M. ENG. CHEM. ENG.

Kenneth Allan Le Mesurier

THE EFFECTS ON THE EXHAUST GAS COMPOSITION AND COMBUSTION PROCESSES OF THE ADDITION OF OXYGEN OR WATER VAPOR TO THE AIR INTAKE OF A DIESEL ENGINE

SHORT TITLE

The title to be placed on the bound copy of the thesis is:

ADDITION OF OXYGEN OR WATER VAPOR TO A DIESEL ENGINE

McGill University April, 1952

THE EFFECTS ON THE EXHAUST GAS COMPOSITION AND COMBUSTION PROCESSES OF THE ADDITION OF OXYGEN OR WATER VAPOR TO THE AIR INTAKE OF A DIESEL ENGINE

THE EFFECTS ON THE EXHAUST GAS COMPOSITION AND COMBUSTION PROCESSES OF THE ADDITION OF OXYGEN OR WATER VAPOR TO THE AIR INTAKE OF A DIESEL ENGINE

A Thesis by

Kenneth Allan Le Mesurier, B.Eng.

Chemical Engineering Laboratory - McGill University

Under Supervision of Dr. W. H. Gauvin

Submitted to the Faculty of Graduate
Studies and Research of McGill University,
in partial fulfillment of the requirements
for the degree of Master of Engineering.

McGill University
Montreal, Canada

April, 1952

ACKNOWLEDGEMENTS

The author wishes to express his sincerest appreciation to all who contributed in any way to the fulfillment of this work.

To Marchak Diesel Locomotives Limited, for providing the Diesel engine and oxygen required for this investigation.

To the Mechanical Engineering Department of McGill University, for the loan of various auxiliary equipment.

To Messrs. Andre Lefebvre and Douglas Lyons, for assistance in the installation and maintenance of equipment and the performance of the experiments.

TABLE OF CONTENTS

HISTORICAL REVIEW

II (continued)

EXPERIMENTAL SECTION

III (continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

HISTORICAL REVIEW

INTRODUCTION

The widespread and ever-increasing use of Diesel engines as a mode of locomotion has brought to the fore the problems presented by their toxic and evil-smelling exhaust gases. During the past 25 years, the Diesel engine has been found to be both mechanically and economically superior to many of the other types of combustion engines, both internal and external, commonly used in heavy-duty haulage trucks and locomotives, and hence, at the present time its use in these fields has become very extensive. However, in underground haulage operations, the use of Diesel engines has been severely curtailed, chiefly because of the problems presented by the noisome and noxious gases that issue from the engines as exhaust. Other difficulties, such as the fire hazards presented by the storage of large quantities of fuel oil or by the possible ignition of gaseous combustible materials, such as methane or coal gas, in contact with the hot engine or its exhaust, have also placed great restrictions on the use of Diesels underground. But the toxicity of the exhaust gases still remains the most pertinent reason inhibiting widespread adoption of Diesel powered locomotives in mines on this continent.

The hazards presented by the use of Diesel engines in mines and tunnels have been investigated extensively in Europe (21,30,66), and later, in America (3,7,8,30,39). As a result of these investigations, considerable research has been carried out in an attempt to eliminate these hazards. These efforts have been successful to the extent that, in general, Diesel engines can now be used in most underground mines with less fire hazard than any other internal-combustion or electrically operated engine (30,39). In regard to the exhaust gas problem, however, no satisfactory solution has been presented for the complete elimination of the dangers encountered when Diesel engines are operated in confined quarters.

In 1940, the U. S. Bureau of Mines initiated an extensive program of investigations into the Diesel exhaust gas problem (5,6,7,8,21,32,44,45). These investigations included a study of the nature of Diesel exhaust gases under both normal and abnormal conditions of engine operation. In addition, a study of the effects on exhaust gas composition of the addition of methane and hot exhaust gases to the intake air was made. The results showed that it was possible to use a Diesel engine in underground operations with safety, provided that the engine was operated properly, and adequate ventilation was available, both to remove the exhaust gases and to provide the engine with pure air (3,7,39).

Much research work has been done in an attempt to reduce or eliminate the obnoxious elements in Diesel exhaust gases by treatment of the gases before they are released to the atmosphere. Numerous patents have been issued in Europe and in America for exhaust conditioners. They consist mainly of liquid scrubbing devices which attempt to remove the objectional components of the exhaust gases by chemical absorption; and catalytic chambers and burners, which attempt to convert the undesirable exhaust gas constituents into less harmful substances. As far as is known, not one of these conditioners has proved efficient enough to obviate the requirement of additional ventilation in tunnels and mines where conditioner-equipped Diesels are being used.

In the reports issued by the Bureau of Mines during their investigation of the nature of Diesel exhaust gases, considerable emphasis was placed on the relation between the combustion process occurring in the engine cylinders and the exhaust gas composition. A study of the theories of the combustion process in relation to the exhaust gas composition indicates that, from a theoretical point of view, oxygen enrichment of the intake air should decrease the concentration of the obnoxious constituents in the exhaust gases, as well as possibly providing more information on the combustion process itself. In the light of these considerations, R. M. Cooper (24) made a preliminary investigation on the effects of oxygen enrichment of the intake air of a commercial Diesel engine. The scope of his experimental work was, however, too restricted to give a complete picture of the effect of oxygen enrichment on exhaust gas composition. An attempt was, therefore, made by the author to extend his data over a wider range of operating conditions, with the intention of making that picture more complete.

The injection of water, in liquid or vapor phase, into the cylinders of internal-combustion engines has been in use for many years, and many reports of the effects produced have been published. A survey of these reports, in conjunction with a study of the reactions between water vapor and the various combustion products, indicates that the addition of water vapor to the intake air of a Diesel engine should decrease the concentration of irritating and toxic constituents of the exhaust gases. As far as is known, the effect of water vapor addition on the exhaust gas composition of a commercial Diesel engine has not been previously studied.

This historical review is written with the intention of presenting a summary of all relevant theories pertaining to the combustion process occurring in a Diesel engine that have been presented up to the present time, as well as a description of the nature of Diesel exhaust gases and their relation to the combustion process. A brief review of water vapor reactions and the effect of water vapor on internal-combustion engines is also given. The mechanical aspects of Diesel engines are discussed only to the extent necessary to explain the several combustion theories.

I THE DIESEL ENGINE

1. GENERAL PRINCIPLES

The Diesel, or compression-ignition engine, may be defined as a prime mover actuated by the gases from the combustion of a liquid or pulverized fuel, injected in a fine state of subdivision into the engine cylinder, or an adjacent combustion chamber, at or about the conclusion of a compression stroke. The high temperature produced by the compression of air to an elevated pressure within the cylinder and chamber provides the sole means of igniting the charge. Following ignition, the charge burns and expands, thus converting the heat energy of the fuel into work (51). At the present time, liquid fuels are used almost exclusively.

Diesel engines operate on both two-stroke and four-stroke cycles, the cycles being similar to those usually associated with ignition engines. In the four-stroke cycle, there is an intake stroke, a compression stroke, an expansion or power stroke, and an exhaust stroke; in the two-stroke cycle, there is an intake-compression stroke and an expansion-exhaust stroke. The two-stroke cycle is slightly less efficient than the four-stroke.

Although the cycles are similar, several fundamental differences exist between spark-ignition and compression-ignition engines. Chief among these are the modes of ignition in the two types of internal combustion engines and the fact that the compression-ignition engine is not equipped with a carburetor: the fuel charge in each cylinder must be injected, evaporated, mixed with air, ignited, and burned in a few degrees of crankshaft travel. Also different is the nature of the cylinder charge: during the compression stroke air only is compressed, not an air-fuel mixture as in the spark-ignition engine.

Two general methods of fuel injection are presently used in Diesel engines: compressed air injection and solid injection. In the former, a blast of compressed air blows a measured amount of fuel into the combustion chamber near, or at, top dead center. The air blast tends to atomize the fuel, thus aiding in the formation of a uniform air-fuel mixture. In the latter and more common method, a measured amount of fuel is injected in the form of a solid jet under high pressure through a nozzle. This solid jet, upon striking the dense compressed air in the chamber, is immediately atomized. In either method, proper injection timing is accomplished by means of a cam shaft arrangement similar to that used in spark-ignition engines to actuate intake and exhaust valves.

To obtain rapid mixing of fuel and air, combustion chambers are designed to promote a high degree of turbulence in the gaseous charge. This air turbulence tends to disperse the atomized fuel throughout the chamber, and hence, aids in the rapid evaporation of the fuel and diffusion of its vapors.

2. THE FUEL-AIR RATIO

It is customary to report much of the compression-ignition engine performance data in terms of the prevailing overall weight ratio of fuel to air (or air to fuel), rather than on the basis of the quantity of fuel consumed per cycle because, although the volume of intake air used per cycle is constant, its weight is not constant and depends on its intake pressure and temperature. The combustion process and the resulting exhaust gases are profoundly affected by the value of this fuel-air ratio.

The composition of the fuel oils commonly used in Diesel engines is usually quite constant, and consists approximately of 86% carbon and 14% hydrogen, by weight. Therefore, for complete combustion of one pound of fuel, about 15 pounds of air are required, corresponding to a fuel-air ratio of 0.067. This value is called the stoichiometric, or chemically correct, ratio and henceforth, fuel-air ratios greater than this value will be designated as ratios (or mixtures) on the rich side, and smaller ratios will be designated as ratios on the lean side. Theoretically, maximum power should be obtained with a fuel-air ratio equal to the stoichiometric value but it is found in practice that use of this value is conducive to incomplete combustion, resulting in poorer efficiency and an increase in the concentration of the undesirable constituents of the exhaust gases (44). In actual operation, excess air is always present and most commercial Diesel engines are adjusted to operate on a maximum fuel-air ratio of approximately 0.05 at maximum rated capacity. When the engine is idling, the ratio is at a minimum.

3. DIESEL FUELS

Diesel fuels are intermediate distillation products of the fractional distillation of petroleum. They are mainly composed of hydrocarbons in the C_{14} - C_{16} range and have the following approximate ultimate analysis: carbon, 85.5 - 86.0%; hydrogen, 14%; sulfur, 0 - 0.4%; and traces of other elements. They have a higher heating value of about 19,000 - 20,000 (B.t.u.)/(lb.). Their physical properties, such as viscosity, molecular structure, etc., as well as their chemical properties, affect the combustion process profoundly (44).

II THE COMBUSTION PROCESS

1. GENERAL PRINCIPLES

To provide the necessary background to the problem of Diesel exhaust purification, a thorough knowledge of the nature and composition of the gases and their source, namely, the combustion process in the cylinders, is necessary. The exact nature and mechanism of the complex reactions occurring during a combustion process are still doubtful; however, several theories have been proposed which will be summarized in the following pages. On the other hand, the nature and composition of the exhaust gases are well known and are presented in another section.

For the purpose of analysis, the overall combustion process in a compression-ignition engine is usually divided into four phases: (a) a period of no apparent combustion activity -- the ignition lag; (b) inflammation of the fuel present, or self-ignition; (c) combustion of the fuel injected; (d) after-burning.

2. IGNITION LAG

The delay period observed subsequent to the beginning of fuel injection but preceding actual inflammation is called the ignition lag. It appears to be divided into two overlapping phases: (i) the physical delay, an endothermic process during which heating and partial evaporation of the liquid fuel, and diffusion of the fuel vapor, ensues; (ii) the chemical delay, an exothermic process during which the fuel and air react without the appearance of flame.

(i) Physical Delay

During this phase, mixture formation occurs. Two terms introduced by Boerlage and Broeze (11,12) may be conveniently used in mixture formation discussion: 'microstructure', the local consideration of the fuel particles in regard to size and whether they are in the liquid or vapor phase; 'macrostructure', the overall distribution of the fuel in the combustion chamber, without regard to whether vaporization has occurred or not.

According to Boerlage and Broeze (11,12), to obtain a good microstructure, the fuel should be injected in such a manner that very fine atomization results. The small droplets will then evaporate quickly on contact with the hot (about 1000°F.) air, hot walls and, if injection continues into the actual inflammation period, the hot combustion gases (up to 3600°F.). In solid injection engines, the following factors have been found to favor the formation of a good microstructure: high injection pressure and air density in the combustion chamber, small injector orifices, and low fuel viscosity. The final microstructure is completed by diffusion of the vapors formed by evaporation throughout the fuel-air mixture.

The macrostructure is obtained with the aid of turbulence in the combustion chamber. One effect of turbulence is to strip the injected fuel jet of its very fine droplets and vapors and distribute them throughout the chamber, thus aiding the formation of a homogeneous fuel-air mixture (11). Excessive turbulence, however, may have the adverse effect of chilling the combustion mixture or even of centrifuging fuel droplets out to the walls where incomplete combustion may take place (59,74).

(ii) Chemical Delay

The fuel vapors formed by evaporation attain the temperature of the surrounding air almost instantaneously and then commence to react with the oxygen in the air. Heat is liberated during this flameless reaction. At a certain locality, or possibly, localities, where the fuel-air ratio is satisfactory, sufficient heat is developed and a flame nucleus appears. Complete inflammation follows immediately. The chemical delay is thus determined by the velocities of the self-ignition, or pre-flame, reactions. Once flames appear the evaporation of the remaining fuel occurs very rapidly (10,11,12,28).

Since the incidence of ignition is markedly localized, the overall fuel-air ratio is not nearly as important in the self-ignition process as might be expected, i.e., there is no critical value for the overall fuel-air ratio which determines the ease with which ignition occurs. Because of the considerable degree of heterogeneity existing in the combustion chamber, the local fuel-air ratios throughout the combustion mixture vary considerably, and apparently, only those local ratios within a specific range of values are suitable as centers of ignition. There is some evidence to indicate that flame nuclei appear at spots where the fuel vapor-air mixture composition is about 150% of the theoretical value (liquid fuel droplets excluded)(11).

It appears that, from considerations of power, fuel economy, carbon deposits, and exhaust gas smoke and smell, the shortest possible ignition lag is desirable since it increases the overall combustion reaction velocity (9,12). It has been found that not only the temperature but also the pressure affect the delay period (49,63), and Lonn (60) reports that the delay is determined primarily by the partial pressure of the oxygen in the fuel-air mixture.

3. PHYSICAL ASPECTS OF IGNITION LAG

During the lag, the pressure in the combustion chamber is more or less constant. The temperature decreases somewhat during the physical delay but rises again during the chemical delay. The occurrence of flame is marked by sudden pressure and temperature increases to maximum values (600 - 800 psi. and about 3600°F. respectively) (12).

4. SELF-IGNITION

Self-ignition may be defined as the process of chemical reactions taking place during the chemical delay which results in inflammation. Several theories have been proposed to explain the mechanism of these reactions and how they are initiated.

