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HYBRID FUELS FOR HIGHWAY TRANSPORTATION

Second Annual Technical Progress Report for Period
June 1, 1979-June 1, 1980

By
T. W. Ryan
W. Likos
C. A. Moses

June 1980

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Southwest Research Institute
San Antonio, Texas

U. S. DEPARTMENT OF ENERGY

Division of Transportation Energy Conservation

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SECOND ANNUAL TECHNICAL PROGRESS REPORT
FOR THE PERIOD
1 JUNE 1979-1 JUNE 1980

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June 1980

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FOREWORD

This report was prepared by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, under Contract No. DEAC04-79CSS4240. The work was administered by the U.S. Department of Energy, Albuquerque Operations Office, P.O. Box 5400, Albuquerque, NM 87115. The Project Director is Mr. E.E. Ecklund, Chief, Alternative Fuels Utilization Branch, DOE Headquarters.

ABSTRACT

A program has been developed to investigate the potential of hybrid fuels for use in highway transportation. Hybrids are fuels derived from combinations of readily available energetic non-conventional materials with petroleum. They are generally formulated as solutions, emulsions, or slurries. The underlying objective of the program is to reduce the use of petroleum-derived fuels and/or to minimize the processing requirements of the finished hybrid fuels.

During the first year of the program, extensive work was done on the development and testing of water and alcohol emulsions and alcohol solutions. In the second year, the emphasis was placed on the development and testing of hybrid fuel slurries. Components evaluated included carbohydrates and various forms of carbon. It was concluded that, of the slurries tested, the carbon (coke, carbon black, etc.) slurries have the most potential for development into finished fuels.

The efforts during the third year will concentrate on advancing the development of the slurries (especially the carbon slurries) to the same point as the solutions and emulsions. This work will include examination of the mechanical difficulties, the stability problems, and the combustion phenomena observed when using slurries in heat engines.

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I. INTRODUCTION

This report describes the second year's progress of a 3-year study to identify and assess the practicality of developing and utilizing hybrid fuels in highway vehicles. Included in the report is a brief description of the historical background, an update of the literature, and an outline of the overall objectives and scope of the project. The program plan followed during the second year is described, and the various technical decisions are discussed in detail. The experimental results are presented, followed by a discussion of the results and a listing of the conclusions. The final section of the report contains the program plan for the third year.

A. Background

The social and economic development of a nation has always been accompanied by an increase in the demand for energy. As more and more nations have emerged as industrialized societies, the accompanying demand for energy has resulted in a continuing tightening of available crude supplies, with a corresponding escalation of energy costs. The Mid-East oil embargo in 1973 heightened the awareness in this country that our domestic energy supply is not sufficient to handle the demand. This is particularly true for the energy needed to operate our complex transportation system.

The transportation sector is the single largest consumer of petroleum-derived energy. Historically, liquid hydrocarbons have evolved as the primary transportation fuel because of its high energy content per unit volume and because of the simplicity of liquid distribution systems as opposed to those required for solid or gaseous fuels. As a result, our present day transportation powerplants have been designed to use liquid fuels, and petroleum refineries have, through an evolutionary process, been tailored to meet the requirements of piston engines. This tailoring of the fuel to meet the requirements must now be reconsidered. As a transitional process, other energy sources must be sought which can be used in modified piston engines. This transitional process could last several decades as new, and yet undefined, transportation systems are developed.

A nationwide research program has been launched to develop alternate domestic energy supplies. Efforts to date have been involved mainly with the development of fuels which are not much different from the petroleum-derived fuels i.e., recovery of liquids from shale and conversion of the coal to liquids. Approaching the problem in this manner requires a great deal of processing energy and expensive technological development. The question then arises as to how much processing is required and are coal and shale oil liquids the only piston engine fuels. This represents a question approaching the short-term problem of producing finished fuels for existing engines. The next step would logically approach the question of optimizing the finished fuel and the engine, where changes in both would be required to obtain satisfactory performance and reductions in the use of petroleum-derived fuels.

The obvious large-scale alternative fuels for transportation are those derived from coal and shale oil. Both of these raw materials are abundant, and the technology exists for conversion to finished liquid fuels. There are several other raw materials available which have energy contents similar to the raw coal and shale oil, but are not considered as feed stock for finished transportation fuels. An example of the use of nontraditional feedstock is the production of ethanol from biomass. Although the overall energy balance for such an application is questionable, the biomass materials do represent a renewable resource. The overall short-term question then reduces to determining the minimum amount of processing required to produce finished fuels for existing engines from each resource, including petroleum, coal, shale oil, and all the nontraditional raw materials. The answers developed for the existing engines will provide guidance as to modification of the existing engines and/or development of new engine concepts.

The nontraditional fuel feedstocks can be used to formulate what have been called hybrid fuels. Hybrid fuels are defined as finished fuels derived from combinations of readily available non-conventional materials with petroleum. The definition allows for all possible formulations including combinations of petroleum with other substances derived from nonpetroleum sources. Figure 1 illustrates some nonpetroleum energy sources. As each component is derived from its parent material, more cost and process energy is involved. The far right column indicates the possible finished fuel composition for the particular compound.

Figure 1. Possible Sources of Hybrid Fuel Components

It must be realized that the overall finished fuel energy content may not be improved by these conversion steps. Likewise, minimal processing may reduce the efficiency of modern engines below a reasonable cost/performance tradeoff level. Figure 1 does not show all the possible processing steps nor does the spacing indicate relative energy requirements for processing.

The direct application of primary components (biomass, coal and oil shale) as transportation fuels is impractical because all are solids and all contain substances which are either damaging to the engine and/or do not contribute to the energy content. In going from left to right, the trend is generally moving towards increasing the hydrogen content and the production of liquids formulations. It is anticipated that liquids will be the preferred fuel forms for several years due to the constraints imposed by the use of existing distribution systems.

Minimal processing of a solid primary component would consist of grinding the material to a size which is compatible with available fuel systems and which is appropriate for complete combustion in the proper time frame. Compatibility with existing fuel systems requires that the fuel be in a liquid form. The far right side of Figure 1 shows the likely formulation of each of the candidates. The possibilities include solutions, emulsions, and slurries. Although the slurries represent a step towards a solid fuel engine, such a development would appear to be several years away due not only to the technical problems associated with the engine but also to the problems associated with the radical changes required in the distribution system.

B. Literature Review

As was indicated previously, the hybrid fuels fall into three general categories with respect to their physical forms. They are: solutions, emulsions, and slurries. The ease with which each of these forms can be used in existing equipment relates mainly to the pumpability (the ability to transport, transfer, and deliver the fuel to the engine combustion system) and metering of the formulation. In this respect, the solutions represent the formulation most similar to the traditional petroleum-derived hydrocarbon fuels. The emulsions represent another class of fuels which have delivery

characteristics very similar to petroleum fuels, but the formulation techniques are more involved due to the required use of surfactants.

The slurries, on the other hand, present not only pumpability and formulation problems relating but also problems to the combustion of the fuel in the engine. The solutions and emulsions behave, at least on the macroscale, very similar to the traditional fuels with regard to the atomization, vaporization, and the subsequent combustion. Due to the finite time available for combustion in heat engines, the solid material contained in slurry fuels must have physical and chemical characteristics which will allow for complete combustion in the available time.

Because of the differences in the physical properties and the formulation techniques of the three types of hybrid fuels, the discussion of each type will be done separately.

1. Solutions

The hybrid components which form solutions with petroleum-derived fuels or with other liquid fuels represent the most straight forward utilization of hybrid components. The two most abundant supplies of these hybrid components are the vegetable oils and certain alcohols.

As was indicated by Engelman, et al.^{(1)*}, the first investigation of the use of vegetable oil as an engine fuel dates back to the 1930's. The production of vegetable oil for use as a fuel is attractive because the processing requirements generally involve mechanical or hydraulic presses to remove the oil from the seeds and caustic wash to remove the gums. These processing requirements are generally much less technically demanding than those for ethanol production.

The physical properties (mainly volatility) of the vegetable oils are such that they are not compatible with spark ignition engines. Therefore, the main

*Numbers in parenthesis designate entries in the reference list on page .

body of the current literature deals with the compatibility of various vegetable oils with compression-ignition engines. Stecher⁽²⁾ reports that sunflower seed oil can be used as a direct replacement for diesel fuel in a four-stroke engine with no apparent durability problems. Chancellor⁽³⁾ reported similar results for a variety of vegetable and plant oils in prechamber types of diesel engines. Engelman, et al.⁽¹⁾ have done a considerable amount of work with vegetable oils, including waste oils from various deep fat fryers. The engine tests were performed using blends of waste soybean oil and diesel fuel with from 70% to 100% soybean oil content. Their results indicate blends of the soybean oil are the most attractive formulations from a performance point of view. Table 1⁽⁴⁾ lists the properties of various vegetable oils and blends of vegetable oil and diesel fuel. These properties are the ones most likely to affect diesel engine performance. As can be seen, the viscosity is much higher and the heating values are somewhat lower for oils than the diesel fuel. The properties of the oils, however, are very similar to each other.

The alcohol solutions have received a great deal of attention in the literature. Most of the work, however, is involved with solutions of methanol and ethanol with gasoline. The gasohol concept, in particular, has received a great deal of attention due to the possibility of legislative action and wide publicity.

The use of alcohol in diesel engines has been attempted using several fuel delivery techniques. Methanol will not go into solution with diesel fuel. Ethanol will go into solution, but the water content must be limited to less than 0.5%.⁽⁵⁾ Three recent papers^(5,6,7) and one report⁽⁸⁾ describe the work done with this contract using ethanol/DF-2 solutions. Additional data will be presented in another section of this report.

2. Emulsions

Most of the more recent work with emulsions has dealt with the water in fuel emulsions. The results of these tests can be summarized as follows: 1) The NO/NO_x and smoke emissions are reduced^(9,10,11) with accompanying increases in the CO and unburned hydrocarbon emissions; 2) the thermal cycle efficiency of the diesel engine is only slightly affected, either increasing or decreasing,

Table 1. Vegetable Oil/Diesel Fuel Blend Properties (4).

	<u>Viscosity</u> 37.8°C, cSt	<u>API Gravity</u> 15.5°C	<u>Flash Point*</u> °F(°C)	<u>Pour Point</u> °F(°C)	<u>Cetane</u> <u>Number</u>	<u>Gross</u> <u>Heat of</u> <u>Combustion</u> kJ/kg	<u>Carbon wt%</u>	<u>Hydrogen wt%</u>
(Railroad Diesel Fuel)**	3.46	32.0	159(71)	-58(-50)	44.3	44694	86.34	12.81
Peanut Oil								
25%	6.60	29.5		5(-15)	41.8			
50%	12.60	27.1	183(84)	16(-9)	40.5			
100%	39.51	22.7	622(328)	28(-2)	39.0	40030	77.13	11.67
Corn Oil								
25%	6.85	28.8		-6(-21)	42.0			
50%	11.37	26.5	181(83)	-6(-21)	40.0			
100%	33.46	21.8	608(320)	-2(-19)	34.4	39460	77.33	11.45
Sunflower Oil								
25%	6.40	29.2		-4(-20)	42.1			
50%	10.75	26.7	177(81)	-2(-19)	40.8			
100%	33.46	21.8	608(320)	16(-9)	33.4	39565	77.36	11.40
Soy Oil								
25%	6.25	29.3		-13(-25)	43.6			
50%	11.28	26.7	179(82)	-2(-19)	41.9			
100%	32.31	21.9	597(314)	16(-9)	41.5	39007	77.39	11.44

* 100% Vegetable Oil - D-92 Cleveland Open Cup Method

Diesel Fuel + Oil Blends - D-93 Pensky-Martin Closed Cup Method.

** This is not the same diesel fuel used in the Hybrid Fuels Program.

depending on the design of the combustion chamber and the injection system.^(11,12,13) The differences in thermal efficiency observed by the various investigators could also be related to the formulation techniques used to produce the emulsions. Some of the work was performed using unstabilized emulsions while other work was performed using emulsions stabilized with surfactants. The results in general indicate that the potential for saving petroleum-derived diesel fuel by the introduction of water is minimal, costly, and possibly detrimental. Work done during the first year of this program⁽⁸⁾, using both partially stabilized (macroemulsion) and a completely stable (micro) emulsions, indicated the same general trend, in which the performance depended upon the operating conditions and the engine design.

