The Relation of Slow Combustion to Knocking in Internal Combustion Engines,

Thesis by

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Summary of Principal Results

A brief consideration of the known facts about knocking indicates that it is due to a nearly simultaneous combustion of a portion of the fuel. An explanation of the great tendency of engines of high compression ratio to knock is suggested. This explanation is based on the idea that maximum temperatures and not mean temperatures are the cause of knocking.

An experimental study shows that lead tetraethyl reduces oxidation of the fuel prior to ignition. The compression pressure, however, is unchanged. A lead deposit on the walls of the combustion chamber does not effect knocking. Aldehydes were observed in samples of explosive gas from an engine in decreased amounts when the fuel contained lead tetraethyl.

A study of oxidation in heated tubes indicates that there is an appreciable cracking of the fuel during slow combustion. Lead oxide on the walls of a heated tube is very effective in reducing oxidation which indicates that all of the oxidation takes place on the walls. Peroxides, formed by slow combustion of gasoline without lead tetraethyl or lead oxide, were found to be ineffective in producing knocking with a mixture of acetone and ether as fuel. Such peroxides were never formed in the presence of lead. Evidence is given which indicates that the formation of peroxides is not the initial step in oxidation.

INTRODUCTION

The main purpose in studying the complicated phenomena of knocking in internal combustion engines has been the practical one of increasing their efficiency. Sir Dugald Clerk first showed that the efficiency is dependent on the compression ratio. But attempts to realize the increased efficiency of higher compression ratios failed whenever a fuel which knocked was used. Interest in the problem was increased greatly when it was discovered by Thomas Midgley Jr. that a small amount of lead tetraethyl in gasoline greatly reduces its tendency to knock. At the present time, a considerable number of substances which reduce knocking have been discovered by various investigators, as well as other substances which greatly increase knocking. Also the knocking of different fuels has been studied extensively.

A considerable number of theories of knocking have been presented and studied. (See the paper by G.L. Clark and W.C. Thee, "Present Status of the Facts and Theories of Detonation," Ind. and Eng. Chem. 17 (1925) p 1219, which gives a concise summary of the known facts and theories at that time.)

Detonation Wave Theory of Knocking

One of the theories is that knocking is due to the formation of true detonation waves such as have been studied by Berthelot, Le Chatelier, Mallard, and Dixon. This theory would account for the facts very satisfactorily if it could be shown that such waves exist in engines. Dixon showed first (Phil. Trans. Roy. Soc. 200 A (1903) 335) that a sudden change in the diameter of a tube causes a detonation wave to be damped. Laffitte (C. R. 179 (1924) 1394) studied this phenomenon in greater detail. Finally, Dumanois (C.R. 182 (1926) 1378) constructed a stepped piston so that the area of the flame front would increase in a series of sudden jumps. His engine had a compression ratio of 6.7 . He stated that he was able to reach a speed of 99 km. per hr. in an automobile with this engine when using a fuel consisting of 77% gasoline and 23% kerosene. Later, (C.R. 182 (1926) 1526) he stated that he found that the engine pre-ignited badly when running with a full load at low speed. It is unfortunate that this is nearly all of the information available concerning the stepped piston, for it is about the best evidence that true detonation waves are formed in engines. The fact that Dumanois did not discover the pre-ignition trouble in his engine until his first paper had been read before the Academy, together with the fact that he drove his car at a high speed, suggests that the reason he did not observe knocking was that the engine speed was high, since it is well known that knocking is less at high engine speed.

While the evidence for the existance of detonation waves is meager, there is much evidence that they do not exist. Woodbury, Lewis, and Canby (J. Soc. Aut. Eng. 8) came to the conclusion that it is very difficult to set up a detonation wave in a vessel as small as an ordinary engine cylinder. Egerton and Gates (Proc. Roy. Soc. 114 A 137) from their experiments with tubes concluded that the anti-knock compounds, lead tetraethyl and diethylselenide, do not affect the position of detonation at ordinary pressures and temperatures. From their further work, and the work of others, Egerton stated (Nature July 7, (1928) 20) that they have abandoned the detonation wave theory of knocking.

Prof. Callendar's Theory

In 1926, Prof. H.L. Callendar, in a series of articles, (Engineering 121 475, 509, 552, 575, 605) presented his theory that knocking is due to the formation of nuclear drops of fuel. There is now general agreement that this theory is not broad enough to explain the behavior of all fuels, for there are fuels that knock badly which certainly remain in the gaseous state. The existance of nuclear drops of ordinary fuel is extremely doubtful. Octane, a fuel which knocks badly, has a critical temperature of 296.2 deg. C., at which temperature the vapor pressure is 18730 mm., (Tables Annuelles Internationales de Constants et Données Numériques vol. 1 , p.69). One mol of octane requires 59.8 mols of air for complete combustion. If such a mixture at a temperature of 100 deg. C. is compressed adiabatically from a volume, 6, at atmospheric pressure to a volume, 1, the final temperature will be approximately 490 deg. C., and the final partial pressure of the octane will be 156 mm. Later, Callendar (Engineering 123 (1927) 210) came to the conclusion that organic peroxides are formed in the nuclear drops during the early stages of combustion. These peroxides will burn later and act as ignition centers for the rest of the unburned fuel, thus causing a very rapid combustion which accounts for the knock. The evidence for the existance of peroxides will be considered later.

Experiments of Tizard and Pye

Tizard and Pye (Phil. Mag. 44 (1922) 79) who studied the ignition of gases by sudden compression, were the first to suggest that whether o~~f~~r not a fuel knocks is determined by the processes of slow combustion which take place before rapid combustion. According to them, not only the ignition temperature is of importance, but also the temperature coefficient of the rate of combustion when the ignition temperature is exceeded. It might be expected reasonably that when a combustible mixture is heated by adiabatic compression, that it would be ignited and burn practically instantaneously. The results of Tizard and Pye show clearly that this is not at all the actual case. If the temperature is just great enough to start combustion, there is a considerable time lag during which the pressure of the mixture remains nearly constant or even decreases after which rapid combustion and increase of pressure follow. If the compression is a little greater than that necessary to start combustion, the time lag is very much reduced. For example, they found that when they compressed a mixture of heptane and air from an initial temperature and pressure of 35 deg. C. and 14.8 lbs./ sq. in. respectively to a pressure of 176 lbs. per sq. in., the time lag was 0.58 sec. while if the same mixture was compressed from an initial temperature of 46.5 deg. C. and an initial pressure of 14.8 lbs./ sq. in. to a pressure of 227 lbs. / sq. in. ignition took place nearly instantaneously. They calculated the difference in temperature to be 58 deg. C. Callendar (Engineering 121 476) gave further results obtained by Tizard on the ignition temperatures of several hydrocarbons by adiabatic compression. The mixture strength is given in terms of fuel to 15 by weight of air in each case.

Tizard's Results for Liquid Hydrocarbons

Hydro-carbon	Wt. fuel	Comp. ratio	Press. ratio	Initial temp.	Final Temp. Mean	Final Temp. Max.
n-pentane	1.0	7.0	12.8	60	336	399
n-hexane	1.0	6.0	10.4	60	306	362
cyclohexane	1.0	6.6	11.8	60	324	384
n-heptane	0.8	5.5	9.34	59	291	325
"	1.6	6.7	11.4	59	292	364
"	0.4	8.0	15.8	13	292	348
"	1.0	6.3	11.2	40	284	335
n-octane	1.0	5.0	8.2	60	275	321
benzene	1.0	9.1	18.7	40	370	430
"	1.0	8.0	15.7	59	380	437
"	1.0	9.4	19.4	39	373	433

In this table, the maximum final temperature was computed on the basis of no heat loss during compression, while the mean was computed from the final pressure.

These results of Tizard are of considerable interest in that the temperatures of ignition of all of these fuels are exceeded in all ordinary engines even if we take the maximum temperatures given here. This will be seen from further considerations of the conditions existing in engines. It follows from this that the time lag is very important, and that it is the only phenomenon which permits us to use as high compression ratios as we do. Callendar's suggestions of nuclear drops and peroxides may be considered as attempts to explain the time lag and the rapid combustion following, as observed by Tizard.

In view of these results, it must be expected that a substance which reduces oxidation in its initial stages will reduce the tendency of the fuel to knock. Conversly, a substance which tends to increase oxidation either by its own early oxidation which would increase the temperature of the remainder of the charge, or by a catalytic effect, will increase knocking.

Thus, experiments have been carried out in the Norman Bridge Laboratory to determine whether or not lead tetraethyl reduces oxidation of the fuel during the compression stroke of an engine. Further experiments on slow oxidation in heated tubes have been performed also. The conclusion from these experiments is that oxidation is reduced in the engine and in the heated tubes. Before describing these experiments, it seems desirable to consider the well established facts about the behavior of combustion in engines from the view-point of the conclusions of Tizard and Pye.

Knocking in Engines

It is generally agreed that when knocking occurs there is a very sudden increase in pressure. Some observers have said that there is a very high instantaneous pressure. H.C. Dickinson (J. Soc. Aut. Eng. 8 (1921) 482) found a pressure of about 1000 lbs./ sq. in. during knocking while normally the pressure was about 450 lbs./ sq. in. He did not mention what kind of an indicator was used. W. S. James (J. Soc. Aut. Eng. 8 (1921) 558) mentioned that a weight placed on a cylinder head was sometimes thrown as high as 1.5 inches from the head. He also stated that the pressure was 550 lbs./sq. in. above normal. From these data, he concluded that the pressure was not uniform throughout the cylinder volume.

However, it seems more reasonable to assume that such high pressures do not exist, at least, not long enough to be measured and that the recorded high pressure is due to the indicator and possible vibrations of the cylinder to which the indicator is fastened. Generally speaking, too little information is given concerning the indicators. Otherwise an estimate of the rate of increase in pressure could be made, for it is well known that the usual indicator will read twice the final value of the pressure if the pressure is applied instantaneously.

The fact that knocking causes an indicator to read high is now used in the familiar Midgley bouncing-pin indicator to compare the knocking of different fuels. The jumping of the pin of such an instrument in itself appears sufficient to justify the conclusion that when an engine is knocking the rate of pressure increase is very high. Such high rates of pressure increase will produce abnormally high elastic stresses in the structure of the engine which may lead to failure. Midgley mentioned (J. Soc. Aut. Eng. 7 489) that pistons have been broken by knocking. A high rate of pressure increase will cause the engine structure to vibrate and emit a sound as if it had been struck a sharp blow.

A high rate of pressure increase means that an appreciable portion of the fuel must burn almost instantaneously. The knock occurs some time after ignition by the spark. During the time between ignition and knocking, the unburned fuel-air mixture is compressed in part by the piston and in part by the expansion of the gases already burned. If the unburned fuel suddenly burns, the hot gases must be put into a violently turbulent condition which accounts for the observation that there is an increase in the amount of heat lost to the cylinder walls, and partly for the loss in power. Some power may be lost due to the ignition being too early. Thus the cylinder walls will become hotter during knocking which will lead to pre-ignition.

Factors Influencing knocking

Apart from the chemical composition of the fuel and the fuel-air ratio, there are several factors which influence knocking in engines. Callendar (Engineering 121 (1926) 509) has given a discussion of these factors. Knocking in increased by:

1. High temperatures
2. Hot pockets in the combustion chamber
3. Placing the spark plug on one side of the cylinder rather than in the center
4. Increasing the compression ratio
5. Increasing the spark advance
6. Reducing the amount of inert gas
7. Decreasing the engine speed
8. Decreasing turbulence
9. Increasing the initial pressure by supercharging

Also, large engines knock more than small engines of the same compression ratio. This is certainly due in part to the higher temperatures existing in the large engines. Making changes opposite to those above decreases knocking. In particular, anything which decreases temperature will reduce knocking.

A consideration of these factors shows that they may be placed into four groups: factors related to temperature, factors related to density of charge, factors related to the time of combustion, and factors relating to the amount of inert gas present.