5. THEORIES OF SELF-IGNITION

(i) The Hydroxylation Theory

This theory, originated by H.E.Armstrong and developed by W.A.Bone and collaborators (15,17,18), postulates that a slow oxidation of the fuel molecule takes place through a series of hydroxylation reactions in which alcohols, aldehydes, and organic acids are successively formed as intermediate products; the final products being carbon monoxide, carbon dioxide, water, and hydrogen. This theory proposes that the oxygen in the air attacks the hydrogen atoms at the ends of hydrocarbon chains of the fuel and a degradation of the chains ensues until only carbon monoxide, carbon dioxide, water vapor, and hydrogen remain, the relative quantities of each depending essentially on the amount of excess air present. For example:

$$RCH_2CH_3 \xrightarrow{\text{oxidation}} RCH_2CH_2OH \xrightarrow{\text{oxidation}} RCH_2CHO + H_2O$$

$$RCH_2CHO \xrightarrow{\text{oxidation}} RCHOHCHO \xrightarrow[\text{decomposition}]{\text{thermal}} RCHO + HCHO$$

$$RCHO + HCHO \xrightarrow[\text{decomposition}]{\text{thermal}} RCHO + H_2 + CO$$

$$H_2 \xrightarrow{\text{oxidation}} H_2O \qquad CO \xrightarrow{\text{oxidation}} CO_2$$

This theory is in good agreement with the experimental results obtained from analyses of exhaust gases, but not with the kinetic considerations of the reactions. Moreover, it does not specify the mechanism by which the initial oxygen attack occurs; presumably, a termolecular collision between two hydrocarbon molecules and an oxygen molecule is required to initiate this reaction (64).

(ii) The Peroxide Theory

At about 200°C. alkyl molecules are capable of forming unstable alkyl peroxides upon collision with oxygen molecules. These peroxides readily explode exothermally, producing alcohols, aldehydes, and organic acids (62,73). This is, in essence, the peroxide theory of self-ignition. It differs from the hydroxylation theory in that it proposes the formation of an intermediate compound, a peroxide, in the initial oxidation of the alkane molecule to the alcohol; thus obviating the assumption of an initial termolecular reaction, as required by the hydroxylation theory mechanism. Several variations of this theory have been proposed in regard to compression-ignition engines.

Callendar (23) proposes that the fuel droplets suffer a distillation in the combustion chamber resulting in the formation of minute droplets of high-boiling constituents surrounded by vapor layers of the more volatile constituents. Alkyl peroxides formed in the vapor layers about the droplets would then be able to recondense, along with some of the vapors, on the surface of the liquid droplets and persist to higher temperatures where they would explode, causing the liquid drops in turn to ignite and act as flame nuclei for the rest of the mixture.

Tausz (73) suggests that partial decomposition occurs before the unstable peroxides are formed, and explosion of the peroxides at the spontaneous ignition temperature of the fuel results in inflammation. Le Mesurier and Stansfield (58) hold that the heat developed by the decomposition of the peroxides gradually raises the temperature and hence, the reaction velocity, until inflammation results.

An energy chain mechanism has been proposed by Egerton (31), according to which an energy transfer occurs upon the decomposition of the active peroxide into active products (aldehydes and water). These active products pass on their energy by collision with other fuel molecules and activate them in turn. However, this proposal does not appear to satisfy the kinetics of the reaction: introduction of a diluent inert gas should slow down the reaction; in actual fact, it does not (64).

Boerlage and Broeze (12) suggest the possibility that "firstly, a tendency to form unstable oxygen compounds at low temperatures plays no role in the ignition process, and secondly that the role of such compounds, if pre-formed, is merely that of introducing active oxygen which may react, after decomposition of the compound, with such active parts of the fuel as are in want of oxygen".

Several arguments against the peroxide theory have been advanced (12). (a) Substances which form peroxides and which, in small quantities, lower the spontaneous ignition temperature of a fuel at atmospheric pressure, do not do so at higher pressures, i.e., at pressures prevailing in compression-ignition engine combustion chambers. (b) Tetralin, a substance which is prone to peroxidation even at normal temperatures, and the peroxide of which has a substantial effect in diminishing the lag of a fuel to which it is admixed, shows no tendency to ignite at all when used as a fuel by itself. (c) It is believed that the time available between fuel injection and fuel ignition is insufficient for the necessary concentration of peroxides to be formed.

(iii) The Atomic Chain Theory

This theory, proposed by Norrish (64), attempts to explain the initial oxygen attack occurring in the hydroxylation theory.

Norrish suggests a chain mechanism in which atomic oxygen, formed by surface reactions, acts as the chain carrier. The overall process can be indicated as follows:

$$\begin{array}{lll}
\text{Induction period:} & RCH_3 + O_2 \xrightarrow{\text{surface}} RCHO + H_2O \\
 & RCHO + O_2 \longrightarrow RCOOH + O \\
\text{Reaction period:} & RCH_3 + O \longrightarrow RCH_2. + H_2O \\
 & RCH_2. + O_2 \longrightarrow RCHO + O \\
\text{Termination:} & RCH_3 + O \xrightarrow{\text{surface}} RCH_2OH \\
\text{Or:} & O \xrightarrow{\text{surface}} \frac{1}{2}O_2
\end{array}$$

Recently, Gaydon (36,37), by spectroscopic analysis of standing flames of burning hydrocarbons, demonstrated that very little atomic oxygen is present during the pre-flame reaction period, thus offering strong evidence against the atomic chain hypothesis.

(iv) Thermal Decomposition Theories

Several decomposition theories have been advanced, the most important of which is probably the thermal stability theory of Boerlage, Broeze, and Van Dijck (13). They suggest that total vaporization of the fuel is unnecessary and that the reaction initiating ignition is due either to the initial stages of cracking, followed by an evolution of heat by the reaction of the free radicals formed with oxygen, or to oxygen reacting with the oil molecules which are in a highly strained state just prior to breaking down, and may be considered as being abnormally sensitive to oxygen. This theory is substantiated by the existence of a definite relation between the initial cracking velocities of fuels and their ignition quality (cetane number) (14). It has been found that oxygen apparently catalyses the decomposition process (12).

(v) The Carbon Nuclear Theory

It is a well-known fact that free carbon particles exist in the combustion chamber along with the fuel-air mixture, the particles originating from cracking reactions of the fuel and, possibly, of the lubricating oil. It has been realized by many that these particles, heated red hot by the exothermic oxidation reactions taking place about them, could act as centers of ignition when the fuel-air ratio near them was sufficient.

Recently, R.O.King (52) presented a theory in which the carbon particles acted not only as heat sources for flame nuclei but also as reaction surfaces. In effect, he substitutes the liquid fuel droplets of the Callendar theory (23) by carbon particles; the products of incipient oxidation, e.g., peroxides, formed in the fuel vapor-air mixture, are assumed to condense on the surface of the particles, react there and raise the temperature sufficiently to cause inflammation in the appropriate fuel-air mixture. King bases his theory on the very safe assumption that pre-flame reactions are essentially surface reactions and that the carbon particles are simply added surfaces on which reaction can take place.

The important difference between the theories of Callendar and King is that the latter applies to vapor phase self-ignition, whereas the former is restricted to partial liquid phase reactions.

The common view at present is that evaporation of the fuel takes place very soon after the latter enters the combustion chamber, and consequently, vapor phase reactions predominate.

6. THEORIES OF COMBUSTION

(i) The Hydroxylation Theory

This theory has already been presented with the theories of self-ignition, since it was originally proposed to cover the complete combustion process, including ignition. It has been found that conditions are most favorable for hydroxylation when the fuel is well vaporized and mixed with air in excess of stoichiometric quantities. A blue flame results (carbon monoxide and carbon dioxide radiations) which has no tendency to soot either from overrichness or chilling (11). When chilling of the flame occurs (possibly from excessive turbulence), there is a possibility of the process being arrested at an intermediate stage, leaving products such as carbon monoxide, aldehydes, and organic acids which make the exhaust gases acrid and noxious (10). Overrich mixtures favor the formation of carbon monoxide and hydrogen (11).

(ii) The Destructive Combustion Theory

This theory, generally attributed to Aufhauser (4), proposes that a decomposition of the fuel by the heat of the flame occurs, followed by oxidation of the destruction products. The conditions favorable for this process are very similar to those occurring in a compression-ignition engine, namely, very sudden exposure of the fuel to flame temperatures resulting in decomposition of the fuel molecules before oxidation. A yellow flame results (double bond radiations) from glowing carbon particles forming soot when chilled and when the mixture is too rich. As in the hydroxylation theory, overrich mixtures favor the formation of carbon monoxide and hydrogen (11,12).

The destructive combustion theory appears to explain combustion in the Diesel engine. However, according to Bone (15) the decomposition products, viz., simple hydrocarbons, burn mainly to carbon monoxide. But Drinkwater and Egerton (29) have shown that carbon dioxide is the main carbon oxide formed, thus disproving the sole existence of destructive combustion. In cold engines, aldehydes and organic acids are produced, indicating that hydroxylation is present. Because of these facts, Haslam and Russel (41) believe that both hydroxylation and destructive combustion occur in compression-ignition engines simultaneously. Sass (69) suggests that partial decomposition takes place, followed by hydroxylation of the fragments.

7. AFTER-BURNING

After the bulk of the fuel has been burned, a period of decelerating combustion, called 'after-burning', occurs. The fuel that has not found oxygen, or whose rate of oxidation has been too low during the burning of the bulk of the fuel, now undergoes combustion.

After-burning is detrimental from both the mechanical and chemical points of view. It decreases engine efficiency, because heat is developed late in the expansion stroke and cannot be completely utilized. Moreover, the process is one of incomplete combustion because the oxygen supply has been nearly exhausted; thus, the amount of undesirable components in the exhaust gases is increased.

Boerlage and Broeze suggest three possible causes of afterburning: dissociation of the fuel, about which little is known; imperfection of the mixture, i.e., faulty microstructure due to slow evaporation of big drops, or faulty macrostructure due to ineffective turbulence; and chilling of the combustion process by contact with cold cylinder walls (12).

III THE EXHAUST GASES

1. GENERAL NATURE

The Diesel exhaust gases consist essentially of nitrogen, oxygen and carbon dioxide, with relatively small amounts of several other gases and solid material. The minor constituent gases are: various aldehydes, carbon monoxide, hydrogen, methane, oxides of nitrogen, oxides of sulfur, and water vapor. Traces of other substances, e.g., organic acids, may also be present. These minor constituents, although present in small quantities, have a great practical importance since some of them have irritating odors, and some are highly toxic. The solid material consists essentially of carbon soot, usually very finely dispersed, but sometimes quite dense. A discussion of each constituent is given below.

2. ALDEHYDES

Aldehydes in the exhaust gases of Diesel engines result from incomplete oxidation of the fuel. They are characterized by their irritating, though not necessarily toxic, effect on eyes and respiratory organs, and are responsible for the 'acrid' odor associated with Diesel exhaust gases.

From the small amount of data available, aldehyde concentration, expressed in terms of formaldehyde, may vary from zero to 50 ppm. by volume, depending on the type of engine and operating conditions. The concentration increases with decreasing fuel-air ratio, the highest values being obtained at the lowest possible fuel-air ratio, i.e., when the engine is idling. In the vicinity of the chemically correct ratio their concentration is very low, and sometimes undetectable for certain engines (39,44).

In the light of the existing combustion theories, aldehydes are formed only in the early stages of hydroxylation, and not at all in destructive combustion. It is therefore believed that the appearance of aldehydes in exhaust gases is due to chilling of the combustion process which causes the hydroxylation of the fuel to stop at the intermediate aldehyde stage. Chilling occurs in lean fuel-air mixtures due to the lower combustion temperatures prevailing, but chilling of richer fuel-air mixtures is probably caused by the cool cylinder walls and/or excessive turbulence (39,44).

The aldehyde concentration is increased by the addition of carbon dioxide or natural gas (85% methane) to the intake air (32). The addition of hot exhaust gases has no significant effect on aldehyde formation (5).

Although aldehydes are not noted for their toxicity, they have an irritating and obnoxious odor that is detectable at concentrations as low as 10 ppm. (32,44).

3. CARBON DIOXIDE

Carbon dioxide results from the complete oxidation of the carbon in the fuel; it is one of the end products of both hydroxylation and destructive combustion. Its important physiological effect is that it tends to increase the lung ventilation, or rate of breathing, of persons exposed to it for any length of time (39,44).

From the data available (44), the carbon dioxide concentration appears to be directly proportional to the fuel-air ratio. It reaches a maximum of about 14% by volume at the chemically correct fuel-air mixture, and then decreases as the mixture becomes richer.

4. CARBON MONOXIDE

Carbon monoxide is a colorless, odorless, extremely toxic gas; it is a product of the incomplete oxidation of carbon in the fuel.

From the available data (39,44), the carbon monoxide content of the exhaust gases may be as high as 6 or 7% for some engines operating with fuel-air ratios on the rich side. In general, the carbon monoxide concentration is a minimum on the lean side, increasing as the mixture becomes richer, and also when the mixture becomes very lean. The carbon monoxide content of a Diesel engine exhaust gas operating normally is usually less than 1%, and is considerably lower than that of a similarly rated gasoline engine. The increase in carbon monoxide for rich mixtures is believed to be due to insufficient oxygen being available for complete combustion. The increase when the mixture becomes very lean is probably due to chilling which prevents oxidation from going to completion.(44).

The carbon monoxide concentration is increased by the addition of hot exhaust gases, carbon dioxide, or natural gas (85% methane) to the intake air (5,32).

Carbon monoxide is toxic to the extent that a concentration of 0.20 - 0.25% of the air breathed causes unconciousness in about thirty minutes; a concentration as low as 0.04% causes headache and discomfort within two to three hours (39).

5. HYDROGEN AND METHANE

These gases occur in very small quantities. The question of their toxicity or explosion hazards is negligible. Small amounts have been reported to be present in the exhaust gases for fuel-air ratios on both sides of the stoichiometric ratio. Small quantities of hydrogen may be produced by the decomposition of water vapor formed during the combustion process or in the intake air (44).

6. NITROGEN

This gas, composing 79% by volume of the intake air, does not take part in the combustion process, and hence comprises the greatest percentage of the exhaust gases. A very small quantity is oxidized, however, resulting in the formation of small amounts of the toxic oxides of nitrogen (39,44).

7. OXIDES OF NITROGEN

These gases, nitric oxide, nitrous oxide, and nitrogen dioxide, are a result of certain high temperature reactions occurring between the oxygen and nitrogen of the air, along with the other combustion processes. Nitric oxide (NO) and nitrogen dioxide (NO_2) are extremely dangerous gases because they tend to form nitrous and nitric acids in the respiratory passages of those exposed to them; nitrous oxide (N_2O) is more or less harmless unless it is present in large quantities, whence it has a soporific effect. NO and N_2O are colorless; NO_2 is reddish-brown. The presence of N_2O in exhaust gases from internal combustion engines has never been proven.

The reaction between nitrogen and oxygen to form NO is endothermic, and is favored by high temperatures and an excess of oxygen. NO_2 is formed at lower temperatures by the oxidation of NO. NO_2 is also formed endothermically from nitrogen and oxygen at high temperatures, but it decomposes to NO which is more stable at those temperatures. Although some NO occurs in the exhaust gases, NO_2 predominates since it is more stable. In normal ranges of operation, the concentration of nitrogen oxides (expressed as equivalent NO_2) varies between 200 and 600 ppm., by volume (44). A review of the kinetics and thermodynamics of the formation of NO in Diesel engines has been presented by Cooper (24).

