OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

Christine RUIZ-CORTES

17715

PREFACE

The present package was prepared taking into consideration the world's increasing market and enormous potential for the production of activated carbon from agricultural wastes.

Coconut shells, in particular, are considered as a raw material that produces one of the highest quality activated carbon.

Developing countries account for over 90% of the annual production of coconuts, however, only a very small proportion of activated carbon is being made from coconut shells and most of that is still produced for industrialized countries.

Close attention should be paid to the first part (1) of this package since it includes references from an up-to-date retrospective literature search covering items published during the last 10 years. 62 references were selected from more than 200 relevant journal articles, patent documents, reports, etc.

An annotated bibliography (1.2, ref.55) produced in Sri Lanka in 1981, already exists.

An information package is intended as a time-saving tool for individuals involved in the development of a specific product since it supplies them with primary information selected from a wide variety of existing sources, which usually is not readily accesible to developing countries.

3115

INTRODUCTION

The ability of various types of carbon from vegetable or animal sources to remove tastes, odors and colours from various liquids and to adsorb gases has been known from ancient times. However, the first industrially manufactured activated carbon in the proper sense was a group of decolourizing carbons (eponit) which were produced at the beginning of this century by R. OSTREJKO (DE pat. 136792) .

Economically, activated carbon is important because at the beginning of this century it was used mainly for the purification of products of the chemical, pharmaceutical and food industries. Purification of drinking water was also an important application at that time.

In recent years it has been increasingly used for the prevention of environmental pollution and for meeting the constantly increasing demand for the purity of natural and synthetical products.

Compared with other commercial adsorbents, activated carbon has a broad spectrum of adsorptive activity with excellent physical and chemical stability, and is easily produced from readily available, frequently waste materials.

Uses of activated carbon are enormous ranging from sugar decolourizing to evaporated emission controls in automobiles.

Activated carbon is rather unique among industrial chemicals in that it can be reused many times before disposal, therefore rather than a raw material it is usually considered as a substrate on which certain materials are deposited during a purification or extraction operation (6.1.4.). The many and varied applications of activated carbon are widely illustrated by the existence of over 1500 manufacturing patents worldwide.

Used with gases, it removes organic vapors and is also used for the recovery of solvents. Many gas purification processes use activated carbon in air conditioning systems to control odours in large public areas (restaurants, auditoriums, airports), in nuclear installations and for desulphurization of flue gases among other uses.

For treatment of liquids and solutions, there are many processes available which utilize activated carbon (batch contact unit operations, continuous layer filtration,percolation) for a wide variety of industrial uses.

Some practical applications in the chemical, pharmaceutical and food industries are : solution purification, such as clean up of cane, beet and corn sugar solutions; removing tastes and odours from water supplies, vegetable and animal fats and oils, alcoholic beverages, chemicals and pharmaceuticals.

Miscellaneous applications include the use of activated carbon as a catalyst and catalyst carrier in certain chemical reactions. Lately, an important use is in gold extraction by the carbon in pulp milling process. It is also used in medicine, in cigarette filters, and so on.

Activated carbons can be subdivided into two broad categories :

- Liquid-phase carbon : used for removal of impurities from solutions.
- Vapor-phase carbon : used for removal of gaseous contaminants and condensible vapours from gas streams.

The most significant physical characteristic of activated carbon is the enormous surface area of the internal pore structure developed during its manufacture by the removal of hydrocarbons.
According to the literature, total surface areas for activated carbon range from 300-2500m^2/g(6.1.3), more commonly from 500-1500 m^2/g(6.1.1.). The large number of very fine pores (micropores) gives the activated carbons a large inner surface area, which is the basis for its remarkable adsorption properties.
Although surface area and adsorption area are interrelated, surface area alone is not always a satisfactory measure of the adsorption capacity of a given carbon for a specific adsorbate. Important factors that determine the adsorption properties of an activated carbon are the pore volume, the pore distribution and the type of functional groups on the surface (surface oxides).
Generally, liquid-phase carbons have a majority of pores of 3nm in diameter or larger, whereas most of the pores of gas-phase adsorbents are 3nm or smaller.
Another reference (6.1.1.) gives 1.2-20nm in diameter for gas-adsorbent carbon or up to 100nm in diameter for decolourizing carbons.
Activated carbon is usually characterized by its appearance as powder granules or pellets of amorphous carbon which has a very large surface area per unit volume.
Almost any carbonaceous raw materials can be converted into activated carbon product although the adsorptive properties will vary greatly, depending both on the raw material and on the processing conditions used. Most industries use chiefly wood (chips or sawdust), nut shells and fruit stones, peat, charcoal, coal, coke, coconut shells and petroleum fractions. Selection of the raw material according to EPI (6.1.4.) depends mainly on :

- Characteristics desired in the end product
- Processing technology required and the attendant operating and equipment costs
- Cost, long term availability and uniformity of the raw material itself

Depending particularly on the moisture content of the starting raw material, yields of activated carbon as a percentage of the raw material volume typically amount to 15-30%.
For economic reasons, lignite, coal, bones, wood, peat and paper mill wastes (lignine) are most often used for the manufacture of liquid-phase or decolourizing carbons. Coconut shells, coal and petroleum in either granular, briqueted or pellet form are used for the manufacture of gas adsorbent carbon.
There are two main methods of producing activated carbon : chemical and gas activation.
Chemical activation depends on the dehydrating action of certain substances such as phosphoric acid, which is the most popular activating agent in the chemical process. The classical zinc chloride process in spite of its advantandges is in decline since the need to avoid [illegible] damaging and the cost to recover [illegible].