There is general agreement that the general correspondence between ignition by sudden compression and knocking is good. But there is considerable difference of opinion concerning the importance of the different factors. Thus

Ricardo (J. Soc. Aut. Eng. 10 (1922) 309) has expressed his opinion that knocking is not dependent on the temperature of compression but on the density of the charge. In support of this, he stated that the temperature at the end of compression is only 40 deg. C. higher in an engine of 6;1 compression ratio than in an engine of 4:1 compression ratio, and that knocking will occur in the engine of high compression ratio even when it is cold, while knocking will not occur in the other even with considerable pre-heating of the charge. Callendar (Engineering 121 (1926) 510) stated that Ricardo has always been of the opinion that pressure is the most important factor, while Tizard concluded that temperature is. While is does not appear possible to decide this question from the available data, still a consideration of the processes occuring in engines, together with the results of Tizard and Pye, may serve to elucidate the question to some extent.

From experiments carried out in the Air Ministry Laboratory, Callendar (Engineering 123 (1927) 211) has calculated the following table for the temperature at the beginning and at the end of compression. Air entered the cylinder at 5 deg. C. which is rather low.

Compression ratio	Temperature at beginning of compression	Temperature at end of compression
3;1	169	377
4:1	133	384
5:1	112	407
6:1	102	429
7:1	95	452
8:1	90	479

It may be noticed that these results are in good agreement with that of Ricardo in that the difference in temperatures, for an engine of 6:1 compression ratio and an engine of 4:1 compression ratio, at the end of compression is 45 deg. C., while Ricardo gave 40 deg. C. Also these temperatures are all greater than the mean values for the ignition temperatures obtained by Tizard, although some are less than his maximum temperatures.This shows that some oxidation preceding ignition is inevitable. The temperature reached in the unburned charge just before it is burned is of interest for knocking occurs an appreciable time after ignition. This may be estimated assuming no oxidation or cooling.

The pressure at the end of combustion cannot be computed with much accuracy. Dumanois (La Technique Aéronautique, Sept. 15, (1928) 182) gave the following results of the measurements of Aubert and Pignot for the maximum pressure produced by combustion by adiabatic compression.

Compression Ratio	5:1	6:1	7:1	8:1
Press. lbs./ sq. in. at end of combustion	540	625	695	740

Using 1.35 for the value of γ in the equation,

$$\frac{T}{T_1} = \left(\frac{P}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

assuming the initial pressure to be 14.7 lbs./sq.in., and using Callendars values for the initial temperatures gives the following results for the maximum temperatures of the last portion of the unburned charge reached by adiabatic compression.

Compression Ratio	5:1	6:1	7:1	8:1
Temperature, deg. C.	706	717	726	737

Thus, even in this extreme case, the temperatures are very much alike for the different compression ratios, which tends to suppost Ricardo's view. But there are other differences between high and low compression engines which seem to have been overlooked. The following explanation of why a high compression engines tends to knock so much worse than one of low compression is suggested.

Possible Temperature Variations

A consideration of the measurements of the usual temperatures existing in engines and Callendar's values for the temperature of the charge before compression shows that there must be a transfer of heat from the walls to the charge. In a Hispano-Suiza water-cooled engine with steel liners in aluminium cylinders, Dr. Gibson (see A.W. Judge,"Automobile and Aircraft Engines" p. 267) found temperatures of the cylinder near the top as high as 241 deg. C.. In another test, he found the temperature to be 172 deg. C.. Judge reported the maximum temperatures of aluminium alloy pistons in a certain engine as 240 deg. C., while the maximum temperatures of cast-iron pistons in the same engine was 400 deg. C. Exhaust valve temperatures, especially in air-cooled engines, are very high. Judge found exhaust valve temperatures in an air-cooled engine as high as 752 deg.C. The temperature of an exhaust valve is ordinarily considerably above the ignition point of the fuel, so that the fuel would be ignited if there were time enough. This is unfortunate, for it makes experiments at engine temperatures impossible with an apparatus such as that used by Tizard and Pye.

Effect of Temperature Variation

A charge comes into the cylinder with an appreciable velocity so that it remains for some time afterwards in motion. Experience shows that this motion lasts long enough to greatly reduce the time of combustion. In fact studies of the rate of propagation of flames in non-turbulent explosive mixtures show that they are too slow to be used in engines. The fact that the motion lasts for an appreciable length of time shows that the motion must be somewhat like a vortex. This motion will bring some of the mixture into contact with the hot walls, valves, and the spark-plug so that portions of the charge will be heated considerably higher than its mean temperature. Because of the short time available, these highly heated portions will not tend to become thoroughly mixed with the rest of the charge. It is impossible to imagine any kind of motion of the charge which will not leave quite stagnant regions near the hot walls at one place or another. Thus, part of the charge will be at nearly the wall temperature. In normal operation, the engine temperatures depend but little on the compression ratio. Furthermore, pre-heating the charge before it enters the cylinder will have very little effect on these maximum temperatures, although it will increase them some. Assuming that the highest temperature in the charge is 200 deg. C., which seems reasonable from the temperatures of the walls, the final temperature by compression can be calculated.

Compression Ratio	3:1	4:1	5:1	6:1	7:1	8:1
Temp. at end of Compression	422	496	559	613	662	717

In view of the results of Tizard and Pye on the decrease of the time of ignition by an increase in temperature beyond the ignition point, the increase in temperature as the compression ratio is increased is far from negligible. As combustion proceeds and the unburned charge is further compressed, the effect of an increase in compression ratio is still greater. From these considerations, it appears that rapid combustion may start in the highly heated portions so that the flame area is so much increased that the combustion of a part of the charge is almost instantaneous. Increased turbulence as a means of reducing knocking has two effects; one is the mechanical distribution of the flame causing quicker combustion, the other is to cause mixing of the gases so that the hot regions will be broken up to a greater extent. Hot pockets, on the other hand, will cause the charge to be highly heated locally, and therefore promote knocking.

At the beginning of the compression, the temperature of the charge is below the wall temperature, but as the compression proceeds, there will be a time when the temperature of the charge exceeds that of the walls, and the heat transfer will be in the opposite direction. Thus, the highest temperature will be in the neighborhood of the wall, but not at the wall. If a substance is to be effective in surpressing knocking, it must act in these regions of highest temperature.

Thus, while there must be some effect of pressure, the factors influencing knocking (except that of the amount of inert gas) can be explained satisfactorily from the effects of temperatures. The inert gases present during combustion, namely the nitrogen of the air and the residual exhaust, act chiefly by reducing the rate and temperature of oxidation. it has been recognized that the decreased amount of residual exhaust in a high compression engine helps to explain why it knocks worse than a low compression engine. The addition of an extra amount of cooled exhaust is the oldest method of preventing knocking.

From these general considerations of the problem of knocking, it seems reasonable to expect that lead tetraethyl acts by reducing the slow oxidation of the fuel. The experiments designed to decide this question will now be considered.

SLOW OXIDATION IN AN ENGINE

General Method of Procedure

The general method of procedure was to cause an ignition miss in the engine one time in four. At the end of the compression stroke during which the charge was not fired, a sample of the explosive mixture was removed and analyzed chemically. Any oxidation would cause a decrease in the oxygen content and perhaps an increase in carbon dioxide.

Engine Used

The engine used in these experiments was a 3/4 kw. air-cooled Delco-light engine having a bore of 2.5 inches and a stroke of 5 inches, making the piston displacement 402 cc. The clearance volume was 105 cc. making the compression ratio 4.83 . The compression pressure was 83 lbs./sq.in. gauge.

The changes from the standard engine were to provide a means of regulating the spark advance, to add a cam and arrangement of links for operating the sampling valve, and to equip the ignition system with a mechanical switch for eliminating the spark every fourth time it should occur. Iron was welded to the head to give sufficient thickness for the threads of the sampling valve.

A variable resistance was connected to the generator as a brake for the engine. When this Delco-light generator was connected in the usual manner, there was insufficient braking force regardless of what resistance was placed in the armature circuit, so it was reconnected as a separately excited generator. It was found that the field coils were so liberally designed that 115 volts could be applied without excessive heating. This gave a sufficiently large braking force to keep the engine speed down to 600 R.P.M. when the throttle was fully opened. Later the generator was connected as a compound cumulative generator to give easier regulation of the load.

There was a little leakage of exhaust gases into the room. While it was not probable that the chemical composition of the air in the room could be changed measurably by these gases, still, to eliminate any possibility of the air to the carburetor being impure, the carburetor intake was connected to the outdoors by a pipe, three inches in diameter.

Carburetor

An attempt was made to use a 3/4 inch Zenith carburetor changed only by adding two fuel tanks with floats and a stop cock for changing from one fuel in one tank to another fuel in the other. It was found that the floats were too erratic in their behavior to give very uniform fuel consumption, so they were discarded. Instead, fuel was added more rapidly than required by the engine and the excess allowed to overflow. The tanks were so constructed that the fuel level could be observed and adjusted. The flow into the fuel tanks was from reservoirs directly above them. The rate of flow was controlled by small orifices which permitted fuel to flow about twice as fast as required by the engine. Still the Zenith carburetor was unsatisfactory, for it did not permit changing quickly from one fuel to another due to its rather large passages for fuel. Another carburetor was constructed.

This carburetor, shown in Fig. 2, was designed to give uniformity of performance together with the possibility of changing very quickly from one gasoline to another. A standard Zenith jet, B, is fastened in a brass stop-cock, D, which may be turned to either of the tubes, C, which lead to the fuel tanks. The venturi tube, A, and the part holding it are from a Zenith carburetor. The total volume of the jet and stop-cock is about 1/5 cc.

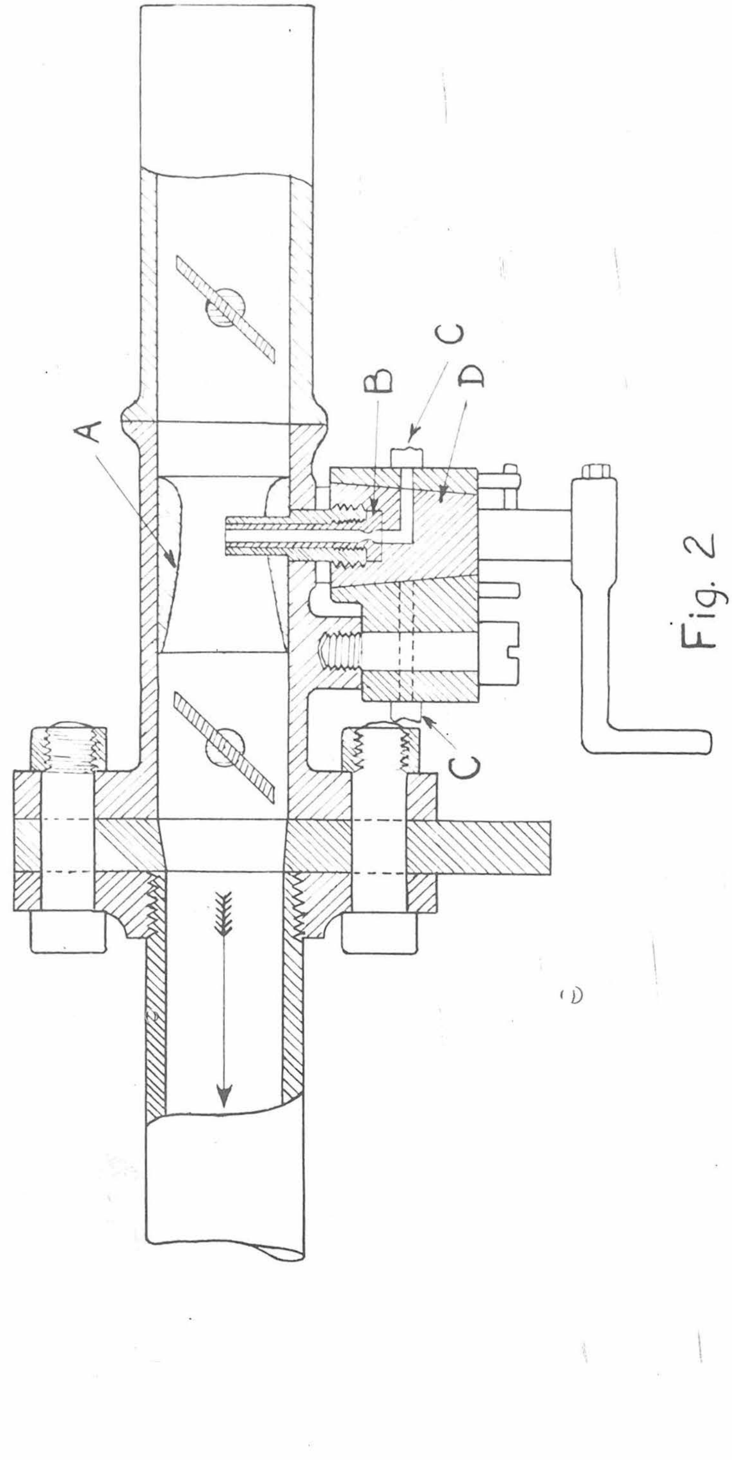

Fig. 2

Sampling Valve

The sampling valve (designed by Mr. W. M. Zaikowsky), used in collecting samples of the unburned mixture from the engine, is shown in Fig. 1. The engine has a cam driven switch in the ignition circuit which causes the engine to miss every fourth time. The sampling valve will open after the miss in ignition unless ignition has taken place spontaneously as it sometimes does. This action is produced as follows.

