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AIRCRAFT FUE
AND
PROPELLANTS

A Report of the AAF Scientific Advisory Group

by
W. J. SWEENEY
L. P. HAMMETT A. J. STOSICK
H. S. TSIEN

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Aircraft FUELS AND PROPELLANTS

A REPORT PREPARED FOR THE AAF SCIENTIFIC ADVISORY GROUP

By

W. J. SWEENEY
Standard Oil Development Company
Research and Development Division

L. P. HAMMETT
Department of Chemistry
Columbia University

A. J. STOSICK
Guggenheim Laboratory
California Institute of Technology

H. S. TSIEN
Guggenheim Laboratory
California Institute of Technology

•

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The AAF Scientific Advisory Group was activated late in 1944 by General of the Army H. H. Arnold. He secured the services of Dr. Theodore von Karman, renowned scientist and consultant in aeronautics, who agreed to organize and direct the group.

Dr. von Karman gathered about him a group of American scientists from every field of research having a bearing on air power. These men then analyzed important developments in the basic sciences, both here and abroad, and attempted to evaluate the effects of their application to air power.

This volume is one of a group of reports made to the Army Air Forces by the Scientific Advisory Group.

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PART I

RESEARCH ON HYDROCARBON FUELS FOR AIRCRAFT PROPULSION

By

W. J. SWEENEY

PART I

RESEARCH ON HYDROCARBON FUELS FOR AIRCRAFT PROPULSION

RECOMMENDATIONS FOR RESEARCH

In hydrocarbon fuels, two natural divisions are (1) fuels for reciprocating engines which require antiknock quality and (2) fuels for gas-turbine power plants which have no such requirement.

FUELS FOR RECIPROCATING ENGINES

The propulsion unit is a combination of engine and fuel. Given a fuel of a certain quality, the best propulsion unit can be obtained only if the engine is built around the fuel. It is, therefore, impossible to divorce fuel characteristics and engine design. At the cruise condition, possibly 30% of the heat in the fuel is converted into power. An approximately equivalent amount is lost by sensible heat through the cylinder walls and through the piston head and by oil cooling. The rest of the heat of the fuel is lost as sensible heat and chemical energy in the exhaust gas. At the high-power rich condition, a relatively large amount of chemical heat is discarded in the form of unburned carbon monoxide and hydrogen. Adequate fuel research should involve, among other things, the following important items:

(1) Discovery of better hydrocarbon structures from the standpoints of antiknock.

(2) Commercial methods of manufacture for these hydrocarbons in large volume.

(3) The fundamentals of combustion.

(4) An understanding of the reasons for unavoidable heat losses through jacket and exhaust gas.

(5) The effects of engine factors such as compression ratio, spark advance, fuel and lead distribution, hot spots, etc., which tend to limit the performance of the fuel-engine combination.

Under item (1), work is presently under way on synthesis of selected hydrocarbons, and their evaluation in reciprocating engines should be continued. Promising compounds studied under such an activity should be referred to development and research organizations with a request that methods be found for manufacturing them on a large scale. Outstanding compounds such as triptane, for which there is presently no worth-while commercial method of manufacture, should demand the attention of the Air Corps, possibly by subsidizing fundamental research in university, government or commercial laboratories. While it presently appears that hydrocarbons, either natural or synthetic, will be the main fuel for propulsion engines, none the less fundamental studies on the preparation, properties, and methods of use of low-weight high-energy-producing materials, such as metallic hydrides, atomic and molecular hydrogen and atomic fissionable materials, should be extended.

Under item (3), among the factors of a fundamental character which should be studied are precombustion reactions which are known to take place in the induction system and in the cylinder during compression, the mechanism of combustion itself, the mechanism of knock, the mechanism of autoignition, and of the action of knock suppressors such as tetraethyl lead and iron carbonyl. Also, study should be made on proknock compounds such as peroxides, ozone, and alkyl nitrates for what they might teach about reciprocating engine knock.

Paralleling fundamental studies on the chemistry of combustion should be item (4), namely, fundamental, physical or engineering studies leading toward an an understanding of the method of heat transfer from burning gas mixtures to cylinder heads and walls so that these losses can be reduced. Such studies should be coordinated with the fundamental studies on combustion, and both should be serviced by physicists and physical equipment such as infrared and ultraviolet spectrometers, mass spectrometers and the like. Physicists and their equipment should be of great help in both the combustion end and in the engine end of the research program.

Items of importance, which are necessary to implement both the pure research and the development research, are those of the nature of background research such as:

(a) Thermodynamic properties of hydrocarbons of different types, and of products of combustion.

(b) Energy balances on reciprocating engines of different types. Important questions are: Where does the heat of the fuel go? How much to power, to sensible heat in exhaust gas, to chemical heat in exhaust gas, to piston head and cylinder walls. Poppet vs. sleeve valve engines, aromatic vs. paraffinic fuels, lean vs. rich mixture are other important problems in the catagorie.

(c) Evaluation of various combustion systems from the standpoint of hot spots (spark plugs, valves, cylinder heads, carbon and lead deposits) and the amount of antiknock degradation they occasion.

(d) Study of manifold and fuel injection equipment (carburetors vs. solid injection) from standpoint of fuel and lead distribution and uniformity of air-fuel ratio.

(e) Schlieren and other photographic studies of flame patterns and speeds: the effects of combustion chamber design, swirl, hot spots, fuel type, antiknock compounds, and mixture strength.

(f) Severity effect of compression ratio, combustion air cooling, cylinder wall cooling, piston head cooling (by lubricating oil), exhaust valve cooling, spark advance, mixture strength, internal coolants, etc., on the antiknock quality of fuels of different types. This study requires knowledge of engine design and construction and might require delegation under direction to some engine manufacturer. Past experience might indicate, however, that it would be better to do at least a part of this work in a separate air service engine laboratory equipped for experimental design and construction, as well as for testing.

As regards item (2), since knowledge of a product is of little practical use without the ability to produce it in useful quantities, the promising leads of pure and background research should immediately become subject of development research. Triptane, for example, which is considered to be the hydrocarbon of highest antiknock quality, was known before the war but was not available for military use. Even at present, there is no satisfactory commercial method of manufacture in sight. Theoretically, it should be possible to make triptane from readily available isobutane and propylene in the same manner as alkylate, the backbone of 100 octane gasoline during the war. From the standpoint of added performance of reciprocating engines, a commercially adequate method of manufacture of triptane would be a most important if not the most important research and development achievement of the next few years.

To a lesser but still appreciable degree, development of (or encouraging environment for) commercial development of processes for the manufacture of other good hydrocarbons such as 2,3 dimethyl butane, 2,2,3 and 2,3,3 trimethyl pentanes is also important. Reasonably good commercial methods for the manufacture of the latter materials are available but they are not being used or perfected because the present price of aviation gasoline will not permit. It might be considered advisable to do what was done in the case of isoöctane ten years ago, namely, subsidize such commercial development by creating a market for higher quality fuels than now contemplated. Commercial development in many cases is every bit as important to the national defense as any other step in the research sequence. Subsidy by creating a market for these presently commercially feasible fuels would probably carry with it added research on processes for producing triptane. When the new level of quality was achieved in sufficient volume, the quality could be lifted again, thereby fostering the development of processes to produce triptane or other superior products later discovered.

Finally, paralleling the development of new fuels for reciprocating engines, power-plant research is needed to develop the best fuel-engine propulsion unit. Better fuel quality can be used in higher compression ratio or higher boost pressures, to get better economy or higher power. Such changes redistribute the heat and drag loads to the jackets, the intake air and cooling air, lubricating oil, the piston head, the valves, the exhaust gas, and the power to propulsion and the power to supercharging. A new engine to get best use out of a new fuel must be tailor-made to fit, to get the optimum performance. When small improvements are made in fuel quality, there is apt to be only a small and fundamentally unimportant improvement in engine design. Much can be said in favor of research and development of a wholly new engine from the ground up, built around the best fuel experimentally obtainable regardless of cost. For example, Dr. Kettering advises that General Motors Corporation is designing a six-cylinder automotive engine of 12 to 1 compression ratio to be powered by triptane (plus lead) which will approach the diesel engine in economy and durability. While this engine is being designed primarily for automotive equipment, Dr. Kettering feels that quite a number of new principles will be developed offering possibility of application to aircraft power plants. The Air Corps should have available to it a group of research engineers capable of and equipped for doing similar work, or at least capable of directing, under subsidy, similar development work in industrial laboratories.

FUELS FOR GAS TURBINES

The fundamental studies listed under the items for reciprocating engines, with the exception of those dealing only with knock, apply also to fuels for gas turbines. In general, gas-turbine fuels are expected to be less volatile than reciprocating-engine fuels, since reciprocating-engine fuels must be completely vaporized before sparking. Atomization, penetration, turbulence and rate of flame propagation appear to be the most important factors in gas-turbine flame tubes. Accordingly, fundamental studies in these fields should be carried out.

An important requirement of gas-turbine flame tubes is to obtain high heat density per unit volume per unit pressure with the least amount of irreversible pressure drop. The aerodynamic principles involved in mixing small amounts of liquid fuel with large amounts of air should be studied. Since there is evidence that the mere presence of a flame enhances such mixing, the study should be made both with flames on and off. Beyond the mixing effect in promoting high heat density, there is also the fundamental effect of ions or flame carriers. The mechanism by which flame is carried from a combustible burning front to a combustible nonburning front should be investigated. This type of work requires the attention of scientists of wide experience and high order of ingenuity. It would be wise to interest outstanding scientific men in universities to study this phenomenon under Air Corps subsidy.

Thermodynamic properties of the hydrocarbons involved and their products of combustion are, of course, important to gas-turbine development. Energy balances on presently available gas-turbine flame tubes should be carried out. One of the best methods of evaluating combustion efficiency of such equipment would be to "freeze" the composition and analyze the combustion products from such tubes. An examination of the unburned fuel should be a much better method of measurement of combustion efficiency than an evaluation from a heat balance, since the latter is a difference between two large quantities, whereas, the former is a direct measurement of the unburned material itself. Evaluation of present flame tubes should, of course, be made over the whole operating range, since it has been found in one laboratory that the General Electric I-16 combustion tube performs very well at an intermediate capacity but suffers carbon deposition and/or liner warping at very high or very low capacities. This is probably to be expected in any piece of equipment, since it is quite difficult to design for equally efficient combustion over a wide range of variables.

It is believed that one of the most important factors in a well-balanced design is that of fuel injectors. It appears that changing fuel rate by changing pressure alone is not adequate, inasmuch as drooling or uneven spray pattern results at low or high rates. Nozzle designs which will embody features to allow a wide range of fuel rates and still maintain good spray pattern appear indicated. In an I-16 tube, at a condition where paraffinic fuel gives good performance, an aromatic fuel gives carbon deposition and warping. By the mere device of changing the nozzle, it has been possible to get as good performance with the armotic fuel at the same heat density. Considerable background information is needed on methods of injection of fuel, and these studies should be made with fuels of different volatility and different degrees of paraffinicity and aromaticity, and at the range of altitude, temperature and pressures expected in the field.

The greater part of the research and development work should be done on full-size equipment because of the difficulty of translating the space relationships from one size to another. Since the single flame tube might burn from 10 to 100 gal/hr, it is rather infeasible to prepare pure hydrocarbons for making fundamental studies such as those carried out in reciprocating engines. It is, however, experimentally feasible to make large amounts of fuels of varying degrees of paraffinicity, napthenicity or aromaticity, by pilot plant hydrogenation, selective solvent extraction, dewaxing and the like. Research and development involving fuels should have available to it supplies of fuels of different types so that any Air Corps agency making such studies should discuss its needs with one or a number of oil companies. Such companies would be only too glad to prepare experimental fuels for test on the pilot plant equipment available to them. In comparing fuels of different types, the comparison should be made in the same combustor under the same conditions of operation.

Another part of the development program should be to test one or possibly two standard fuels in combustors of different design. The present combustor in either the General Electric or the Westinghouse units is a good practical design by present standards, but it is to be expected that much better combustion tubes will become available as time goes on. Any adequate program on the development of flame tubes will involve design, construction, and testing of a great number of types.

The efficiency of a gas-turbine power plant can, of course, be increased markedly if the turbine-blade temperature can be allowed to rise. The present turbine-blade temperature is dictated by the materials of construction, and any adequate development program on gas turbines will require the services of a metallurgical laboratory and metallurgic consultants of the highest grade.

In any research and development activity, success is largely dependent on the quality of the research and engineering personnel. Successful organizations exert a major effort in their recruiting of young technical men, even to the extent of having each prospect interviewed by several key men, such as managers or directors of research and engineering departments. Seldom is this important job delegated to a general personnel department, although the latter sometimes makes the early contacts, gathers the information on training, scholastic record, extracurricular activities and personality, and schedules the tour of interviews and other details. The object of this effort is to obtain young men who are superior in the attributes of intelligence, training, and personality (for group activities) and integrity.

Where the effort of the organization encompasses all categories from pure research to commercial development, and therefore demands coordination and integration, it is exceedingly important that a good quota of men of superior personal characteristics and broad judgment be included. However, these men should be qualified to compete technically with the best of the research or development group when occasion demands, so that they will have the respect and backing necessary to effective liaison or coordinating jobs when and if attained. The military probably know more about such matters generally than industrial people but it is pointed out here to be certain that men put in liaison jobs involving research and development on fuels, power plants and related matters will not be chosen for their ability to get along without regard to their scientific and engineering qualifications.

The difficulty faced by the Air Corps in effecting superior technical recruiting is the matter of opportunity and salary. It appears necessary, if the upper 10% of the quality group is to be tapped, to institute some sort of incentive system, based on salary, on opportunities for technical development, retirement benefits, or public prestige.

PART II

PETROLEUM: ITS USE FOR MOTIVE POWER

By

W. J. SWEENEY

PART II

PETROLEUM: ITS USE FOR MOTIVE POWER

1 JUNE 1945

SUMMARY

To power the nation's military aircraft, liquid fuel of high heating value is needed in very large quantities. Petroleum is the most practical source of such fuel today. It consists of liquid compounds of carbon and hydrogen, which have higher heating values than any other liquid, except liquefied hydrogen gas. The annual tonnage of petroleum, over 200,000,000 tons, produced in the United States is greater than that of any other article of commerce except coal.

If the supply of petroleum should ever become exhausted, liquid hydrocarbons similar to those in petroleum could be made from coal. The processes for making liquid hydrocarbons are well developed. At present, however, they are more costly than the refining of crude petroleum. Domestic supplies of petroleum are adequate, even in the most pessimistic estimates which assume no further oil discoveries, for at least fifteen years. The supply of synthetic oil from coal would be about two hundred times as much.

For conversion to mechanical power, the energy in petroleum is released by combustion. The highest heat of combustion per pound is found in paraffinic hydrocarbons, and per gallon, in aromatic hydrocarbons. Intermediate between the two types are the naphthenic hydrocarbons. All these types occur in petroleum, the heating value of which can be estimated very accurately from measurements of density and boiling points. Per pound of reagents, i.e., fuel and air, more energy is developed from a hydrocarbon than from TNT.

The energy in petroleum, released by combustion, is converted into work for aircraft propulsion in two types of engines, the reciprocating engine and the gas-turbine. The efficiency of the latter depends upon the temperature of the hot gases entering it and the efficiency of the former depends upon the compression pressure in its cylinders. Obviously, in order to design engines of still greater efficiency an intimate knowledge of the mechanism of combustion is needed. This report includes a bibliography of combustion studies. Increasing the turbulence of the mixture of fuel and air is the most rewarding approach to the problem of speeding up the rate of combustion.

In the reciprocating engine, using gasoline fuel and spark ignition, it has been found that certain types of hydrocarbons are particularly desirable components of the fuel. As shown in the detailed table in the Appendix of this report, these are the iso-paraffinic and the aromatic types. Accordingly, petroleum refining processes have been developed for producing gasolines containing the desirable proportions of these hydrocarbons. Two examples are the manufacture of isoöctane by combining isobutane with butene and the manufacture of toluene by stripping hydrogen atoms from the naturally occurring petroleum-hydrocarbon, methyl cyclohexane.

The principal reason for the desirability of these hydrocarbon types is their resistance to knock in engines. Knock is the limiting property at present in the development of more efficient reciprocating engines. It is the result of an untimely explosion of the combustible mixture. Apart from the choice of specifically resistant hydrocarbons, knock can be minimized by cooling the engine or by using a given fuel less efficiently, as by the use of richer than ideal fuel-air ratio for take-off power.

For the combustion turbine and jet propulsion, knock is not a limiting factor; but there are other fuel properties which need particular consideration from the viewpoint of practice. One such consideration is whether the maximum heat content should be attained in a given weight of fuel, from the viewpoint of airplane load, or in a given volume, from the viewpoint of wing design and fuel-tank capacity. Another consideration is explosion hazard, since the fuel may be chosen either to be so volatile as to keep the vapor space always above the upper inflammability limit, or to be so nonvolatile as to keep the vapor space below the lower inflammability limit. Again, the volatility should not be so great as to cause excessive vaporization loss from fuel tanks at high altitude. These and other practical items which should be the subject of further research are listed at the end of this report.

DISCUSSION

AVAILABLE ENERGY

Petroleum has two properties which make it the most practical source of energy for motive power. These are its liquid form and its high heat of combustion. Motive power for aircraft is obtained, of course, by expansion of air which is heated by fuel combustion.

The wide variety of liquid hydrocarbons present in petroleum permits a choice to be made so that the volatility and the viscosity of the liquid fuel can be accurately controlled. This control makes the liquid ideally suited for either intermittent or continuous feeding at controllable rates.

As a practical combustible, petroleum is in a class by itself and, on the basis of heat contents or BTU per pound, it is excelled only by hydrogen. The latter, however, is at a disadvantage in respect to its container requirements, due to its being a gas and having low density. The possibilities of hydrogen as a fuel for special purposes should not be entirely neglected. All that is needed is a practical method of lowering its bulk volume to compare with hydrocarbon in heat of combustion per unit volume. Liquefaction and adsorption on a self-combustile material (activated carbon) are conceivable devices. However, as an example of the latter, there is presently no practical competitor for hydrogen chemically combined with carbon to form oil.

A few comparative heating values are shown in the following tabulation:

	Heating Value, BTU/lb	
	Higher Qv (*Gross*)	*Lower Qp* (*Net*)
Petroleum Products		
Aviation Gasoline	20,310	18,900
Kerosene	19,620	18,340
Fuel Oil, Bunker C	18,150	17,200
Other Organic Compounds		
Coal (Anthracite)	12,450	12,240
Coal (Bituminous)	11,700	11,310
Wood	8,670	8,120
Ethyl Alcohol	12,770	11,585
Ethyl Ether	15,880	14,650
Chemical Elements		
Sodium	3,900	....
Hydrogen	61,600	52,450
Hydrogen, Atomic*	152,500	143,400
Aluminum	12,650	....
Magnesium	10,820	....

*Atomic hydrogen is a transient state and not known in mass.

In the above tabulation, Qv is the higher heating value at constant volume, the water formed during combustion being condensed; and Qp is the lower heating value at constant pressure.

In addition, petroleum is relatively abundant as a raw material, and its peacetime economy offers established facilities for production, processing and distribution which can be converted to war economy quickly. In the speed of such conversion, the degree of slack represented by the luxury factors of relatively nonessential driving, household heating, and the like, plays no small part. In the early days of a new war the nation that is over-built in petroleum capacity, to supply civilian demand, is in a fortunate position indeed.

However, once a war has begun, volume of products alone is not sufficient. Performance quality comes to be of great importance. The premium grade suddenly becomes the basic grade, and a balance must be struck between quality and quantity until new capacity is made available. Under good conditions this takes 18 months to two years. While this may seem slow, the invested manpower hours per BTU of fuel produced by the petroleum route is only a fraction of what would be required by any conventional chemical route. The fact is that the tonnage of petroleum required for peace or war dwarfs all chemical industries, as shown in the following tabulation and in Plate I:

	Estimated Production, Tons per Year	
	U. S. Peace	*U. S. War*
Petroleum (Total)	175,000,000	242,000,000
Aviation Gasoline	2,190,000	28,700,000
Motor Gasoline	86,500,000	100,000,000
Fuel Oil	70,000,000	99,000,000
Rubber	600,000	800,000
Explosives	300,000	1,500,000
Synthetic Resins	238,500	400,000
Sulfuric Acid, 50° Baume	9,000,000	15,500,000
Ethyl Alcohol	1,000,000	2,000,000
Pig Iron	45,000,000	60,000,000
Paints and Varnishes	1,950,000	2,000,000
Hydrogen Peroxide	20,000	....
Manganese	60,000	....
Nitric Acid	200,000	....
Ammonia (Anhydrous)	113,500	....
Ammonia (Total)	338,000	....

Not only does the tonnage of petroleum exceed that of any other material in the above list, but the mechanical power actually obtainable by burning this petroleum tonnage is nearly double all the horsepower that could theoretically be produced in all the central power stations in the United States, including both coal- and water-power stations, if they were operated continuously at 100% of installed capacity. The following figures illustrate the foregoing statement:

	Yearly Horsepower Hours
100% of Installed Capacity of Central Stations	438,000,000,000
20% of BTU in 242,000,000 T Petroleum	704,000,000,000
33% of BTU in 28,700,000 T Aviation Gasoline	139,000,000,000
28% of BTU in 100,000,000 T Motor Gasoline	400,000,000,000

The last two items in the foregoing tabulation show that the actual mechanical power developed from gasoline annually exceeds the theoretical limit that central power stations could attain at 100% service factor.

OIL FOR THE FUTURE

In view of the huge and increasing demands for petroleum, there has recently been considerable speculation about the proven, and the anticipated ultimate, reserves of petroleum crude oil. A rapid depletion of U. S. petroleum reserves could be a serious matter in case of war only if there should have been no peacetime installation of manufacturing capacity for "Synthetic Crude." This crude oil can be made from natural gas or coal, and steam. It can be processed to yield the required products by methods very similar to those now used for petroleum. Plant investment and the delivered cost of fuel in cents per gallon will be higher than from petroleum crude oil at present price levels for crude oil, but the cost per BTU will still be cheaper than in any other normally liquid fuel. It appears safe to conclude that the basic fuel for war will continue to be made from hydrocarbons, whether natural or synthetic.

To equal one year's production of ENERGY FROM OIL in the United States, we would need:

The annual oil production of the United States develops energy amounting to

7,500,000,000,000,000 B.t.u.'s

B.t.u. stan[illegible] for British thermal unit. This is the standard commonly employed by [illegible]neers in the measurement of energy. It expresses energy in terms of heat, [illegible]d is defined as the quantity of heat required to raise the temperature [illegible]ne pound of water by one degree Fahrenheit. Crude oil contains abou[illegible],000 B.t.u.'s of energy per pound.

Above is [illegible]aphic comparison of the energy developed by the annual production of [illegible]de oil in the United States with that developed by other important sou[illegible] of energy. To avoid the distorted picture which would be presented by [illegible] abnormal production of the war years, the last year of normal productio[illegible] — 1939 — has been chosen as the basis of comparison. In 1939 the Unite[illegible] States produced 1,260,000,000 barrels of crude oil. The total energy con[illegible]t of this volume of production was 7,500,000,000,000,000 B.t.u.'s. If so m[illegible]h energy had to be obtained from any one of the following sources, it wou[illegible] require, in round numbers:

- **96,000,000,000** gallons of grain alcohol, at 11,760 B.t.u.'s per pou[illegible]
- **2,950,000,000,000** H.P. hours of electricity, at 2,545 B.t.u.[illegible]
- **2,200,000,000,000** pounds of nitroglycerine, at 3,400 B.[illegible]; or
- **4,000,000,000,000** pounds of guncotton, at 1,900 B.t.[illegible] pound; or
- **27,000,000,000** cubic feet of wood, assuming 7,500 [illegible] per pound; or
- **250,000,000** tons of coal, at an average value of 1[illegible] B.t.u.'s per lb.

Plate 1

Nothing could be of greater concern to the petroleum industry than the amount of the reserve of its raw material. Facing the realities of war, of future transport and of new, broad uses of petroleum, it is well to examine future prospects.

No one knows how much petroleum lies undiscovered in the earth, or where and when and how fast it will be discovered. All the statements, estimates, and statistics which have been published deal only with oil already discovered. Notwithstanding all the remarkable advances in methods to aid in locating oil, no one yet can tell anything even approaching certainty whether or where oil exists until it is actually produced.

With this as a background, one may interpret estimates and statistics either optimistically or pessimistically, as he chooses.

The pessimistic view allows only 15 years, although this assumes that, suddenly, discovery of new oil fields will cease entirely, an unlikely assumption. Optimists believe that the reserves, increased by reasonable new discovery rates as time goes on, will be adequate for generations to come. For this discussion, however, let it be assumed that the pessimists are right, and that the domestic oil supply is in serious danger of rapid depletion.

To date, over 60% of the total world production of petroleum has come from the U.S.A. For years the bulk of the world's known petroleum resources were in the United States. This is no longer true; known reserves elsewhere in the world, even after far less intensive exploration than here, exceed our own. Yet U.S. per capita consumption of petroleum far exceeds that of any other nation. It seems inevitable, therefore, that the U. S. will continue to import oil, as in the past.

Gradual increase of oil imports need not affect the domestic industry adversely. As the excess of demand over supply creates favorable price levels, increased conversion of domestic crudes to higher value products, such as gasoline, burning oils, distillate fuels, solvents and lubricants, will be possible at the expense of products such as industrial and bunker fuel oils, which are largely competitive with coal. The resulting shortage of the heavy liquid fuels could be met in two immediate ways' conversion to coal by many larger power generating plants and by utilizing low-grade foreign crudes for those marine and industrial uses where liquid fuels are essential. Heavy fuels constitute nearly half the present yield from domestic crudes.

Naturally, there are important military and political reasons why the U.S. should not be dependent on foreign oil. Foreign supplies of crude are not inexhaustible. Ultimately, it will be necessary to look elsewhere than to crude petroleum for a supply of liquid fuels.

Fortunately, petroleum is only one of several forms in which nature has stored an almost inexhaustible supply of hydrocarbons within the boundaries of this country. Buried in American earth are other vast resources of carbon and hydrogen in an almost infinite series of combinations ranging from anthracite coals, semibituminous coals, cannel coals, lignites, oil shales and natural gas. To be sure, petroleum is by far the most useful form of these hydrocarbons. An all-important fact is that almost any of the other hydrocarbon resources can be converted into convenient liquid form.

Which of these other hydrocarbon resources is to be converted to liquids, and how and when, will be determined not by the technical ability to do it, but by economic factors.

An idea of the relative supply of these hydrocarbons and a picture of the economics of their conversion may be gained from a study of the Plates 2 to 5.

The change from petroleum to other sources of liquid fuels will not come suddenly. Inevitably, crude oil in its natural state will become more difficult and more costly to find. Reduction in reserves will increase the value of the existing oil. This increased value of liquid petroleum will encourage conversion of other hydrocarbons to liquid form. Some engineers believe that the liquefaction of the natural gas reserves may be undertaken as soon as men and materials are available, even at present price levels.

Next, from the cost standpoint, will probably come recovery of oil from many sources, from the vast western oil shale deposits, by recovery of petroleum from Canadian and domestic oil sand deposits. And, as soon as the economics permit it, the U.S. can turn to the liquefaction of coal, which, although entirely practical from a technical standpoint, appears too costly at present.

None of these developments will come overnight, yet they are all factors in the complex of our petroleum economy. Out of the interplay of economic forces and alternate sources of petroleum there is assured this one important result: enough petroleum and products to meet national needs as far into the future as can be seen.

If the present known reserves of natural gas were liquefied, U.S. petroleum reserves would be increased by 50 to 60%. It is likely that the relative proportion of gas reserves will increase in the future. As deeper wells are drilled in the more pressing quest for oil, the ratio of natural gas occurring with the crude oil is growing.

Today only a small percentage of the resources of natural gas is employed usefully. Although its use is increasing, the great bulk of it is closed in gas fields whose production is far below potential.

Among several methods for liquefying natural gas the most promising is probably the Fischer-Tropsch Process, originally developed in Germany for the liquefaction of coal. In this process, natural gas is converted to hydrogen and carbon monoxide by processes now in use on a large commercial scale. These gases are then combined with the aid of catalysts to form synthetic petroleum fractions.

Another of the processes for recovering liquid hydrocarbons is the working of the enormous deposits of oil-bearing shales in the Western U.S.A. About 20 years ago, during another period of apparent shortage of petroleum, these oil shales were considered the next logical source of oil. Many groups, including Standard Oil Company (N.J.), were working on processes of extracting shale oil from these vast deposits, estimated today to be equivalent to at least five times the present known crude oil reserves in this country.

The better western shales average an oil content of about 10% by weight, which can be separated by heating to a proper temperature.

Shales of this type have been mined and treated to extract oil in a numberof countries, including Scotland, France and Australia. A few semicommercial plants

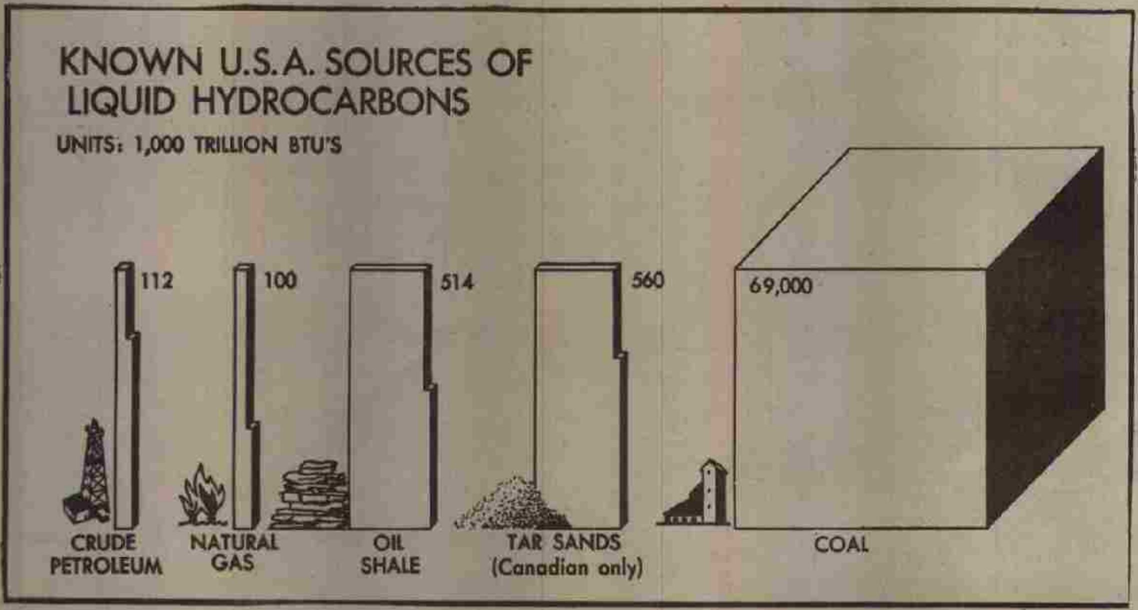


Plate 2

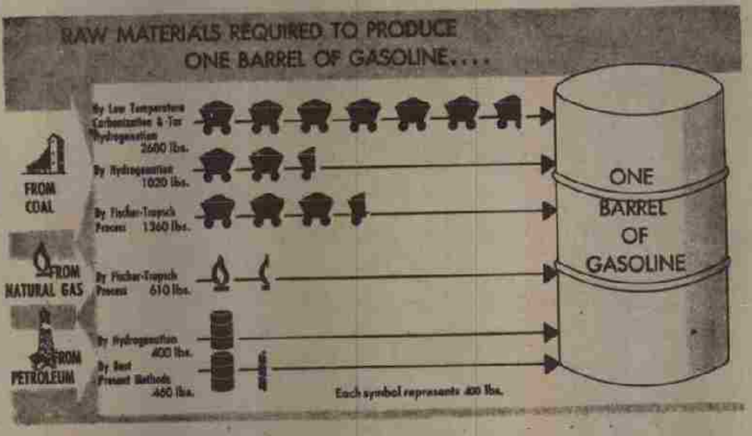


Plate 3

Estimated INVESTMENT REQUIRED FOR PLANTS to produce 1,000,000 barrels of Gasoline per day

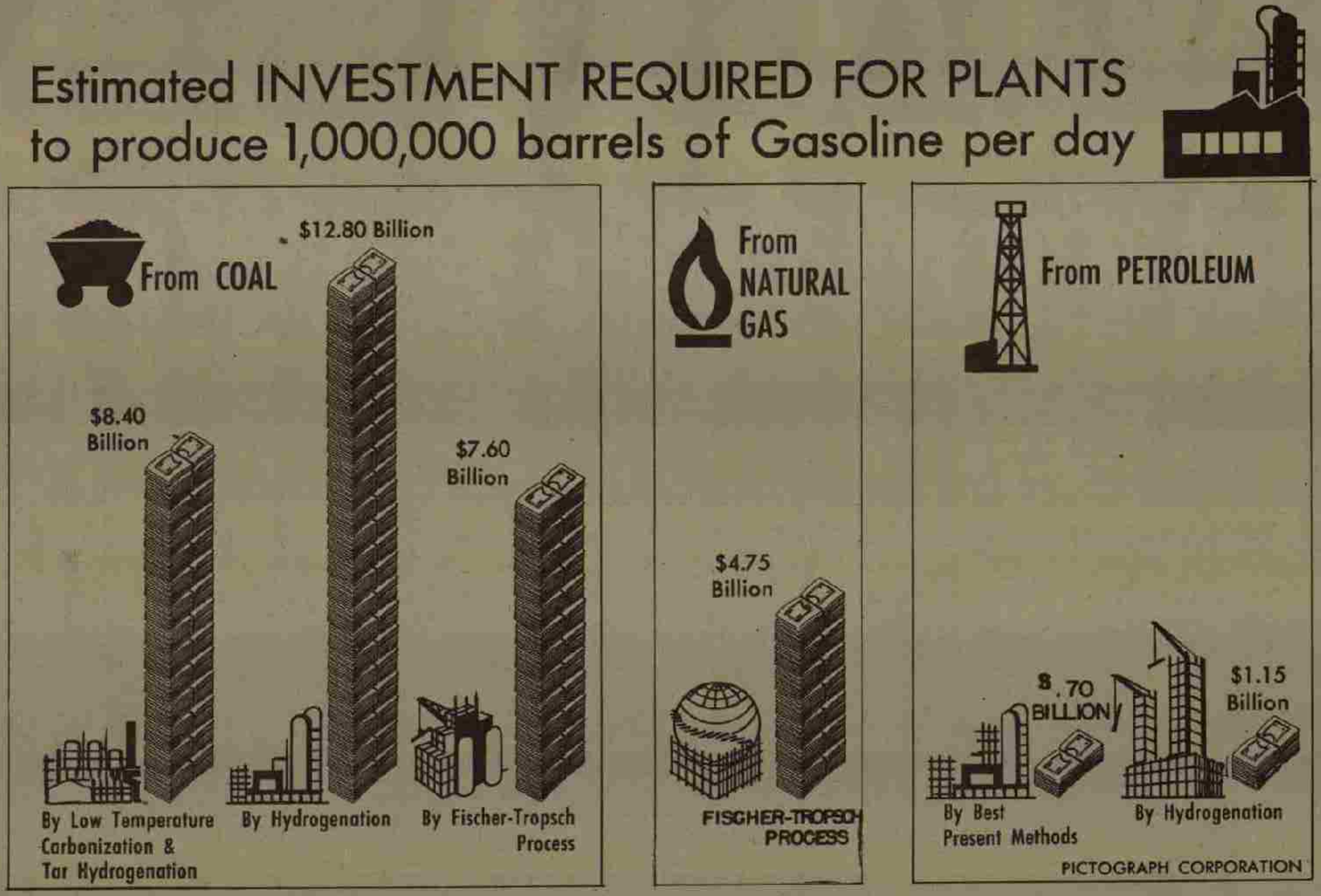
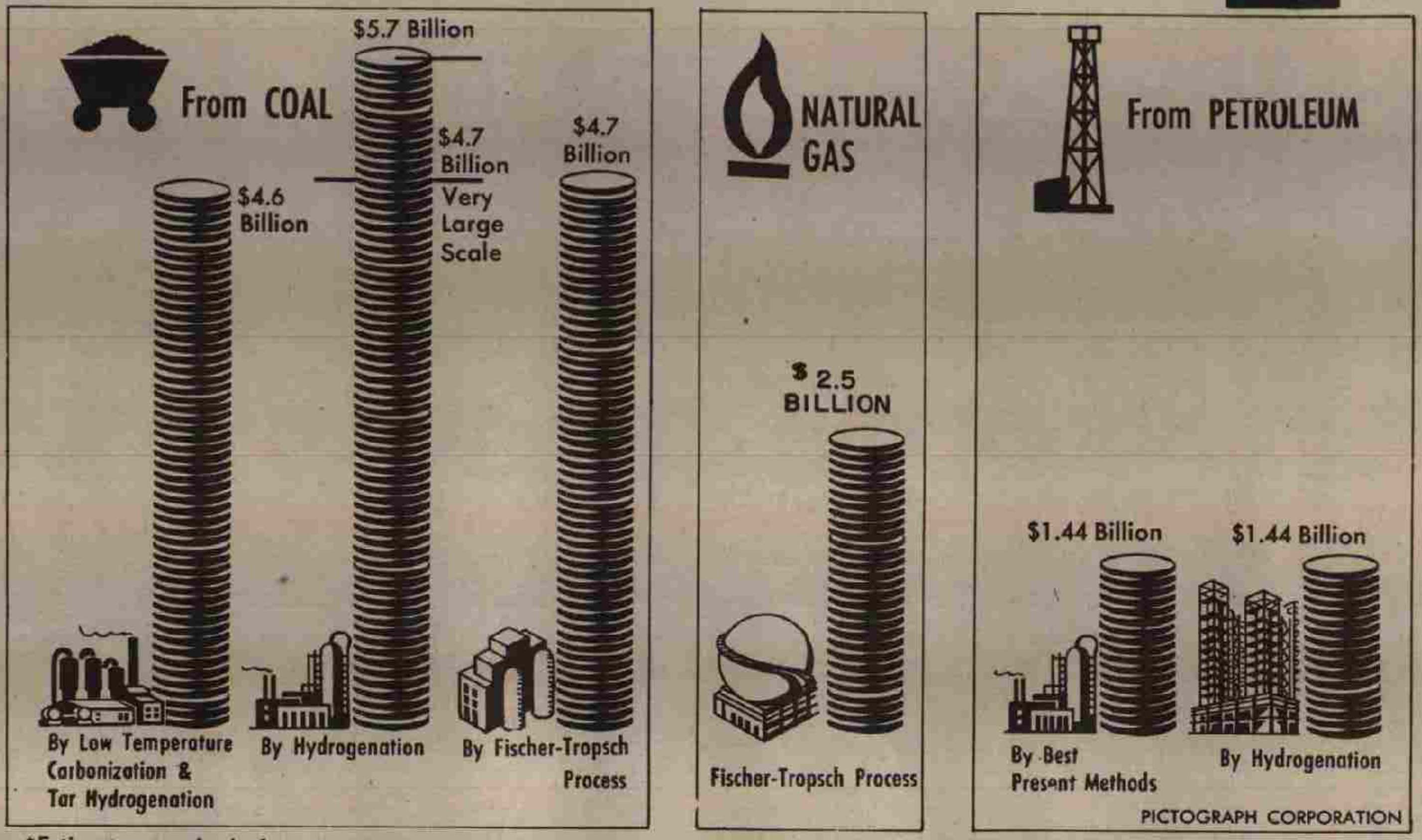


Plate 4

WHAT OUR GASOLINE BILL WOULD BE*

(At Refineries Using Various Processes)



*Estimates made before Taxes and without profit to the Refiner based on 1941 Gasoline Consumption.

