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AVIATION SPIRIT - PAST, PRESENT AND FUTURE.

By A. E. Dunstan and F. B. Thole.

Paper read at International Air Congress, June, 1923.

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

TECHNICAL MEMORANDUM NO. 229.

AVIATION SPIRIT - PAST, PRESENT AND FUTURE.

By A. E. Dunstan and F. B. Thole.

The volatile fuel of the high-speed internal combustion engine has, in the past, consisted almost exclusively of the lighter distillates from crude petroleum. In earlier days, when the value of kerosene far exceeded that of gasoline, the latter being practically a waste by-product, motor fuel had a final boiling point averaging 120°C. With increasing demand for motor spirit the upper limit of boiling point of this fraction steadily rose till today it frequently reaches 220°C. This increase in average boiling point of the fuel has both advantages and disadvantages. It means that a much larger proportion of crude petroleum can be utilized as motor fuel, while the higher specific gravity of modern gasoline means that a larger quantity of energy, measured in British thermal units, is contained in a gallon of the spirit than was formerly the case. On the other hand, the higher proportion of less volatile hydrocarbons renders starting less easy and effective vaporization more difficult, with the consequent troubles of uneven carburetion and possibly even dilution of the lubricating oil. These last-mentioned drawbacks are more or less overcome in modern engines by heating the inlet manifold, a somewhat unsatisfactory compromise since for fullest efficiency the explosive mixture should be as cold as is permissible.

* Read before International Air Congress, London, 1923.

A more serious difficulty lies in the fact that the heavier "paraffinoid" hydrocarbons in gasoline, when vaporized and mixed with air, give a mixture somewhat susceptible to "detonation," i.e., propagation of the explosion with a velocity far greater than that of the normal explosive wave. This excessively rapid explosion, instead of being converted into effective propulsive power, gives a hammer-like blow to the cylinder and piston resulting in the well-known "pinking." This tendency to "detonation" increases rapidly as the compression ratio is raised, and as higher efficiency results from increased compression ratio the trend of modern aircraft engineering is to produce engines with so high a compression that normal straight-run petroleum distillates consisting of paraffin hydrocarbons can hardly be used.

The limitation of final boiling point to 150°C laid down in the Air Ministry specification for engine spirit has the twofold object of obtaining a readily vaporizable fuel and of excluding these higher boiling paraffin hydrocarbons which are prone to detonation in aircraft engines. It has the serious result, however, of limiting the amount of gasoline available both for aircraft and for transport purposes, for an increase in the demand for the aviation "cream" involves a disproportionately greater limitation in the volume of transport "milk" available, since the latter cannot be skimmed beyond a certain degree. Modern fuel research is directed to the double problem of increasing the supplies of gasoline and of discovering ingredients - which may or may not be fuels - which will overcome the detonation difficulty and so enable heavier grades of pe-

troleum to be used.

Much of our knowledge regarding the effects of compression ratio on the efficiency of engines and on the suitability of the various fuels employed is due to Ricardo. He proved by using a variable compression engine that, while paraffinic hydrocarbons, and to a somewhat less degree naphthenic hydrocarbons, are rather prone to detonation, benzole, toluol and xylol will withstand very high compression ratios without detonation occurring. The presence of these aromatic hydrocarbons is therefore of considerable value in a motor spirit, and especially in an aviation spirit. In order to obtain a spirit which can be used without marked tendency to detonation in high-compression engines, the Air Ministry specifications, besides excluding hydrocarbons boiling above 150°C , insist on the presence of a certain minimum proportion of aromatic hydrocarbons. Some spirits from Borneo, Sumatra, Burmah and Persia already contain these aromatic hydrocarbons, but most other spirits have to be blended with the benzole and toluol derived from coal to fulfill the requirements.

The question at once arises as to the possibility of procuring sufficient material to fulfill these requirements in the event of war or of widely increased development of aircraft. Obviously, in the former case the demands on aromatic hydrocarbons for explosives' supply will be enormous, and will create a serious strain not only on the coal tar, coal gas and coke oven industries, but also on those petroleums which contain notable amounts of benzene and toluene. Benzole is, however, by no means the only substance which

possesses "anti-detonating" qualities. A considerable range of alternative fuels capable of incorporation with gasoline are available to serve the double function of increasing the volume of spirit at our disposal and improving its qualities for aircraft use.

Alternative and Supplementary Engine Fuels.

Tetralin, Dekalin and Tetralin-Extra.