A member of a link mechanism, driven by a cam which in turn is driven by the cam shaft of the engine, presses on the knob, A. Usually, this mechanism was so adjusted that A starts to move down at the top dead center following the compression stroke, and returns to its top position before the exhaust valve starts to open. However, this will not open the sampling valve, G, unless the gas pressure applied to the chamber, B, is great enough to hold the valve, C, on its seat against the combined effects of inertia, the upward force of the weak spring, E, and, which is more important, the pressure of the gases in the engine cylinder against G. The gas pressure in B is adjusted so that the valve will open only when there is no explosion. In case of explosion, the valve, G, remains against its seat while C is opened allowing the gas in B to escape through the openings, D. When the link is not pressing against A, the spring, I,

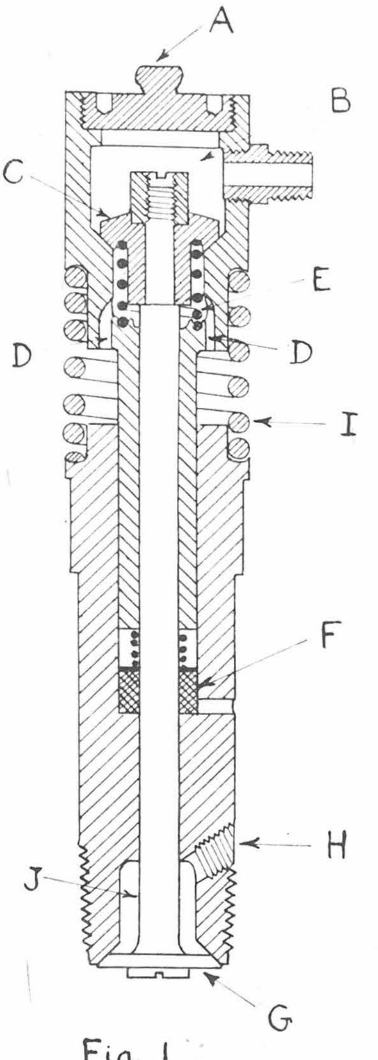

Fig. 1

holds both valves firmly closed. The sample is taken from a pipe connected to the opening, H. Packing, F, is placed around the valve stem to partially prevent air leaking into J which tends to take place to a small extent.

Having the sampling valve operate on the power stroke allows the heating by compression to have its full effect, if any, and allows some time for the mixing of the fresh charge with the residual exhaust.

The gas pressure used in B is supplied from an ordinary commercial nitrogen tank with a pressure reducing valve. A 1/4 in. dia. copper tube having several coils gives enough flexibility for the connection to the valve.

Sampling Bottles

Four sampling bottles of the type shown in Fig. 3 were used in collecting the samples from the engine. An inverted glass bell with a two way stop-cock is placed in a container made from seamless steel tubing. The bell is sealed with mercury. By moving the bell up, a fairly large sample of 400 cc. can be collected with less mercury than required for displacement. There are the further advantages that samples can be collected by equal portions and that they may be stored under a slight pressure so that any leakage of the stop-cocks will be from the bottle and hence unimportant.

Engine Speed Indicator

A small belt-driven Tetco magneto and a milliammeter was used to give the engine speed in most of the runs. In

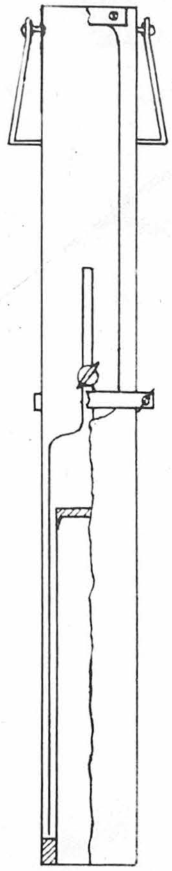

Fig. 3

the runs when this was not used, an ordinary shaft-driven electric tachometer was used.

Maximum Pressure Indicator

In the tests for measuring the maximum pressure at the end of compression, an Okill gauge was used. The Okill gauge has a small piston which is pressed against a seat by a calibrated spring, the tension of which is adjusted so that the pressure just fails to move the piston. Settings can be made with an accuracy of about 1/2 lb./sq. in. if the adjustment is made by placing a finger on the top of a rod which rests on the piston in order to detect any motion

Apparatus for Measuring Intake Air

Pressure fluctuations in the suction of the engine were damped out fairly completely by connecting the carburetor intake to a wooden box having inside dimensions 8.5 by 8.5 by 45 inches. Air entered the box through a venturi meter having a throat about 8.6 mm. in diameter. A water manometer measured the drop in pressure at the throat. Since this apparatus was used only to see if there was any variation in the volumetric efficiency of the engine due to dope in the fuel, it was unnecessary to calibrate the venturi meter.

Revolution Counter

A small revolution counter was mounted so that when it was placed in an "in" position it would turn at engine speed, and when it was placed in an "out" position it would stop.

Engine Temperature Measurement

A mercury thermometer was placed in an oil well in the engine head. The reading of the thermometer served only to give a check on the engine temperature so that conditions could be approximately duplicated.

Gas Analysis Apparatus

Precision gas analysis apparatus using mercury as the confining medium was used to analyze the samples. An oil manometer was used with the measuring burette to give accuracy in temperature and pressure correction.

Necessary Conditions for Comparable Explosive Samples

Several conditions must be satisfied if samples of partially oxidized mixture are to be the same except for the effect of dope in the fuel: for both samples, a) the air-fuel ratio must remain the same, b) the engine speed must be the same, C) the engine temperature must be the same, d) the chemical composition of the exhaust must either be the same of the differences definitely known, e) the ratio of the mols of exhaust to the mols of fresh charge must either be the same or the differences definitely known.

Quite a little work was necessary to be certain that these conditions were satisfied. To get the same air-fuel ratio for pure and doped gasolines was simply a matter of adjusting the carburetor. The ratio of the mols of residual exhaust will be constant if its temperature is not dependent on the use of dope in the fuel, and if the volumetric efficiency of the engine is not changed. The procedure in sampling was designed to greatly reduce the effects of changes in engine temperature.

Procedure in Collecting Explosive Samples

Before the collection of samples, the engine was always allowed to run partially throttled until the engine temperature became constant as observed by the mercury thermometer in the oil well in the head. The single-jet carburetor does not give a sufficiently rich mixture when partially throttled if it is adjusted to give a slightly lean mixture at full throttle, so the engine was operated on city gas while warming up.

Two of the sampling bottles of the floating bell type were connected by a Y-joint to the sampling valve. A wash bottle, filled with water, was connected between the Y-joint and the sampling valve so that the full pressure of the engine could not be exerted of the sampling bottle. The sampling bottles were completely filled with mercury before the start of the collection. The arrangement was such that the explosive gas could be passed through the connecting tubes up to the stop-cocks in the sampling bottles so that after one sample in one bottle was collected, the remaining gas could be passed through the stop-cock and completely removed before the collection of the other sample. It was thus made certain that all of the gas taken into the sampling bottles came from the engine and that there was no mixing of the samples.

The wash bottle allowed much more of the gas to excape from the engine than could be taken into the sampling bottle which tends to give a more representative sample than would be obtained if only a small amount of gas was taken from the cylinder and all of it taken into the sampling bottle. The idea was to take from the engine as much gas as the dimensions of the valve would permit, and take a small part of this into the sampling bottle. As may be seen from the sketch of the sampling valve, there are no pockets for the trapping of gas in it. This method of collecting samples should give representative samples, a matter of prime importance in these experiments.

With the air-cooled engine, the temperature increases when the throttle is fully opened until the engine becomes too hot to run. Since steady temperatures are not obtainable with it, the samples from doped and non-doped gasoline were collected alternately in approximately equal portions, quick changes from one fuel to another being possible with the apparatus used. The attempt was made to collect these equal portions in the same number of openings of the valve for uniformity. Each sample, about 400 cc., was collected in eight portions. No significance is attached to the number eight; it was merely convenient. If one starts collecting one sample first, for example a doped one, and then collects a portion for the non-doped, the average temperature for the latter is greater than for the former. To eliminate this small effect, samples were collected in both orders.

When a change was made from one fuel to another, knocking did not start or stop immediately. The cause for this will be considered below. It was necessary to wait until the change had audibly taken place. Preliminary tests showed how long a time was required, and a selected time was used to give uniformity. The most convenient way to measure this was to count the number of openings of the sampling valve which made enough noise to be heard distinctly.

Collection of Exhaust Samples

Collection of exhaust samples was more simple. For the sake of uniformity, they were collected in portions as in the case of the explosive samples. The sampling bottles were connected near the engine to the long exhaust pipe which carried the exhaust outdoors. It was not possible with the apparatus to collect exhaust samples and explosive samples simultaneously, so the effect of dope on the composition of the exhaust was studied first. As mentioned above, it is necessary that this effect be known if explosive samples are to be compared.

Measurement of Fuel Consumption

An attempt was made to measure the fuel consumption of the engine when using the overflow fuel tanks by passing a measured amount of fuel into the carburetor and measuring the overflow. This cannot be very accurate because of evaporation of part of the fuel, and unavoidable errors. The following results were obtained for one fuel tank.

Run	R.P.M.	Room temp.	Engine head temperature	cc. fuel burned	Revs.	cc. per explosion
1	690	29	170	20.85	1491	.0281
2	690	29	171	21.20	1548	.0274
3	690	29	171	27.10	1961	.0277
4	690	31	169	26.80	1987	.0270
5	690	29	168	26.05	1940	.0269
6	690	30	170	23.55	1715	.0275
7	690	29	157	14.55	1019	.0285
8	690	29	165	18.70	1353	.0277
9	690	26	152	26.05	1884	.0276
10	690	27	162	26.30	1917	.0274
11	690	26	153	27.15	1946	.0278
12	690	26	162	25.80	1851	.0279
13	690	26	162	25.00	1801	.0277

The average volume of fuel per explosion is 0.0276 cc. The variation in the readings is considerable due in part to the method of measurement and also to actual differences in the behavior of the engine.

The following are measurements for the other fuel tank.