Phosphoric acid has become more popular in recent years specially be cause of new methods to recovery it. Unfortunately these methods have hardly been reported in the literature. The "know how" is a trade secret among producers.

Many decolourizing carbons are made by this process and are usually employed as powders. Thus, the raw material for this type is either structureless or has a weak structure. Sawdust and lignite yield carbon of this kind.

Temperatures in the range 400-1000°C are required for this process.

The economic viability of many processes often depends on whether the economics of regeneration are favourable. Contributing to the importance of regeneration is the rising cost of virgin carbon and the energy needed for regeneration.

Chemical activation is most widely practiced in Europe and the economics of the process requires recovery of the chemical agent.

Gas activation involves the use of gases containing oxygen, usually steam or carbon dioxide. Oxidation is usually preceded by a primary carbonization of the raw material.

Vapor-adsorbent carbons used in the form of hard granules are usually made by this process and are generally produced from coconut shells, fruit pits, briqueted coal and charcoal.

Temperatures for this process are 400-900°C for the carbonization step and 750-1000°C for the activation step. Steam is usually used as an oxidizing gas, and less frequently, carbon dioxide.

Production of activated carbon can be carried out in various kiln designs with each one depending on the basic raw material. At the present time, internally heated rotary kilns are the most commonly used since these are suitable for production of activated carbon having a large range of particle sizes, from powder and granular material up to molded shapes.

With respect to coconut shells as a raw material for manufacturing activated carbon, experts agree that it is a well-acknowledged and practical fact that coconut shell charcoal makes first quality activated carbon. It is considered superior to that obtained from other sources mainly because of its finer pore structure, which renders it more effective for the adsorption of gas/vapor and for the removal of taste and odour of compounds.

Activated carbon production is concentrated in Japan, U.S.A. and Europe, utilizing imported coconut charcoal. The world market for activated carbon and its potential for development is enormous. Only a very small proportion of the annual world production is made from coconut growing countries.

The smallest commercially viable activated carbon plant produces 7-10 tons of activated carbon a week from 28-40 tons of wood quality charcoal; this in turn is produced from 100-150 tons of raw material. Experts recommend that an integrated processing is required for a rational coconut agro-industry, they claim, "It is not only necessary, but will also be feasible, profitable and socially beneficial".

ACTIVATED CARBON FROM AGRICULTURAL WASTES

1. [illegible] 1980-1988 *

2.1 ABSTRACTS INDEX

* [illegible]

1.2 ABSTRACTS*:

1.- 109: 152415w **Preparation of activated carbon.** Arakawa, Hideo; Hasebe, Tatsuo (Nippon Enji K. K.) **Jpn. Kokai Tokkyo Koho JP 63,134,510 [88,134,510]** (Cl. C01B31/10), 07 Jun 1988, Appl. 86/280,849, 27 Nov 1986; 3 pp. Activated C is prepd. by heating carbonaceous feedstocks with an acidic gas in an app. comprising a rotary kiln equipped with a burner, a steam-supply pipe, and means for blowing the acidic gas into the carbon particle bed. Suitable acid gas is CO_2. Thus coconut-shell was carbonized in the app. at 920° for ~12 h, the yield of activated C was 290 kg/day, vs. 173 kg/day for a conventional app.

2.- 109: 131632z **Activated carbon from soybean cake.** Ishibashi, Osamu (Mitoyo K. K.) **Jpn. Kokai Tokkyo Koho JP 63,123,803 [88,123,803]** (Cl. C01B31/08), 27 May 1988, Appl. 86/269,302, 11 Nov 1986; 6 pp. Soybean cake is dried, mixed with 300-400% $ZnCl_2$ soln. as activating agent heated at 500-600°, and carbonized to obtain activated C. Thus, typical activated C manufd. from soybean cake had calomel decoloration index 98.1 and methylene blue decoloration index 24, vs. 85-95.3 and 20-24 for a com. one.

3.- 109: 112873n **Method of producing activated coal.** Romanov, Yu. A.; Galkin, V. A.; Zorina, E. I.; Fomin, A. V.; Chizhevskii, S. V. **U.S.S.R. SU 1,401,277** (Cl. C01B31/08), 07 Jun 1988, Appl. 4,196,806, 19 Dec 1986. From *Otkrytiya, Izobret.* **1988**, (21), 166. Activated C is produced by treating C-contg. material with air at 280-420° until the combustion loss becomes 15-35% and then activating with steam at 800-900°. To improve the adsorption capacity of the C, charcoal is used as the C-contg. material. The treatment is carried out at a combination loss rate of 7-35% for 1 h and then activated until the loss becomes 15-43%.

