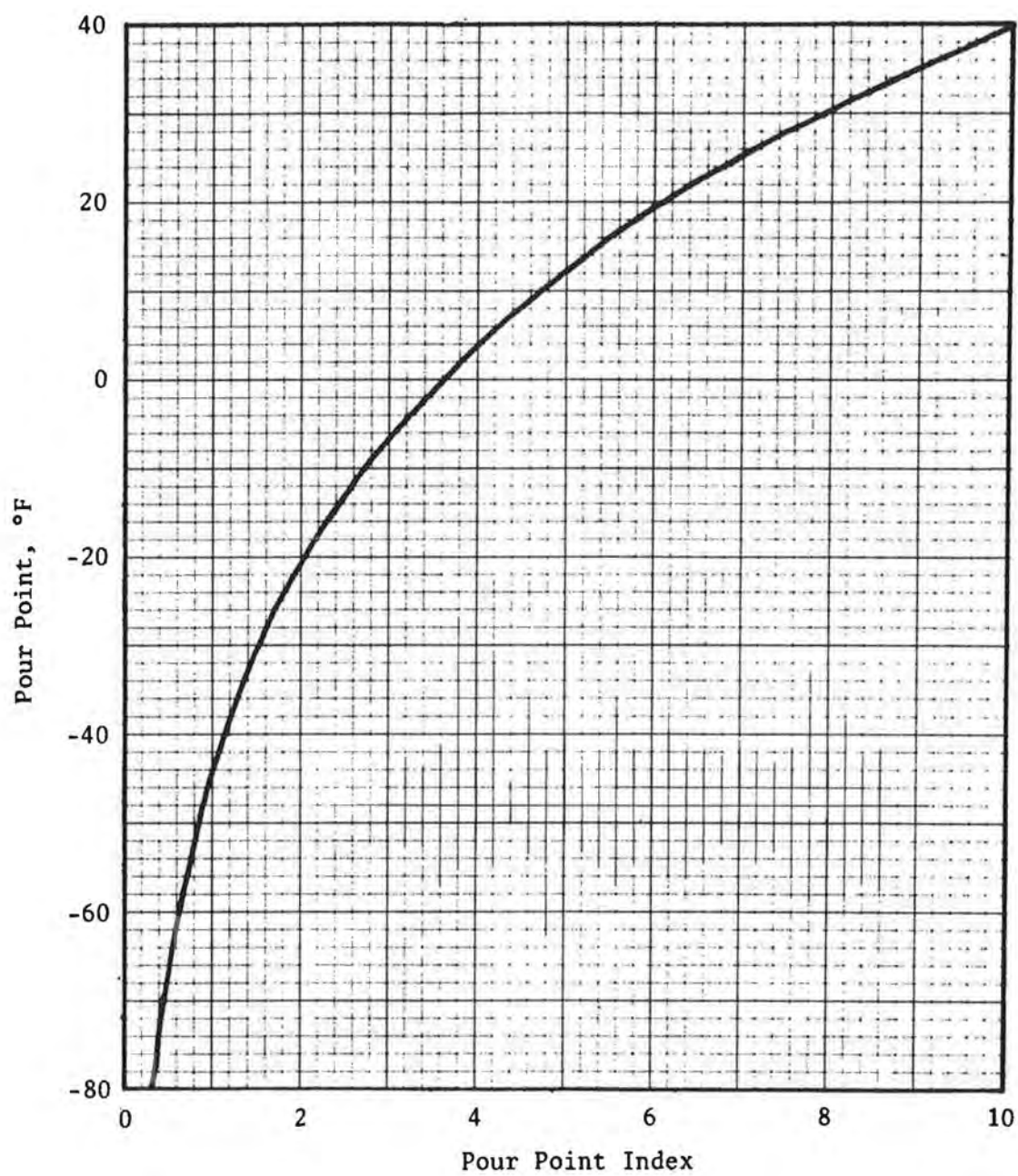


FIGURE D-2 Graph of pour point index for blend calculations (data from ref. 84).