Run	R.P.M.	Room temp.	Engine Head temperature	cc. fuel burned	Revs.	cc. per explosion
1	690	27	150	22.00	1598	.0275
2	690	26	158	18.20	1292	.0283
3	690	27	158	20.05	1481	.0271
4	690	27	160	18.60	1371	.0272
5	690	27	160	21.85	1605	.0273
6	690	27	160	21.95	1658	.0265
7	690	27	160	21.70	1596	.0272
8	690	27	160	23.75	1774	.0268
9	690	27.5	160	21.40	1613	.0266
10	690	27.5	160	22.55	1698	.0266

The average here is 0.0271 cc. per explosion. The engine head temperatures are the temperatures of the head at the beginning of the runs. The engine was idled before each run until this temperature was nearly constant. It was not easy to keep this temperature very uniform. One of the troubles in getting a uniform fuel consumption is the variation in temperature of the engine which changes the volumetric efficiency. For this reason, an air cooled engine is rather unsatisfactory for experimental purposes.

Adjusting the Fuel Tanks

The inaccuracies in this method of measuring the fuel consumption made it useless in adjusting the fuel tanks to give the same air-fuel ratio, so another method was used. When a lean mixture is burned, the power developed is quite sensitive to small changes in the air-fuel ratio. So if the speed of the engine is measured, keeping the resistance in the generator circuit constant, small differences in power may be detected although the power delivered by a generator varies approximately as the square of the speed. The following readings of speed were taken when the level of the fuel in tank, No. 1, was 0.3 mm. below that of tank, No. 2, as measured by a cathetometer. The fuel was the same in both tanks, namely Red Crown gasoline with 1/4% of lead tetraethyl. Readings of speed were taken alternately starting with tank No. 2.

No.	R.P.M.	
	Tank 2	Tank 1
1	690	684
2	681	673
3	674	669
4	671	666
5	666	661
6	666	661
7	664	658
8	664	656
9	658	653
10	658	653

The levels of the two tanks were then adjusted so that the difference was less than 0.1 mm. and the following readings were taken alternately starting with tank No.2.

No.	R.P.M.	
	Tank 2	Tank 1
1	705	705
2	695	686
3	684	684
4	676	679
5	671	671
6	671	659
7	664	664
8	664	664
9	664	659
10	658	653
11	654	653

The readings for tank No.1 are less in both cases due partly to the increase in temperature of the engine. When an average is made on an approximate time basis, the speed with tank No. 2 was 0.6% greater than with tank No.1 before adjusting the levels, while after adjustment, this difference was reduced to 0.1% . This shows how sensitive the behavior of an engine is to variations of the fuel level and helps to explain the irregular performance observed when floats were used in the fuel tanks.

Volumetric Efficiency as Dependent on the Fuel

Because of the high temperature of the residual exhaust, it seemed possible that some of the fresh mixture may be burned before the intake valve closes. If the oxidation depends of the presence of dope in the fuel, the volume of the fresh charge will be different. It was considered necessary to settle this question using the apparatus previously described. The following readings were taken.

No.	Manometer Readings		Speed R.P.M.
	Pure Fuel	Doped Fuel	
1	63	65	990
2	62	63	990
3	61	62	990
4	60	62	990
5	59	60	990
6	60	61	990
7	59	61	990
8	59	60	990

Pure fuel was in one tank and doped in the other. The readings were taken alternately starting with the doped. The use of the fuel tanks was interchanged and the following readings were taken.

No.	Manometer Readings		Speed R.P.M.
	Pure Fuel	Doped Fuel	
1	64	63	990
2	62	62	990
3	62	62	990
4	61	61	990
5	61	60	990
6	60	60	990
7	59	60	990
8	59	60	990
9	59	60	990

These readings were taken alternately starting with the pure fuel. The unit for the manometer readings is 1/20 inch of water.

During the runs, the engine temperature increased causing a decreased flow thru the venturi. The readings were plotted assuming that the rate of decrease was independent of the fuel used but a function of time and that the readings were taken at equal intervals. The result is that when pure fuel is used the volume entering is 0.9% less than when doped fuel is used under the conditions of these measurements. This may indicate oxidation of the pure fuel, but it is more probable that it is due to errors in measuring for the manometer was never quite steady. At any rate, as it shall be shown later, this difference is not great enough to account for the difference in the samples of doped and non-doped explosive mixtures.

Variation in the Temperature of the Exhaust

It seemed possible in view of the great difference in the behavior of an engine when knocking and not knocking that there may be an appreciable difference in the temperature of the exhaust. If this were the case, it would change the ratio of the mols of exhaust to the mols of fresh charge, and hence, for comparing exlosive samples, the difference in the exhaust temperatures must be known.

A thermo-couple, covered with insolute cement, was placed in the exhaust pipe about 5 cm. from the engine head. The exhaust temperature varied with the speed of the engine, but there was no difference caused by a change from pure gasoline which knocked badly to the same gasoline doped with lead tetraethyl so that it did not knock. At 750 R.P.M., the temperature was 560 deg. C. which is certainly hotter than the exhaust pipe. Since there was no difference in temperature under these conditions, the conclusion is that the mols of residual exhaust does not depend on the fuel.

Results of Analysis of Exhaust Samples

The results of analysis of six pairs of exhaust samples are given in the following table. For convenience of expression, the samples from the mixture containing dope will be refered to as the red sample, while the one from the mixture not containing dope will be called the blue sample as these colors were used for marking sampling bottles etc.

No.		CO_2	O_2	CO	N_2	R.P.M.	Temp.	% dope
1	red	16.62	0.95	0.40	100	630	---	1/5
	blue	16.52	0.46	1.15	100			
2	red	16.22	2.35	0.16	100	690	162	1/5
	blue	16.80	1.15	0.67	100			
3	red	16.91	1.18	0.49	100	690	177	1/5
	blue	16.90	0.48	0.94	100			
4	red	16.51	1.60	0.08	100	690	170	1/4
	blue	16.78	0.73	0.55	100			
5	red	16.42	1.42	0.00	100	690	167	1/4
	blue	16.56	0.88	0.69	100			
6	red	15.95	3.07	0.00	100	690	162	1/4
	blue	15.66	3.38	0.00	100			

The dope was lead tetraethyl and the percentage is given on the basis of volumes.The temperatures given are those of the engine head reached when the engine was warming up on partial throttle just before going to full throttle and the collection of samples. The gasolines used all had a density of approximately 0.75

Conclusions From Analyses of Exhaust

By comparing the results for the red with the corresponding results for the blue, it is seen that there is no great difference in the samples, although it is also seen that the total carbon varies somewhat. This is not entirely due to errors in gas analysis for the engine behaved somewhat unevenly. There was some difference in the two fuel tanks. Considerable time was spent in trying to get more uniform results from the air-cooled engine, but the variations in performance could never be made as small as desired. These samples were taken before it was found that the fuel consumption is sensitive to small differences in the fuel levels. But the temperature variation is the main source of trouble with the air-cooled Delco-light engine. The conditions under which the samples of exhaust were collected were less favorable for uniform results than the conditions for the explosive samples. However, an error of 2% in the mixture strength will change the amount of CO_2 in the explosive samples only 2%, an unimportant amount there.

It is considered that the measurements are sufficiently accurate to justify the conclusion that there is no difference in the composition of the exhaust if the mixture is lean, as it was for sample number 6. This carburetor adjustment was used in the collection of the explosive samples although the engine will not run as uniformly as it will with a richer mixture. From the average for the red and blue, and the known composition of air, the air-fuel ratio was 16.8:1.

Conclusions from Preliminary Experiments

From the results of the preliminary experiments, the conclusion is that the conditions for comparable explosive samples are satisfied fairly well, although the behavior of the air-cooled engine was never very uniform. Before giving the results of analyses of explosive samples, some incidental questions will be considered.

Time Required to Change from Knocking to not-Knocking

As mentioned above, knocking does not start immediately when changing from a doped fuel to a pure fuel, and does not stop immediately when the inverse change is made. With the single-jet carburetor, there was only enough gasoline trapped for about seven explosions. But about ten times this number were required for the change to be made, as audibly determined. It was decided to investigate this more fully, for this may be considered to be a result of lead oxide on the walls of the combustion chamber, which would be of importance if clearly established.

Before the single-jet carburetor was constructed, the Zenith carburetor was used. It was observed that the time required for the appearance of the knock and its disappearance was greater than it should be for removing one fuel from the passages of the carburetor and start using the other. However, the construction of the passages would prevent any really sudden change in fuels. One object in constructing the single-jet carburetor was to give a small passage for the gasoline with no pockets so that the actual change would be very quick.

When the single-jet carburetor was tried, it was found that the commencement and cessation of the knock was very gradual, requiring about 20 seconds for the knock to become completely established or removed when using gasoline and gasoline containing lead tetraethyl as fuels. A comparison of a knocking gasoline and benzole as the two fuels when the engine was hot enough to cause the gasoline to knock intensly showed that the knock starts immediately, although it needs a little time to reach its full intensity, and that the knock ceased immediately in changing to benzole.

It was found also that knocking starts and stops more quickly when iron pentacarbonyl (Unless otherwise mentioned, the word, dope, means lead tetraethyl) was used as the anti-knocking dope thanwhen lead tetraethyl was used in the same gasoline. The gasoline contains some hydrocarbons which are not very volatile. These can collect to some extent on the walls of the passage from the carburetor to the head of the engine. Since lead tetraethyl is less volatile than iron pentacarbonyl, there is a greater tendency for it to remain with the gasoline, thus explaining the difference in the behavior. This view is supported further by the observation of the way in which knocking starts and stops when lead tetraethyl is introduced as a vapor with the air rather than with the fuel,in which case the addition of dope caused the knock to disappear at once and ceasing the addition caused it to appear at once. The change was so quick that it is not possible to ascribe it to differences in the surface conditions in the engine. It was found later that lead oxide on the surface of a combustion tube greatly reduces oxidation. Since lead oxide on the walls of the combustion chamber is not effective is stopping knocking, this result is in complete agreement with the hypothesis that rapid combustion starts in hot regions which may be near but not at the walls.

Effect of Lead Tetraethyl on Residual Exhaust

It was noticed that when the engine was missing every fourth explosion, knocking occured in the first explosion following the miss with an intensity a little greater than in the other two explosions, if pure gasoline was used. When doped fuel was used, there was no knocking following the miss. In this first explosion following the miss, the thermal effects of the residual exhaust are negligible and any chemical effects greatly reduced. Thus, if lead tetraethyl has any effect on the residual exhaust, it is not the only effect it has in an engine. One cannot say from these observations that lead tetraethyl has no effect on the residual exhaust, for mixing the exhaust gases with a fresh charge has effects which tend to overcome each other; because it is hot, it will increase the temperature of the mixture which is favorable to knocking, because it dilutes the mixture, it tends to decrease knocking. Nevertheless, the observations suggest strongly that the important effect of lead tetraethyl is on the air-fuel mixture. The results of analyses of explosive samples will now be considered.

Explosive Samples

Explosive samples were collected in the manner explained above, using first one fuel tank for one fuel, say doped, and then using the other fuel tank for the doped so that two pairs of samples could be collected under the same conditions as possible. Two analyses of each sample were made, and the results given in the table are the mean of the two. These results are given on the basis that the residual after the absorption of carbon dioxide and oxygen is 100 cc. The analysis of the residue for combustible gases showed that their volume was small, less than 1% . Of the results given, No. 4 are most reliable. As before, red refers to doped fuel and blue to pure fuel.

No.	R.P.M.	Temp.		First Pair		Second Pair	
				CO_2	O_2	CO_2	O_2
1	800	167	red	1.07	25.77	1.43	25.33
			blue	1.85	24.67	1.69	24.92
2	640	152	red	1.54	23.71	----	-----
			blue	1.65	23.93	----	-----
3	640	157	red	2.43	23.32	2.17	22.72
			blue	2.56	22.47	2.43	23.01
4	640	155	red	2.64	22.76	2.57	23.06
			blue	2.70	22.68	2.77	22.13

The temperature given above are the temperatures of the engine head reached while the engine was idling just before taking the samples.