The concentration of nitrogen oxides appears to be a maximum at intermediate fuel-air ratios. The fuel-air ratio at which this maximum occurs is dependent upon the type of engine and the engine speed. An explanation of the variation of the concentration of nitrogen oxides can be obtained from the fact that both high temperatures and excess oxygen favor the formation of NO. As the fuel-air ratio increases, the temperature of the combustion process increases, and the formation of NO also increases. But when intermediate fuel-air ratios are reached, the effect of the excess oxygen is decreased, and hence the formation of NO is also decreased (39,44).

The concentration of nitrogen oxides is decreased by the addition of hot exhaust gases to the intake air (5). The addition of natural gas (85% methane) to the intake air does not affect the nitrogen oxide concentration significantly (32).

8. OXIDES OF SULFUR

Any sulfur in the fuel oil is oxidized to sulfur dioxide and sulfur trioxide which appear in the exhaust gases. Since fuels can be obtained that are almost entirely free of sulfur, the oxides of sulfur are of little concern and will not be discussed further.

9. OXYGEN

The oxygen content of the exhaust gases is always relatively high -- from 7 to 18% -- since excess air is always used in Diesel engines. Its concentration decreases with increasing fuel-air ratios. If a Diesel engine is to be used in a confined space, adequate ventilation must be maintained to replace the oxygen consumed by the engine as well as to remove the exhaust gases (39,44).

10. SMOKE AND SOOT

Exhaust smoke is composed almost entirely of aldehydes and minute carbon particles suspended in the exhaust gases. It originates from two sources: lubricating oil that has been carried past the piston rings into the combustion chamber, or from excess oil on the inlet valve stems; and improper combustion of the fuel oil.

Smoke from the first source is usually a blue color and has an obnoxious odor; smoke from the second source may be white, blue, or black, or a combination of the three. The white smoke comes from very slight oxidation of the fuel spray, or from slow combustion. Blue smoke, consisting mostly of aldehydes, results from the combustion of chilled fuel-air mixtures such as occur with fuel droplets that have struck the cool chamber walls. Black smoke, composed mostly of minute carbon particles, is produced by the combustion of overrich mixtures, and may be due to faulty injection, or improper mixing of the fuel and air (75). Certain mechanical features of compression-ignition engines are often responsible for excessive exhaust smoke; thus, some Diesels are inherently more smoky than others.

11. WATER VAPOR

Water is one of the products of complete combustion of Diesel fuel oils, and hence, is produced in relatively large amounts as vapor in the combustion chamber. It is condensed, however, in the exhaust cooling system and, consequently, does not represent a large proportion of the exhaust gases. A small quantity of water vapor probably dissociates into hydrogen and oxygen at the high temperatures prevailing in the combustion chamber.

IV PREVIOUS INVESTIGATIONS OF OXYGEN ENRICHMENT

The operation of internal-combustion engines using intake air that had been enriched by the addition of pure oxygen, has been studied by a few investigators with the intention of improving the operating efficiency of the engines. As a result of these experiments, several patents have been issued describing ways and means of enriching the intake air of Diesels to give increased power and efficiency (76). Other advantages claimed by the patents include a reduction of carbon deposits in the cylinder, and the possibility of utilizing heavier grades of fuel.

References to oxygen enrichment of internal-combustion engines in the research literature are infrequent. In 1940, Schweitzer (71) reported the results of his investigations on the effect of increasing the oxygen content of the intake air of a four-stroke, C.F.R. Diesel engine from 21% to 45% by volume. The engine was run at 890 R.P.M., and the exhaust temperature was found to increase from 620°F. to 1000°F., while the ignition lag was shortened by 47%. Other observations were: an increase of ten cetane numbers in the ignition quality of the fuel; increases in the indicated and brake horsepower, maximum cylinder pressure and fuel consumption per horsepower-hour. In 1946, Hawthorne (42) reported that the addition of oxygen to an aircraft engine increased its speed 30 to 35 mph. Kuzminov (54), in 1947, stated that, from theoretical considerations, oxygen enrichment is more applicable to gas engines than either Diesel or carburetor type engines.

However, up to 1950, no data had ever been published concerning the effect of oxygen enrichment on the composition of internal-combustion engine exhaust gases. In that year, Cooper (24) reported the results of preliminary investigations along those lines on a commercial, four-stroke, Diesel engine. His investigations covered the effect of a constant oxygen enrichment at constant speed and variable brake loads, and that of a variable oxygen enrichment at no load and medium load, both at constant speeds. He found that, for a constant enrichment of 0.8% (i.e., the enriched intake air contained 21.8% oxygen instead of the normal 21.0%), a decrease resulted in both the carbon monoxide and aldehyde concentrations, accompanied by an increase in the oxides of nitrogen concentration in the exhaust gases. However, as the oxygen enrichment was increased to a maximum of 3.2%, the aldehyde concentration appeared to pass through a minimum at about 1% enrichment and began to increase; the carbon monoxide concentration appeared to approach a minimum limiting value, and the oxides of nitrogen increased steadily. A small temperature increase in the exhaust gases was also observed for each successive enrichment. These results were obtained for brake loads varying from no load at 792 R.P.M. to about 22 horsepower at a constant speed of 1000 R.P.M. Cooper concluded that the main reason for the observed trends appeared to be an increase in the temperature level at which the combustion reactions occurred. He stated that this increase in temperature was due to decreased heterogeneity of the fuel-air mixture, caused by the addition of extra oxygen, which led to shorter ignition delays and decreased after-burning, and hence to higher reaction velocities and shorter reaction times. Obviously, this investigation must be extended to include greater brake loads at higher speeds and larger oxygen enrichments before any final conclusions can be drawn concerning the effect of oxygen enrichment on the composition of Diesel exhaust gases.

V PREVIOUS INVESTIGATIONS OF WATER VAPOR ADDITION

The addition of water vapor to internal-combustion engines has been in use for many years. Water was added to the fuel-air mixture of a spark-ignition engine as far back as 1866 (38), and is still being introduced into many automobile and aeroplane engines at the present time. The reasons presented in favor of its addition to spark-ignition engines are that it acts as an internal coolant, permitting greater power output, and that it suppresses knocking and makes it possible to use lower octane fuels in high compression ratio engines (38,53,68). The same effect is obtained whether the water is added as a liquid or as a vapor (68). A satisfactory explanation, accompanied by experimental proof, of the effect of water vapor on the performance of spark-ignition engines could not be found in the research literature.

Water vapor has been added to semi-Diesels to increase their power outputs. Sass (69) attributes this effect to dissociation of the water vapor, the products of which lead to a more complete combustion of the fuel. Le Mesurier and Stansfield (57,58) contend that the effect is one of cooling the hot bulb; thereby preventing pre-ignition and subsequent loss of power.

There have been reports that the addition of water vapor to a semi-Diesel decreases carbon formation (57), but the effect of water vapor addition to the intake air on the exhaust gas composition of internal-combustion engines has apparently never been studied, so far as can be ascertained from the research literature.

VI WATER VAPOR AND COMBUSTION

The influence of water vapor on the characteristics of combustion processes has been observed and investigated for many years. In 1880, H.B.Dixon (27) first reported that the presence of water vapor in a mixture of carbon monoxide and oxygen (in the stoichiometric ratio of 2:1) definitely aids the ignition of that mixture by an electric spark. Bone and Weston (17) studied this phenomenon very thoroughly and found that the ease of ignition of a carbon monoxide-oxygen mixture by a spark was proportional to the amount of water vapor present, up to saturation. In 1927, Bone and Townend (16) reviewed all research done on the effect of water vapor on the spark-ignition and combustion of a carbon monoxide-oxygen mixture. They concluded that the presence of water vapor, although not essential, definitely aided ignition and combustion. They reported no satisfactory theory to explain the phenomenon.

In 1928, Bonhoeffer and Reichardt (20) reported that, at temperatures above 1200°C. (2200°F.), water vapor dissociated into hydrogen and hydroxyl (OH) radicals as well as into hydrogen and oxygen. This immediately suggested the possibility that the hydroxyl radical was responsible for the ease of ignition of the carbon monoxide-oxygen mixtures in the presence of water vapor.

Reactions of dissociated water vapor have been studied by many investigators in the last twenty years. In 1929, Urey and Lavin (77) observed that dissociated water vapor had a marked reducing action on many substances, and, in 1931, Lavin and Reid (56) reported that dissociated water vapor readily converted liquid vegetable oils to solids. Thus, dissociated water vapor appeared to be able to act both as a reducing and an oxidizing agent. This was confirmed in 1931 and in succeeding years, when several investigators reported that carbon monoxide could be converted to carbon dioxide by dissociated water vapor, the amount converted being reported as high as 65% (46, 55,67). The apparent explanation for this dual role played by dissociated water vapor is that the hydrogen produced by the dissociation is the reducing agent, and the hydroxyl radical is the oxidizing agent. The suggestion that atomic oxygen, formed as an intermediate product in the dissociation of water vapor, was the true oxidizing agent has been refuted by Harteck and Kopsch (40) who demonstrated that atomic oxygen was a very poor oxidizing agent.

The effects of the presence of water vapor in the ignition and combustion of methane and other hydrocarbons has also been studied. Jones and Seaman (48) found that the ignition temperatures of dry methane-oxygen mixtures were lowered by the presence of water vapor. David and Mann (25), in 1943, reported that the flame temperatures of many burning hydrocarbon mixtures have been raised by the presence of moisture in the mixtures. No theoretical explanations were given for these phenomena. Another manifestation of the effect of water vapor on combustion is mentioned in a report by Boerlage and Broeze (12): if steam is injected into the air-holes of an oil-burning lamp, the flame immediately becomes soot-free and less radiant; thus, "the addition of water vapor influences the chemical processes in the direction of hydroxylation".

In 1947, Frank-Kamenetzky (34) reported the effect of the presence of water vapor and hydrogen on the formation of nitric oxide during the explosion of mixtures of carbon monoxide, oxygen and nitrogen. He found that small amounts of water vapor, or hydrogen, caused an increase in nitric oxide formation, but that further additions of water vapor resulted in a decrease. This latter effect was not observed with hydrogen. All the observations were made at a pressure of 200 mm. of mercury.

In brief, it may be said that the presence of water vapor in combustible mixtures definitely improves the ignitability of the mixtures, by spark-ignition at least, and that dissociated water vapor is a good oxidizing agent. It appears, although it has not been proved conclusively, that it is not the water vapor itself that increases the ease of ignition of combustible mixtures, but rather the products formed from the dissociation of the water vapor by the high temperatures of the ignition source.

EXPERIMENTAL SECTION

I EQUIPMENT AND PROCEDURE

The equipment used in this investigation consisted essentially of a Diesel engine equipped with a dynamometer and the apparatus necessary for the chemical analysis of the exhaust gases. A photograph of the complete set-up is shown in Fig. 1. .

1. THE DIESEL ENGINE AND ACCESSORIES

The Diesel engine was a standard Hercules, four-stroke engine, model DOOD, the characteristics of which are tabulated in Table I.

TABLE I

ENGINE CHARACTERISTICS

Type	Four-stroke cycle
Number of cylinders	Four
Cylinder bore, inches	$4\frac{1}{4}$
Piston stroke, inches	$4\frac{1}{2}$
Piston displacement, cu. in.	255
Maximum rated speed, R.P.M.	2600
Maximum rated B.H.P. (without accessories)	79
Fuel pump	Individual pump for each cylinder; fuel delivery controlled by pump plunger by-pass.
Type of injection valve	Pintle nozzle
Opening pressure of injection valve discharging into air at atmospheric pressure, lb. per sq. in.	1650
Combustion system	Spherical turbulence
Cooling system	Positive circulation, thermostatically controlled
Lubrication	S.A.E. 30

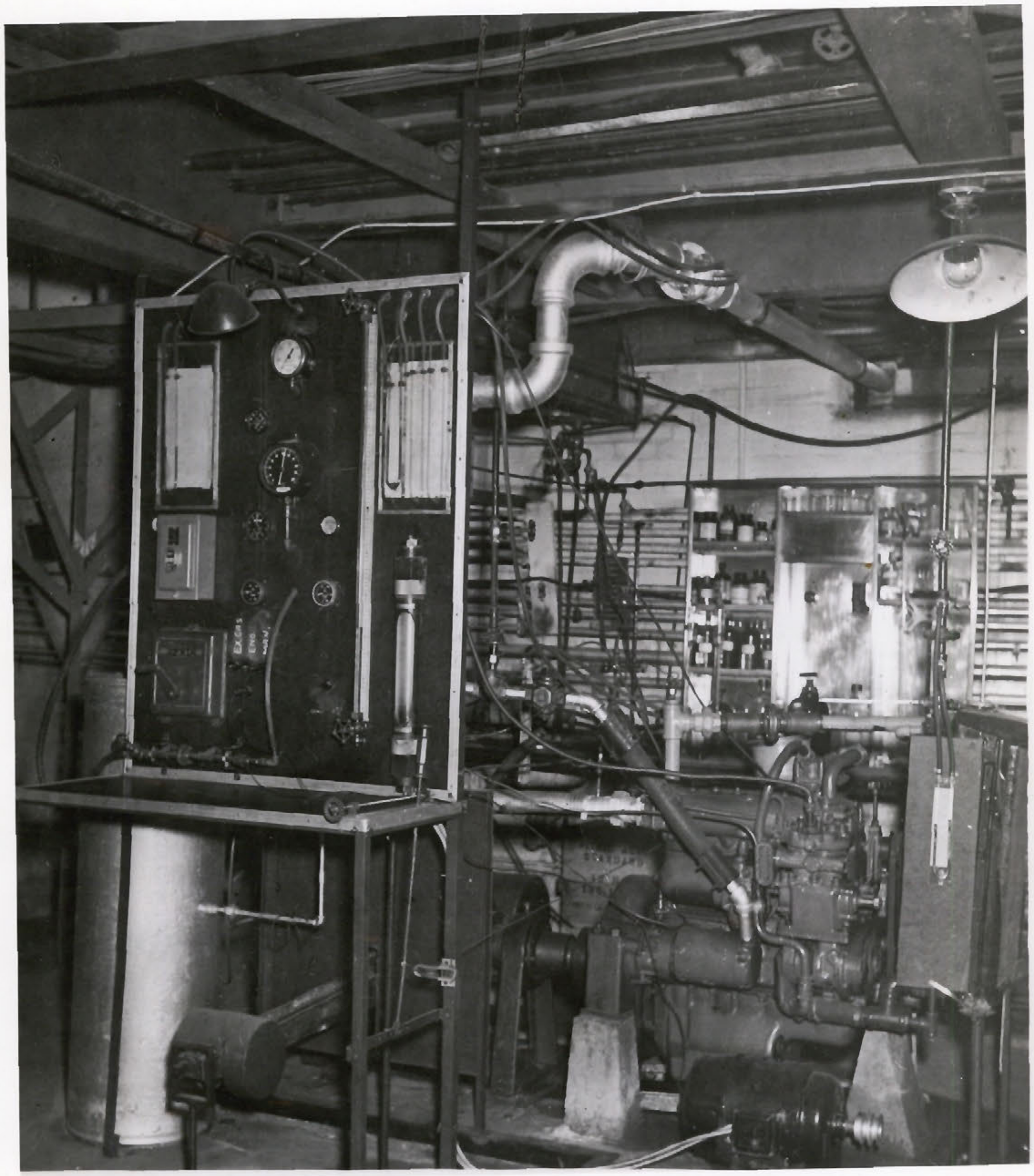

FIG. 1. THE DIESEL ENGINE, CONTROL PANEL, AND ACCESSORIES

The engine was mounted on three short concrete pedestals, and was anchored firmly by six 12-inch bolts passing through the pedestals to the concrete floor beneath. Rubber pads, placed between the supports and the engine proper, helped to minimize vibrations.