Comparisons are approximate, since all data are not for plants of same capacity.

Plate 5

were erected in the United States in the early 1920's. Further development was arrested by the discovery of new oil fields, but enough was done to demonstrate that U.S. oil shales are a thoroughly practical source of petroleum.

Even when the time comes to utilize these oil shale resources, the U. S. will only have begun to dip into the storehouse of hydrocarbons.

In northern Saskatchewan lie the Athabasca tar sands, deposits so enormous that their oil-bearing potential has been estimated at over 100 billion barrels, or more than five times the known petroleum reserves of the United States. When broken up by blasting, mined and processed, they yield something over 10% of heavy oil.

Operations on a commercial scale are now being carried on only in one corner of the Saskatchewan fields, in the vicinity of Fort MacMurray. Strictly local in character and economically feasible only because of the cost of transporting oil to the region from other areas, these operations could be extended when needed.

Important as are the reserves of natural gas, oil shales and tar sands, in the long-range picture they represent only a tiny fraction of the enormous deposits of hydrocarbons in the form of coal and lignite. These are by far the greatest sources of energy. All the coal mined to date has but scratched the ultimate potential. With mining still confined to the most easily accessible beds, and those highest in heating value, there remain largely undeveloped the vast subbituminous and lignite coal deposits of the West.

Coal can be converted into petroleum by the chemical addition of hydrogen, utilizing processes widely known and commercially proven.

These processes stem from the original work of a German scientist, Dr. Frederich Bergius, who first demonstrated the possibility of converting coal into oil in 1913: His discoveries were developed by Badische Anilin Soda Fabrik, later merged with I. G. Farbenindustrie, A.G., the German dye manufacturers' association.

Improved catalysts and methods were worked out and in the 1920's high-pressure catalytic techniques for coal hydrogenation had been perfected on a commercial scale. At this time, with the United States facing another threat of a petroleum shortage, Standard Oil Company (N.J.) purchased the patents and "know-how" for these processes, and made them available to the entire petroleum industry shortly thereafter.

Two plants for hydrogenation of oil were constructed by Standard at that time, and one of these is still in operation. The discovery of large new deposits of oil in this country in the early 1930's removed the economic necessity for liquefaction of coal, but the techniques have been fully developed and await only economic justification for application.

Also available when the time comes is the Fischer-Tropsch Process (already referred to in connection with liquefaction of natural gas) for the liquefaction of coal. This process now appears in many ways competitive with hydrogenation for the liquefaction of coal.

If a greater consumption of coal can be tolerated, in view of the enormous deposits of coal and lignite, many chemical engineers feel that another possibility should be considered. Coal can be heated at low temperature to distill off a substantial yield of tar, which can be hydrogenated to produce gasoline. While the yield of gasoline per ton of coal would not be as great, a substantial amount of coke is recovered as a by-product, and it is not too difficult to imagine conversion of this coke to water-gas and using this to extend the supply of natural gas being distributed through the expected network of gas pipe lines covering the country. In effect, this would achieve complete utilization of coal. The costs by this process now appear competitive with the complete liquefaction processes.

FUNDAMENTALS OF COMBUSTION

a. Heating Value.

In the section on "Available Energy" a few typical values were tabulated to illustrate the fact that petroleum hydrocarbons have higher heats of combustion than any other fuel except hydrogen. A more complete tabulation of the heats of combustion of hydrocarbons is presented herewith in Tables I and II. These tables are compiled from the most recent values reported by the National Bureau of Standards.

The first generalization to be deduced from Table I is that the heating value per pound of paraffinic hydrocarbons decreases as the density increases and as the molecular size or the boiling point increases. On the other hand, for aromatic hydrocarbons in Table II the trend is partly reversed, in that the heating value per pound increases slightly with increasing molecular weight, at least for monocyclic aromatics. Naphthenic hydrocarbons show very little variation in heating value, averaging about 18,750 net BTU per pound.

These three types of hydrocarbons constitute the principal components of petroleum. Consequently, the trends for petroleum distillates are the resultants of those just discussed. For instance, Fig. 1 illustrates for two constant values of net BTU per pound, how the densities of petroleum distillates may be expected to vary with their average boiling points. The densities are plotted in terms of degrees API, which is the density scale commercially used in the petroleum industry. The relationship between degrees API and specific gravity at 60°F. is as follows:

$$\text{Sp. Gr. at } 60^\circ\text{F}/60^\circ\text{F} = 141.5/(131.5 + {}^\circ\text{API})$$

so that the API gravity of water 60°F is 10°API.

In view of the foregoing observations, it follows that, for a given type of petroleum distillate with closely controlled volatility characteristics, as, for example, aviation gasoline of Grade 100/130, the net heating value per pound is a reasonably precise function of the density. Figure 2 shows this average function as determined empirically at the Esso Laboratories by actual measurements on a large number of aviation gasoline samples. To indicate the relative effect of changes in the average boiling point, a similar function is shown in Fig. 2 for safety fuel, which is an aviation gasoline having a relatively high average boiling point of about 332°F as compared with about 212°F for Grade 100/130.

This figure indicates that the general relationship is as follows, between values of 212° and 332°F for the average boiling point: Net BTU/lb at Constant Pressure, $Q_p = 44.79({}^\circ\text{API}) + 15.894 + 4.25$ (average boiling point 212°F).

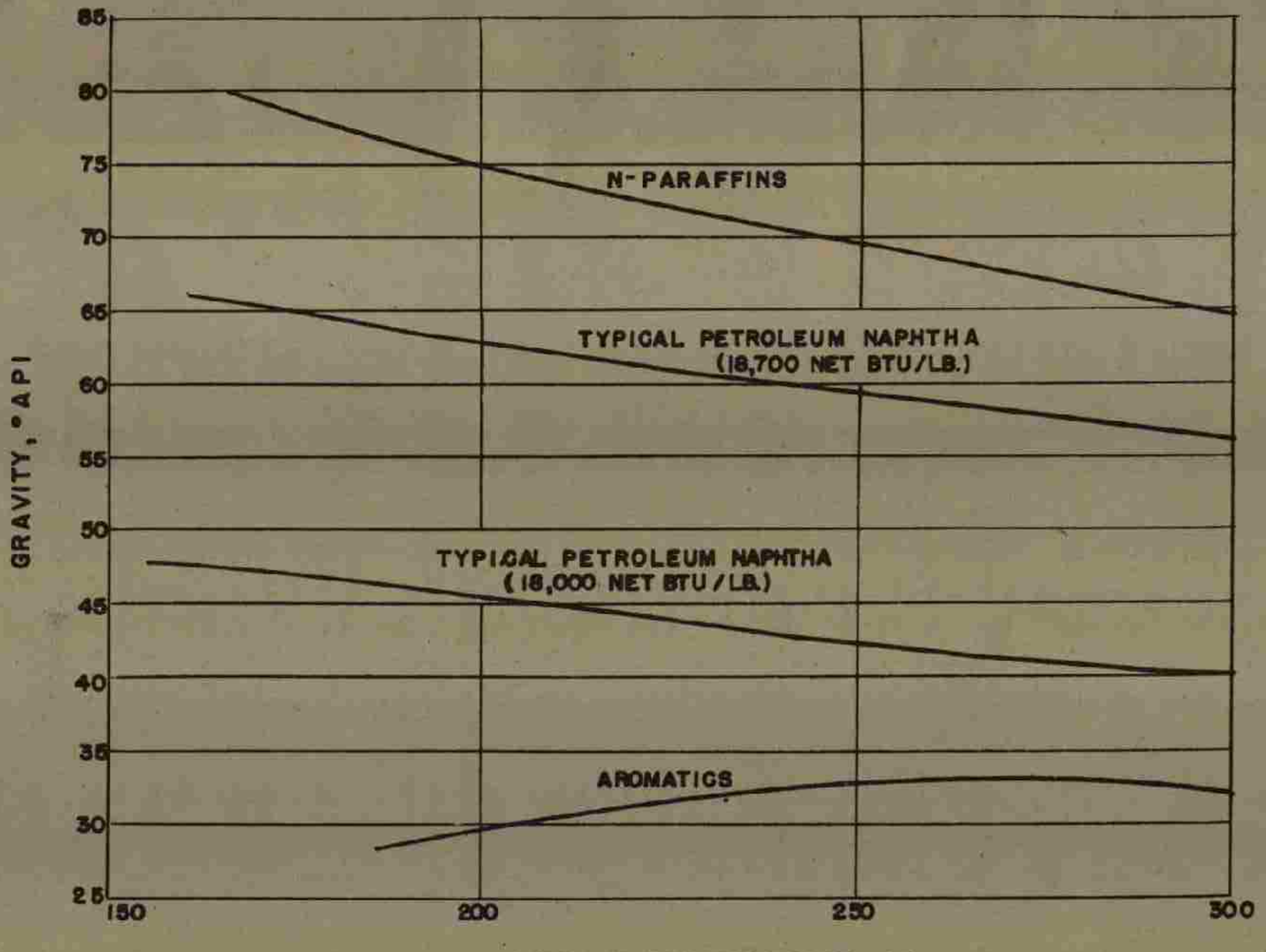


Figure 1— Trends of Density of Hydrocarbons vs. Boiling Point

TABLE I

HEATS OF COMBUSTION OF HYDROCARBONS

Paraffins (C_nH_{2n+2})	Density at 25°C		Net BTU at 25°C and Constant Pressure	
	Gm/Ml	*Lb/Gal*	*Per Lb Liquid*	*Per Gal Liquid*
Methane		....	21,502 (as gas)	....
Ethane		....	20,416 (as gas)	....
Propane	0.4930	4.11	19,774	81,271
n-Butane	0.5730	4.76	19,506	92,849
Isobutane	0.5510	4.59	19,468	89,358
n-Pentane	0.6213	5.17	19,340	99,988
Isopentane	0.6146	5.11	19,303	98,638
Neopentane		....	19,253	....
n-Hexane	0.6549	5.45	19,233	104,820
2-Methylpentane	0.6484	5.40	19,206	103,712
3-Methylpentane	0.6597	5.50	19,218	105,699
2,2-Dimethylbutane	0.6445	5.36	19,161	102,703
2,3-Dimethylbutane	0.6570	5.47	19,192	104,980
n-Heptane	0.6795	5.65	19,157	108,237
2-Methylhexane	0.6745	5.61	19,134	107,342
3-Methylhexane	0.6828	5.68	19,145	108,744
3-Ethylpentane	0.6938	5.78	19,155	110,716
2,2-Dimethylpentane	0.6696	5.57	19,096	106,365
2,3-Dimethylpentane	0.6909	5.75	19,118	109,928
2,4-Dimethylpentane	0.6686	5.56	19,112	106,263
3,3-Dimethylpentane	0.6892	5.73	19,114	109,523
2,2,3-Trimethylbutane	0.6858	5.71	19,104	109,084
n-Octane	0.6985	5.82	19,100	111,162
2-Methylheptane	0.6939	5.78	19,080	110,282
3-Methylheptane	0.7017	5.85	19,091	111,682
4-Methylheptane	0.7005	5.83	19,093	111,312
3-Ethylhexane	0.7094	5.91	19,098	112,869
2,2-Dimethylhexane	0.6911	5.75	19,055	109,566
2,3-Dimethylhexane	0.7092	5.91	19,090	112,822
2,4-Dimethylhexane	0.6961	5.79	19,073	110,433
2,5-Dimethylhexane	0.6893	5.74	19,060	109,404
3,3-Dimethylhexane	0.7060	5.88	19,071	112,137
3,4-Dimethylhexane	0.7152	5.96	19,092	113,788
2-Methyl-3-Ethylpentane	0.7152	5.96	19,101	113,842
3-Methyl-3-Ethylpentane	0.7235	6.02	19,089	114,916
2,2,3-Trimethylpentane	0.7121	5.92	19,073	112,912
2,2,4-Trimethylpentane	0.6878	5.72	19,065	109,052
2,3,3-Trimethylpentane	0.7223	6.01	19,086	114,707
2,3,4-Trimethylpentane	0.7150	5.95	19,080	113,526
2,2,3,4-Tetramethylbutane		....	19,029	....
n-Nonane	0.7139	5.94	19,063	113,234
n-Decane	0.7301*	....	19,030	....
n-Undecane	0.7403*	....	18,997	....
n-Dodecane		....	18,982	....

*At 20°C.

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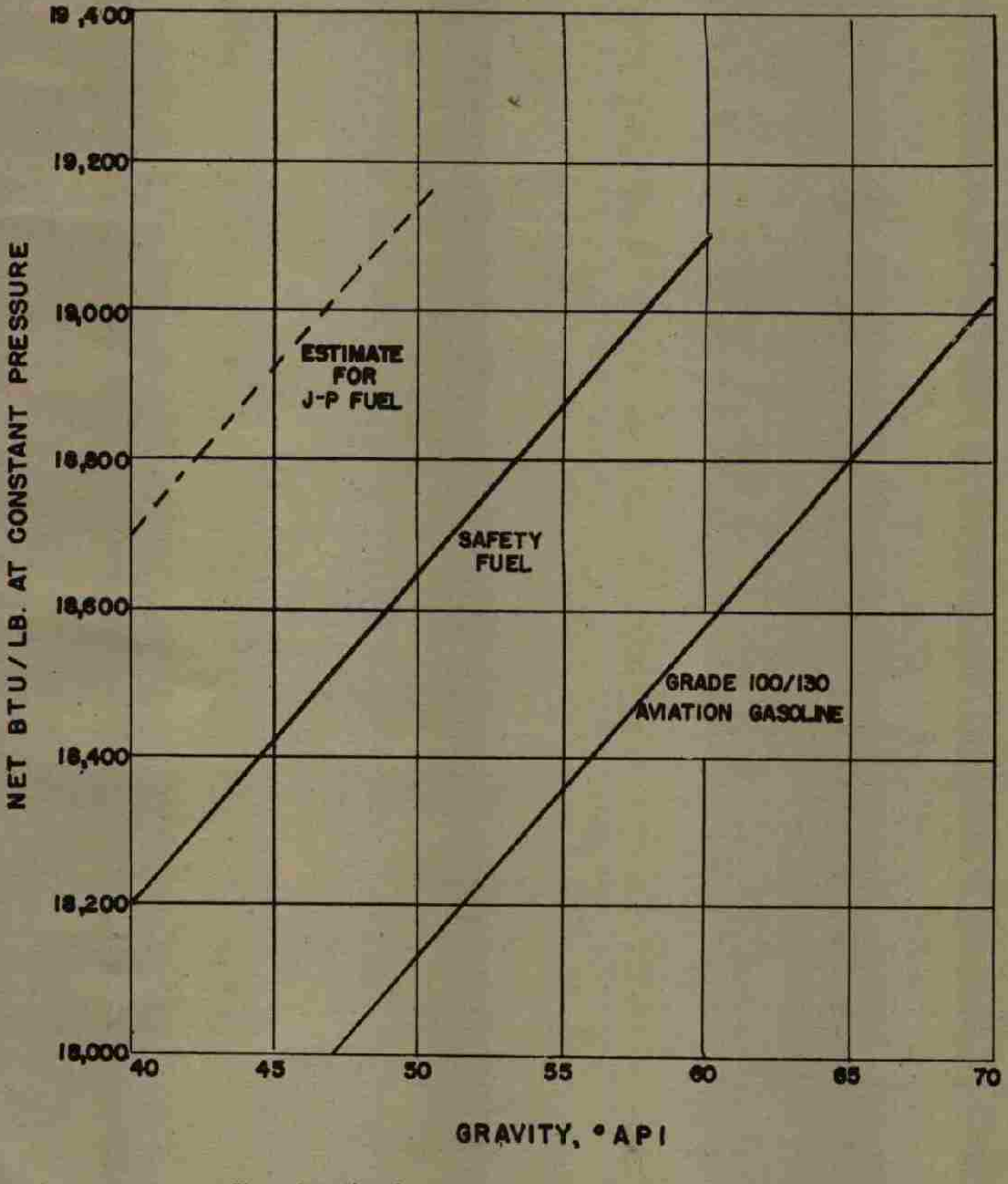


Figure 2 — Chart for Estimating Heating Value from Gravity

TABLE II

HEATS OF COMBUSTION OF HYDROCARBONS

	Density at 25°C		*Net BTU 25°C and Constant Pressure*	
	Gm/Ml	*Lb/Gal*	*Per Lb Liquid*	*Per Gal Liquid*
Olefins (C_nH_{2n-2})				
Ethene		....	19,980 (as gas)	....
Propene	0.5053	4.19	19,960 (as gas)	83,700
1-Butene	0.5888	4.88	19,450 (as gas)	95,000
n-Hexene	0.6688	5.55	19,070	105,800
1-Octene	0.7113	5.90	18,965	112,000
Decene		....	18,920	....
Naphthenes (C_nH_{2n})				
Cyclopentane	0.745	6.17	18,809	116,100
Methylcyclopentane	0.748	6.21	18,750	116,300
Cyclohexane	0.7739	6.44	18,750	120,600
1,2-Dimethylcyclopentane	0.76 (ave.)	6.31	18,790	118,400
Dimethylcyclohexane	9.77 (ave.)	6.44	18,740	120,500
Aromatics (C_nH_{2n-6})				
Benzene	0.8737	7.27	17,325	125,900
Toluene	0.8621	7.18	17,470	125,400
Xylene	0.86 (ave.)	7.15	17,570	125,500
Cymene	0.8577	7.14	17,824	127,200
Hexamethylbenzene	solid	solid	17,850	....
Hexaethylbenzene	0.823	6.83	18,150	124,000

T-329-45

Reference to Fig. 1 shows that the last term in the above equation (page 20) is only an approximation, since the relationship in that figure between °API and average boiling point is not a straight line for constant heating value, but as a first approximation the above equation can be used conveniently for estimating the heating values of petroleum distillate having different average boiling points. Actually Fig. 2 may be more reliable than Fig. 1, since the former is based on actual analyses of gasolines containing mixtures of hydrocarbons while the latter is based on interpolation between data obtained on individual hydrocarbons. As an example of the usefulness of Fig. 2 and its equation, the following comparison is pertinent:

Petroleum J-P Fuels	*Gravity °API*	*Midboiling Point, °F*	*Net Heating Value, BTU/lb*	
			Estimated from Eq.	*Determined*
Typical	41.7	384	18,492	18,643
Experimental	32.0	419	18,207	18,209

The second generalization to be deduced from the tables and the figures is that, for a given heating value per pound, the higher boiling petroleum distillates have greater density (lower degrees API). This means, of course, that for equal heating value per pound, J-P fuel will have more BTU per gallon than aviation gasoline. This characteristic may assume great importance for jet-propelled aircraft operating at very high speeds, if the requirements of speed necessitate a limitation on wing size and consequently on wing-tank volume. Then the J-P fuel, for equal weight and equal number of BTU, will occupy less volume, as follows:

	BTU/Lb	*Gravity API*	*Lb/Gal*	*Relative Volumes for Equal* Q_p
J-P Fuel	18,700	40.0	6.870	88.5
Safety Fuel	18,700	51.2	6.448	94.3
Grade 100/130	18,700	62.5	6.072	100

Reference to Tables I and II will reveal that heating value per pound is closely related to the hydrogen content of the hydrocarbon molecule. Paraffins, with the generic composition, C_nH_{n2+2}, have the highest heating value per pound, and aromatics with the type formula, C_nH_{n2-6}, have the lowest heating value per pound. However, since hydrogen is very light, the paraffins have the lowest density and the aromatics have such high density that they have highest heating value per gallon.

The close relationship between heating value and hydrogen content can be expressed by a linear equation as shown in Fig. 3 for the averaged analytical data on a large number of aviation gasoline samples. The equation is as follows:

$$\text{Net BTU/lb } Q_p = 228.8\ (\%H) + 15{,}450.$$

Generally, distillates from petroleum crude oils have a predominance of saturated hydrocarbons, namely paraffins and naphthenes or cycloparaffins, with a minor proportion of the unsaturated hydrocarbons, principally aromatics. A typical distillate, therefore, may be considered as being composed, on the average, of hydrocarbons having the formula. C_nH_{2n}. A hydrocarbon of this composition will contain 14.28% hydrogen by weight and about 18,700 net BTU/lb.

To burn substances of this general formula, say C_8H_{16} for Grade 100/130 and $C_{12}H_{24}$ for J-P fuel, the following oxygen weights are required stoichiometrically:

$$C_8H_{16} + 12\ O_2 \longrightarrow 8\ CO_2 + 8\ H_2O$$

$$(112) + (384) \longrightarrow (352) + (144) = 496 \text{ lb or } 2{,}094.4\text{M BTU}$$

and:

$$C_{12}H_{24} + 18\ O_2 \longrightarrow 12\ CO_2 + 12\ H_2O$$

$$(168) + (576) \longrightarrow (528) + (216) = 744 \text{ lb or } 3{,}141.6\text{M BTU}$$

Therefore, in the case of these petroleum products, one pound of the reagents, fuel and oxygen, develops 4222 net BTU. This comparison on the basis of reagents instead of fuel alone is useful when studying the case of rockets carrying oxygen for combustion. If the fuel were TNT for instance, its heating value would be 5298 net BTU/lb and the stoichiometric relations are as follows:

$$(NO_2)_3 \cdot C_7H_5 + 5.25\ O_2 \longrightarrow 1.5\ N_2 + 2.5\ H_2O + 7\ CO_2$$

$$(227) + (168) \longrightarrow (42) + (45) + (308) = 395 \text{ lb or } 1202.6\text{M BTU}$$

In this case, one pound of reagents develops at most 3044 net BTU. For fuel value, therefore, a petroleum distillate is preferable to TNT.

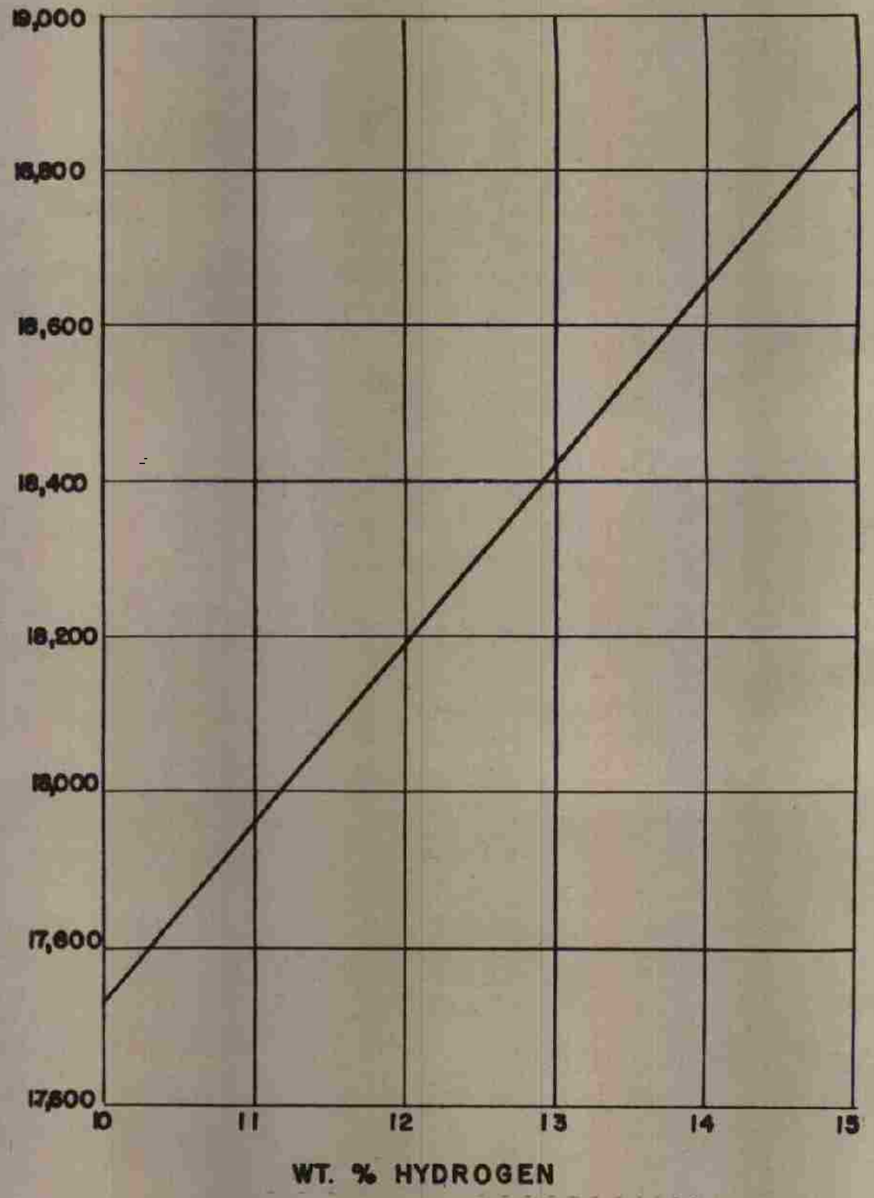


Figure 3 — Relationship Between Heating Value and Hydrogen Content for Aviation Gasoline.

b. Application.

The energy released by the combustion of fuels may be converted to power by four main methods. These are the steam turbine, the gasoline engine, the diesel engine and the combustion gas turbine. Of these the first three are in general use while the fourth method is only just coming into prominence, despite the fact that for over a century it has been known that theoretically its efficiency should be very high.

Mechanically the combustion gas-turbine power plant is very simple, consisting of a compressor, a combustion chamber and a turbine. Air is compressed to combustion-chamber pressures, fuel is admitted and burned, and the expanded, heated gases are passed through the turbine. The mechanical simplicity and theoretically attainable efficiencies have intrigued engineers for a long time; in fact, the first patent was taken out in 1791. However, the early inventors were severely handicapped on each of the three points involved, that is, compressor, combustor and turbine efficiencies, and were unable to obtain any net power output. This may be readily understood by reference to the following table, (Ref. 59), if one remembers that until very recently turbine temperatures were limited to 1000-1200°F and efficiencies for both turbines and compressors were very low.

Combined Mechanical Eff., Turb. & Compr.	*Thermal Efficiencies at Various Turbine Inlet Temp.*					
	1000°	*1200°*	*1400°*	*1600°*	*1800°*	*2000°*
50	—	—	—	3	7	11
60	6	9	12	16	19	22
70	15	18	21	24	27	30
80	23	26	28	31	34	37
90	30	33	35	37	40	43

However, development of the axial flow compressor with its high efficiencies and improvement in turbine design had changed the situation enough so that at least two applications had been reported before the war. The first was as a stand-by power plant where low investment and quick starting could offset efficiencies somewhat lower than those of a steam plant. The second was a power source for locomotives where simplicity, ease of maintenance, low weight, low cost and easy application of regenerative braking could justify lower efficiencies than those obtainable with diesel engines.

There are several ways of improving the efficiency of the simple combustion gas-turbine plant. Briefly, the compressor efficiencies may be improved by cooling between stages, the turbine efficiencies by reheating between stages and the over-all efficiencies could be theoretically improved by operating the unit as a closed cycle at higher pressures. The following table gives a comparison between the best steam power plant efficiencies and expected combustion gas-turbine plant efficiencies when operating on a closed cycle.

EFFICIENCIES AT VARIOUS TURBINE INLET TEMPERATURES

	1000°	*1200°*	*1400°*	*1600°*	*1800°*	*2000°*
Combined Gas Turb.	32	38	44	49	53	57
Steam Plant	34	37	38	39	40	41

In view of high-temperature alloys which have been developed during the war it is very probable that the combustion gas turbine will become one of the chief sources of postwar power. The jet-propulsion plane and the exhaust-gas turbosupercharger are very good evidence that such materials exist and that we may consider the higher temperature ranges of the above tabulations.

However, one of the factors which must be considered is the combustion step. Both of the above tables assumed 100% combustion efficiency and the thermal efficiencies would, of course, be reduced proportionally for any lower combustion efficiency. It must also be remembered that not only are high conversions of fuel energy to heat needed, but that the reactor itself must be kept small in size and weight. This is particularly important when the combustion gas-turbine plant is to be used to power aircraft.

The soundest approach to improved design of combustion reactors and higher combustion efficiencies would appear to be through a study of the fundamentals of combustion. In order to do this with the greatest expediency a brief literature survey has been made which emphasizes the variables to be considered and experimental techniques which have been used.

c. *Data on Combustion Processes.*

(1) GENERAL. The early workers on combustion processes were severely handicapped since modern equipment (spectrographs, etc.) was not available, and they were forced to work with slow combustion so that chemical sampling of the intermediate reaction products would have maximum validity. In a high temperature, and consequently fast, reaction, it was impossible to take and cool a sample quickly enough to freeze the reaction in the status quo. Therefore, their work was limited to cool or slow combustion and to deductions made from rather superficial observations of the faster reactions.

However, during the decade from 1920 to 1930 two factors combined to spur and facilitate research on oxidation processes. First, methods were developed which enabled the scientist actually to look into a flame front and detect the changes which were taking place there. Second, increased importance of fuel quality and performance in automobile, airplane and diesel engines forced industrial research to investigate these phenomena. Thus, the more recent research work may be divided roughly into two parts, that done in engines and that work not directly connected with engines. When this is done and the effects of the various variables are compared according to the findings of these two groups some very interesting discrepancies are found.

(2) COMPARISON OF ENGINE AND FLAME DATA. In both cases, the usual criterion of combustion rate was flame speed. Those people who investigated combustion in engines measured total flame speed, that is the actual speed of the flame relative to the gases plus the speed of the gases, while the other investigators measured the more fundamental property or actual flame speed. Bearing this in mind, the effects of various variables on flame speed were found to be as follows:

(a) *Increasing Reaction Temperature.* In engines, total flame speed went down (Ref. 12), while the nonengine data indicated an increase in actual flame speed. Two suggested reasons for this deviation are the increase of inert diluents in an engine with increasing temperature and a decrease in turbulence. In the engine studies an increase in temperature was obtained by increasing inlet temperature.

(b) *Increasing Combustion Pressure.* When tests were made on an engine in which both exhaust and inlet pressure were varied together, the flame velocities were found to increase with pressure (Ref. 12). By comparison, laboratory work has indicated that there is no variation of actual flame velocity with pressure over a wide range (Ref. 118). These variations could have been caused either by turbulence effects or might not be real but due to the different definitions of flame velocity.

(c) *Increasing Diluents.* Here both approaches give the same answer: addition of inert gases reduces flame velocities. This was done by increasing exhaust pressure in engines and thus increasing the proportion of residual gases (Ref. 12). In fundamental work this has been done by addition of inert gases to normal combustion mixtures (Ref. 121,40), and has also been noted in explosive mixtures (Ref. 73).

(d) *Increasing Humidity.* There is considerable deviation in results on the effect of humidity due apparently to varied conditions of test and fuels. In engine work the flame speed decreased as humidity went up (Ref. 12), which checks other work on hydrocarbons (Ref. 126). However, since water vapor takes part in some oxidation reactions, it may increase flame speeds, for example in combustion of CO. It is probable that no fundamental disagreement exists but merely a lack of data.

(e) *Increase in Turbulence.* Although there is no good method for measuring turbulence, a large amount of data exists which shows a definite increase in flame speed with increasing turbulence. Many variations in determining the effects of other variables are known to be due to turbulence as has been mentioned previously. Some work has been done in which turbulence in an engine was varied by raising inlet velocities and thus obtaining an increase in flame velocities without changing other variables (Ref. 108,109).

This has also been shown in flow experiments on petroleum products (Ref. 68) where increasing turbulence actually decreased the temperature at which reaction took place. Work in glass tubes on slow burning mixtures has also shown that increasing turbulence can produce supersonic flame speeds in mixtures which ordinarily would burn very slowly (Ref. 31). These results seem to indicate that turbulence may increase the actual as well as the total flame velocities.

(f) *Increase in Engine Speed.* Here several tests are in agreement and show an increase in total flame speed with engine speed (Ref. 78, 13). This is believed to be due to turbulence in the cylinder head and is probably mainly due to an increase in flame front area as discussed in "Increase in Turbulence." In this case it is difficult to determine whether the actual flame velocities are affected or not.

Although the data available seem to conflict they point strongly to the need for additional work. It is evident that many of these discrepancies could be eliminated by judging all tests on the basis of the more fundamental variable of actual flame speed relative to the burning gases and by devising some means of measuring the turbulence present during combustion. It is also apparent that the experimental procedures used must be carefully considered.

(3) THEORETICAL MECHANISMS OF COMBUSTION. Considerable controversy exists with respect to the mechanism of combustion. The most pouplar theories explain initiation of combustion reactions by formation of hydroxyls or peroxides and have many variations. Egerton (Ref. 36), Norrish (Ref. 86), Bone and Gardner (Ref. 10), Ubbelohde (Ref. 128) and von Elbe and Lewis (Ref. 134) have all contributed to these theories. Gaydon (Ref. 51) discusses these theories briefly and makes the interesting comment that, despite the evidence in their favor, they all ignore the CH and C_2 radicals which are the strongest found in flame spectra.

In connection with the question of the efficiency of conversion of the combustion energy of fuels into mechanical energy, it must be pointed out that the reciprocating engine has not reached the limit of attainable efficiency. It is true that for practical purposes, present limitations of engine design, fuel antiknock quality and construction materials restrict the advances in efficiency that can be realized; but the combustion turbine also has similar limitations to overcome. There is likely to be, therefore, lively competition among designers of prime movers for aircraft power, as a result of which contest more efficient reciprocating engines are almost certain to be developed. Figure 4 indicates what can be hoped for along this line. In modern aircraft engines, the over-all value of K, the polytropic exponent, is about 1.23 and the compression ratio is nearly 7. Consequently an increase in compression ratio from 7 to 10 might permit an increase in efficiency from about 35 to 40 or possibly an improvement of 14% in fuel economy.

AVIATION GASOLINE MANUFACTURE

For powering aircraft, aviation gasoline of the 100-octane grade is at present the most important fuel. As indicated above in the section on "Available Energy" the volume of aviation gasoline required is immense. It constitutes about 11% of each barrel of petroleum produced and amounts to more than one half million barrels per day. This gasoline is largely a synthetic product in that it is chiefly composed of hydrocarbons which do not occur naturally in petroleum. Out of the millions of possible hydrocarbons, only a few are outstanding in antiknock quality and in the refining of petroleum these desirable hydrocarbons are obtained by converting the less desirable ones. The principal hydrocarbons included in 100-octane gasoline are isopentane, the isohexanes, the isoöctanes and the aromatics, toluene, xylene and cumene. The antiknock quality of these hydrocarbons is further enhanced by the addition of 0.12% of the synthetic hydrocarbon derivative, tetraethyl lead. The manufacture of the desired hydrocarbons may be represented schematically for the following processes:

Desired Hydrocarbon	*Schematic Process*	*Name of Process in First Step*
Isopentane	$n\text{-}C_5H_{12} \longrightarrow iso\text{-}C_5H_{12}$	Isomerization
Isohexane	$n\text{-}C_6H_{14} \longrightarrow iso\text{-}C_6H_{14}$(2,2-dimethylbutane)	Isomerization
Isohexane	$C_2H_4 + i\text{-}C_4H_{10} \longrightarrow iso\text{-}C_6H_{14}$(2,3-dimethylbutane)	Alkylation
Isoöctane	$2(i\text{-}C_4H_8) \longrightarrow C_8H_{16} \xrightarrow{H_2} C_8H_{18}$	Polymerization
Isoöctane	$i\text{-}C_4H_8 + n\text{-}C_4H_8 \longrightarrow C_8H_{16} \xrightarrow{H_2} C_8H_{18}$	Copolymerization
Isoöctane	$i\text{-}C_4H_{10} + C_4H_8 \longrightarrow C_8H_{18}$	Alkylation
Toluene	Methylcyclohexane $\longrightarrow C_6H_5 \cdot CH_3 + H_2$	Hydroforming

CYCLES

$E = 1 - \left(\frac{1}{CR}\right)^{K-1}$

$K = \frac{C_p}{C_V}$

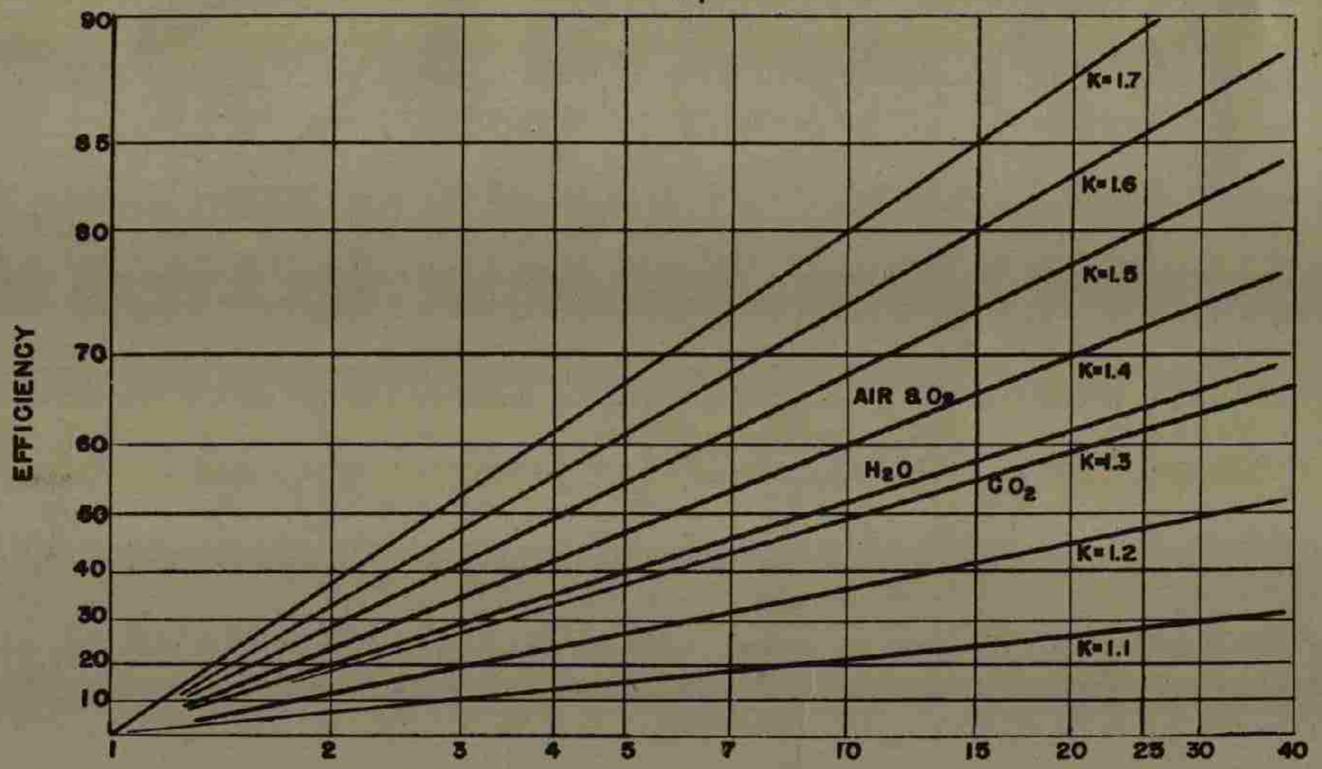


Figure 4 — Efficiency vs. Compression Ratio Constant Volume and Constant Pressure

Feed stock preparation, as applied to the raw materials subjected to the above processes, represents a considerable proportion of the over-all refining effort. This preparation involves such operations as fractional distillation, thermal cracking, catalytic cracking and the manufacture of catalysts used in the processes. In spite of the apparent complexity of the processes, however, the blending agents, which are the proper mixtures of these desirable hydrocarbons, can be manufactured at costs of about only three cents per pound. It is evident that the manpower involved in making a specific hydrocarbon in relatively pure form is moderate in comparison with the labor required in the manufacture of conventional chemicals. Should other hydrocarbons of different types prove desirable in the future, there is reason to be confident that satisfactory processes can be developed to manufacture them economically and in volume.

