

Many of us believe that the future happiness of the world rests largely in the hands of scientists, who are the modern magicians and miracle-workers; it is not their fault that others at times pervert to ignoble uses the gifts which science gives us. It is with this in our thoughts that the University offers them its greetings and its welcome to-day."

Outlining the true function of universities, Sir Maurice declared: "I hope too that this year's meeting of the Science Congress will mark the beginning of a reorientation of the attitude of Indian universities towards scientific studies. There has been, I think, too great a pre-occupation with lectures and degrees, to the prejudice of true learning and research. None denies the importance of learning and research; but there is still room for the more complete recognition of the fact that the greatest and most vital function of a university is to increase the bounds of human knowledge, to be a centre of culture in the broadest sense, to be the guardian of fundamental values and to set the standards for its generation."

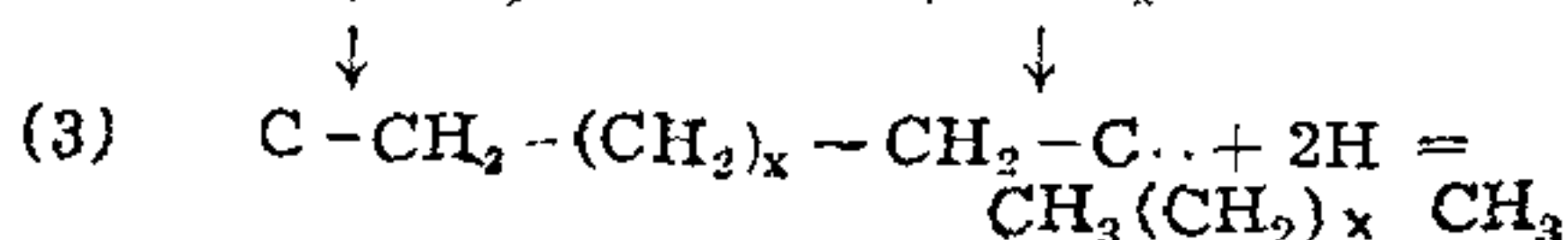
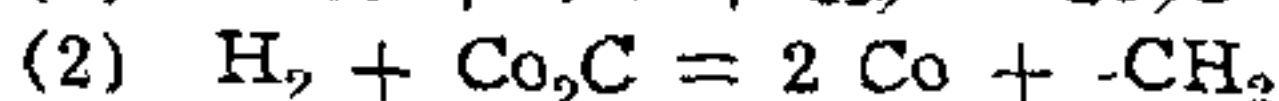
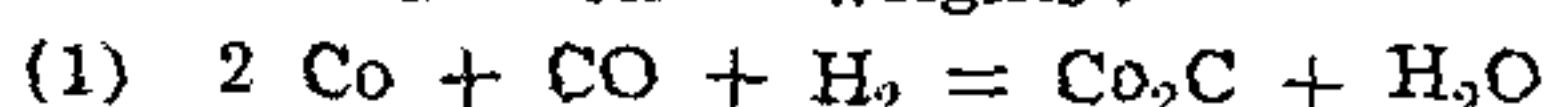
This is the true idea and conception of a university not only in India but in every land. To achieve it will be made more easy by the new attitude of the authorities here towards the universities and by the munificent grants which by a welcome change in policy they are now beginning to make.

If the assistance thus generously given is not allowed to prejudice the autonomy of the universities, for that is a precious possession which they could never yield up without being false to everything for which they stand, a future lies before us incomparably greater than anything which the universities have known in the past. They will become what they ought to be, homes for original research and for the promotion of learning, wherein a true academic atmosphere in which intrigue and jealousies have no place, men may have freedom to develop all the talents which God has given them, serving faithfully their own generation and handing on the torch undimmed to the generations which come after."