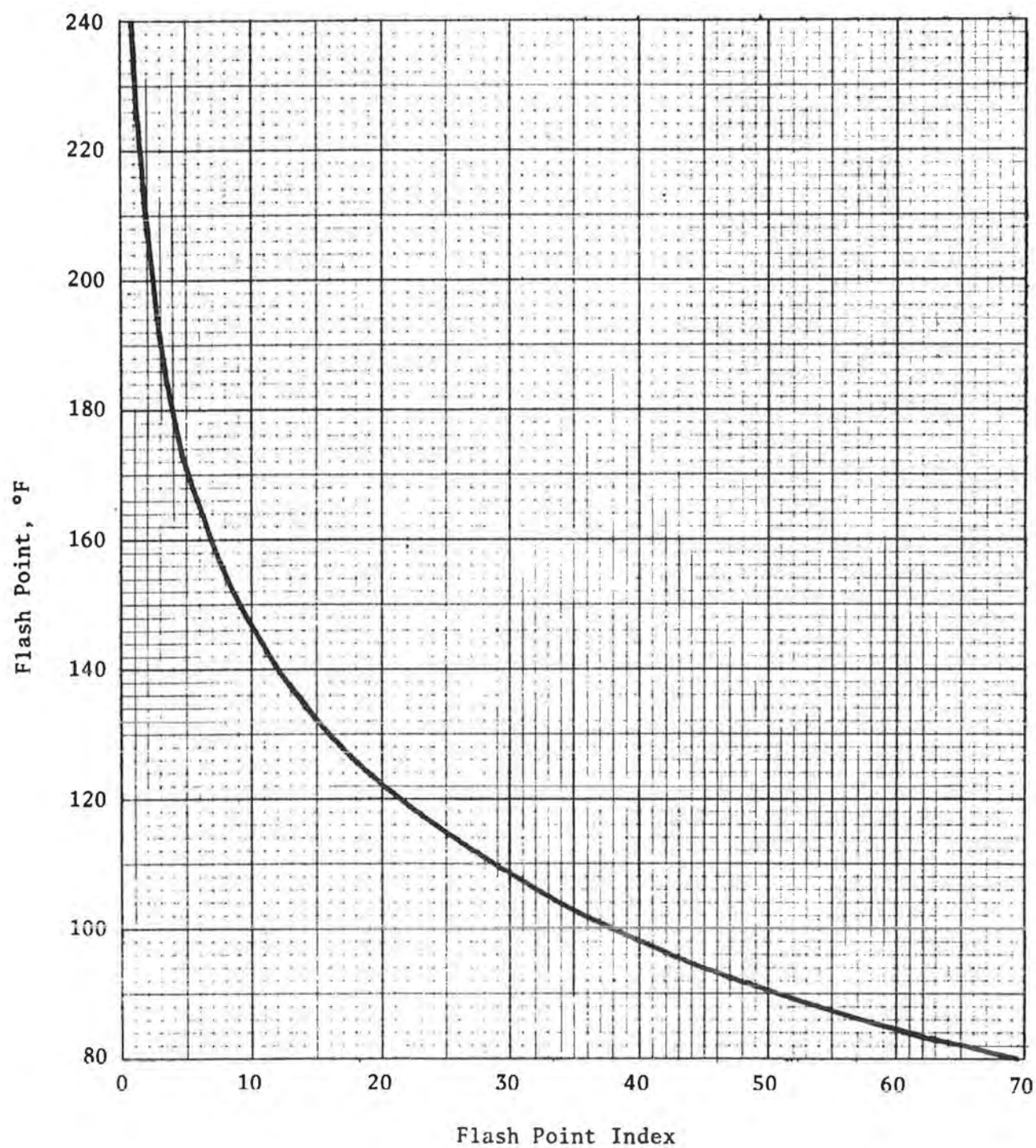


FIGURE D-3 Graph of flash point index for blend calculations (data from ref. 84).



## APPENDIX E

### EXXON'S LOW-TEMPERATURE FLOW PROCEDURE

#### Low Temperature Flow Test (LTFT) For Diesel Fuels

##### A. Description of Method

###### Introduction

This test was developed by Exxon Research and Engineering Co. to determine the low temperature operability of diesel fuels in autodiesel equipment. Results obtained by this test correlate with those obtained at the 1970-1971 Bemidji, Minnesota auto-diesel field test.

###### Scope

The method is applicable to all diesel fuels. Fuels passing the test are expected to provide satisfactory operability (free of wax plugging) in auto-diesel equipment at fuel temperatures equal to or higher than that of the test.

###### Summary of Method

The sample is brought to the desired test temperature by cooling it at a rate of  $2^{\circ}\text{F}$  per hour in a cold box. At that temperature the filterability of the test fuel through a screen of 40 micron openings at a vacuum of 6 inches of mercury is determined.

Low temperature operability of the test fuel at a given temperature is considered satisfactory if passage of the fuel through the screen is completed in less than 60 seconds.

###### Precision

Data not available yet.