The engine was started by means of a small compressed air turbine. The compressed air, obtained from a laboratory compressor, was stored in a steel cylinder adjacent to the engine, and was admitted to the turbine through a fast-acting, on-off, check valve. The exhaust gases, leaving the engine via the exhaust manifold, were conducted through five feet of 2-inch pipe followed by nineteen feet of 3-inch pipe to the atmosphere outside the laboratory. Fuel was supplied by gravity feed from a calibrated fuel tank equipped with a graduated sight-glass. The fuel used was standard Diesel fuel which met the American Society for Testing Materials specifications. Its properties are listed in Table II.

TABLE II

FUEL PROPERTIES

Specific gravity, °A.P.I. @60°F.	35.8
Flash point P.M., °F.	160
Viscosity S.U. @100°F.	36
Cloud point, °F.	-35
Pour point, °F.	-50
Dissolved soaps, mg.	2.1
Sulfur, Bomb, %	0.490
C.C. residue on 10% bottoms, %	0.047
Diesel index	52.8
Cetane number	44
I.B.P., °F.	385
F.B.P., °F.	635
Higher heating value, B.t.u./lb.	19,700
Carbon, wt. %	85.4
Hydrogen, wt. %	13.6

To make satisfactory heat measurements on the engine the fan was disconnected and cooling was accomplished by means of a steady stream of water passing through the engine cooling system. Water from the mains was supplied to the engine through standard ½-inch pipe, and its rate of circulation was determined by means of a calibrated orifice. The cooling-water rate was adjusted to maintain the temperature of the water leaving the engine constant at 50°C. (122°F.).

The engine was coupled directly to a dynamometer which consisted of a modified Froude water-brake. The water-brake had a four-foot arm and a 200-pound counter-weight, and was mounted on a steel plate which was bolted to the floor. The engine loads were varied by adjusting the water level in the brake, the loads being measured by balancing the brake with weights placed on the end of the four-foot arm.

Addition of oxygen or water vapor to the intake air was effected through a tapped hole in the air intake duct, between the air filter and the engine air manifold. A ¼-inch stop-cock was also provided in this line to allow operation of the engine with normal air.

2. INSTRUMENTATION

The engine was equipped with the usual continous reading instruments, namely, an oil pressure gauge, an oil viscosity gauge, and a tachometer. In addition, several temperature measuring and flow rating instruments were installed. The exhaust manifold temperature was measured by a chromel-alumel thermocouple situated directly in the exhaust gas stream as it left the manifold. The engine block temperature was obtained from a copper-constantan thermocouple embedded in the surface of the engine casting. Another copper-constantan thermocouple was installed in the exhaust line at the point of sampling. The temperature of the cooling water leaving the engine was measured by a gas-bulb type thermometer, as was the oil temperature in the oil pan and the ambient air temperature. The inlet cooling-water temperature was measured by a mercury-filled glass thermometer installed in the water line, and its flow rate was measured by a calibrated orifice with a mercury-filled manometer.

All the above instruments, with the exception of the inlet cooling-water thermometer and orifice manometer, were mounted on a central control panel. Also installed on this panel was a calibrated orifice and its water-filled manometer for metering the oxygen added to the engine in some of the tests. A Bourdon gauge, indicating the pressure in the compressed air storage tank, completed the panel instrumentation. All the thermocouple leads terminated in plug-in jacks mounted on the panel, connected to a portable Leeds and Northrup potentiometer.

The amount of fuel admitted to the engine was regulated from the control panel by means of a hand-lever connected to the governor control lever on the engine by a cable and pulley arrangement. This made it possible to maintain any engine speed, from idling to maximum, for any period of time.

3. ADDITION OF OXYGEN

Oxygen was added to the engine from a standard commercial, 240 cu. ft. capacity, cylinder situated beside the panel bench. Its flow was regulated by a standard oxygen duplex gauge attached to the cylinder, and also by a $\frac{1}{4}$-inch globe valve just preceding the metering orifice described above. From the orifice, the oxygen passed through rubber tubing to the engine, entering through the tube provided in the air intake duct.

4. ADDITION OF WATER VAPOR

Water vapor was added to the engine in the form of steam. Instead of using steam from the laboratory lines, which proved too difficult to meter and control in the small quantities required, a small generator was constructed to provide a constant supply of steam at any desired rate. The generator consisted essentially of a four-liter Erlenmeyer flask with side-arm and an Nichrome wire internal heating coil which was made by winding the required length of wire into a $\frac{1}{4}$-inch spiral. Current was conducted to the heating coil through heavy copper leads passing through a rubber stopper in the neck of the flask. Water was admitted to the flask through a glass tube in the rubber stopper from a reservoir above the flask, the rate being regulated by a glass stop-cock. The steam generated passed out through the side-arm and was conducted directly to the engine through a short length of rubber tubing. The steam rate was determined by the amount of power supplied to the heating coil, and was measured by the amount of water evaporated in a given time.

5. SAMPLING THE EXHAUST GASES

All gas samples were drawn from a point in the exhaust line about fifteen feet from the outlet. This precaution is necessary in sampling the exhaust gases from an internal-combustion engine to prevent contamination of the sample by outside air which is known to be drawn a considerable distance into the pipe between pulsations in the flow of exhaust gases from the engine (44). The sampling tube was permanently inserted in the 3-inch exhaust pipe and consisted of standard $\frac{1}{4}$-inch iron pipe with eight 1/8-inch holes drilled along its length. The sampling line carried the gases to a finned, air-cooled, spiral condenser where they were cooled to room temperature and condensation of most of the moisture present took place. The gases then passed through a glass trap, and thence to a glass manifold equipped with two two-way glass stop-cocks from which samples were drawn to be analysed. This arrangement permitted the collection of two samples simultaneously, when necessary.

6. METHODS OF ANALYSIS

The analytical procedures employed for the determination of carbon dioxide, oxygen, nitrogen, methane, hydrogen, carbon monoxide, and the oxides of nitrogen were similar to those used by other investigators in this field. The aldehydes were determined by a method used chiefly in the bio-chemical field but also applicable to exhaust gas analysis.

(i) Carbon Dioxide, Oxygen, Nitrogen, Hydrogen, Methane

A single sample for the determination of these gases was collected by displacement of an acidified sodium sulfate solution in a standard 250-ml. gas sampling bulb. The acidified sodium sulfate solution was used rather than water because carbon dioxide is slightly soluble in the latter. The sample was analysed in a commercial Burrell gas analyser which operates on the two principles of (1) the selective absorption of carbon dioxide and oxygen, the volume changes accompanying the absorption of these gases (in Oxorbent and potassium hydroxide solution, respectively) being proportional to the amount of each gas present; and (2) the catalytic combustion of the hydrogen and methane to water and carbon dioxide. Nitrogen was obtained by difference.

(ii) Carbon Monoxide

Carbon monoxide was analysed by the common iodine pentoxide method (2,50). A gas sample was collected by water displacement in a standard 250-ml. gas sampling bulb. The sample was then passed slowly through a train of apparatus consisting of: (a) a flow meter to control the flow rate, (b) a bubbler containing concentrated sulfuric acid, (c) a liquid-oxygen cooled trap, (d) a U-tube containing activated alumina and Ascarite, (e) a U-tube containing iodine pentoxide maintained at a temperature of 150°C. by a thermostatically controlled external electrical heating element, and finally, through (f) a Bowen absorption bulb containing potassium iodide solution. The sulfuric acid acted as a dessicant, the liquid oxygen trap condensed any undesirable hydrocarbon vapors which might have been present, as well as any remaining moisture, and the alumina and Ascarite acted as final drying agents to remove the last traces of water vapor. It was essential that all water vapor be removed before exposing the gases to the iodine pentoxide, as the latter's effectiveness is destroyed by exposure to water vapor. When the dried gases were passed through the hot iodine pentoxide, any carbon monoxide present reacted with the pentoxide, liberating iodine vapor which was subsequently absorbed in the potassium iodide solution. At the end of the analysis, which required about one hour and forty-five minutes, the potassium iodide solution was titrated with standard sodium thiosulfate solution to determine its iodine content. Knowing the amount of gas analysed and the quantity of iodine liberated, the amount of carbon monoxide present in the exhaust gases was calculated.

(iii) Oxides of Nitrogen

The phenoldisulfonic acid method (1,65) was used for the determination of the oxides of nitrogen (excluding nitrous oxide). This is a common method used in gas analysis. A gas sample was collected, by displacement with the aid of suction, in a one-liter, three-neck flask. A solution of water, dilute sulfuric acid and hydrogen peroxide was then added to the flask, and a period of two hours was allowed to permit complete absorption of the oxides in the sample by the solution. The latter was then washed into a beaker, made slightly alkaline with potassium hydroxide solution, and evaporated to dryness. To the dry residue was added a small amount of phenoldisulfonic acid, and the resulting solution was then washed into a Nessler tube and made up to volume with ammonium hydroxide solution and water. The final solution was compared with a standard solution in a Dubosq colorimeter to determine its concentration of oxides of nitrogen, from which the oxides of nitrogen concentration in the exhaust gas sample could be calculated. The results were reported in parts per million, by volume, of equivalent nitrogen dioxide (NO_2).

(iv) Aldehydes

The method adopted for the determination of aldehydes, although common in quantitative organic analysis (35), has, as far as is known, been used by only one other investigator (24) in the analysis of Diesel exhaust gases. The method consisted of slowly bubbling about two liters of exhaust gases through a solution of sodium bisulfite. Any aldehydes present formed addition products with the bisulfite. The free, or unbound, bisulfite was then titrated with iodine solution to the starch indicator end-point. Sodium bicarbonate was added to release the bound bisulfite which was subsequently titrated with standard iodine solution. From this final titration, the amount of aldehydes in the exhaust gases was calculated, and was reported as parts per million, by volume, of equivalent formaldehyde (HCHO). This method is probably more accurate than the Schiff-Elvove reagent method (33), and much easier to perform than the silver precipitation method (43) -- the two most common methods used in gas analysis for aldehydes (2).

The chief drawback to this procedure was the large gas sample required. Since aldehydes are either soluble in, or react with, most common liquids, the gas sample could not be conveniently collected by liquid displacement and analysed at a more suitable time. Mercury could have been used, but the amount required would have been difficult to handle. Consequently, the gas sample had to be drawn directly from the sampling manifold, and through a calibrated flow meter and the bisulfite solution at a constant rate for a definite period of time with the aid of suction -- an operation which required about twenty minutes per sample and one operator's almost undivided attention.

7. ACCURACY OF THE ANALYTICAL RESULTS

From a consideration of the experimental errors inherent to the analytical procedures employed in this investigation, and from the results of a large number of preliminary blank titrations, the respective accuracies of the analytical determinations have been estimated to be as follows: 6% for oxides of nitrogen, 10% for aldehydes, 8% for carbon monoxide, and 2% for carbon dioxide, oxygen, and nitrogen. Comparison of the results obtained with those reported by other investigators using similar engines and operating conditions showed good agreement.

8. TEST PROCEDURE

Before any exhaust gas samples were taken, the engine was run under the required operating conditions of speed and load until steady state conditions had been reached, which required about half an hour. If oxygen or water vapor were to be added during the run, the addition began about five minutes before sampling commenced.

The samples taken consisted of: two samples for oxides of nitrogen determination, two samples for carbon monoxide determination, two samples for aldehyde determination, and one sample for the combined determination of carbon dioxide, oxygen, nitrogen, hydrogen and methane. The order of sampling was done in such a manner as to insure good average samples being obtained in the least possible time. As soon as the engine operating conditions became stable the first oxides of nitrogen determination sample was taken. About six minutes were required to obtain a pure sample. As soon as collection of this sample was completed, the first aldehyde sample was begun. During this sampling, which took about seventeen minutes, the first carbon monoxide sample and the sample to be analysed in the Burrell analyser were taken through the second stop-cock on the sampling manifold. At the completion of the first aldehyde sampling, the second oxides of nitrogen sample was taken, followed immediately by the second aldehyde sampling. During the second aldehyde sampling the second carbon monoxide sample was taken. At the end of the second aldehyde sampling the engine was shut down. The total time required for sampling was about forty-five minutes.

During the period in which the samples were being taken, a second operator was operating the engine and brake and taking the following readings at five-minute intervals: air temperature, engine oil temperature and pressure, cooling water temperature at inlet and outlet, thermocouple readings, and inlet cooling water rate. When oxygen or water vapor were being added this operator controlled the rate of addition as well. The engine operating conditions were kept constant by keeping the engine speed, brake load, and outlet cooling water temperature (50°C.) constant. These three factors were controlled by proper regulation of the fuel consumption, water rate to the brake, and inlet cooling water rate, respectively. During this period, the fuel consumption rate was measured several times by the operator.

As soon as the engine was shut down, the chemical analysis of the exhaust gases was begun. The total time required for a complete run, including the chemical analysis, was about six and a half hours.

9. TERMINOLOGY

To facilitate the interpretation of the results, the definitions of two terms peculiar to the problem should be borne in mind:

Enriched Air is normal air to which has been added a fixed amount of pure oxygen. Since normal air has an oxygen content of very nearly 21% by volume, enriched air will always have an oxygen content greater than 21%.

Percent Oxygen Enrichment is the percent increase in the oxygen content of normal air, following addition of pure oxygen; thus, a 10% oxygen enrichment of the intake air is equivalent to an increase in the oxygen composition from 21.0% to $100 \frac{(21 + 0.10 \times 21)}{(100 + 0.10 \times 21)} = 22.6\%$ -- an increase of only 1.6 percentage points in the oxygen content of the intake air.

II RESULTS

The results of the tests carried out under variable oxygen enrichment of the intake air are recorded in Tables III, IV, V, and VI on the pages immediately following. In order to facilitate interpretation of the experimental data, the results are reproduced graphically (Fig. 2-7) at the appropriate places in the discussion. The tests fall into three groups, according to the constant power output of the engine maintained during the test runs: Group I consisted of runs made at 1200 R.P.M. and 30 B.H.P.; Group II at 1250 R.P.M. and 35 B.H.P.; and Group III at 1350 R.P.M. and 40 B.H.P. The variation in oxygen enrichment was the same for each group: from zero to 38%, approximately.