Conclusions from Analyses of Explosive Samples

From these results, the amount of carbon dioxide is greater in the blue sample although exhaust from doped fuel usually contains slightly more of carbon dioxide. However, from experiments with combustion tubes, which experiments will be considered below, it is probable that what is recorded is not entirely CO_2 but a mixture of CO_2 and some organic acids formed in slow combustion. Also from the combustion tube experiments, it was learned that compounds are formed in slow combustion which are absorbed very slowly by the KOH solution. It is possible that this is due to the polymerization of aldehydes. If this is also true for the engine, the results support the conclusion that lead tetraethyl decreases the slow oxidation of the charge.

In two of the pairs of analyses, the oxygen content is greater in the blue than in the red by a small amount, while in the other five pairs the blue contains less oxygen. The average difference for all of the samples is 0.41 cc. while that of No. 4, which is the most reliable as the behavior of the engine and the carburetor were best, is 0.50 cc., which is about 2% of the total oxygen present.

There was some oxygen left in the residual exhaust, but this may be neglected for the purpose of estimating how much the volumetric efficiency of the engine would have to be decreased to account for the difference in oxygen content. The ratio of nitrogen to oxygen in the air is 79.1 : 20.9 or, which is the same thing, 86.1 : 22.75 . To get the ratio 100 : 22.75 by adding nitrogen requires 13.9 parts of nitrogen for the 22.75 parts of oxygen. Assume that this amount of nitrogen comes from the residual exhaust and that air is added to give the ratio of nitrogen to oxygen, 100 : 22.25 . Then

$$\frac{20.9x}{79.1x + 13.9} = \frac{22.25}{100}$$

from which $x = 0.937$. To get the ratio 22.75 : 100 for the oxygen-nitrogen ratio, x must be 1.088. Hence to account for the difference in oxygen content, the volumetric efficience must be reduced

$$\frac{1.088 - 0.937}{1.088} = 0.139$$

Thus the observed difference if volumetric efficiency, 0.009, is not nearly enough to account for the difference of 2% in oxygen.

If the temperature of the residual exhaust were not the same, it is possible for it to be different enough to account for the difference in oxygen content. A calculation shows that the exhaust with a pure fuel would have to be cooler by something of the order of 150 deg. C. The measurement of the exhaust temperature would have shown some difference if this temperature really existed.

Since the difference in oxygen content cannot be accounted for by decreased volumetric efficiency or by a change in the temperature of the residual exhaust, it must be due to a decreased rate of oxidation when lead tetraethyl is present.

Maximum Possible Heat of Reaction

The maximum possible heat of reaction that can be realized in the combustion of a hydrocarbon-air mixture occurs when all of the oxygen is used to react with the hydrogen to form water. In the explosive mixture of the ordinary engine, not scavanged, of about 5 : 1 compression ratio, there is about 18% of oxygen by volume present. Taking the temperature of the explosive mixture as 300 deg. C. at which the heat of formation of H_2O is 58 cal., the raise of the temperature due to the reaction of each percent of O_2 is about 170 deg. C., or it will be about 30 deg. C. for each hundredth part of the oxygen present. That is, it will be about 60 deg. C. for the oxidation observed. In the Delco-light engine, the temperature at the end of compression will be about 600 deg. C. absolute while the pressure is 97 lbs./sq.in. absolute. This increase in temperature would increase the pressure

$$(660/600 - 1) \times 97 = 9.7 \text{ lbs./sq.in.}$$

Measurement of the Compression Pressure

In view of the calculation for the maximum possible increase in pressure due to oxidation for a pure fuel beyond that of a doped fuel, it was decided to measure the pressure in the two cases using the Okill gauge previously described. The gauge was connected to the sampling valve so that the compression pressure could be measured while the engine was running normally except for the miss in ignition every fourth time. Since the carburetor with the two fuel tanks permitted quick changes in fuel, effects of any change in the temperature were avoided.

No difference in the compression pressure was observed. The engine knocked badly with the pure fuel and did not with the doped. To be certain that this was not due to any differences in the fuel tanks, the use of the fuel tanks was reversed. No difference in pressure was observed even when the pure fuel was nearly at the point of auto-ignition.

Conclusion from Pressure Measurements

Since no difference in pressure was observed, it must be concluded that the thermal effects calculated on the assumption that all of the oxygen goes to form water are not realized. There seem to be only two possible explanations; a) the oxidation takes place on the walls of the combustion chamber and the heat goes to them, b) the assumption that only hydrogen burns is not valid. Cracking of the fuel may happen but the effect on the pressure should not be large. While the cooling of the walls may have some effect, it is doubtful that all of the heat could go to them because of the turbulent motion of the charge. Just what the reactions that take place in the early stages of oxidation are, is unknown at present. The lack of a difference in pressure indicates that the heat of reaction must be small. No calculations of thermal effects can be made until more is known about the reactions.

General Conclusions

The general conclusions from the previous experiments is that lead tetraethyl decreases the rate of slow oxidation before ignition and the passage of the flame. This accounts in general for the anti-knock effect of the lead tetraethyl but the experiments tell nothing about the manner in which the rate of oxidation is reduced. Further experiments with slow combustion in heated tubes have yielded some results of interest, but this part of the problem is still unsolved. Before considering these experiments, two other experiments will be considered; one concerns the evaporation of the fuel in the Delco-light engine, the other the presence of aldehydes in the explosive samples.

Evaporation of Fuel

The carburetor of the Delco-light engine is connected to the head by a straight pipe about five inches long. If one looks into this pipe through the carburetor while the engine is running, the fuel is seen to leave the jet as a white mist and pass through the pipe, much of the mist staying near the middle. Thus the chances of fuel entering the cylinder unevaporated are very good.

With the apparatus, it was possible to switch off the ignition and generator load quickly and use the generator as a motor to turn the engine. When the compression pressure was measured under these conditions, it was found to depend on whether or not fuel entered with the air. With air alone, when the engine was hot, a pressure of 70 lbs. gauge was measured, with benzole 68 lbs, and with gasoline 66 lbs. If the pressure measurements were taken when the engine was cold, the difference in pressure for air, and air with gasoline was 2 lbs. It appears that the difference must be due to evaporation of the fuel.

A numerical calculation should give approximate agreement. Complete agreement cannot be expected, for the time when the fuel evaporates and the heating of the walls are unknown. Assume that the fuel air ratio was 15;1 and that the evaporation of all of the fuel takes place at the beginning of the compression stroke, using heat from the air only. Since no hot exhaust was mixed with the air, the temperature may be considered to be 300 deg. C. abs. Gurwitch, in "Petroleum Technology" gives 68 cal./gram as the heat of evaporation of the constituent of gasoline having a density, 0.7428 . The specific heat of a diatomic gas is 5 cal./mol or 5/28.7 = 0.174 cal./gram for air. As a result of evaporation, the temperature is approximately

$$\frac{15 \times 0.174 \times 300 - 68}{15 \times 0.174} = 274^{\circ}\text{C abs.}$$

The pressure will be reduced from 14.5 lbs./sq.in. to

$$14.5 \times \frac{274}{300} = 13.25$$

The partial pressure of the fuel will increase this about 2% making the pressure 13.5 lbs./sq.in.

The connections of the gauge increase the clearance volume of the engine. The compression ratio with the gauge must be about

$$\frac{v_1}{v} = \left(\frac{P}{P_1}\right)^{1/\gamma} = \left(\frac{84.5}{14.5}\right)^{\frac{1}{1.35}} = (5.83)^{\frac{1}{1.35}}$$

Considering the reduction in pressure

$$P = \left(\frac{v_1}{v}\right)^{\gamma} P_1 = 5.83 \times 13.5 = 78.8 \text{ lbs./sq. in.}$$

The calculated pressure difference is 84.5 - 78.8 = 5.7 lbs. per sq. in.. If it is assumed that the fuel is evaporated at the end of compression, the difference is less than that observed. It appears that some of the fuel is evaporated before the intake valve closes and the rest soon afterwards. This is in general agreement with the conclusions of H.C. Dickinson (J. Soc. Aut. Eng. 8 (1921) 450) and contrary to the conclusion of Callendar that the fuel will condense in the cylinder.

Tests for Aldehydes in Explosive Samples

The samples of explosive mixture were collected into evacuated gas sampling bottles of about 475 cc. capacity. A small capillary tube was fastened to the entrance cock of the bottle so that the time required to fill it was about one minute. Colorimetric tests seemed to indicate that more aldehyde was present when pure fuel was used than when doped was used, which agrees with Callendar's observations (Engineering 123 (1927) 210), and is in agreement with the conclusion that lead tetraethyl decreases the rate of oxidation.

OXIDATION IN HEATED TUBES

Apparatus Used

The combustion tubes and apparatus for making the

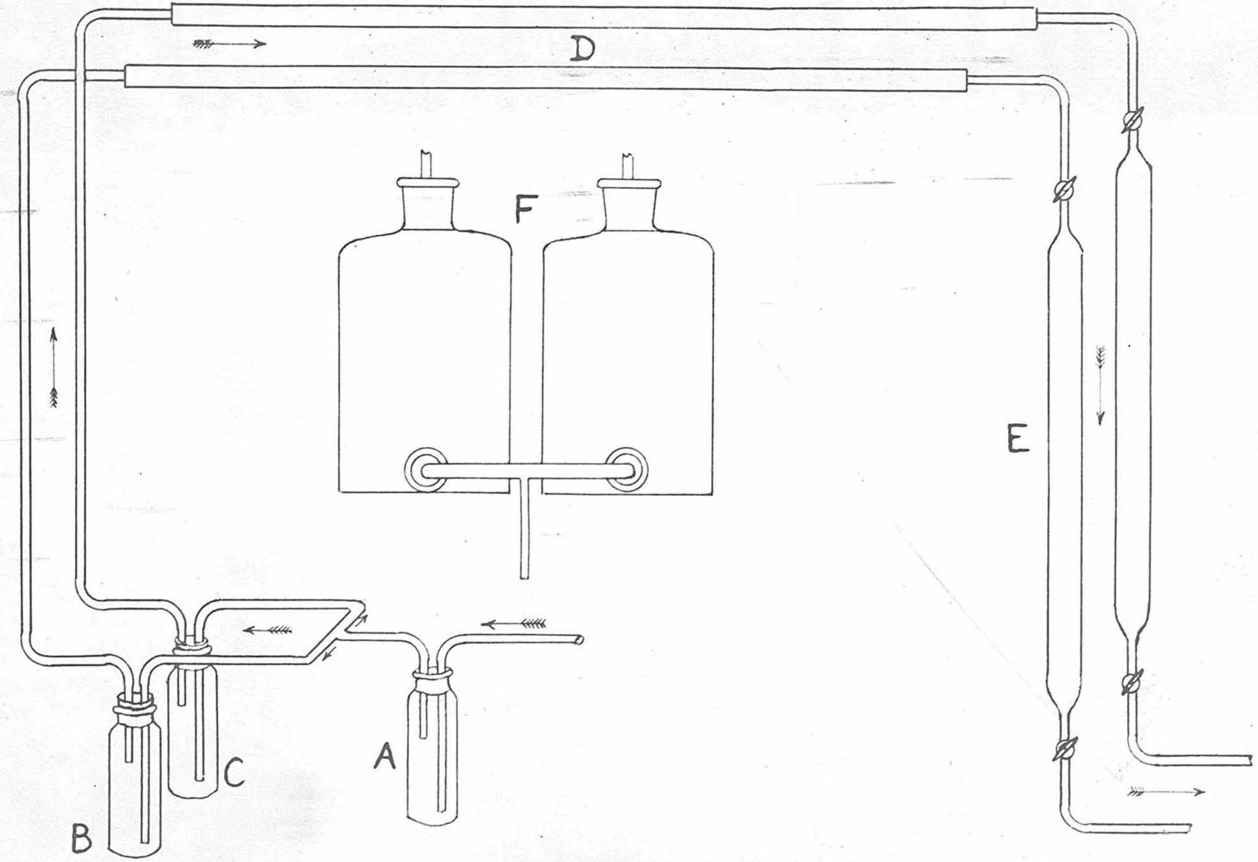

Fig. 4

samples in the first experiments on slow oxidation are shown in Fig. 4. A bottle, A, contains gasoline and glass beads through which air is passed. The resulting mixture of fuel and air is divided into two equal parts by having equal rates of flow through the two combustion tubes, D. One of the two parts, in passing through the bottle, B, in which there is some lead tetraethyl absorbed by some loose asbestos, becomes doped. The other bottle, C, is the same as B except that it contains no lead tetraethyl, the purpose of C being to keep the two sides of the apparatus similar. Between the bottles, B and C, and the combustion tubes, D, a length of about 10 cm. of 2 mm. capillary tubing through which a copper wire of about 0.5 mm. is passed, is placed so that a flame can not reach the bottles, A, B, and C.