The preliminary work with macro and microemulsions of both methanol and ethanol was reported previously.^(5,6,7,8) The macroemulsions were unstable and presented problems with regard to obtaining repeatable results. The microemulsions, on the other hand, were completely stable. The results of the methanol and ethanol microemulsion work indicated that savings in diesel fuel could be realized both by direct energy replacement and possible improvements in the thermal cycle efficiency were possible. The cost of these fuels were very high, however, due to the requirement for large concentration of expensive surfactant (surface active agent). Recent work by Lawson and Last⁽¹⁴⁾ showed that an on-board emulsifier could be used to produce unstabilized methanol emulsions which showed a reduction in particulate matter and an increase in the thermal efficiency. They also found that small quantities (2%) of water present in the alcohol produced further improvement in the efficiency.

Work done at the Indian Institute of Technology⁽¹⁵⁾ indicates that pure methanol or ethanol can be used to fuel a diesel engine if surface ignition is initiated. In this work, an electrically heated surface was placed in a manufactured prechamber which was added to a normally direct injection engine. The results show that the thermal efficiency is basically the same for diesel fuel, methanol or ethanol.

3. Slurries

Slurry fuels represent the epitome of hybrid fuel formulation. The differences between the various components are not only chemical but physical, in that the slurry represents a mixture of a solid and a liquid phase. In examining the resources available for fuel formulation, the vast majority of material available for its energy content is in solid form (i.e., coal, shale oil, and biomass). The most direct conversion of these energy forms would be direct conversion to heat, but existing transportation engines are not readily adaptable for use of solid fuels. The slurry represents a compromise between existing technology and the reduction of processing energy requirements.

The vast majority of the recent work in the development of slurry fuel technology has been directed at utilization in stationary Rankine cycles. The objective of that work is to utilize pulverized coal mixed with heavy fuel oil as a fuel for boilers designed to be oil fired. This coal-oil-mixture work is summarized in Reference 16. Although the final product of a COM production plant is not compatible with diesel engines, the work demonstrates the potential for utilization of slurries in systems designed to handle liquid fuels.

Another area which has received a great deal of attention in the past few years is the use of slurries, or colloidal fuels, as high-energy density fuels. These fuels are of interest for use in applications where volume constraints place limits on the amount of energy which can be carried on board the vehicle, e.g. cruise-missiles fuels. Frainier and Colling⁽¹⁷⁾ prepared slurries of carbon powder in RJ-4 (MIL-F-82522A) with up to 75 percent carbon loading. The heating value of this fuel was 191,000 Btu/gallon (53235 kJ/liter). The slurry was stabilized using 2-percent surfactant. The slurry was stable, but highly thixotropic with apparent viscosities several times higher than that of diesel fuel. No combustion or engine experiments were reported. At SwRI, carbon slurries in fire-resistant fuels (water-diesel fuel micro-emulsions) have been formulated and tested in diesel engines. The preliminary work with these fuels have indicated that the pumpability problems present the most severe limitations on utilization in diesel engines; again the viscosities were very high compared to straight diesel fuel.

Foster, et al.⁽¹⁸⁾ have presented a very thorough bibliography on the development of coal-based colloidal fuels. They also presented a review of a new process for grinding and removing the ash and sulfur from coal. In this process (ILOK process), the coal is reduced to particles which are less than 4 microns and which are also free of ash and sulfur. The ILOK Process is reported to require only 0.7 percent of the process energy generally required for such processes. If the claims for the ILOK process are only partially true, the slurry fuel technology would be advanced beyond one of its most difficult problems; i.e., economical size reductions of the solid phase.

Soehngen⁽¹⁹⁾ presented an excellent review of the German work done on the development of a coal dust diesel engine. The conclusions drawn from the review indicates that high-speed coal dust engines are possible. A similar review of the literature by Rich and Walker⁽²⁰⁾ resulted in the development of a low-compression ratio coal dust diesel engine which used a pilot injection of diesel fuel and fumigation of the coal into the intake air. The test results were less than satisfactory due to coal delivery problems and what appears to be the relatively large size of the coal particles (large percentages in excess of 200 mesh).

A 15-percent slurry of solvent-refined coal in JP-4 was produced and tested in a prechamber engine by Marshall and Walters.⁽²¹⁾ The combustion and engine efficiency data were not presented, but it appears that satisfactory performance was obtained using the slurry fuel. Although it was not indicated in the paper, the refined coal was apparently SRC-I. The particle size was not reported. The authors indicated that some difficulties were encountered with fouling and sticking of the injection system. Possible causes for these problems were excessive particle size and/or melting and refusion of the SRC-I solids in the tight clearances in the system [fusion temperature of SRC-I is 177°C (350°F)].

Tataiah and Wood⁽²²⁾ recently tested 10-, 20- and 30-percent coal slurries in a 4-stroke direct injection engine. The suspended coal particles were reported to be 100 percent below 10 microns. Heat release calculation, based on the pressure diagrams, indicated that the coal was either not undergoing complete combustion or that the heat transfer to the coolant was increased due

to radiation from the solid particles. These data were obtained at 800 rpm in the test engine. At the test conditions, there is maximum (based on 90° of revolution for combustion) of 18 msec available for combustion. From well stirred reactor data, Essenhigh⁽²³⁾ indicates that the maximum coal particle size which will burn out in 18 msec is approximately 10 microns. It should be realized that the actual time available for useful combustion is much less than that based on 90° of revolution. In addition, the well stirred reactor data are based on dry particles. In the engine combustion of coal slurry, the particles are wetted by the liquid fuel. If there is no separation of the solids and the liquid during the injection event, the combustion of the solid material will not begin until the liquid coating is evaporated and possibly burned. This process could add considerably to the time required for complete combustion. These considerations could explain the incomplete combustion observed by Tataiah and Wood⁽²²⁾ and could also suggest improvements in performance by further reduction of particle sizes or improvements in the injection system (ultra high pressure).

Figure 2⁽²³⁾ is a plot of the combustion time versus particle diameter for coal particles. Figure 3⁽²⁴⁾ is a similar plot of carbon and kerosene particles. Although the data do not apply directly to diesel engine combustion, they would represent the minimum burnout times for given size particles when used in a diesel engine. Additional theoretical and fundamental and experimental work is currently being performed to identify the mechanisms by which carbon particles and carbon slurries react with oxygen.^(25,26) Although these studies do not account for the complex fluid mechanics and the rapid transients encountered in an operating diesel engine, they, and similar studies, will provide important information which will be useful in the development and utilization of slurry fuels.

In summary, the solution type of hybrid fuels present a fairly straight forward utilization effort. The properties of several of the more abundant oils show similarities which indicate that the engine performance would be similar for those considered. Engine experiments with various vegetable oils and various concentrations were required to expand the data base.

Figure 2. Variation of Combustion Time with Particle Diameter from Various Experimental and Theoretical Sources (23).

Figure 3. Burnout Times for Carbon and Kerosene Particles of Various Diameters (2.4)

The use of the alcohols as fuel additives were successfully demonstrated during the first year of the project. Additional engine tests were required to quantify the results and examine the mechanisms involved in their combustion in the engine. In addition, efforts were required to optimize or reduce the costs of the surfactants used in the preparation of the micro-emulsions.

The slurries required a great deal of effort both from the point of view of identification of possible components as well as the determination of the requirements imposed by the fuel delivery system and the combustion process. The considerations included minor modifications of the fuel delivery system, possible major modifications, the interaction of the fuel, the injection system, the atomization of the fuel and the combustion process, and the combined effects on the engine performance.

II. TECHNICAL PROGRAM

As it was in the first year's work, the logical development of hybrid fuels during the second year followed a course of:

1. Identification
2. Formulation
3. Engine Performance Testing
4. Evaluation

Figure 4, repeated from the first annual report, illustrates the technical approach of the program showing the development cycle of the initial generation of hybrid fuels followed by a more complete evaluation of more mature second generation fuels. Included in the figure is an indication of the status of the project at the end of this second year.

A. Fuel Component Selection and Fuel Formulation

The criteria for selecting fuel components remained the same as during the first year. The primary goal was the selection of materials which had a potential for reducing the demand for petroleum. This can be done in three ways:

Figure 4. Program Flow Chart

1. by replacing some of the petroleum in the finished fuel, e.g., a carbon/fuel slurry;
2. by improving the thermal efficiency of the engine, e.g., water/fuel emulsions; and
3. by improving the utilization of lower quality fuels, thus reducing the energy requirements for refining.

Materials which meet one or more of these objectives are considered as components for formulating hybrid fuels. Questions of cost, formulation, fabrication, handling, and stability are not deterrents during this initial process of identification to reduce the possibility of overlooking candidates. Some candidates that are ultimately infeasible may suggest others that were not considered in the initial search.

As was indicated previously, the hybrid fuels can be generally categorized into three groups, i.e. solutions, emulsions, or slurries. Table 2 shows a listing of the various materials which were considered during the second year of the program, listed in categories and subcategories. In addition to the selection criteria listed previously, the choice of the materials listed in Table 1 was affected by the availability of the materials and whether the various materials were representative of the various subcategories. Since most of the materials (especially the slurries) were not compatible with carburetion systems, the formulation was directed towards diesel or gas turbine utilization.

1. Solutions

A number of different solutions were formulated and tested over the past year. All successful solutions (would operate in the diesel engine) were formulated using various percentages of the base fuel. Table 3 is a listing of the properties of the base diesel fuel. It is a military specification referee No. 2 diesel fuel. The various hybrid solutions are listed in Table 4 along with the properties that are most pertinent for use in a diesel engine. The properties of the SRC-II are listed in Table 5.

Table 2. Hybrid Fuel Components Considered During the Second Year

Solutions

1. Miscible Liquids
 - A. Alcohols
 - a) Ethanol
 - B. Vegetable Oils
 - a) Cottonseed Oil
 - b) Peanut Oil
 - C. Coal or Shale Derived Liquids
 - a) SRC-II

Emulsions

2. Immiscible Liquids
 - A. Alcohols
 - a) Methanol
 - b) Ethanol
 - B. Water
 - a) Sugar-Water Solution

Slurries

- A. Starches
 - a) Wheat Starch
 - b) Corn Starch
 - c) Processed Starch (Clear Gel)
- B. "Cellulose"
 - a) Microcrystalline Cellulose
 - b) Mesquite Wood Fiber
 - c) Grain Elevator Dust
- C. Carbon
 - a) Coal
 - b) Carbon Black
 - c) Coke

Table 3. Referee Grade II Diesel Fuel (AL-8064-F)

Property	MIL-F-46162A(MR) Specifications	Analysis
Gravity, API°	33-37	36.2 at 15.5°C
Flash Point, °C(°F)	569(133) min	58.2°C
Cloud Point, °C(°F)	-13(9) max	-15°C
Pour Point, °C(°F)	-18(0) max	-24°C
K. Viscosity, cSt at 37.8°C (100°F)	2.2 to 3.2	2.17
Distribution, °C(°F)		
IBP	171-204(340-400)	170(339)
10% Evaporated	204-238(400-460)	221(430)
20	---	229(445)
30	---	235(455)
40	243-282(470-540)	239(462)
50	---	244(471)
60	---	251(483)
70	---	258(497)
80	---	271(519)
90	288-321(550-610)	293(559)
95	---	317(603)
EP	304-349(560-660)	334(634)
Recovered, %	---	98.5
Residue, %	---	1.5
Loss, %	---	0
Carbon Residue on 10%		
Bottoms, wt%	0.20 max	0.10
Sulfur, wt%	0.35 to 0.70	0.34
Ash, wt%	0.02 max	0.0
Water & Sediment, vol%	0.01 max	0.0
Accelerated Stability, total insolubles		
mg/100 ml D 2274	1.0 max	0.04
Neutral No., TAN, mg/100 ml	0.01 max	0.01
Aromatics, vol%	27 min	26.0
Aromatics by HPLC, wt%	---	26.0
Heat of Combustion, gross, (kJ/kg)	---	45124(19400 Btu/lb)
Particulate Contamination, mg/l	8 max	1.26
Cetane No.	---	47.6
Existent Gum, mg/100 ml	---	6.7