An examination of the power charts supplied by the manufacturer of the Hercules engine showed that in Groups II and III the engine was operated at about maximum load capacity for the respective engine speeds, whereas, in Group I, the engine was only run at about 85% of the maximum rated load capacity. The significance of this fact is made more apparent in the ensuing discussion of the results.

The results of the tests made with water vapor addition to the intake air are presented in Tables VIII and IX and Figure 8. Two groups of runs were made: Group I was carried out at 1000 R.P.M. and no load (the dynamometer was disconnected from the engine), and Group II at 1200 R.P.M. and 30 B.H.P. In Group I the rate of water vapor addition was varied from zero to four pounds per hour, and in Group II it was varied from zero to eight pounds per hour.

TABLE III

OPERATING DATA

VARIABLE OXYGEN ENRICHMENT - CONSTANT LOAD

Test No.	Engine Speed R.P.M.	Load B.H.P.	Oxygen Enrich't % v/v	O_2 in Intake Air % v/v	Fuel Rate lb./hr.	Fuel-O_2 Ratio lb./lb.	Exh. Gas Rate lb./hr.	Exh. Gas Temp. °F.
1	1200	30	0	21.0	13.90	0.173	337	796
2	1200	30	0	21.0	14.80	0.181	351	770
3	1200	30	4.2	21.7	14.88	0.166	342	772
4	1200	30	5.9	22.0	14.80	0.167	365	754
5	1200	30	10.8	22.8	13.96	0.159	344	748
6	1200	30	12.0	23.0	14.52	0.158	364	719
7	1200	30	37.0	26.7	14.70	0.149	335	774
8	1250	35	0	21.0	16.44	0.195	356	858
9	1250	35	5.6	21.9	17.44	0.185	380	908
10	1250	35	10.8	22.8	16.42	0.174	369	859
11	1250	35	38.3	26.9	17.41	0.162	361	859
12	1350	40	0	21.0	18.51	0.213	360	912
13	1350	40	0	21.0	20.08	0.215	393	939
14	1350	40	6.0	22.0	20.40	0.205	399	1003
15	1350	40	6.1	22.0	19.06	0.200	374	898
16	1350	40	11.7	22.9	20.05	0.195	398	918
17	1350	40	37.5	26.8	18.73	0.170	373	866

TABLE IV

HEAT BALANCES

VARIABLE OXYGEN ENRICHMENT - CONSTANT LOAD

	HEAT IN	HEAT OUT			HEAT LOSSES	
Test No.	Heat from Fuel	Heat to Cooling Water	Heat to Exhaust Gas	Heat to work	Radiation, Conduction, etc.	
	B.t.u./hr.	B.t.u./hr.	B.t.u./hr.	B.t.u./hr.	B.t.u./hr.	%
1	274,000	107,800	88,250	76,400	1,550	0.6
2	291,700	109,700	90,120	76,400	15,480	5.3
3	273,400	115,200	85,670	76,400	-3,870	-1.4
4	291,700	109,000	91,120	76,400	15,180	5.2
5	275,000	107,950	85,300	76,400	5,350	2.0
6	291,200	110,400	85,350	76,400	19,050	6.5
7	289,700	111,800	86,820	76,400	14,680	5.1
8	323,800	123,900	97,200	89,050	13,650	4.2
9	343,300	131,000	114,740	89,050	8,510	2.5
10	323,600	123,700	105,700	89,050	5,150	1.6
11	343,000	132,300	105,400	89,050	16,250	4.7
12	357,500	130,000	112,780	101,850	12,870	3.6
13	395,200	145,200	128,600	101,850	19,550	5.0
14	402,000	150,100	135,380	101,850	14,670	3.6
15	375,700	145,100	115,800	101,850	13,050	3.5
16	395,000	151,900	124,620	101,850	16,630	4.2
17	369,000	150,150	111,080	101,850	5,920	1.6

TABLE V

ANALYTICAL DATA

VARIABLE OXYGEN ENRICHMENT - CONSTANT LOAD

Test No.	Carbon Monoxide	Aldehydes	Oxides of Nitrogen	Carbon Dioxide	Oxygen	Nitrogen
	Parts per Million by Volume			Percent by Volume		
1	270	7.0	382	8.7	8.1	83.2
2	286	4.4	381	9.1	7.9	83.0
3	347	4.2	424	8.6	9.0	82.4
4	237	4.3	632	8.9	9.3	81.8
5	151	11.5	422	8.6	10.6	80.8
6	205	4.5	755	8.6	10.8	80.6
7	139	16.8	1168	9.4	14.4	76.2
8	591	6.8	125	9.8	6.9	83.3
9	365	2.8	186	9.7	7.8	82.5
10	185	18.4	359	9.5	9.3	81.2
11	241	11.5	1446	10.4	12.8	76.8
12	554	5.2	315	10.7	5.9	83.4
13	452	4.7	126	10.9	5.3	83.8
14	496	3.6	-	10.9	6.3	82.8
15	215	3.2	459	10.6	6.8	82.6
16	256	16.7	338	10.8	7.5	81.7
17	148	17.5	1109	10.8	13.4	75.8

TABLE VI

HEAT IN COOLING WATER PER POUND OF FUEL USED

VARIABLE OXYGEN ENRICHMENT - CONSTANT LOAD

Test No.	Engine Speed R.P.M.	Load B.H.P.	Oxygen in Intake Air % v/v	Heat to Cooling Water B.t.u./hr.	Fuel Rate lb./hr.	Heat to Water per lb. of Fuel B.t.u./lb.
12	1350	40	21.0	130,000	18.51	7020
13	1350	40	21.0	145,200	20.08	7240
14	1350	40	22.0	150,100	20.40	7360
15	1350	40	22.0	145,000	19.06	7560
16	1350	40	22.9	151,900	20.05	7575
17	1350	40	26.8	150,150	18.73	8020

TABLE VII

OPERATING DATA

VARIABLE WATER VAPOR ADDITION - CONSTANT LOAD

Test No.	Engine Speed R.P.M.	Load B.H.P.	Water Added lb./hr.	Humidity of Intake Air lb./lb.	Fuel Rate lb./hr.	Fuel-Air Ratio lb./lb.	Exh. Gas Temp. °F.
18	1000	0	0	0.011	3.62	0.0089	245
19	1000	0	0	0.011	4.94	-	254
20	1000	0	0	0.010	3.06	-	236
21	1000	0	1	0.015	3.08	0.0095	251
22	1000	0	4	0.022[1]	3.26	0.0094	246
23	1200	30	0	0.011	14.80	0.0420	770
24	1200	30	0	0.011	13.90	0.0413	796
25	1200	30	4	0.021[1]	14.52	0.0388	800
26	1200	30	4	0.023[1]	13.97	-	795
27	1200	30	8	0.032[2]	14.88	0.0399	787

1. Saturated air.
2. Wet air.

TABLE VIII

HEAT BALANCES

VARIABLE WATER VAPOR ADDITION - CONSTANT LOAD

	HEAT IN	HEAT OUT			HEAT LOSSES	
Test No.	Heat from Fuel B.t.u./hr.	Heat to Cooling Water B.t.u./hr.	Heat to Exhaust Gas B.t.u./hr.	Heat to work B.t.u./hr.	Radiation, Conduction, etc. B.t.u./hr.	%
18	77,800	33,000	23,710	0	11,090	14.3
19	97,300	30,420	-	0	-	-
20	60,000	-	-	0	-	-
21	60,650	31,900	19,575	0	10,175	16.5
22	64,200	33,000	23,615	0	11,585	17.0
23	291,700	109,700	90,120	76,400	15,480	5.3
24	274,000	107,800	88,250	76,400	1,550	0.6
25	286,000	110,400	97,200	76,400	2,000	0.7
26	274,100	105,700	-	76,400	-	-
27	293,000	110,600	102,050	76,400	10,950	3.7

TABLE IX

ANALYTICAL DATA

VARIABLE WATER VAPOR ADDITION - CONSTANT LOAD

Test No.	Carbon Monoxide	Aldehydes	Oxides of Nitrogen	Carbon Dioxide	Oxygen	Nitrogen
	Parts per Million by Volume			Percent by Volume		
18	730	13.3	-	1.9	17.9	80.2
19	798	12.7	70	1.9	17.8	80.3
20	-	11.5	75	1.9	18.4	79.7
21	952	12.1	32	2.0	18.0	80.0
22	852	14.5	24	2.0	17.6	80.4
23	286	4.4	381	9.1	7.9	83.0
24	270	7.0	382	8.7	8.1	83.2
25	288	4.0	306	8.5	8.3	83.2
26	-	-	274	8.6	8.3	83.1
27	287	3.0	195	8.7	7.9	83.4

III DISCUSSION

Proper interpretation of the results presented can only be made in the light of the chemical aspects of the processes occurring during combustion, which were previously discussed at some length in the historical review. Summarizing briefly, two general theories of combustion have been developed to account for the chemical reactions and observed behavior in compression-ignition engines: the hydroxylation, or direct oxidation theory, and the destructive combustion theory. There is considerable evidence to suggest that both hydroxylation and destructive combustion occur simultaneously during the combustion process, and this is the general belief prevailing at the present time.

Consideration of these two theories shows that if chilling of the combustion process occurs, the reactions in both mechanisms will be partially arrested at some intermediate stage, and the presence of carbon monoxide, aldehydes, and organic acids from the intermediate hydroxylation reactions, and soot from the destructive combustion reactions, can be anticipated in the exhaust gases. Also, if overrich conditions exist in the combustion mixture, the formation of soot by destructive combustion and carbon monoxide and hydrogen by both destructive combustion and hydroxylation can be expected. It should be noted that the presence of air in excess of the stoichiometric requirements for complete combustion does not insure against the formation of the products resulting from overrichness, since locally overrich regions can occur because of the heterogeneous conditions accompanying the injection of liquid fuel. Somewhat similarly, chilling, with its attendant incomplete combustion, can occur locally, e.g., near the relatively cool cylinder walls, although the average temperature level during combustion may be normal or even higher.

In direct contrast with the formation of the other exhaust gas constituents, the oxides of nitrogen found in exhaust gases do not result directly from the chemical reactions of combustion: they are products from certain endothermic reactions occurring between the oxygen and nitrogen in the air present during combustion. The course of these reactions is determined mainly by the prevailing temperature and the relative proportions of oxygen and nitrogen present.

1. EFFECT OF ENRICHMENT ON THE COMBUSTION PROCESSES

An examination of the heat balances made for the three groups of runs (Table IV) reveals that, in general, the heat absorbed by the engine cooling water increased as the amount of oxygen enrichment increased. This indicates an increase in the amount of heat liberated per unit quantity of fuel consumed, and the consequent attainment of a higher temperature level in the engine cylinders during combustion. This increased engine temperature was not accompanied by a similar behavior in the exhaust gases, however, since the engine cooling water passing through the exhaust manifold jacket was deliberately maintained at a constant temperature (50°C.). Figure 2 shows graphically the

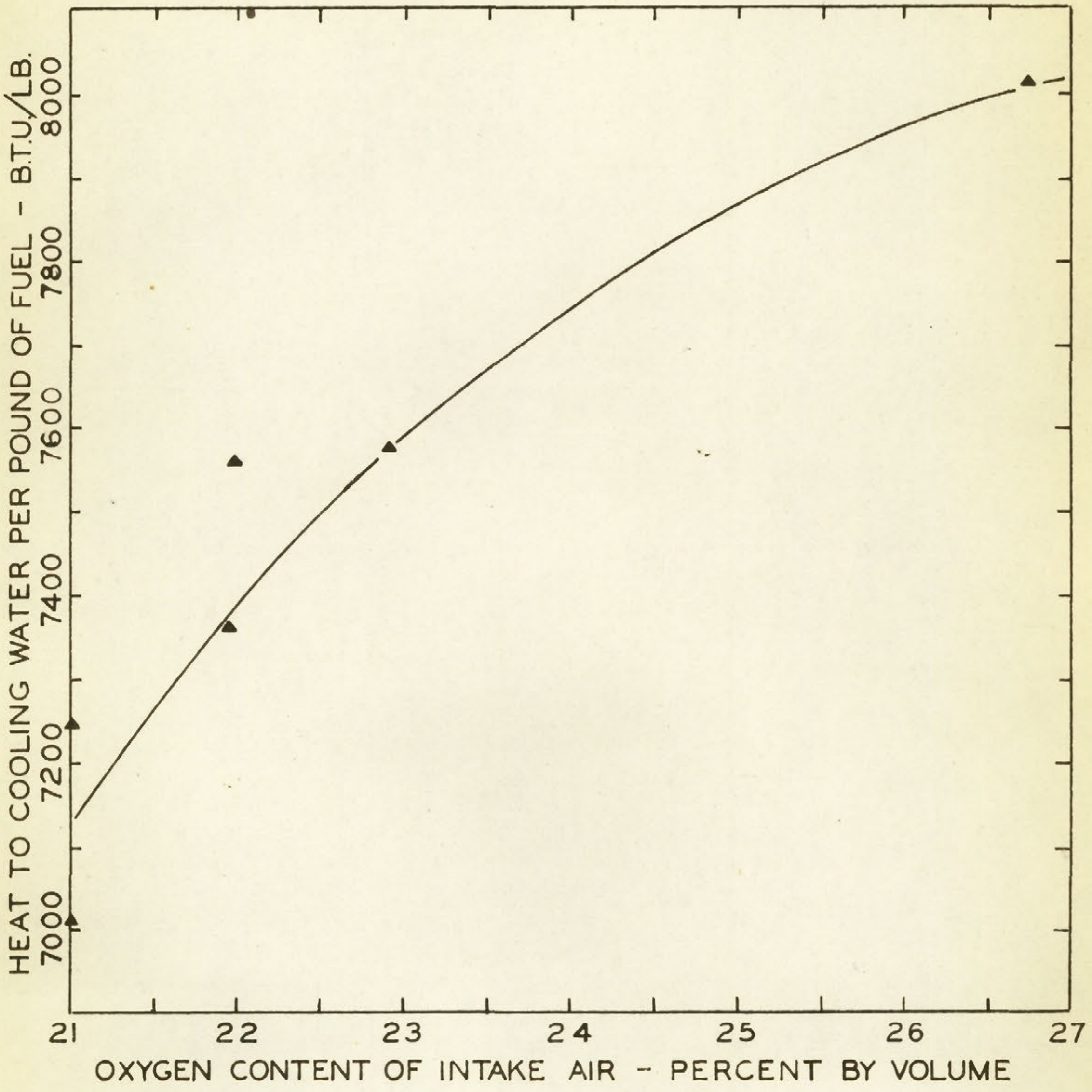

FIG. 2. VARIATION OF HEAT TO COOLING WATER WITH OXYGEN IN INTAKE AIR, AT 1350 R.P.M. AND 40 B.H.P.

increase in the heat removed by the cooling water with increasing enrichment for one group of runs.