KNOCK-LIMITED POWER

The foregoing discussion has been predicated upon the need for a plentiful liquid fuel of high energy content and more particularly upon the use of this liquid in an internal combustion aircraft engine. To perform its function, the aircraft engine must produce the maximum amount of power, consume the least amount of fuel and weigh as little as is consistent with the strength it must have to withstand the strains imposed upon it.

The chief limiting factor in aviation fuel performance is the familiar tendency of most petroleum hydrocarbons to knock under increased power conditions, thus to threaten destruction of the very engines they operate.

The true mechanism of knock is not well understood, but the phenomenon can be roughly described as follows. A tube of fuel-air mixture ignited at one end by a spark plug is shown in Fig. 5. The following sequence of events occurs: (a) Ignition of the mixture by the spark plug. (b) Relatively slow burning of the mixture, progressing away from the spark plug. (c) Rapid increase in pressure and temperature of the unburned portion of the mixture ahead of the flame front until a condition is reached which makes that unburned mixture explode violently or detonate. (d) Pressure waves set up within cylinder, resulting in knock; rapid scrubbing of walls by vibrating gas, rise in temperature of walls, loss in engine power and eventual destruction of parts.

An aircraft engine is a device for converting heat energy into useful work. Its working fluid is air, or more accurately, nitrogen from air plus the products of combustion. These combustion products are the gases, carbon dioxide, carbon monoxide, water vapor and hydrogen, in varying proportions depending on the conditions of burning in the cylinders. It is a fact not generally appreciated, that the power output of a gasoline engine is more nearly proportional to the amount of air (oxygen in the air) burned than to the amount of gasoline consumed. It is the reason why aircraft engines are supercharged or boosted to increase manifold pressure for take-off and for operation at high altitudes.

A very much simplified calculation of the thermal efficiency of an actual engine, as compared with that of the theoretical Carnot cycle is the following:

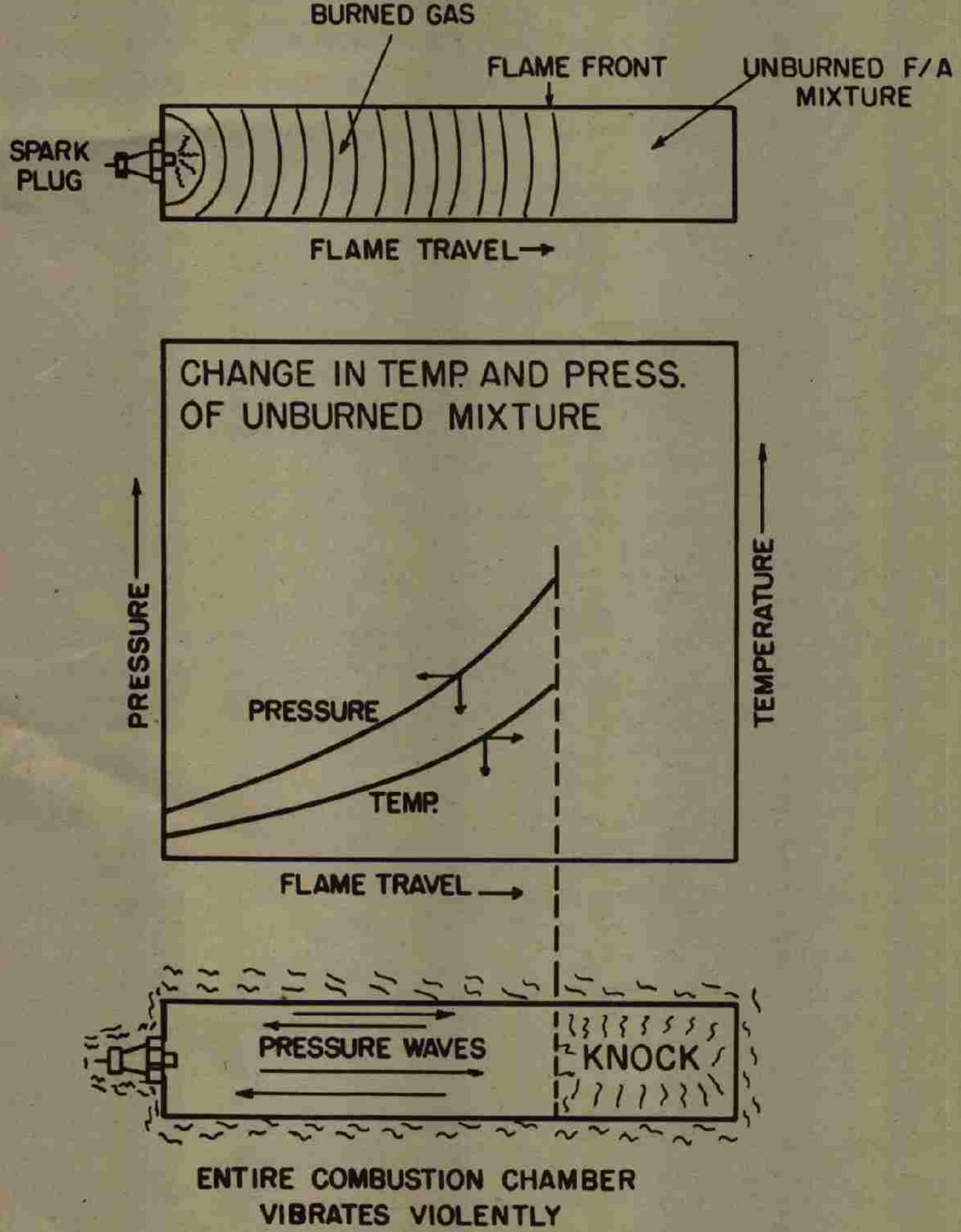

BURNED GAS
FLAME FRONT
UNBURNED F/A MIXTURE
SPARK PLUG
FLAME TRAVEL→
CHANGE IN TEMP. AND PRESS. OF UNBURNED MIXTURE
PRESSURE
TEMPERATURE
PRESSURE
TEMP.
FLAME TRAVEL
PRESSURE WAVES
KNOCK
ENTIRE COMBUSTION CHAMBER VIBRATES VIOLENTLY

Figure 5

ACTUAL VS. THEORETICAL ENGINE (7 TO 1 COMPRESSION RATIO)

	Actual		*Theoretical*	
Total heat in fuel, BTU/lb.		19,000		19,000
Heat lost in exhaust, BTU	6,500		8,500	
Heat lost in cylinder cooling, BTU	6,000		0	
Total heat lost, BTU		12,500		8,500
Usable heat: available to produce work		6,500		10,500
Thermal Efficiency, $\frac{\text{Usable heat}}{\text{Total heat}}$	34%		55%	
Theoretical pounds of fuel per brake horsepower hour (no heat losses)			0.134	
Pounds of fuel per brake horsepower hour at stated efficiency	0.394		0.244	

The actual engine is naturally much less efficient than the theoretical engine, since it has mechanically operated valves which require time to open and close, thus permitting dilution of the fuel charge with exhaust gases, and because the mixture will not burn instantaneously after ignition. Moreover, it is impossible in an actual engine to prevent heat loss from the gas to the walls and the temperatures that the metal parts of the engine can stand are limited so heat must be removed in order to keep temperatures of cylinders and pistons within safe limits. This means a need for cooling fins, to cool cylinders and lubricating oil, which place an added drag on the airplane; also for special metals to withstand high temperatures; for engine lubricants to function under these severe conditions. Many other problems which the designer, the metallurgist and the oil refiner must solve, result from this unavoidable heat loss.

At least theoretically there is big room for improvement in the efficiency of reciprocating engines beyond that given by increased compression ratio. Roughly speaking, the total heat in a pound of fuel is divided as shown above. This, however, applies only to operation with the theoretically correct ratio of fuel to air, typified in practice by cruising conditions at low power output. For high power output, as at take-off, an engine designed to give maximum fuel economy at cruising conditions must run with a rich mixture (a higher ratio of fuel to air) for otherwise it would knock, overheat and quickly be destroyed.

The following simple chemical equations show why rich mixtures produce less heat, hence less knock. They show the relative volumes of gases produced and the relative quantities of heat evolved when a given volume of oxygen in the air combines with or burns a hydrocarbon in lean mixture and in rich mixture respectively.

100% of Theoretical Fuel

(Cruise or maximum economy lean mixture
Fuel/Air ratio = 0.067) (1)

$$\text{(Fuel)} + \text{(Air)} \longrightarrow \text{(Exhaust Gas)}$$

$$1\ CH_2 + 1.5\ O_2 \longrightarrow CO_2 + H_2O$$

Heat evolved = 19,000 BTU/lb fuel
or 1,270 BTU/lb air

150% of Theoretical Fuel

(Take-off or full power rich mixture (2)
Fuel/Air ratio = 0.10)

$$\text{(Excess Fuel)} + \text{(Air)} \longrightarrow (\ldots\ldots\ldots\ldots\text{Exhaust Gas}\ldots\ldots\ldots\ldots\ldots\ldots)$$

$$1.5\ CH_2 + 1.5\ O_2 \longrightarrow 0.53\ CO_2 + 0.97\ H_2O + 0.97\ CO + 0.53\ H_2$$

Heat evolved = 10,900 BTU/lb fuel
or 1,090 BTU/lb air

These equations show that, with rich mixtures, the heat evolved per pound of fuel or per pound of air is reduced. This produces less temperature rise in the cylinders, and less tendency to knock. This also permits an increase in air supplied to the engine by means of added boost or supercharging, and added fuel, and this in turn permits greater power outputs before knocking occurs again.

Although all fuels will knock less in rich mixtures than at the theoretically correct fuel-air ratio, some are better than others in this respect.

The following table shows what this means in terms of power output and fuel consumption in an aircraft engine of 2000 rated brake horsepower:

	Cruise	*Rated Continuous*	*Take-Off*
Horsepower delivered	1,400	2,000	2,400
Lb fuel consumed per hr	560	1,050	1,600
Gallons fuel consumed per hr (assuming 6 lb/gal)	94	175	266
Fuel/Air ratio	0.07	0.085	0.10
Total heat in fuel, BTU (assuming 19,000 BTU/lb)	10,600,000	20,000,000	30,400,000
Heat to produce power, BTU	3,600,000	5,100,000	6,100,000
Heat lost, BTU (difference)	7,000,000	14,900,000	24,300,000
Fuel consumption rate, over-all lb/BHP hr	0.40	0.525	0.67
Thermal efficiency, over-all	34%	26%	20%

The fuel consumption at cruise, the condition of best economy, is 0.40 lb of fuel /bhp-hr. For the increase of 600 hp to bring the engine to rated continuous power, fuel consumption is at the rate of 0.82 lb/bhp-hr, and thermal efficiency at this rate is reduced to 16%. The rate of fuel consumption for the increment from rated 2000 to 2400 take-off horsepower jumps to 1.38 lb/bhp-hr, and thermal efficiency for the same range drops to 10%.

This indicates where improvements in fuel quality can, in present conventional power plants, help reduce airplane operating costs or improve performance. There are a number of ways that these benefits might be effected:

(a) Same cruise quality but better rich mixture quality, so that same power as at present can be obtained with less enrichment. Result: better economy.

(b) Same cruise quality but better rich mixture quality, so that greater power can be obtained with same enrichment as at present. Result: better performance.

(c) Better cruise quality and same rich mixture quality. Result: greater range of operation.

(d) Better cruise quality and better rich mixture quality. Result: greater range and better performance.

However, the above data also indicate the possibilities open for subsidiary power plants for take-off and combat performance. With light, dependable, and moderately economical rockets or thermal jets available the reciprocating engine could be designed for one purpose, namely, economical cruise with reduction in weight and possibly improved efficiency. Another possibility is that suggested by equations (1) and (2) previously given. It will be noted that at the very rich condition only 10,900/19,000 or 58% of the chemical heat of the fuel has been used. A large proportion, namely, 42% of the heat available in the fuel still remains as unburned CO and H_2 in the exhaust gas. Air, under suitable pressure, added to the exhaust gas during the rich condition should make some of this energy available as thrust by jet action in exchange for added boost power. Suitable combustors, possibly catalytic in nature, would have to be developed, but this should not be difficult. A third possibility is always to operate the conventional reciprocating engine partially rich with the advantage of higher power per cubic inch, recovering the excess fuel in a thermal jet power plant operating in series.

Figure 6 shows how knock affects economy (or range of operation) of an aircraft. The higher the compression ratio, and the higher the temperature, the better will be the resulting economy for a given power output. Neglecting mechanical considerations, the tendency of a fuel to knock limits the compression ratio with which it can be used, and hence the economy or range that can be attained.

Figure 7 presents three schematic indicator cards showing the increased cylinder pressures, and hence greater powers, which are obtainable without knocking when richer mixtures are used. (For simplicity, the power increase that is gained in practice by increasing rpm has been neglected.) Three work areas are shown: the area surrounded by the light solid line is work (power developed) at cruise conditions; the area surrounded by the dotted line is work at rated continuous power conditions; and the unshaded area surrounded by the solid line is work at take-off conditions. These roughly represent the three conditions listed in the above table. In each case the limit of permissible power is due to knock, but different fuels will show different rates of change in permissible power with rate of change in fuel-air ratio.

The necessary adjustments to handle these changes in fuel-air ratio are complicated and to relieve the pilot the carburetor is designed to take care of them, automatically, as shown in Fig. 8. There are two settings, "automatic lean" and "automatic rich," determined by experience, and the pilot has the choice of either to obtain economy or power as required. With these settings the carburetor automatically supplies enough fuel based on the quantity of air passing through its throat to prevent knock under any normal condition when running on the proper fuel. In certain large long-range aircraft, however, the flight engineer may override the controls manually and approach incipient knock as closely as he dares in order to obtain maximum economy and hence greatest range. In Fig. 8, the three points at successively higher power outputs represent conditions for cruise, rated continuous and take-off power respectively.

A comparison of fuel quality on a lean mixture performance and a rich mixture performance basis is admittedly an oversimplification of the knock problem because other variables enter, such as compression ratio, spark advance, cylinder cooling,

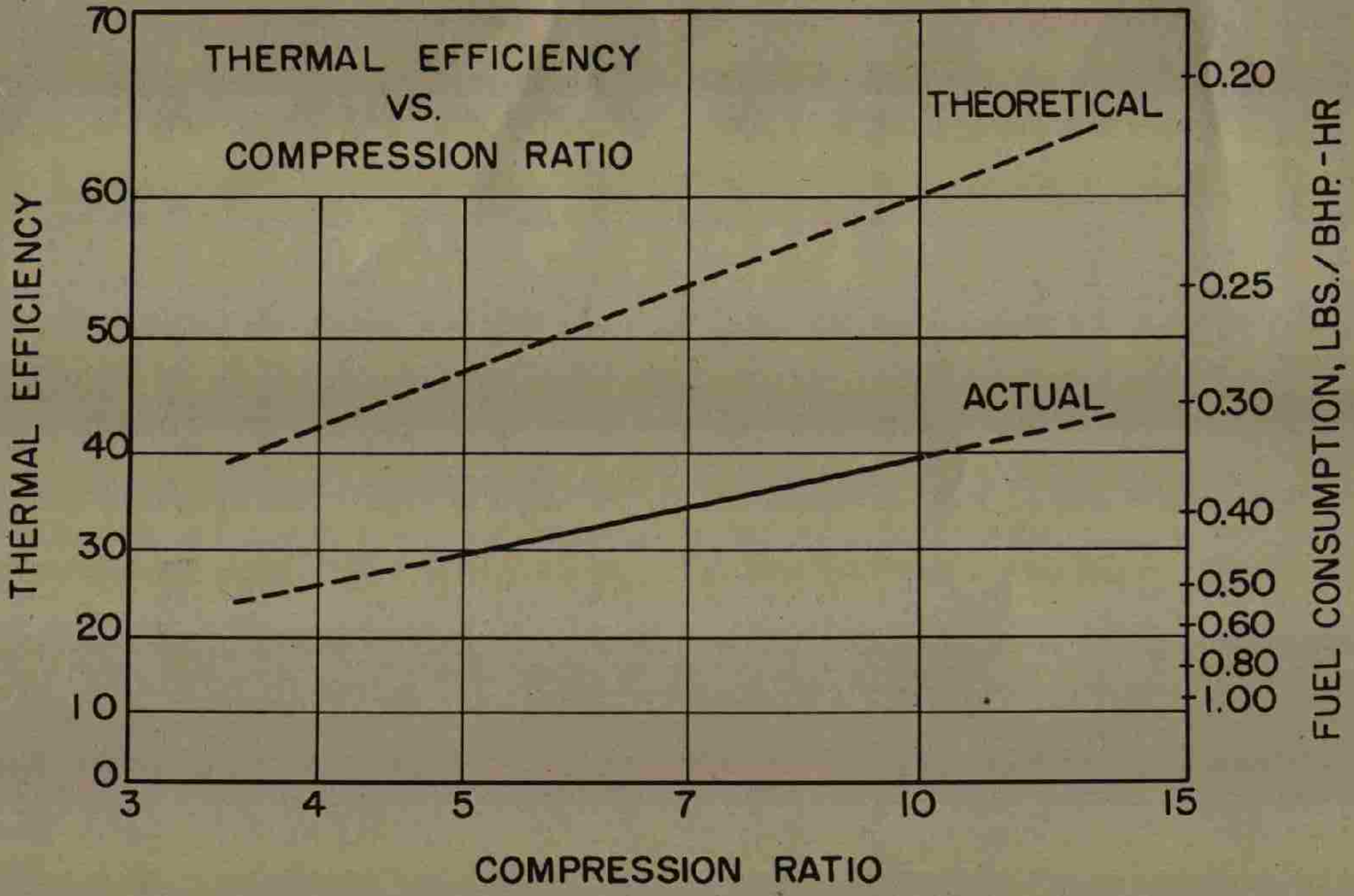


Figure 6 — Thermal Efficiency vs. Compression Ratio

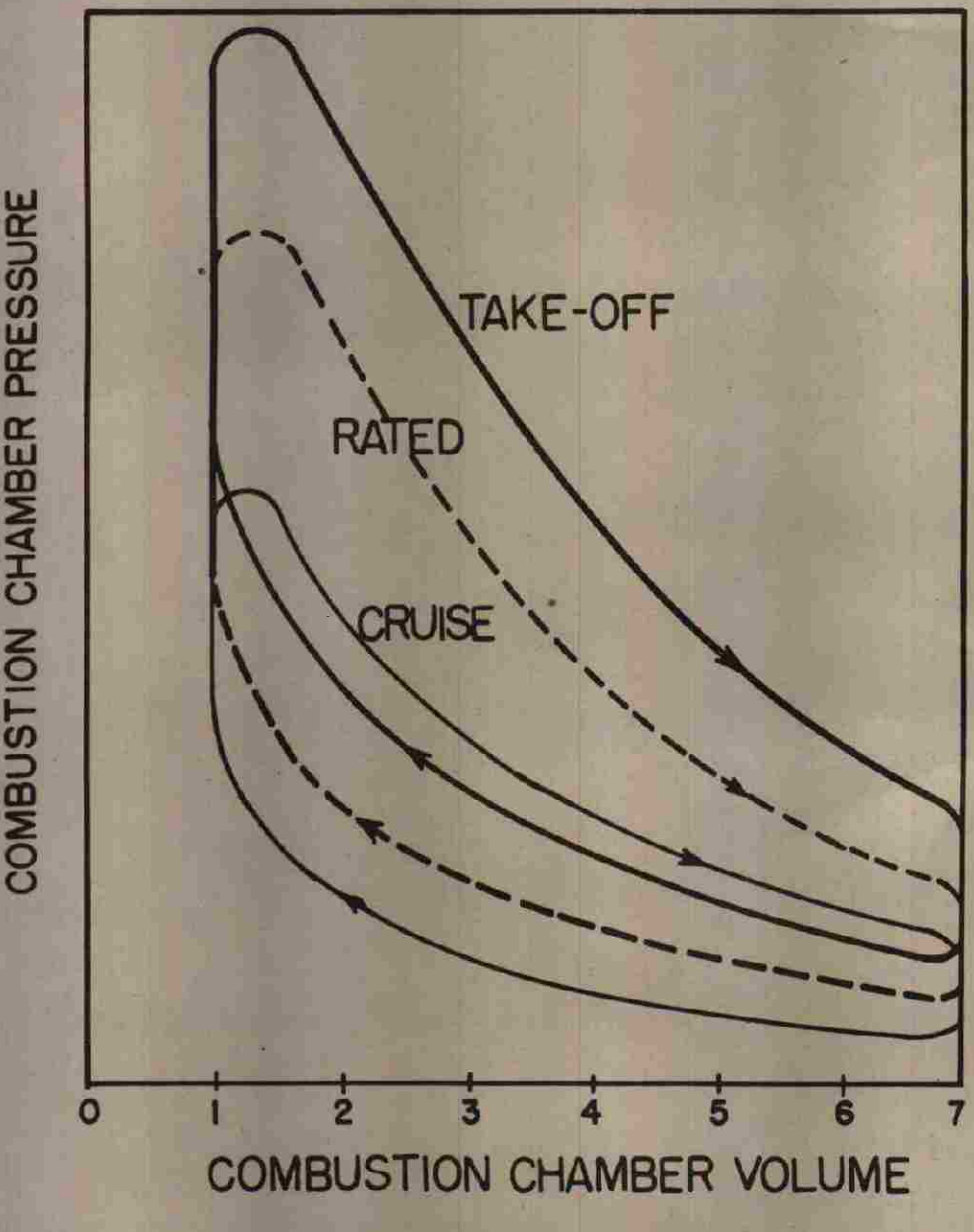


Figure 7 — Pressure-Volume Relationship

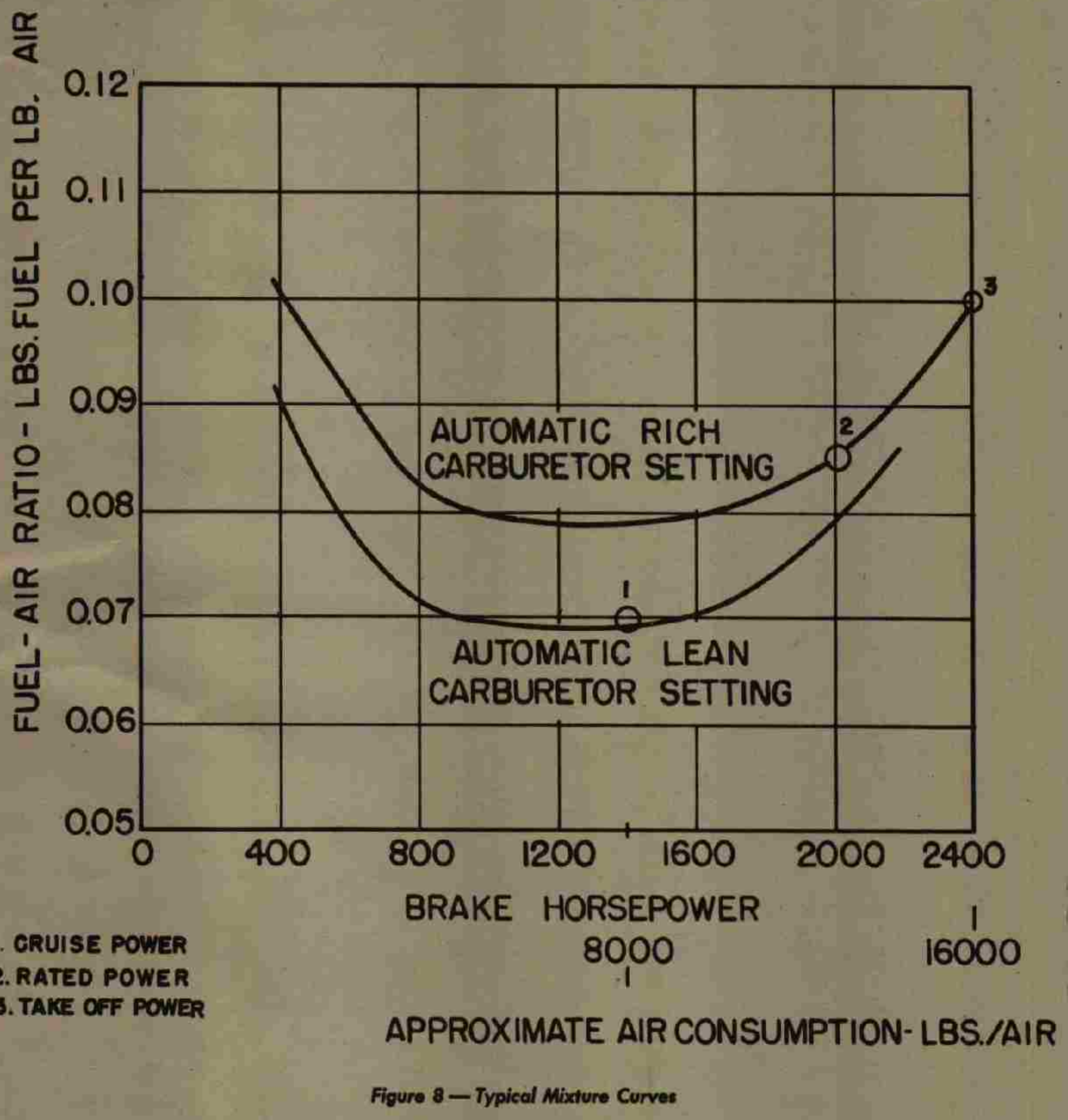


Figure 8 — Typical Mixture Curves

mixture temperature, rpm, hot spots, etc. Nevertheless, the wide differences in fuel quality under different operating conditions can readily be shown by such a comparison.

There are millions of individual hydrocarbon compounds possible and the number present in petroleum is probably in the hundreds of thousands. In the gasoline boiling range alone, the number possible is around 5000. Of these, however, only a few dozen are known to be of superior antiknock quality. The following table gives a comparison of the relative antiknock quality of some of these hydrocarbons and of some typical aviation gasolines:

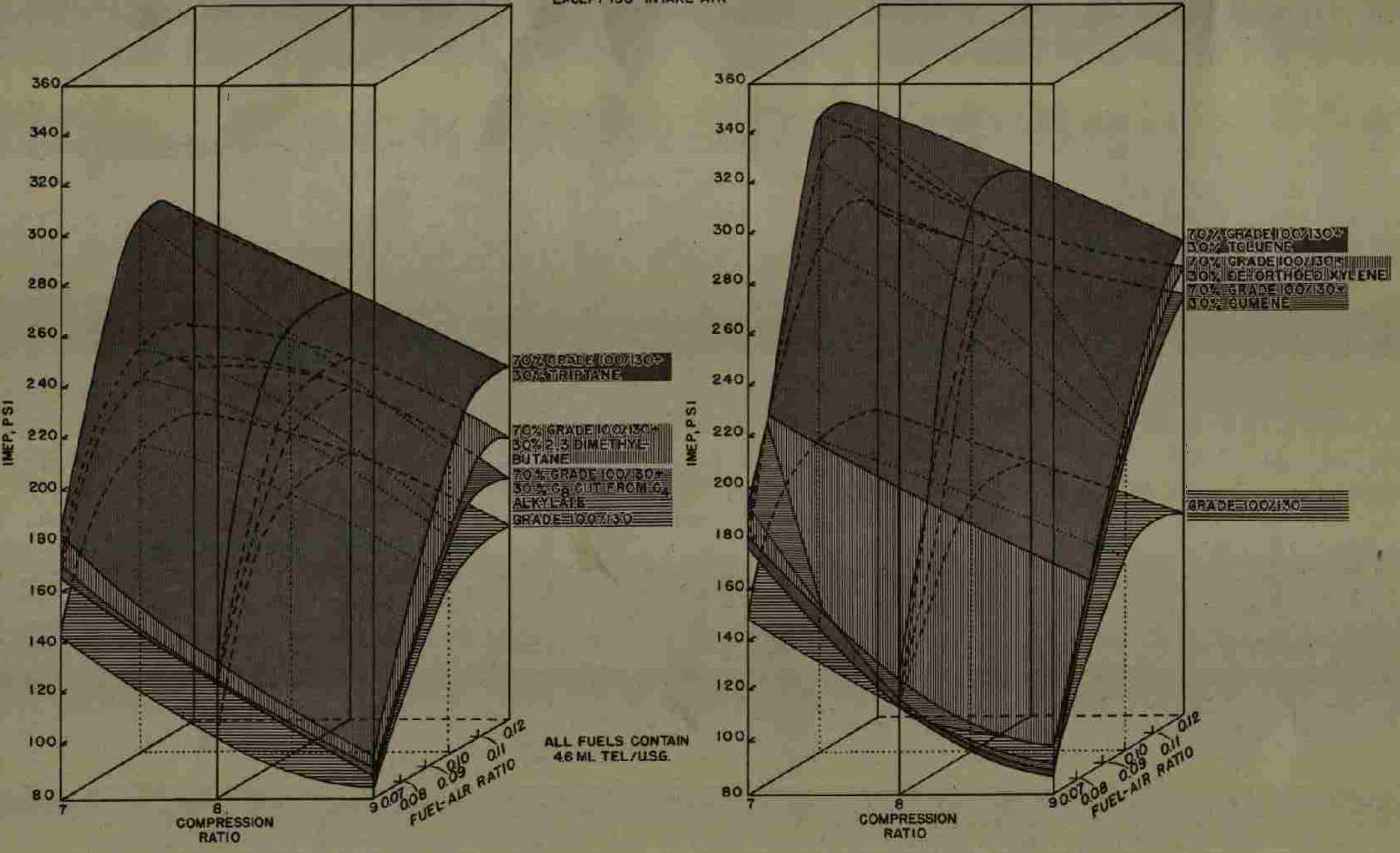
COMPARISON IN ANTIKNOCK QUALITY OF PURE HYDROCARBONS AND AVIATION FUELS

	Performance Numbers with 4-cc Ethyl Lead/Gal		
Substance Tested	*Lean Mixture (F-3 Test)*	*Rich Mixture (F-4 Test)*	*Increment (Rich-Lean)*
Cumene	103	246	143
m- and p-Xylene	128	246	118
Toluene	103	240	137
Triptane	160	240	80
Diisopropyl	139	190	51
Isoöctane (Reference)	153	153	0
Neohexane	137	139	2
2,3-Dimethylpentane	100	141	41
100/130 Aviation Fuel Base	100	130	30
Methyl Cyclohexane	76	128	52
91/96 Aviation Fuel Base	76	88	12

These ratings serve to indicate the wide variations in fuel performance that can be obtained by varying engine operating conditions. Assuming that between the two extremes lie the actual knocking conditions experienced in flight, it is obviously important to know just where incipient knock is reached under different flight conditions and in different engines. Plate 6, here presented, further illustrates the variation in antiknock quality of some of the above substances when the compression ratio of the engine and the strength of the fuel-air mixture are varied. The Appendix presents a more complete record of the variation of antiknock quality of individual hydrocarbons under different conditions of test. This table was compiled by the Hydrocarbon Research Project of the American Petroleum Institute.

To redesign engines and aircraft to take full advantage of fuel improvements is no easy task. One phase of the job is to prove by adequate full-scale engine tests that the fuel has the added quality, how much and under what conditions of operation. Another is to determine what changes in superchargers, carburetors, ignition systems, coolers, etc., must be made to get the most from the new fuel, new engine combination. The fuel and the engine are, in a sense, like the hen and the egg: which comes first?

The engine manufacturer cannot build his engine in production quantities until the fuel it needs is commercially available. The refiner cannot build the equipment for making the fuel without knowing what its composition must be to meet the needs of the engine.



EFFECT OF COMPRESSION RATIO
AND MIXTURE STRENGTH
ON PERMISSIBLE POWER OUTPUT

SUPERCHARGED C.F.R. ENGINE
STANDARD F-4 OPERATING CONDITIONS
EXCEPT 150° INTAKE AIR

ALL FUELS CONTAIN
4.6 ML. TEL/USG.

Plate 6 — Effect of Compression ratio and mixture strength on permissible Power Outfit

REACTION, PROPULSION

If the present progress towards elimination of knock as the principal limitation of the reciprocating engine should lag, the rapid strides concurrently being made in jet propulsion and rocket propulsion might conceivably result in the gradual obsolescence of the reciprocating engine. However, it is more likely that combinations of the different methods of propulsion will be developed to give maximum over-all efficiency in aircraft operation.

As long as the weight of the fuel to be carried aboard aircraft is a major consideration in airplane design, aviation gasoline will continue to be the most desirable fuel, irrespective of the type of engine used, because it is the liquid combustible having the most BTU per pound. This desideratum may have to be modified, as in present JP-1 fuel, for design reasons; but generally the most volatile and most paraffinic liquid fuels that can be burned will be chosen because they have the highest BTU per pound.

Eventually, for flight at very high speeds, the design of airplane wings will be so slenderized that space limitations will control the amount of fuel that can be stowed aboard. In such cases, the fuel having the most BTU per cubic foot or per gallon will be desired and a nonvolatile fuel will be used, provided that its pour point, viscosity and burning characteristics are satisfactory. The present JP-1 fuel is a good example of this type of fuel. In order to have the optimum combination of properties, it is likely that such a fuel will be predominantly naphthenic in its hydrocarbon structure. This means, of course, that it will have relatively high density due to the cyclic structure of the hydrocarbon molecules and relatively high BTU per pound due to the relatively high ratio (about 1:6) of hydrogen to carbon in these molecules. The net result is high BTU content per gallon.

Generally speaking, the choice of a suitable petroleum liquid can be made by reference to existing compilations of data on the interrelations of the physical properties of various petroleum products. For example, the attached chart, Fig. 9, on the "Related Properties of Diesel Fuels" shows how two out of five physical properties can fix the other three. This particular chart was drawn up for diesel fuels, but it includes fuels of volatility comparable with that of JP-1. The characteristics of "Cetane Number" is largely a measure of paraffinicity, the paraffin "Cetane" or hexadecane having 100 Cetane Number by definition. Of course, the chart presents average relationships and it is therefore possible to select an individual hydrocarbon with properties that do not conform with the chart. Nevertheless, it is unlikely that any fuel, falling within the scope of this chart and yet departing significantly from the average relationship, can be made available in the tonnage that would be necessary for powering our aircraft.

PRACTICAL CONSIDERATIONS

a. Relative Fire Hazard of Aviation Gasoline and Kerosene Fuel.

The question of the relative hazards of using volatile and nonvolatile fuels for aircraft has been under discussion in the technical literature for the past fifteen years without reaching a final answer. The difficulty of decision has been due to the fact that each type of fuel is more hazardous than the other in certain circumstances. Consequently, the person whose responsibility it is to choose one of the two for a certain

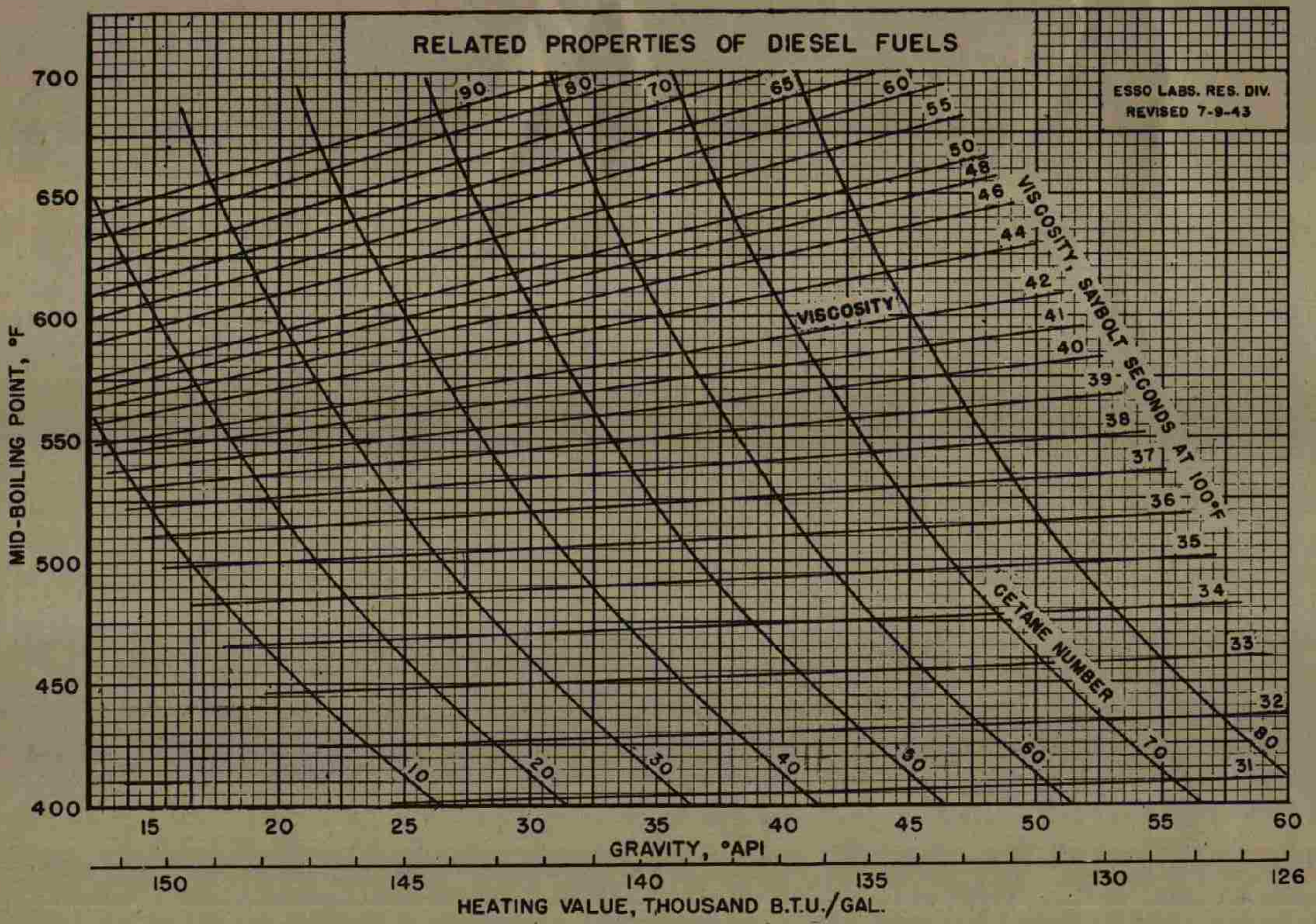


Figure 9 — Related properties of Diesel Fuels

type of service must make his decision after considering which fuel offers the lesser hazard in that service. The purpose of this section is to summarize the characteristics of the two fuels, pointing out the circumstances in which these characteristics may be critically significant with respect to fire or explosion hazards.