Table 4. Properties of the Various Solution Test Fuels

<u>Fuel</u>	<u>Net Heat of Combustion, (kJ/kg)</u>	<u>H, wt%</u>	<u>C, wt%</u>
Ethanol			
10% v/v	40947	12.85	83.44
20% v/v	39640	12.87	80.15
30% v/v	38322	12.88	76.87
40% v/v	36974	12.90	73.51
100% v/v	28545	12.99	52.40
SRC-II			
50% v/v	40942		
Peanut Oil			
20% w/w	41259	12.77	84.82
60% w/w	39623	12.32	81.21
80% w/w	38702	12.09	79.4
100% w/w	37420	11.87	77.60
Cotton Seed Oil			
20% w/w	41232	12.75	84.73
60% w/w	39684	12.27	80.94
80% w/w	38784	12.03	79.04
100% w/w	37285	11.79	77.15
DF-2 Base fuel	42219	12.99	86.62

Table 5. SRC-II Middle Distillate Inspections

Specific Gravity 15.5°C/15.5°C	0.9840	Ash, wt%	0.0023
Gravity, °API	12.3	Steam Jet Gum, mg/100 ml	25.1
Viscosity		Accelerated Stability, mg/100 ml	10.5
cSt at 37.8°C(100°F)	3.83	Particulate Matter, mg/l	77.5
cSt at 40°C(104°F)	3.68	Total Acid No., mg KOH/gm	0.31
Flash Point, (D 93), °C(°F)	80(176)	Cetane Number	16
Aniline Point, °C(°F)	-9(16)	Carbon Residue, 10% Btms, wt%	0.52
Pour Point, °C(°F)	-48(-54)	Water, wt%	0.08
Cloud Point, °C(°F)	Too dark	Copper Strip Corrosion, 50°C (122°F)	1a
Hydrocarbon Type FIA, vol%		Net Heat of Combustion	
Aromatics	91.2	MJ/kg	40.007
Olefins	0.7	Btu/lb	17,200
Elemental Analysis, wt%		Visual	
Carbon	86.15	Color (D 1500)	8.0
Hydrogen	8.64	Appearance	Dark gray, turns opaque. Black
Oxygen	3.9	IR Curve	Spectrum indicates mixture of aromatic compounds with significant hydroxyl sub- stitutions on aromatic rings. No organic acids.
Nitrogen	0.82		
Sulfur	0.26		
Ring Carbons, wt%			
Monoaromatic	30.5		
Diaromatic	22.6		
Triaromatic	0.95		
Distillation	ASTM D 86	GC Distribution	
	°C °F	°C °F	
IBP	187 368	151 304	
5% Recovered	204 400	187 368	
10	211 412	197 387	
15	216 420	210 410	
20	220 428	216 420	
30	228 442	232 450	
40	237 459	244 471	
50	245 473	258 497	
60	254 489	268 514	
70	262 504	280 536	
80	274 525	295 563	
90	289 553	311 592	
95	303 577	324 615	
EP	323 613	377 710	

All of the fuels which have been formulated are described in this section of the report, regardless of the outcome of the engine tests. It is felt that the failures encountered in a research program such as this one are as important as the successes. The outcome of all of the engine tests are discussed in another section of the report.

2. Emulsions

Two different emulsions were formulated for testing in the past year. They were a 20-percent and a 30-percent microemulsion of ethanol in the base fuel. These fuels and the corresponding solutions were formulated and tested to examine the results of a zero-dimensional thermodynamic model which was developed this past year and which is described in another section. The composition and the properties of the two emulsions are listed in Table 6. An emulsion of sugar-water-ethanol in diesel fuel was also formulated. The composition by mass was 31.7% DF-2, 29.5% ethanol, 18.8% water, 15% sugar, and 5% surfactant (Span 85). Preliminary engine tests with this fuel were unsuccessful, therefore the properties were not determined.

3. Slurries

Ten slurry fuels were formulated and tested in the engine. Experience gained during the first year of the program indicated that the problems of forming completely stable slurries were beyond the scope of this project. Therefore, the stability criterion used for the formulation of the fuels was that they remain homogeneous with mild stirring over the duration of the tests. This criterion was verified, for those fuels which received extensive engine testing, by measuring the hydrogen to carbon ratios before and after the engine tests.

Several of the slurry fuels tested during the first year caused malfunctions of the injection system. The two problems, which can be called pumpability problems, were plugging of the injector nozzle holes or sticking of the injector nozzle check valve. Both problems manifested themselves by erratic performance of the engine and, in severe cases, an engine shut down. In examining the previous data and considering the combustion literature, (23,24)

Table 6. Properties of the Emulsion Test Fuels

<u>Fuel</u>	<u>Net Heat of Combustion (kJ/kg)</u>	<u>H, wt%</u>	<u>C, wt%</u>
DF-2 Basefuel	42219	12.99	86.62
SOA (Surfactant)	35555	11.79	71.03
Ethanol	28545	12.99	52.4
20% v/v Ethanol	38753	12.78	78.18
0.6% v/v Water			
8.0% v/v SOA			
71.4% v/v DF-2			
30% v/v Ethanol	37006	12.68	73.94
0.9% v/v Water			
12.0% v/v SOA			
57.1% v/v DF-2			

it was decided to limit the particle size of the solids in the slurries to less than 10 microns. It was felt that particles below this size would pass through the injection system and, in addition, would have burnout times which were within the time available for combustion in the engine. As an added step, the clearance between the nozzle valve and the nozzle body was increased by 0.25 mm. This added clearance was enough to allow for sufficient bypass of the fuel to prevent nozzle valve sticking.

In examining the various solid materials which could be potential hybrid candidates, it was realized that the materials could be classified into two groups with respect to size reduction. They are: (1) the hard, frangible materials, and (2) the soft fibrous materials. In general, the carbons fall into the first category while the raw biomass materials fall into the second category. The carbonaceous materials, therefore, can be reduced in size by any number of the methods currently available for size reduction by fracture or attrition. Efforts were made to use several of the methods to accomplish the desired size reductions for several of the biomass materials. These methods included prolonged processing in an attrition mill (ball mill), ultra high pressure operation in a homogenizer, multiple passes through an air impaction device and multiple passes through a cutting mill. All techniques were unsuccessful.

The biomass materials which were tested in the engine were those which were commercially available (by chemical processing) or were available in size ranges close to the desired 10-micron limit.

Table 7 is a listing of the slurry fuel formulations and the properties of the various mixtures. All of the information which is available on the various unorthodox solid and liquid components is listed in Table 8. The carbonaceous materials are all thermally formed in gas phase processes and are therefore available in very small particles, as shown in the table. Figures 5 through 9 are photomicrograms of several of the fuel formulations. Due to the transparent nature of the cellulose, attempts to photograph that formulation were unsuccessful. Careful microscopic examination of the cellulose slurry revealed, however, that the particle size distribution was below 20 microns, with the majority of the particles below 10 microns. Summarizing the results

Table 7. Properties of the Slurry Fuel Formulations

<u>Fuel</u>	<u>Net Heat of Combustion (kJ/kg)</u>	<u>H, wt%</u>	<u>C, wt%</u>
10% Coke	41556	11.56	87.96
20% Coke	40728	10.27	89.29
10% Carbon Black	41349	11.56	87.96
20% Carbon Black	40060	10.27	89.29
20% Coal	39607	11.82	83.89
20% Cellulose	37467	13.3	86.75
20% Starch*	---	---	---
20% Mesquite Wood*	---	---	---
20% Flour, 1% Lecithin	36751	---	---
20% Coke, 80% Methanol*	---	---	---

* These fuels would not run in the engine.

Table 8. Available Information on the Hybrid Components Which Were Obtained Commercially

<u>Component</u>	<u>Trade Name</u>	<u>Manufacturer</u>	<u>Pertinent Information</u>
Peanut Oil	100% Pure Peanut Oil	Planters Standard Brands Inc New York, NY 10022	Food Quality
Cottonseed Oil	Pure Cottonseed Oil	Hunt-Wesson Food Inc. Fullerton, CA 92634	Food Quality Polyglycerides added as a cloud inhibitor
Coke	---	Coastal States Corp. Houston, TX 77046	Petroleum Coke
Cellulose	Signacelli Type 20	Sigma Chemical Co. St. Louis, MO 63178	Microcrystalline Cellulose
Carbon Black	Mogul-L	Cabot Corporation Boston, MA 02110	Long Flow Type 24 millimicron particles 60 cc/100 gm DBP
Carbon Black	Monarch 1300	Cabot Corporation Boston, MA 02110	Channel Black 13 millimicron particles 121 cc/100 gm DBP
Starch	Clear Gel	National Starch & Chemical Corp. Bridgewater, NJ 08807	Food Quality Refined from waxy corn.

Figure 5. Photomicrogram of the 20% Flour, 1% Lecithin Slurry diluted 1000:1 in Baseline Diesel Fuel. Scale = 50 μ m/Division.

Magnification = X100

Magnification = X430

Figure 6. Photomicrograms of 20% Starch Slurry Diluted 1000: 1 in Baseline Diesel Fuel. Scale = 50 μ m/Division.

Magnification = X100

Magnification = X430

Figure 7. Photomicrograms of 10% Coke Slurry - diluted 1000: 1 in baseline Diesel Fuel. Scale = 50 μ m/Division.

Magnification = X 100

Magnification = X 430

Figure 8. Photomicrograms of 10% Carbon Black (Mogul-L) Slurry diluted 1000:1 in Baseline Diesel Fuel. Scale = 50 μ m/Division.

Magnification $\approx$ X 100

Magnification = X 430

Figure 9. Photomicrograms of 10% Carbon Black (Monarch) Slurry -Diluted 1000: 1 in Baseline Diesel Fuel. Scale = 50 μ m/Division.

Magnification = X100

Magnification = X 430

of the photomicrograms, the flour had particles much larger than 10 microns, the starch particles were distributed close to 10 microns, and the carbonaceous materials were all well below 10 microns. Microscopic analysis of the mesquite wood revealed that the particle size distribution was well in excess of 10 microns. (The particles were generally in excess of 50 microns even after several passes through a dry airjet micronizer and one pass through a high-pressure homogenizer). It should be noted that several other types of commercially available wood powders were examined and found to have excessive particle size distributions. In addition, dusts from various processes (such as grain elevators) were examined and were also found to have very large particle size distributions.

An attempt was made to standardize the fuel preparation and handling processes used in developing the slurry fuels. In all cases, the solid material was added to the diesel fuel and stirred. This mixture was allowed to stand for at least 24 hours to allow for absorption and adsorption of the fuel. Immediately before engine testing, the fuels were homogenized in a laboratory homogenizer for at least 0.5 hour to accomplish deflocculation of the particles. From that point on, including the time in which the fuels were being tested, they were continually agitated using a magnetic stirrer.

Based on visual observations of the various mixtures, the carbons appeared to form the most stable slurries. It appears to be possible to form stable slurries of the carbon black by judicious selection of the base particle sizes, the oil absorption characteristics, and the concentration of the carbon black. Viscosity restraints of the current injection systems may prevent the utilization of such slurries in existing systems, but these problems could be overcome by modified injector designs. Viscosity measurement of some of the slurries is discussed in the next subsection.

Preliminary work was started during the second year on the design of a system which could be used to determine the settling rates of the slurry fuels. The system is based on the attenuation of ultrasonic signals as they pass through and are reflected by materials of different density. A prototype system was assembled and tested producing results which were promising. The calibration of the apparatus is fairly complex and highly dependent on the density of

suspended material. Since several different materials were being tested, it was decided that the utilization of the apparatus would be too time consuming until the number of candidates was reduced.

4. Viscosity Characteristics of Slurries

A colloid is generally defined as a dispersion of solid particles, of less than one micron, in a liquid phase.⁽²⁷⁾ Although the particle sizes of the solids which have been considered appear to be larger than one micron (see Figures 5-9), the carbon slurries would obviously have a large proportion of the particles below one micron. The carbon black, in particular, has a base particle size of 24 millimicrons, well below the size which is observable on an optical microscope. Those particles which are visible are agglomerations of thousands of the base particles. Since colloids are generally non-Newtonian fluids,⁽²⁷⁾ it was felt that the carbon slurries could also be non-Newtonian.

This theory was examined using a Weissenberg Rheogoniometer. The device is a cone and plate viscometer⁽²⁸⁾ which can be used to measure the shear stress versus shear rate characteristics of liquid samples, and thus give an indication of non-Newtonian behavior. The instrument was used to measure shear stress versus shear rate and shear stress versus time characteristics of the base fuel and a number of the hybrid fuel samples. Of particular interest were the carbon black slurries, which were expected to demonstrate the rheological characteristics of colloidal mixtures.