The combustion tubes, which are of pyrex glass, are 80 cm. long, with an internal diameter of about 13 mm. They are covered on the outside with a 2 mm. layer of asbestos paper to reduce the loss of heat.Each tube contains a helical heater of No. 20 B&S chromel wire of approximately 13.5 ohms resistance. The heaters were connected in series so that the heating of the two tubes would be the same. Generally, the attempt was made to duplicate the two combustion tubes etc. so that any difference in the two samples would be caused only by the presence of dope. A thermocouple was placed next to the glass wall of one tube so that temperature conditions could be reproduced for different mixtures.

Since only partial oxidation takes place in the heated tubes, it is important to have the rates of flow in the two tubes identical. This was realized by connecting the suction bottles, shown by F of Fig. 4, to the lower ends of the sampling bottles. The suction bottles, after being filled with water, were allowed to drain through a 5 mm. glass tube, the lower end of which was placed about 40 cm. below the bottoms of the bottles. Any inequality in the rates of flow could be observed by the difference in levels of the water, and corrected by partially clamping the tube connected to the sampling bottle on the side which flowed fastest.

The sampling bottles, E, are cylindrical having a length of about 50 cm. and a volume of about 475 cc. They are provided with a stop-cock at each end.

In the case of perfact diffusion of the fresh gas with the original gas in the sampling bottle, the amount of the original gas left is very small for it may be shown easily that

$$R = e^{-\frac{V}{Q}}$$

where R is the ratio of the original gas present at any time in the gas collected, and V/Q is the ratio of the volume of the gas passed through to the volume of the container. For these experiments, V/Q was about 7.5 which gives $R = 1/1800$, an upper limit for the amount of gas left in the sample. It was not considered necessary to evacuate the bottles.

Procedure

Since the purpose of these experiments was to determine differences in the effect of heating fuel-air mixtures with and without dope, no attempt was made to prepare mixtures of given fuel-air ratios. The mixture, prepared as mentioned above,was passed by blowing through the combustion tubes at room temperature at approximately the rate of flow produced by the suction bottles, and ignited at the end of the combustion tubes, the sampling bottles being disconnected. The strength of the mixture was judged from the appearance of the flame. The gasoline used contained some very volatile constituents so that the mixture was very rich at first. To give a leaner mixture, an additional tube was passed through the stopper of the mixing bottle, A, of Fig. 4 through which air could be passed without bubbling it whrough the gasoline. This method was used in the preparation of some of the samples. It has however the disadvantage that the strength of the mixture changes very rapidly at first when fresh gasoline is used. After the most volatile constituents have been removed, the rate of change in the strength is much reduced. It was found better to pass air through the gasoline until the strength of the mixture, when all of the air was passed through the gasoline, was the one desired.

The rate of flow used and the dimensions of the combustion tubes gave approximately 3 seconds for the time of exposure of the air fuel mixture to the action of heat.

The current used in the heater was 4 amperes for all of the samples analyzed.

Observations with Heated Tubes

The conditions, under which the samples were collected, were selected because it was found in preliminary work with the apparatus that, as the current in the heater was increased from zero, there was a value of current at which a dense white smoke and a strong acrolein odor were produced in the combustion tube for the pure gasoline, while none of the smoke was produced in the combustion tube for the doped gasoline and the acrolein odor was very faint. It was found that under no conditions could this same smoke be produced with dope present although there was a small amount of smoke which can be attributed to the presence of lead oxides. This white smoke was formed in the tube for pure gasoline for a rather wide range of temperature and strength of the mixture. If the heater current is great enough, there is no smoke, and water vapor collects in the sampling bottle. As before, the sample from gasoline with dope will be refered to as red, while the other will be called blue.

The white smoke was observed in both samples from the engine, but the experiments do not permit a statement as to whether the red or the blue had the greater amount. Part of the smoke must come from the lubricating oil which complicates the matter. The acrolein odor was also observed in the explosive samples, which indicates that the combustion tubes may produce effects comparable with those occuring in the engine during compression.

Tests for Peroxides

The products of slow oxidation of a very rich air and gasoline mixture from the combustion tubes were bubbled at different rates through solutions of KI. The mixture which contained no lead tetraethyl gave a dark brown color to the KI solution, but the addition of starch solution gave no blue coloration. Furthermore, distilled water alone acquired exactly the same color as the KI solution under the same circumstances. The mixture containing lead tetraethyl gave no coloration at all.

After the tubes had been used for a little time, the tube for the blue became covered with a dark brown viscous fluid on the cool part of the exit end, while the other tube became covered with a light colored lead oxide deposit only. The coloration of the KI solution and distilled water was due to this dark brown substance and not to the oxidation of iodine in these cases. However, further experiments have shown that a substance which oxidizes iodine can be made by passing a mixture of gasoline and air through heated tubes. These experiments will be considered later.

Effect of Lead on the Walls of the Tube

An important observation which has a bearing on all experiments of this nature was made. After a mixture containing a small amount of lead tetraethyl has been passed through a tube for some time so that lead oxide has been deposited on it, a mixture containing no lead tetraethyl does not give the white smoke and intense acrolein odor, as it does under the same temperature conditions in a tube which never has come into contact with lead, However, if the chromel wire heater was heated for a short time by a current about 1.5 times as great as was used in the collection of the samples, while an air-gasoline mixture of city gas was passed through it, and then brought to normal temperature, it would produce the white smoke and acrolein odor exactly like a tube which never came into contact with lead, in so far as could be determined without analysis of the samples. In this treatment, the lead oxides will be reduced and removed as a vapor. If the temperature of the tube is not too great, the effect of the lead is noticable for a very long time.

Method of Analysis of Samples

The samples, red and blue, were each analyzed in two ways. In one analysis, oxygen of known purity was added to the original sample and the mixture was burned by a heated platinum wire. The resulting contraction of volume, CO_2, and the amount of O_2 used in combustion were determined. This will be spoken of as direct combustion. In the other analysis, CO_2 and O_2 were absorbed first, after which the sample was burned etc. as before. This will be spoken of as indirect combustion. The results are given on the basis that the residual N_2 is 100 cc.

Results of Analysis

		Red Sample		Blue Sample	
No.		Direct	Indirect	Direct	Indirect
1	W	132.05	132.71	129.09	128.13
2	O_2 in air	26.42	26.42	26.42	26.42
3	O_2 added	19.15	42.80	16.12	32.40
4	O_2 absorbed	-----	27.05	-----	20.56
5	CO_2 absorbed	-----	0.64	-----	1.83
6	T.C.	22.02	20.20	18.90	17.21
7	CO_2	29.10	27.65	26.25	20.93
8	N_2	100.00	100.00	100.00	100.00
9	O_2 total	45.57	42.80	42.54	32.40
10	O_2 for H_2	16.47	15.15	16.34	11.47

The quantity, W, is the volume of the sample and T.C. is the thtal contraction of the sample by combustion. Numbers, 4 and 5 were abslrbed before combustion. Number 2, the oxygen in the air, is from the known composition of air. The variation of the quantity, W, for a given sample represents the inaccuracy of the analysis. This variation may be due in part to processes occuring in the sample during its storage during the time between collection and analysis. Number 10, O_2 for H_2, is obtained by subtracting from the total volume of O_2 used, No. 9, the volume of CO_2, as oxygen not used for the combustion of carbon is used for the combustion of hydrogen.

Discussion of Results

The value of W for the red sample is greater than for the blue. This is due to the greater oxidation of the blue sample in the combustion tube so that it contracted more. The amount of $O_2 + CO_2$ absorbed in the indirect is 27.69 which exceeds the possible maximum of 26.42 . One concludes that some compound was absorbed with the CO_2 and O_2 . The absorption of part of the fuel is shown still more clearly by the fact that the direct combustion gave more CO_2 than the indirect, which shows that products of oxidation were absorbed before combustion. Later experiments show that acids are formed. There is also the possibility that the fuel was cracked by the heating and that the products of cracking were absorbed. Moreover, the difference in the amount of CO_2 absorbed in the blue direct and the blue indirect combustions is greater than in the case of the red, which indicates a greater degree or difference of oxidation or cracking in the case of non-doped samples.

To test whether or not the gases absorbed could be gasoline vapors, a sample of air-gasoline mixture was collected under the usual conditions except that the combustion tubes were at room temperature. The results were as follows:

Volume of sample	99.05 cc.
After KOH absorption	99.06 cc.
After 3 combustions	95.27 cc.

These results show that the gases absorbed by the KOH were not gasoline vapors, but some products of cracking or oxidation. The combustion of the sample was made to make sure that it contained enough fuel to give a fair sixed T.C..

Unfortunately, the accuracy of the analysis is not great enough to determine with much accuracy what the hydrogen-carbon ratio of the absorbed fuel is. One may compute this ratio in the following manner. The volume of the fuel which was absorbed is $27.05 + 0.64 - 26.42 = 1.27$ cc. Since 26.42 is the volume of O_2 in air corresponding to 100 cc. N_2, there cannot be any CO_2 included in the 1.27 cc. The volume of CO_2 formed by this amount of fuel is the difference in the direct and indirect combustions, namely 29.05 - 27.64 or 1.45 cc. The difference in the amounts of O_2 for H_2, $16.47 - 15.16 = 1.31$ cc. is the amount of O_2 required for the combustion of the hydrogen in it. These data give the empirical formula, $C_{1.1}H_4$, i.e. it is methane. But the data are not consistent. The volume of the fuel burned in the direct can be computed, and also the volume in the indirect after the absorptions of CO_2 and O_2 and their difference should be the volume of the fuel that was absorbed. In the red direct, the volume of fuel is

$$V = T.C. - (O_2 - CO_2) = 5.55 \text{ cc.}$$

In the red indirect after absorption, it is

$$V = T.C. - (O_2 - CO_2) = 5.04 \text{ cc.}$$

The difference is $5.55 - 5.04 = 0.51$ cc. which is quite different from 1.27, and gives an absurd formula for the fuel.

The data can be brought into a more consistent form by correcting for the differences in the two values of W by averaging. Subtracting the value of N_2 from the value of W, and taking the mean for the two gives 32.38 and so the correction factor is 0.0103 for the red. The following is obtained:

		Red Sample		Blue Sample	
No.		Direct	Indirect	Direct	Indirect
1	W	132.38	132.38	128.61	128.61
2	O_2 in air	26.42	26.42	26.42	26.42
3	O_2 added	19.35	42.36	15.85	32.94
4	O_2 absorbed	-----	26.77	-----	20.90
5	CO_2 absorbed	-----	0.63	-----	1.86
6	T.C.	22.25	19.99	18.58	17.50
7	CO_2	29.40	27.36	25.76	21.28
8	N_2	100.00	100.00	100.00	100.00
9	O_2 total	45.77	42.36	42.27	32.94
10	O_2 for H_2	16.37	15.00	16.51	11.66

From this, using the first manner of computation, the volume of the fuel absorbed is 0.98 cc. and by the second method of computing it is 0.89 cc.. The difference in the CO_2 is 2.04 cc. and the difference in O_2 for H_2 is 1.37 cc. The first value for the volume gives the formula $C_{2.08}H_{5.59}$ and the second value for the volume gives $C_{2.29}H_{6.05}$. This indicates that the fuel is ethane. While these computations are not very accurate since they depend on differences, it is permissible to say that the fuel absorbed is a light hydrocarbon. This shows that a tempory exposure of a very rich doped mixture of air and gasoline to a hot chromel wire can produce a measurable degree of cracking without much oxidation.