THE THEORY OF THE FISCHER-TROPSCH SYNTHESIS

By M. V. C. SASTRI

IN a contribution¹ to the Discussion on "Hydrocarbon Chemistry", held in 1939 by the Faraday Society, London, Dr. S. R. Craxford of the Fuel Research Station, Greenwich, put forward a theory of the Fischer-Tropsch synthesis, depicting the formation of long chain hydrocarbons in essentially three stages, namely: (1) the formation of a carbide-surface (usually cobalt carbide), (2) the limited reduction of the carbide to form long chains of $-CH_2$ groups on the surface, and (3) the disruptive reduction of the CH_2 chains with chemisorbed hydrogen atoms to yield hydrocarbons of suitable molecular weights:



This mechanism has been successful in accounting for most of the phenomena connected with the Fischer-Tropsch synthesis.^{1,2} By employing the *ortho-para* hydrogen conversion as a tracer reaction for ascertaining the presence of chemisorbed hydrogen atoms, it was shown that oil formation proceeded only when the surface was almost completely covered by carbide. In the presence of chemisorbed hydrogen, methane was the chief product. Carbide-free surface also facilitated the water-gas-shift reaction



which accounts for most of the carbon dioxide formed and is obviously an unnecessary side-reaction.

A plentiful accumulation of carbide-centres on the surface of the catalyst is, therefore, essential for maximum yield of oil and this is actually what happens during the so-called "running in" process, in which the freshly reduced catalyst is given a prolonged prelimi-

nary treatment with synthesis gas at below the reaction temperature. The importance of the surface-carbide has received further emphasis in two recent papers of Dr. Craxford published by the Faraday Society. In the first paper,³ it is demonstrated that as the rate of passing the synthesis gas over the catalyst bed is increased the yield of oil passes through a sharp maximum. Simultaneously, the amount of carbon dioxide formed drops abruptly as the velocity is increased beyond the value required for maximum yield of oil. The explanation given is that at low gas-rates oil-synthesis is nearly completed over the first part of the catalyst bed, leaving the succeeding parts free from carbide and, therefore, able to promote the formation of methane and carbon dioxide. At the optimum gas-rate there is obtained a uniform distribution of carbide centres and the whole of the catalyst is thus actively engaged in oil-formation. At higher gas-rates the yield of oil naturally falls off rapidly due to the time of contact with the catalyst surface being too short. With continued use, the catalyst deteriorates, presumably as a result of wax-formation and carbon-deposition, so that the surface available for the synthesis and the side reactions alike dwindles continuously. In consequence, the length of the catalyst bed required for good yield of oil becomes greater and greater and the position of the optimum gas-rate shifts in the direction of lower values. This explains why, if the gas-rate is maintained at a steady value below the initial optimum, the yield of oil at first rises to a peak value after a few days' use and then falls off slowly—a result which is quite familiar to experimenters in this field and which is often reported mistakenly as the "rise and fall in the activity of the catalyst". The advantage of conducting the process in stages can also be appreciated in the light of the carbide theory.

In the second paper,⁴ the function of the promoters, thoria and kieselguhr, has been examined by kinetic measurements. The results emphasise the salient fact that although the primary consideration for an active Fischer catalyst is a high rate of carbide-formation, this must be coupled with a relatively slow rate of reduction of the carbide in order that oils and not gases may be produced. A catalyst containing cobalt with 18 per cent. thoria and no kieselguhr, in spite of its high rate of carbide formation, is rendered unsuitable by an excessive rate of reduction. On the other hand, a catalyst containing cobalt with 21 per cent. thoria and 100 per cent. kieselguhr is poor in both respects, slow carbidisation and fast reduction. The catalyst commonly used containing cobalt with 18 per cent. thoria and 100 per cent. kieselguhr has a relatively rapid carbide formation which, together with slow reduction, accounts for good yields of oil.

The emphasis placed so strongly on the importance of surface-carbides should not obscure the equally important role of chemisorbed hydrogen atoms which, though relatively few in number, are no less vital to the formation of oil. The fragmentation of the giant chains of $-CH_2$ groups chemisorbed on the surface into hydrocarbon molecules of suitable size is due to attack by these hydrogen atoms, as shown in reaction (3) above. Lack of chemi-

sorbed hydrogen would result in the formation of waxes of indefinitely large molecular weight, with consequent deterioration of the catalyst, while an excess of it would lead to gaseous products.