Figures 10 and 11 show the results of the rheological examination of the carbon black slurries, the cellulose slurry, and the base fuel. In Figure 10, the shear stress is plotted versus the shear rate. In all cases, the viscosity of the slurries is higher than that of the base fuel. In addition, all of the slurries demonstrated non-Newtonian behavior in that the shear stress versus shear rate curves were not straight lines. The Monarch carbon black indicated a higher viscosity than the Mogul L, due possibly to the high oil adsorption characteristics of the monarch. In Figure 11, the hysteresis effects of the various slurries are demonstrated. The cellulose was the only slurry which showed a shear thinning effect with time, explaining the hyster-

Figure 10. Shear Stress versus Shear Rate for the Base Fuel and Several Slurry Fuels.

Figure 11. Shear Stress versus Shear Rate for Three of the Slurry Fuels as the Shear Rate was Increased and the Decreased to Demonstrate Hysteresis Effects.

esis effect for that fuel. The carbon blacks showed hysteresis but did not demonstrate any time effects on the viscosity.

B. Engine Test Apparatus

The primary concern of the engine experiments was the measurement of the thermal efficiency of the engine when different fuels were being used. As a result of the first year's work, it was realized that in many cases the differences in performance of the various fuels were very small. An effort was made during the second year to increase the precision of the experimental measurements and to improve the repeatability of the experimental results.

The engine used in this study was a single-cylinder, four-stroke, CLR engine equipped as a direct-injection diesel. The engine, manufactured by Laboratory Equipment Co., was originally designed for evaluation of lubricants. This engine was chosen because of the easy access to the cylinder for pressure measurements and because of the capability of converting very easily to a divided chamber configuration. The engine specifications are listed in Table 9. The relatively low compression ratio of 14:1, which was used during the first year, was also used during the second year to maintain a standard data base.

The fuel injection system consisted of an American Bosch-type APEIB-50P-5625A injection pump and a Bosch-type DDL-150-S-315 nozzle. The nozzle was equipped with a proximity sensor to record the injection timing and duration.

The engine was started, motored, and controlled using an eddy-current dynamometer which was directly coupled to the crankshaft. The dynamometer controller was designed to maintain the speed within ± 5 rpm at any of the test conditions.

Two problems which plagued the experiment during the first year were variations in the inlet air properties and drifting of the load measurements due to changes in ambient temperature. Originally, the inlet air was drawn into the engine through a laminar flow instrument. Variations in the atmospheric pressure, temperature, and humidity were measured, but no provisions were made

Table 9. Engine Specifications

Bore	9.65 cm
Stroke	9.53 cm
Connecting Rod Length	17.46 cm ₃
Displacement	400.4 cm ³
Compression Ratio	14:1
Intake Valve	
Opening	18° BTDC
Closing	58° ABDC
Exhaust Valve	
Opening	56° BBDC
Closing	20° ATDC

Table 10. Engine Conditions Which Were Held Constant Over the Duration of a Test

Inlet Air Temperature	56.7°C(100°F)
Inlet Air Pressure	101.3 kPa(14.4 Psia)
Oil Temperature	71.1°C(160°F)
Injection Timing	
1000 rpm	16° BTC
1500 rpm	17° BTC
2000 rpm	18° BTC
Coolant Temperature	82.2°C(180°F)

for controlling these variables in the inlet air to the engine. During the second year, an inlet air conditioning system was designed and installed in the test cell. Figure 12 is a schematic of the system. Using this system, the pressure and temperature of the inlet air is controlled and the relative humidity is maintained below a value of 30 percent. In addition, the installation of the precision rotameter allows for measurement of the air flow to $\pm 1\%$ of the reading.

The torque transmitted to the cradled dynamometer was measured using a strain gauge load cell. It was determined that the load cell readings were strongly affected by variations in the ambient temperatures. This problem was eliminated by the installation of an enclosure which allowed for control of the load cell temperature.

The fuel flow rate was determined gravimetrically using an Analog model AN5322 Load Cell Digitizer in conjunction with GSE Model 4400 weighing platform. The supply and return lines for the injection system were run to a common container on the weighing platform. The digitizer provided digital readout of the change in the weight of container as a function of time. These readings were integrated over a precisely determined time increment to give the net rate of fuel flow to the engine.

C. Data Acquisition Systems

A water-cooled piezoelectric pressure transducer was installed in the head of the CLR engine (AVL Model 12 QP300CYK). The charge generated in the transducer was amplified using a Kistler Model 504 charge amplifier. The output from the charge amplifier was displayed on a multibeam oscilloscope along with a TDC mark and the injector needle lift signal. The pressure signal was also supplied to an A-D converter installed on a Computer Automation microcomputer. A shift encoder (Disc Rotary Switch), coupled to the crankshaft of the engine, provided a trigger pulse every degree of revolution. These pulses triggered the A-D converter and initiated storage of the readings in the computer memory. The resulting record consisted of 720 pressure readings every engine cycle. The pressure records from 10 cycles were averaged and then used to compute the apparent heat release rate using the methods described by

Figure 12. Schematic of the Inlet Air Preparation System.

Obert⁽²⁹⁾ and other authors.^(30,31,32) Statistical analysis of the averaged pressure data indicated that averaging over ten cycles was optimum with respect to time required to take the data and minimization of the standard deviations of the resulting averages.

Attempts to correlate the apparent heat release rates and the performance data based on the brake measurements met with only limited success. During the second year, a new computer system was installed which allowed for the computation of the indicated horsepower as well as the apparent heat release from the cylinder pressure measurements. It was hoped that this data would be more meaningful and would allow for the development of combustion correlations which would provide insight into the effects of the various fuels on the combustion process. Using the new system, it was possible to compare the integrated performance data (ihp) and the heat release data, where both were based upon the measurement of the cylinder pressure. The new computer system is based on a Data General Micro Nova computer. A Biomation Model 1015 Waveform Recorder was used as an A-D converter and a buffer for recording 1024 reading of the pressure signal over a given cycle. The Biomation unit triggered 1024 times a cycle using a shaft encoder coupled to the engine crankshaft. Figure 13 is a schematic of the data system. As with the old system the data from ten cycles was averaged and used to compute the apparent heat release rates. In addition, the average pressure data was used to compute the indicated horsepower.

Equation (1) is the form of the First Law of Thermodynamics which was used to compute the apparent heat release rate.

$$dQ/d\theta = [1 + C_v/R] P(dV/d\theta) + (C_v/R) V dp/d\theta \quad (1)$$

where: Q = heat release

θ = crank angle

C_v = specific heat at constant volume of the working fluid

R = gas constant of working fluid

V = instantaneous volume of the working fluid

P = instantaneous pressure of the working fluid

Figure 13. The MicroNova Based Data Acquisition System.

The crank angle position was determined from the shaft encoder. The specific heat and the gas constant of air were used in the equation. The pressure was measured and the volume and the rate of change of volume were computed using the volume-crank angle relationship. In the original system, $dQ/d\theta$ was computed using every degree of revolution. In the new system, $dQ/d\theta$ was computed every 0.7 degrees of revolution. In addition, the indicated horsepower was computed every 0.7 degrees in the new system using equation (2),

$$\dot{W} = P(dV/d\theta) \quad (2)$$

where $\dot{W}$ = instantaneous rate of doing work (instantaneous power)

The total indicated horsepower over the average cycle was computed using equation (3),

$$I_{hp} = \int_0^{720} P (dV/d\theta) d\theta \quad (3)$$

The new data acquisition system also provided mass storage and graphics capabilities which were not possible on the original system. Since the development of the system was not completed until late in the second year, only a limited amount of data was available for this report. This data is presented in another section, separate from other engine data.

D. Exhaust Emissions Measurement

A gas phase emissions bench was designed and constructed during the second year. The exhaust gases were analyzed for CO , CO_2 , O_2 , NO/NO_x , and unburned hydrocarbons. The original design of the system included ice baths in the sample lines to the nondispersive infrared analyzers (CO/CO_2) only. Difficulties were encountered with condensation in the chemiluminescent NO/NO_x detector. The final design of the system, shown in Figure 14, included the installation of an ice bath between the FID hydrocarbon detector and the NO/NO_x analyzer. The calibration curves for the instruments are programmed into the Micro Nova computer. By inputting the raw meter readings and the concentration of the calibration gases into the computer, the concentrations of the various species could be output as ppm, gm/Bhp-hr and gm/Ihp-hr. In addition, the computer was programmed to compute the air-fuel ratio based on the exhaust gas composition.

Figure 14. Schematic of the Gas Phase Emissions Analysis System.

Comparison of the air fuel ratios computed from the measurement of the air and fuel flow rates, and those computed from the exhaust analysis, revealed that the exhaust analysis always indicated higher air-fuel ratios than those determined from the air and fuel flow rates. One possible explanation for this difference was the fact that the solid carbon present in the exhaust was not accounted for in the computations. A system was designed late in the second year which would allow for measurement of the particulate matter in the exhaust. Figure 15 is a schematic of the system. Basically, a known volume of the exhaust gas is drawn through the filter paper. Typically, 30 to 40 liters of gas were passed through the system. The filter material was Whatman Qualitative No. 2 papers with a pore size of less than 8 microns. The procedure consisted of desicating the filters for 24 hours, weighing the dry papers immediately before collecting a sample, drying the papers and sample for an additional 24 hours, and finally weighing the dried paper and sample. The differences in the two weights and the volume of gas passed through the filter gave the concentration of solids in units of g/liter. The results of the gas phase and solid emissions measurements are given in another section of the report.

E. Experimental Procedure

The objective of the engine experiments was to compare the performance of the test fuels to that of a standard baseline diesel fuel. During the first year, engine tests with the base fuel were run intermixed with the tests with the hybrid fuels. This bracketing provided a compensation for the day to day variability in the ambient conditions and in the experimental apparatus. This procedure was cumbersome, however, and became unnecessary when the inlet air preparation system was installed. As a result, the general procedure was modified in that a baseline was established and used as a basis of comparison for the test fuels. Verification runs were made at the beginning and end of each day to insure that a constant baseline was maintained. Additional baseline data were generated if changes were made to the engine or the injection system, but the test fuels were always compared to the baseline prevailing at the time of the experiment.

Figure 15. Sampling System for Solids In the Exhaust.

The procedure consisted of operating the engine on the test fuel and adjusting the rack position until the brake horsepower measurement matched that obtained with the base fuel. Full load was defined as the load generated by the engine when operating on the base fuel at an air-fuel ratio of 20:1. Three-quarter and one-half loads were defined as the appropriate portions of the full load. Once the desired load was reached and maintained, the data acquisition system was started, the fuel and air flow measurements were made, and the exhaust emissions measurements were made. Table 10 is a listing of the variables which were maintained at constant values over the duration of a test.

In the later tests, where the Ihp was computed, the baseline and the test data were based on Ihp rather than Bhp; this provided internal consistency between the performance data and the heat release data.

As the test fuels were formulated, they were tested in the engine at 1500 rpm and three loads. Emissions data were not collected during these runs because they were meant to be screening tests for performance characteristics and evaluation of pumpability characteristics of the test fuels. Based on the results of the screening tests, additional engine testing was done with a test fuel if it displayed good performance and pumpability characteristics. The full-scale tests included three speeds and three loads at each speed with full sets of emission and heat release data.

III. TECHNICAL PROGRESS

During the second year of the program, approximately twenty-seven fuel formulations were tested in the engine. The majority of these fuels were in the slurry and solution categories. Efforts were made to evaluate the fuels and judge which were the most promising candidates for further testing and development. This judgment was based not only on the ease with which the fuels could be used in existing systems but also on the thermal efficiency of the fuels in the engine.

1. Screening Test Results

The performance data of the various test fuels were normalized using corresponding data for the base fuel. Two definitions result from this normalization which provide a convenient means of comparing the results. The definitions are:

Relative Specific Energy Consumption (REC)

$$= \frac{\text{Brake Specific Energy Consumption (Test Fuel)}}{\text{Brake Specific Energy Consumption (Base Fuel)}}$$

and,

Relative Specific Diesel Fuel Consumption (RDC)

$$= \frac{\text{Brake Specific Diesel Fuel Consumption (Test Fuel)}}{\text{Brake Specific Diesel Fuel Consumption (Base Fuel)}}$$

where both REC and RDC were determined under the same conditions of speed and load for the test as well as the base fuel.

