

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.*, 1933, **35**, 946.
2. Henington E. F. G., and Woodward, L. A., *ibid.*, p. 958.
3. —, *ibid.*, 1946, **42**, 576.
4. —, *ibid.*, p. 530.
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.⁶⁸⁻⁷⁶

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

density of the raw material; of fifty or more materials investigated, coconut shells had the highest density and gave the most active charcoal. As supplies of coconut shells were limited by transport difficulties other raw materials were also used in practice, including various nut materials such as cohune nuts, cherry stones, apricot stones and vegetable ivory, and (later) anthracite coal. These papers carry photomicrographs of interest including some of coconut shell, primary charcoal and charcoal at various stages of activation.

It was briefly mentioned in the previous article⁶⁷ that preliminary investigations had been carried out in coconut-producing countries on the possible local production of active carbons. In the Philippines the subject was studied, especially by Clemente and his colleagues at the University. In 1930⁸⁸ experimental results were published on the relative adsorption of acids and bases from aqueous solution by forty-one different kinds of Philippine wood charcoal (not chemically treated). Coconut shell charcoal had the highest adsorption for potassium hydroxide and the lowest for hydrochloric and acetic acids. Decolorizing charcoals were prepared by Clemente and Pascual (1939)⁸⁹ from coconut shells, husks and cake, by impregnating with zinc chloride and carbonizing. Tested by their adsorption of Sudan III from kerosene and methylene blue from aqueous solution they were about as active as Norit. Charcoal prepared by other treatments were less effective. Clemente and Galang⁹⁰ prepared active charcoals by the zinc chloride method from various agricultural by-products, including coconut shells, and compared their adsorption of methylene blue, Congo red, methyl-violet and iodine from aqueous solutions and of colour from coconut oil; the adsorptive properties of these charcoals for vapours of ether, benzene, alcohol and chloroform were also studied.⁹¹ Similar work was reported by Samaniego and de Leon (1940),⁹² who prepared charcoals activated in various ways from rice bran, rice hulls, coconut shells, corn-cobs, lumbang* (candlenut) shells and pilinut† shells. The best decolorizing carbon, as estimated by its adsorption of iodine, was coconut shell charcoal prepared by impregnating with phosphoric acid; satisfactory gas adsorbents were obtained from all three nut shells impregnated with caustic soda. It was stated in 1939⁹⁰ that there was then no commercial production in the Philippines of activated carbon from coconut shell charcoal. The "Cochar" Products Inc., were, however, stated to be ready to undertake production if a market could be found; the Company were understood to have patented a process utilizing the combustible gases from the primary carbonization to make the activated carbon (see below).

Rao in India (1939)⁹³ studied various raw materials, including coconut shells, as sources of active charcoal suitable for sugar refining. Satisfactory gas adsorbent charcoal was prepared by Neubauer and Rands⁹⁴ in New Zealand by steam activation of crude coconut

charcoal from Samoa. Similar laboratory scale work is believed to have been carried out by the Department of Commerce and Industries in Ceylon but nothing has been published.

METHODS OF PREPARATION

Methods of preparation of decolorizing carbons have been classified by Mantell (*loc. cit.*, 1941, 1298-99) as follows:—

Class 1.—Carbon is deposited on a porous inorganic base to produce materials analogous to bone chars. Natural high-ash products such as rice hulls, which contain an appreciable amount of silica, may be used directly as raw material (*cf.* Clemente's work in the Philippines). Vegetable materials such as saw-dust, sea-weed, bagasse, etc., may be mixed with porous substances such as pumice or diatomite; the mixture is strongly heated whereby the carbon is deposited throughout the porous base.

Class 2. Impregnation Methods.—Suitable carbonizable materials are impregnated with chemical reagents such as sulphuric acid, phosphoric acid, metallic (especially zinc) chlorides, etc.; after carbonization at comparatively low temperatures, the resultant carbons are washed free from inorganic compounds. A second carbonization is sometimes given.