4.- 109: 40211v **The importance of reaction conditions in activated carbon manufacture from fruit stones.** Born, Manfred; Klose, Eberhard (Sekt. Verfahrenstech. Silikatech., Bergakad. Freiberg, DDR-9200 Freiberg, Ger. Dem. Rep.). *Chem. Tech. (Leipzig)* **1988**, 40(5), 218-21 (Ger). Active C was made from cherry stone by coking at 500-1000° and coke activation by steam, CO_2, CO_2-steam mixts., and a CO_2-steam-N mixt. (10:20:70). Activation by pure steam at the optimum temp. of 850° is impractical in spite of the high conversion rate. Activation by steam with a decreased partial pressure and by CO_2 requires a substantially longer activation time to reach the same conversion, but the active-C quality is better. The optimum conversion by steam is 60-70%. The conversion with a steam fraction of <40% for the same quality can be decreased by 10%.

5.- 109: 40200r **Activated carbon from a tropical carbonaceous material.** Chughtai, Fiyyaz Ahmad; Fakhar-un-Nisa; Illahi, Afzal; Ejaz-ul-Haque; Parveen, Najma (Dep. Chem., Univ. Agriculture, Faisalabad, Pak.). *J. Pure Appl. Sci.* **1987**, 6(1), 57-60 (Eng). Active C can be made from *Saccharum munja* by a chem. treatment and pyrolysis at 400-750°, leaching by 2M HCl, washing by H_2O, heating 1/2 h in an oven at 110°, and thermal activation. The chem. treatment consists of 1-h soaking in either com. H_2SO_4, pure H_2SO_4 (5-9N), or $ZnCl_2$ (1-5N).

---

* Complete documents can be obtained from: British Library Lending Division,
Boston Spa, Wetherby, West Yorkshire,
United Kingdom, LS23 7BQ.

6._ 109: 8846v **Study of the preparation of active carbon from wheat straw.** Bueno Cordero, Jose; Estevez Sanchez, Angel M.; Fernandez Tena, Angel; Martin Sanchez, Jose Luis; Ramos Castellanos, Pedro (Fac. Cienc. Quim., Univ. Salamanca, Salamanca, Spain 37008). *Afinidad* **1988**, 45(413), 78-80 (Span). Activated C was prepd. from straw by thermal pretreatment of <2-cm particulates at 150-550° under N, sifting (25 mesh), impregnation with $ZnCl_2$ soln., and activation by heating to 130° and then to 350 for 3 h under N. The material has an absorption capacity of 553 mg methylene blue/g activated C.

7._ 109: 8330x **Present state and future prospects of activated carbon production from wastes.** Berger, Lutz Michael; Klushin, V. N.; Rodionov, A. I. (Moscow Inst. Chem.-Technol., Moscow, USSR). *Chem. Tech. (Leipzig)* **1988**, 40(4), 143-9 (Ger). A review with 148 refs. dealing with the prodn. of activated C from various waste products, e.g. byproducts from the pulp and paper industry, sludges from wastewater treatment, municipal refuse, and waste rubber, plastics, and textile fibers. Problems of the utilization of these waste products for the prodn. of activated C are discussed. see p.52

8._ 108: 97149q **Method of producing active carbon.** Ogurtsov, A. V.; Bobrova, V. N.; Koroleva, L. P. (Kalinin Polytechnic Institute) U.S.S.R. SU 1,351,876 (Cl. C01B31/08), 15 Nov 1987, Appl. 3,985,779, 23 Oct 1985. From *Otkrytiya, Izobret.* **1987**, (42), 74. The process includes mixing of org. and lignocellulose materials, adding to the mixt. 40-60% $ZnCl_2$, granulation of the mixt., drying, carbonization, and washing of the product. In order to improve the clarification property of the C, the stabilized sludge from biol. treatment of wastewater is used as the org. material and flux fibers (35-75%), as the lignocellulose material.

9._ 106: 216355z **Utilization of cereal straw for the preparation of activated carbon.** Martin Sanchez, J. L.; Estevez Sanchez, A.; Fernandez Tena, A.; Bueno Cordero, J.; Ramos Castellanos, P.; Rodriguez Martin, E. (Fac. Cienc. Quim., Univ. Salamanca, Salamanca, Spain). *Ing Quim (Madrid)* **1987**, 19(214), 189-92 (Span). Wheat straw is suitable raw material for prepn. of activated C. Thermal pretreatment of the straw decreases its wt. and vol. and reduces the amt. of the activating agent ($ZnCl_2$) needed. The adsorption capacity of the activated C prepd. is increased by an increased concn. of the $ZnCl_2$ soln. used, an increased heating rate in the thermal treatment, and an increased activation temp., but is decreased by an increased temp. of thermal treatment. Wheat straw pretreated thermally at 230°, heated at a rate of 10°/min, and activated at 400° with an 80% $ZnCl_2$ soln. gave an activated C with a methylene blue adsorption capacity of 670 mg/g activated C.