Coal tar contains a large amount of naphthalene, the potential production in this country being of the order of 50,000 tons per year, although the present demand is small. The quantity could be greatly increased in all coal-producing countries. Although an admirable fuel, it is a solid melting at 80°C and not readily soluble in petrol, so that its utilization as such has obvious disadvantages.

By union with hydrogen, the solid naphthalene is converted into a mobile liquid, and two distinct compounds are obtained according to whether one or both of the benzene rings are hydrogenated. These are tetrahydronaphthalene or tetralin, $\text{C}_{10}\text{H}_{12}$ (b.p. 206°C), and decahydronaphthalene or dekaline, $\text{C}_{10}\text{H}_{18}$ (b.p. 175°C). As in the case of the hydrogenation products of benzene, there is a complete change in the characteristic odor on hydrogenation and alteration in the physical properties, there being a steady lowering of the boiling point and the specific gravity as the substance is hydrogenated. The hydrogenation seems to take place in two stages only, either one or both of the benzene rings being saturated, no intermediate partially-saturated rings being formed. There is, however, an intermediate product between tetralin and dekaline, known

as "tetralin extra," a mixture of about 20 per cent tetralin and 80 per cent dekalin. Dekalin is a completely saturated body and therefore practically chemically inert, but tetralin is partially unsaturated, and is therefore capable of reaction in many ways.

Tetralin acts as a benzole homologue, except as regards its reaction with oxygen. An alkaline solution of tetralin, unlike benzene and hexahydrobenzene, decolorizes potassium permanganate. Tetralin is also capable of autoxidation in the same way as unsaturated hydrocarbons such as turpentine. If exposed to the air for a long time or evaporated over a water bath at a low temperature, it resinifies.

Tetralin has been suggested as an engine fuel when mixed with benzene, alcohol or petrol. Its high boiling point would preclude its use undiluted.

Cyclo-hexene.

When phenol is reduced by hydrogen in the presence of nickel, the alcohol cyclohexanol is produced. Catalytic dehydration of this yields cyclo-hexene, which, boiling at 82 - 84°C, is a colorless liquid resembling petroleum. In a similar way the homologues of phenol yield tetrahydro-aromatic hydrocarbons.

Alcohol Fuel Derived from Coke Oven Gases.

It is very well known that coke oven gas, coal gas and the gases from cracking heavy oil, and from general distillation plant, contain unsaturated hydrocarbons, particularly ethylene and propylene. These reactive bodies are soluble in sulphuric acid yielding alkyl hydrogen sulphates, which after hydrolysis give alcohols.

The alkyl sulphates are hydrolyzed by means of superheated steam and the alcohol distilled off. The residual diluted acid is reconcentrated. The experiments at Skinningrove, where coke oven gas was purified from hydrogen sulphide, carbon bisulphide and carbon dioxide, and then passed through 95 per cent sulphuric acid at 60°C - 80°C , showed that 70 to 80 per cent of the ethylene was absorbed quite rapidly. The concentration of the acid was reduced to 77 per cent during the absorption and after hydrolysis to 74 per cent.

In the case of gases from cracking processes, the problem is complicated because in addition to ethylene there are present propylenes, butylenes, and also diolefines such as butadiene, all of which are soluble in and combine with sulphuric acid. Selective treatment of the purified gases with different strengths of acid and at different temperatures will yield the desired alkyl compounds from which the alcohols may be obtained in the usual way. A further line of attack is to convert the olefines into chlorhydrins by the action of aqueous hypochlorous acid. The chlorhydrins are reactive compounds, and by regulated treatment with alkalis they yield inner ethers. These ethers are combustible and potential fuels. The first member of the series, ethylene oxide, boils at 12°C and has specific gravity 0.898. Propylene oxide boils at 35°C and isobutylene at 51°C .

The great potentialities in the production of alcohol from the fermentation of sugar waste and from the hydrolysis of various naturally occurring bodies (wood, starch, etc.) has been so widely described and discussed that the matter need not be elaborated here.

Alcohol per se will probably not be used as a motor fuel at any rate in the near future. Its immediate advantage appears to lie in the fact that it withstands high compressions and is exceedingly reluctant to detonate. It would therefore find its ideal use in a gasoline blend or for subsidiary use in cases where detonation has already set in. A serious difficulty lies in the fact that owing to its inevitable water content, commercial alcohol will not readily blend in small proportions with gasoline. Much research is yet needed on this subject.

Various mixtures of alcohol with liquids of high vapor tensions have been proposed. The obvious liquid, ether, is used in natalite, and can very readily be obtained by passing alcohol vapor over heated alumina.