The composition of the fuel which burned in the red indirect combustion may be computed more accurately. Its volume was 5.04 cc., it produced 27.64 cc. of CO_2 and required 15.16 cc. of O_2 for the combustion of the hydrogen in it. So its formula is $C_{5.48}H_{12}$ which corresponds to a mixture of pentane and hexylene.

Passing now to the blue sample, it is seen that the amount of oxygen used was 26.42 - 20.56 = 5.86 cc. So unlike the red sample, oxidation here is very appreciable, and any computations based on assuming it negligible would be meaningless. The acrolein odor indicates that part of it has been used for the formation of aldehydes.

Part of the fuel is absorbed by the KOH, for the difference in the CO_2 absorbed in the direct and indirect is 26.25 - 20.93 = 5.32 cc. Assuming that the 1.83 cc. absorbed by the KOH is all CO_2, still the difference is 3.49 cc., but the data is insufficient for determining its composition even approximately.

The composition of the fuel which burned in the indirect combustion for the blue, may be computed in the same manner as for the red, which gives $C_{3.64}H_8$. Comparing this with that of the red, namely $C_{5.48}H_{12}$, shows clearly that cracking has taken plece to a greater extent in the blue than in the red.

Comparing the CO_2 formed in the direct combustions shows that more has been formed in the red than in the blue, while a comparison of the O_2 for H_2 shows that the amount is nearly the same for the two. This shows that the fuel lost in the viscous tar is mostly carbon. But the T.C. for the red direct is greater than for the blue direct, which shows that more of the H_2 was burned in the combustion tube for the blue. While this shows that the presence of dope decreases the oxidation of the light hydrocarbons, it also suggests that in this slow oxidation hydrogen burns first.

The main results of these first incomplete analyses may be summarized by saying that cracking of gasoline in an air-gasoline mixture, and the combustion of the products of cracking is less in the case when lead tetraethyl has been added to the mixture under the conditions of these experiments.

Another Experiment

The following experiment was performed. A rich mixture of air and gasoline doped with lead tetraethyl was passed through one of the hot combustion tubes, then through a sampling bottle where it was cooled to nearly room temperature, after which it was passed through another combustion tube identical with the first in every respect except that it was free from any deposit of lead oxide, and finally through another sampling bottle. Unfortunately, very fresh gasoline was used in the preparation of the air-gasoline mixture so that the strength of the mixture was decreasing rapidly. Samples were taken simply by closing the stop-cocks of the sampling bottles so the second sample, the one which passed through both combustion tubes, was richer than the first, as the analysis shows.

It was observed in taking the samples that there was smoke in the sampling botthe after the mixture had passed through both combustion tubes. It was considered that all of the lead tetraethyl present would be decomposed by heat in the first tube and that very little lead would be carried into the second combustion tube, so that the action of heat in the second tube would be different.

<u>Results of Analysis.</u>

No.		Ist Sample		2nd Sample	
		Direct	Indirect	Direct	Indirect
1	W	140.5	140.5	137.0	137.0
2	O_2 in air	26.42	26.42	26.42	26.42
3	O_2 added	108.18	115.10	120.40	112.10
4	O_2 absorbed	------	25.90	------	15.23
5	CO_2 absorbed	------	1.32	------	5.51
6	T.C.	65.05	56.00	65.95	56.20
7	CO_2	83.40	72.70	87.60	71.90
8	N_2	100.00	100.00	100.00	100.00
9	O_2	134.60	115.10	146.82	112.10
10	O_2 for H_2	51.10	42.40	59.22	40.20

Discussion of Results

These results show that the time during which lead tetraethyl remains effective is short provided there is no deposit of lead on the heated surface.

Computations of the empirical formulas of the fuels which burned in the indirect combustions give $C_{5.3}H_{12.5}$ and $C_{4.5}H_{10}$ respectively for the first sample and the second, showing that cracking proceeded in the second tube.

As a result of passing the sample through the first tube,

$$\frac{26.42 - 25.90}{26.42} \times 100 = 1.97$$

or about 2% of the total oxygen present went to oxidation. After the passage through the second tube,

$$\frac{25.90 - 15.23}{26.42} \times 100 = 40.4$$

or about 40% of the oxygen was used in the second tube. The oxidation proceeded 20 times as fast without dope as with it.

Formation of Peroxides

It was first suggested by Callendar (Engineering 123 (1927) 210) that knocking in engines may be due to the formation of peroxides in the early stages of slow oxidation. A series of observations concerning such peroxides have been made.

The rate of flow of an air-gasoline mixture and the temperature of the combustion tube with the chromel wire helix inside were varied while the products of oxidation were passed through an acidified solution of KI with starch as an indicator. Sometimes there was a sudden coloration. This coloration was never observed unless the run was sufficiently long to contaminate the tube with condensed products of oxidation. The tube with the chromel helix was not very suitable for this experiment for the condensed products could not flow freely from it.

Another pyrex glass combustion tube about 40 inches long was made with an electric heater about 20 inches long at the entrance end. The other end, being exposed to the air of the room, remained quite cool. The tube was inclined at an angle of about 20 degrees so that the condensed products could flow out. After several hours of blowing air-gasoline mixture through the tube, several cc. of condensate were received. The condensation started about 5 cm. from the end of the heater, and the rest of the tube was filled with a white fog. If some of the condensate was placed in a test tube and heated gently, it produced the white smoke.

When tested idiometrically, one drop of the condensate was found to require as many as 176 drops of 0.02 N sodium thiosulphate solution to decolorize the solution. Further preparation of condensate showed that the amount of peroxide is very much dependent on the conditions of temperature and rate of blowing, but no attempt was made to determine the most advantageous conditions. The reaction with KI proceeds very slowly, several hours being required to complete the determination.

Some of the condensate was dissolved in water and boiled for about ten minutes. The peroxide content was unchanged which shows that the peroxide must be quite stable at 100 deg. C.

From the manner of getting the condensate, it is not certain whether the peroxide is formed in the gaseous or liquid phase. The fact that there was no coloration when the products of oxidation without the liquid condensate were passed through KI solution with starch as the indicator suggests that the formation is in the condensate.

Effect of Peroxide in Fuel

The peroxide does not appear to be at all of the explosive nature of the peroxides tested in an engine by Callendar (Engineering 123 (1927) 210). The condensate will burn when ignited about the same as kerosene.Unfortunately it does not dissolve in gasoline to any extent. It dissolves readily in a mixture of acetone and ether, so it was tried with this mixture in the Delco-light engine. Since acetone does not knock in this engine, it was necessary to add the ether. The mixture consisted of 2 parts of acetone to one part of ether for the fuel without peroxides.For the other fuel, about 12 cc. of the condensate prepared from n-hexane was added to 78 cc. of the acetone-ether mixture. The peroxide content of this, calculated as hydrogen peroxide, was 5.6 g./ liter.

But when this mixture with the condensate was tried in the engine,using the acetone- ether mixture to compare it with, there was no difference as determined audibly when making sudden changes from one fuel to the other. Trials were made when the engine was cool enough to give a very slight knock, when it was knocking moderately, and when it was knocking quite badly. In the latter case the knocking was slightly less for the mixture with condensate.

S.F. Birch and R. Stansfield (Nature Mar, 30, 1929, p 491) found that when cyclohexane had been exposed to light and air for six months that the highest useful compression ratio was reduced from 5.6 to 5.46. A rough analysis gave a peroxide oxygen content of 0.2 g./ liter. Callender tried known peroxides in an engine and found that the highest useful compression ratio was reduced in all cases.

There does not appear to be sufficient experimental evidence to show entirely what caused this difference in results. The peroxides tried by Callendar (Engineering 123 (1927) 210) produced a considerable effect if they were very unstable. The peroxides found in the condensate seem to be fairly stable, so it must be expected that their effect must be less than the unstable ones. Another explanation may be that the peroxides act differently in the mixture of acetone and ether mixture than they would in gasoline. This could be tested experimentally by by building a carburetor with two jets, one for gasoline and one for the condensate.

It is not surprising that unstable peroxides should cause an engine to knock in view of the well known effect of increasing the temperature. When the experiment with the acetone and ether was tried, it was expected that there would be increased knocking. Since there was no increase, the conclusion seems to be justified that the peroxides formed in the slow oxidation in tubes are fairly stable at the temperatures in the engine. There is the possibility that the condensate contains some other compounds which completely compensate for any knock promoting effect of its peroxides. If one were adopting the peroxide theory of knocking and if this were the case, it would be necessary to show why this could not happen in an engine.

The fact that Birch and Stansfield found that cyclohexane containing peroxides knocked worse than cyclohexane which did not, does not justify in itself the conclusion that the peroxides increased the knocking. It is conceivable that there were other molecular changes in the fuel ~~other~~ than the formation of the peroxides.

At any rate, the comparatively large amount of peroxide in the acetone ether mixture, together with the fact that they are apparently quite stable peroxides, makes the hypothesis that they are responsible for knocking seem quite improbable. However, peroxides were formed in no case when lead was present either as a deposit of lead oxide on the walls of the combustion tube or as lead tetraethyl vapor with the fuel.

Oxidation on the Walls of the Combustion Tubes

The fact that lead oxide on the walls of the combustion tubes greatly decreases oxidation and lasts for a very long time indicates clearly that all, or at least nearly all, of the oxidation in tubes takes place at the walls. This means that the effect of lead tetraethyl on the combustion in an engine must be studied in such a manner that the effect of walls will be eliminated in future experiments. It is possible also that the temperature of rapid oxidation at the walls is less than in the volume, but the observation that lead on t the walls of an engine has no effect on knocking makes this appear unimportant.

Acids in Condensate

The condensate and the vapor above it were distinctly acid. This acid will give a very vigorous reaction with iron or copper filings. There is some other effect than that of the acid on iron, for if the condensate is made slightly alkaline, a reaction with production of gas takes place and a precipitate is formed. The precipitate appears to be iron hydroxide.

The fact that acid is formed during slow combustion helps to account for some of the fuel being absorbed by the KOH solution and makes the analysis for CO_2 by absorption of very doubtful accuracy.

In another experiment, a mixture of n-hexane and air, about three times rich, was passed through two heaters, the first being heated at a higher temperature than the first. After the oxidation in the first of the two heaters, the mixture was divided into two parts and passed at equal rates through two equally heated tubes of pyrex glass in the second heater. The second heater was 16 inches long, and the inside diameter of the pyrex glass tubes was 11 mm. The temperature of the second heater was 254 deg. C.. The temperature of the first heater was not measured, but judging from an analysis of the products and the rate of flow, together with other observations with the apparatus, it must have been about 380 deg. C. The rate of flow through the first heater was about 600 cc./min. measured at room temperature. One tube in the second heater was clean while the other was covered with a thin layer of lead oxide.

There was condensate from both tubes in the second heater. But the condensate from the tube with lead was neutral while that from the other was acid. Also a test for peroxides showed that they were not present in the condensate from the tube with lead. Unless the acids and peroxides are formed in the liquid phase, this proves that lead will distroy them when they are once formed.

Peroxides not Formed Initially in Oxidation

The following simple experiment appears to show quite conclusively that while peroxides can be formed by slow oxidation in tubes, that their formation is not the initial step in oxidation. Two tubes, alike in all respects, were placed in a heater so that the external temperatures were the same. A n-hexane and air mixture was passed through one tube and then into a vessel where condensation could be observed if it took place, and where the mixture would be cooled to room temperature. It was then passed through the second heated tube.