This indication of more complete fuel combustion immediately suggests that the rates of the pre-flame reactions of the combustion processes occurring in the engine cylinders were increased approximately in proportion to the amount of oxygen enrichment, and thus allowing more time for the fuel to be consumed during the succeeding inflammation period. This is in accord with the decrease in ignition lag observed by Schweitzer (71) during his studies of the possible use of oxygen enrichment for power boosting in Diesel engines.

2. EFFECT OF ENRICHMENT ON THE CARBON MONOXIDE CONCENTRATION

The results of oxygen enrichment on the carbon monoxide concentration in the exhaust gases at various power outputs are presented graphically in Fig. 3.

An examination of these curves indicates that oxygen enrichment effected a definite decrease in carbon monoxide in the exhaust gases under all of the operating conditions studied. The maximum decrease, occurring at the maximum oxygen enrichment, amounted to approximately 55% for Group I, 65% for Group II, and 69% for Group III, based on the carbon monoxide concentrations obtained at zero enrichment (i.e., using normal air).

From a consideration of the combustion processes believed to occur in a compression-ignition engine, it is evident that the presence of extra oxygen should tend to reduce the formation of locally overrich regions, while generally increasing the temperature level existing in

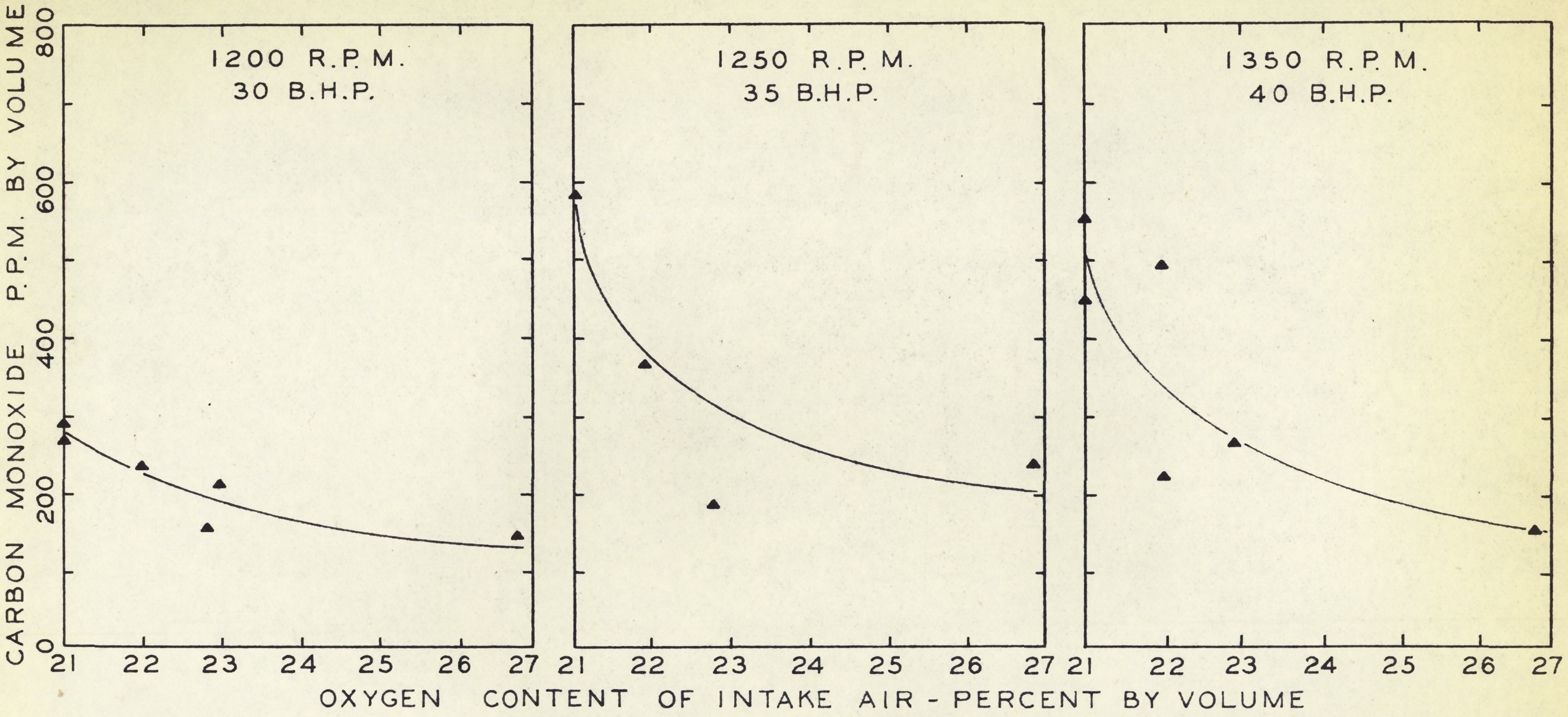

FIG. 3. VARIATION OF CARBON MONOXIDE WITH OXYGEN IN INTAKE AIR AT THREE DIFFERENT POWER OUTPUTS

the cylinders. Therefore, chilling, with its undesirable effects on the exhaust gas composition, should be lessened. If, in addition, the rate of combustion is increased and the combustion reactions are made more complete, lower carbon monoxide concentrations should be observed in the exhaust gases, as indicated by the results.

The curves obtained all appear to be levelling off at the points of maximum enrichment, i.e., at the minimum fuel-oxygen ratios studied. This is in accord with the results of other investigators (44) who found that, using normal air, the carbon monoxide concentration reached a minimum at a fuel-oxygen ratio of about 0.13, regardless of the type of engine and of its speed. In Table III it is seen that the minimum fuel-oxygen ratios obtained were 0.149, 0.162, and 0.170 respectively, for the three sets of runs.

The apparent discrepancy between the relatively low carbon monoxide concentrations obtained in Group I using normal air, and the concentrations obtained in Group II and Group III respectively under the same conditions, is satisfactorily explained when the engine operating characteristics supplied by the manufacturer are studied in conjunction with the effect of brake load on carbon monoxide concentration in the exhaust gases. It has been found that the carbon monoxide concentration in most Diesel exhausts remains low (less than 350 ppm.) when the engine is moderately loaded. However, as the load is increased at a constant speed, the carbon monoxide concentration begins to increase rapidly as soon as it reaches about 80% of the maximum rated load for which the engine was adjusted by the manufacturer. Past this point, the carbon monoxide concentration increases rapidly as the engine approaches and finally exceeds the maximum rated load (44). Now, in the test runs in Group I the engine was only operating at about 85% of its maximum rated capacity for that speed (1200 R.P.M.), compared with approximately 100% for runs in Groups II and III. Hence, in the light of these facts, the carbon monoxide concentrations obtained at zero enrichment for Group I should be lower than those of Groups II and III under the same conditions of enrichment.

It is believed that the carbon monoxide concentrations obtained at the maximum enrichment are minimum values, or very nearly so; any further increase in enrichment would not lower the concentrations appreciably. In fact, further increases in oxygen enrichment would result in combustion mixtures so lean as to cause increases in the carbon monoxide concentrations, as has been previously observed in studies of combustion of lean mixtures in Diesel engines (24,44).

3. EFFECT OF ENRICHMENT ON ALDEHYDE FORMATION

The effects of oxygen enrichment on aldehyde concentrations in the exhaust gases are shown graphically in Fig. 4.

From the results obtained it is seen that variable oxygen enrichment had the same general effect at the three power outputs studied: an initial decrease in aldehyde concentration to a minimum value, followed by a definite increase as the oxygen enrichment was increased. Thus, there appears to have been two opposing reactions operating during oxygen enrichment with regard to aldehyde formation. One reaction, tending to suppress aldehyde formation, predominated during

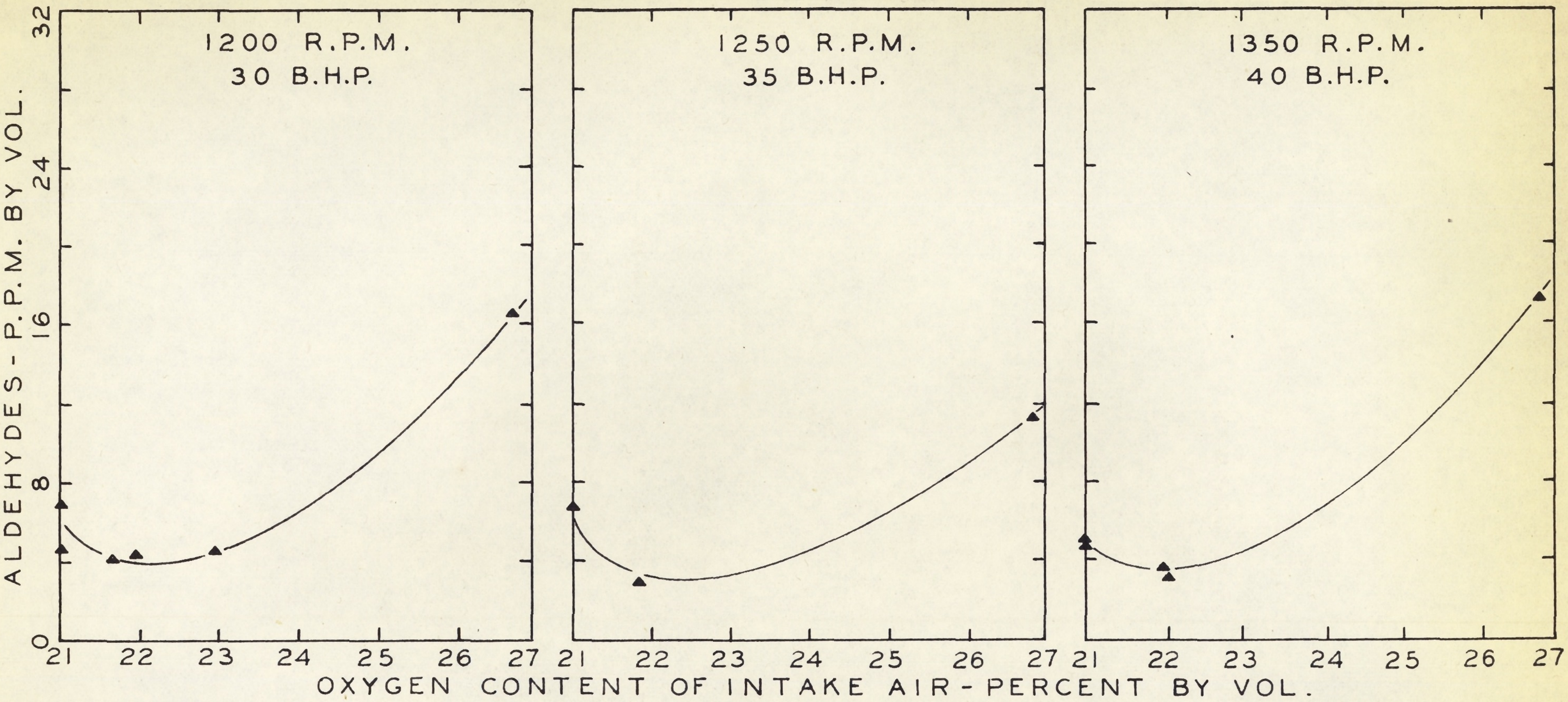

FIG. 4. VARIATION OF ALDEHYDES WITH OXYGEN IN INTAKE AIR
AT THREE DIFFERENT POWER OUTPUTS

low oxygen enrichment, whereas the other, tending to increase aldehyde formation, prevailed during high oxygen enrichment. These two reactions, which were not anticipated, are probably due to the effect of oxygen on the relative rates of the various intermediate reactions occurring in the hydroxylation, or direct oxidation, process of combustion which is believed to be responsible for the formation of aldehydes in compression-ignition engines.

The various steps of the hydroxylation combustion process may be summarized as follows:

$$\text{Hydrocarbons(fuel)} \xrightarrow{\text{oxidation}} \text{Alcohols} \xrightarrow{\text{oxidation}} \text{Aldehydes}$$

$$\text{Aldehydes} \xrightarrow{\text{oxidation}} \text{Acids and Lower Aldehydes}$$

$$\text{Acids and Lower Aldehydes} \xrightarrow[\text{and dissociation}]{\text{thermal decomposition}} CO,\ CO_2,\ H_2O,\ H_2$$

According to this mechanism, the first stage of the process, up to the formation of the lower aldehydes, consists of a series of direct oxidation reactions whose rates would naturally be increased by an increase in oxygen concentration, with a corresponding increase in the rate of lower aldehydes formation. The second stage consists of the thermal decomposition of the lower aldehydes to form carbon monoxide, carbon dioxide, etc. The concentration of aldehydes in the exhaust gases will thus depend essentially on the relative rates of the two stages. That aldehydes can be detected at all indicates that the decomposition reaction is not a relatively fast one. Its equilibrium yield is probably further depressed in the presence of the high pressures prevailing in the Diesel engine. Finally, chilling in certain parts of the combustion chamber will arrest it completely. In the presence of normal air, the slow rate of the decomposition reaction is controlling, and, in addition to chilling, is responsible for the presence of undecomposed aldehydes in the exhaust gases.

If the addition of oxygen to the air intake is now considered, the ignition lag is decreased, chilling is reduced, and although the rate of formation of aldehydes is increased, the rate of the decomposition reaction is also increased. As an overall result of the complex changes during low oxygen enrichment, the concentration of aldehydes appearing in the exhaust gases is decreased relative to normal air conditions.

However, as oxygen enrichment is increased the rate of aldehyde formation continues to increase, and a point is reached where the rate of decomposition of the aldehydes is exceeded to such an extent by the rate of formation that the amount of aldehydes remaining at the end of the expansion stroke begin to increase again. This is the point at which the minimum aldehyde concentrations obtained in the experimental curves (Fig. 4) are believed to occur.

4. EFFECT OF ENRICHMENT ON THE OXIDES OF NITROGEN

The effect of oxygen enrichment on the concentration of the oxides of nitrogen in the Diesel exhaust gases is shown graphically in Fig. 5. It is seen that the oxides increased in direct proportion to the amount of enrichment. This result was not unexpected, and agrees with previous investigations in this field (24).