Values of REC greater than unity indicate a decrease in the thermal efficiency when using the test fuel, while REC values less than unity indicate improvement in the efficiency. Similarly, RDC values greater than one indicate that more diesel fuel is being consumed by using the test fuel than if straight diesel fuel were used. The ideal cases are those in which both the REC and the RDC are less than one.

The REC and the RDC provide a very good means for quantizing the performance results. The pumpability characteristics were much more difficult to quantize. Table 11 is a listing of the test fuels according to type. To the right of each fuel are a series of columns indicating the difficulties encountered with the particular fuel. As would be expected, the solutions and emulsions presented no problems with pumpability. The slurries, on the other hand, were generally more difficult to handle; this was especially true for the noncarbon components. The inability to operate the engine on a particular fuel resulted from either ignition problems (pure vegetable oils) or injection system problems (mesquitewood). In many cases, engine data were obtained, but injection system problems made it necessary to stop the testing to clean the injection system (coal, cellulose, flour).

Table 11. Summary of the Difficulties Encountered With the Test Fuels*

Fuel	Ignition	Misfire	Knock	Nozzle Sticking	Nozzle Plugging	Engine Operable	Fuel Type	Concentration Mass or Volume
10% Coke	Y	N	N	N	N	Y	Slurry	M
20% Coke	Y	N	N	N	N	Y	Slurry	M
10% Carbon Black	Y	N	N	N	N	Y	Slurry	M
20% Carbon Black	Y	N	N	N	N	Y	Slurry	M
20% Coal	Y	N	N	Y	N	Y	Slurry	M
20% Cellulose	Y	N	N	Y	N	Y	Slurry	M
20% Starch	N	--	--	Y	Y	N	Slurry	M
20% Mesquite	N	--	--	Y	Y	N	Slurry	M
20% Flour	Y	N	--	N	Y	Y	Slurry	M
20% Coke, 80% Methanol	N	--	--	N	N	N	Slurry	M
10% Carbon Black in H ₂ O Emulsion	Y	N	N	Y	N	Y	Slurry	M
100% SRC-II	N	--	--	--	--	N	Solution	M
50% SRC-II	Y	N	Y	N	N	Y	Soluton	M
10% Ethanol	Y	N	N	N	N	Y	Solution	V
20% Ethanol	Y	N	N	N	N	Y	Solution	V
30% Ethanol	Y	N	N	N	N	Y	Solution	V
40% Ethanol	Y	N	N	N	N	Y	Solution	V
20% Cottonseed Oil	Y	N	N	N	N	Y	Solution	M
60% Cottonseed Oil	Y	N	N	N	N	Y	Solution	M
80% Cottonseed Oil	Y	N	N	N	N	Y	Solution	M
20% Peanut Oil	Y	N	N	N	N	Y	Solution	M
60% Peanut Oil	Y	N	N	N	N	Y	Solution	M
80% Peanut Oil	N	--	--	N	N	N	Solution	M
100% Cottonseed Oil	N	--	--	N	N	N	Solution	M
100% Cottonseed Oil	N	--	--	N	N	N	Solution	M
20% Ethanol	Y	N	N	N	N	Y	Emulsion	V
30% Ethanol	Y	N	N	N	N	Y	Emulsion	V
31.7% DF-2, 29.5% Ethanol, 18.8% Water, 15% Sugar, and 5% Surfactant	N	--	--	--	--	N	Emulsion	M

* Y = Yes; N = No

In the course of the screening tests, it was realized that the injection system problems (especially nozzle sticking) could be reduced by increasing the clearance between the nozzle valve and the nozzle body by 0.025 mm. All of the slurry results, presented in Table 11 and elsewhere in the report, were obtained with the modified nozzle. Exceptions to this are the flour and the mesquite wood. These fuels had particle size distributions which were so large that nozzle plugging was the main problem. The solutions and emulsions were all tested using the standard nozzle.

The starch slurry was an unusual case in which the particle size distribution was in the acceptable range, but engine operation was impossible. This slurry formed a thick viscous material in the injection nozzle which could not be cleared by operation on the base fuel. It appears that the high temperatures and shear rates encountered in the nozzle caused the starch particles to swell and possibly fracture, resulting in the formation of the gum; a similar material could be formed by adding the starch to hot water.

The sugar-water-ethanol emulsion was a case in which the fuel could not be ignited and, in addition, caused the engine to seize. During the preliminary attempts to test the fuel, a syrup was formed between the piston and the cylinder liner. As the engine cooled, this material hardened, seizing the piston to the liner.

Tables 12 through 14 contain the screening test results for the solutions, emulsions, and slurries, respectively. In all cases, except the 10% carbon black-water slurry, the RDC values are less than unity, indicating that all of the fuels demonstrate a tendency to reduce the diesel fuel consumption required to produce a given amount of power. The REC values, on the other hand, vary from 0.885 to 1.20, indicating that the thermal efficiencies are either increased or decreased depending on the fuel and/or the load conditions.

In order to compare the results for all of the test fuels, the REC and RDC values were arranged over the load conditions of the screening test (1500 rpm - full, 3/4, 1/2 loads). The averaged REC values give an indication of the relative thermal efficiencies, while the averaged RDC values give an indication of the potential for reducing diesel fuel consumption. The results

Table 12. Engine Performance Data for Various Fuel Solutions at 1500 rpm

<u>Fuel No.</u>	<u>Fuel Composition</u>	<u>BMEP</u>	<u>REC</u>	<u>RDC</u>
S1	100% SRC-II	---	---	---
S2	50% SRC-II	528	0.895	0.464
	50% SRC-II	396	0.836	0.433
	50% SRC-II	263	1.097	0.568
S3	10% Ethanol**	528	0.969	0.906
	10% Ethanol	396	0.974	0.909
	10% Ethanol	263	0.985	0.921
S4	20% Ethanol**	528	0.926	0.802
	20% Ethanol	396	0.890	0.772
	20% Ethanol	203	0.921	0.798
S5	30% Ethanol**	528	0.892	0.709
	30% Ethanol	396	0.898	0.714
	30% Ethanol	263	0.933	0.741
S6	40% Ethanol**	528	0.888	0.635
	40% Ethanol	396	0.885	0.632
	40% Ethanol	263	0.991	0.709
S7	20% Cottonseed Oil	528	0.988	0.805
	20% Cottonseed Oil	396	0.988	0.813
	20% Cottonseed Oil	253	1.006	0.819
S8	20% Peanut Oil	528	0.946	0.770
	20% Peanut Oil	396	0.923	0.752
	20% Peanut Oil	263	0.954	0.777
S9	60% Cottonseed Oil	528	0.948	0.404
	60% Cottonseed Oil	396	0.929	0.395
	60% Cottonseed Oil	263	0.892	0.379
S10	60% Peanut Oil	528	0.895	0.358
	60% Peanut Oil	396	0.893	0.381
	60% Peanut Oil	263	0.951	0.405
S11	80% Cottonseed Oil	514	0.977	0.213
	80% Cottonseed Oil	396	0.939	0.205
	80% Cottonseed Oil	263	0.989	0.215
S12	80% Peanut Oil	514	0.925	0.202
S4	20% Ethanol***	550	0.961	0.831
	20% Ethanol***	413	1.002	0.866
	20% Ethanol***	276	0.992	0.858
S5	30% Ethanol***	528	0.987	0.798
	30% Ethanol***	396	0.989	0.800
	30% Ethanol***	263	1.001	0.809

* Concentration on a volume bases, all others on a mass basis.

** Injection timing varied for these fuels.

*** This data presented in Figures 16 and 17.

Table 13. Engine Performance Data for Various Fuel Emulsions at 1500 rpm

<u>Fuel No.</u>	<u>Fuel Composition</u>	<u>BMEP</u>	<u>REC</u>	<u>RDC</u>
E1	20% v/v Ethanol Micro	550	0.915	0.706
		413	0.989	0.763
		276	0.973	0.750
E2	30% v/v Ethanol Micro	550	1.022	0.831
		413	1.005	0.866
		276	0.986	0.858
E3	31.7% w/w DF-2			
	29.5% w/w Ethanol			
	18.8% w/w Water			
	15.0% w/w Sugar			
	5.0% Surfactant			

Table 14. Engine Performance Data for Various Fuel Slurries at 1500 rpm

<u>Fuel No.</u>	<u>Fuel Composition</u>	<u>BMEP</u>	<u>REC</u>	<u>RDC</u>
SL1	10% Coke*	528	0.918	0.857
		396	0.918	0.857
		263	0.924	0.862
SL2	20% Coke*	528	1.086	0.901
		396	0.956	0.793
		263	0.936	0.777
SL3	10% Carbon Black*	528	0.976	0.900
		396	0.994	0.917
		263	0.988	0.912
SL4	20% Carbon Black*	514	1.157	0.975
		411	1.054	0.889
		258	1.066	0.898
SL5	20% Coal*	528	1.137	0.969
		396	1.124	0.958
SL6	20% Cellulose*	528	0.99	0.896
		396	1.009	0.910
		263	1.078	0.973
SL7	20% Starch*	---	---	---
SL8	20% Mesquite Wood*	---	---	---
SL9	20% Flour, 1% Lecithin*	528	1.052	0.955
		396	0.931	0.845
		263	1.083	0.983
SL10	20% Coke, 80% Methanol*	---	---	---
SL11	10% Carbon Black	528	1.10	1.18
	10.4% Water	396	1.10	1.17
	6.1% Surfactant	263	1.20	1.18

* See Table 8 for details on the properties of the various solids. All concentrations are on a mass basis.

of the averaging for REC are presented in Figure 16 in the form of a bar chart. Based on these results, the test fuels fall into the ranking presented in Table 15, with number 1 indicating the highest efficiency and number 19 indicating the lowest efficiency. Following the same procedure, the RDC averages are presented in the bar chart of Figure 17, and ranked according to minimum RDC in Table 16.

Except for the 10% coke slurry, the nine best fuels (based on REC and RDC) are either solutions or emulsions. The 60% peanut oil solution was the best. Even though the 80% cottonseed oil had a better RDC, its REC ranked eighth. Examining the slurry fuel results, the carbons were better than the biomass slurries in both thermal efficiency and replacement of diesel fuel.

2. Zero-Dimensional Thermodynamic Model

In an effort to explain the results obtained in the screening tests, a simple zero dimensional diesel cycle model was developed. Equation (4) is the equation for first law of thermodynamics (conservation of energy):

$$Q = W + \Delta U \quad (4)$$

where Q = apparent energy input due to chemical reactions and W and U are the work done on the system and the change in its internal energy. Assuming an ideal gas working fluid and applying the equation to a control volume where

$$V = V(\theta),$$

$$dQ/d\theta = [k/(k-1)] dV/d\theta + (1/k-1) V dP/d\theta \quad (1)$$

which is equation (1), defining the apparent heat release rate. Rearranging equation (1) results in the differential equation,

$$dP/d\theta + k/V \cdot (dV/d\theta)P - [(k-1)/V] \cdot dQ/d\theta = 0 \quad (5)$$

If it is assumed that V , $dV/d\theta$, and $dQ/d\theta$ are constant over an integration interval of $\Delta\theta$, then Equation 5 can be integrated to give,

Figure 16. Average Values of REC for the Fuels Tested During the Second Year. Averages are over the Load range at 1500 rpm.

Table 15. Rating of the Various Formulations Based on the Average
REC Values at 1500 rpm

1. 60% Peanut Oil Solution
2. 10% Coke Slurry
3. 40% Ethanol Solution
4. 60% Cottonseed Oil Solution
5. 20% Peanut Oil Solution
6. 50% SRC-II
7. 20% Ethanol Microemulsion
8. 80% Cottonseed Oil Solution
9. 10% Ethanol Solution
10. 10% Carbon Black Slurry
11. 20% Ethanol Solution
12. 20% Coke Slurry
13. 30% Ethanol Solution
14. 20% Cottonseed Oil Solution
15. 30% Ethanol Microemulsion
16. 20% Flour, 1% Lecithin Slurry
17. 20% Cellulose Slurry
18. 20% Carbon Black Slurry
19. 20% Coal Slurry

Figure 17. Average Values of RDC for the Fuels Tested During the Second Year. Averages are over the Load Range at 1500 rpm.