The chief property of a liquid fuel which determines the ease with which it can be ignited is the vapor pressure of the liquid. This property varies with the temperature, the higher the temperature the higher the vapor pressure. Every liquid fuel has a certain critical vapor pressure which determines its lower inflammability limit in air. When this limit is reached, the concentration of inflammable vapor in the air directly above the surface of the liquid is just great enough to permit ignition by a spark or flame. If the container is closed, it is possible, by further increasing the temperature, further to increase the concentration of vapor in the air space until the upper inflammability limit is reached, at which point the ratio of air to fuel is too small to permit ignition of the fuel. The effect of altitude is to decrease the pressure of the air, with the result that increasing the altitude lowers the two temperatures at which each fuel just enters and then leaves the inflammable range.

The foregoing paragraph succinctly states the principles governing the degree of explosion hazard for a given fuel in a given set of circumstances. All it is necessary to know is (1) the inflammability limits of the fuel, (2) the vapor pressure of the liquid at different temperatures, (3) the temperature of the liquid, (4) the altitude or the air pressure, and (5) the length of time at the temperature and altitude given. With this information and a knowledge of the aircraft operations, for example, whether the source of ignition is most likely to come from static electricity while fueling on the ground or from incendiary bullets at ceiling altitudes, a proper choice of fuel can be made. The following table compares an aviation gasoline of the type AN-F-28 with AN-F-32 fuel of the kerosene type (having exceptionally high flash point as compared with the minimum requirement of 110°F) on the basis of the above listed properties:

	Typical Properties	
	Aviation Gasoline	*Kerosene*
Vapor Pressure, lb/sq in.		
at 140°F	14.7	0.07
100°F	7.0	0.015
60°F	3.0	0.0017
20°F	1.1	—
−20°F	0.3	—
−60°F	0.07	—
Lower Inflammability Limit, lb fuel/lb air		
at sea level	0.035	0.035
at 20,000 ft	0.043	0.040
at 40,000 ft	0.049	0.048
at 60,000 ft	0.061	0.059
Upper Inflammability Limit, lb fuel/lb air		
at sea level	0.245	0.250
at 20,000 ft	0.225	0.232
at 40,000 ft	0.206	0.213
at 60,000 ft	0.190	0.194

	Typical Properties	
	Aviation Gasoline	*Kerosene*
Temperature Range, °F, from Lower to Upper Limit		
at sea level	−45 to +14	145 to −
at 20,000 ft	−55 to −14	130 to −
at 40,000 ft	−75 to −45	108 to 145
at 60,000 ft	− to −65	97 to 128
True Sea Level Flash Point, °F	−45	+145

The foregoing table shows that kerosene has much lower vapor pressure than aviation gasoline and, since the inflammability limits of the two fuels in air are substantially the same, the kerosene needs to be heated considerably more than the aviation gasoline in order to enter the inflammable limits. Of course, the relative safety of kerosene in respect to explosion hazard at sea level has long been recognized. Various governmental and private agencies, such as the Interstate Commerce Commission or the National Fire Protection Association, have made more lenient rulings for the handling of liquids having flash points higher than atmospheric temperature, than for the handling of liquids like gasoline which flash at low temperatures.

Flash point when accurately determined is really a measure of the temperature at which the liquid reaches the lower inflammability limit. However, this point alone does not give complete information about the relative fire hazards of fuels. A glance at the table will show that at 140°F the aviation gasoline begins to boil (14.7 lb vapor pressure) while the kerosene is only just reaching its flash point, at which point the concentration of its vapor in the layer of air just above the surface is only about 0.6%. Assuming that the vapor space above the liquid is 1 cu ft capacity and that at 140°F this space is burst open and its vapor contents allowed to diffuse uniformly in the form of a hemispherical envelope around the central point where the liquid remains, the vapor from the aviation gasoline would form an explosive hemisphere 7 ft in diam, while the vapor from the kerosene would be too attenuated to flash even at the liquid surface.

The chief advantage of a fuel with a flash point of 145°F is that it will not form an inflammable mixture with air as long as no part of the liquid is heated as high as 145°F at sea level or 97° F at 60,000-ft altitude. Generally, therefore, no fire or explosion will occur with kerosene if a source of ignition should be brought close to the liquid at ordinary ambient temperatures. It must be emphasized, however, that if any portion of the liquid is heated hot enough to ignite, it can provide heat to propagate combustion of the remainder. This may be borne out by an informal report that the Air Corps has been able to explode leak-proof tanks of a kerosene of 105°F flash point by firing incendiary bullets into the vapor space at temperatures well below the flash point: presumably the impact of the bullet sets up a fine spray of the liquid and the spray is heated sufficiently to set up a focus of combustion.

Fundamentally, however, the lower vapor pressure of the AN-F-32 fuel is a safety factor. In addition to the greater difficulty of ignition by accidental sparks or flames introduced in the vapor space, the AN-F-32 fuel by virtue of its low vapor pressure is subject to less loss by vaporization at high altitudes. In the case of ordinary aviation gasoline it has been noted that if an airplane takes off from sea level with the gasoline at 100°F and makes a fast climb to 40,000-ft altitude, the pressure in the vapor space of the fuel tank may be as high as 3 lb/sq in. in spite of the vent, and the loss through the vent may be as much as 10% of the gasoline in the tank. Obviously in such circumstances there is a plume of combustible vapor near the vent and the fire hazard is real.

Aviation gasoline provides another explosive hazard in that its inflammability limits at certain altitudes occur at temperatures which are frequently encountered in practice. For example, at 40,000-ft altitude, the explosive range of gasoline vapors lies between −75° and −45°F, whereas, the AAF standard summer air temperature at 40,000 ft is −45°F, and the fuel might get down to that temperature. As another example, during the Battle of France in 1940, there was a case reported of aircraft which had just landed from high altitudes so that the temperature of the fuel in the tanks had lowered to about 0°F, which is within the explosive range at sea level, and this cold gasoline was ignited by ground-strafing enemy aircraft.

However, aviation gasoline has two advantages over kerosene for fueling aircraft. One great advantage is that present manufacturing facilities are geared for producing many times more aviation gasoline than kerosene. Much development work remains to be done before a satisfactory fuel of 145°F could be produced in volume comparable with the present half million barrels of aviation gasoline per day. A minor advantage of the aviation gasoline is its higher spontaneous ignition temperature. If fuel is spilled in a crash and the liquid comes in contact with a hot metallic surface, for example a combustion tube in a jet-propelled aircraft, aviation gasoline ignites spontaneously only if the surface is hotter than 960°F, whereas kerosene ignites spontaneously at temperatures as low as 520°F (Moore Test Method).

In summary, a fuel of 145°F flash point is generally safer to handle than a fuel of lower flash point. The one exception is in respect to spontaneous ignition by a hot surface as distinct from ignition by a spark or flame. However, the present availability of fuels of 145°F is limited and, since any lowering of the flash point would result in an increase in the hazard from explosion in fuel tanks at high altitudes, probably without a greatly countervailing advantage in increased availability, the present outlook is that a volatile fuel of the type of aviation gasoline will have to be retained. Nevertheless, since the Air Corps at Wright Field and the National Advisory Committee for Aeronautics have carried out tests to investigate the relative hazards of handling different types of fuels, it is recommended that their data should be reviewed before making final decision on the choice of the least hazardous type of fuel.

b. *Vaporization Losses.*

One important practical consideration that affects the actual or over-all fuel consumption of aircraft is the matter of vaporization loss at high altitudes. With Grade 100/130 fuel having vapor pressures of 6 to 7 lb/sq in. at 100°F, actual boiling of the liquid fuel can occur during operation of aircraft at very high altitudes. For this reason, the Army Air Forces specify vent capacities for aircraft fuel tanks so that excessive internal pressures may be avoided. The present permissible limit of pressure in the tank is 7 in. of water. With vents of such capacity, fuel losses exceeding 5% of the tank contents have been actually observed.

Recent surveys made by the Aviation Fuels Division of the Coordinating Research Council have permitted the derivation of an equation to express the relationship between fuel loss by vaporization and the characteristics of the fuel, as follows:

$$L = \frac{T^2}{4ST + 16T' - 0.02T'(T\text{-}560)} \times \log \frac{p}{P} + 1$$

In the above equation, L is per cent loss by weight. T is the initial temperature, in degrees Rankine, of the fuel at take-off. S is the slope of the ASTM distillation curve at the 10% point. It is expressed in degrees Fahrenheit for each 1% evaporated between the 5% point and the 15% point on the ASTM distillation curve of "Temperature" vs. "% Evaporated," or $S = (t_{15\%} - t_{5\%})/10$. T′ is the temperature in degrees Rankine at the 10% point on the ASTM distillation curve and p is the true vapor pressure, of fuel at the initial fuel temperature, in lb/sq in. absolute. P is the absolute ambient pressure in the fuel tank, in lb/sq in. absolute.

The values derived by applying this equation correspond within 1% to the values actually measured in tests with nine different fuels. This equation shows that the vapor pressure alone does not give a complete measure of the fuel loss. The slope of the distillation curve at the 10% point is important. The higher the slope, the lower will be the evaporation loss for fuels of the same vapor pressure, other conditions being constant. However, since the loss is also a function of the log p/P, it is obvious that the loss of fuels of the type of J-P fuel with very low vapor pressures will be almost negligible compared with those encountered when using Grade 100/130 Fuel.

ITEMS FOR AVIATION FUEL STUDIES

Some of the major problems in the development of fuels for aircraft engines, both present and future, are presented graphically in Fig. 10.

Figure 10 — (Sheet 1) Post War Aviation Fuels — Items Suggested for Discussion

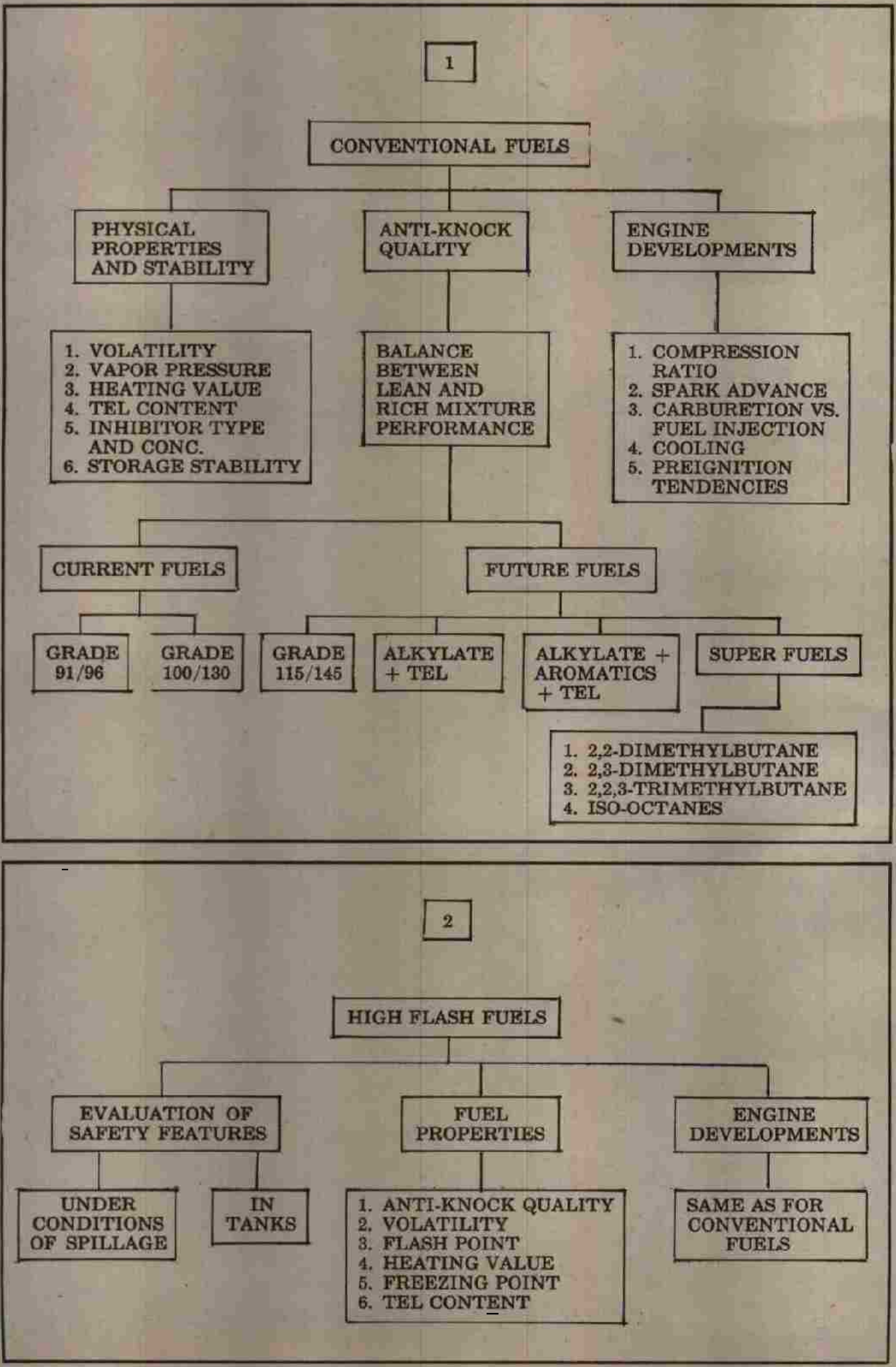


Figure 10 — (Sheet 2) Post War Aviation Fuels — Items Suggested for Discussion

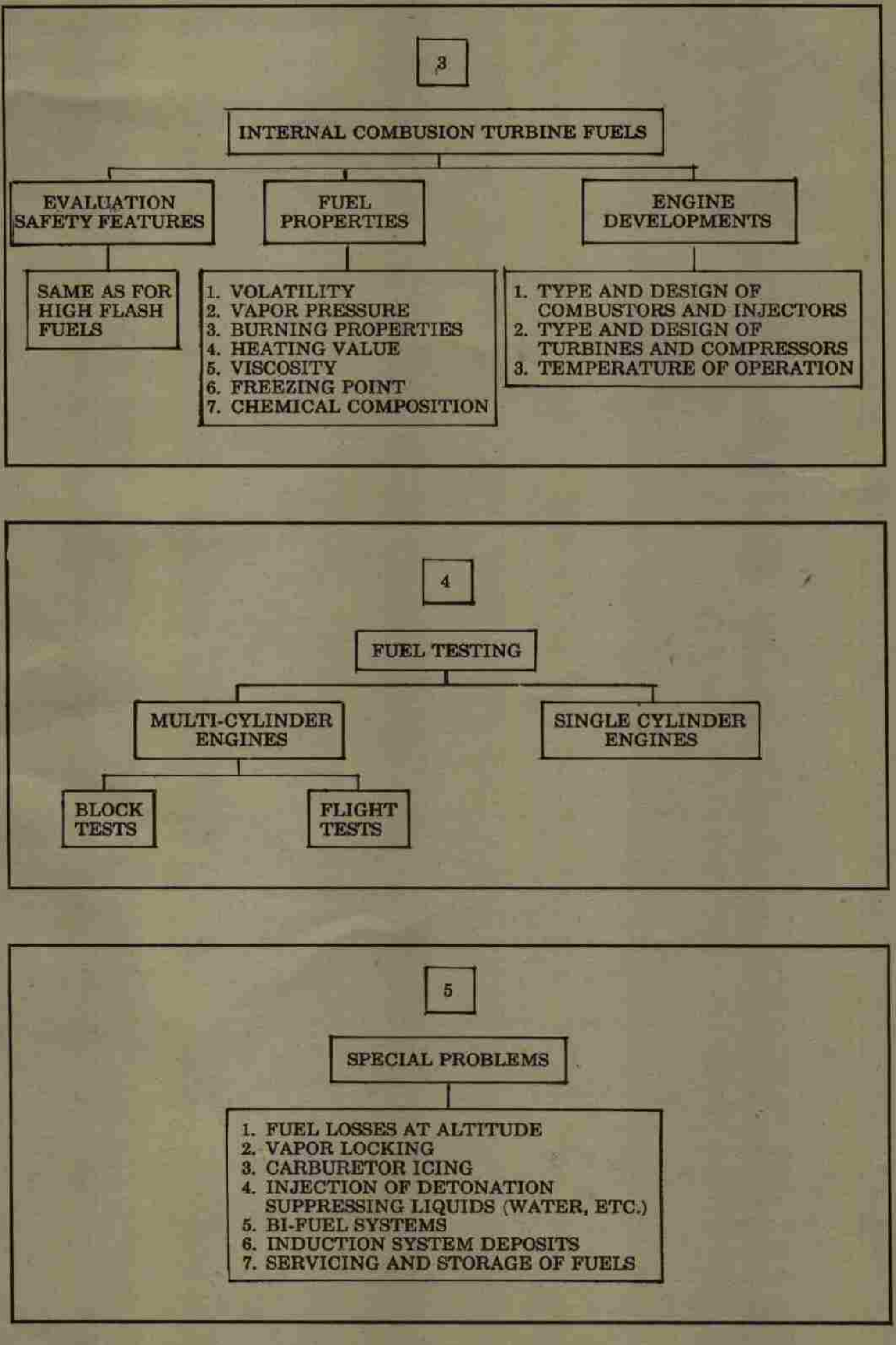


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TABLE I — API HYDROCARBON RESEARCH PROJECT — TABULATED

Hydrocarbon	*Manifest Number*	*Customary CFR Octane Numbers*										*Critical Compression Ratios*						
		Research Method					*Motor Method*					*600 rpm; 212°F.*			*600 rpm; 350°F.*			*2000*
cc TEL Added		0.0	1.0	3.0.	*	**	0.0	1.0	3.0	*	**	0.0	1.0	3.0	0.0	1.0	3.0	0.0
n-Pentane	61	61.7	—	88.7	60.3	62	61.9	—	—	61.3	67	3.95	—	4.8	3.2	—	4.5	4.75
2-Methylbutane	62	92.3	+0.37	+1.00	67.9	99	90.3	100+	—	68.7	104	5.65	—	8.4	5.1	—	7.6	7.35
n-Hexane	49	24.8	43.4	65.3	—	—	26.0	51.1	65.2	—	—	3.25	—	3.8	3.0	—	3.8	4.05
2-Methylpentane	68	73.4	84.6	93.1	64.5	83	73.5	87.3	91.1	63.7	79	4.3	—	5.95	3.65	—	5.4	5.5
3-Methylpentane	56	74.5	85.0	93.4	65.1	86	74.3	87.5	91.3	64.1	81	4.2	—	5.65	3.7	—	5.35	5.45
2,2-Dimethylbutane (h)	39	91.8	+0.15	+0.59	—	—	93.4	+0.58	+2.10	67.4	97	5.95	—	9.6	5.1d	6.5d	7.8d	7.95
2,3-Dimethylbutane	50	+0.32	+2.15	—	67.2	96	94.3	+0.42	+1.79	69.3	107	8.95	11.9	—	7.45	10.6	—	9.7
n-Heptane	32	0.0	—	—	48.0	0	0.0	—	—	48.0	0	3.0	3.2	3.5	—	—	—	3.8
2,3-Dimethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	6.2	—	8.85	5.6	—	8.35	7.95
2,4-Dimethylpentane	73	83.1	93.7	96.6	63.3	77	83.8	93.0	99.1	63.7	78	4.9	—	6.9	4.35	—	—	—
3-Ethylpentane	104	65.0	75.2	85.0	60.9	64	69.3	81.2	88.0	62.5	—	3.95	—	5.05d	3.6d	—	4.85d	5.25
2,2,3-Trimethylbutane	41	+1.83	—	—	70.5	113	+0.07	—	+3.07	70.5	113	14.4	—	—	10.5	11.5	—	10.9
n-Octane	6	—	0.0e	24.8	—	—	—	0.7	28.1	—	—	2.9	—	3.4	—	—	3.0	3.5
2-Methylheptane	5	21.7	34.4	57.6	—	—	23.8	45.0	61.4	—	—	3.3	3.55	4.05	—	2.95	3.65	4.15
3-Methylheptane	4	26.8	37.5	59.6	—	—	35.0	53.5	68.0	—	—	3.4	3.65	4.10	—	3.05	3.75	4.30
4-Methylheptane	3	26.7	38.7	61.1	54.1	31	39.0	55.4	70.1	57.5	48	3.5	3.75	4.15	—	3.15	3.85	4.45
3-Ethylhexane	8	33.5	46.3	61.1	—	—	52.4	65.9	80.0	—	—	3.5	3.7	4.15	3.0	3.5	4.1	4.7
2,2-Dimethylhexane	29	72.5	85.4	93.3	61.4	67	77.4	90.0	95.2	63.2	76	4.4	—	6.25	3.95	—	5.55	5.9
2,3-Dimethylhexane	16	71.3	82.5	91.7	62.1	71	78.9	88.4	93.7	63.2	76	4.5	5.2	6.2	4.1	4.6	5.4	5.9
2,4-Dimethylhexane	12	65.2	77.6	87.3	60.9	65	69.9	83.8	89.0	62.0	70	4.3	—	5.85	3.9	—	5.2	5.3
2,5-Dimethylhexane	7	55.5	68.0	81.6	—	—	55.7	71.6	82.9	—	—	3.95	4.3	5.0	3.2	3.8	4.65	5.0
3,3-Dimethylhexane	33	75.5	86.2	94.6	62.5	73	83.4	95.4	+0.02	64.2	81	4.65	—	6.6	4.35	—	5.65	6.55
3,4-Dimethylhexane	20	76.3	88.4	94.7	61.4	67	81.7	92.5	97.1	64.0	80	4.7	—	5.95	4.15	—	5.7	6.35
2-Methyl-3-ethylpentane	17	87.3	95.6	+0.02	63.2	76	88.1	96.5	+0.09	65.0	85	5.8	6.4	7.3	4.9	6.0	7.2	7.4
3-Methyl-3-ethylpentane	35	80.8	87.8	95.9	63.3	77	88.7	99.7	+0.17	65.7	89	5.05	—	6.55	4.55	—	6.05	7.2
2,2,3-Trimethylpentane	36	+1.18	+3.70e	—	68.9	105	99.9	+0.67	+2.05	70.3	112	10.8	15.9	—	8.95	11.15	—	10.05
2,2,4-Trimethylpentane	31	100.0	+1.00	+3.00	68.0	100	100.0	+1.00	+3.00	68.0	100	7.3	9.6	11.2	6.6	8.8	10.6	9.0
2,3,3-Trimethyplentane	27	+0.61	+2.75	—	68.0	100	99.4	+0.57	+1.95	69.9	110	8.6	12.5	—	7.85	10.55	—	10.15
2,3,4-Trimethylpentane	9	+0.22	+1.25	—	67.4	97	95.9	+0.18	+0.72	68.4	102	8.3	11.3	12.5	6.7	8.3	10.2	9.3
2,2,3,3-Tetramethylbutane(n)	40	—	—	—	—	—	—	—	—	—	—	13.0	—	—	9.8	—	—	—
2,2,5-Trimethylhexane	NACA	—	—	—	—	—	—	—	—	—	—	—	—	—	5.35	—	8.45	—
2,3,5-Trimethylhexane	NACA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2,2-Dimethyl-3-ethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	12.95	—	—	9.25	10.1	—	—
2,4-Dimethyl-3-ethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	8.8	—	12.6	7.2	—	10.3	9.35
2,2,3,3-Tetramethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2,2,3,4-Tetramethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2,2,4,4-Tetramethylpentance	NACA	—	—	—	—	—	—	—	—	—	—	7.05	—	10.05	5.75	—	7.7	—
2,3,3,4-Tetramethylpentane	NACA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3,3-Diethylpentane	99	—	—	—	—	—	—	—	—	—	—	5.25	—	6.5	4.65	—	6.4	8.1
Cyclopentane	63	—	—	—	76.2	141	85.0	91.4	95.2	76.2	141	12.4	13.1e	—	7.6	9.2	—	9.45
Methylcyclopentane	66	91.3	99.5	+0.5	69.4	107	80.0	89.4	93.0	67.8	99	6.25	—	10.4	5.45	—	8.8	7.45
Dimethylcyclopentanes	96	84.2	—	95.9	67.3	96	76.9	—	88.7	65.1	86	5.0	—	6.7	4.8	—	6.05	6.2
Ethylcyclopentane	55	67.2	72.3	79.5	62.9	75	61.2	72.7	80.7	61.4	67	4.0	—	4.7	3.55	—	5.0	5.2
n-Propylcyclopentane	18	31.2	43.1	59.8	—	—	28.1	43.3	60.5	—	—	3.5	3.7	4.1	—	3.1	3.6	4.3
Isopropylcyclopentane	19	81.1	89.6	94.3	64.6	83	76.2	85.7	89.4	64.2	81	5.1	—	6.35	4.45	—	5.5	6.55
Cyclohexane	10	83.0	92.9	97.4	69.9	110	77.2	85.4	87.3	67.4	97	4.9	5.7	6.65	4.7	5.5	6.0	6.7
Methylcyclohexane	11	74.8	83.5	88.2	68.8	104	71.1	82.0	86.2	64.8	84	4.55	4.95	5.4	4.0	4.65	5.35	5.9
Ethylcyclohexane	2	46.5	54.0	65.1	56.6	43	40.8	52.3	65.4	55.9	39	3.55	3.8	4.1	—	3.1	3.55	4.55
cis-1,2-Dimethylcyclohexane	23	80.9	89.2	94.3	64.9	85	78.6	87.2	90.7	64.4	82	4.65	—	6.05	4.45	—	5.65	6.1
trans-1,2-Dimethylcyclohexane	24	80.9	89.8	94.5	65.0	85	78.7	87.3	90.8	64.8	84	4.7	—	6.0	4.35	—	5.6	6.1
cis-1,3-Dimethylcyclohexane	30	71.7	—	—	—	—	71.0	—	—	—	—	4.5	—	—	3.8	—	—	—

For explanation of notes see Table III

KNOCK-TEST DATA TO 1 SEPTEMBER 1943.—PARAFFINS AND NAPHTHENES

					Approximate Octane Numbers Obtained from Critical Compression Ratios												*Supercharge Relative IMEP % of Isooctane (f)*			*Supercharge Equivalent Octane Numbers (f)*			*Manifest Number*
rpm; 212°F		*2000 rpm; 350°F*			*600 rpm; 212°F*			*600 rpm; 350°F*			*2000 rpm; 212°F*			*2000 rpm; 350°F*									
1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	
—	6.25	4.3	—	5.7	55	—	78	54	—	85	54	—	83	57	—	86	40d	54	—	60d	79d	—	61
—	10.7	6.2	—	8.4	90	—	+0.4	92	—	+0.4	92	—	+1.1	91	—	+1.6	79d	101d	—	93d	100d	—	62
—	5.15	3.55	—	4.7	18	—	48	46	—	72	19	—	66	26	—	29	—	—	—	—	—	—	49
—	7.7	4.95	—	6.35	66	—	92	68	—	94	73	—	94	74	—	93	—	—	—	—	—	—	68
—	7.6	5.0	—	6.45	64	—	90	69	—	94	72	—	93	76	—	94	57d	70d	—	75d	85d	—	56
—	12.1	6.8d	8.4d	9.7d	92	—	+1.0	92	100	+0.4	95	—	+2.7	97	+1.6	+5	79d	103d	—	92d	+0.05d	—	39
11.6	—	7.05	8.0	—	+0.6	> +4	—	+0.3	+3.0	—	+0.4	+2.0	—	100	+1.0	—	111d	153d	—	+0.25	+3.75	—	50
—	4.7	3.0	3.2	3.85	0	15	33	0	—	—	0	—	52	0	8	40	—	—	—	—	—	—	32
—	11.5	6.4	—	7.9	94	—	+0.6	95	—	+0.7	95	—	+1.8	93	—	+0.8	74	101	—	91	100	—	NACA
—	—	—	—	—	80	—	98	83	—	—	—	—	—	—	—	—	65d	82d	—	86d	94d	—	73
—	6.85	4.8d	—	5.9	55	—	82	66	—	89	68	—	88	71	—	88	46	56d	—	71d	80d	—	104
12.6	—	7.5	8.9	9.4	> +6	—	—	+2.8	> +5	—	+1.3	+3.5	—	+0.4	+2.5	+4	162d	207d	—	> +6	> +6	—	41
—	4.2	2.75	2.95	3.5	—	—	27	—	—	46	—	—	28	—	—	23	—	—	—	—	—	—	6
—	5.15	3.6	—	4.55	21	36	59	—	—	68	25	—	66	28	—	65	—	—	—	—	—	—	5
—	5.3	3.85	—	4.7	29	41	60	—	48	71	33	—	69	40	—	69	—	—	—	—	—	—	4
—	5.45	3.95	—	4.8	33	46	62	—	52	73	41	—	72	44	—	71	—	—	—	—	—	—	3
5.3	6.1	4.3	4.6	5.2	33	43	62	46	63	78	52	69	81	57	66	79	—	—	—	—	—	—	8
—	8.35	5.1	—	6.95	70	—	95	75	—	95	79	—	97	77	—	99	—	—	—	—	—	—	29
6.7	8.0	5.1	5.5	6.8	72	85	94	78	86	94	79	87	95	77	84	97	—	—	—	—	—	—	16
—	7.4	4.7	—	6.1	67	—	92	74	—	92	69	—	92	69	—	90	—	—	—	—	—	—	12
—	6.8	4.35	4.8	5.7	54	67	82	54	72	87	62	—	88	59	71	86	—	—	—	—	—	—	7
—	9.15	5.7	—	7.25	75	—	97	83	—	96	86	—	+0.1	86	—	+0.1	—	—	—	—	—	—	33
—	8.3	5.5	—	7.85	76	—	92	79	—	96	84	—	97	84	—	+0.8	—	—	—	—	—	—	20
8.9	10.1	6.0	6.7	7.5	91	95	100	90	98	+0.2	92	99	+0.6	89	96	+0.4	75d	92d	—	91d	97d	—	17
—	9.9	6.0	—	7.65	82	—	96	86	—	98	91	—	+0.5	89	—	+0.6	—	—	—	—	—	—	35
11.6	—	7.45	8.1	—	+2.3	> +6	—	+1.1	+4	—	+0.6	+2.0	—	+0.3	+1.1	—	82d	101d	—	+1.7d	> +6d	—	36
10.5	12.3	7.1	8.0	9.1	100	+1.0	+3.0	100	+1.0	+3.0	100	+1.0	+3.0	100	+1.0	+3.0	100d	126d	138d	100d	+1.0d	+3.0d	31
11.8	—	7.6	8.15	—	+0.5	+6	—	+0.5	+2.9	—	+0.7	+2.2	—	+0.5	+1.2	—	73d	91d	—	+0.6	+3.4	—	27
10.1	11.7	6.8	7.7	8.7	+0.4	+3.1	+6	+0.1	+0.7	+2.4	+0.2	+0.6	+2.1	97	+0.6	+2.1	66d	82d	—	+0.15d	+1.7d	—	9
—	—	—	—	—	> +6	—	—	+1.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	40
—	—	6.85	—	9.1	—	—	—	94	—	+0.7	—	—	—	98	—	+3.0	80	100	—	93	100	—	NACA
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	63	76	—	85	92	—	NACA
—	—	7.2	—	—	> +6	—	—	+1.2	+2.2	—	—	—	—	+0.1	—	—	120	151	—	+1.2	> +6	—	NACA
—	—	7.05	—	—	+0.6	—	+6	+0.2	—	+2.5	+0.2	—	—	99	—	—	103	130	—	+0.5	+1.3	—	NACA
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	156	185	—	+4.2	> +6	—	NACA
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	143	178	—	+2.7	> +6	—	NACA
—	—	6.35	—	—	99	—	+1.4	96	—	+0.4	—	—	—	93	—	—	84	103	—	94	+0.05	—	NACA
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	150	—	—	+3.7	—	—	NACA
—	—	6.7	—	—	85	—	96	87	—	99	96	—	—	96	—	—	—	—	—	—	—	—	99
9.9	—	5.9	6.95	—	+6	> +6	—	+0.4	+1.3	—	+0.3	+0.5	—	88	99	—	90	110	—	97	+0.25	—	63
—	10.35	5.55	—	7.1	94	—	+1.7	95	—	+1.0	93	—	+0.9	85	—	100	68	84	—	87	95	—	66
—	8.7	5.2	—	6.05	82	—	97	89	—	98	83	—	98	79	—	90	—	—	—	—	—	—	96
—	7.0	4.55	—	—	56	—	76	65	—	92	67	—	89	66	—	—	—	—	—	—	—	—	55
4.6	5.2	3.6	3.9	4.5	33	43	60	—	50	66	33	48	67	28	42	63	—	—	—	—	—	—	18
—	9.0	5.1	—	6.2	83	—	95	85	—	95	86	—	100	77	—	91	57	71	—	81	89	—	19
7.6	9.0	5.1	5.5	6.3	80	90	96	88	95	98	87	93	100	77	84	92	62	77	—	85c	92c	—	10
6.6	8.1	4.9	5.3	6.15	73	81	87	76	87	94	79	86	96	73	81	91	—	—	—	—	—	—	11
4.95	5.55	4.0	4.25	4.85	36	48	60	—	50	65	46	61	74	46	55	72	—	—	—	—	—	—	2
—	8.15	4.9	—	5.85	75	—	93	85	—	96	81	—	96	73	—	88	—	—	—	—	—	—	23
—	8.4	4.95	—	6.2	76	—	92	83	—	95	81	—	97	74	—	91	—	—	—	—	—	—	24
—	—	—	—	—	72	—	—	72	—	—	—	—	—	—	—	—	—	—	—	—	—	—	30

E I — Continued

					Approximate Octane Numbers Obtained from Critical Compression Ratios												Supercharge Relative IMEP % of Isooctane (f)			Supercharge Equivalent Octane Numbers (f)			Manifest Number
0 rpm; 212°F		2000 rpm; 350°F			600 rpm; 212°F			600 rpm; 350°F			2000 rpm; 212°F			2000 rpm; 350°F									
—	6.5	4.6	—	5.85	60	—	81	63	—	87	66	—	85	66	—	88	—	—	—	—	—	—	21
—	7.25	4.7	—	6.05	72	—	86	72	—	89	76	—	91	69	—	90	—	—	—	—	—	—	26
—	6.5	4.55	—	5.8	60	—	81	63	—	86	63	—	85	65	—	87	—	—	—	—	—	—	22
—	4.65	3.45	—	4.25	15	—	33	46	—	48	19	—	50	21	—	55	—	—	—	—	—	—	67
—	6.25	4.55	—	5.35	64	—	80	57	—	81	68	—	83	65	—	82	—	—	—	—	—	—	34
—	8.9	5.45	—	7.05	82	—	94	85	—	97	85	—	99	83	—	100	61	75	—	84	91	—	51
—	6.5	4.45	—	5.3	48	—	80	68	—	86	68	—	85	62	—	81	—	—	—	—	—	—	69
—	4.35	3.05a	—	3.75	21	—	30	—	—	45a	5	—	36	0a	—	35	—	—	—	—	—	—	101
—	—	—	—	—	67	—	—	71	—	81	—	—	—	—	—	—	—	—	—	—	—	—	72
—	—	—	—	—	—	—	—	70	—	86	—	—	—	—	—	—	47	56	—	71	80	—	E
—	5.95	4.35	—	5.25	50	—	70	52	—	75	60	—	80	58	—	80	—	—	—	—	—	—	97
—	7.05	4.7	—	5.5	74	—	90	78	—	90	76	—	90	68	—	84	—	—	—	—	—	—	71

KNOCK-TEST DATA TO 1 SEPTEMBER 1943.—UNSATURATES AND AROMATICS

0 rpm; 212°F		2000 rpm; 350°F			600 rpm; 212°F			600 rpm; 350°F			2000 rpm; 212°F			2000 rpm; 350°F			Supercharge Relative IMEP % of Isooctane (f)			Supercharge Equivalent Octane Numbers (f)			Manifest Number
1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	
—	—	5.15	—	—	99	—	+1.4	93	—	97	90	—	—	78	—	—	—	—	—	—	—	—	86
9.95	10.4	6.45	—	7.25	+3.8	—	—	+0.4	—	+1.1	+0.2	+0.5	+0.8	94	—	+0.1	—	—	—	—	—	—	81
—	4.9	3.4	—	4.2	24	—	57	--	--	57	19	—	59	18	—	53	—	—	—	—	—	—	37
—	5.4	4.05	—	4.85	52	—	66	55	—	76	50	—	71	21	—	72	—	—	—	—	—	—	43
—	6.15	4.55	—	5.35	65	—	76	66	—	84	65	—	82	64	—	81	—	—	—	—	—	—	53
—	6.4	4.7	—	5.4	65	—	76	69	—	86	69	—	85	68	—	83	—	—	—	—	—	—	54
—	6.2	4.4	—	5.2	68	—	83	72	—	84	69	—	83	60	—	79	—	—	—	—	—	—	45
—	—	4.65	—	—	65	—	89	69	—	81	72	—	—	68	—	—	—	—	—	—	—	—	46
—	6.3	4.3	—	5.15	64	—	81	68	—	87	63	—	83	57	—	78	—	—	—	—	—	—	44
—	—	4.55	—	5.35	65	—	87	72	—	89	69	—	—	65	—	82	—	—	—	—	—	—	59
—	—	—	—	—	96	—	+0.4	92	—	+0.2	—	—	—	—	—	—	—	—	—	—	—	—	60
9.15	10.2	5.7	5.9	6.05	+4	>+6	—	+0.2	+0.4	+0.7	98	100	+0.7	86	88	90	99c	113c	—	100c	+0.35c	—	74
—	9.6	5.6	—	6.0	+6.0	—	—	+0.6	—	+1.1	98	—	+0.3	85	—	89	109	120	—	+0.2	+0.7	—	NACA
—	9.0	5.9	—	6.45	+0.9	—	+1.4	100	—	+0.2	96	—	100	88	—	94	—	—	—	—	—	—	NACA
—	6.3	4.2	—	4.65	92	—	99	86	—	91	77	—	83	53	—	68	—	—	—	—	—	—	47
—	6.45	4.55	—	4.95	92	—	93	88	—	90	83	—	85	65	—	74	—	—	—	—	—	—	48
—	7.5	4.7	—	5.0	99	—	+0.6	89	—	94	85	—	93	68	—	76	—	—	—	—	—	—	65
—	—	—	—	—	—	—	—	88	—	96	—	—	—	—	—	—	—	—	—	—	—	—	118S
—	7.05	4.5	—	—	95	—	100	88	—	94	84	—	90	63	—	—	—	—	—	—	—	—	87
—	6.55	4.45	—	4.8	88	—	97	87	—	91	81	—	86	62	—	71	49	56	—	74	80	—	38
—	—	—	—	—	93	—	97	83	—	91	—	—	—	—	—	—	—	—	—	—	—	—	117S
—	8.05	6.4	—	5.55	+1.4	—	+0.4	100	—	96	+0.2	—	96	93	—	85	106	95	—	+0.15	99	—	64
—	8.9	6.65	—	6.25	+5.2a	—	+2.6	+0.4	—	99	+0.7	—	99	96	—	92	—	—	—	—	—	—	116
—	5.1	3.7	—	3.9	86	—	88	74	—	76	55	—	64	33	—	42	—	—	—	—	—	—	83
—	4.95	3.3	—	3.8	82	—	88	76	—	79	49	—	60	13	—	37	—	—	—	—	—	—	88
—	10.55	7.65	—	7.45	>+6	—	+5.6	+1.0	—	+0.7	+1.2	—	+0.9	+0.5	—	+0.3	—	—	—	—	—	—	100
—	6.6	4.45	—	4.9	90	—	98	85	—	90	81	—	86	61	—	73	—	—	—	—	—	—	70
—	5.8	4.5	—	4.65	87	—	89	81	—	83	75	—	77	63	—	67	—	—	—	—	—	—	78
—	5.6	4.15	—	4.3	85	—	89	77	—	82	71	—	74	51	—	56	—	—	—	—	—	—	79
—	—	6.0	—	—	+0.3	—	+0.8	88	—	93	96	—	—	89	—	—	—	—	—	—	—	—	82
—	—	—	—	—	—	—	—	97	—	99	—	—	—	—	—	—	84	85	—	95	95	—	E
—	5.4	3.9	—	4.95	43	—	57	55	—	82	41	—	71	42	—	74	—	—	—	—	—	—	57
—	5.55	4.35	—	5.0	46	—	58	57	—	79	57	—	74	58	—	76	—	—	—	—	—	—	58
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	242c	238c	—	>+6c	>+6c	—	25
—	—	9.0	—	—	>+6	—	—	+5	—	—	+5	—	—	+2.8	—	—	189c	252c	—	>+6c	>+6c	—	42
—	10.2	7.2	—	7.7	>+6	—	—	+0.2	—	+0.3	+0.6	—	+0.7	100	—	+0.6	116k	118k	—	+0.5k	+0.6k	—	13
—	13.8	9.3	—	10.8	>+6	—	—	+5	—	>+6	+2.9	—	>+6	+3.6	—	>+6	213	245	—	>+6	>+6	—	14
—	14.3	9.3	—	10.8	>+6	—	—	+5	—	>+6	+5	—	>+6	+3.6	—	>+6	197	246	—	>+6	>+6	—	15