10._ 106: 215747s **Preparation of activated carbon. Kinetics of activation reaction of carbonaceous materials with steam.** Shi, Yinrui; Tang, Qifeng; Zhao, Yuming (Res. Inst. Chem. Process. Util. For. Prod., Chin. Acad. For., Nanjing, Peop. Rep. China). *Linchan Huaxue Yu Gongye* **1986**, 6(4), 8-16 (Ch). The activation rates of the charcoals prepd. from the pine wood, coconut shell, almond kernel, olive kernel, and bituminous coal were strongly influenced by steam concn. except those of brown coal and anthracitic coal. The reaction of steam and C followed zeroth order kinetics.

11.– 106: 178998b **Active carbon.** Wienhaus, Otto; Klose, Erhard; Born, Manfred; Hennig, Friedhelm; Blossfeld, Otfried; Seidel, Hans; Riedel, Dietrich; Fischer, Friedrich; Zimmer, Joerg; et al. (Technische Universitaet Dresden) **Ger. Offen. DE 3,604,320** (Cl. C01B31/10), 19 Mar 1987, DD Appl. 280,774, 19 Sep 1985; 4 pp. Active C is prepd. from fresh wood chips, e.g., conifer, and optionally a lignocellulosic binder, e.g., sawdust, by a continuous process in a shaft kiln which includes a combustion chamber. At least part of the fuel gases from the kiln are combusted to give a water vapor-contg. hot gas with O ≤0.5, CO ~1 vol.%, and a temp. 10–30° higher than the activation zone (AZ) temp., that is fed back to the kiln and entered below the AZ at 0.1–0.6 m/s. Active C of sp. surface area 900 m^2/g, methylene blue absorption value 96 mL/100 mg, molasses value 420 mg, I absorption 655 mg/L, and ash content ~8.5%, was prepd. from pine chips according to the invention. The app. for the process is described with a flow diagram.

12.– 106: 122368d **Method of producing active carbon.** Ryk, V. A.; Akhmina, E. I.; Guseva, V. I.; Shokhireva, V. S. (Scientific-Industrial Enterprises of Hydrolysis) **U.S.S.R. SU 1,279,959** (Cl. C01B31/08), 30 Dec 1986, Appl. 3,723,679, 09 Feb 1984. From *Otkrytiya, Izobret.* **1986**, (48), 88. The process consists of drying of lignin-contg. feedstock, heating and carbonization, cooling, and activation. In order to improve the clarifying properties of the carbon, heating is done at a rate of 1000–3000°/min. In one embodiment, the heating is carried out first at up to 500–700° followed by activation by flue gases and steam at 800–900° or by a mixt. of flue gases and steam in the presence of O_2 at 700–800°.

13.– 106: 104679b **Wood pellets for manufacturing activated carbon.** Fujimori, Hidekazu (Japan Steel Works, Ltd.) **Jpn. Kokai Tokkyo Koho JP 61,220,727 [86,220,727]** (Cl. B01J2/20), 01 Oct 1986, Appl. 85/58,134, 25 Mar 1985; 4 pp. Wood pellets for manuf. of activated C are prepd. by mixing powd. wood contg. <10wt% water with 5-20 wt.% coal tar and powd. pitch, and pelletizing the mixt. by extruding. Thus, wood pellets were prepd. by mixing 200 kg wood powder with 8 kg tar and 12 kg powd. pitch in a mixer equipped with a steam jacket, and extruding the mixt. at 3550 kg/cm^2. Upon heating 2 kg pellet at 5°/min to 550° in N and cooling to 100°, 710 g product contg. 83.2% fixed C was obtained.

14.– 106: 38919b **Production of activated carbon from walnut shells. II. Pore structure investigations.** Kutics, K.; Kotsis, L.; Argyelan, J.; Szolcsanyi, P. (Dep. Chem. Process Eng., Veszprem Univ. Chem. Eng., Veszprem, Hung.). *Hung. J. Ind. Chem.* **1986**, 14(3), 353–62 (Eng). Various activated C species were prepd. from walnut shells. On the basis of pore structure investigations a quasi-bidisperse pore model is proposed. By taking geometric considerations into account, the increases of the micropore diams. due to activation were estd. Micropore distributions are calcd. by means of adsorption isotherms. Activated carbon samples have high micro- and macropore vol. and negligible mesoporosity, i.e. the assumption of a bidisperse structure is correct.

15.– 106: 35965c **Manufacture of charcoal, coke, or activated carbon in a shaft furnace.** Kossatz, Klaus; Blossfeld, Otfried; Gubatz, Fritz; Wienhaus, Otto; Urban, Harry; Henning, Friedrich; Klose, Erhard; Born, Manfred; Ganserra, Benno; Fischer, Friedrich **Ger. (East) DD 238,162** (Cl. C01B31/10), 13 Aug 1986, Appl. 210,577, 22 Jan 1979; 6 pp. Flexible pyrolysis of a no. of feedstocks is described in which the feedstock is pyrolyzed in a shaft furnace with a rotating grate in which the pyrolysis gases and condensates can be used as a supplemental fuel for the prodn. of combustion gases, which are used for the pyrolysis. The process can be used for the pyrolysis of wood and timber wastes (at 600°) to charcoal, cellulose wastes (e.g., straw, sawdust, etc.), secondary wastes from coal briquetting, old tires, and raw brown coal and peat (to 950°). The process can include a predrying step (e.g., in which the pyrolysis gases are used to heat the feedstock until the condensate temp. reaches 140 180°).