Table 16. Rating of the Various Formulations Based on the Average
RDC Values at 1500 rpm

1. 80% Cottonseed Oil Solution
2. 60% Peanut Oil Solution
3. 60% Cottonseed Oil Solution
4. 50% SRC-II
5. 40% Ethanol Solution
6. 20% Ethanol Microemulsion
7. 20% Peanut Oil Solution
8. 30% Ethanol Solution
9. 20% Cottonseed Oil Solution
10. 20% Coke Slurry
11. 30% Ethanol Microemulsion
12. 20% Ethanol Solution
13. 10% Coke Slurry
14. 10% Ethanol Solution
15. 10% Carbon Black Slurry
16. 20% Carbon Black Slurry
17. 20% Flour, 1% Lecithin Slurry
18. 20% Cellulose Slurry
19. 20% Coal Slurry

$$P = (P_i - B/A) \exp(-A \cdot \Delta\theta) + B/A \quad (6)$$

where $A = (k/V) (dV/d\theta)$

$$B = [(k-1)/V] (dQ/d\theta)$$

and where the ratio of specific heats is computed as

$$k = k(N_2, O_2, CO_2, H_2O, \text{Fuel}, \text{Temp}).$$

The heat transfer is assumed to be 33 percent of the total heat release; thus, variations in heat transfer rates were not accounted for in the model.

Summarizing the model, the first Law equation is rearranged and integrated to give the cylinder pressure in terms of the volume-crank angle relationship and the rate of energy input. In this form, the cylinder pressure can be examined using different energy input schedules and different fuels. In the model, the ratio of specific heats of the working fluid was computed as a function of composition and temperature. The temperature and composition of the working fluid were computed using the energy input schedule assuming that the reaction went to completion for each increment of fuel injected. The latent heat of vaporization of the fuel was accounted for by assuming that the total mass of fuel which was injected, vaporized during the crank angle increment just prior to ignition.

In the first annual report, four mechanisms were suggested which could explain the improvements in thermal efficiency observed with the alcohol and water/diesel fuel blends. They are:

1. If the microexplosion phenomena occurred with the emulsions, the improved air-fuel mixing would result in higher burning rates, resulting in more heat release at constant volume which is a more efficient conversion process of heat into work.
2. The cooling effect of the vaporizing water or alcohol results in a lower ratio of specific heats of the working fluid; this also is in the direction of a more efficient conversion of heat into work although the lower temperature also means a lower pressure.

3. The expansion effect of the water or alcohol results in more moles of gas and hence higher pressures in the cylinder.
4. Observed increase in the physical delay portion of ignition delay period allow more time for fuel to vaporize before ignition. This means more of the fuel burns in a pre-mixed flame very rapidly, resulting again in higher heat release rates and more efficient conversion.

The zero-dimensional model was used to examine the second and third items. This was accomplished by including the alcohol, and its high latent heat of vaporization, in the computations of the combustion pressure from a simulated fuel delivery schedule. If the efficiency improvements result from either item two or three, the peak cylinder pressure should be higher when the alcohol is added to the fuel. This is demonstrated in Figure 18 which is a pressure versus crank angle diagram for the base fuel compared to that of the 20% ethanol solution. The diagrams represent actual engine data obtained at the same speed and brake load conditions. The REC value for the solution was less than one, indicating an improvement in the efficiency.

Using the base fuel with the 20 percent ethanol solution and the corresponding fuel delivery schedules in the model produced no significant change in the pressure diagrams as seen in Figure 19. The computed pressure traces overlaid one another almost exactly. Water was then studied in order to examine the effects of the cooling and mole changes in an extreme case. When 20% water is added to the base fuel, the computations result in a pressure diagram which has lower pressures than the base fuel, as seen in Figure 20. It is obvious from these results that items two and three can no longer be considered as explanations for the improvements in efficiency observed with the alcohol fuels--or for that matter, with the water fuels.

The results shown in Figure 18 would tend to indicate that the increased ignition delay, with the ethanol fuel, was the cause of the efficiency improvement. This improvement obviously resulted from the more rapid rate of heat release (approaching constant volume combustion) encountered with the ethanol fuel. The question as to whether the increase in heat release rate

Figure 18. Comparison of Cylinder Pressure Data.

Figure 19. Baseline Diesel Fuel and 20% Ethanol and Diesel Fuel

Figure 20. Baseline Diesel Fuel and 20% Water and Diesel Fuel.

resulted from the ignition delay or from microexplosion cannot be answered using the model. The question will be discussed further in the next section.

Some questions arose as to the optimum heat release schedule. Theoretically, constant volume combustion at top dead center would provide the most power output for a given amount of energy input. In practice, the combustion process takes a finite amount of time. In examining the actual heat release data for several of the fuels, it was realized that timing and the shape of the diagrams affect the power output. In addition, the timing, shape, and total apparent energy input are all coupled and therefore pose a difficult task when attempting to determine optimum heat release rates.

A baseline fuel heat release diagram was used to construct a simulated heat release diagram which was input into the zero dimensional model. The shape of the diagram was held constant (constant total energy input), but the timing was varied from 10 degrees before the actual events to 10 degrees after. These diagrams are shown in Figure 21. The model was used to compare the indicated horsepower developed in each case. The computed indicated horsepower are plotted with respect to the standard timing in Figure 22. As can be seen, the optimum timing for the given shaped diagram is approximately three degrees retarded from actual timing. In the engine, a shift in the heat release can be accomplished by changing the injection timing but that also results in a change in the shape of the diagram. Based on the results of the computations, it appears that the optimum timing for the occurrence of the peak heat release rate is 6 to 7 degrees before top dead center.

Three very simple heat release diagrams were used to examine the effects of the peak heat release rate and the shape of the heat release diagrams. The hypothetical diagrams are shown in Figure 23. The total heat release was the same in all cases. The occurrence of the peak was always at 7 degrees before top center. If the indicated horsepower computed for each of the heat release schedules is normalized with respect to diagram A, and plotted versus the peak heat release rate, it can be seen that the value of the peak and the shape of the diagram do not have as strong an effect on the work output (see Figure 24) as the timing of the peak heat release rate (see Figure 22).

Figure 21. Hypothetical Heat Release Diagram. Total Energy input is the Same for all Five Cases (21.8KJ).

Figure 22. Normalized I_{hp} versus timing of the Heat Release event using the Heat Release Diagrams Presented in Figure 21.

Figure 23. Hypothetical Heat Release Diagrams. Same Total Energy and the Same Timing for the Occurance of the Peak Rate of Heat Release.

Figure 24. Normalized Ihps versus Peak Heat Release Rate Using the Heat Release Diagrams Presented in Figure 23.

3. Discussion of the Screening Test Results

The experimental results for the three general types of hybrid fuels are discussed separately. It should be noted that all tests were performed using a diesel engine optimized for operation on diesel fuel. The comparison of all the test fuels was previously presented in section III.A.1.

Solutions

Based on the average results presented in Figure 16, the overall performance of the 60% peanut oil solution was better than any of the other test fuels. The heat release diagrams for the base fuel and the 60% peanut oil solution are shown in Figure 25. Both tests were performed using the same speed, load and other engine conditions. The REC for the peanut oil was 0.954 for the run displayed in the figure. Even though the peak heat release rate was higher for the base fuel, the peanut oil solution performed better than the base fuel. Based upon the results of the zero dimensional model analysis, it appears that the superior performance of the peanut oil solution resulted from the fact that the peak heat release occurred closer to the optimum timing described in the previous section. Physically, these results indicate that the peanut oil solution has a shorter ignition delay time, resulting in more heat release early in the cycle and a corresponding higher thermal efficiency.

Heat release rate data, at selected points near the peak value, is presented in Figure 26 for the peanut oil solutions at 1500 rpm and 530 kPa BMEP. As can be seen, as the concentration of peanut oil increases, the occurrence of the peak heat release rate advances before top center. Based on the model analysis, this would indicate that under the conditions of the test the order of best efficiency would be 80% as the most efficient and 20% as the least efficient. The 80% and the 60% solutions were more efficient than the 20% solution, but the 60% was more efficient than the 80% solution, as shown in Figure 27. As can also be seen, the 80% solution would run only at the 530 kPa BMEP condition. In addition to the heat release event timing effects, the 80% solution had a lower total apparent heat release (the total energy computed from equation one and integrated over the time that the valves were closed) than the 60% solution. Both the 60% and the 80% solutions had higher total apparent heat releases than the 20% solution. These results indicate

Figure 25. $\dot{Q}$ versus Crankangle for the Basefuel and the 60% Peanut Oil Solution at 1500 rpm and 528 KPa BMEP.

Figure 26. Selected Heat Release Data for the Peanut Oil Solutions near the Peak Value. Engine Speed = 1500 rpm, BMEP=530KPa.

Figure 27. REC versus BMEP for the Peanut Oil Solutions at 1500 rpm.

that 60% solution of peanut oil underwent more complete combustion than either 20% or the 80% solution, assuming that the heat transfer was the same in all cases.

The results for the cottonseed oil were very similar to those for the peanut oil. Figure 28 is a plot of REC versus BMEP for the cottonseed oil solutions. Again the results for the 80% concentration fell between those for the 20 and 60% solutions. The only major difference was that the engine would operate at part load on the 80% cottonseed oil solution.

The ethanol solution data presented at the top of Table 12 represent an attempt to optimize the injection timing for the various ethanol solutions. The ethanol data at the end of the table was obtained at the standard injection timing. At 1500 rpm, the standard injection timing was 17 degrees before top center. Due to the long ignition delay times encountered with the ethanol fuels, the injection timing was advanced to 18 degrees BTC for the 10, 20, and 30 percent solutions and to 24 degrees BTC for the 40 percent solution. Figure 29 shows the heat release data for the ethanol solutions near the peak values, at 1500 rpm and 530 kPa BMEP. Since the ignition delay times were so long and the injection timing advanced so far, there was a relatively long period of time for the physical delay. As a result of this, the heat release rates were very rapid, thus compensating for the fact that the peak value did not occur at the optimum time. In going from the 10- to the 40-percent solutions, the REC's decreased due to the fact that the total apparent heat release increased. The attempt to optimize the injection timing for the ethanol solution resulted in an improvement in performance over that of the standard timing. In general, the REC values for the 20 and 30% solutions were higher at the standard timing than with the advanced timing. This effect manifests itself in lower total apparent heat releases and delayed peak heat release rates for the standard timing.

Emulsions

The only emulsions which were tested during the second year were the ethanol microemulsions and the ethanol-sugar-water emulsion. The sugar emulsion was unsuccessful, and the ethanol performance data were repeats of tests made

Figure 28. REC versus BMEP for the Cottonseed Oil Solutions at 1500 rpm.

Figure 29. Heat Release Data for the Ethanol Solutions, Selected Points near the Peak Value. 1500 rpm, 530 KPa BMEP.

during the first year. The ethanol microemulsions were retested during the second year mainly to obtain the exhaust emission characteristics of these fuels. These results are reported in another section.

One interesting comparison between the various solutions and emulsions is the REC's versus ignition delay times for these fuels. Figure 30 is a plot of REC versus ignition delay for the ethanol and methanol microemulsions, the ethanol solution and some depressed octane number diesel fuels. The ethanol solutions and the low cetane fuels behaved very similar to one another, while the emulsions display much steeper slopes. If the ignition delay time was the only contributor to the rapid heat release rates and the corresponding low values of REC, all of the fuels would fall within a narrow band around the low cetane fuel data. The fact that the microemulsions displayed lower REC values indicates that there is another factor contributing to the improved performance. Recalling the four possible causes for the efficiency improvements, and the fact that the zero dimensional model eliminated the possibility of cooling or mole change effects, the results presented in Figure 30 tend to verify the presence of improved atomization resulting from disruptions in the combustion ("microexplosions").

Slurries

The operational characteristics of the slurries was discussed in previous sections. Based upon that discussion, the "carbon" (coke and carbon black) slurries were the only ones which allowed for continual operation with little or no injection system problems. This was accomplished using a slightly modified injection nozzle (clearances opened by 0.025 mm). The modified nozzle did not, however, improve the operational characteristics of the starches and cellulose.

An attempt was made to use the heat release data to generate combustion efficiency information. It must be realized that the heat release equations do not account for heat transfer effects. It was expected, however, that the solid materials in the slurries would increase the heat transfer rates to the coolant due to radiation from the solid particles. This fact must be kept in mind when interpreting the heat release data.