TABLE II — API HYDROCARBON RESEARCH PROJECT — TABULATED

Hydrocarbon	Manifest Number	Customary CFR Octane Numbers										Critical Compression Ratios						
		Research Method					Motor Method					600 rpm; 212°F.			600 rpm; 350°F.			200
trans-1,3-Dimethylcyclohexane	21	66.9	75.7	83.5	61.3	67	64.2	78.3	83.8	60.9	65	4.1	—	4.95	3.5	—	4.65	5.15
cis-1,4-Dimethylcyclohexane	26	67.2	78.0	84.7	61.6	68	68.2	80.0	85.0	61.2	66	4.5	—	5.3	3.8	—	4.8	5.7
trans-1,4-Dimethylcyclohexane	22	68.3	75.1	82.8	60.7	64	62.2	77.4	83.4	59.8	59	4.1	—	4.95	3.5	—	4.6	5.05
n-Propylcyclohexane	67	17.8	25.6	42.8	—	—	14.0	29.4	47.7	—	—	3.2	—	3.5	3.0	—	3.05	4.05
iso-Propylcyclohexane	34	62.8	70.1	79.6	60.4	62	61.1	74.3	81.4	60.4	62	4.2	—	4.9	3.3	—	4.25	5.25
1,1,3-Trimethylcyclohexane	51	81.3	89.5	94.8	64.9	85	82.6	91.2	95.8	66.4	92	5.05	—	6.2	4.45	—	5.85	6.5
1-Methyl-4-isopropylcyclohexane	69	67.3	70.2	78.5	—	—	60.5	71.4	81.4	—	—	3.8	—	4.9	3.65	—	4.6	5.25
n-Butyl cyclohexane	101	—	—	22.5	46.4	−8	—	4.4	25.3	47.3	−4	3.3	—	3.45	—	—	2.95a	3.85
Bicyclo (2,2,1) heptane (n)	72	—	—	—	58.9	55	—	—	—	58.5	53	4.3	—	—	3.8	—	4.25	—
2-Methyl bicyclo (2,2,1) heptane	E	—	—	—	—	—	—	—	—	—	—	—	—	—	3.75	—	4.55	—
2-Ethyl bicyclo (2,2,1) heptane	97	51.9	60.2	71.5	57.7	48	49.7	60.6	70.9	59.2	56	3.85	—	4.4	3.2	—	3.95	4.95
Pinane	71	77.7	85.7	91.3	59.8	59	65.9	75.4	78.8	60.5	63	4.6	—	5.75	4.1	—	4.95	5.7
cc TEL Added	—	0.0	1.0	3.0	*	**	0.0	1.0	3.0	*	**	0.0	1.0	3.0	0.0	1.0	3.0	0.0
2,3-Dimethyl-2-butene	86	97.4	98.1	98.5	85.0	185	80.5	83.4	84.0	76.8	144	7.2m	—	10.0	5.25m	—	5.85	7.05
2,2,3-Trimethyl-3-butene	81	+0.5	+0.7	+1.2	76.9	145	90.5	92.3	93.7	73.9	130	11.65	—	—	7.8	—	9.0	9.4
1-Octene	37	28.7	43.8	63.5	—	—	34.7	46.6	57.7	—	—	3.35	—	4.0	2.85	2.9	3.3	4.05
2-Octene	43	56.3	69.9	78.7	62.9	75	56.5	67.9	73.0	61.6	68	3.9	—	4.25	3.25	—	4.0	4.65
3-Octene (trans)	53	72.5	84.6	89.4	67.0	95	68.1	77.7	81.2	65.0	85	4.25	—	5.05	3.6	—	4.45	5.15
4-Octene (trans)	54	73.3	85.4	91.8	67.8	99	74.3	82.8	84.2	68.2	101	4.25	—	5.05	3.7	—	4.6	5.3
2-Methyl-1-heptene	45	70.2	79.6	87.9	63.4	77	66.3	73.3	79.6	—	—	4.35	—	5.1	3.8	—	4.4	5.3
2-Methyl-2-heptene	46	75.9	—	—	66.2	91	71.0	—	—	68.4	102	4.25	—	5.55	3.7	—	4.25	5.45
6-Methyl-1-heptene	44	63.8	74.8	87.2	62.8	74	62.6	69.9	76.6	61.8	69	4.2	—	4.95	3.65	—	4.65	5.05
6-Methyl-2-heptene	59	71.3	84.6	90.2	63.0	75	65.5	77.0	80.5	—	—	4.25	—	5.4	3.8	—	4.75	5.3
2,3-Dimethyl-1-hexene	60	96.3	—	—	71.5	118	83.6	86.7	88.1	69.8	109	6.6	—	8.4	5.2	—	7.15	—
Diisobutylene (b)	74	+0.5	+0.9	+1.1	81.5	168	88.6	89.1	90.1	78.1	151	11.95	12.95	—	7.3	7.9	8.45	8.55
2,4,4-Trimethyl-1-pentene	NACA	—	—	—	—	—	—	—	—	—	—	12.5a	—	—	8.25	—	9.0	8.55
2,4,4-Trimethyl-2-pentene	NACA	—	—	—	—	—	—	—	—	—	—	9.45	—	10.9	6.5	—	7.25	8.2
2,5-Dimethylhexadiene-1,5	47	90.2	93.3	94.3	77.0	145	65.5	70.8	70.4	70.5	111	5.95	—	7.2	4.55	—	4.95	5.75
2,5-Dimethylhexadiene-2,4	48	94.3	95.2	95.5	85.4	187	78.9	79.9	81.7	78.3	152	5.85	—	6.05	4.7	—	4.9	6.2
Cyclopentene	65	93.3	94.5	94.8	82.2	171	69.7	72.7	73.4	73.2	126	7.2	—	8.95	4.85	—	5.35	6.45
1-Methyl cyclopentene	118S	—	—	—	84.9	184	—	—	—	77.3	147	—	—	—	4.75	—	5.7	—
1-Ethyl cyclopentene	87	90.3	94.2	95.7	80.8	164	72.0	75.3	78.2	74.4	138	6.45	—	7.3	4.75	—	5.4	6.35
Cyclohexene	38	83.9	87.5	88.4	75.4	137	63.0	67.3	68.1	68.4	102	5.45	—	6.7	4.65	—	4.95	6.1
1-Methyl cyclohexene	117S	—	—	—	80.3	161	—	—	—	73.7	129	6.15	—	6.75	4.4	—	5.0	—
1,3-Cyclopentadiene	64	+0.3	—	98.7	91.5	218	86.1	—	83.2	77.8	149	10.5	—	8.5	6.6	—	5.7	9.25
Dicyclopentadiene	116	+0.77	+0.34	+0.28	93.8	229	95.9	94.3	91.0	81.4	167	12.15a	—	11.0	7.7	—	6.4	10.15
1,4-Cyclohexadiene	83	75.4	77.5	78.1	89.4	207	39.9	43.5	50.0	77.4	147	5.35	—	5.5	3.9	—	4.0	4.8
1-Methyl-1,4-cyclohexadiene	88	75.0	76.1	76.8	87.2	196	42.1	49.2	55.7	74.3	131	5.05	—	5.45	4.0	—	4.15	4.65
Benzocyclopentadiene	100	+2.29	+1.47	+1.38	80.7	163	+0.74	+0.35	+0.35	76.2	141	12.8a	—	12.1a	8.9	—	8.35	10.9
Dipentene	70	90.6	92.2	93.7	77.7	149	73.2	75.7	77.7	73.2	126	5.65	—	6.95	4.5	—	4.95	6.05
Alpha-Pinene	78	83.1	86.7	88.4	71.8	119	68.6	70.0	71.4	67.9	100	5.4	—	5.65	4.25	—	4.4	5.65
Beta-Pinene	79	80.6	83.8	84.4	70.3	112	60.3	62.3	63.9	67.1	96	5.25	—	5.6	4.05	—	4.3	5.4
Bicyclo (2,2,1) heptene	82	—	—	—	65.9	90	—	—	—	66.3	92	8.2	—	9.2	4.75	—	5.35	8.15
2-Methyl bicyclo-(2,2,1)-2-heptene	E	—	—	—	—	—	—	—	—	—	—	—	—	—	5.95	—	6.4	—
1-Octyne	57	50.5	63.0	75.2	59.0	55	51.5	58.8	66.1	58.4	52	3.7	—	4.0	3.25	—	4.3	4.45
4-Octyne	58	59.6	67.0	76.4	67.0	95	65.9	74.2	79.6	69.3	107	3.75	—	4.05	3.3	—	4.15	4.85
Benzene	25	—	—	—	67.7	99	+2.75	—	—	66.1	91	—	—	—	—	—	—	—
Toluene	42	+5.82	—	—	72.7	124	+0.27	+1.00	+1.72	70.3	112	15	—	—	11.35	—	—	13.5
ortho-Xylene	13	—	—	—	72.0	120	100.0	—	+0.05	68.5	103	13.0	—	—	7.1	—	7.4	10.0
meta-Xylene	14	—	—	—	76.9	145	—	—	—	72.8	124	15.5	—	—	11.5	—	12.7	12.3
para-Xylene	15	—	—	—	77.1	146	—	—	—	73.3	127	15.7	—	—	11.5	—	12.7	13.4

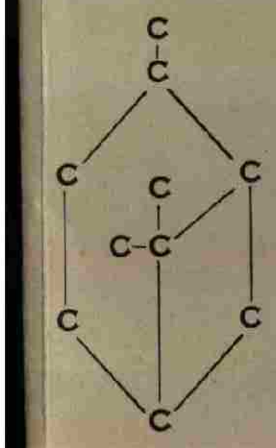
For explanation of notes, see Table III

— Continued

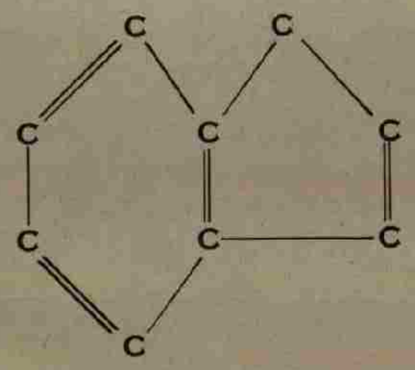
					Approximate Octane Numbers Obtained from Critical Compression Ratios													*Supercharge Relative IMEP % of Isooctane (f)*			*Supercharge Equivalent Octane Numbers (f)*			*Manifest Number*
m; 212°F		*2000 rpm; 350°F*			*600 rpm; 212°F*			*600 rpm; 350°F*			*2000 rpm; 212°F*			*2000 rpm; 350°F*										
.4	—	6.9	7.8	8.6	>+6	>+6	—	+0.6	+1.2	+4	+0.2	+1.8	—	98	+0.7	+1.9	141	188	—	+2.5	>+6	—	1
.8	—	7.35	8.1	—	+4	—	—	+0.9	+3.5	—	+0.5	+2.2	—	+0.2	+1.1	—	125	166	—	+1.0	>+6	—	52
0.95	—	7.3	7.9	—	>+6	—	—	+1.0	+3.1	—	+0.6	+1.4	—	+0.1	+0.8	—	127	173	—	+1.0	>+6	—	28
—	—	6.5	6.8	—	+3.6	+5.8a	—	100	+0.3	—	+0.3	—	—	94	97	—	—	—	—	—	—	—	92
—	—	—	—	—	>+6	—	—	+0.9	+1.9	—	—	—	—	—	—	—	145	190	—	+3.0	>+6	—	85
—	—	—	—	—	>+6	—	—	+2.0	—	—	—	—	—	—	—	—	181	213	—	>+6	>+6	—	EK
—	—	—	—	—	100	—	—	95	—	—	—	—	—	—	—	—	85	117	—	95	+0.5	—	EK
—	—	7.25	—	—	>+6	—	—	+0.8	—	+2.4	+0.9	—	—	+0.1	—	—	—	—	—	—	—	—	98
—	—	7.1	—	—	>+6	—	—	+0.6	—	+2.1	+0.7	—	—	100	—	—	148k	—	—	+3.5k	—	—	94
—	—	7.85	—	9.05	>+6	—	—	+1.8	—	—	+3.3a	—	—	+0.7	—	+2.9	225k	256k	—	>+6	>+6	—	95
—	—	—	—	—	>+6	—	—	+0.2	—	—	—	—	—	—	—	—	114	166	—	+0.4	>+6	—	EK
—	—	7.05	—	—	>+6	—	—	+0.9	+2.3	—	+0.7	—	—	99	—	—	155	216	—	+4.8	>+6	—	91
—	—	—	—	—	+2.5	—	—	+0.2	—	—	—	—	—	—	—	—	120	129	—	+0.7	+1.25	—	EK
—	—	—	—	—	>+6	—	—	+0.9	—	—	—	—	—	—	—	—	148	175	—	+3.5	>+6	—	EK
—	—	—	—	—	>+6	—	—	+0.3	—	—	—	—	—	—	—	—	147	181	—	+3.5	>+6	—	EK
—	—	—	—	—	+0.6	—	—	98	—	—	—	—	—	—	—	—	86	82	—	95	94	—	EK
—	—	7.5	—	7.4	>+6	—	+5.8a	+1.1	—	+1.1	+1.6	—	—	+0.4	—	+0.2	—	—	—	—	—	—	103

NOCK-TEST DATA TO 1 SEPTEMBER 1943.—MISCELLANEOUS COMPOUNDS

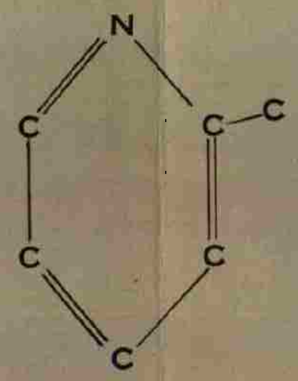
.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	0.0	1.0	3.0	
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	189	180	—	>+6	>+6	—	c
—	—	8.4	—	—	>+6	—	—	+3	—	—	+3	—	—	+1.6	—	—	201c	269c	—	>+6c	>+6c	—	72
.6	—	7.25	8.05	—	97	—	+3.6	+0.4	+1.1	—	+0.6	+2.0	—	+0.1	+1.0	—	—	—	—	—	—	—	E
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	235	326	—	>+6	>+6	—	S
—	11.7	6.75	—	7.3	>+6	—	—	+1.1	—	+2.0	+1.4	—	+2.1	97	—	+0.1	—	—	—	—	—	—	102
—	9.3	5.8	—	6.5	+3.4	—	—	+0.2	—	+ .08	93	—	+0.2	87	—	94	91	106	—	97	+0.1	—	89
—	8.2	5.15	—	5.95	92	—	+0.1	91	—	97	86	—	96	78	—	89	—	—	—	—	—	—	90
—	—	9.2	—	—	>+6.0	—	—	+4.0	—	—	>+6.0	—	—	+3.3	—	—	186	186	—	>+6	>+6	—	80
—	—	—	—	—	+4.5	—	—	+1.9	—	+1.7	+3.2	—	—	—	—	—	184	184	—	>+6	>+6	—	84
—	5.55	3.9	—	4.4	35	—	43	40	—	63	57	—	74	42	—	60	—	—	—	—	—	—	76
—	5.15	3.75	—	4.2	56	—	59	63	—	76	51	—	65	35	—	53	—	—	—	—	—	—	75



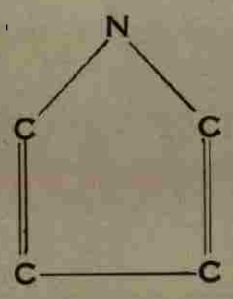
PINANE



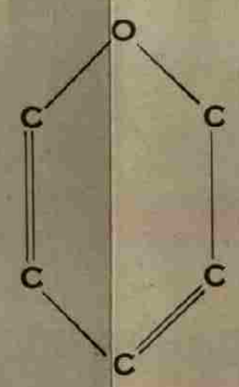
BENZOCYCLOPENTADIENE



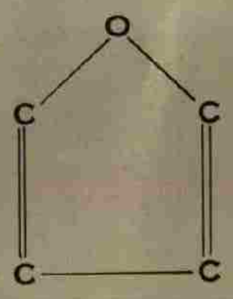
Alpha-PICOLINE



PYRROLE



PYRAN



FURAN

TABLE

Hydrocarbon	Manifest Number	Customary CFR Octane Numbers										Critical Compression Ratios						
		Research Method					Motor Method					600 rpm; 212°F.			600 rpm; 350°F.			2000 r
Ethyl benzene	1	+0.8	+0.8	+0.8	72.8	124	97.9	100.0	+0.2	69.4	107	13.5	15.1	—	8.2	9.1	11.0	9.3
n-Propyl benzene	52	+1.52	+3.84	+4.27	73.4	127	98.7	+0.12	+0.24	73.8	129	11.9	—	—	8.7	10.8	—	9.8
iso-Propyl benzene	28	+2.08	+3.41	—	74.4	132	99.3	+0.16	+0.50	72.8	124	14.5	—	—	8.9	10.65	—	9.95
ortho-Methyl ethyl benzene	92	—	—	—	73.1	125	—	—	—	70.3	111	11.5	12.3a	—	6.55	7.5	—	9.55
para-Methyl etyhl benzene	85	—	—	—	79.0	155	97.0	—	—	71.1	115	> 13	—	—	8.65	9.9	—	—
1,3,5-Trimethyl benzene	EK	—	—	—	—	—	—	—	—	—	—	14.5	—	—	10.0	—	—	—
n-Butyl benzene	EK	—	—	—	—	—	—	—	—	—	—	7.25	—	—	5.6	—	—	—
iso-Butyl benzene	98	—	—	—	—	—	—	—	—	—	—	13.5a	—	—	8.6	—	10.25	10.4
sec-Butyl benzene	94	—	—	—	—	—	—	—	—	—	—	12.5a	—	—	8.25	—	10.05	10.2
tert-Butyl benzene	95	> +3	—	—	75.7	138	+0.84	—	—	73.4	126	13.2a	—	—	9.8	—	—	12.5a
Diethyl benzene	EK	—	—	—	—	—	—	—	—	—	—	12.7	—	—	7.3	—	—	—
para-Methyl isopropyl benzen	91	+1.42	—	—	78.0	150	97.7	—	—	74.5	133	12.9a	—	—	8.7	10.2	—	10.3
sec-Amyl benzene	EK	—	—	—	—	—	—	—	—	—	—	10.95	—	—	7.2	—	—	—
tert-Amyl benzene	EK	—	—	—	—	—	—	—	—	—	—	14.2	—	—	9.0	—	—	—
meta-Diisopropyl benzene	EK	—	—	—	—	—	—	—	—	—	—	13.1	—	—	7.5	—	—	—
Triethyl benzene	EK	—	—	—	—	—	—	—	—	—	—	8.9	—	—	6.0	—	—	—
isopropenyl benzene	103	+2.08	+1.90	+1.78	83.9	169	+0.13	+0.04	+0.01	77.9	150	12.9a	—	12.3a	9.05	—	9.0	11.25

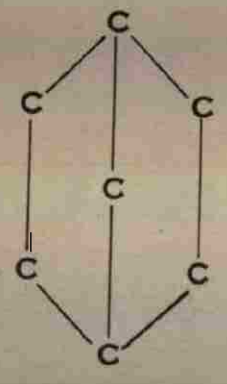
TABLE III — API HYDROCARBON RESEARCH PROJECT — TABULATED K

cc TEL Added		0.0	1.0	3.0	*	**	0.0	1.0	3.0	*	**	0.0	1.0	3.0	0.0	1.0	3.0	0.0
Methanol	c	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Methyl-tert-butyl ether	72	+4.5	—	—	77.3	147	+0.1	+2.9	+4.9	77.1	146	+13	—	—	10.6	—	—	12.4
Diiso-propyl ether	E	+0.24	+1.0	—	69.1	105	98.9	+1.0	+3.45	71.4	117	6.7	—	11.55	7.65	9.05	—	10.05
isopropyl tert-butyl ether	S	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Methyl phenyl ether	102	> +3	—	—	76.4	142	96.0	96.4	96.7	73.9	130	12.7a	—	—	9.0	—	9.95	11.05
2,5-Dimethyl furane	89	+0.14	—	—	91.0	215	88.1	—	—	83.5	178	11.45	—	—	7.2	—	8.6	7.65
2,5-Dimethyl tetrahydro furane	90	92.2	—	99.6	69.2	106	80.2	—	90.3	67.6	98	5.9	—	7.4	5.0	—	5.9	6.6
alpha-Picoline (p)	80	—	—	—	74.2	131	+3.9	—	—	70.5	113	12.7	—	—	11.0	—	—	14.2
Pyrrole (p)	84	—	—	—	81.5g	168	—	—	—	73.6g	128	11.95	—	—	9.9	—	—	12.45
Tetrahydropyran	76	52.2	—	71.0	—	—	35.4	45.3	58.3	52.8	24	3.55	—	3.7	2.9	—	3.5	4.85
Dihydropyran	75	66.5	73.3	79.9	67.9	100	48.7	54.7	60.8	64.6	83.	4.0	—	4.4	3.5	—	4.0	4.7

NOTES FOR TABLES I, II, AND III

a—Approximate.
b—Approximately 85% 2,4,4-trimethyl-1-pentene
15% 2,4,4-trimethyl-2-pentene
c—Sample from another source.
d—Data on different but similar sample from NACA.
e—With 0.5 cc tetraethyl lead instead of 1. 0 cc.
f—In Ethyl Corporation 17.6 Engine at 900 rpm and 300 °F.
g—20% in 52% C-12 + 48% A-6, which has 60 octane number.
h—Contained a small amount of impurity.
k—Data obtained on a similar sample from another source.
m—Corrected data obtained after 1 September 1943.

n—Data on these solid compounds obtained with a special carburetor, but are probably comparable.
p—Values for undiluted compounds are approximate; observed knock not critical.
E—Sample from Ethyl Corporation.
EK—Sample from Eastman Kodak Co.
S—Sample from Shell Development Co.
+—Values preceded by a plus (+) indicate equivalent cc tetraethyl lead in isooctane.
>—Greater than.
*—Rating of 20% hydrocarbon + 80% 60:40 mixture of isoocatane: n-heptane.
**—Calculated blending octaine number of 20% hydrocarbon in above (*) primary reference fuel.
---Knock rating too low for conversion chart.
— Not determined.



BICYCLO(2,2,1)HEPTANE

PART III

SOLID PROPELLANTS FOR ROCKETS AND OTHER JET PROPELLED DEVICES

By

LOUIS P. HAMMETT

PART III

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SUMMARY

There is great opportunity for the improvement of existing solid propellants for rockets and other jet-propelled devices in the sense of making possible the use of a lower ratio of motor weight to propellant wieght. A decrease in this ratio can increase the pay load materially or the velocity of the rocket or decrease the total weight of the motor required to yield a given performance. There are also large opportunities for improved methods of production, especially of large charges, which will decrease the cost of the product and lessen the burden on the country's manpower and ability to produce heavy machinery. In both these directions promising lines of attack are already apparent and have been partially explored.

INTRODUCTION

This report is primarily concerned with the lines of research and development which may profitably be pursued in the search for better solid propellants for rockets and other jet-propelled devices. For this purpose it discusses, first, those general properties of propellants which are critical for their use in such devices, and, second, the specific properties of existing propellants.

PROPERTIES OF SOLID PROPELLANTS

CRITICAL PROPERTIES OF SOLID PROPELLANTS

1. *Basic Prerequisites for a Useful Propellant.*

In order to come into consideration as a solid propellant for jet propulsion, a material must be capable of being formed into masses, called grains, of a suitable size and geometry. These grains must when ignited undergo a self-sustaining combustion reaction which produces hot gaseous products, and the reaction must maintain itself at rocket pressures and preferably at pressures of 500 psi or less. The combustion reaction must occur only on the surface of the grain and the linear rate of recession of the surface must be essentially constant under constant external conditions. The burning must, therefore, not go over to detonation or penetrate through pores in the solid. The grain must have a certain minimum resistance to distortion under slowly applied forces and to rupture under impact. The composition must satisfy the same requirements of chemical stability and resistance to ignition from impact and friction as does a high explosive.

These properties cannot be predicted in advance of experiment. The combination is rare enough so that the first sifting of candidate materials for use as propellants may well be by way of the preparation of grains and investigation of their burning properties. For instance, it has been impossible so far to burn at rocket pressures many materials which are thermodynamically suitable for propellants even though, in some cases, they are useful gun propellants (e.g. RDX-nitrocellulose compositions).

2. *Effective Gas Velocity or Specific Impulse.*

The velocity V imparted to a rocket or other jet-propelled device is given by

$$V = w \ln \frac{M+m}{M} \approx \frac{mw}{M + (m/2)} \qquad (1)$$

in which M is the mass of the object propelled exclusive of propellant and m is the mass of propellant. The effective gas velocity, w, is the mementum of the gas issuing from the jet per unit weight of propellant consumed. (Specific Impulse $I = w/g$.) The value of w depends on the geometry of the nozzle and on the pressure in the motor chamber. It is, however, always possible to employ a nozzle which for a given pressure yields the maximum value of w (optimum expansion ratio) and this maximum value is not very sensitive to the pressure. (It increases by 17% between 300 and 1500 psi and the effect is essentially the same for all propellants.)

The effective gas velocity is, therefore, a characteristic measure of the ability of a propellant to impart momentum to a rocket projectile or other object and the highest possible value is desirable. The values for propellants currently in use range from 5500 to 7500.

Given sufficiently complete and precise thermochemical data a theoretical effective gas velocity may be calculated with a high degree of precision if all of the products of combustion are gaseous, and to a rough approximation if some are solid or if the thermochemical data are incomplete. In most cases these computed values, with small corrections for heat losses and the like, agree well with experiment; some discrepancies are attributed to a failure of the system to attain chemical equilibrium, to which state alone the calculations apply. With these reservations the value of w is to a useful approximation proportional to $\sqrt{n\ T_c}$ where n is the number of moles of gas produced per unit weight of propellant and T_c is the flame temperature. With carbon compounds T_c cannot be greatly increased over values already available with double-base propellants because of heat absorbing dissociation reactions. The value of n might be increased by employing compounds of high energy and hydrogen content such as cyclonite or nitroguanidine if their reluctance to burn can be overcome. It seems most unlikely, however, that an increase of as much as 10% over the effective gas velocity of double-base powder can be attained in this way. The use of materials with high heats of oxidation such as aluminum, boron, or beryllium or of oxidizing agents of high energy and oxygen content such as potassium perchlorate does not appear to offer much prospect of large increases in effective gas velocity because much of the reaction product is not gaseous. It appears probable, therefore, that the upper limit of effective gas velocity obtainable from ordinary chemical reactions has already been nearly, if not quite attained.

3. *Factors Affecting Loading Density and Motor Weight.*

There are a variety of ways in which better propellants can improve rocket performance without any increase in effective gas velocity over values now available. For existing types of artillery rockets, projectile velocity at constant pay load or pay load at constant velocity is increased nearly as rapidly by an increase in weight of propellant as by an increase in effective gas velocity and is increased about half as rapidly by a decrease in motor weight. The percentage effects of given changes in these factors upon velocity and pay load are illustrated in Figs. 1 and 2 using the existing 5.0 in. HVAR as a point of reference. Similar effects would be obtained with any other currently used rocket.

It is obvious that any change in propellant properties which decreases the ratio of motor weight to propellant weight has an effect comparable to that produced by an increase in effective gas velocity. That there is room for much variation in this ratio is evidenced by the data of the following table for various existing rocket motors.

TABLE I

Designation	*Powder*	*Motor Wt Mm*	*Propellant Wt Mp*	*Mn/Mp*
5.0 in. HVAR (CIT)	Double-base dry extruded	64.4	24.0	2.68
11.75 in. Tiny Tim (CIT)	Double-base dry extruded	445	146	3.05
115-mm Rocket (ABL)	Double-base solvent type	47	14	3.35
115-mm Rocket (ABL)	Solvent composite MJ	47	20.5	2.29
Galcit 12-sec 1000-lb thrust unit	Galcit	137.5	64.5	2.12
JB-2 Launching motor, current	Molded Composite 492	204	121	1.69
JB-2 Launching motor, projected	Molded Composite 492	125	121	1.03

Figure 1

Effect of changes in effective gas velocity in propellant weight, and in motor weight on velocity of 5.0 in HVAR. Ordinates are rocket velocities.

Curve I—Effect of variation in effective gas velocity over range from 50 to 150% of value for existing rocket (7130 ft/sec). All weights constant.

Curve II—Effect of variation in weight of proellant over range from 50 to 150% of value for existing rocket (24.0 lb). Effective gas velocity (7130 ft/sec) pay load (48.2 lb), and motor weight (64.4 lb) constant.

Curve III—Effect of variation in weight of motor over range from 50 to 150% of value for existing rocket (64.4 lb). Effective gas velocity (7130 ft/sec), pay load (48.2 lb), and propellant weight (24.0 lb) constant.

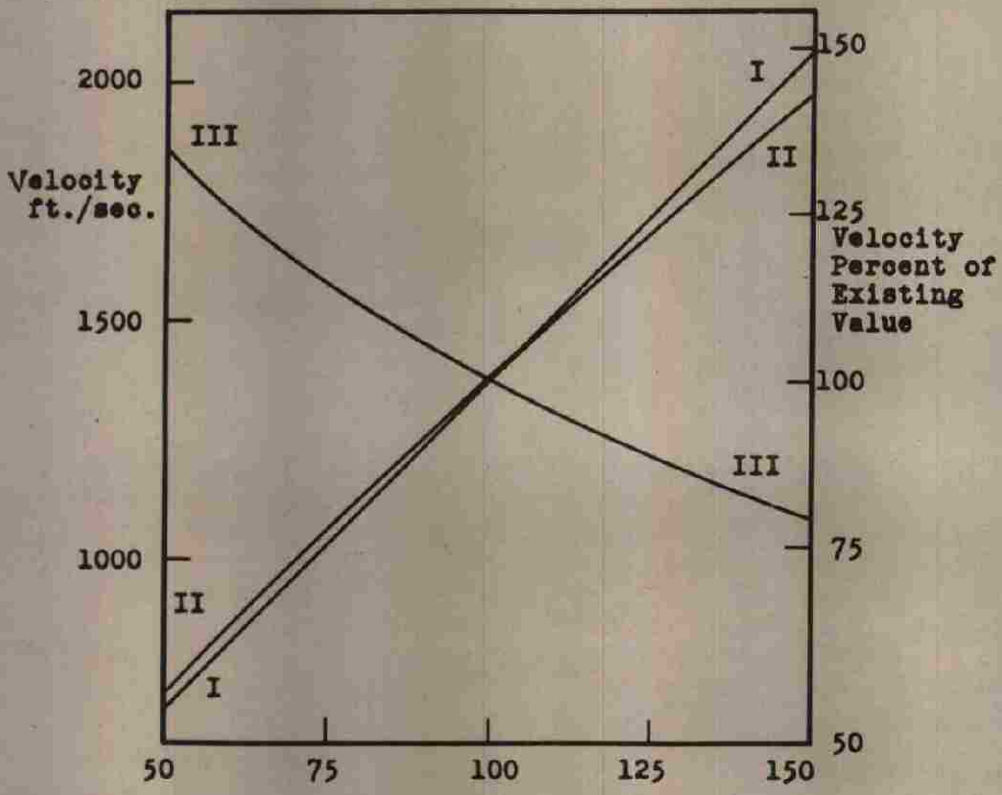

Figure 1 — Percent of Value for Existing Rocket

Figure 2

Effect of changes in effective gas velocity, in propellant weight, and in motor weight on pay load of 5.0 in HVAR. Ordinates are values of pay load.

Curve I—Effect of variation in effective gas velocity over range from 50 to 150% of value for existing 5.0 in. HVAR (7130 ft/sec). Motor weight (64.4 lb), propellant weight (24.0 lb), and projectile velocity constant (1375 ft/sec).

Curve II—Effect of variation in weight of propellant over range from 50 to 150% of value for existing rocket (24.0 lb). Effective gas velocity (7130 ft/sec), projectile velocity (1375 ft/sec), and motor weight (64.4 lb) constant.

Curve III—Effect of variation in weight of motor over range from 50 to 150% of value for existing rocket (64.4 lb). Effective gas velocity (7130 ft/sec), projectile velocity (1375 ft/sec), and propellant weight (24.0 lb) constant.

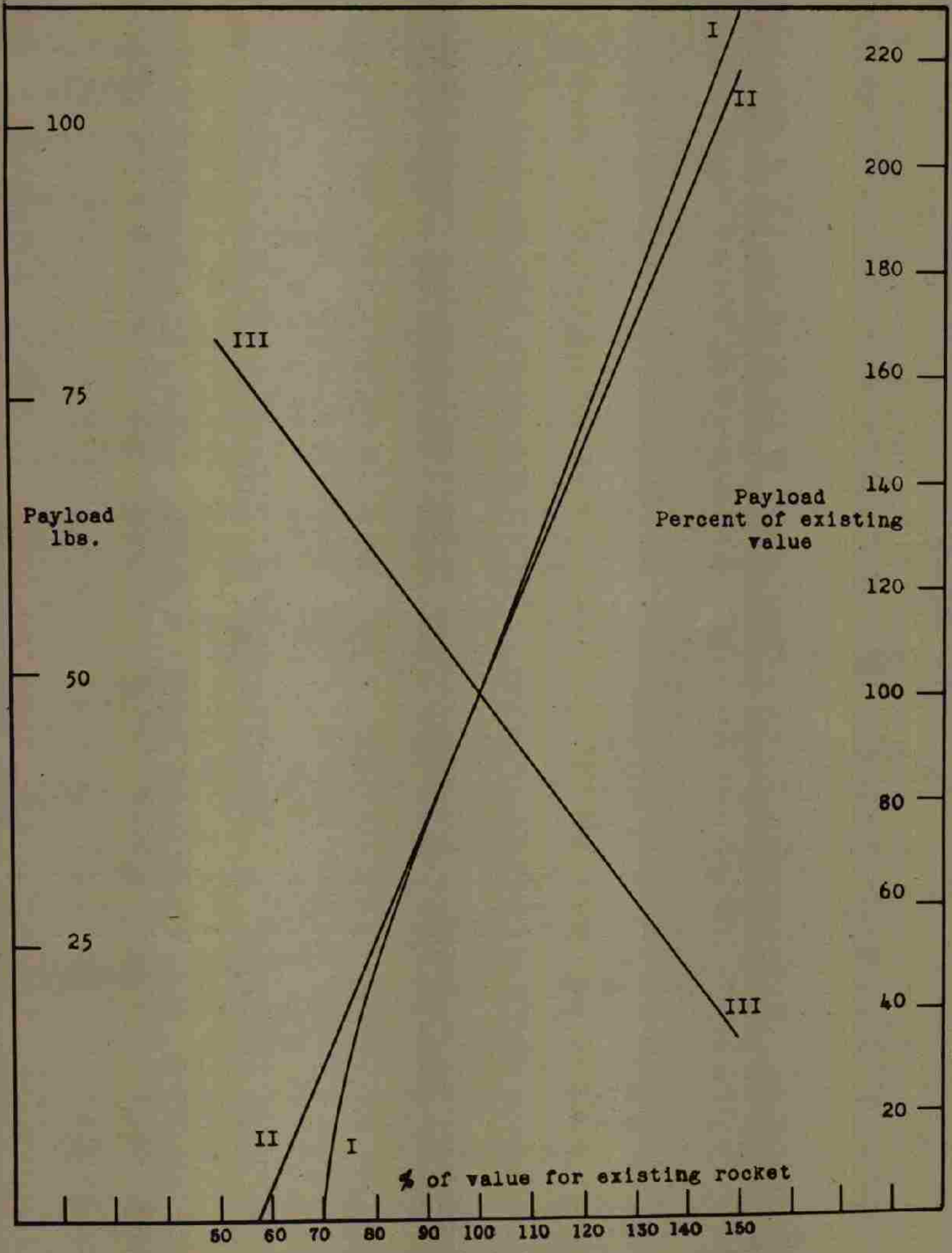

Figure 2 — Percent of Value for Existing Rocket

The profit derivable from this source does decrease at very high projectile velocities for which the ratio of propellant weight to total weight is large, but remains important for any probable rocket projectiles. It also decreases for airplane take-off and similar systems in which the weight of the rocket motors is a small fraction of the total weight. Here, however, the logistic advantage of a low motor-propellant weight ratio is obvious since both motor and propellant must be shipped to the point of use.

The following properties of propellant materials are important in this respect:

(a) Since the weight of a rocket motor increases approximately in direct proportion to the gas pressure, while the effective gas velocity varies much less rapidly, a decrease in operating pressure is favorable until it reaches the point where other forces than bursting pressure become important factors in motor design, certainly as far down as 500 psi. In general solid propellants possess a lower pressure limit, which depends on size and geometry of motor as well as on the propellant, below which they fail to burn or burn irregularly and incompletely. Obviously a low value of this limit is a desirable property of a propellant. In some cases, as in the bazooka, high-operating pressures (10,000 psi) are employed to keep the burning time short. A faster burning propellant would permit a lower operating pressure.