Acetone also is of service in this connection, and is obtained by the destructive distillation of calcium acetate.

Important work on the production of acetone by fermentation has been carried out by Fernbach, who, by means of a special bacillus, has been able to ferment starch into butyl alcohol and acetone. Acetone boils at 56°C, and is therefore sufficiently volatile to ensure easy starting.

A fuel blend containing acetone is described by Ricardo (E.P. 183577) as containing 60 per cent alcohol, 20 per cent acetone, 10 percent water.

A new field of supplies is opened out by the work of Pergusa, who claims to have successfully hydrogenated not only heavy petroleum residues, but also coal, and to have produced considerable amounts

of light hydrocarbons therefrom. The operation consists in heating heavy oil or coal to its incipient cracking temperature, and then hydrogenating at the moment when the molecules are at the point of scission. The pressure needed for this procedure is relatively immense and of the order of 100 atmospheres. Consequently, the plant must be constructed to withstand very great stresses and must be isolated when working. The work of Bergius may be of the greatest importance, seeing that every coal field becomes a potential oil field. It has yet to be proved that the light fractions are equivalent to straight-run gasoline in operation, but it is clear that if or when large amounts of spirit are produced by this process, the motor industry would be able to utilize it.

Somewhat analogous to the research of Bergius is the investigation of Fischer, who has shown that coal, heated with sodium formate or with carbon monoxide and steam, yielded very considerable amounts of oil, and within the same category comes the production of coal oil by the various low temperature carbonization processes which are slowly advancing towards the goal of commercial success.

Although the time is not ripe for the production and utilization of oil derived from coal, the period approaches when shale products will prove an inevitable adjunct to petroleum, ultimately perhaps to supplant it. The venerable Scottish oil industry is still with us, and will remain for all time a monument to the persistence, skill, foresight and courage of its founders and operators. The present yield of shale oil is, however, a very small part indeed of that needed to supply the country's demand, and it is to the great

deposits of Utah, Colorado, Australia, etc., that industry must look for supplies. Just as we are now living in the petroleum age, so without any doubt will the immediately following generations have their being in the oils derived from coal and shale.

Engineering progress will be fully tested in developing aircraft and road motors for the utilization of heavier fuels than gasoline; already, in fact, have interesting experiments been carried out in the direction of employing both road and aero-engines of the Diesel type. There is a huge reservoir of intermediate oil yet to be made use of, since for every ton of gasoline the average crude petroleum yields from five to twenty tons of kerosene and heavier oils. Much attention is at present directed to cracking these heavy oils in order to convert them partly into gasoline, but it would clearly be more logical to devise engines to suit the fuel available rather than to convert the latter into gasoline at the expense of costly plant and considerable losses in material.

The work of Ricardo on the resisting powers of various fuels and fuel blends to detonation at high compression has been continued by Midgeley and Boyd, and results of the highest potential value have been obtained.

Ricardo has demonstrated that certain fuels such as benzole, and more particularly alcohol, when mixed with kerosene or heavy grade petrol, diminish its tendency to detonate, but the quantity of "anti-detonating fuel" necessary is considerable, little improvement resulting until 10 per cent or more of the new component is

added. Considerable interest attaches to the value of hydrogen in this connection, since as the fuel of an airship is consumed the lifting power necessary diminishes and hydrogen becomes available and may have to be blown to waste. Since hydrogen is not prone to detonation, the ingenious and effective scheme has been suggested of supplying the engines of an airship with a mixture of heavy grade petrol, or even kerosene, with hydrogen in appropriate quantity to balance fuel load against lifting capacity.

Midgeley and Boyd's researches have been directed not only to the moderate anti-detonating qualities of fuels such as benzole, but also the extraordinarily effective anti-detonating influence of very small quantities of "dopes." Thus, 1 per cent of xylydine is as effective as an anti-detonator as 15 per cent of benzole. Certain organic compounds of tin, selenium, tellurium and lead have a still greater value, the relative efficiencies for this purpose of benzole, xylydine, diethyl selenide and lead tetraethyl being represented by the figures 1, 15, 1,200 and 22,000. It would indeed seem not improbable that in the near future heavy grades of gasoline or gasoline-kerosene blends containing an infinitesimal quantity of "anti-detonator" will be available for use in ultra high efficiency engines provided with auxiliary vaporizing and supercharging devices. Cooperation in such research between chemists and engineers should give us a power unit as far ahead of the present aircraft engine as that is from the steam engine of the earliest flying machines.