Figure 30. Effect of Increasing Ignition Delay on the Thermal Cycle Efficiency.

The relative energy consumption versus BMEP is plotted in Figures 31 and 32 for the coke and carbon black slurries, respectively. Both components displayed a tendency towards degraded performance at the higher concentrations. These effects could be related to the greatly increased viscosities at the high concentrations, and the resulting degradation of the injection process.

If the total apparent heat release is divided by the energy input per cycle (via the fuel heating value), an efficiency is obtained which is related to the combustion efficiency, assuming that the heat transfer rates are the same. Figure 33 shows the apparent combustion efficiency versus concentration for the coke and carbon black at 1500 rpm and 528 kPa BMEP. The shape of the curve for the coke is unknown due to a lack of heat release data at the 10-percent concentration. The results show, however, that the percentage of the input energy which appears in the working fluid decreases rapidly with concentration. In addition, the timing of the heat release events move away from the optimum (discussed previously), contributing to the decrease in thermal efficiency. Figure 34 shows the heat release rate data for the 10- and 20-percent carbon black slurries and the base fuel, and Figure 35 shows the effects of concentration on the REC for both the coke and the carbon black.

As can be seen in Figure 34, the ignition delay time (time from start of injection to the first indication of heat release) was unaffected by the 10% carbon black, indicating that the atomization and ignition of the diesel fuel was not affected by the carbon black. At 20-percent concentration, the ignition delay time was increased and the early rate of heat release was decreased by the presence of the carbon black. In addition, the heat release event was more spread out in the early stages of combustion, indicating that the carbon (at 20% concentration) was affecting the combustion process. These effects are demonstrated in Figure 35 where the REC first decreases (at 10%) and then increases with concentration. Using the existing fuel formulations, the results in Figure 35 indicate an optimum concentration of 7.5 percent for the carbon black and 10 percent for the coke. These results are somewhat affected by the load, but the general trends are similar at all loads.

Due to the fact that the ignition delay times and the early stages of combustion were affected by the higher concentrations of "carbon," the degra-

Figure 31. REC versus BMEP for 10 and 20 Percent Coke Slurries of 1500 rpm.

Figure 32. REC versus BMEP for 10 and 20% Carbon Black Slurries at 1500 rpm.

Figure 33. The Apparent Combustion Efficiency versus Concentration for the Coke and Carbon Black Slurries.

Figure 34. Heat Release Rate Data for the Basefuel and the Carbon Black Slurries. At 1500 rpm and 528 KPa BMEP.

Figure 35. REC versus Concentration for the Coke and Carbon Black Slurries. At 1500 rpm and 528 KPa BMEP.

dation in performance encountered with these fuels can be attributed to a degradation in the atomization of the fuel. This theory is somewhat verified by the fact that the viscosity of the high concentration fuels was higher than the lower concentrations fuels, and the fact that the 10-percent concentrations gave lower REC values (higher thermal efficiencies) than the base fuel. The viscosity of the 10-percent carbon black was slightly higher than that of the base fuel while the 20-percent carbon black was two orders of magnitude more viscous than the base fuel.

The results of the screening tests on the 20 percent cellulose slurry were somewhat scattered due to operational difficulties (nozzle sticking) which required repeated shutdowns for clearing the injection system.

B. Discussion of Additional Speed and Load Tests

Five test fuels were selected for testing under a range of speeds and loads. The test matrix included three loads at each speed (1000, 1500, and 2000 rpm) with complete heat release and emissions measurements. The selection of the fuels was based on the operational and performance characteristics observed during the screening tests and an awareness of the potentials represented by each formulation. The test fuels included the 10- and 20-percent carbon black slurries (Mogul L), the 20 percent cellulose slurry, the 20-percent ethanol solution and the 20-percent ethanol microemulsions. The ethanol fuels were run mainly to obtain emission data and to examine the microexplosion phenomena.

Table 17 is a listing of the performance data for the five fuels at 1000 rpm, and Table 18 is a listing of the data at 2000 rpm. The 1500-rpm data is listed in Tables 12 through 14. The REC averages for each fuel, over the entire speeds and load matrix, is presented in Figure 36, which also shows the data presented in Figure 16 (REC averaged at 1500 rpm). Using only the 1500-rpm data, the 20-percent cellulose performed better than the 20 percent carbon black. When the averages are taken over the entire matrix, the 20-percent cellulose slurry and the 20-percent carbon black slurry both have the same average REC values. The cellulose slurry, however, demonstrated added operational difficulties noted previously. In addition, while running the 20-

Table 17. Engine Performance Data at 1000 rpm

<u>Fuel No.</u>	<u>Fuel Composition</u>	<u>BMEP</u>	<u>REC</u>	<u>RDC</u>
SL3	10% w/w Carbon Black	481	0.909	0.838
	10% w/w Carbon Black	370	0.974	0.898
	10% w/w Carbon Black	262	1.059	0.976
SL4	20% w/w Carbon Black	481	1.048	0.883
	20% w/w Carbon Black	370	1.081	0.911
	20% w/w Carbon Black	262	1.150	0.969
SL6	20% w/w Cellulose	459	0.992	0.894
	20% w/w Cellulose	345	1.158	1.044
	20% w/w Cellulose	229	1.511	1.362
E1	20% v/v Ethanol Micro-emulsion	528	0.954	0.736
	20% v/v Ethanol Micro-emulsion	396	0.957	0.738
	20% v/v Ethanol Micro-emulsion	264	0.975	0.752
S4	20% v/v Ethanol Solution	528	0.974	0.841
	20% v/v Ethanol Solution	395	0.962	0.832
	20% v/v Ethanol Solution	264	0.971	0.839

Table 18. Engine Performance Data 2000 rpm

<u>Fuel No.</u>	<u>Fuel Composition</u>	<u>BMEP</u>	<u>REC</u>	<u>RDC</u>
SL3	10% w/w Carbon Black	530	0.989	0.913
	10% w/w Carbon Black	362	0.984	0.907
	10% w/w Carbon Black	240	0.966	0.891
SL4	20% w/w Carbon Black	530	1.186	1.000
	20% w/w Carbon Black	362	1.104	0.930
	20% w/w Carbon Black	240	1.229	1.036
SL6	20% w/w Cellulose	505	1.081	0.974
	20% w/w Cellulose	379	1.132	1.020
	20% w/w Cellulose	253	1.115	1.006
E1	20% v/v Ethanol Micro-emulsion	482	0.915	0.706
	20% v/v Ethanol Micro-emulsion	362	0.915	0.706
	20% v/v Ethanol Micro-emulsion	241	0.938	0.724
S4	20% v/v Ethanol Solution	482	1.007	0.871
	20% v/v Ethanol Solution	362	0.941	0.813
	20% v/v Ethanol Solution	241	0.960	0.827

Figure 36. Comparison of the REC Averaged over the Load Range at 1500 rpm and the REC Averaged over the Entire Speed and Load Range.

percent cellulose slurry, it was noted that the engine baseline changed with time. Figure 37 shows the baseline shift observed after several hours of operation on the cellulose. The baseline data at 1500 rpm were taken first in the test series. Under those conditions, the baseline had decreased, indicating a slight improvement in the thermal efficiency due possibly to a compression ratio increase caused by deposit formation. Shafizadch and De-Groot⁽³³⁾ have indicated that up to 25% of the heating value of cellulose is contained in char material, which has a very slow reaction rate. This would tend to support the theory that deposits would form rapidly with a cellulose fuel. The 1000- and 2000-rpm data were taken after several hours of operation on the 20% cellulose. In both cases, the BSFC values were higher after operation on the cellulose fuel. It is theorized that the deposit formation in both of these cases was severe enough to degrade the atomization of the fuel. This is supported by the larger differences in the 1000-rpm data. This low speed is accompanied by a decrease in turbulence and mixing and is more sensitive to the atomization accomplished by the nozzle.

After the test with the 20% cellulose slurry, the engine was run using a microemulsion of ethanol. In previous tests with these fuels⁽⁶⁾, they displayed a tendency to remove engine deposits. After several hours of operation on the alcohol fuels, the engine returned to the original baseline performance.

The ethanol fuels presented no operational problems over the speed and load range. Figures 38 and 39 show the REC values versus BMEP at the three engine speeds for the 20-percent solution and the 20-percent microemulsion, respectively. The data for the solution was obtained using the standard injection timings. The noteworthy results for the ethanol fuels were the facts that the trends were similar in both cases and that the microemulsion demonstrated a higher thermal efficiency (lower REC) than the solution. In addition, there was a general increase in the thermal efficiency as the speed increased, due possibly to the increase in turbulent mixing and atomization as the speed is increased.

The carbon black slurries demonstrated no operational difficulties and gave performance results very similar to those obtained at 1500 rpm. The REC

Figure 37. BSFC Versus Load for the Baseline Fuel Before and After the Baseline Shift.

Figure 38. REC versus BMEP for the 20% Ethanol Solution at the Three Engine Speeds.

Figure 39. REC versus BMEP for the 20% Ethanol Microemulsion at the Three Engine Speeds.

values for the 20-percent carbon black were always greater than unity, as shown in Figure 40, but the 10 percent carbon black had only one point greater than unity, as shown in Figure 41. The slope of the 1000 rpm data in Figure 41, is a result of the sensitivity of the engine at 1000 rpm to changes in load (the fuel delivery and atomization are characteristically bad at 1000 rpm on the test engine).

Additional speed and load tests were performed using the 10-percent carbon black slurry (Mogul L carbon black), as well as a 10-percent slurry of the Monarch 1300 carbon black. Since the Monarch had smaller base particle sizes, it was hoped that the combustion efficiency would be improved somewhat. In these tests, the computer was used to calculate the indicated horsepower from the pressure data. The load matching, between the base fuel and the test fuel, was done using the Ihp rather than the Bhp. It was felt that basing the performance data (Ihp) and the heat release rates on the measurement of the cylinder pressure would provide for internal consistency of the two results and would provide for better diagnosis of the combustion process. The results of these tests are presented in the next section.

1. Discussion of Data Based on Engine Indicator Diagrams

Due to the difficulty encountered in attempting to correlate the heat release data to the brake measurements, a series of runs on base fuel and 10% Mogul carbon black were made where the operating point for the engine was set according to the Ihp values determined by the digitally processed cylinder pressure data. It was felt that using the Ihp rather than the Bhp would allow for comparisons, of a quantitative nature, between the base fuel and the test fuel heat release data. Previously runs with slightly different Ihp values, due to experimental variation in setting the brake level, frustrated attempts to obtain quantitative comparisons. The difficulty, it was felt, was not in the accuracy of the data, but rather lacking a means to "normalize" the data to the Ihp. In other words, the Ihp needed to be an independent variable, not a dependent. It was found that setting the operating condition by brake horsepower did not yield consistent indicated horsepowers.

Figure 40. REC versus BMEP for the 20% Carbon Black Slurry at the Three Engine Speeds.

Figure 41. REC versus BMEP for the 10% Carbon Black Slurry at the Three Engine Speeds.

2. Relative Diesel Fuel and Energy Consumption Figures for the
10% Mogul L Carbon Blacks

The new data for the 10% carbon black, reduced to the form presented in the previous section, is presented in Figures 42 and 43. Definitions of IREC and IRDC are based on the indicated power and defined as:

Indicated Relative Specific Energy Consumption (IREC)

$$= \frac{\text{Indicated Specific Energy Consumption (Test Fuel)}}{\text{Indicated Specific Energy Consumption (Base Fuel)}}$$

and,

Indicated Relative Specific Diesel Fuel Consumption (IRDC)

$$= \frac{\text{Indicated Specific Diesel Fuel Consumption (Test Fuel)}}{\text{Indicated Specific Diesel Fuel Consumption (Base Fuel)}}$$

where both IREC and IRDC were determined under the same conditions of speed and load for the test, as well as the base fuel.

The IREC and IRDC curves are the result of 2nd order least squares criteria curve fits of ISFC versus IMEP data. These curve fits are presented in Figure 44. Note that the ISFC versus IMEP curves for the standard nozzle and the 10% carbon black are similar in their shape, differing mainly in their height. The 10% carbon black has a higher ISFC value than that of the base fuel with the standard nozzle. The base fuel runs with the modified nozzle showed lower efficiencies than the standard nozzle, particularly at high loads. The same trends were noted in the curves for the 20% carbon black. It is apparent that the poor injection performance introduced by increasing the leakage at the injector nozzle on base fuel is compensated for by the complex flow characteristics of the slurries. The higher viscosities may reduce the leakage. No measurements of leakage rates were made, however. Other possible explanations involve alterations in the spray patterns and/or effects on the combustion.