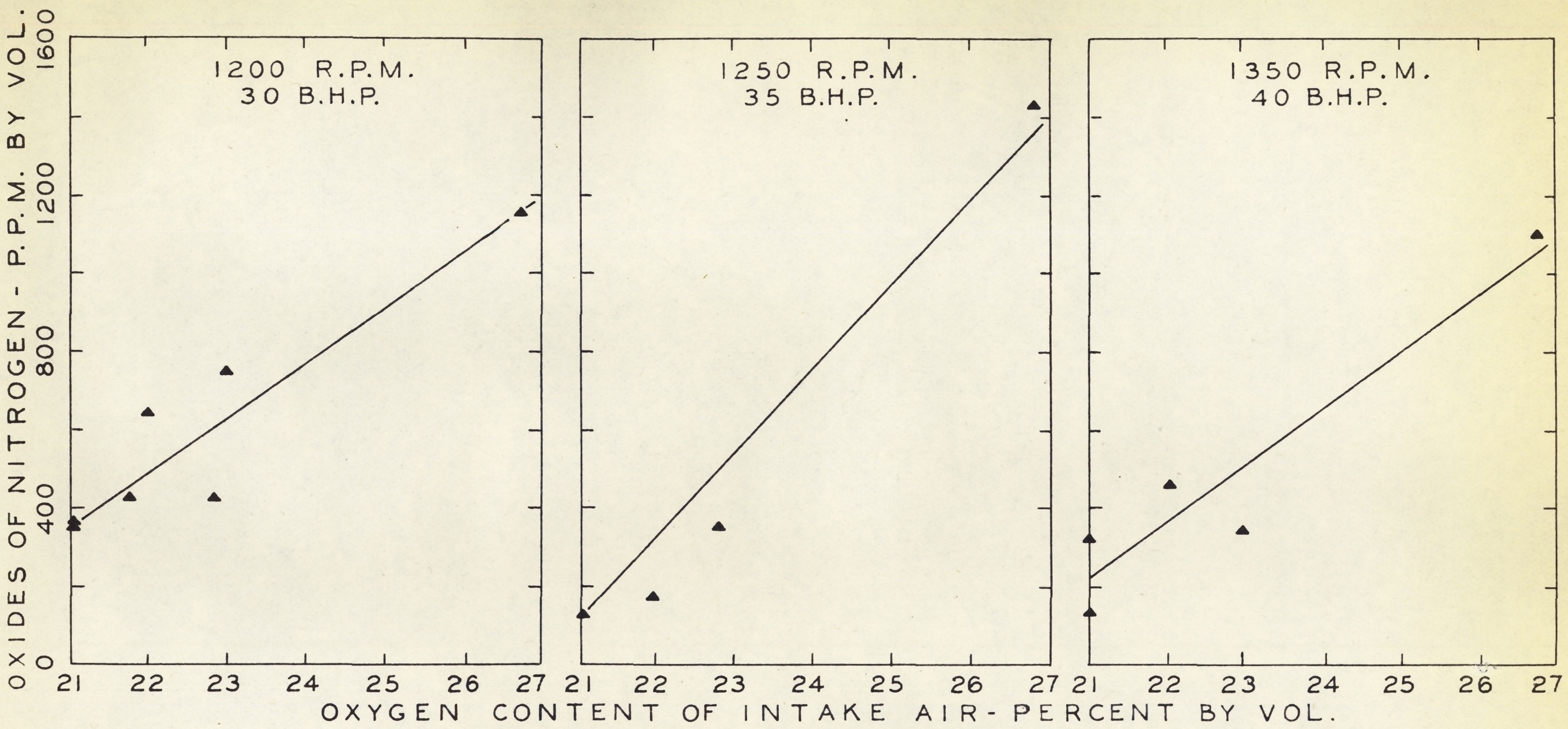

FIG. 5. VARIATION OF OXIDES OF NITROGEN WITH OXYGEN IN INTAKE AIR AT THREE DIFFERENT POWER OUTPUTS

The reason for the increase in the oxides of nitrogen concentration is made evident when the chief chemical reaction leading to their formation is considered. As was explained previously, this reaction,

$$N_2 + O_2 \longrightarrow NO$$

is favoured by high temperatures and increased oxygen or nitrogen concentrations. Since, during oxygen enrichment, both factors combine to increase the rate of reaction, the nitrogen oxides are bound to increase in proportion to the amount of enrichment.

5. EFFECT OF ENRICHMENT ON THE CO_2,O_2, AND N_2 CONCENTRATIONS

Figures 6 and 7 indicate the effect of oxygen enrichment on the concentrations of the major constituents of Diesel exhaust gases: carbon dioxide, oxygen, and nitrogen, at the various power outputs studied. It is seen that the carbon dioxide remained relatively constant for each group of runs, a result that is in agreement with the essentially constant fuel consumption for each group. A natural increase in the oxygen and a corresponding decrease in the nitrogen concentrations occurred in each group, as was anticipated.

6. EFFECT OF WATER VAPOR ADDITION

The results obtained from the limited number of runs with water vapor added to the intake air of the Diesel engine were mainly negative, as can be seen in Tables VII, VIII, and IX. In both groups of runs there was no appreciable effect observed on the quantity of heat removed by the engine cooling water, or on the concentrations of the various exhaust gas constituents, except the oxides of nitrogen.

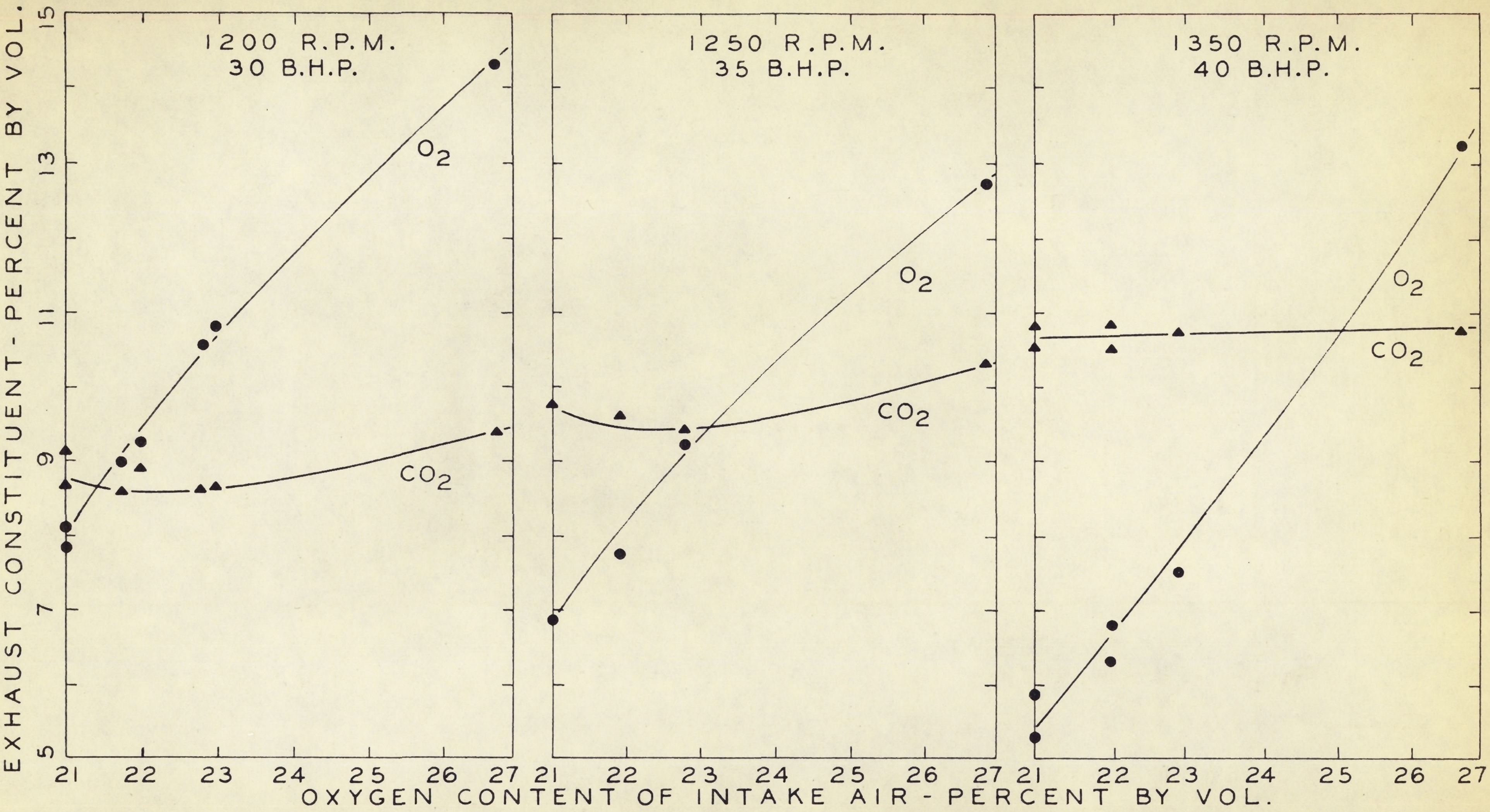

FIG. 6. VARIATION OF OXYGEN AND CARBON DIOXIDE WITH OXYGEN IN INTAKE AIR AT THREE DIFFERENT POWER OUTPUTS

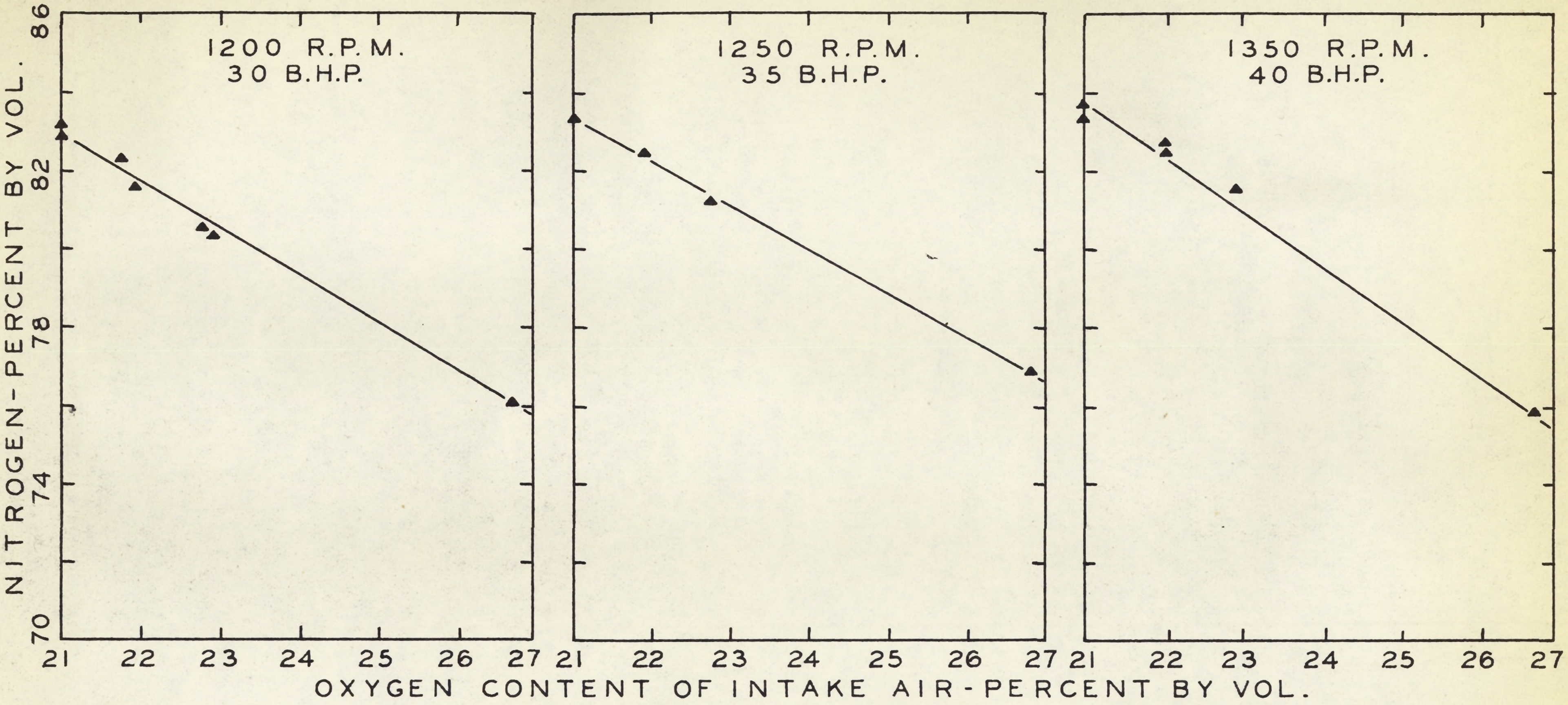

FIG. 7. VARIATION OF NITROGEN WITH OXYGEN IN INTAKE AIR
AT THREE DIFFERENT POWER OUTPUTS

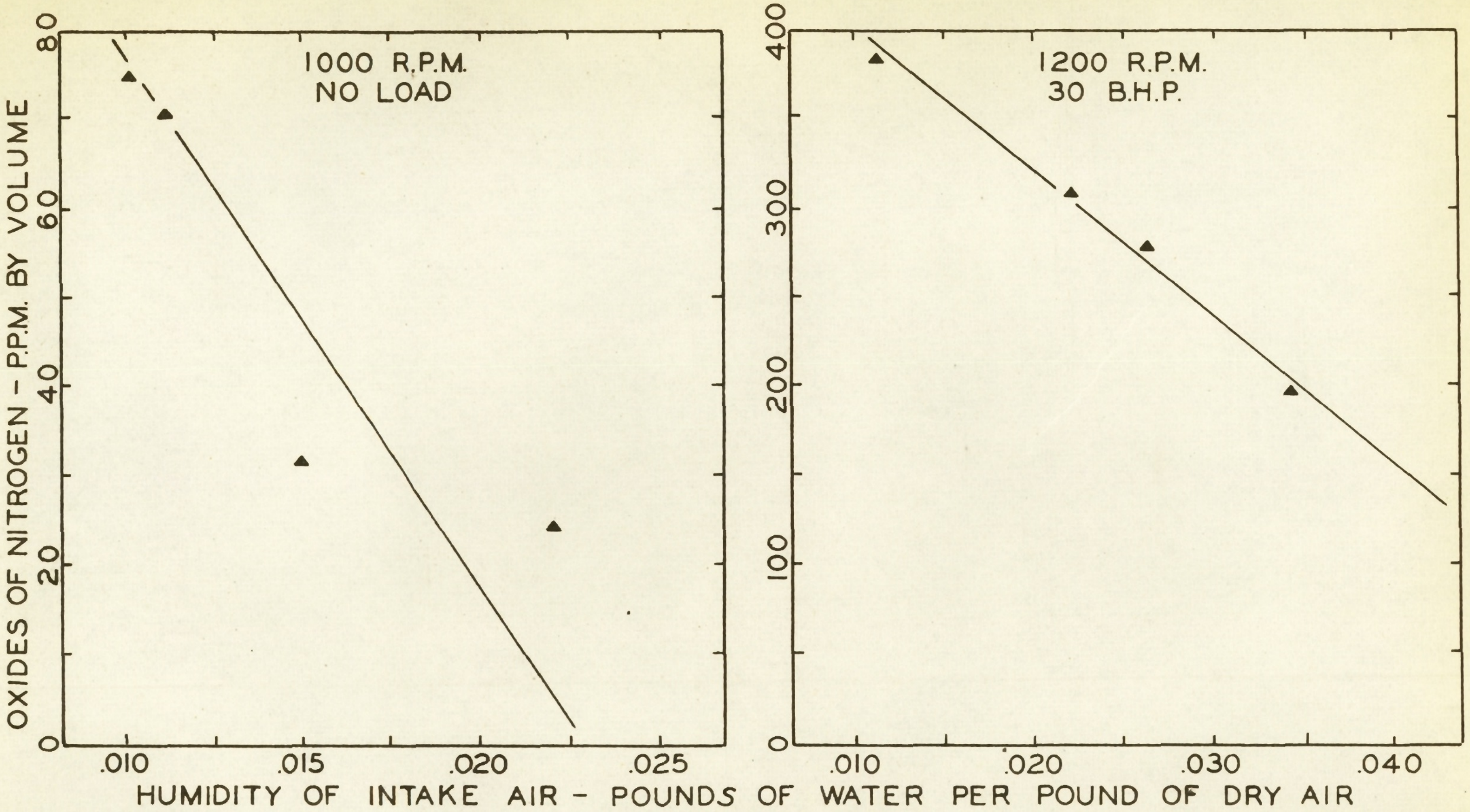

FIG. 8. VARIATION OF OXIDES OF NITROGEN WITH HUMIDITY OF INTAKE AIR AT TWO DIFFERENT POWER OUTPUTS

In the latter case, however, a definite decrease was effected by water vapor addition in both groups of runs (Fig. 8).