16._ 106: **6673a Preparation of activated carbon.** Buerger, Alex; Thom, Karl Friedrich; Schmidt, Peter (Bayer A.-G.) **Ger. Offen. DE 3,501,073** (Cl. C01B31/12), 17 Jul 1986, Appl. 15 Jan 1985; 15 pp. Activated C is prepd. by H_3PO_4 (e.g., ≤50% H_3PO_4) activation of C-contg. fuels at high temp. in which the fuel-H_3PO_4-water mash, is pretreated at 80-250° in presence of water vapor and O with heating to the final temp. in <30 min before activation at 250-550°, preferably 350-550°. The O and water vapor content may be 3-15 and ≤20, preferably 25-40 vol.%, in the gas phase during pretreatment and the mash may be dried to <15% water content by the pretreatment. The product is washed with water, neutralized, treated with desalinated water, removed from the liq., and dried. Thus, 250 g wood shavings (contg. natural moisture content and 178 g dry substances) was stirred with 475 g 50% H_3PO_4 soln. (172 g P_2O_5) and the 1:0.966 ratio mash was heated to 170° in 20 min in contact with 1 L/min water vapor stream contg. 6 vol.% O to decrease water content to 5.5%; the dried mash was heated to 330-450° for 15 min to activate and then cooled, washed, dried, and ground. The product was used to bleach molasses.

17._ 105: **211198v Activated carbon.** Sato, Eiichi **U.S. US 4,616,001** (Cl. 502-437; B01J20/20), 07 Oct 1986, JP Appl. 85/136,323, 21 Jun 1985; 4 pp. Activated C is manufd. by carbonization and activation of macadamia nut shells using conventional carbonization and activation methods. Macadamia nut shells 1000 g were carbonized and activated with steam at 900° for 120 min to give 20% yield of activated C with ash content 0.5% and sp. surface area 1320 m^2/g vs. 18%, 1.2 and 1200, resp., for activated C from coconut shells.

18._ 105: **45707p Manufacture of activated carbon.** Watanabe, Fujio; Murase, Hiroki (Amano Pharmaceutical Co., Ltd.) **Jpn. Kokai Tokkyo Koho JP 61 14,113 [86 14,113]** (Cl. C01B31/08), 22 Jan 1986, Appl. 84/136,153, 29 Jun 1984; 4 pp. Activated C is prepd. from wheat bran or the extn. residue of wheat bran koji by carbonizing and activating with steam. Thus, activated C was prepd. by drying the extn. residue of wheat bran koji at 110°, carbonizing 100 g residue at 820°, and passing steam at 820° and 2.1 kg/h for 1 h. The product had a large portion of its pore vol. due to pores of 10-100 Å diam. The activated C can adsorb a wide range of low and high mol.-wt. adsorbates.

19._ 105: **26056j Charcoal-making in a home, and the utilization for activated carbon.** Satonaka, Seiichi; Sako, Chizuko; Kawase, Kiyoshi (Coll. Exp. For., Hokkaido Univ., Sapporo, Japan). *Enshurin Kenkyu Hokoku (Hokkaido Daigaku Nogakubu)* **1985**, 42(4), 1135-51 (Eng). Carbonization of woods of 19 tree species in a conventional firewood stove gave charcoal in a 25-38% yield with d. 0.16-0.47, moisture content 0.7-3.3% at the next morning, methylene blue (I) adsorption 11-74 mg/g, and shrinkage in radial direction 10-24%. Activation of charcoal as above by steam gave activated C in 23-65% yield, and with lignin adsorption from spent liquor 5-61%. A strong pos. correlation was found between the wood and charcoal d., as well as between I and lignin and sorption. Neg. correlations between activated C yield and I and lignin adsorption were obsd. see p.45

20._ 105: **8945u Kinetics of activated carbon gasification and regeneration.** Cheng, Alan Tat Yan (Cornell Univ., Ithaca, NY USA). **1985.** 272 pp. (Eng). Avail. Univ. Microfilms Int. Order No. DA8516957. From *Diss. Abstr. Int. B* **1986**, 46(7), 2394.

21.- 105: 3130z **Activated carbon from sal (Shorea robusta) seed husks.** Hossain, M. Altaf; Mustafa, A. I.; Alam, M. Zahangir (Dep. Appl. Chem., Dhaka Univ., Dhaka, Bangladesh). *Dhaka Univ. Stud., Part B* **1985**, 33(2), 279-85 (Eng). Good quality activated C was prepd. from sal seed husks in 41% yield using $ZnCl_2$ as activating agent. The adsorption capacity of this C was better than that of the com. available samples. The C produced also showed good adsorption of color from molasses soln.