It is clear that the advantage of operating at a low pressure at low temperatures vanishes if the pressure becomes four or five times greater at temperatures in the upper part of the operating range. This is one of the advantages of a powder of low-temperature coefficient.

(b) The rate of burning of a solid propellant varies as a power n with the pressure of the gas surrounding it, while the flow of gas through the nozzle varies as the first power of the pressure. This situation admits of a stable steady state only if n is less than unity, and the state is the more stable and the less sensitive to disturbing influences such as variations in the burning surface the greater the value of 1-n. In this sense the difference between the exponent 0.75 of most double-base powders and the 0.4-0.5 exhibited by composite propellants is a large and important one which leads to materially greater reproducibility and reliability with the latter material. A lower factor of safety and a lighter motor are, therefore, permissible.

The value of a low exponent is especially great in the usual type of artillery rocket in which a tubular or cruciform grain burning over all or nearly all of its surface is contained in a long motor of small diameter. When the attempt is made to reach the highest possible ratio of propellant weight to motor weight the limiting factor becomes the space available for flow of gases toward the nozzle (the port area). If this is small a pressure differential is set up, the burning rate increases in the high-pressure region, and the whole effect is magnified by an amount which is greater the greater the exponent. Consequently a low exponent permits a higher propellant-motor weight ratio for a specified time of burning. A high-density propellant is, of course, desirable for the same reason, as is one resistant to distortion under applied forces, since any bulging of the grain under the forces of setback and pressure drop reduces the port area.

(c) By all odds the most effective way of obtaining a high loading density and hence an optimum propellant-motor weight ratio is to employ a cylindrical grain burning from one end only. Such a grain can fill the cross section of the motor completely and the whole cross section is likewise available as port area in the region between the burning surface and the nozzle. Furthermore, the material need not be stiff since bulging will not infringe on the port area. This arrangement requires a method of restriction to prevent burning on other surfaces than the cylinder base. Restriction appears to be practicable with the propellants now available and is a desirable property for a new one.

With currently available propellants, rates of burning are such that end-burning charges are entirely suitable for the long-burning charges (8 to 40 sec) required for assisted take-off of airplanes and for propulsion of guided missiles, mine-clearing snakes, hydrobombs and the like. For artillery rockets, burning rates of from one to two orders of magnitude greater than those now available will be necessary if the total burning times of such charges are to be brought down to the necessary one to two seconds.

For end-burning charges, and hence at present only for take-off and similar applications, there is much advantage in a single large diameter charge as compared to a multiple of smaller cylinders. In the latter case the motor diameter and, hence, the motor weight must be materially greater. For purposes requiring large thrust the possibility of fabrication in charges of large diameters (8 to 16 in.) is, therefore, an important property of a propellant. The advantage of a single charge largely disappears in artillery-type rockets in which the requirement of sufficient port area enforces a low loading density which can be met either by a single or by a multiple charge.

(d) Another method by which motors might be lightened is to reduce the temperature to which the motor walls are heated by the propellant gases, since the strength of metals decreases materially at temperatures easily reached by the motor walls in conventional designs. By all means the most effective insulating material is the propellant itself. If this burns from a central perforation and the exterior is essentially in contact with the walls, light but low-melting and inflammable materials like magnesium and plastics become practicable. If the perforation has a star-shaped cross section, nearly neutral burning and reasonably constant pressure may be attained with a propellant of low exponent. The propellant requirements are, therefore, low exponent and the practicability of restricting the external surface and bringing it in close contact with the motor wall.

4. *Temperature Coefficient.*

The rate of burning of a propellant increases with increasing temperature of the solid material. With the usual double-base propellants the pressure in a rocket motor and the thrust obtained from it are five times as great at 140°F as at -40°F, and the time of burning is one-fifth as great at the higher temperature as it is at the lower. With the composite propellants and with Galcit, the corresponding factors are 1.5 and 0.67. A low coefficient is indispensable for airplane take-off applications and other cases in which the individual values of thrust and burning time and not merely the thrust-time product are important. With artillery rockets it simplifies design, lightens motors, and eliminates or greatly reduces the aiming correction for the tempreature of the propellant.

5. *Miscellaneous.*

Smoke is an undesirable feature for some applications, as for ground-fired rockets, but is unimportant for others, such as airborne missiles. The same considerations apply to flash, i.e., a luminous jet.

For long-burning charges for assisted take-off, guided missiles, and the like, a low gas temperature is desirable, since it eases the problem of materials for the construction of nozzles and other metal parts. The decrease in flame temperature may generally be compensated partially by an increase in the number of moles of gas formed per unit weight of propellant so that the loss in effective gas velocity which results is not large. A cool propellant is usually, however, a slow burning one, which is frequently a disadvantage. The nozzle problem does not, however, appear to be insoluble even for the hottest existing propellants, although highly refractory and relatively expensive materials such as molybdenum may be required.

In so far as tests have been made all known solid propellants as loaded in metal motors can be ignited by the impact of a rifle bullet. It would be desirable to eliminate this sensitivity.

PROPERTIES OF EXISTING PROPELLANTS

1. *Double-Base Powders.*

Double-base powder is a plastic material containing nitrocellulose and nitroglycerin or a nitroglycerin equivalent, such as diethylene glycol dinitrate. It always contains a small proportion of a stabilizer such as Centralite and may contain up to 20% of other plasticizers called coolants, such as Centralite, phthalate esters, triacetin, dinitrotoluene or the like. The product is stiffer the higher the proportion of nitrocellulose, the usual proportion being from 40 to 50%. It is not brittle, not easily ignited by impact, except when very finely subdivided, and its chemical stability is adequate but could be improved with advantage. The effective gas velocity of a 40% nitroglycerin, 60% nitrocellulose powder (7500 ft/sec) is not likely to be exceeded to any large extent by any new propellant composition depending upon ordinary chemical reaction. The value drops somewhat but not very rapidly as the content of nitroglycerine is decreased or as coolants are added.

Until recently all known double-base powders had high exponents (0.70 to 0.75) and high-temperature coefficients (1.5%/°C). Lately a powder has been developed by the Allegany Ballistics Laboratory and the Hercules Powder Company with an exponent of 0.5 and a temperature coefficient of 0.5%/°C. An investigation of a captured Japanese propellant has shown it to possess a similarly low-temperature coefficient. Both of these propellants are relatively slow-burning ones, which somewhat limits their usefulness, and the effective gas velocities are about 10% below that of hotter powders. The fact that they differ only by very small variations in composition from other powders with high exponents and temperature coefficients suggests strongly that these limitations may be removed by further investigation. It has further been pointed out by Pauling that a charge containing particles or strands of small diameter composed of a fast-burning powder of low temperature coefficient embedded in a matrix of slower burning powder of high temperature coefficient possesses as a whole the low coefficient of the particles. In this case, the grain does not burn by recession of a plane surface but by the formation of a broken surface whose magnitude is determined by the behavior of the faster burning powder. This procedure, already proven experimentally, makes it possible to eliminate the undesirably high temperature coefficient of double-base powder by the addition of a proportion of solvent extruded composite propellant so small as to produce negligible amounts of smoke.

The lower pressure limit below which double-base powder will not burn regularly and completely is undesirably high, especially where small grains are concerned. The available range of burning rates is from 0.1 to 4 in./sec, the higher values being attained only at undesirably high pressures. Restriction of the burning surface by application of a plastic material such as cellulose acetate is possible, although the ability of restricted grains to maintain the desired properties over long periods of storage has not been completely proven.

There are four available methods for forming grains of double-base powder:

(a) In the solvent extrusion process the ingredients are mixed with volatile solvents to a soft dough and pressed through a die to form strands. These are then dried to remove the solvent. The machinery required for this process is relatively easily constructed and is currently available for the production of very large quantities of powder. Unfortunately, the process is limited to the preparation of grains of not much over 1 in. in diameter, because larger sizes crack or distort badly during the removal of the solvent.

(b) In the dry extrusion process the ingredients of the powder are mixed on roll mills and the product is pressed warm through suitable dies. In order to obtain a satisfactory product a certain minimum ratio of press diameter to grain diameter must be maintained. Since explosions destroy the presses, apparently inevitably, at intervals, and since their cost and the damage produced by an explosion increase rapidly with the size of the press, it is perhaps impracticable to produce grains of much larger diameter than 5 in. by this process. In addition to the presses, which are heavy and expensive equipment, large numbers of expensive roll mills are required. Because the material must be soft enough to extrude at a reasonable pressure at a temperature which is limited by the instability of the material, dry extruded double-base powder is not as stiff at service temperature as is desirable. A propellant used by the Germans has the remarkable property of becoming much stiffer on storage after extrusion than when freshly extruded. This property appears to depend upon some very special choice of the type of nitrocellulose used in this composition.

(c) The cast double-base process invented by Kincaid and Shuey of the Explosives Research Laboratory is still in an experimental stage but offers every promise of successful development. In this, small particles of a nitrocelluloise-nitroglycerine powder are mixed with a sufficient quantity of a mixture of nitro-glycerine with an active solvent for nitrocellulose, such as triacetin, to form a pourable slurry. This is cast in a mold, or in a plastic tube which serves as a restricting material where this is desired. On heating for one day at 60°C the mass sets up to a tough grain with completely satisfactory burning properties. There appear to be no limits to the size and shape of charge that may be produced by this process, and it is particularly advantageous for very large charges. The actual casting process requires no heavy equipment of any sort and should be an exceptionally cheap and simple manufacturing technique. The small granules which are the raw material may be made by the solvent process in the same way as rifle powder is manufactured and can probably be made by an even simpler and cheaper process developed by the Western Cartridge Company (ball powder). The casting process is exceptionally suitable for the preparation of charges of low temperature coefficient of the Pauling type.

(d) In the molded double-base process of the Western Cartridge Company small granules of "ball powder" are mixed with a few percent of a plasticizer and compression-molded to form grains. Details of the process are not available for publication and the product has not been tested on any large scale. The process deserves further investigation.

Double-base powder is smokeless, except that some of the cooler powders produce limited amounts of black smoke. The flame temperature and, hence, the destructive effect upon nozzles roughly parallels the burning rate.

The raw materials required for double-base powder, namely nitroglycerine and nitrocellulose, are articles of commerce prepared in very great quantities, and the cellulose, glycerine, and the nitric and sulphuric acids from which they are prepared are widely available.

Solvent extruded powder is currently used in the Bazooka and in the 4.5 in. Army rocket. Dry extruded powder is employed in enormous quantities in rockets now widely used in service and notably in the 5.0 in. HVAR, the Tiny Tim, and in various spinner rockets. Cast double-base powder is being developed with the immediate aim of producing a unit for airplane take-off delivering 1000-lb thrust for 8 sec or more.

2. *Cast Perchlorate Powders.*

The Galcit propellant is prepared by stirring together finely ground potassium perchlorate and a hot asphalt-oil mixture, pouring into the motor which has been lined with a layer of asphalt, and allowing to cool. Alternatively it may be cast in a mold, removed and coated with asphalt and tape. The product is too soft at the higher service temperatures to be employed in applications where it is not directly supported by the motor wall. It is not brittle enough even at low temperatures to be easily fractured by rough handling. It is extremely stable and is difficult to ignite. The effective gas velocity is of the order of 5400 to 5900 ft/sec, but its high density partially compensates for this. The exponent is undesirably high, 0.75, which leads to considerable variability in performance. The temperature coefficient is low (0.5%/°C). The powder produces large quantities of white smoke (potassium chloride). The greatest weakness of the propellant is inherent in the nature of asphalt, namely that it flows at high temperatures and becomes hard and cracks from shrinkage at low ones. Consequently, the range of temperatures over which it may be used is undesirably narrow. It does not burn satisfactorily below 1000 psi and the motors must, therefore, be relatively heavy. It has a high burning rate (1.0 to 1.6 in./sec), which is suitable for end-burning grains for airplane take-off and similar applications. Restriction of the burning surface is practicable by methods already described.

The outstanding advantage of the material is the extraordinarily simple process by which it is produced. The supply of potassium perchlorate is currently limited but it could be very largely expanded, since it is produced by an electrolytic process from protassium chloride. It is of interest that this is the only solid propellant known whose preparation does not depend ultimately upon nitric acid.

The propellant produces a great deal of white smoke and the flame temperature is high enough to make nozzle erosion a problem which has, nevertheless, been solved for burning times up to 30 sec. The Galcit propellant is currently in service use for the assisted take-off of Navy planes.

It has been found at the Explosives Research Laboratory that the substitution of materials containing long chain polymeric molecules for the asphalt of the Galcit propellant materially widens the temperature range over which it may be used, and, furthermore, that the addition of 5% of flake aluminum reduces the exponent to approximately 0.60. A mixture of potassium perchlorate, aluminum, and a fusible ethylcellulose castor oil composition may be cast in the same way as Galcit and shows a material increase in the range of temperature over which it may be used. If the GE Permafil resin is employed instead of the ethylcellulose castor oil composition, the composition may be cast at room temperature and hardens without shrinkage by chemical action to a rubbery material of essentially unlimited temperature range. These materials are still in the experimental stage but should be capable of very rapid development and application. The necessary raw materials are available in large quantities and the costs are not prohibitive.

3. *Molded Composite Propellants.*

These propellants, developed by the Monsanto Chemical Company and the Explosives Reserch Laboratory, are prepared by milling together in edge runner mills a mixture of ammonium picrate, alkali nitrate, and a small proportion of a resinous binder. The powdery product of the mills is then formed by compression molding at about 10,000 psi into grains of the desired shape and size. The material is exceptionally hard and resistant to distortion but is somewhat brittle. By the use of compressed cork supports, however, the grains may be made to withstand any reasonable rough handling. The effective gas velocity is of the order of 5500 ft/sec, but the high density and low exponent make it possible to obtain the same velocity with this propellant in a given rocket as with a double-base powder charge of the same burning time. Substitution of alkali perchlorate and nitroguanidine for alkali nitrate and ammonium picrate would bring the gas velocity approximately up to that of double-base powders, but these compositions have been investigated on the laboratory scale only. The compositions burn completely and smoothly at pressures at least as low as 500 psi. Restriction of the burning surface can be carried out with relative ease and is thoroughly proven. By varying the proportions of alkali nitrate and ammonium picrate and the particle size of the nitrate, a range of burning rates from 0.25 to 1.0 in./sec at 1000 psi is readily accessible, and a still wider range of rates may be attained by operation at low and high pressures.

The propellant produces considerable amounts of white smoke, the quantity being smaller with the slower burning compositions which contain smaller proportions of alkali nitrate.

The fabrication of this propellant requires large numbers of small edge runner mills, although improved techniques may probably be developed by further investigation. It also requires large presses, but a press capable of producing not over 3-in. diameter double-base charges is suitable for the production of 8.5-in. diameter composite propellant charges. The press operation is, however, materially slower in terms of powder produced per unit time with the composite propellant than with double-base powders.

The raw materials for this propellant are all currently manufactured in large amounts and ammonium picrate is perhaps the only available raw material for propellants in which a surplus exists.

This powder is currently employed in the experimental launching of JB-2 bombs. The launching requires four rockets, each containing an 8-1/2 in. OD, 2-1/2 in. ID, 37 in. long grain weighing 120 lb and burning 1.75 sec. Applications involving end-burning grains of 8-1/2 in. or 12 in. OD and with burning time up to 50 sec are also being developed.

4. *British Plastic Propellant.*

This is similar in composition and in ballistic properties to the molded composite propellant which indeed derives historically from early British experiments on picrate propellants. In contrast the resinous binder is larger in amount and more fluid. The materials are milled on roll mills and pug mills to yield a putty-like product, which is molded directly into the motor at relatively low pressures (approximately 1000 psi). The presses may, therefore, be lighter and more easily constructed than with the molded composite propellant. It is currently being developed in the form of central burning charges which insulate the motor wall and are restricted from burning on the outer surface of the charge by the wall itself. (See section on "Temperature Coefficient," p. 67.)

5. *Solvent-Extruded Composite Propellants.*

These consist of a filler composed of carbon black and either potassium perchlorate or potassium nitrate dispersed in a binder (35% or more of the total) composed of double-base powder. They have the ballistic advantages of low exponent and temperature coefficient characteristic of composite propellants but are prepared in the standard equipment and by the normal methods used for solvent-extruded double-base powder. As such the grain diameter is limited but the limit is probably higher than with straight double-base powder because these powders shrink less on drying. Some experiments indicate that the solvent-extruded powder may be reextruded by the dry process in any granulation desired. The powder produces white smoke in an amount dependent upon the proportion of potassium salt present.

EJA powder contains 56% potassium perchlorate and 9% carbon. It was developed for use in the Army 4.5-in. rocket in which it gave excellent performance, but the development has been side-tracked by decreased interest in the use of the rocket. The powder is also important for use as fast-burning low temperature coefficient particles or strands in charges of the Pauling type. (See section on "Double-Base Powders," p. 68.)

MJA powder contains 43% potassium nitrate and 7% carbon. In the Allegany Ballistic Laboratory 115-mm rocket, this powder gives a rocket velocity of 1200 ft/sec compared with 950 ft/sec for a double-base charge, because its low exponent and temperature coefficient and high density permit a higher loading density.

BBP powder contains only 7.8% potassium perchlorate and 1.2% carbon and is nearly enough smokeless to be employed in the Bazooka for which it has been adopted for service use. The temperature coefficient is approximately one-half of that shown by double-base powder in the same weapon. With it the bazooka may be employed in cool weather without the injury to the gunner and the high dispersion which occur when burning is not completed inside the projector. These advantages are retained even with a 15% increase in propellant weight which permits the use of a higher pay load and a materially greater effectiveness of the projectile.

6. *The Aberdeen Propellant.*

This consists of a mixture of potassium perchlorate, metallic aluminum and metallic titanium with a resinous binder. It may be molded directly into a metal motor to form an end-burning charge and is claimed to have a burning rate of the order of 50 in./sec. If these claims are substantiated the material is an answer to the problem stated on page 66, paragraph (C).

CONCLUSIONS AND RECOMMENDATIONS

The following recommendations serve only to indicate that numerous lines of investigation which have high promise of developing improved performance are immediately obvious. Any active and effective research organization may be expected to uncover further directions of advance which would be more profitable than those listed. Since the effect of improved propellants upon rocket performance is for the most part indirect, and by way of permitting improved motor design, it is most desirable that any research group working on propellants should cooperate closely with workers in the field of rocket design.

ARTILLERY ROCKETS

In this field the present situation is that nearly all American rockets in service employ a single propellant, a particular composition of double-base powder. There had been, during the war, the most effective activity in designing motors around this powder contrasted with relatively little progress in the direction of using better powders. It is, therefore, probable that the limit of performance of this powder has been reached, but, as the preceding discussion shows, materially improved performance may be expected from the use of different powders. Promising lines of investigation are:

1. The design of motors and projectiles around the propellants of low exponent, low temperature coefficient, high density and low pressure limit which already exist in order to exploit to the fullest the potentialities of these powders.

2. The development of powder charges of the Pauling type which combine the advantages of low temperature coefficient and of high effective gas velocity and burning rate with an essentially complete absence of smoke.

3. The development of rocket charges burning outwardly from a central perforation in which the propellant insulates the motor tube from the hot gases.

4. The search for propellants of much higher burning rate than are now available so that end-burning charges may be employed in artillery rockets.

5. Studies looking toward the elimination of flash.

LARGE AND LONG-BURNING CHARGES

The techniques of production of charges of this sort are in their infancy. The only fully developed and demonstrated types are Galcit units of 1000-pound thrust and 8 or 12 second burning time and Monsanto units of 11,000-pound thrust 2-second burning time. The possible applications of larger and longer burning charges are myriad and their military importance is extremely high.

1. The cast double-base process for producing charges of the Pauling type is still in an experimental stage. A successful development will permit the production at relatively low price of units of any desired thrust and burning time which are essentially smokeless and which have a low flame temperature.

2. The replacement of the Galcit asphalt by other materials can eliminate the objectionable narrowness of the temperature range within which the Galcit propellants are usable, and a decrease in the exponent may be expected to improve the reproducibility of these units. The simple and inexpensive casting process by which these charges are produced justifies a great deal of effort to improve the quality of the product.

3. The Monsanto molded composite propellant has been made in units burning up to 50 seconds on an experimental scale. Completion of this development is clearly desirable.

4. In view of the difficulties encountered from nozzle erosion, investigations looking toward the development of compositions of low flame temperature are most desirable.

GENERAL

1. The most important advance that may be hoped for in solid propellants in general is the development of techniques of production which will materially reduce the cost of preparing the charges and the requirements in manpower and heavy machinery. The Galcit propellants and the cast double-base process clearly indicate the possibility of very great economies in this direction which should be applicable to rocket charges as well as to larger units. It appears probable that the cost of cast double-base powder charges will be not over one-fifth of that of dry extruded powder.

2. The existence of isolated compositions of double-base powder having low temperature coefficients and low exponents indicates the desirability of a continuing search for other compositions which possess these qualities, but which have higher effective gas velocities and burning rates.

3. In this direction and generally for the whole field of solid propellants the most serious deficiency is the complete lack of any satisfactory theory of the factors which determine the burning rate. Theoretical investigations of this problem carried out

in connection with empirical studies of rates, exponents, and temperature coefficients should be of extreme value.

4. The nitrocellulose-nitroglycerine plastic of double-base powder is not in principle the only composition which would have similar mechanical properites and a sufficiently high effective gas velocity. It has the disadvantage inherent in compositions consisting of nitrate esters of a relatively low stability. The search for plastic or high-polymer materials based upon other structures is desirable. Particularly from the side of the Navy there is interest in the development of propellants which do not contain nitroglycerine, whose volatility is a potential hazard.

5. A search for solid propellant compositions which are not ignited by the impact of a rifle bullet is desirable.

PART IV

LIQUID PROPELLANTS FOR ROCKET TYPE MOTORS

By

A. J. STOSICK

PART IV

LIQUID PROPELLANTS FOR ROCKET TYPE MOTORS

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INTRODUCTION

SIMPLICITY OF THE ROCKET MOTOR

Rocket motors are among the most recently developed and simplest sources of motive power, involving no moving parts except for accessories such as valves or pumps. A complete rocket power plant consists of a tank or set of tanks for storage of the propellant, a system for forcing the propellant into the reaction chamber, a reaction chamber in which the propellant produces hot gases, and an expanding exhaust nozzle through which the gases escape. The motor proper is merely a hollow chamber, which may be double walled to permit it to be cooled by the influent propellant, and the exhaust nozzle. The propellant can be introduced into the chamber either by pumps or by gas pressure. Some propellants require, in addition, an ignition device as part of the motor system.

The simplicity of the rocket motor, with no moving parts, as compared with a conventional gasoline engine is obvious. A consequence of this simplicity is the small size of a rocket motor as compared with other engines. Thus, a rocket motor capable of exerting 1000 lb of thrust has about the same size as a single cylinder of a large aircraft engine.

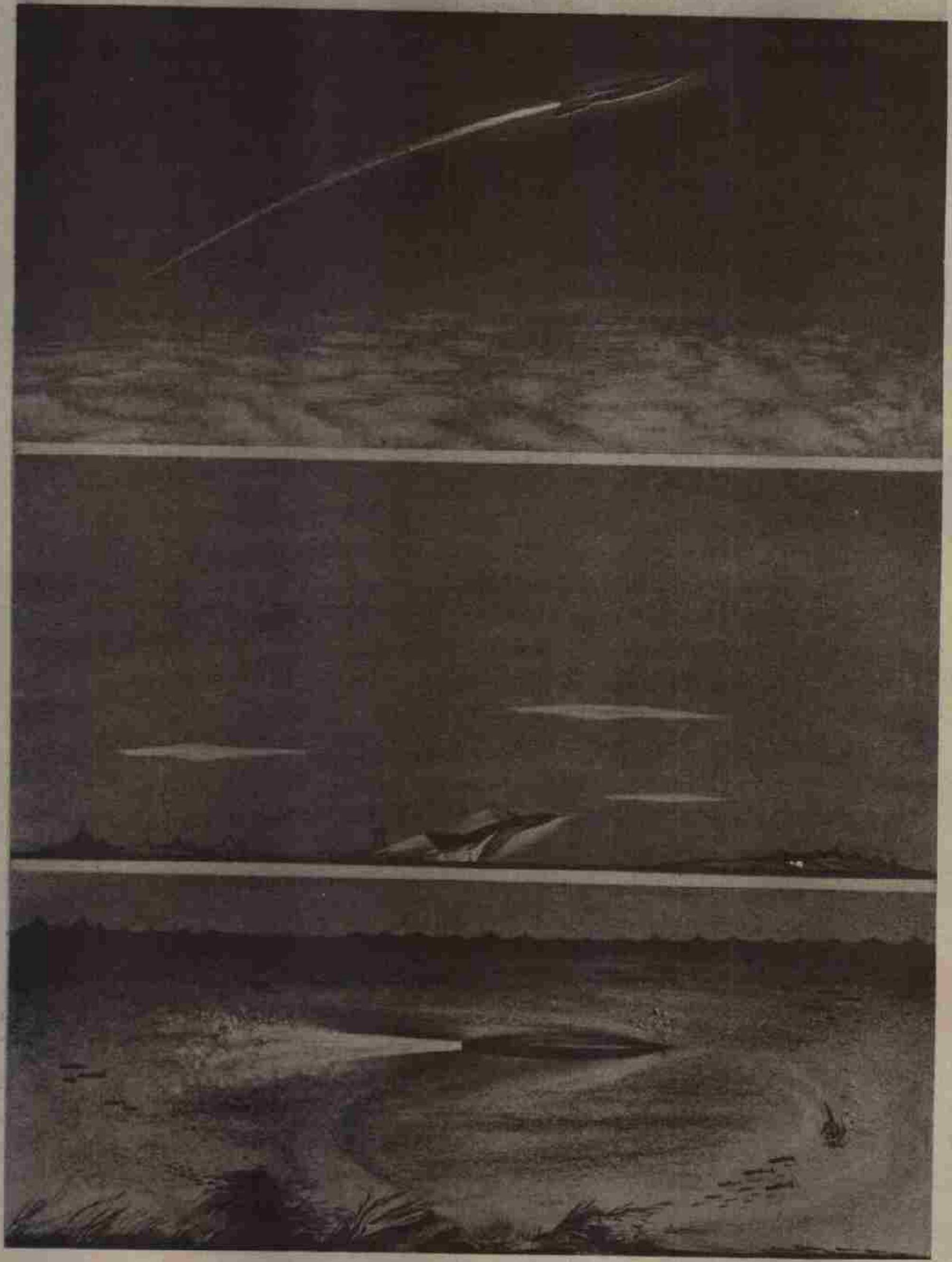
INDEPENDENT OF NATURE OF SURROUNDING MEDIUM

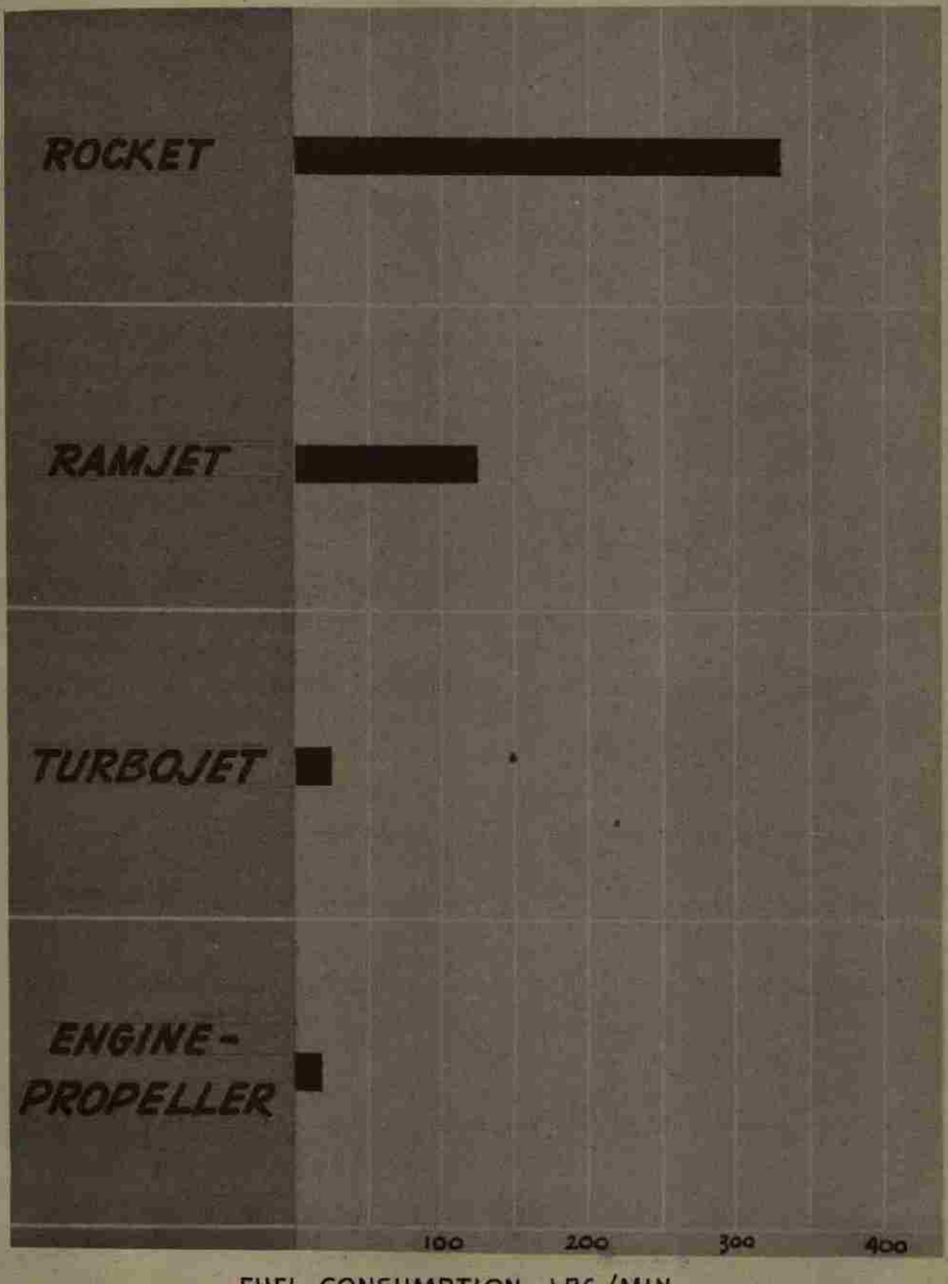
Conventional engines and jet engines depend on the presence of air at substantially normal atmospheric pressure. For operation at high altitudes use is made of turbosuperchargers and of ram pressure to provide these engines with such an atmosphere. Rockets are free of this limitation since their heat-producing chemicals are all transported with the rocket as components of the propellant. By virtue of this property rocket motors have been run successfully in air, underwater, and in the near-vacuum of the stratosphere.

DISADVANTAGES AND ADVANTAGES

The principal disadvantage of a rocket is the high rate of consumption of chemicals as compared with other engines. The following numbers, obtained from Memorandum JPL-2, Jet-Propulsion Laboratory, GALCIT, by Karman Malina, Summer-

Versatility of a Rocket Motor





FUEL CONSUMPTION - LBS./MIN.

Fuel consumption based on rate necessary to produce 1000 lbs. thrust at a flight speed of Mach Number = 0.65 at sea level.

field and Tsien, very strongly demonstrate this weakness of rockets. These numbers list the fuel or propellant-consumption rates necessary to produce 1000 lb of thrust at a flight speed of Mach number 0.65 at sea level:

Rocket	340 lb/min
Ramjet	127 lb/min
Turbojet	24 lb/min
Engine-Propeller	17 lb/min

For the rocket a propellant with a specific impulse (cf. later) of 176 sec was assumed. Even if a specific impulse twice as great is assumed (the propellant consumption rate is then halved) the rocket is still grossly inefficient in its propellant requirements. Moreover, it is almost a certainty that no practical chemical propellant system with such a specific impulse will ever be found. It follows that the rocket will always be hopelessly inferior to other engines with respect to fuel economy.

The reason for the superiority of the other engines is a consequence of the fact that they derive the major part of their chemical system from the air and carry only their fuel. Thus, for each pound of gasoline consumed, approximately 15 lb of air are required. In the rocket the equivalent of this entire chemical system is contained in the propellant and is transported by the rocket. Several investigators have suggested arrangements for burning combustible gases found in the rocket exhaust in a duct with auxiliary air. Since this secondary combustion requires the presence of air such a device cannot be considered a pure rocket.

The numbers presented in the foregoing table do not take into account the weight of the motor installations, and hence are applicable as they stand only to long-duration devices in which motor weight is small compared to propellant weight. For short-duration uses the comparison is less unfavorable for the rocket by virture of its simple low-weight construction. Thus, the rocket is seen to be particuarly suited for use in missiles, for superperformance of aircraft, for assisted take-off of aircraft, or for other uses in which an air-fuel system is impractical or impossible.

Further improvements in devices such as the turbojet are likely since the necessary improvements are largely metallurigcal or mechanical. No major improvement in rockets using chemical systems is foreseeable, since the barrier to increased performance of rockets is a fundamental chemical limitation rather than mechanical. Stated in other words, present rocket propellants are already very near to the maximum in energy release which can be obtained from chemical systems.

PROPELLANT PROPERTIES

The remainder of this report will be devoted to a discussion, from a chemical point of view, of various typical liquid propellants. The discussion will be restricted to representative examples of the various types and will not be a catalog of all tested or proposed combinations. Instead the discussion will emphasize those factors which limit propellant performance. Detailed lists of various propellants, both proposed and tested, are available in the numerous reports prepared by various rocket research groups in this country and abroad.

GENERAL REMARKS

Any chemical reaction which results in the production of hot gases is a possible basis for a rocket propellant. The greater the amount of gases per unit mass of chemical and the higher the temperature of the gases, the better the propellant will be. Thus a reaction such as

$$4\ Al\ (\text{solid}) + 3\ 0_2\ (\text{gas}) \longrightarrow 2\ Al_2\ 0_3\ (\text{solid}) + \text{Energy}$$

would not be suitable for a propellant since gases are not produced except by minor side reactions.

It is immaterial whether the initial chemicals are solid, liquid, or gaseous except from the standpoint of practical matters relating to storage and handling of the chemicals. Because gases are of low density even when compressed to reasonably high pressure they have not been considered to be suitable for rocket propellants, and only liquids or solids have been tested extensively.

The distinction between liquid and solid types of propellants does not imply any fundamental differences in their chemistry, but it is only a matter of practical convenience occasioned by necessary differences in the methods of their use. Two obvious differences are the following:

(1) The reaction or combustion chamber of a liquid-propellant rocket motor need only be large enough to accomplish the desired combustion, whereas, a solid-propellant rocket combustion chamber must initially contain all of the propellant. This, in part, restricts the places of location of solid-type units and implies a freedom of choice for the liquid type.

(2) A liquid-type rocket motor can, in principle, be cooled by jacketing it with channels for the influent propellant. This cannot be done for a solid-type rocket.

QUANTITATIVE EVALUATION OF PROPELLANTS

To constitute an effective propellant, the chamicals which react in the rocket motor must liberate, in the combustion process, an amount of energy of the order of 1 kcal/gm, approximately 50% of which is converted into thrust effort. Less efficient reactions, e.g., German use of hydrogen-peroxide at 0.20 kcal/gm, have been used because of some other compensating advantage. In the case mentioned the reaction temperature is so low that an uncooled steel reaction chamber can be used for sustained operation of at least one minute and probably for an indefinitely longer period. However, to obtain high performance, the goal to be sought is a chemical reaction releasing the maximum energy per unit of mass with products which are entirely or mostly gases.

Two methods of evaluating propellants are available; the first, and historically the earlier, is by direct experimentation, the second is by calculation. The calculation of performance, based on chemical equilibrium in the cumbustion chamber, is in most cases straightforward although occasionally tedious. It serves the very important function of directing and guiding experimental work by selecting those combinations which are most likely to produce useful results. In some cases the proposed chemicals are not available, or are too expensive because of limited production to permit satisfactory tests and immediate direct experimentation is not feasible. In another case, that of nitromethane (cf. later), about a year of experimentation by several rocket groups was required to find means for achieving combustion. Calculations had shown that this substance would be a desirable propellant and these experiments were undertaken on the basis of the results of the calculations.

QUANTITATIVE CHARACTERISTICS OF PROPELLANTS

Four numerical data are usually used in comparing propellants. These are: (1) effective jet velocity, c; (2) specific impulse, I_{sp}; (3) characteristic velocity, c*; and (4) temperature in the combustion chamber, T_c, and at the exit of the nozzle, T_e. From engineering considerations other properties such as density, boiling point and freezing point, heat and shock sensitivity, viscosity, etc., are also of practical importance. These properties, however, are in a different category from those listed above.

The effective jet velocity, c, is the velocity of the escaping gas averaged over the exhaust nozzle escape area. This is the most important number describing propellant performance since it can be used directly to calculate the thrust of a rocket motor. Thus, from Newton's second law:

$$\text{Force} = F = \frac{d\,(mv)}{dt} = m\frac{dv}{dt} + v\frac{dm}{dt}. \qquad (1)$$

When the jet velocity has become stable $\frac{dv}{dt} = O$, $v = c$, and the force becomes

$$\text{Force} = F = c\,\frac{dm}{dt} \qquad (2)$$

in which $\frac{dm}{dt}$ is the mass flow rate of propellant exhaust. The value of c for various known tested propellants ranges from 4000 to about 8000 ft sec.

The specific impulse, I_{sp}, is defined by

$$I_{sp} = \frac{c}{g} \qquad (3)$$

where g is the acceleration of gravity. The use of I_{sp} is one of engineering convenience permitting the use of conventional weight rather than mass units for the flow rates. Thus,

$$F = c\,\frac{dm}{dt} = \frac{c}{g}\left(g\,\frac{dm}{dt}\right) = I_{sp}\,\frac{dw}{dt}. \qquad (4)$$

It follows that c and I_{sp} basically provide the same information about a propellant since they are related by equation (3).

The characteristic velocity, c*, as its name implies, is a number characteristic of the propellant and it is theoretically almost independent of the conditions of use of the propellant so long as equilibrium combustion is achieved. In particular it is essentially independent of nozzle geometry and of chamber pressure, p_c. Thus, c* is of greater interest to the propellant chemist than to the engineer since the measured valve of c* provides a useful index of the efficiency of the combustion process.

The theoretical expression for c^* is

$$c^* = \sqrt{\frac{RT_c}{\overline{M}\delta_c}}\;\frac{1}{\left(\frac{2}{\delta_c + 1}\right)^{\frac{\delta_c + 1}{2(\delta_c - 1)}}} \tag{5}$$

in which

R = universal gas constant,
T_c = chamber temperature on an absolute scale,
$\overline{M}$ = average molecular weight of chamber gas, and
$\delta_c = \delta$, the ratio of the isobaric and isochoric heat capacities of propellant gas at $T = T_c$.

The corresponding experimental expression is

$$c^* = \frac{p_c f_t}{\left(\frac{dm}{dt}\right)} \tag{6}$$

in which

p_c = chamber pressure (absolute)
f_t = cross section of nozzle throat, and
$\frac{dm}{dt}$ = mass flow rate of propellant exhaust.