Since water vapor addition had no significant effect on the heat removed by the cooling water or on the concentrations of carbon monoxide, carbon dioxide, and aldehydes in the exhaust gases, it apparently did not decrease the ignition lag, and consequently, did not improve the rate of combustion. These conclusions are in apparent contradiction with the experimental evidence described on page 33 et seq. It will be remembered that a number of investigators (16,17,27,48) had found that the presence of water vapor in combustible hydrocarbon-air mixtures definitely aided in the ignition of these mixtures when they were ignited by an electric spark. It might appear, therefore, that water vapor improves combustion only when ignition results from such a source. The high temperatures associated with the spark probably cause dissociation of the water vapor, the products of which help to ignite the mixture. The relatively low temperature levels reached just prior to ignition in a compression-ignition engine are presumably of insufficient magnitude to cause appreciable dissociation of the water vapor and consequent improvement in combustion.

The pronounced decrease in the oxides of nitrogen concentrations with increasing water vapor addition are in agreement with the results obtained by Frank-Kamenetzky (34). Briefly, he found that the presence of water vapor during explosions of mixtures of carbon monoxide, oxygen, and nitrogen caused an initial increase in nitric oxide formation, followed by a marked decrease with increasing water vapor addition.

Thus, extending his results to this investigation, when no water vapor was added the small quantity of water vapor occurring naturally in the intake air would presumably tend to increase nitric oxide formation, but upon addition of water vapor to the air, the oxides would be reduced, as was experimentally observed. An explanation of the mechanism of nitric oxide reduction by water vapor cannot be attempted with the limited amount of data available.

It must be mentioned that immediately upon addition of water vapor to the Diesel engine used in this investigation smoother operation of the engine was observed, and the exhaust gases became practically invisible. Thus, although the analytical results revealed no improvement in combustion, these qualitative results indicate that more even combustion was produced, and the soot concentration in the exhaust gases was decreased. These results are in agreement with those obtained by other investigators (38,53,57,58,68,69) who have studied the effect of water vapor addition to high compression spark-ignition and semi-Diesel engines with the view to increasing engine efficiency and performance.

CONCLUSIONS

The results of this investigation indicate that, as the intake air of a commercial Diesel engine is enriched by the addition of pure oxygen in increasing amounts (from zero to 38% enrichment, by volume), the exhaust gas composition is affected as follows: (1) the carbon monoxide concentration is decreased to an apparently limiting value; (2) the aldehydes are decreased to a minimum value, occurring at about 10% enrichment, and then are increased to concentrations exceeding those obtained at zero enrichment; (3) the oxides of nitrogen are increased in direct proportion to the enrichment; (4) the carbon dioxide concentration is not significantly affected. It is evident that the optimum conditions, with respect to purification, occur during low oxygen enrichment, at about 10%. At this enrichment, the aldehydes are at a minimum, the carbon monoxide concentration has nearly reached its limiting value, and the oxides of nitrogen have not increased to excessive amounts.

From an academic viewpoint, the results are of importance in that they tend to substantiate the existing theories of the combustion process since these theories satisfactorily explain all the observed trends. It is believed that the use of oxygen-enriched intake air caused an increase in the rates of the pre-ignition reactions, thus reducing the ignition lag in accordance with previous observations made by Schweitzer (71), resulting in more time being available for the actual combustion reactions in the presence of a greater oxygen concentration. As a consequence, more complete combustion of the fuel was obtained, producing higher maximum temperatures in the cylinders, and hence, reducing chilling and after-burning with their attendant undesirable effects on exhaust gas composition.

One unavoidable result of increased oxygen concentrations was the production of higher nitrogen oxides concentrations. This effect is not too serious in practical exhaust gas purification, however, when it is remembered that the oxides are very soluble in water, and hence, can be easily scrubbed out of the exhaust gases.

The experimental results obtained indicate that, in general, the addition of water vapor to the intake air of a Diesel engine is an ineffective method of improving exhaust gas purity. No appreciable effects on the primary chemical reactions of the combustion processes were observed, although there was some evidence to indicate that more even combustion with a reduction in engine knock was effected.

The definite reduction in the nitrogen oxides concentration, although gratifying with respect to exhaust gas purification, is chiefly of academic interest since their removal presents no problem. The results offer further substantiating evidence in support of the observations made by Frank-Kamenetzky (34) in his study of the chemical kinetics of combustion in an oxygen-nitrogen-water vapor atmosphere.

It must be mentioned that certain mechanical difficulties (not caused by water vapor addition) were encountered which considerably curtailed the study of water vapor addition. However, the continuation of the tests at higher humidities (i.e., using wet air) and more varied operating conditions does not appear promising in the light of the results already obtained.

On the basis of the experimental data obtained, both oxygen enrichment and water vapor addition appear to be impractical for the purification of Diesel exhaust gases. Although oxygen enrichment does improve the exhaust gas purity somewhat, the improvement, from an economic point of view, does not warrant the added cost of the installation, the maintenance of the necessary equipment, and the oxygen requirements to achieve it. However, a reduction in the total concentration of the evil-smelling and toxic exhaust gas constituents was effected by the addition of small quantities of pure oxygen, indicating that the application of oxygen enrichment to those Diesel engines whose exhaust gases are inherently, and hence, unavoidably obnoxious might prove advantageous.

This investigation further indicates that, from a study of the changes produced in the exhaust gas composition of compression-ignition engines by the addition of various substances to the fuel-air mixture, considerable information can be obtained regarding the mechanisms of the combustion processes taking place in the cylinders. It is believed that further study along these lines should be carried out using different additions and a more refined analytical procedure.

BIBLIOGRAPHY

1. Allison, V.C., Parker, W.L. and Jones, G.W., U.S. Bur. Mines Tech. Paper 249: 12 pp. 1921.

2. American Gas Association, Research Bulletin 15: 110 pp. 1942.

3. Ash, S.H. and Naus, L.L., U.S. Bur. Mines Inform. Circ. 7222, 26 pp. 1942.

4. Aufhausser, D., Brennstoff und Verbrennung, Springer, Berlin, 1928.

5. Berger, L.B., Elliott, M.A., Holtz, J.C., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 3541: 18 pp. 1940.

6. Berger, L.B., Elliott, M.A., Holtz, J.C., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 3713: 13 pp. 1943.

7. Berger, L.B., Elliott, M.A., Holtz., J.C., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 4032: 26 pp. 1947.

8. Berger, L.B. and McGuire, L.H., U.S. Bur. Mines Rept. Invest. 3887: 20 pp. 1946.

9. Blume, Deutche Kraftfahrtforschung Technische, Forschung bericht, Zwischen bericht, 91: 43-59, 1940.

10. Boerlage, G.D. and Broeze, J.J., Ind. Eng. Chem. 28: 1229-1234, 1936.

11. Boerlage, G.D. and Broeze, J.J., Chem. Revs. 22: 61-85, 1938.

12. Boerlage, G.D. and Broeze, J.J., The Science of Petroleum 4: 2894-2907, Oxford University Press, 1938.

13. Boerlage, G.D., Broeze, J.J. and Van Dijck, W.J.D., J. Soc. Automotive Engrs., July 1932.

14. Boerlage, G.D., and Van Dijck, W.J.D., J. Roy. Aero. Soc., Dec. 1934.

15. Bone, W.A., Proc. Roy. Soc. 137A: 243, 1932.

16. Bone, W.A. and Townend, D.T.A., Flame and Combustion in Gases, Longman's, Green and Co. Ltd., London 1927.

17. Bone, W.A. and Wheeler, R.V., J. Chem. Soc. 81, 1902.

18. Bone, W.A. and Wheeler, R.V., Proc. Chem. Soc. 19, 1903.

19. Bone, W.A. and Weston, F.R., Proc. Roy. Soc. 110A: 615, 1926.

20. Bonhoeffer, K.F. and Reichardt, H., Z. physik Chem. 139A: 75-97, 1928.

21. Breyre, A. and Fripiat, J., U.S. Bur. Mines Rept. Invest. 3527: 17 pp. 1940.

22. Busch, H.W., and Berger, L.B., U.S. Bur. Mines Rept. Invest. 4531: 9 pp. 1949.

23. Callendar, H.L., Engineering 123: 147, 1927.

24. Cooper, R.M., Lean Mixture Combustion of Diesel Engines, McGill University Thesis, 1950.

25. David, W.T. and Mann, J., Nature 151: 392, 1943.

26. Davis, R.F. and Elliott, M.A., Paper 47-A-108 Presented at Annual Meeting of Am. Soc. Mech. Engrs., Dec. 1947.

27. Dixon, H.B., Brit. Assoc. Repts. 503, 1880.

28. Dreyhaupt, F., Motortech. Z. 4: 333-339, 1942.

29. Drinkwater, J.W. and Egerton, A.C., Proc. Inst. Mech. Engrs. 138: 415-459, 1938.

30. East, J.H., Jr., U.S. Bur. Mines Inform. Circ. 7378: 13 pp. 1946.

31. Egerton, A.C., Nature 121: 19, 1928.

32. Elliott, M.A., Holtz, J.C., Berger, L.B., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 3584: 50 pp. 1941.

33. Elvove, E., Ind. Eng. Chem. 9: 295-297, 1917.

34. Frank-Kamenetzky, D., Acta Physicochimica U.R.S.S. 22: 27-44, 1947.

35. Friedemann, F.E., Cotonio, M., and Shaffer, P.A., J. Biol. Chem. 73: 335-358, 1927.

36. Gaydon, A.G., Proc. Roy. Soc. London 183A: 111-124, 1944.

37. Gaydon, A.G., Trans. Faraday Soc. 42: 292-297, 1946.

38. Green, W.P. and Shreeve, C.A., Am. Soc. Mech. Engrs. 68: 541-545, 1946.

39. Harrington, D. and East, J.H., Jr., U.S. Bur. Mines Inform. Circ. 7406: 87 pp. 1947.

40. Harteck, P. and Kopsch, U., Z. physik. Chem. Abt. 12B: 327-347, 1931.

41. Haslam, R.T. and Russel, R.P., Fuels and Their Combustion, McGraw-Hill Book Company, Inc., New York, 1926.

42. Hawthorne, E.P., Aircraft Eng. 18: 330-335, 1946.

43. Heim, Ind. Eng. Chem. Anal. Ed. 10: 431, 1938.

44. Holtz, J.C., Berger, L.B., Elliott, M.A., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 3508: 48 pp. 1940.

45. Holtz, J.C., Berger, L.B., Elliott, M.A., and Schrenk, H.H., U.S. Bur. Mines Rept. Invest. 3700: 24 pp. 1943.

46. Jackson, W.F., J. Am. Chem. Soc. 57: 82, 1935.

47. Jones, R.A., Reactions in Dissociated Water Vapor, McGill University Thesis, 1950.

48. Jones, G.W. and Seaman, H., Ind. Eng. Chem. 26: 71-72, 1934.

49. Jost, W., Rogener, H., and Weber, U., Schrifton der deutschen Akademie der Luftfahrtforschung 54: 2-10, 1941.

50. Katz, M. and Katzman, J., Can. J. Research, 26F: 318-330, 1948.

51. Kent, R.T., Mech. Engrs. Handbook, Power, 12-03, 1936.

52. King, R.O., Can. J. Research, 26F: 228-240, 1948.

53. Kuhring, M.S., Can. J. Research, 16A: 149-176, 1938.

54. Kuzminov, G.P., Kislorod 4: 36-43, 1947.

55. Lavin, G.I. and Jackson, W.F., J. Am. Chem. Soc. 53: 383-384, 1931.

56. Lavin, G.I. and Reid, E.E., J. Am. Chem. Soc. 52: 2454, 1930.

57. Le Mesurier, L.J. and Stansfield, R., J. Inst. Pet. Tech.: Fuel Testing in Slow and High Speed Diesel Engines, 1931.

58. Le Mesurier, L.J. and Stansfield, R., North-East Coast Inst.: Combustion in Heavy Oil Engines, 1932.

59. Lewis, B. and Von Elbe, G., Combustion, Flames, and Explosions in Gases, Cambridge University Press, London, 1938.

60. Lonn, O.A., Luftfahrtforschung, p. 344, 1942.

61. Mardles, F.W.J. and Stern, W.J., Rep. and Memo. Aeron. Res. Comm. 1062: Dopes and Detonation, 1926.

62. Mardles, F.W.J. and Stern, W.J., Trans. Faraday Soc. 27: 681, 1931.

63. Miller, C.D., J. Soc. Automotive Engr. 53: 719, 1945.

64. Norrish, R.W., Proc. Roy. Soc. London 150A: 36-57, 1935.

65. Piccard, J., Peterson, E.G., and Bitting, C.D., Ind. Eng. Chem. Anal. Ed. 2: 294-295, 1930.

66. Rice, G.S. and Harris, F.E., Bur. Mines Rept. Invest. 3320: 52 pp., 1936.

67. Rodebush, Wende, C.W., and Campbell, R.W., J. Am. Chem. Soc. 59: 1924, 1937.

68. Rowe, M.R. and Ladd, G.T., J. Soc. Automotive Engr. Trans. 54: 26, 1946.

69. Sass, F., Kompressorlose Dieselmaschinen, Springer, Berlin, 1928.

70. Schmidt, F.A.F., Schriften der deutschen Akademie der Luftfahrtforschung 54: 77-88, 1941.

71. Schweitzer, P.H., Automobile Engr. 30: 395-397, 1940.

72. Schweitzer, P.H., Soc. Automotive Engr. Quart. Trans. 1: 476-87, 1947.

73. Tausz, J. and Schulte, F., Uber Zundpunkte und Verbrennungsvorgrange in Dieselmotor, Knapp, Halle, 1924.

74. Taylor, C.F. and Taylor, E.S., The Internal Combustion Engine, International Textbook Company, Scranton, Pa. 1938, 292 pp.

75. Treiber, O.D., J. Soc. Automotive Engr., Oct. 1935.

76. U.S. Patents: 670,311; 883,240; 970,153; 1,232,215; 1,262,034; 1,459,306; 1,496,591; 1,632,285; 1,973,979; 2,062,859; 2,376,479; 2,444,222.

77. Urey, H.C. and Lavin, G.I., J. Am. Chem. Soc. 51: 3293, 1929.