22.- 104: 115845m **Activated carbon preparation for filtering materials and products.** Eichner, Otto Friedrich **Braz. Pedido PI BR 85 00,055** (Cl. C01B31/08), 29 Oct 1985, Appl. 85/55, 08 Jan 1985; 13 pp. Activated C is prepd. by distn. of ground resinous wood with conc. H_2SO_4 3-6 wt %, in water 15-20 vol. %, based on the acid, at 450-700°. The product can be refrigerated and then reactivated in a furnace in contact with air for ≥20 min at ≥50°. The filtering material is esp. useful for water treatment, e.g., surfactants. Thus, pine sawdust 1000 g was treated with 500 cm^3 of 10% aq. soln. of H_2SO_4, carefully homogenized, and dried to decrease the wt. to 1200 g, distd. in contact with air in a furnace at 500-550° for 3 h until gas evolution ends and then allowed to cool to ~200° and then to cool in free air to ambient temp. The straw-like C obtained was used in a 100-cm filter layer for filtration at 10-12 m/h.

23.- 104: 112156c **Low ash activated carbon from rice husk.** Beg, M. Arshad Ali; Usmani, Tanzil H. (PCSIR Lab., Karachi, Pak. 39). *Pak. J. Sci. Ind. Res.* **1985**, 28(4), 282-7 (Eng). Rice husk char obtained in the absence of air at 600-800° was leached with a 10-15% soln. of NaOH to remove 90% of the SiO_2. The adsorption activity of leached activated C was greater than that of the untreated char but less than that of a com. activated C. The leached product should be useful for adsorption of low-mol.-wt. gases and vapors from air and for purifn. of water contg. lower-mol.-wt. org. contaminants.

24.- Utilization of non-kernel **products** of the coconuts (Cocos nucifera; Sri Lanka).
Yatawara, R. (Harley Ltd., Sri Lanka).
En
Cocoa and coconut: progress and outlook. Pushparajah, E.; Chew, P.S. (eds.).
Kuala Lumpur (Malaysia). Incorporated Society of Planters. 1986. p. 917-932.
Summary (En). Appendices.
(International Conference on Cocoa and Coconuts: Progress and Outlook. Kuala Lumpur (Malaysia). 15-17 Oct 1984.)
In theory, laboratory research studies, and folklore, the versatile coconut had a myriad uses. This paper was confined to its commercial uses in building up rural and national economies. The coir fibre industry and **activated carbon** from charcoal, was dealt with, in some depth, and only a few examples of others are cited. (EN)

25.- 104: 71160d **Activated carbons.** Fujimagari, Hitoshi; Katada, Nobuaki; Okabayashi, Hiroaki (Pentel Co., Ltd.) **Jpn. Kokai Tokkyo Koho JP 60,161,316 [85,161,316]** (Cl. C01B31/12), 23 Aug 1985, Appl. 84/15,841, 31 Jan 1984; 3 pp. The raw materials with water-repelling surface property is pulverized and then impregnated with activators. Thus, peanut shells were pulverized to 1000 μ, stirred for 1 h at 90-95° in an aq. $ZnCl_2$ soln. (sp. gr. 1.8), dried at 110°, and heat-treated for 60 min at 600° in N_2 to give 56% (the raw material wt.) activated carbon with 230 mL/g methylene blue adsorption, as compared with 110 mL/g without the pulverization.

26. 104: 52897h **Preparation of activated carbon from the by-products of agricultural industry.** Noszko, Laszlo H.; Bota, Attila; Simay, Agnes; Nagy, Lajos Gyorgy (Dep. Appl. Chem., Tech. Univ., H-1521 Budapest, Hung.). *Period. Polytech., Chem. Eng.* 1984, 28(3-4), 293-7 (Eng). Activated C with adsorptivity properties that are satisfactory for use in water treatment was prepd. from the seeds of stone fruit by carbonization and subsequent activation with steam. Also, sawdust treated in a similar manner gave a product that was less dense and had a greater adsorptivity.

27. 103: 73286c **Activated carbon from walnut shells.** Khan, A.; Singh, Harbans; Bhatia, A. K. (Reg. Res. Lab., Jammu Tawi, 180 001 India). *Res. Ind.* 1985, 30(1), 13-16 (Eng). Walnut shells, after being digested in solns. of H_3PO_4, $ZnCl_2$, and HCl, were carbonized at 500° for making activated C. The products had a kinetic behavior for removal of color from sugar similar to that of a com. activated C but their capacity for color removal was less.

28. 102: 64716v **Comparison of activated carbons produced by partial steam gasification of various carbonaceous materials.** Wigmans, T. (Neth.). *Act. Carbon ... Fascinating Mater.* 1983, 58-80 (Eng). Edited by Capelle, A.; De Vooys, F. Norit: Amersfoort, Neth. This study evaluates lab. activation results of peat coke, lignite coke, wood char and preoxidized coal as feedstocks for the prodn. of powd., broken, and extruded activated C. Results are interpreted in terms of specific gas phase and liq. phase applications, based on C_6H_6 adsorption and C burn-off data. In order to put into a proper context the influence of the feedstock type on the characteristics of the activated C produced, the lab. expts. are characterized by activation over a broad range of temps. and of steam partial pressures. This study confirms that peat coke is the most universally applicable, feedstock among the alternatives studied for producing large variety of C.