In general the observed value of c^* is 90-95% of the calculated value when combustion is satisfactory.

The effective jet velocity, c, is related to c^* in accordance with

$$c = C_F\, c^* \tag{7}$$

where C_F is the nozzle thrust coefficient. For a nozzle with no expanding section $C_F \simeq 1.2$, with an expanding exhaust section $C_F \simeq 1.4$ when p_c is near 300 psia and p_e (exhaust pressure, absolute) is near 15 psia. Thus the effect on c of the expansion ratio, p_c/p_e, is all contained in C_F since c^* is essentially independent of p_c. The value of C_F increases slowly with increasing p_c/p_e to a value of roughly 2 for infinite p_c/p_e. Thus C_F, c, and I_{sp} increase if the chamber pressure is increased or if the exit pressure is decreased. The usual value for the chamber pressure of a liquid-type rocket is about 300 psia, but this could probably be raised to 600 psia without undue mechanical difficulties. For an assisted-take-off rocket, for which p_e is 15 psia, using nitromethane raising the chamber pressure from 300 to 600 psia would increase the thrust by nearly 8%. For the lower pressure $C_F = 1.396$; for the higher pressure $C_F = 1.503$. The value of c^* is the same for the two cases. A similar increase in C_F would also arise if p_e decreased, for example, in the case of a rocket missile rising to a high altitude. To achieve these predicted values for C_F requires that the nozzle be designed for the desired expansion ratio.

Returning to the theoretical expression of c^* given in equation (5) it can easily be shown that the quantity outside of the square-root sign is essentially constant with a value of 1.70 for all values of δ encountered in propellant gases. Thus, c^* is determined by the magnitude of the quantity under the square-root sign. Since δ usually does not vary by much more than 10-20% from one propellant to another, variations in δ change c^* by only 5-10%. Therefore, c^* is determined largely by the value of $T_c/\overline{M}$. Hence, the principal requirement for a high c^*, and therefore a high c and I_{sp}, is that $T_c/\overline{M}$ be a maximum. In a following section we shall see that there is a fundamental limitation on the value of T_c attainable by chemical systems. The remaining controllable parameter is $\overline{M}$.

The remaining quantities characterizing a propellant are T_c and T_e. Of these T_c is of greater importance, because of its connection with the problem of cooling the rocket motor for long-duration operation.

CALCULATION OF PROPELLANT CHARACTERISTICS

The methods used for calculating T_c, T_e, c, c^*, and I_{sp} have been discussed in whole or in part in the following:

(1) A. J. Stosick; Jet-Propulsion Laboratory, GALCIT, Progess Report 1-25, 2 April 1945;

(2) Hirschfelder, et al; "Thermodynamic Properties of Propellant Gases," OSRD Report No. 547; and

(3) Lewis and von Elbe; "Combustion, Flames, and Explosions of Gases," Cambridge Press, 1938.

The calculation of T_c presents no difficulties for systems containing only carbon, hydrogen, oxygen, and nitrogen since reliable thermodynamic data are available for the various possible combustion products up to 5000°K. This is more than adequate for any system involving only C, H, O, and N. If the propellant contains other elements such as Al, Mg, Li, B, Be, Cl, F, S, etc., the situation is much different. For compounds of these elements the high-temperature thermodynamic data are meager or nonexistent. In essence, the calculation of T_c assumes that chemical equilibrium, without loss of energy, is achieved in the combustion chamber. Since the time of passage of the propellant through the combustion chamber, from injection to exhaust, is of the order of 0.01-0.02 sec, this assumption is a reasonable one.

The calculation of T_e is subject to some ambiguity when T_c is greater than 2500°K. The source of the ambiguity is the absence of knowledge as to whether the combustion gases remain in thermodynamic equilibrium during expansion or whether the gas composition is "frozen" at the composition existing in the combustion chamber. The uncertainty is twofold inasmuch as the term thermodynamic equilibrium implies: (1) Equilibrium chemical composition with recombination of dissociation products such as atomic hydrogen, hydroxyl molecule, etc. and (2) equilibrium adjustment of energy between the various degrees of freedom of component gases, i.e., translation, vibration, and rotation. The time required for the exhaust gas to pass from the combustion chamber and out of the nozzle is of the order of 0.0001 sec. This may well be inadequate for either or both of the requisite changes to occur.

The relation which is assumed to relate T_e to T_c is the adiabatic expansion equation derived for a perfect gas with a constant heat capacity. Since heat capacities vary with temperaure, δ, an average value of $\delta = \frac{cp}{cv}$ over the range T_c to T_e is used. As an example of the dependence of T_e and δ on the assumed nature of the expansion process the following results are of interest:

Propellant: 62 parts by weight liquid methylamine
128 parts by weight liquid oxygen
Chamber temperature: $T_c = 3393°K$
Chamber pressure: $p_c = 300$ psia
Exist pressure: $p_e = 14.69$ psia
(a) "Frozen" composition: $\delta = 1.220$; $T_e = 1974°K$
(b) Equilibrium: $\delta = 1.089$; $T_e = 2630°K$

The jet velocity is calculated from the equation

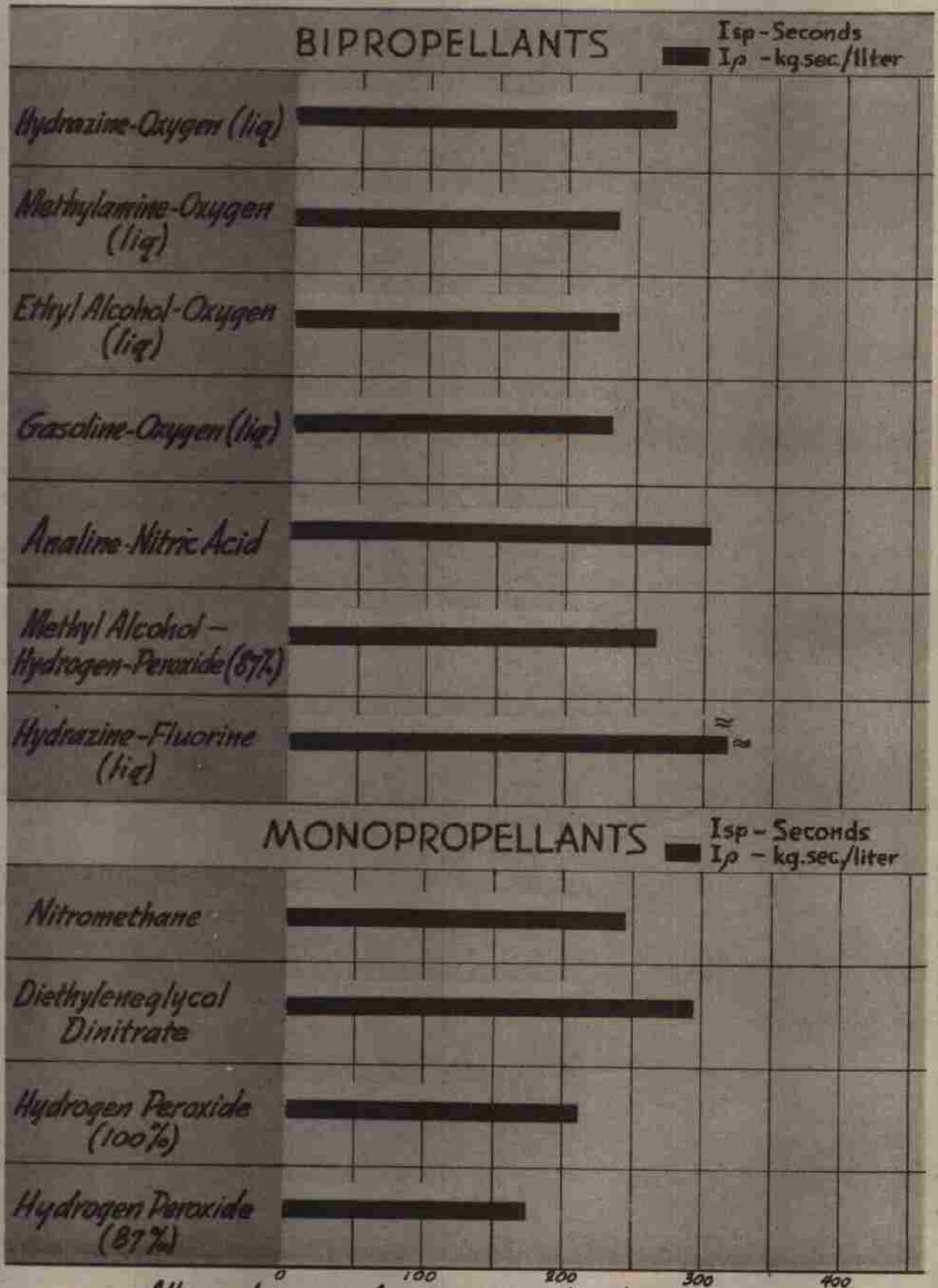
$$c = \sqrt{\frac{2\,\Delta H_{T_e}^{T_c} J}{m}} \qquad (8)$$

using a value of $\Delta H_{T_e}^{T_c}$ (enthalpy change on expansion) appropriate to assumption (a) or (b) above. In equation (8) J is the proper mechanical equivalent of heat and $\Delta H_{T_e}^{T_c}/m$ is the enthalpy change per unit mass of propellant. For the propellant listed above assumption (a) leads to the values c = 8100 ft/sec, I_{sp} = 251.5 sec, and assumption (b) leads to the values c = 8605 ft/sec, I_{sp} = 267.3 sec.

PROPELLANT TYPES

As a matter of convenience, liquid propellants are divided into two classes, the monopropellants and the bipropellants. Monopropellants contain in a single liquid, which may be a mixture or a pure compound, all of the requisite elements for a high-energy, gas-producing reaction. It automatically follows that monopropellants are potentially high explosives, but this hazard is considered to be small for some examples. Bipropellants consist of comparable quantities of two separately injected substances, one of which is a fuel, the other an oxidizer component. In principle they are less hazardous since the separate components are usually not capable of releasing energy explosively, but the components may be hazardous in other respects.

Some further minor operating differences distinguish the two classes. Monopropellants require only a single storage, pumping, and injection system; bipropellants require a dual system. If chemical stability permits, the entire flow of a monopropellant can be used for cooling the motor. With a bipropellant it is usually convenient to use only one of the two components, thereby reducing the cooling capacity. All monopropellants tested thus far require some initial ignition device such as spark plus oxygen, a hot spot, a pyrotechnic ignitor, or a catalyst surface or fluid,



All numbers are for 300 PSIA chamber pressure and 14.69 PSIA exhaust pressure assuming "frozen" composition on expansion.

Some bipropellants, such as nitric acid and aniline or other fuels, ignite spontaneously on mixing in the combustion chamber, and no other ignition device is needed.

At present it does not appear likely that a monopropellant will be found which will surpass bipropellants in performance. There are two reasons for this belief. Those monopropellants which contain all their energy-producing elements in each of their molecules almost invariably have a positive heat of formation. They are, hence, in a more degraded condition on an energy scale than their separated elements. These elements presumably could be combined to make components of a bipropellant with a greater energy release thereby achieving a higher propellant performance. Those monopropellants which consist of a mixture of an oxidizer and a fuel are limited by increasing sensitivity to detonation as their chemical potential is increased. The increasing sensitivity thus limits the chemical potential which can safely be used at a value less than that which can be attained if the components are not mixed. The following is an example of this effect:

$$1.\quad \left.\begin{array}{l}\text{H}_2\text{O}_2\ 87\%\text{ by wt}\\ \text{H}_2\text{O}\ 13\%\text{ by wt}\end{array}\right\}\ \text{—insensitive to shock}$$

$$2.\quad \left.\begin{array}{ll}\left.\begin{array}{l}\text{H}_2\text{O}_2\ 87\%\text{ by wt}\\ \text{H}_2\text{O}\ 13\%\text{ by wt}\end{array}\right\} & \text{— 92\% or less by wt of total}\\ \text{CH}_3\text{OH}\qquad\qquad\ \} & \text{— 8\% or more by wt of total)}\end{array}\right\}\ \text{—sensitive to shock}$$

British practice, as of several months ago, limited the amount of added methyl alcohol to about 5% by weight. If the peroxide and methyl alcohol components are injected separately as a bipropellant the entire useful range of mixture ratios can be used. In particular the mixture ratio giving best performance, 21% by weight of methyl alcohol and 79% by weight of peroxide component (87:13), is ruled out as a single-fluid propellant by its great shock sensitivity.

MONOPROPELLANTS

The following list includes the various types of substances suggested or tested as monopropellants. Each class will be discussed in the sections immediately following: (1) organic nitro compounds, (2) organic nitrate or nitrite compounds, (3) organic perchlorates, (4) nitroalcohols and nitroalcohol intrates, (5) hydrogen peroxide, (6) miscellaneous: hydroxylamine, ammonium nitrate dissolved in liquid ammonia, etc.

Organic Nitro Compounds.

The outstanding example of this class is nitromethane which is produced from natural gas and nitric acid on a pilot plant scale by the Commercial Solvents Corporation. The development of motors to use nitromethane is in progress and appears to be approaching a satisfactory solution. The experimental value of c, the jet velocity, is about 10% less than the calculated value of 7000 ft/sec for $p_c = 300$ psia, and the experimental value of c^* is about 5% less than the calculated value of 5000 ft/sec.

The thermal stability of nitromethane is sufficiently great to permit cooling the reaction chamber with the influent propellant. With a motor having a carbon liner, sustained operation for a period of five minutes has been achieved at Jet-Propulsion Laboratory, GALCIT. Similar cooled motor operation for shorter periods has been achieved without the carbon liner. The success of these experiments indicates that a long-duration propellant-cooled motor could be developed without undue difficulty. These experiments have all been performed with motors of 200-lb thrust, but the cooling problem for larger motors may be less severe because of a decrease of the surface to volume ratio on increasing the motor size.

In other types of experiments the unusual thermal stability of nitromethane is confirmed. The material has been heated to 538°F without exploding while under pressure in a flow system such that the average time of exposure to this temperature was of the order of one minute. Higher temperatures were not investigated in this set of experiments. In other experiments in which confined samples were slowly heated, explosions occurred at 600 ± 50° F. In these experiments liquid and vapor were both presumed to be present. When the explosions occurred the evidence suggested that they were of low order since in most cases unexploded liquid remained.

If nitromethane is subjected to strong impact, for example, with a blasting cap in a heavy-walled steel vessel, a high order detonation can result. With much stronger initiation the detonation can be caused to propagate through filled metal tubes. However, such detonations have never been obtained in entirely light-walled vessels, and methods for desensitizing the nitromethane and traps for stopping the detonations have been devised.

Recently impact sensitivity tests have been made with nitromethane at the Explosives Research Laboratory at Bruceton, Pennsylvania. In these tests nitromethane failed to explode in a drop-weight test with a drop distance of 337 cm, whereas, 50% explosion incidence for nitroglycerin occurred at 9 cm, and for diethyleneglycol dinitrate at 30 cm. The insensitivity of the nitromethane is remarkable considering its latent chemical energy.

Currently 1-2% of chromium acetylacetonate is dissolved in nitromethane for use as a propellant. This chromium compound produces smoother combustion at lower operating pressures, presumably because Cr_2O_3 is formed during combustion. The latter, Cr_2O_3, as well as CeO_2, ThO_2, MnO_2, and others are known to be excellent catalysts forthe decomposition of nitromethane at somewhat elevated termpatures.

The combustion process for nitromethane is effected by changing the pressure in the combustion chamber, and by changing the size of the combustion chamber. For a given size and shape of the chamber, and for a given injection system, there is minimum value for the chamber pressure below which combustion is not stable.

The volume of a rocket motor chamber in its relation to the amount of propellant to be reacted in unit time is measured by a number, called L*, which is defined as the ratio of the chamber volume in cubic inches to the exhaust-nozzle throat area in square inches. Since L* is proportional to the time the propellant spends in passing through the reaction chamber the minimum usable value for L* is, in part, a characteristic of the propellant. For nitromethane containing chromium acetylacetonate an L^* of roughly 300 in. is required at 300 psia. The minimum value required for L^* for nitromethane has been found to depend on factors such as the shape of the reaction chamber, the type, number, and location of the injectors, the injector pressure drop, the chamber pressure, and the presence or absence of potential catalysts such as the chromium acetylacetonate. Increasing the chamber pressure reduces somewhat the minimum L^* required for stable combustion of nitromethane.

For comparison, the L^* required for nitric acid - aniline at 300 psia is about 60 in., and it is not greatly dependent on chamber pressure. Although nitromethane requires an L^* about five times as great, this does not mean a motor chamber need be five times as great in linear dimensions, but more nearly only $\sqrt[3]{5}$ times as great.

Since nitromethane does not decompose spontaneously at ordinary temperatures, initial ignition devices are needed on the rocket motor. Four types have been used, some only on very small scale units:

(a) Electric spark + oxygen (air + spark fails).
(b) Hot oxygen from decomposing concentrated hydrogen-peroxide solutions.
(c) Hot catalyst bed or surface.
(d) Pilot ignitor (ballistite, etc.).

Of these (a) and (b) have proven very satisfactory. The ignition aid is needed only for a second or less while the chamber pressure rises to its normal operating value, after which the combustion is self-sustaining.

The higher nitroparaffins, such as nitroethane, do not contain sufficient oxygen to be useful monopropellants. Polynitroparaffins, such as dinitromethane, are generally much less stable than the mononitroparaffins and are not suitable as propellants or components of propellants.

The use of tetranitromethane as a component of propellants has frequently been suggested. By itself it would be a very poor propellant, but it could be considered as an oxygen source. It contains 65% of oxygen by weight and most of this would be available in combustion of a fuel. At present the material is obtainable only in very small research quantities.

The possibility of using tetranitromethane as a component of monopropellants has also been proposed. This is likely to be hazardous since it is well established that mixtures of tetranitromethane and hydrocarbons such as toluene are the most brisant explosives known. It has also been reported that addition of tetranitromethane to nitromethane sensitizes the latter with respect to the ease of inducing detonation.

All nitroarmoatics having the requisite oxygen balance are solids, and hence are not included in this report. They are familiar to us as high explosives such as TNT or picric acid.

Organic Nitrate or Nitrite Compounds.

A typical organic nitrate compound which is a possible monopropellant is the substance diethyleneglycol dinitrate (DEGN). Its calculated performance is practically equivalent to that calculated for nitromethane. The sensitivity of DEGN to detonation on impact is much greater than that of nitromethane as was mentioned in a previous section. The sensitivity to impact and the sensitivity to heat are common properties of the organic nitrates which render them too hazardous to be considered seriously as monopropellants or components of liquid propellants unless they are considerably diluted. In the latter event it is questionable whether they have any value. In a heat-sensitivity test performed at the Jet-Propulsion Laboratory, GALCIT, DEGN exploded violently and completely at 365°F compared to the milder and only partial explosions of nitromethane at 600 ± 50°F.

If DEGN were to be used as a monopropellant, an initial ignition system would be required as in the case of nitromethane. Because of the lower vapor pressure of DEGN the use of oxygen and an electric spark might not work, but other methods might be satisfactory.

The combustion of DEGN does not appear to differ in any major respect from that of nitromethane. Nitromethane containing DEGN (70:30 by weight) does not "burn" more smoothly than nitromethane alone, as shown by tests at Jet-Propulsion Laboratory, GALCIT. So far as is known no tests have been made with pure DEGN in this country, and only a limited amount of testing has been done in England. The latter tests showed little promise since there were frequent cases of flash-back resulting in explosion of the propellant tanks. In America DEGN is not normally produced in large quantities, but it could easily be made if it were found to have a propellant use.

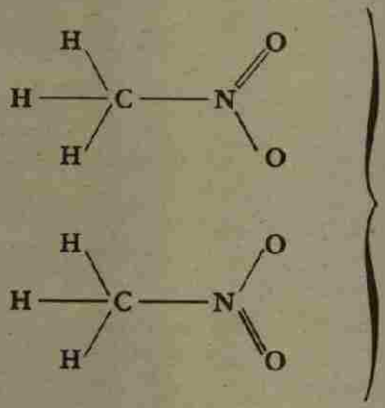
Another proposed nitrate-type propellant originating with the Germans, and tested somewhat by the British, are mixtures of methyl nitrate and methyl alcohol. The preferred composition tested by the Germans contained about 75% of methyl nitrate and 25% of methyl alcohol. This composition is close to the azeotropic composition, and was therefore easily manufactured by the continuous esterification-rectification process employed. A second and more important consideration for diluting with methyl alcohol was the necessity of reducing the sensitivity of the methyl nitrate to detonation by impact.

Pure methyl nitrate is also very sensitive to heat. According to a handbook the material explodes about 2°C above its normal boiling point of 65°C. Another source, the book on explosives written by Tenney L. Davis, states that the vapor explodes at 150°C (302°F). It is not reasonable to expect that dilution with methyl alcohol will significantly alter the susceptibility to thermal explosion. This conclusion with respect to thermal instability is supported by recent British experiences with small-scale test motors. In many cases flash-back explosions which destroyed the propellant tank occurred, notably at the end of the tests. In general these tests have had a duration not longer than five to seven seconds. These investigators appreciate the fact that the material is sensitive to heat and they were making no plans to cool the reaction chamber with the influent propellant.

The Germans designated this type of propellant by the name Myrol followed by a number expressing the weight percent of methyl nitrate. Thus pure methyl nitrate was called Myrol-100, or simply Myrol, and the mixture with methyl alcohol containing 75% of methyl nitrate was called Myrol-75. The results of German tests on Myrol-75 did not show great promise of developing the material as a propellant.

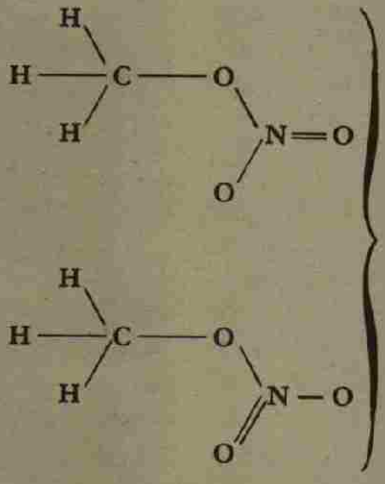
The material, Myrol-75, has several other disadvantages as compared to nitromethane. It has a higher vapor pressure, and this coupled with its greater inflammability confer upon it a great fire hazard. The density of the mixture is also much less than that of nitromethane. Furthermore the performance, on a weight basis, is less than that of nitromethane. The calculated jet velocity, found in the German documents, is 6385 ft/sec for $p_c = 235$ psia.

Of the organic nitrates only methyl nitrite enters into consideration. This material has the same empirical composition as nitromethane, but has a different molecular structure. For comparison, the structural formulas of the nitro, nitrate, and nitrite compounds are given below:



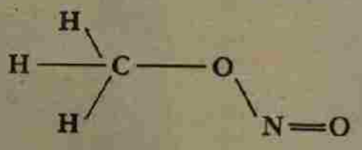
Principal
Structures
of
Resonance
Hybrid

Nitromethane



Principal
Structures
of
Resonance
Hybrid

Methyl Nitrate



Methyl Nitrite

It may be seen from these diagrams that the nitrite is similar to the nitrate and not to the nitro compound. The similarity of the nitrite and nitrate with respect to thermal instability and heat-induced explosion is, therefore, not surprising. The nitrite at ordinary pressure and temperature is, moreover, a gas. The propellant characteristics for the nitrite have not been calculated so far as is known, but they certainly cannot differ by more than a few percent from those of nitromethane. The material will in all probability never be used as a propellant because of its thermal instability and probable sensitivity to impact detonation when liquefied.

Organic Perchlorate Compounds.

A few organic perchlorates, such as ethyl perchlorate, have been prepared. They all exhibit great thermal instability and sensitivity to impact. These undesirable properties, as well as the absence of good preparative techniques, render them unsuitable as propellants, although the performance of ethyl perchlorate should be quite good.

Nitroalcohols and Their Nitrates.

The only nitroalcohols which are of potential interest as monopropellants are nitroethanol and bis-(hydroxymethyl)-nitromethane. However, both substances have a composition and structure such that they would be poor propellants. Moreover, no good method of synthesis and isolation of these substances exists or is likely to be found. This conclusion is based on the results of a several months' examination of the most promising method of synthesis at Jet-Propulsion Laboratory, GALCIT, and is in accord with a pricate communication from Professor Hass of Purdue University, a specialist in aliphatic nitro compounds.

Nitroethanol nitrate and similar compounds might slightly surpass nitromethane in performance, but it is doubtful that they could be manufactured in quantity or that they would be safe to use as propellants. They would, without doubt, possess all the undesirable properties of organic nitrates discussed in a previous section.

Hydrogen Peroxide.

The German military services made wide use of hydrogen peroxide as a propellant component. In several devices the material was used essentially as a monopropellant since in addition to this chemical only a much smaller amount of a catalytic agent, calcium permanganate, was used. The devices in which the Germans used hydrogen peroxide are (1) the rocket unit of the glider bomb Hs-293, (2) an assisted take-off unit for aircraft, (3) a launcher for the flying-bomb, V-1, and (4) the gas turbine used for driving the propellant pumps of the rocket bomb, V-2. In addition, there were other devices where the peroxide was used as the oxidizer component of bipropellants.

Hydrogen peroxide is not a high-performance monopropellant. The maximum calculated jet velocity for $p_c = 300$ psia is 4710 ft/sec, obtained for pure hydrogen peroxide. Dilution with water further diminishes this already low jet velocity. Thus, for an aqueous solution containing 87% by weight of peroxide and 13% by weight of water the corresponding calculated jet velocity is only 4065 ft/sec. It is known that the Germans used an 80% solution which had an even lower jet velocity, approximately 3700 ft/sec.

The great advantage of hydrogen peroxide is the fact that it produces rather low chamber temperatures which make possible the use of uncooled steel motors. Thus, the chamber temperature for 100% peroxide is 1252°K (1793°F), for 87% it is 931°K (1214°F), and for 80% it is even lower.

7-7-Bo

Apart from the problem of concentrating peroxide to nearly 100% concentration the fact that the Germans used a maximum concentration of only 80% indicates that they considered simplicity of motor design and use to be at least as important as high performance.

In order to cause the peroxide to decompose,

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 + \text{energy},$$

it was necessary to inject simultaneously an initiating fluid such as a concentrated calcium or sodium permanganate solution. The amount of initiating fluid is of the order of five percent of the amount of the peroxide solution, but the exact amount is not critical. The initiating fluid probably reacts with peroxide producing catalytic products as well as directly catalyzing the decomposition.

In experiments at Jet-Propulsion Laboratory, GALCIT, successful motor tests have been made in which the decomposition is caused to occur by means of a manganese-dioxide-impregnated alumina refractory placed in the motor chamber. This improvement promises to simplify the motor by eliminating the need for a permanganate system and will also simplify logistic requirements. Reports subsequently received from Germany indicate that the Germans had indeed developed such a system (used in the Me-163), not for the rocket motor but for a turbine unit. In the latter case the products of the permanganate solution would have formed an undesirable gritty slag prohibiting long-duration operation.

In a subsequent section peroxide will be discussed again as an oxidizer for bipropellants.

Miscellaneous Monopropellants.

A number of other materials have been suggested from time to time as monopropellants. So far as is known none have been developed to the point of usefulness, and indeed some have never been tested even in a preliminary way.

Hydroxylamine, NH_2OH, from purely energetic considerations, is a potential monopropellant of good calculated performance. The calculated jet velocity for $p_c = 300$ psia is 7104 ft/sec and the chamber temperature is 2090°K (3302°F). This is superior to nitromethane in so far as c is greater and T_c is lower. However, the thermal stability of hydroxylamine is low (explodes above 56°C), its availability is very poor, and its freezing point is high, 33°C (91°F). All these factors make it impractical to use.

Mixtures of benzene, nitric acid, and water, which are known as Dithekites, have been suggested as monopropellants. Dithekite 13 has an initial composition corresponding to

Nitric acid	72.2% by wt
Water	9.3% by wt
Benzene	15.5% by wt.

On standing, this mixture undoubtedly becomes a mixture of nitric acid, nitrobenzene, dinitrobenzene, and water. According to an OSRD report on explosives (OSRD Report No. 2014) the mixture flashes but does not ignite when dropped on a surface heated to 125°C (257°F). The performance of such a mixture as a propellant is not known, but it probably would not differ much from those of nitromethane or of nitric acid with aniline.

Diver's solution, ammonium nitrate dissolved in liquid ammonia, is an interesting possible monopropellant. In it the ammonium nitrate is an oxidizer component, and the ammonia a fuel component. The most interesting feature is the absence of carbon in the system. Depending on the composition chosen, the exhaust gas would contain principally nitrogen and steam, and either hydrogen or oxygen. Its calculated performance should be quite good, possibly exceeding that of nitromethane. So far as is known the mixture has never been used successfully.

BIPROPELLANTS

As mentioned earlier, propellants for which a fuel and an oxidizer are injected into the motor separately are called bipropellants. Since there are several good oxidizers and a very great number of possible fuels, there is an almost unlimited number of possible useful bipropellants. However, it is not necessary to consider each of these combinations separately as will be seen in the discussion to follow.

Oxidizers.

The principal liquid oxidizers which merit discussion are the following: (a) liquid oxygen, (b) nitric acid, (c) mixed acid (HNO_3 containing H_2SO_4), (d) liquid nitrogen dioxide (NO_2), (e) hydrogen peroxide, (f) tetranitromethane, (g) perchloric acid or soluble perchlorates, and (h) liquid halogens or their oxides. The first five of this list have been tested in America, some only to a very limited extent. The most highly developed propellants tested in this country use either nitric acid oxidizers or liquid oxygen. Of these two the latter has probably not been sufficiently emphasized thus far. Lately work with hydrogen peroxide has been started, first at Jet-Propulsion Laboratory, GALCIT, and a number of interesting propellants based on it have been tested successfully. The last three oxidizers have not been tested either here or abroad so far as is known.

If we exclude class (h) oxidizers for the moment, of those remaining, liquid oxygen is undoubtedly the best for carbonaceous fuels when the criterion of comparison is the maximum jet velocity obtainable. However, it can easily be shown that propellant performance is not limited by the particular oxidizer used if the oxidizer is used at its maxmimum effectiveness.

For a propellant using methyl alcohol as the fuel and 87% hydrogen peroxide as the oxidizer the maximum calculated jet velocity for $p_c = 300$ psia is 7200 ft/sec. If 100% hydrogen peroxide were used instead of the 87% concentration the calculated jet velocity would probably rise to about 7500 ft/sec or a little more. It is estimated that the maximum calculated jet velocity for methyl alcohol with liquid oxygen, at the same chamber pressure, would be 7700 ft/sec. These figures very strikingly show a low order of dependence of jet velocity on the nature of the oxidizer. The 87% peroxide contains only 41% of free oxygen, and has a heat of formation of 165.1 kcal/100 gm, whereas liquid oxygen is entirely free oxygen and at its normal boiling point has a heat of formation of only 9.6 kcal/100 gm. Even this extreme change in the nature of the oxidizer produces only a minor change in propellant performance.

It is evident from this comparison of an apparently poor oxidizer with a very good oxidizer that propellant performance is not limited solely by the nature of the oxidizer.

The limitation arises from another and more fundamental cause. Conventional fuel-oxidizer combinations derive their energy largely from the formation of water and carbon dioxide as combustion products. However, at the very high temperatures obtained in rocket motors these substances are not stable. Water, in part, decomposes or is otherwise removed from the combustion products by the reactions

$$2\,H_2O \longrightarrow H_2 + 2\,OH$$

$$H_2O \longrightarrow H_2 + O$$

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

$$N_2 + 2\,H_2O \longrightarrow 2\,H_2 + 2\,NO,$$

and the accumulation of hydrogen is removed by two other reactions

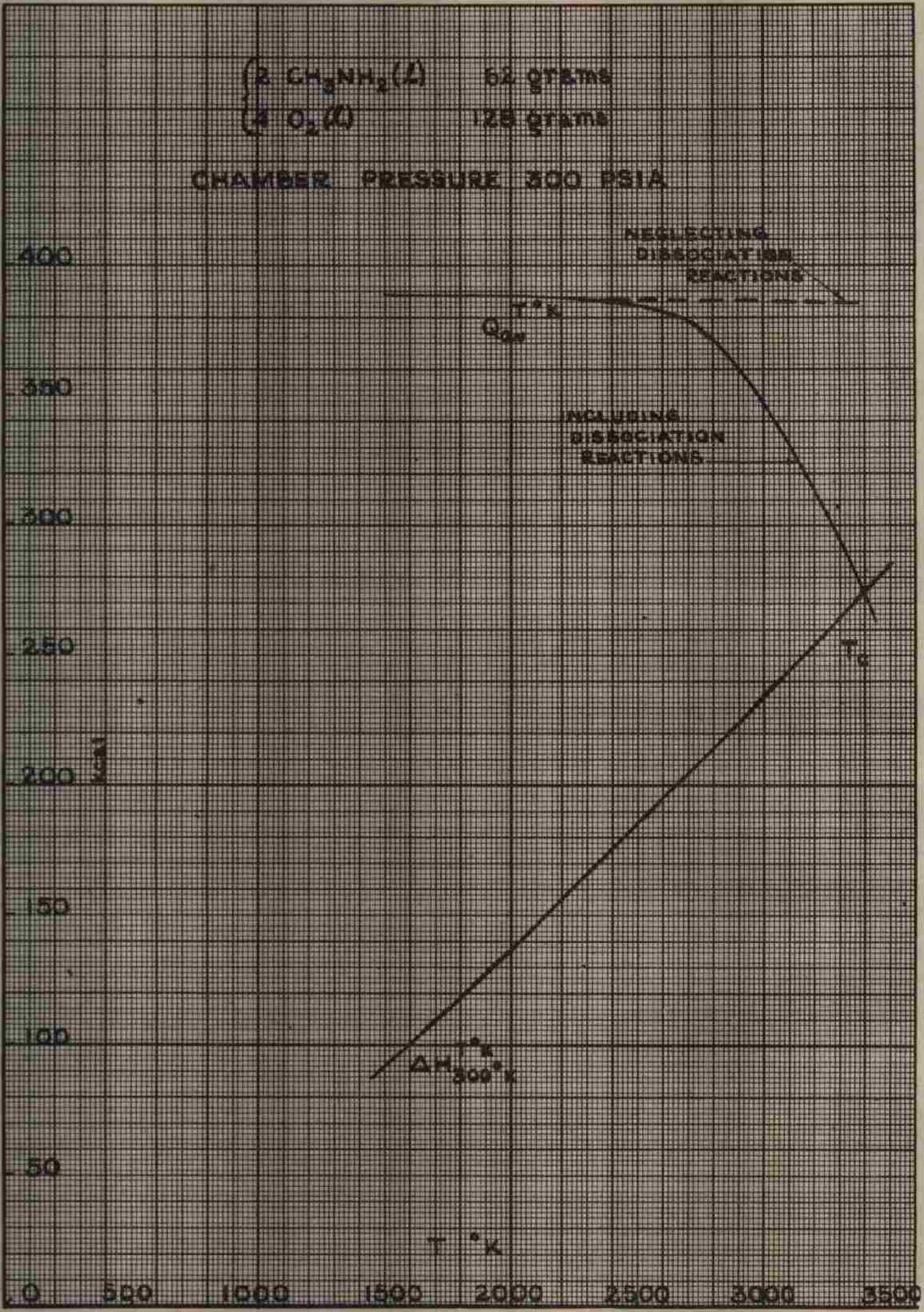
$$H_2 \longrightarrow 2\,H$$

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

The last reaction also removes carbon dioxide and converts it to carbon monoxide.

These reactions leading to dissociation products begin to be important near 2500°K (ca 4000°F), and their extent rises at an accelerating rate with a further increase in temperature. The net result is that these reactions, with their attendant large losses in the amount of energy released, limit the temperatures which can be attained in the combustion of carbon-hydrogen-oxygen systems to approximately 3400°K (5660°F) for a chamber pressure of 300 psia. Since increased pressure exerts only a minor inhibiting effect on these reactions, increasing the chamber pressure will not result in a significant change. It follows that this limit on maximum combustion temperatures for carbon-hydrogen-oxygen systems is essentially independent of the particular oxidizer and fuel used so long as the system derives its energy from carbon, hydrogen and oxygen. The presence of nitrogen in addition does not alter this conclusion since the nitrogen appears in the products almost entirely as N_2. The remainder is almost completely accounted for by the energy-absorbing reaction above which results in the formation of NO.

The effect of these limitations on energy release is shown in the curves of the accompanying figure. The curve labeled $Q_{av}^{T^\circ K}$ represents the heat available from the reaction when the products are in thermodynamic equilibrium at chamber pressure and at a temperature of T°K. The curve labeled $\Delta H\frac{T^\circ K}{300^\circ K}$ is the heat absorbed in heating this gas from 300°K to T°K. The intersection of these two curves determines the temperature of the gases in the combustion chamber, assuming no heat losses. The rapid decline of $Q_{av}^{T^\circ K}$ beginning at about 2500°K is the result of these dissociation reactions. If no dissociation occurred, the curve for $Q_{av}^{T^\circ K}$ would be almost straight and nearly horizontal, and in that case T_c would be nearly 4400°K (ca 7500°F) instead of 3393°K (5647°F). These curves and data also demonstrate the common fallacy


$2\ CH_3NH_2(l)$ 62 grams
$4\ O_2(l)$ 128 grams
CHAMBER PRESSURE 300 PSIA
NEGLECTING DISSOCIATION REACTIONS
$Q^{T°K}$
INCLUDING DISSOCIATION REACTIONS
T_c
$\Delta H^{T°K}_{300°K}$
kcal
400
350
300
250
200
150
100
50
0
500
1000
1500
2000
2500
3000
3500
T °K

of attempting to estimate rocket-propellant performances on the basis of the heat liberated on complete stoichiometric combustion of a fuel in oxygen.

The example shown is for a propellant consisting of two moles (62 gm) of liquid methylamine, CH_3NH_2, and four moles (128 gm) of liquid oxygen. If no dissociation reactions occurred the gas composition at 3400°K would be:

Hydrogen $^{n}H_2 = 0.306$ moles
Water $^{n}H_2O = 4.694$ moles
Carbon Monoxide $^{n}CO = 0.694$ moles
Carbon Dioxide $^{n}CO_2 = 1.306$ moles
Nitrogen $^{n}N_2 = 1.000$ moles

When all dissociation reactions of importance at this temperature are considered, the gas composition becomes:

Hydrogen $^{n}H_2 = 0.723$ moles
Water $^{n}H_2O = 3.837$ moles
Carbon Monoxide $^{n}CO = 1.214$ moles
Carbon Dioxide $^{n}CO_2 = 0.786$ moles
Nitrogen $^{n}N_2 = 0.952$ moles
Hydroxyl $^{n}OH = 0.618$ moles
Atomic Hydrogen $^{n}H = 0.262$ moles
Nitric Oxide $^{n}NO = 0.096$ moles
Oxygen $^{n}O_2 = 0.264$ moles
Atomic Oxygen $^{n}O = 0.135$ moles

It is to be noted that free oxygen is stable in the presence of unburned hydrogen and carbon monoxide at this temperature. The example presented is typical of the effect demonstrated.