###### Apparatus

(1) Cold Box (Low Temperature Bath) capable of providing a cooling rate of  $2^{\circ}\text{F}/\text{hour}$  between  $30^{\circ}\text{F}$  and  $-20^{\circ}\text{F}$ , with air circulation to provide uniform temperatures throughout the box.

(2) Temperature Controller, Rotax M-40, Cam. Set Controller, obtainable from Foxboro Co., Foxboro, Massachusetts, under catalog number M-40 is recommended. This controller has a range  $-30^{\circ}\text{F}$  to  $+70^{\circ}\text{F}$  and is equipped with a double pole, single throw switch wired so as to cut off power to the chart drive only.

(3) Temperature Controller Cam. Prepare the cam by marking the chart for  $1^{\circ}\text{F}$  drop in temperature for each 30 minutes ( $2^{\circ}\text{F}/\text{hour}$  cooling rate). Cut the cam along a smooth curve through the points.

(4) Filtering Assembly, shown in Figure E-1.

#### Procedure

1. Fill sample container (Figure E-1) with 200 ml of clean, dry fuel to be tested.
2. Equip the filter with a screen of 40 micron openings, and place this filter and the tubing attached to it in the sample container. Cover the top of the bottle with aluminum foil to exclude contamination with condensed water.
3. Place the container into a cold box kept at a temperature at least  $15^{\circ}\text{F}$  above the WAP\* of the test fuel.
4. Insert a thermometer or thermocouple in a separate bottle of fuel oil for recording test temperature and place it in the cold box next to the first bottle.
5. Close the cold box and start programmer to lower temperature at a rate of  $2^{\circ}\text{F}$  per hour.

\*WAP = "wax appearance point" or cloud point.

6. When fuel temperature reached the desired last temperature, remove bottle containing test fuel and filter from the cold box.

7. Using the filter assembly, gently stir the oil to disperse settled wax crystals. Attach the filter assembly at B as shown in Figure E-1.

8. Connect a vacuum system providing a suction equivalent to 6 inches of mercury. Open pinch-clamp "C" (Figure E-1) and simultaneously start the timing with a stop watch.

9. Determine the time required for all of the fuel to pass through the filter.

#### Reporting

Report the time in seconds that was required for the filtration of the fuel.

The fuel is considered to have "passed the LTFT" if 80% of the fuel passed through the screen in 60 seconds or less.

