

The Production of Motor Spirit from Heavy Oils.

By Dr. A. E. DUNSTAN.

IT is obvious that the provision of adequate supplies of motor fuel is a fundamental necessity of modern civilisation. Thirty years ago the light fractions of petroleum were not only a by-product in the preparation of kerosene, but also a positive nuisance, and vast quantities were deliberately burnt. In the interim the demand for motor spirit has steadily increased, and to-day has reached the colossal figure of eleven thousand million gallons per annum, Great Britain consuming nearly four hundred and fifty million gallons in the year.

This demand is increasing at the rate of about 30 per cent. a year in Britain alone, whilst the rate of increase on the Continent when trade becomes prosperous will inevitably be steeper than that in England. Last year, of the total amount of petrol produced in the United States, the straight-run gasoline distilled from the crude amounted to 56 per cent., cracked gasoline 33 per cent., natural gas or casing-head gasoline 10 per cent., and benzene 1 per cent.

It is clear that "cracking," *i.e.* the conversion of heavy oil into lighter products, is playing a more and more important part in the provision of motor spirit. The first successful attempts to bring about the conversion of heavy oils into lighter products were achieved by Dewar and Redwood in 1889 (English Patent 10277), and the object of this operation was the conversion of gas oil into burning oil. It was many years later that the conversion of burning oil and gas oil into petrol became desirable and practicable.

Although Redwood's patent was taken out in 1889, the writer had the advantage of seeing some time ago in Edinburgh a lay-out of a shale oil refinery in which this operation was actually provided for so far back as 1865.

The actual origin of cracking in the United States is supposed to be due to the carelessness of a stillman who, having left a still running, returned some hours later and found that a lighter distillate was being produced, and this was traced to condensate dripping from the upper cooler part of the still on to the hot residue. Between this early discovery and present-day big-scale cracking lies a period of intensive development, and it was only the perseverance of Dr. Burton that led to a refinery procedure being established on a large scale. The Burton process is really indistinguishable from that put forward by Dewar and Redwood; in effect, Burton merely heated petroleum residues at a temperature of 700° F. under a pressure of 4-5 atmospheres, the pressure being maintained right up to the outlet of the condenser. The real difference lies in the fact that Burton had developed the same procedure, but to a different end—the production of gasoline.

The first Burton patent was taken out in 1912. For a long time the Burton process was regarded with some disfavour, because of the relatively high pressure maintained in the still and the somewhat serious risks incurred by heating large masses of oil under these conditions, and the attention of innumerable investigators was directed to the cracking of hydrocarbons under atmospheric pressure. In Great Britain, for example, about the years 1913 to 1916, two at least of such processes were in operation. They failed, how-

ever, because the serious drawback of low pressure operation is a high yield of gas with corresponding low yield of gasoline, and that of a nature which makes refining extremely difficult. As will be seen in the sequel, it is by no means certain that vapour-phase cracking at atmospheric temperature is entirely defunct, because the nature of the spirit produced does offer certain advantages as a fuel for modern high-compression engines.

During the War, quite a considerable amount of attention was paid to vapour-phase cracking from an entirely different point of view. It has long been known that at temperatures in the neighbourhood of 750° C., paraffinoid hydrocarbons may be cracked, yielding considerable percentages of aromatic hydrocarbons. In a large-scale experimental plant operated at Thameshaven in 1916, working with heavy Persian oil distillates, a spirit was produced which contained no less than 16 per cent. of toluene.

Between 1916 and the last few years, however, the attention of inventors has been almost entirely directed to cracking under pressure, because it has been found that the spirit produced in this way is not only higher in yield but is also accompanied by far less gas and coke.

One or two typical methods of procedure may be very briefly outlined. In essence, all these processes consist of two parts: A pipe-still through which the oil is passed with considerable velocity at high temperature and pressure into a reaction vessel, in which it is maintained under pressure for varying lengths of time.

In the Cross apparatus—which is one of the most popular types—the oil is raised in the pipe-still to a temperature of about 470° C. and then passes into a reactor, which consists of a horizontal steel cylinder 40 ft. long, 38 in. in diameter, with walls 3 in. thick. The reactor is not directly heated, but is heavily lagged, and the oil is held in this chamber long enough to establish equilibrium between the liquid and vapour phases. This period is about 15-20 minutes, and the oil falls in temperature 50° between the inlet and the outlet. The operating pressure may amount to 750 lb. to the square inch. Normally in this process the amount of coke produced is less than 1 per cent.

After the reaction is complete, the oil is discharged into a separator and thence the vapours pass to the dephlegmator, where the temperature is regulated to yield gasoline to the required specification. The gas that is produced is nearly sufficient to maintain the necessary temperature in the plant. A modern unit will process 2000 barrels of oil per day, and if the intermediate oils produced in the operation be recycled to the plant, it is claimed that the yield of gasoline from a gas oil fraction may reach 65 per cent.

The Carleton-Ellis developments have led to the adoption of a vertical reactor which may be in duplicate. Oil is fed through the pipe-still under a pressure of 350 lb. and passes into vertical steel vessels, in which again the time factor is allowed to have its effect. After the reactor comes the dephlegmator.