29. 102: 64309q **Preparation of granular activated carbon from wood pellets.** Hayashi, Katsumi; Abe, Ikuo; Nakano, Shigekazu; Kitagawa, Mutsuo; Hirashima, Tsuneaki (Osaka Munic. Tech. Res. Inst., Osaka, Japan 536). *Tanso* 1984, 119, 185-9 (Japan). Granular activated C was prepd. from wood pellets which were prepd. in an extruder from wood scrap by adding pitch and tar as binders. The wood pellets were carbonized at 550° and activated with steam in a batch-type rotary kiln. The exptl. conditions were as follows: activation temp. 850°, steam rate 0.55 g/g char-h, and activation time 1.5-3 h. The relationship between the activation yield and the activation time was linear. The activated C, obtained at a yield of ~45% had surface area 900 m^2/g, and adsorption capacities for methylene blue, I, and benzene 200 mL/g, 1300 mg/g, and 34%, resp. Addn. of the binders gave activated C harder than the activated C prepd. only from wood scrap; the hardness was >95% of that obtained by the JIS K 1474 method at a yield of ~45%.

30. 102: 48183p **Shaped activated carbon.** Japan Steel Works, Ltd. **Jpn. Kokai Tokkyo Koho JP 59,164,611 [84,164,611]** (Cl. C01B31/08), 17 Sep 1984, Appl. 83/38,356, 10 Mar 1983; 4 pp. Wood is pulverized, dried to contain ≤10% H_2O, mixed with 5-20% coal tar and/or pitch, pelletized, carbonized, and activated with high-temp. steam to give shaped activated C for adsorption.

31. 101: 194505r **Production of activated carbon from plant waste.** Chaparro Beltran, Manuel; Moreno B., Tomas R. (Univ. Oriente, Puerto la Cruz, Venez.). *Ing. Quim. (Madrid)* 1984, 16(183), 85-7 (Span). Dried coconut shell, previously triturated, is activated by impregnation with $ZnCl_2$ soln., then filtered and dried at 90° in a vacuum oven, carbonized at 350° in an elec. furnace in a N_2 atm., cooled in the absence of air, pulverized in a mortar, washed with distd. water and 4% HCl to remove residual $ZnCl_2$, and dried at 80°. The optimum C is impregnated with 80 wt.% $ZnCl_2$ for 1 h and activated at 350°.

32. 101: 178138t **The two-stage air-carbon dioxide activation in the preparation of activated carbons. II. Characterization by adsorption from solution.** Linares-Solano, A.; Rodriguez-Reinoso, F.; Molina-Sabio, M.; Lopez-Gonzalez, J. de D. (Dep. Quim. Inorg., Univ. Alicante, Alicante, Spain). *Adsorpt. Sci. Technol.* **1984**, 1(3), 223-34 (Eng). Olive stones and almond shells were used as raw materials to prep. activated C following the methods of (*1*) carbonization in N_2 followed by activation in CO_2, (*2*) direct activation in CO_2, and (*3*) treatment in dry air at 573 K followed by activation in CO_2. The C is characterized by the adsorption of *p*-$NO_2C_6H_4OH$, Methylene Blue, Orange II, Crystal Violet, and Victoria Blue in aq. soln. Methods (*1*) and (*2*) yield C with very similar adsorptive capacities and method (*3*) yields C with larger adsorptive capacities for similar overall yields. On the other hand, C from almond shells (more microporous) would be more suitable for adsorption of small solutes and C from olive stones (more macroporous and consequently, with larger rate of adsorption) for larger dimension mols.

33. 101: 113151x **Preparation of activated carbon from bagasse and its adsorption characteristics.** Khan, M. I.; Nawaz, R. (Dep. Chem., Univ. Agric., Faisalabad, Pak.). *J. Pharm. (Univ. Karachi)* **1983**, 2(1), 41-4 (Eng). Bagasse was converted to activated C by being treated with H_2SO_4 and $ZnCl_2$ at various concns. and 400-900°. The best activation occurred when 1 part of bagasse was treated with 3 parts H_2SO_4 at 900°. At activation temps. >900° both the combustion loss and adsorption power were increased.

34. 101: 93000s **Regeneration of activated carbon.** Gomella, Cyril (Paris, Fr.). *Water Supply* **1983**, 1(2-3, World Water Supply), SS12/1-SS12/15 (Eng/Fr). A review without refs. covers thermal, chem., solvent, and biol. regeneration of activated C.