The importance of chemisorbed hydrogen in the Fischer-Tropsch synthesis has been brought out more eloquently by the recent work of Sir J. C. Ghosh at the Indian Institute of Science, Bangalore. By incorporating 4 to 5 per cent. of chromium oxide in a typical cobalt-thoria-kieselguhr catalyst, very good yields of oil have been obtained, using water-gas as such without the usual addition of hydrogen.⁵ The gain in economy that accrues from this development is obvious. Chromium oxide is a powerful chemisorbent for hydrogen and acts presumably as a "surface-enricher" for hydrogen, helping to maintain the necessary concentration of active hydrogen at the seat of the reaction, while at the same time allowing a higher partial pressure of carbon monoxide in the gas-phase. That this is so in fact is borne out by adsorption measurements.

1. Craxford, S.R., *Trans. Faraday Soc.*, 1931, **35**, 946.
2. Herrington E. F. G., and Woodward, L. A., *ibid.*, p. 958.
3. —, *ibid.*, 1946, **42**, 576.
4. —, *ibid.*, p. 580.
5. Ghosh, J. C., and Sastry, S. L., *Nature*, 1945, **156**, 506.

COCONUT SHELLS AS AN INDUSTRIAL RAW MATERIAL

IV. COCONUT SHELL CHARCOAL: (B) ACTIVATED CARBON

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THE first part⁶⁷ of this the fourth article of the series dealt with Coconut Shell Charcoal so far as concerned the preparation of the crude (primary) charcoal and some of its uses. Only brief reference was made to its principal application as "activated carbon".

A general account of activated carbon is not here possible. What is attempted is a discussion of the position coconut shell charcoal occupies in this field. References to the more important published reviews of the general subject are given.⁶⁸⁻⁷⁰

The power of freshly made wood charcoal to absorb gases was certainly known in the late eighteenth century, as was its property of removing colouring matter and impurities from solutions. The volumes of different gases absorbed by a unit volume of charcoal were measured by Th. de Saussure⁷⁷ (1814) and his figures are still quoted, often without acknowledgement or any indication of their date.^{77a} It was known, too, that charcoals from different woods varied considerably in their absorptive capacity (cf. Brande, 1821)⁷⁸

The superiority of coconut shell charcoal was established by J. Hunter, who published between 1863 and 1872 a series of papers⁷⁹ on the absorption of gases and vapours by charcoal. Since then it has been utilised in many researches, both academic and applied. Dewar observed the extraordinary absorptive power of coconut charcoal at low temperatures and

applied this property to the production of high vacua and the separation of gases.⁸⁰ Rutherford used the same method in his work on radium emanation and J. J. Thomson testified that Dewar's method of exhaustion by strongly cooled charcoal had been almost a main contributory cause to the progress of modern physics.⁸¹

Although it is only since the war of 1914-18 that activated carbons have been widely developed industrially, there were prior to this a number of scattered observations on "activation". Thus de Saussure's boxwood charcoal samples were heated to redness and cooled under mercury before each absorption measurement. De Bussy⁸² in 1827 described several methods of increasing the decolorizing power of vegetable charcoals. An early example of "chemical activation", using metal chlorides, is that of Ostrejko (1900).⁸³ Halse (1903) similarly employed sulphuric acid.⁸⁴ Dewar's coconut charcoal was steam activated; an interesting discussion of the nature of Dewar's charcoal has been given by Hase et al. (1939).⁸⁵

Reference has been made in the previous article^{67,49} to the developments in 1914-18, when active carbons were required for gas masks. Accounts of the work of the U.S. Chemical Warfare Service were published in 1919 by Dorsey⁸⁶ and by Lamb et al.⁸⁷ Preliminary experiments had shown that the activity of charcoal increased with the apparent