The Dubbs' system is particularly adapted to the

cracking of residue oils, although of course it will function on distillates. The process is simple in that the oil, after leaving the pipe-still, passes into a large reactor under a much lower pressure than that used by the Cross system. In the standard plant the oil enters the reaction chamber at 450°C ., and the vessel is 10 ft. in diameter and may reach 30 ft. in height, with a capacity for coke ranging from 30 tons upwards. From the reactor again the vapours are subjected to dephlegmation, and a heavy condensate can be passed along with the incoming crude oil to the pipe-still.

The question of temperature in liquid-phase cracking is decided by the particular oil under treatment and the amount of gasoline required, because there appears to be a definite relationship between the variables time, temperature, and yield. It is interesting to note that the percentage of spirit obtained, after the oil has reached a definite cracking temperature, appears to double, within limits, for an increase of 10°C .

There has been little advance in our knowledge of cracking from a chemical point of view during the past ten years, because problems connected with cracking processes have been more often of an engineering nature, and the most urgent question to the majority of operators is the possibility of elimination—or at any rate the diminution—of coke, so that the plant may run continuously without the necessity for frequent shut-downs for cleaning.

It is surprising how little progress has been made in the examination of the residues left after the cracked gasoline has been removed from the synthetic crude oil, and investigators would do well to bear in mind that herein lies reactive material of unknown constitution, knowledge of which would probably amply repay intensive research.

Recent development in the design of the high speed, high compression, and high efficiency light car engine has brought to notice the importance of suitable fuel. It is in this connexion that cracked spirit shows particular advantages over straight run gasoline, in that it withstands high compression and is less prone to detonation, and it is a fact that, at the moment, quite considerable quantities of this material

are being marketed as "anti-knock" motor spirit. The vapour phase product, having been processed at considerably higher temperatures, is specially noteworthy from this point of view.

No account of the present position of oil-cracking to-day would be complete without some consideration of the Bergius process, about which such far-reaching claims have been made. From the early work of Bergius there emerged the formation of artificial coal from cellulose at temperatures of 350°C . and pressures of more than 100 atmospheres. This substance was capable of hydrogenation by being heated to 400°C . in the presence of hydrogen at very high pressures. From this observation naturally led the application of hydrogenation to coal itself.

An entirely new technique had to be developed in this research and its later development, and only the discovery of a new method of joint construction rendered possible the application of very high pressures to this problem.

A commercial plant has been set up at Rheinau, and consists of an autoclave 30 ft. long \times 3 ft. in diameter, fitted with stirring device and capable of handling 50 tons of material a day, under a pressure which may reach nearly 300 atmospheres.

In the case of coal, the material is ground to pass a 400-mesh sieve and is mixed with oil to permit of its passage through pipes. The autoclave is heated very ingeniously by surrounding it with heated nitrogen under pressure. Bergius has claimed that any coal containing less than 84 per cent. of carbon on an ash-free basis can be successfully hydrogenated.

In this connexion a good deal of work has been carried out the last few years in Great Britain, more particularly in the University of Birmingham, which more or less substantiates claims advanced by Bergius, and a variety of coals, lignites, and so on have been liquefied; but it should be borne in mind that the liquid product, whatever it may be, is certainly not petroleum, seeing that it contains liquid compounds of oxygen, sulphur, and nitrogen; and at the moment of writing it can be safely stated that the process has not yet been placed on a commercial basis.

Obituary.

PROF. EDMUND KNECHT.

BY the death of Prof. Edmund Knecht, associate-professor of technological chemistry in the College of Technology, University of Manchester, chemistry, as applied to dyeing and other branches of textile industry, has lost one of its chief exponents.

Henry Edmund Knecht was the third son of Gustave Knecht, B.Sc. (Lond.), a Swiss who became a naturalised Englishman and for many years had a large private school in Liverpool, where Dr. Knecht was born in 1861. His mother was English. On leaving school he matriculated at the University of Zürich, studying chemistry under Victor Mayer, to whom later he acted as assistant. He graduated Ph.D. at the Swiss Federal Polytechnic in 1882, and returned to England in 1883 on his appointment as Head of the Department of Chemistry and Dyeing of the then newly opened Bradford Technical College. In 1890 he entered upon the long period of service at the Man-

chester College of Technology which ended only with his death.

When the Society of Dyers and Colourists was formed in 1884, Dr. Knecht became the first editor of the journal of the Society, a position which he held continuously for forty-one years and was the source of great satisfaction to him. To commemorate the completion of the fortieth year of his editorship, an excellent portrait of Dr. Knecht was issued with the journal and a valuable presentation was made to him, towards which subscriptions were received from the United States, Canada, India, Japan, and most European countries—for he had friends and admirers the world over.

Dr. Knecht was an indefatigable and prolific worker, his published researches, which number more than one hundred, appearing in the *Journal of the Society of Dyers and Colourists*, the *Journal of the Chemical Society*, the *Berichte*, and elsewhere. They cover a