Because of these fundamental limitations on carbon-hydrogen-oxygen systems, oxidizers of class (h) are listed. From purely energetic considerations they might show some value, in particular liquid fluorine, when used with noncarbonaceous fuels. As an example, we might consider the reaction of fluorine with hydrogen.

$$H_2 + F_2 \longrightarrow 2\,HF$$

The hydrogen fluoride formed liberates 3.2 kcal/gm, which happens to be the same as the energy released when a gram of water is formed from hydrogen and oxygen. However, the hydrogen fluoride is more stable at high temperatures than water and less energy is lost through dissociation. Hence, fluorine provides a sort of chemical limit for oxidizers.

The use of liquid fluorine as an oxidizer is at present completely impractical for a variety of reasons. This substance is toxic, and too, it is probably the most reactive chemical known, thereby causing severe handling difficulties. Hydrogen fluoride, the product of the reaction of fluorine with hydrogen, is in itself sufficiently toxic to have warranted considering it as a possible agent in chemical warfare. These objections could probably be met if the need were sufficiently great, particularly for use in missiles operated from a remote-control point.

Liquid ozone, O_3, has intentionally been omitted from the list of oxidizers since this material is exceedingly unstable. The liquid has been handled only in carefully cleaned glass, and contamination even with a few grains of dust has caused violent explosions. The normal boiling point of liquid ozone is $-112°C$ compared to $-183°C$ for liquid oxygen. In accordance with the previous discussion of oxidizers, it is evident that the use of liquid ozone would not cause any major improvement in propellant performance in spite of its negative heat of formation.

The fact that T_c is limited by virtue of the previously discussed dissociation reactions also limits propellant performance. This follows from the expression for c^* given in "Quantitative Characteristics of Propellants," page 84, and the relation between c and c^*.

Fuels.

A very great number of possible fuels are available for consideration for bipropellants. However, this multiplicity of choice is only apparent since they are all members of only a few general classes, the individual examples differing only in secondary details. These classes are (a) carbonaceous fuels, (b) noncarbonaceous fuels, and (c) metals or metal compounds. Combinations of members of two or more classes are of course possible but this in no way alters the discussion.

CARBONACEOUS FUELS. The carbonaceous fuels include substances such as hydrocarbons, alcohols, amines, acetylene-ammonia mixtures, etc. There is no reason to expect major differences between various carbonaceous fuels if the comparison is made with regard to the maximum attainable jet velocity. As an example, we can compare gasoline (octane) and ethyl alcohol, each used with liquid oxygen. At their optimum mixture ratios of fuel to oxidizer both propellants have almost identical calculated jet velocities (frozen composition), the difference amounting to less than one-half percent. To make the comparison more extreme, it appears that the maximum calculated jet velocity for liquid oxygen and methyl alcohol will differ from these by not more than abut one percent.

In this series the fuel has changed from C_8H_{18} to C_2H_5OH or to CH_3OH, from a completely unoxidized fuel to a fuel already substantially oxidized, with no significant change in performance. From this comparison it is clear that the nature of the fuel is not a major factor in limiting propellant performance. This evidence further supports the previous arguments which show that propellants are limited by product instability rather than poorness of the fuel or the oxidizer. By increasing the H-C ratio, e.g., methylamine, a slight increase in jet velocity results, but no major improvement can be expected. By increasing the H-C ratio the limiting temperature is achieved without having an unduly high-average molecular weight, $\overline{M}$, and hence the value of c^* shows a slight improvement. From these considerations it appears that fuels of class (a), when used with liquid oxygen, will have a maximum calculated jet velocity of about 8700 ft/sec ($I_{sp} = 270$ sec) for $p_c = 300$ psia. In an actual rocket motor the observed jet velocity would probably be about 90% of the calculated value.

Apart from these considerations based only on jet velocities there are other factors involved in choosing a fuel for a given oxidizer. One very important factor is the question of whether or not the fuel and oxidizer ignite spontaneously on mixing in the rocket motor. Thus two fuels may have equal merit as far as jet velocities and other properties are concerned, but if one ignites spontaneously with the oxidizer and the other does not the choice is obvious. The combination gasoline-nitric acid is not spontaneous and experiments with this mixture were discontinued for this reason. This combination was succeeded by aniline-nitric acid which does ignite spontaneously even at very low temperatures. Quite a large number of fuels are known which ignite spontaneously with various oxidizers. With nitric acid there are many, including aniline, xylidine, cyclohexylamine, aliphatic amines, unsaturated hydrocarbons, furfuryl alcohol, hydrazine, and others. With peroxide there are a smaller number, including hydrazine, thioglycolic acid, methyl alcohol containing thioglycolic acid and metal salts, methyl alcohol containing hydrazine with or without metal salts, and others.

Another consideration of practical importance is the relative proportion of fuel and oxidizer at the optimum jet velocity. This ratio varies from one fuel to another, and it may be a deciding factor in choosing between two equally good propellants. The weight ratio for liquid oxygen-gasoline corresponding to maximum jet velocity is 2.5, whereas for liquid oxygen-ethyl alcohol the weight ratio is 1.5. In the latter case the fuel comprises a larger weight fraction of the total propellant. If the rocket motor is to be cooled by the influent fuel, as in V-2, the choice of alcohol rather than gasoline is self-evident, other factors such as price, availability, etc., being equal.

From this discussion it may be concluded that the choice of a carbonaceous fuel is not determined primarily by the maximum attainable jet velocity, which is almost the same for all such fuels, but rather the choice is determined primarily by secondary characteristics of the kinds mentioned. The same argument does not apply to the choice of a fuel for other jet-engine devices, since for these devices high-temperature dissociation is of minor importance.

The most highly developed propellants using carbonaceous fuels are (1) aniline with nitric acid, (2) alcohol with liquid oxygen, (3) methyl alcohol with hydrogen peroxide, (4) methyl alcohol - hydrazine hydrate with hydrogen peroxide, (5) nitromethane-methyl alcohol with hydrogen peroxide, and (6) furfuryl alcohol with nitric acid.

The first of these has been highly developed in America and was also examined extensively in Germany. Other amines may be substituted in whole or part for the aniline and the combination still shows spontaneous ignition. It is interesting to note that in this country interest in this type of propellant was decreasing, largely because of objections on the part of our military services, until it was learned that the Germans were beginning to prefer this type rather than the liquid-oxygen type.

The second type was a German development and is best exemplified by its use in the V-2 rocket as well as in other rocket devices used for a variety of purposes.

The third type has been tested in America in motors up to 200-lb thrust. It was undoubtedly considered by the Germans but probably was not used in any applications. The fourth type was used by the Germans in the Me-163B, a rocket-propelled interceptor. It was the apparent original intention of using hydrazine hydrate with hydrogen peroxide, a mixture which ignites spontaneously, but the shortage of hydrazine made the use of a diluent necessary. The mixture actually employed was also spontaneously ignitable with peroxide particularly if a minute amount of a heavy-metal catalyst is included in the fuel.

The fifth type is the result of an effort to use a desensitized form of nitromethane as the major part of a propellant. When methyl alcohol is used as the desensitizer the oxygen balance is seriously disturbed so that a satisfactory monopropellant is no longer obtained. If this oxygen deficiency is made up by an oxidizer, in this case hydrogen peroxide, a suitable jet velocity can be obtained. This propellant is an American development and has been tested in motors having up to 200-lb thrust.

The sixth type, furfuryl alcohol with nitric acid, has been tested in this country only very recently. It was known for several years that this combination was spontaneously ignitable, but nothing was done with this propellant until the trend of German developments became known. This probably is a result of the interest in short-time developments and the lack of encouragement of longer-range research on propellants in this country. After the very detailed German test data become available this combination was tested here and has been found to be superior to acid-aniline in many respects. The ignition lag is shorter, less concentrated nitric acid can be used, the fuel has a much lower freezing point, the fuel density is greater, the fuel is far less toxic, and the ignition lag is not appreciably effected if moderate amounts of water are placed in either or both of the components. Another advantage is the favorable mixture ratio at the optimum jet velocity. For furfuryl alcohol and white fuming nitric acid the optimum ratio of fuel to oxidizer is about 1 to 2.3; for aniline and red fuming nitric acid the optimum ratio is about 1 to 2.9. The former pair, therefore, has available a larger proportion of the propellants to use as coolant for a fuel-cooled rocket motor.

NONCARBONACEOUS FUELS. There are three good examples of noncarbonaceous fuels. These are hydrogen, hydrazine, and ammonia. The main advantage to be gained from using these fuels is a low-average molecular weight of combustion products. From the previous discussion of c^* it was seen that the jet velocity of a propellant is largely determined by the ratio $T_c/\overline{M}$, where $\overline{M}$ is the average molecular weight of propellant gas. Thus, for a given T_c a better propellant results if this also corresponds to a low value of $\overline{M}$. Such a circumstance is possible for noncarbonaceous fuels.

The highest jet velocity calculated to date for chemical systems is for a propellant consisting of liquid hydrogen and liquid oxygen. The maximum calculated jet velocity is approximately 11,000 ft/sec for $p_c = 300$ psia. This corresponds to a specific impulse of approximately 340 sec. However, because of the very low density of liquid hydrogen (sp.g. = 0.07) as well as other undesirable properties this combination cannot be considered practical by present standards. The low density of liquid hydrogen will make pumping a very great problem if centrifugal pumps are contemplated.

The possible poorness of this propellant is apparent if we adopt an additional figure of merit for propellants which includes a factor dependent on the mean density of the propellant. This is of great importance since for some applications of rockets the volume of the propellant is of greater concern than the weight of propellant. Thus, the increase in weight of the propellant container and associated structures may outweigh the potential decrease in the weight of propellant required.

The ordinary specific impulse, I_{sp}, has the dimension of time, i.e., seconds, which is equivalent to (lb) (sec)/(lb) or (kg) (sec)/(kg). If we use the latter and multiply by the density in kg/liter (which is essentially equal numerically to the specific gravity), we have

$$I\rho = I_{sp} \times \rho = \frac{(\text{kg})\,(\text{sec})}{(\text{kg})} \times \frac{(\text{kg})}{(\text{liter})} = \frac{(\text{kg})\,(\text{sec})}{(\text{liter})},$$

a specific impulse on a volume basis. We see that if two propellants have the same value of I_{sp} that which has the greater density will have the greater value of $I\rho$. If we use this system for the hydrogen-oxygen propellant, we find $I\rho$ is 84 kg sec/liter when I_{sp} is a maximum. For nitromethane $I\rho$ is 246 and for nitric acid-aniline $I\rho$ is 305 at) maximum I_{sp}). If the two components of the propellant have equal densities the mixture ratio for maximum I_{sp} will also be correct for maximum $I\rho$. If the densities differ greatly the mixture ratios corresponding to maximum $I\rho$ and to maximum I_{sp} will not be the same, but this will not alter the essential conclusion (above) regarding hydrogen as a fuel.

In spite of these objections to this propellant, the calculation has served a useful purpose in establishing a limit of fuel performance for rockets. The importance of $T_c/\overline{M}$ in getting a high I_{sp} is also strikingly apparent. For hydrogen-oxygen, at maximum I_{sp}, $T_c/\overline{M}$ is about 270°K moles/gm; for nitromethane the value is 121°K moles/gm.

Hydrazine, N_2H_4, is a fuel which shows great promise provided an adequate manufacturing process can be devised. Of all the fuels considered for rockets, excluding hydrogen, hydrazine produces the highest jet velocity. Two factors contribute to its high performance. First, hydrazine contains no carbon and it therefore follows that low molecular weight combustion products can be formed. Second, hydrazine is endothermic, i.e., it can release energy on decomposing into its elements in their normal state. Thus, the reaction

$$N_2H_4(\text{liq}) \longrightarrow N_2\ (\text{gas}) + 2\ H_2\ (\text{gas})$$

would liberate 12.05 kcal/32 gm. If the decomposition occurred as written, this reaction would result in a specific impulse of approximately 168 sec with a chamber temperature of 855°K (1080°F); this would be a monopropellant involving no oxygen. If an oxidizer is used higher temperatures and higher performance results. For the hypothetical case above $\overline{M}$ is 10.7 gm/mole, about half the value for usual propellants, and $T_c/\overline{M}$ has the value 80°K moles/gm.

If liquid oxygen is chosen as the oxidizer, the maximum calculated jet velocity is about 8500 ft/sec (mean of frozen and equilibrium results) for $p_c = 300$ psia. For the combination resulting in optimum jet velocity $T_c/\overline{M}$ is 176°K moles/gm compared with 121°K moles/gm for nitromethane.

The known physical and chemical properties of hydrazine do not indicate that any insurmountable obstacles would bar its use as a fuel for rockets. Since the first drafting of this report the fact has become known that the Germans used hydrazine as a fuel component of propellants with hydrogen peroxide as the oxidizer. Recently at Jet-Propulsion Laboratory, GALCIT, hydrazine (anhydrous) has been successfully operated in a small rocket motor with oxygen and also with hydrogen peroxide. With oxygen, ignition was achieved using an electric spark; with peroxide, ignition is spontaneous. Hydrazine hydrate (100%) has also been tested successfully with peroxide, again with spontaneous ignition. These tests gave results which were found to be in satisfactory agreement with the predictions.

The density of hydrazine is quite favorable; it is about 1-2% more dense than water. Its stability to heat (of interest in operating fuel-cooled rocket motors) appears to be satisfactory on the basis of indirect evidence. Its critical constants have been measured, and its vapor pressure at high temperatures has been determined. This is good presumptive evidence that hydrazine is not particularly sensitive to heat decomposition, and could probably be used to cool the rocket motor. The mixture ratio of fuel to oxidizer is also very favorable, from 1:1 to 4:1 with liquid oxygen compared with 1:1.5 for alcohol - liquid oxygen or 1:2.5 for gasoline - liquid oxygen. Thus the larger part of the propellant is the fuel when hydrazine is used in contrast with the other fuels where the reverse is true.

The satisfactory density of the fuel together with the high jet velocities which are calculated, result in very favorable values of I_ρ (287) as well as high I_{sp}. This makes the hydrazine-oxygen or the hydrazine - nitric acid combination very well suited for use in missiles where both the weight and volume of propellant are important. The calculation for hydrazine - nitric acid has not been made yet but the results should be very good. Other systems of interest are hydrazine - liquid NO_2, and hydrazine - hydrogen peroxide. Anhydrous hydrazine ignites spontaneously with nitric acid, liquid NO_2, and hydrogen peroxide. It also ignites in air (or oxygen) if certain metal oxide catalysts are present as has been shown in recent tests at Jet-Propulsion Laboratory, GALCIT.

If liquid flourine can ever be used as a liquid oxidizer with hydrazine a very effective propellant should result. The maximum calculated jet velocity for this pair is near 10,000 ft/sec for $p_c = 300$ psia. Moreover, such a combination would have a satisfactory density and I_ρ would be approximately 340.

Another example of a noncarbonaceous fuel is afforded by ammonia. With liquid oxygen its performance would be poorer than that for hydrazine, and only slightly better than that for gasoline. Its low density, toxicity, low boiling point, as well as its price compared with other common fuels, do not indicate any great advantages if high rocket performance is sought. If the goal is to obtain hot gases for running turbines or other devices it has some virtue. At Jet-Propulsion Laboratory, GALCIT, an ordinary laboratory ammonium-hydroxide solution has been successfully used as a fuel with hydrogen peroxide. Such a combination would not constitute a high performance propellant, but its simplicity and low chamber temperature are factors to make further tests desirable.

METALS OR METALLIC COMPOUNDS AS FUELS. The possibility of using metals or metal compounds as a part of the fuel for rockets is suggested by the large heats of combustion of metals. In the discussion of carbonaceous fuels we have seen that carbon is never fully oxidized to CO_2 at the termpatures associated with high-performance propellants. If carbon were oxidized to CO_2 each gram atom of oxygen used would liberate 47 kcal of energy. Actually the oxidation in most cases proceeds only somewhat past the CO stage in which each gram atom of oxygen liberates only 27 kcal. On the other hand if a metal, aluminum for example, were oxidized to Al_2O_3 (solid or gas), the energy per gram atom of oxygen would be about 126 kcal. A large part of this energy is crystal lattice energy which would not be released if the metal oxide appeared as a vapor in the rocket motor. Such would be the case if the reaction temperature exceeded some temperature determined by propellant composition and the vapor pressure of the metal oxide. If Al_2O_3 formed as a vapor rather than the solid form only 86 kcal/gm atom of oxygen would result.

In an early part of this report it was pointed out that the mere release of energy does not produce a propellant, since a gaseous medium or working substance is also required. It follows that the utility of including a metal fuel in a propellant is not self-evident and must be invesitgated in further detail. It is not possible to make predictions for such fuels with the same degree of reliability as for more conventional examples. This inability arises from a lack of reliable knowledge of the high-temperature thermodynamics of metal compounds. There is, for example, no assurance that Al_2O_3 would be a stable combustion product at high temperatures in the presence of reducing agents, such as H_2 or CO, which are common components of rocket gases.

An example of a liquid fuel of the sort under discussion is provided by aluminum trimethyl, $Al_2(CH_3)_6$. This substance, still somewhat of a chemical curiosity, has the property of igniting spontaneously in air. This is both an advantage and a disadvantage; it makes for easy ignition in a rocket motor, but adds hazard to handling operations. The material might find use when used in conjunction with other fuels such as gasoline or other conventional examples.

Inadequate thermodynamic data are available for calculating the optimum performance characteristics of aluminum trimethyl with an oxidizer such as liquid oxygen. However, a few calculations have been made for propellants in which the aluminum compound was considered to be used along with another fuel, liquid ammonia, and for which liquid oxygen was the oxidizer.

In these calculations it was assumed that the heat of formation of aluminum trimethyl was zero. The calculations are insensitive to reasonable variations in this quantity, and no significant error is introduced by this reasonable assumption. The compositions examined were adjusted so that T_c was close to 2500°K. Even at this temperature, some extrapolation of the available thermal data for Al_2O_3 was required. It was also assumed that the aluminum was oxidized to solid Al_2O_3, with the remainder of the system in thermodynamic equilibrium. The results for these systems are not appreciably better than for ammonia-oxygen systems which have the same chamber temperatures.

A propellant with the following composition,

$\left[Al(CH_3)_3\right]_2$	21% by wt
NH_3	37% by wt
O_2	42% by wt,

has a calculated specific impulse of 240 sec with a chamber temperature of 2257°K (3600°F). The following ammoni-oxygen combination has the same chamber temperature and a specific impulse of 235 sec:

NH_3	54% by wt
O_2	46% by wt

Other pairs are the following:

$\left[Al\ (CH_3)_3\right]_2$	19% by wt
NH_3	34% by wt
O_2	47% by wt
T_c	2630°K
I_{sp}	251 sec

compared with

NH_3	50% by wt
O_2	50% by wt
T_c	2630°K
I_{sp}	246 sec

and

$\left[Al\ (CH_3)_3\right]_2$	31% by wt
NH_3	29% by wt
O_2	40% by wt
T_c	2320°K
I_{sp}	243 sec

compared with

NH_3	53% by wt
O_2	47% by wt
T_c	2320°K
I_{sp}	236 sec

Compounds of this sort probably could never compete economically with fuels, such as gasoline or alcohol, particularly since the results above show no great gain in performance when the metal compound is included.

Other possible metal-type fuels are the borohydrides, particularly $Al\ (BH_4)_3$. This is indeed a remote possibility, since at present, the production even of small research quantities is a great problem. This material is also said to ignite spontaneously in air. The nature of the combustion products is very obscure; it is not known whether the aluminum and boron would form separate oxides, combined oxides, or compounds such as an aluminum boride.

CONCLUSIONS

Arguments have been presented in previous sections showing that present rocket propellants are very near to the maximum performance which can be expected from chemical systems. For the monopropellants (propellants consisting of a single fluid), the barrier to using systems of higher energy is mainly the increasing sensitivity to detonation either by heat or by shock. A successful monopropellant is really nothing more than a controllable liquid explosive whose sensitivity to explosion is considered to be low enough to permit safe handling. Thus, nitromethane and hydrogen peroxide are each considered to be relatively safe to use as monopropellants whereas nitroglycerine is not.

In the case of the bipropellants (systems employing a separate fuel and a separate oxidizer), the limit arises from the instability of the combustion products at high temperatures. Since this limit arises from properties of the products rather than of the reactants, it is not surprising that wide variations in the nature of the fuel or of the oxidizer can be made with only minor changes in the effective jet velocity. Examples illustrating this behavior were presented. These remarks apply with particular emphasis to systems using carbonaceous fuels.

Another class of fuels (those not containing carbon) was examined and one example, hydrazine, was found to have particular merit. Fuels of this class are capable of high rocket performance because they produce combustion products of somewhat lower average molecular weight than carbonaceous fuels. Of the examples cited hydrazine is most deserving of future development. The principal barrier to its immediate use is its present high cost. This cost is high in part because of the very small amount normally produced in this country.

In the discussion of oxidizers it was shown that there is not a great difference between the various possible substances available. Liquid oxygen is slightly superior to nitric acid or hydrogen peroxide, but the margin of superiority is small. All of the possible chemicals which can serve as oxidizers have one or more undesirable properties, and the choice is in part one of selecting the least undesirable one for each particular application. Liquid oxygen is difficult to store and transport without large losses; nitric acid is highly corrosive to most metals and causes severe burns; hydrogen peroxide must be stored and handled under conditions of extreme cleanliness, and can also cause burns which are less severe than nitric acid burns. There is little prospect of finding any other oxidizer which does not have more objections. One of the liquefied halogens, liquid fluorine, was mentioned because it would result in higher jet velocities when used with noncarbonaceous fuels. However, this chemical possesses hazards many times greater than those of the other chemicals just listed, and probably will never be used.

These facts are too little appreciated by those branches of the services most interested in rocket devices. The gains in rocketry will be largely a result of many small improvements and the various possible avenues of betterment should be all explored. One direction of possible improvement is a careful examination of the combustion process and its dependence on the geometry of the reaction chamber, so as to insure full use of the available energy. The brilliant luminosity of the jet from a nitric acid - aniline motor, without much doubt, indicates the presence of solid carbon in the exhaust. This fuel should be burned in the motor. Another direction for development is a more widespread experimentation with liquid oxygen, the best of the safer oxidizers. A wider variety of fuels should also be examined. Much useful information concerning ignition characteristics, etc., can be obtained with little expenditure of effort. Only very improvised tests of this sort have been done in this country and these tests have little quantitive significance. In contrast to this, the Germans made precise measurements on a very great number of fuels for use either with nitric acid or with hydrogen peroxide. Thus the Germans discovered the beneficial effect of small amounts of iron in nitric acid in promoting ignition. In this country nitric acid which was found to contain metals arising from storage drums was arbitrarily declared unsuitable for propellant use.

The German propellant chemists developed solid catalyst surfaces, notably for hydrogen peroxide, which were stacked in the reaction chamber. Such a device was used to provide hot gases for driving a turbine in the Me-163. In this country the idea of using solid catalysts in a reaction chamber was not acceptable to rocket engineers. The use of combustion catalysts deserves further study.

Since the first drafting of this report, the release of a part of the energy of atomic nuclei has been achieved on a large scale. The advent of muclear power, if it may be said to be here, does not imply rockets of unlimited performance. While it is true that nuclear reactions have an energy release of the order of a million times as great as chemical reactions, this does not imply that rockets are better than present ones by the same ratio. A simple calculation will show that this is not to be expected. If we assume a conventional rocket based on the usual adiabatic expansion process, this rocket requires a source of energy and a working fluid. If we further assume that this energy source has no weight and we choose hydrogen (which has the lowest molecular weight of the fixed gases), and in addition choose a value of the chamber temperature comparable to present practice, we do not find improvement by even an order of magnitude. Thus, for hydrogen expanding adiabatically from 300 psia and 2500°K to 14.69 psia the jet velocity would be 21,600 ft/sec. This is only about 2.5 times the value which might be obtained from the better chemical systems. For other devices, such as ramjet, etc., the gain would be more nearly that expected intuitively since these devices would not need to transport their working fluid.

The table at the end of this report lists some representative examples of the various types of chemical propellants. For the bipropellants the fuel component is indicated by the letter (a) and the oxidizer by the letter (b). The performance data are given for compositions yielding the maximum jet velocity for each system. For the hydrazine-oxygen and hydrazine-fluorine systems less favorable mixture ratios are also given, because even at these less favorable compositions they roughly match the optimum performance of other more common propellants.

The letter (e) following a number in the table signifies that the products of combustion are assumed to remain in thermodynamic equilibrium; the letter (f) signifies that the composition is assumed to be frozen at chamber conditions. When no letter follows the number, the two assumptions lead to equivalent results.

Propellant	Wt%	Ref	c ft/sec	I_{sp} sec	c* ft/sec	T_c °K	T_c °F	Iρ kg sec liter	p_c/p_e	p_c psia
MONOPROPELLANTS										
Nitromethane	100	1	7008	217.9	5020	2450	3950	246	20.4	300
Nitromethane	100	1	7546	236.6	5020	2455	3960	268	40.8	600
Diethyleneglycol Dinitrate	100	2	6865	213.1	4895	2521	4078	294	20.4	300
Hydrogen Peroxide	100	2	4710	146.3	3260	1252	1794	212	20.4	300
{Hydrogen Peroxide {Water	87 13	2	4065	126.3	2950	931	1216	176	20.4	300
BIPROPELLANTS										
(a) Hydrazine (b) Liquid Oxygen	50 50	3	8720 e 8285 f	270 e 257 f	6280 e 5910 f	3283	5449	290 e 276 f	20.4	300
(a) Hydrazine (b) Liquid Oxygen	80 20	3	7620	237	5460	1970	3085	245	20.4	300
(a) Methylamine (b) Liquid Oxygen	32.6 67.4	7	8605 e 8100 f	267 e 251 f	6040 e 5765 f	3393	5647	250 e 236 f	20.4	300
(a) Ethyl Alcohol (b) Liquid Oxygen	40 60	4	7830 f	243.5 f	......	3180	5260	236 f	20.4	300
(a) Gasoline (b) Liquid Oxygen	29 71	4.6	7780 f	242 f	5527 f	3294	5470	234 f	20.4	300
(a) Liquid Ammonia (b) Liquid Oxygen	41.5 58.5	7	8220 e 8000 f	255 e 248 f	5980 e 5700 f	3006	4950	212 e 206 f	20.4	300
(Liquid Ammonia 79.8)	40	7	8640 e	268 e	......	3270	5462	241 e	20.4	300
(a) (Liquid Acetylene 20.2) (b) Liquid Oxygen	 60		8280 f	257 f	......			232 f		

Propellant	Wt%	Ref	c ft/sec	I_{sp} sec	c^* ft/sec	T_c		$I\rho$ kg sec liter	p_c/p_e	p_c psia
						°K	°F			
BIPROPELLANTS (Cont)										
(a) Methyl Alcohol (b) (Hydrogen Peroxide 87) (Water 13)	21.4 78.6	2	7140	222.0	5130	2543	4117	265	20.4	300
(a) Aniline (b) Red Fuming Nitric Acid — 15% NO_2	25 75	5	7091 f	220.5 f	5015 f	3070	5065	305 f	21.3	300
(a) Aniline (b) Red Fuming Nitric Acid — 15% NO_2	25 75	5	7694 f	239.2 f	5062 f	3118	5150	331 f	42.6	600
(a) Hydrazine (b) Liquid Fluorine	77 23	7	7830	243	5690	2075	3275	251	20.4	300
(a) Hydrazine (b) Liquid Fluorine	31 69	7	9980 e	310 e	......	4000	6700	334 e	20.4	300

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PART V

POSSIBILITIES OF ATOMIC FUELS FOR AIRCRAFT PROPULSION POWER PLANTS

By

HSUE-SHEN TSIEN

PART V

POSSIBILITIES OF ATOMIC FUELS FOR AIRCRAFT PROPULSION POWER PLANTS

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INTRODUCTION

Since the success of the atomic bomb, the possibility of the use of atomic energy in power plants is a much discussed subject. However, in the information now available outside of the atomic bomb project, there seems to be no adequate analysis comparing atomic fuels with conventional molecular fuels for aircraft application. This report is an attempt to offer such an analysis. Of course, since the great volume of data and studies made for the bomb project is not available, the analysis has to be based upon results published before the secrecy regulation on nuclear phenomena was in effect. On the other hand, the general principles of nuclear reactions were well understood before 1940, and it is known that no essentially new phenomena have been discovered since that time. Therefore, the results of the following analysis should be essentially correct, especially if the interest is not on a definite quantitative answer, but rather on the qualitative conclusion as to likely directions of research and development on atomic fuels for aircraft power plants.

CHARACTERISTICS OF POSSIBLE ATOMIC FUELS FOR POWER GENERATION

The binding energy between the electrons in the outer shell and the nucleus of an atom is generally of the order of a few electron-volts per electron. But the binding energy between the protons and the neutrons in the atomic nuclei themselves is of the order of a few million electron-volts per nuclear particle. Any molecular reaction, such as combustion of hydrocarbon fuels with air, involves a rearrangement of electrons in the outer shells of the reacting atoms, while any nuclear reaction, such as fission, involves a rearrangement of the nuclear particles. Therefore, the energy involved in a molecular reaction should be of the order of a few electron-volts per process, while that of a nuclear reaction should be of the order of a few million electron-volts per process. In other words, the nuclear reactions should have an energy release or heat value about a million times that of conventional fuels. Experimentally, this is found to be true. For instance, the published measured value[*] of the energy release of fission of uranium-235 is 177 million electron-volts per process. By converting into engineering units, the heat value of U^{235} is 3.120×10^{10} BTU/lb. Even a much lower energy atomic fuel, such as polonium-210, which decomposes into lead-206 and alpha particles, gives a heat value of 3.30×10^{8} BTU/lb. The heat value of gasoline is only 1.87×10^{4} BTU/lb.

Such an enormous increase in the heat value would mean that in all engineering practice the "fuel" consumption would be reduced to a negligibly small quantity and the range of an atomically powered aircraft would be almost infinite. This, however, does not mean that atomic fuels will be used for all aircraft and missiles, even excluding the economical aspect of the problem. The key of the situation is the rate of energy release, a consideration necessitated by the ever-present importance of the weight of the fuel to be carried in the aircraft. For a given type of power plant, if atomic fuel is to be used in place of the conventional fuel, the atomic fuel must release heat at the same rate as the conventional fuel it replaces. If the rate of heat release per pound of the atomic fuel is small, large mass or weight of the atomic fuel is necessary to supply the required total rate. Then, for short-duration operation, the conventional fuel might give a smaller weight of fuel to be carried than that of the atomic fuel. In these cases, the atomic fuel should not be used.

What is, then, the rate of energy release for atomic fuel?

The simplest nuclear reactions are those of natural radioactivity. These reactions are not controllable and the rates are determined by the intrinsic structure of the decomposing atoms. For instance, the element polonium-210[†] decomposes by emitting alpha particles, with total energy generation of 3.30×10^{8} BTU/lb, and a half life of 136 days. The average initial rate of energy release is 5.06×10^{4} BTU/hr/lb. The lack of controllability of this atomic fuel is, however, a disadvantage, because high wastage will be inevitable during the handling of the fuel. On the other hand, the fact that the fuel emits only alpha particles, which are easily absorbed, is a great advantage in not requiring heavy shielding for the pilot and other human occupants of the aircraft. To transfer the heat from the material to the working fluid, we can use sheets of polonium placed parallel to the fluid flow and constructed so as to give enough surface for this purpose.

The other type of nuclear reaction possible for energy generation is the chain reaction of nuclear fission. The reaction rate of this type of reaction can be controlled by artificial means, such as inserting sheets or bars of neutron-absorbing materials

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[*] Henderson, M. C., "The Heat of Fission of Uranium," *Physical Review*, vol. 58, pp. 774–780 (1940).

[†] Polonium-210 can be manufactured from bismuth by using the neutron source in a uranium pile, according to the following equation:

$$ {}_{83}Bi^{209} + {}_{0}n^{1} \longrightarrow {}_{83}Bi^{210} \xrightarrow{\qquad\qquad} {}_{84}Po^{210} + {}_{-1}e^{0} \qquad (1)$$

This fuel was first suggested to the author by Dr. G. Gamow of the George Washington University, Washington, D. C.

into the reacting chamber. High reaction rates can be secured. In fact, the atomic bomb is the extreme example. For power generation, the rate need not be as high as that in the bomb explosion, and for safety, the rate should not be too high. The material can be used, here again, as sheets parallel to the fluid flow in the reacting chamber. Here two factors for efficient reaction must be considered in the design: (1) the critical overall dimension of the reacting chamber and (2) the necessary thickness of the sheets. In the absence of accurate data and calculations, we may assume that the total mass of the reacting material must be greater than that corresponding to a cube of 10 cm. The free path of a neutron in pure fissionable material is approximately 10 cm. If U^{235} is used, the minimum total mass for continuous reaction will then be 40 lb. To calculate the heat-release rate that could be reached in such a reacting chamber, we assume that the surface heat transfer rate is 1 BTU/sec/sq/in.* and the thickness of the sheet is 1/2 cm. Then the rate of heat release is 5.44×10^4 BTU/hr/lb.

The preceding discussion shows that while the rate of radioactive decomposition cannot be controlled, but depends upon the material itself, the rate of the fission chain reaction process can be regulated according to design. The two cases considered both give a rate of heat release of approximately 5×10^4 BTU/hr/lb of atomic fuel. By using this value as the probable rate of heat release, the feasibility of atomic fuel for aircraft propulsion can be estimated.

FEASIBILITY OF ATOMIC FUELS FOR THERMAL JET POWER PLANTS

For the thermal-jet engine, such as the ramjet or turbojet, the combustion chamber can be replaced by the nuclear reacting chamber mentioned in the previous section If the thermal jet has a specific fuel consumption of s pounds of gasoline per hour per pound of thrust, then, since the lower heat value of gasoline is 18,700 BTU/lb for 1 lb of thrust, a heat rate of 18,700 s BTU/hr is required. The necessary mass of atomic fuel is then

$$\frac{18{,}700\ s}{5 \times 10^4}\ \text{lb.} \tag{2}$$

where 5×10^4 is the heat rate in BTU per hour for 1 lb of atomic fuel, as calculated previously. The operating duration, t, for equal weights of atomic fuel and gasoline is then given by the equation

$$\frac{18{,}700\ s}{5 \times 10^4} = st \tag{3}$$

or

$$t = \frac{18{,}700}{5 \times 10^4}\ \text{hr} = 22.4\ \text{min.} \tag{4}$$

Therefore, if the operating duration is longer than 22 minutes, it is more advantageous, from the pure weight point of view, to use atomic fuel than to use gasoline.

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* This value corresponds very closely to the heat-transfer rate to the walls of a rocket motor.

Then it seems the first application of atomic fuels will be for long-duration engines, such as turbopropellers and turbojets. Ramjets generally operate for short duration. The use of atomic energy, then, seems less probable until the rate of heat release of atomic fuels can be increased from the preceding estimated value. Of course, here the economic aspect of the problem is not considered at all. The fact that, according to the preceding calculation, a 1000-lb thrust turbojet would require approximately 300 lb of atomic fuel, must be noted. If the cost of atomic fuel is very high, its application will not be feasible except for aircraft of extremely long range.

FEASIBILITY OF ATOMIC FUELS FOR ROCKETS

The investigation of the feasibility of atomic fuels for rockets is complicated by the necessity of supplying the working fluid. For the calculation, we assume the chamber pressure and chamber temperature in the atomic rocket to be 40 atm and 5000°R. Then the discharge velocity, c, of the rocket can be calculated by assuming isentropic expansion from the chamber conditions. Thus

$$c = 10^4 \sqrt{\frac{\delta}{\delta-1} \frac{4.96}{m} \left[1 - \left(\frac{1}{40}\right) \frac{\delta-1}{\delta}\right]} \qquad (5)$$

where m is the molecular weight of the working fluid and δ is the ratio of specific heats. First, we consider hydrogen as a working fluid. Then $m = 2$, $\delta = 1.4$; then the discharge velocity is

$$c = 23{,}800 \text{ ft/sec}$$

The specific consumption is then 4.87 lb/hr/lb-thrust.

By using helium with $m = 4$ and $\delta = 5/3$, as a working fluid, under the same chamber conditions, the discharge velocity is

$$c = 15{,}000 \text{ ft/sec}$$

The specific consumption is then 7.48 lb/hr/lb-thrust.

The boiling temperatures of liquid hydrogen and liquid helium are very low; therefore, if the working fluid is stored in liquid form, only negligible errors are involved by calculating the heat added per pound of working fluid as $C_p.5000$, where C_p is the specific heat at constant pressure. For a perfect gas

$$C_p = \frac{\delta}{\delta-1} \frac{1.984}{m} \qquad (6)$$

Hence, for hydrogen the heat added is 17,350 BTU/lb; for helium the heat added is 6200 BTU/lb.

The equations for the time, t, in hours, for equal weight of fuel for an atomic rocket and a conventional rocket, are as follows, assuming the specific consumption for conventional rockets to be 15 lb/hr/lb-thrust.

$$\text{for hydrogen} \quad \left(\frac{17{,}350}{5 \times 10^4} + t\right) 4.87 = 15\, t \qquad (7)$$

$$\text{for helium} \quad \left(\frac{6{,}200}{5 \times 10^4} + t\right) 7.48 = 15\,t \tag{8}$$

By solving these equations, one obtains:

$$\text{for hydrogen} \quad t = 0.167 \text{ hr} = 10 \text{ min} \tag{9}$$

$$\text{for helium} \quad t = 0.123 \text{ hr} = 7.4 \text{ min.} \tag{10}$$

Since the operating time for rockets is generally very much less than 10 minutes, it seems, then, that atomic fuels will not be used in rockets unless the heat-release rate of atomic fuel is much higher than the estimated 5×10^4 BTU/hr/lb.

CONCLUDING REMARKS

The primary factor which determines the feasibility of replacing hydrocarbon fuels by atomic fuels is not the heat value of the atomic fuel, but rather its rate of heat release. With the estimated heat-release rate of 5×10^4 BTU/hr/lb, pure weight considerations would make the atomic turbopropeller and the atomic turbojet possibilities. Atomic ramjets are much less probable, while atomic rockets, with either hydrogen or helium as working fluid, are definitely unwieldy.

The preceding conclusion is based upon the concept of a nuclear reacting chamber design now considered definitely possible. However, the art of utilizing atomic energy, or atomic engineering, is still in its infancy. Much better energy-generation methods can be expected in the future. For instance, for rocket application one could inject a very small amount of gaseous uranium fluoride of isotope U^{235} into a stream of deuterium. If the dimension of the deuterium stream is large, once the uranium compound is thoroughly mixed with the stream, the whole mass will be of overcritical size and the reaction will be completed in a fraction of a second, with the deuterium acting as the moderator. At the exit end of the reacting chamber, the deuterium gas, together with the fission products, will be heated to a very high temperature. This high-temperature gas then expands through a nozzle, as in the conventional rocket. Here one has a true analogy with conventional combustion, with the heat release controlled by the amount of uranium compound injected. Fission cannot be started in the injector, because the dimension of the flow there is subcritical. Such a reacting chamber will also be self-igniting, as any spontaneous fission can start the reaction. The deuterium is chosen because of its good moderating character. If air could be used as the moderator, then the same scheme could also be used for thermal jets. The superiority of this system of atomic energy generation over the previously mentioned "conventional" system certainly warrants further investigation to determine its practicability.