Figure 42. Indicated Relative Diesel Fuel Consumption for 10% Mogul-L Carbon Black.

Figure 43. Indicated Relative Energy Consumption for 10% Mogul-L Carbon Black.

Figure 44. ISFC versus IMEP.

3. Correlation of Cylinder Pressure Data to Thermal Efficiency

The computer model discussed in a previous section of this report revealed how the thermal efficiency is related to the heat release profile for this engine. In the model, the point of heat release was varied until the optimum point was found. This agrees with observation of the engine heat release data. Attempts to correlate the degradation in thermal efficiency when not operating at the optimum timing have been unsuccessful. Such information would be useful, for then, all of the engine data on any fuel could be corrected to their optimum efficiency. This would save a great deal of testing since it is time consuming to locate the best timing for each fuel at each test condition.

It was felt that the difficulty encountered above may have been due to the sensitivity of the heat release data to noise. In the calculation of the apparent heat release, the difference in two consecutive pressure readings is used. Such numerical derivatives are notorious for erratic behavior. This problem does not arise in the computer model since the pressure profile is a continuous function. For this reason, an attempt was made to correlate various regions of the heat release diagram to thermal efficiency. The regions of point of injection to 360° (TDC), 360° to 375° to 490° were chosen. The computer calculated the apparent heat release between these three points. 490° is the exhaust valve opening defined as the point of 0.001" lift. Total "Q" apparent is defined as the total heat release calculated from the point of injection to the exhaust valve opening.

No correlation was apparent between thermal efficiency and heat release for the spans of crank angle chosen. The next approach would be to look at smaller regions of the heat release diagrams and perhaps curve fit the data, then take the derivative of the resulting function for the calculation of the heat release.

C. Discussion of Exhaust Emissions Results

In this section, the results of the emissions testing are discussed. The apparatus has been described in a previous section of this report. Emission data were obtained for the following fuels: base fuel (reference grade DF-2)

with the standard nozzle and modified nozzle, 20% ethanol microemulsion, 20% ethanol solution, 10% carbon black (Mogul L), and 20% carbon black slurry. Total particulates were collected during the base fuel and carbon black test series.

1. Comparative Steady State Exhaust Emissions

Throughout this report, the test fuels performance has been qualitatively compared and normalized to the base fuels. In this section, the test fuels are again compared to the base fuel. The majority of the emissions data is presented in the form of graphs of grams per indicated horsepower-hour versus the equivalence ratio. Equivalence ratio being defined as fuel-air ratio actual divided by the fuel-air ratio stoichiometric. An equivalence ratio greater than one is rich and less than one is lean. The plots are based on the equivalence ratio calculated from the inlet air and fuel measurements. Hydrocarbons are represented as HC.

Data for all three speeds and loads are represented by a least squares curve fit. A first order polynomial was found to yield the best fit. The lines, therefore, represent the overall emissions characteristics for three rpms (1000, 1500, and 2000), as compared to the base fuel.

As discussed earlier, the baseline runs were either interdispersed through the test matrix or complete series of baseline runs were performed before and after the test fuel.

Figure 45 through 50 show the gram per indicated horsepower for the 10% and 20% carbon black for HC, CO, and NO_x . Included is the baseline data curve fit. The particulate sampling train was not operational at the time the 20% Mogul L carbon black was tested.

Hydrocarbons and carbon monoxide for the base fuel are slightly less than both the 10 and 20 percent Mogul L carbon black results. The carbon black did produce higher NO_x than the baseline. It was, as depicted in Figures 45 and 48, 2 g/Ihp-hr higher for both fuels. This represents an approximate 50% increase for the 20 percent slurry and a 25% increase for the 10 percent slurry.

Figure 45. 10% Carbon Black NO_x Emissions.

Figure 46. 10% Carbon Black HC Emissions.

Figure 47. 10% Carbon Black CO Emissions.

Figure 48. 20% Carbon Black NO_x Emissions.

Figure 49. 20% Carbon Black HC Emission.

Figure 50... 10% Carbon Black CO Emissions.

Particulate matter was collected via the technique described in the Experimental Methods Section. This data is presented in Figure 51. Fourteen percent higher total particulate matter was collected as compared to the base fuel for the 10 percent carbon black fuel.

Baseline comparisons of 20% ethanol solutions and 20% microemulsions are presented in Figures 52 through 57. The FID hydrocarbons for both the solution and microemulsions were the same as the base fuel. Corrections for the lowered FID responsive for the oxygenated fuels were not made. Note that the base fuel runs encompass a greater range of equivalence ratios than the normal. For this series, a wider range of loads was run in the hope of obtaining a better mapping of the engine performance.

The CO curves are significantly different for both test fuels. At an equivalence ratio of 0.42 the base and test fuels produced equal amounts of CO as the g/Ihp-hr, but as the load was increased, the test fuels CO levels became significantly less than the base. At the maximum load condition, the 20% ethanol emulsion produced 50 percent, and the 20% ethanol solution produced 60% of CO produced with the base fuels. Smokemeter readings on a Public Health Type instrument were half of that obtained with the base fuel. The NO_x g/Ihp-hr for the test fuels were higher than the base. At the leaner equivalence ratios 40% to 50% more NO_x (g/Ihp-hr) was produced.

D. Engine Component Evaluation

Although wear studies were not included in the program, cursory evaluations of component malfunctions and wear were accomplished. As was indicated previously, the injection system was the most susceptible area for malfunction when using the slurry fuels. The two most common problems were sticking of the nozzle valve and plugging of the nozzle holes. Figure 58 is a photograph of an injection nozzle which has been cut in cross section. The nozzle, which was standard, malfunctioned during operation on the coal slurry; the nozzle valve stuck. The coal particles had gotten into the clearance between the valve and the body and formed a hard coating which caused the valve to seize to the body. These deposits can be seen in the top section of the nozzle body. The deposits were obviously formed by the heat and shearing action of

Figure 51. 10% Carbon Black Particulates Emissions.

Figure 52. 20% Ethanol Emulsion CO Emissions.

Figure 53. 20% Ethanol Emulsion NO_x Emissions.

Figure 54. 20% Ethanol Emulsion HC Emissions.

Figure 55. 20% Ethanol Solution CO Emissions.

Figure 56. 20% Ethanol Solution NO_x Emissions.

Figure 57. 20% Ethanol Solution HC Emissions.

the valve as the particles were forced into the clearance at very high pressure. This problem was eliminated by increasing the valve clearance, thereby allowing for sufficient leakage to prevent the deposit formation.

The injection pump performed perfectly for the entire second year of the project, except for the very last series of tests with the 10% slurry of Monarch 1300 carbon black. During these tests, it was noted that the rack position had to be continually increased to accomplish a constant fuel delivery rate. Examination of the injection pump plunger revealed that the clearance had increased dramatically, thus allowing for more and more leakage past the plunger. Figures 59 and 60 are photographs of the pump plunger and the pump cam, respectively. Both pieces show obvious signs of wear. It is felt that most of this wear occurred during the tests with the Monarch 1300 carbon black.

Figure 61 and 62 are photographs of the top of the piston and the thrust side of the piston, respectively. This piston has been in the engine for two years and shows no signs of wear. The cylinder liner showed only normal wear rates. The deposits, seen in Figure 61, are significant but they are not as bad as expected. The last fuels to be tested before the photograph were the Mogul L and Monarch carbon blacks.

Figure 63 is a photograph of the valves. The exhaust valve (right) was clean and free of deposits, while the intake valve (left) was coated with a hard, carbonaceous deposit. The presence of the deposit on the intake valve can only be explained by the flow of combustion products into the intake during the valve overlap period.

After two years of operation on a variety of hybrid fuels, the overall wear effects of these fuels appear to be minimal. The deposit formation tendencies are somewhat higher than diesel fuel but overall they do not appear to present deposit formation problems (the exception is the cellulose).

Figure 58. Photograph of An Injection Nozzle which has been cut in Cross Section.

Figure 59. Photograph of the Injection Pump Plunger.

Figure 60. Photograph of the Injection Pump Cam Lobe.

Figure 61. Photograph of the Top of the Piston.

Figure 62. Photograph of the Thrust Side of the Piston.

Figure 63. Photograph of the Intake (Left) and Exhaust (Right) Valves.

IV. SUMMARY AND PLANS FOR THIRD YEAR

Approximately fifty different fuel formulations have been tested in the CLR diesel engine. The test fuels have included solutions (of ethanol, various vegetable oils, and SRC-II), emulsions (of methanol and ethanol), and slurries (of flour, starch, cellulose, carbon black, coke, coal, etc.). These fuels have been tested at 1500 rpm and three loads with the CLR in the direct injection configuration.

It is felt that the feasibility of producing finished hybrid fuels containing alcohol has been demonstrated. One area in the use of alcohols which has not been addressed is the optimization of the surfactants. These fuels required the use of appreciable amounts of surfactant, greatly increasing the fuel costs. There appears to be a potential for reduction of fuel costs if the surfactant (composition and/or concentration) can be optimized. It was felt, however, that a major effort in that area was too specific for this program.

The various vegetable oils which were examined proved to be fairly good compression-ignition fuels. There were no major differences in the performance data between the various types. The types which were studied had very similar hydrogen-to-carbon ratios possibly accounting for the similarities in engine performance. Future tests will include the studies using minimally processed oils, with different hydrogen-to-carbon ratios. If these tests produce results similar to the tests with the high hydrogen content materials, then additional testing would not appear to be necessary due to the straight-forward utilization of these materials.

The solid substances which were formulated as slurries can be classified in three general groups. The ranking of these groups, in order of best performance in the engine, can be given as:

1. Carbons
2. Cellulose
3. Starches

Of the three, the carbons appear to have the most promise due to a number of findings including engine performance, energy content, burnout time, ashing or deposit formation, availability in the correct particle size range, and potential supply.

Figure 64 is an outline of the status of the various fuel categories discussed above. If any new potential candidates in the solution or emulsion categories become available during the third year of the program, it is felt that the investigation should be limited to cursory formulation and testing. The work required to produce finished economically viable fuels in either of these categories appears to be beyond the scope of this program.

During the initial testing of the slurries, it was realized that the combustion characteristics of the various materials was the primary criteria for future formulations. As was indicated previously, the carbon materials (coke, carbon black, coal) displayed the most promise as indicated by the performance of these materials in the engine. Another consideration is the availability of these materials, from a number of sources, in the correct size range. The starches and cellulose are soft fibrous materials which are difficult to grind or cut. In addition, these materials have very slow reaction rates leading to incomplete combustion in the engine and a decrease in the cycle efficiency. Because of the number of solid materials being tested, it was impossible to develop fully-stable slurries for each formulation. The stability criteria was simply that the slurry fuels remain homogeneous with mild stirring over the duration of the tests.

A number of questions must be answered before the slurry fuels can be advanced to the same point as the solutions and emulsions. These questions relate to the interaction of the solid particles and the liquid in the injection and atomization processes and the mechanisms of ignition and combustion. The physical form (particle sizes, oil absorption, agglomeration tendency) of the slurries are affected by the source and manufacturing techniques of the carbon materials; these characteristics affect the stability and pumpability as well as the combustion of the slurries. Based on the results of the initial testing and the considerations presented above, it is felt that future testing should be involved mainly with carbon slurries.

Figure 64. Status Review of the Various Hybrid Fuel Forms.

Figure 65. Experimental Plan for the Third Year of the Program.

The experimental plan, shown in Figure 65, allows for testing of new formulations of other materials if they become available. These other materials would receive more attention if they show as much promise as the carbons.

The third-year test plan includes studies of the effects of particle size and source of the carbon, concentration studies, and studies of the effects of the form of the carbon (agglomerations of very small particles or fines from carbon grinding). These parameters will be examined in relationship to the physical properties, the spray characteristics, the combustion characteristics and the stability of the slurries.

The experimental plan, shown in Figure 65, initially addresses the combustion problems in detail. The final stages of the work include attempts at producing stable slurries utilizing the combustion data to establish the carbon (other solid) forms to be used. The final evaluation will involve engine tests of the stable or partially stabilized slurries.

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