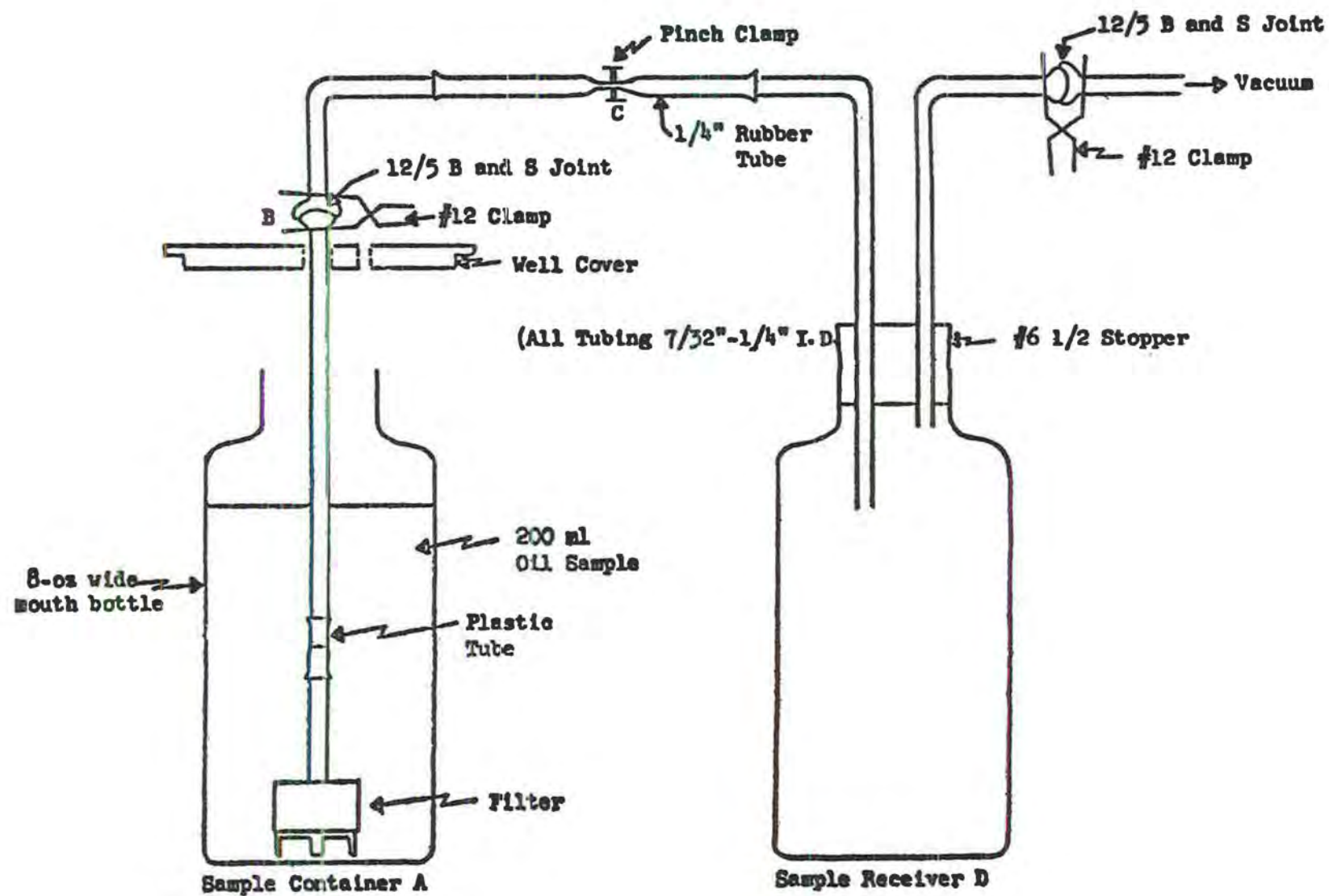


FIGURE E-1 Filter assembly filtering.



## APPENDIX F

### SURVEY OF FUEL AND ADDITIVES USED BY TRANSIT OPERATORS

#### FUEL ADDITIVES INFORMATION SURVEY

Effects of Fuel Additives and Alternative Fuel Grades for Transit Buses

Topic TS-3, Subcontract No. TR 60-1/3

1. What types of diesel fuel do you use?
  - No. 1 \_\_\_\_\_
  - No. 2 \_\_\_\_\_
  - Blend of 1 and 2 \_\_\_\_\_
  - Other \_\_\_\_\_
2. Does your fuel supplier provide fuel inspection results?
  - Yes \_\_\_\_\_
  - No \_\_\_\_\_
3. What fuel inspections or in house tests do you make?
  - None \_\_\_\_\_
  - Appearance & odor \_\_\_\_\_
  - Laboratory Tests \_\_\_\_\_
  - Other \_\_\_\_\_
4. Do you send out samples for laboratory testing or analysis?
  - Yes \_\_\_\_\_
  - No \_\_\_\_\_
5. What additives, if any, does your fuel supplier put into your fuel?
  - \_\_\_\_\_
  - \_\_\_\_\_
  - \_\_\_\_\_
  - Unknown \_\_\_\_\_
6. What additives, if any, do you put into your fuel?
  - \_\_\_\_\_
  - \_\_\_\_\_
  - \_\_\_\_\_
7. Do you filter the fuel?
  - To remove particulates \_\_\_\_\_
  - To remove water \_\_\_\_\_
  - Other \_\_\_\_\_

8. If you put in your own additive, how do you determine the additive amount?

Fuel inspection results \_\_\_\_\_  
 In house tests \_\_\_\_\_  
 Prior experience \_\_\_\_\_  
 Additive suppliers  
     recommendations \_\_\_\_\_  
 Other \_\_\_\_\_

9. What procedure is used for mixing the additive with the fuel?

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

10. What problems have you experienced that might be related to fuel quality, or to the presence or lack of fuel additives?

Fuel stability in storage? \_\_\_\_\_  
 Excess smoke? \_\_\_\_\_  
 Injector sticking? \_\_\_\_\_  
 Starting problems? \_\_\_\_\_  
 Other (specify): \_\_\_\_\_

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

11. If you or someone in your organization can supply additional information about your experience with either fuels or additives by telephone, please list the following:

Best time to call \_\_\_\_\_  
 Name of Person \_\_\_\_\_  
 Telephone Number \_\_\_\_\_

Please return to:

David S. Moulton, Division 05, Bldg. 63  
 Southwest Research Institute  
 6220 Culebra Road, P.O. Drawer 28510  
 San Antonio, TX 78284  
 Phone: (512) 684-5111 Ext. 3504