It was possible to adjust the heater temperature and the rate of flow so that there was no smoke, no condensation, and only a slight acrolein odor after the mixture had passed through the first combustion tube. But when it had passed through the second tube, there was much smoke, the odor was strongly acrolein, and there was condensation. The condensate gave a reaction for peroxides. No analysis was made of the products after the first heating, but it has been observed many times that unless there is smoke and a strong acrolein odor, the oxidation is small.

In another run, the rate of flow was adjusted so that there was about one tenth as much condensate after one combustion as after two. A rough test for peroxides showed that their concentration was considerably greater after the second heating.

Hydrogen Evolved from Condensate

It was noticed as soon as several cubic centimeters of the condensate were collected that small bubbles were evolved from it at room temperature. This production of gas would continue for about a week. Investigation showed that this gas was not absorbed noticable by KOH, pyrogallol, or acid cuprous chloride solutions, so it was decided to use combustion analysis. It was observed that this evolution of gas was more rapid at reduced pressure than at atmospheric pressure. Sometimes the volume of gas produced, measured at atmospheric pressure, was about ten times the volume of the condensate. The amount of gas is considerably dependent on the temperature of the heater, the strength of the mixture and the rate of flow used in making the condensate. In the following analyses the gas was evolved at reduced pressure. The apparatus was not entirely tight and so there was some air mixed with the gas which can be corrected for from the analyses.

In the following analysis, the gas was evolved from condensate made from gasoline. A liquid air trap was used to condense any products which could be condensed at liquid air temperatures.

Volume of Gas	25.20 cc.
Volume after passing thru liquid air trap	21.52 "
Air added for combustion	66.19 "
Total volume	87.71 "
Volume after combustion	64.10 "
Contraction of volume by combustion	23.61 "
Volume after carbon dioxide absorption	63.08 "
Volume of " " absorbed	1.02 "
Volume after oxygen absorption	57.00 "
" of " absorbed	6.08 "

Total air used, 57.00 x 1.2642,	72.06 cc.
Air in gas, 72.06 - 66.19,	5.87 "
Volume of combustible gas	15.65 "
O_2 used in combustion	8.98 "
Ratio of contraction to oxygen used	2.63

In the combustible gas had been methane, the hydrocarbon giving the greatest contraction of volume, the following results would have been observed:

Volume of CH_4	15.65 cc.
O_2 used in combustion	31.30 "
CO_2	15.65 "
Contraction in volume	31.30 "
Ratio of contraction to O_2 used	1.00

If hydrogen only were burned, the ratio of the contraction to the oxygen used would be 3.00 . Thus, it must be concluded that the gas was mostly hydrogen, although it contained some compound containing carbon.

The gas in the following two analyses was obtained from the condensate by adding $KMnO_4$ crystals which accelerate the evolution of gas. The condensate was not evolving much gas before the addition of the $KMnO_4$, and with the $KMnO_4$ the production of gas was slow.

Volume of gas	10.95 cc.
Volume of air for combustion	54.85 "
Total volume	65.80 "
Volume after combustion	63.10 "

Contraction in volume	2.70 cc.
Volume after CO_2 absorption	60.00 "
Volume of "	3.10 "
Volume after O_2 absorption	48.82 "
" of "	11.18 "
Total air used 48.82 x 1.2642	61.72 "
Volume of combustible gas	4.08 "
O_2 used in combustion	1.70 "
Ratio of contraction to O_2 used	1.59

Unless free O_2 came from the $KMnO_4$, this analysis shows that there was free hydrogen in the gas. Another sample of gas evolved from the same condensate with $KMnO_4$ gave the following results:

Volume of gas	7.10 cc.
Volume after CO_2 absorption	5.70 "
Volume of air for combustion	41.80 "
Total volume	47.50 "
Volume after combustion	46.10 "
Contraction in volume	1.40 "
Volume after CO_2 absorption	45.50 "
" of "	0.60 "
Volume after O_2 absorption	36.75 "
" of "	8.75 "
Total air, 36.75 x 1.2642,	46.46 "
Volume of combustible gas	2.44 "
Volume of gas - gas absorbed by KOH	1.04 "
O_2 used in combustion	0.96 "

Ratio of contraction to O_2 used	1.46

This shows again that there was free H_2 in the gas. It cannot be concluded that the gas absorbed by the KOH was CO_2 due to the presence of acids in the condensate.

In the following analysis, the gas was evolved from the condensate without the addition of anything.

Volume of gas	7.70 cc.
Volume of air for combustion	68.30 "
Total volume	76.00 "
Volume after CO_2 absorption	75.60 "
Volume absorbed by KOH	0.40 "
Volume after combustion	73.30 "
Contraction in volume	2.30 "
Volume after CO_2 absorption	72.54 "
" of "	0.76 "
Volume after O_2 absorption	58. 55 "
Total air	74.03 "
Volume of combustible gas	1.97 "
Volume of gas - volume absorbed by KOH	1.57 "
Ratio of contraction to O_2 used	1.55

In the next two analyses, PbO_2 was added to the condensate. PbO_2 accelerates the evolution of gas.

Volume of gas	11.60 cc.
Volume of air for combustion	56.15 cc.
Total volume	67.75 "
Volume after combustion	64.70 "

Contraction in volume	3.05 cc.
Volume after CO_2 absorption	62.98 "
" of "	1.72 "
" after O_2 absorption	52.10 "
" of "	10.88 "
Total air	65.86 "
Volume of combustible gas	1.89 "
O_2 used in combustion	2.91 "
Ratio of contraction to O_2 used	1.05

This is so little greater than the contraction for methane that it cannot be said that there certainly was H_2 present.

Volume of gas	8.90 cc.
Volume of air for combustion	67.68 "
Total volume	76.58 "
Volume after combustion	73.85 "
Contraction in volume	2.73 "
Volume after CO_2 absorption	71.60 "
" of "	2.25 "
Total air	73.70 "
Volume after O_2 absorption	58.30 "
" of "	13.30 "
Volume of combustible gas	2.88 "
O_2 used in combustion	2.10 "
Ratio of contraction to O_2 used	1.30

This analysis shows that H_2 was originally present. Since the volume of carbon dioxide after combustion is greater than the amount of oxygen used in combustion, there must have been carbon dioxide in the original gas.

The gas in the following two analyses was obtained from condensate prepared in the following manner. A mixture of n-hexane abd air, about ten times rich, was passed through two combustion tubes arranged in series. (See page 71) Condensate was collected after both heatings. The gas in the following analysis was from the condensate after one heating.

Volume of gas	8.80 cc.
Volume of air for combustion	69.15 cc.
Total volume	77.95 cc.
Volume after combustion	76.90 cc.
Contraction in volume	1.05 cc.
Volume after CO_2 absorption	75.60 cc.
" of "	1.30 cc.
Volume after O_2 absorption	61.40 cc.
" of "	14.20 cc.
Total air	77.62 cc.
O_2 used	2.02 cc.
Volume of combustible gas	0.33 cc.

The very small volume of the fuel makes this analysis very questionable. It is included here only for completeness. The following is an analysis of gas from condensate from the twice oxidized mixture.

Volume of gas	12.41 cc.
Volume of air for combustion	68.05 "
Total volume	80.46 "
Volume after combustion	72.40 "
Contraction in volume	8.06 "
Volume after CO_2 absorption	71.10 "
" of "	1.30 "
" after O_2 absorption	58.90 "
" of "	12.20 "
Total air	74.46 "
Volume of combustible gas	6.00 "
O_2 used in combustion	3.36 "
Ratio of contraction to O_2 used	2.40 "

This analysis clearly supports the conclusion that there was free H_2 present.

The condensate which evolved the gas in the following analysis had a volume of about 7 cc. and required 50 cc. of n-hexane to produce it.

Volume of gas	35.80 cc.
Volume of air for combustion	63.10 "
Total volume	98.90 "
Volume after combustion	75.34 "
Volume after CO_2 absorption	68.90 "
Contraction in volume	23.56 "
Volume of CO_2	6.44 "
Air added to complete combustion	33.20 "
Total volume	102.10 "

Volume after combustion	92.18	cc.
Contraction in volume	9.92	"
Volume after CO_2 absorption	89.52	"
" of "	2.66	"
Air added to complete combustion	14.08	"
Total volume	103.60	"
Volume after combustion	99.64	"
Contraction in volume	3.96	"
Volume after CO_2 absorption	98.25	"
" of "	1.39	"
" after O_2 absorption	97.98	"
" of "	0.27	"
" after CO absorption	96.70	"
" of "	1.28	"
Total air used	122.26	"
Total O_2 used	25.28	"
Total contraction in volume	37.44	"
Total CO_2 absorbed	10.44	"
Volume of combustible gas	23.92	"
Total contraction corrected for incomplete carbon combustion	38.08	"
O_2 used for carbon combustion	11.13	"
O_2 " " H_2 "	14.15	"
Ratio of Contraction (corrected) to O_2 for H_2	2.69	

In the case of methane, which gives the greatest of contractions of any of the hydrocarbons, the ratio of the contraction to the O_2 for H_2 is 2.00 . Thus this analysis, in spite of the piece-meal combustion which was caused by an error in estimating the amount of oxygen needed, clearly supports the conclusion that there was H_2 in the gas from the condensate. The following is another analysis of the same gas.

Volume of gas	12.35 cc.
Volume of air for combustion	82.30 "
Total volume	94.65 "
Volume after combustion	76.20 "
Contraction in volume	18.45 "
Volume after CO_2 absorption	70.82 "
Volume of CO_2	5.38 "
Volume after O_2 absorption	64.80 "
Volume of O_2 absorbed	6.02 "
Total O_2	17.11 "
O_2 used	11.09 "
Ratio of contraction to O_2 used	1.67

The condensate which evolved the gas in the following two analyses, evolved gas more rapidly and in larger amounts than usual.

Volume of gas	13.35cc
Volume of air for combustion	74.00 "
Total volume	87.35 "
Volume after combustion	75.00 "
Volume after CO_2 absorption	71.45 "
Contraction in volume	12.35 "
Volume of CO_2	3.55 "

Volume after O_2 absorption	61.85 cc.
" of "	9.60 "
Total Air	78.19 "
Volume of combustible gas	9.16 "
O_2 for combustion	6.74 "
Ratio of contraction to O_2 used	1.83

This shows again that H_2 was present. The following are the results of another analysis of the same gas.

Volume of gas	18.40 cc.
Volume of air for combustion	66.85 "
Total volume	85.25 "
Volume after combustion	63.60 "
Contraction in volume	21.65 "
Volume after CO_2 absorption	57.40 "
" of "	6.20 "
" after O_2 absorption	55.00 "
" of "	2.40 "
Total air	69.53 "
Volume of combustible gas	15.72 "
O_2 used in combustion	12.13 "
Ratio of contraction to O_2 used	1.78

If a very concentrated KOH solution is added to the condensate, there is a violent reaction which evolves gas and the condensate turns a dark, reddish brown color. The gas in the following analysis was evolved by this reaction.

Volume of gas	11.87 cc.
Volume of air for combustion	69.40 "
Total volume	81.27 "
Volume after combustion	66.35 "
Contraction in volume	14.92 "
Volume after CO_2 absorption	61.25 "
" of "	5.10 "
" after O_2 absorption	57.05 "
" of "	4.20 "
Total air	72.12 "
Volume of combustible gas	9.15 "
O_2 used in combustion	10.87 "
Ratio of contraction to O_2 used	1.38

These results show that there was free H_2 in the gas.

The foregoing results show conclusively that free hydrogen is evolved from the condensate from the products of slow oxidation. It is probable that the reaction is that of peroxide with aldehyde. Rough tests for peroxides showed that the condensates which evolved hydrogen most freely contained the most peroxides.

Conclusion

As stated previously, sufficient knowledge of the processes of slow oxidation has not yet been obtained to show in just what manner lead tetraethyl acts to decrease oxidation. From the present state of the problem, it appears that it will be solved when this is determined.

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