Class 3.—Primary charcoals are prepared by heating suitable materials (wood, lignite, waste sulphite liquors, etc.) in retorts. The properties of the final carbons vary considerably with the conditions of carbonization. The primary charcoals are activated by air, oxides of carbon, chlorine, superheated steam, or mixtures of steam and air, the effect being one of selective removal of the residual hydrocarbons on the internal surfaces of the charcoal. When oxides of carbon are employed there may be re-deposition of active carbon on the surfaces of the material undergoing activation (*cf.* the Cochlar process mentioned above).

The preparation of gas-adsorbent carbons usually follows the lines of class 3. Further information on laboratory and commercial methods will be found in the references given.⁶⁸⁻⁷⁶

The dense hard charcoals derived from coconut and similar "nut" shells, whilst pre-eminent as gas adsorbents, are not generally so effective in decolorizing solutions, for which purpose soft and highly porous carbons are preferred. Chaney, Ray and St. John (1923)⁹⁵ attempted to correlate decolorizing and gas-adsorptive efficiencies; but there is considerable specificity in adsorptive action in liquids; a charcoal active in decolorizing one type of solution will not necessarily be equally effective in other types.

METHODS OF EXAMINATION

(a) Gas-Adsorbent Carbons—

Particular attention may be drawn to a useful paper by Stone and Clinton (1942).⁹⁶ The most reliable data for assessing the efficiency of gas-adsorbing carbons are:—

(1) *Service time*, which is the time required for the break through of a vapour (usually chloropicrin) under specified standard conditions.

(2) *Adsorption Value*.—The weight of a vapour (usually carbon tetrachloride) adsorbed by a carbon under conditions of saturation.

* *Aleurites moluccana*, Willd.

† *Canarium ovatum*, Engl.

(3) *Retentivity*.—The residual weight of vapour retained under standard conditions of temperature and pressure. Stone and Clinton correlate these with the heat of wetting in *m*-xylene for coconut carbons and provide a convenient method for evaluating them on this basis.

(b) *Decolorizing Carbons*—

Mantell (*loc. cit.*, 1941, p. 1300) states that "in the present state of our knowledge, data regarding the action of carbons on one solution cannot be applied to a different solution, but each one to be decolorized must be tested separately. The so-called standard methods of estimation have little practical value".

Density of Activated Coconut Shell Charcoal.—The apparent density (gms. per ml.) is generally measured on dry samples screened between 8 and 14-mesh. Stone and Clinton (*loc. cit.*) quote a range of 0.38-0.54 for gas-adsorbing carbons derived from coconut shells.

The true density tends to a limit of 2.1⁹⁷ (graphite has s.g. 2.25).

Industrial Applications.—The dry distillation products of coconut shells form the subject of the next article projected in this series. The prospects of an industry based on coconut shell distillation depend largely on the existence of a satisfactory outlet for the charcoal.

In the past the demand for coconut shell charcoal has been for the preparation of gas-adsorbent carbons for war purposes, and there is reason to suppose that the bulk of the nearly sixty thousand tons of crude charcoal exported from Ceylon between 1937 and 1940 inclusive was so utilized. As a supplement to the table showing exports of shell charcoal from Ceylon (1933-41) which appeared in the previous article,⁶⁷ the following table gives the exports from 1942-45.

TABLE I

Exports of Coconut Shell Charcoal (crude)
from Ceylon

Year	Amount Tons	Value Rs.	Value per Ton Rs.
1942	2,334	111,422	47.74
1943	1,562	94,044	60.21
1944	470	29,900	63.62
1945	1	70	70.00

Industrial uses of gas-adsorbent carbons include: purifying carbon dioxide from fermentation processes; purifying air; solvent recovery in extraction and similar plants; recovery of gasoline from natural gas and benzene from coal gas; and in vacuum work, e.g., manufacture of radio valves, X-ray tubes, etc.

Decolorizing carbons are used in water purification, refining of edible oils, and the purification of such materials as glycerine and pharmaceutical chemicals. The largest potential application is in sugar refining; the refining process using bone charcoal is very old-established, but in recent years activated vegetable carbons have been found capable of handling economically smaller outputs than the charcoal process and involving less capital investment

on equipment and buildings.

Alkali-activated charcoals can be prepared which are able to remove metals such as gold from their solutions. Avery (1908)⁹⁸ used coconut shell charcoal in an investigation of the decomposition of gold chloride in this manner.

Active carbons act as contact catalysts in a number of chemical reactions of industrial importance. Hassler (*loc. cit.*, pp. 56, 111-113) gives examples and a bibliography.

There is an extensive literature, both in technical journals and in patent records, on active carbons. This is useful on industrial applications, but less so on methods of preparation. It is probable that much information is unpublished in the records of firms actually engaged in manufacture.

Previous articles in this series have been:—

17. Child, R., "Coconut Shells as an Industrial Raw Material. I. Composition of Shells." *Curr. Sci.*, 1943, **12**, 292-94.

(See this article for references 1-16).

31. Child, R. II. "Miscellaneous uses: Fuel." *Ibid.*, 1944, **13**, 4-6. (for references 17-30).

41. Child, R. III. "Estimated World Production", *Ibid.*, 1944, **13**, 150-52. (for references 31-40).

67. Child, R., IV. "Coconut Shell Charcoal: (a) Commercial". *Ibid.*, 1944, **13**, 245-50. (for references 41-66.)

68. Strachan, J. T., "Activated Carbon: Some Industrial Applications." *Chemistry and Industry*, 1923, **47**, (New series,) 1203-1214. 69. Mantell, C. L., "Industrial Carbon." (New York, 1928.) See chapters 15, 16, 18, 19, 20; *Chemical Engineer's Handbook Sec. 11*, "Adsorption", pp. 1298-1322 (New York, 1941.) 70. Raychoudhury, S., "Activated Charcoal." p. 42. a reprint, Calcutta, 1931. 71. Kausch, O., "Die Aktive Kohle: ihre Herstellung und Verwendung." (Halle, 1928. *Erganzband 1932*) Reprinted, 1946 in U.S.A. under authority of the Custodian of Enemy Property. 72. Bailleul, G., Herbert, W., and Reismann, R., "Aktive Kohle." (Stuttgart, 1937). 73. Wohryzek, O., "Die aktivierten Entfärbungskohlen." Stuttgart, 1937). 74. Chaplin, R., Article, "Active Charcoal" in "Thorpe's Dictionary of Applied Chemistry," 4th Edn., Vol. II, 1918, pp. 315-320. 75. Hassler, J. W., "Active Carbon: the modern Purifier." 1941. Trace publication of West Virginia Pulp and Paper Co., New York. 76. Ramat, A., "Les Charbons Actifs." (Danod, Paris, 1943).

77. Th. de Saussure. *Thomson's Annals of Philosophy*, Vol. VI. 1814. (a) See for example Kingzett's: "Chemical Encyclopaedia", Fifth edition, 1932 p. 139. 78. Brande, W. T., "Manual of Chemistry", second edition, 1821, Vol. I, p. 419. 79. Hunter J., "On the Absorption of Gases by Charcoal". *Phil. Mag.*, 1863, **25**, (4) 364-363. *J. Chem. Soc.*, 1865, **18**, 285; 1867, **20**, 160; 1868, **21**, 186; 1870, **23**, 73; 1871, **24**, 76; 1872, **25**, 649. 80. Dewar, J., "The Adsorption and Thermal Evolution of Gases occluded in Charcoal at low Temperature". *Proc. Roy. Soc. (London)*, 1904, **A74**, 122-127; *Comptes rendus*, 1904, **133**, 261. "Improved method of absorbing gases and the application thereof to the production of High vacua and the Separation of Gases," English Patent, 12,638/16 June, 1904. (*J. Soc. Chem. Ind.*, 1905, **24**, 793). See also *Proc. Roy. Inst.*, 1905, **18**, 184; 1906, **18**, 437 and 756. "Use of Charcoal in Vapour Density Determinations", *Proc. Roy. Soc.*, 1908, **A80**, 229-238. 81. Lord Rayleigh., "The Life of Sir J. J. Thomson, O.M." (Cambridge Univ. Press,