35. 101: 25245a **Pyrolysis and transformation of wood chips to activated carbon.** Onofrio, Maurizio; Gozzelino, Giuseppe; Fasoli, Ugo (Dip. Sci. Mater. Ing. Chim. Politec. Torino, Turin, Italy). *Chim. Ind. (Milan)* **1984**, 66(2), 84-9 (Ital). Activated carbon was obtained from wood chips by pyrolysis at 400° and activation at 900° in a CO_2-N_2 medium; the activation energy of the activation process was 23 kcal/mol. Max. adsorption capacity for methylene blue was attained by activation of carbon at 870° for 25 min. The activated carbon obtained from wood chips had properties comparable to those of com. activated carbons.

36. 100: 194370x **Activated carbon from almond shells. Chemical activation. 2. Zinc chloride activation temperature influence.** Ruiz Bevia, F.; Prats Rico, D.; Marcilla Gomis, A. F. (Dep. Quim. Tec., Univ. Alicante, Alicante, Spain). *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, 23(2), 269-71 (Eng). Activated C, obtained by treating ground almond shells with an aq. soln. of $ZnCl_2$ and heating at 500°, showed max. adsorption capacity. The adsorption capacity was equiv. to those of com. products.

37. 100: 193865a **Preparation and absorption capacity of active carbons from palm nut fibers.** Avom, Jerome; Hajal, Issam (Fac. Sci., Univ. Yaounde, Yaounde, Cameroon) *Rev. Sci. Tech.* **1983**, 3(1-2), 71-7 (Fr). The carbonization (heating rate 300°/h, 5.5 h at 700°) of dry palm nut fibers (residue from expression of *Elaeis Guineensis*), washing with 5% HCl and water, grinding to 0.2 mm, and activation for 30 min in 80% H_3PO_4 + 5% H_2SO_4 gave an adsorbent carbon with sp. surface area 875 m^2/g, I sorption 100.9 g/100 g, and methylene blue sorption 23.2 mg/g. Activation with 60% $ZnCl_2$ was also effective.

38. Studies on the effects of CaCl2 and ZnCl2 concentration and activation process on the yield and the quality of coconut shell activated carbon.
Suryani, A.; Ketaren, S.
in
Buletin Penelitian Tehnologi Industri, Bogor (Indonesia). ISSN 0216- 3160. (1982).
v. 1(2) p. 16-30. Received Oct 1983.
7 ill.; 6 ref. Summary (En).

39. 100: 105850p **Dual production of active carbon and hydrogen by steam gasification of palm stones.** Rabah, M. A.; Eldighidy, S. M.; Gahin, S. (Coll. Eng., King Abdulaziz Univ., Jeddah, Saudi Arabia). *Energy Res.* **1983**, 3(Altern. Energy Sources 5, Pt. D) 429–42 (Eng). Palm stones were carbonized at 700° in an O_2-Free atm. The carbonized palm stones, after being crushed to a particle size of 5 mm, were treated with steam at 950°. The gas from the steam treatment, contg. H_2O, CO_2, CO, H_2, and S compds., was dried and treated with 33% aq. caustic potash. The gas remaining was H_2 contg. 3.5–4% CO. The yield from 1 ton of palm stones is 112.8 kg active C and 46.7 kg H_2. The surface area of the active C is >1200 m²/g.

40. 100: 12976u **New uses for activated carbon.** Wilkins, C. S. H. (Sutcliffe Speakman Eng. Ltd., UK). *Chem. Eng. (Rugby, Engl.)* **1983**, 396, 15, 23 (Eng). A review on adsorption on activated C in recovery of inorg. materials or in nuclear industry with 11 refs.

41. 99: 197419s **Manufacture of active carb.- pellet from wood.** Japan Steel Works, Ltd. **Jpn. Kokai Tokkyo Koho JP 58,140,311 [83,140,311]** (Cl. C01B31/08), 20 Aug 1983, Appl. 82/19,721, 12 Feb 1982; 4 pp. Wood is crushed to a particle size of 5–30 mm and dried to a H_2O content of 12–18 wt.% in a rotary kiln. The wood particles are extruded at 150–200° and 400–8000 kg/cm² through a die having 5–7 mm holes. The pellets are self-bonding because they contain a resin and have a d. of 1.4 g/cm³. The pellets are carbonized at 400–700° in the absence of O_2 and activated with steam at 800–1000°.

42. 99: 107378a **A summary of the recent work of French laboratories presented as a tribute to Prof. Mrozowski.** Pacault, A.; Marchand, A. (Cent. Rech. Paul Pascal, 33 Talence, Fr.). *Carbon* **1983**, 21(4), 367–98 (Eng/Fr). A review is given with 282 refs. of work published by individuals from French research centers relating to C.

43. 99: 90296w **Preparation of activated carbon from sawdust and coal.** Cardona, Gloria E.; Pena, Ana B. (Dep. Quim., Univ. Antioquia, Medellin, Colombia). *Rev. Colomb. Quim.* **1982**, 11(2), 93–4 (Span). Activated C in powder and granular form was prepd. by using sawdust or coal as the raw material. For powd. activated C, the sawdust (or coal) was put into a mech. agitator with the activating agent ($CaCl_2$ or $ZnCl_2$) at 5:2 ratio for 2 h. After agitation, the mixt. was dried at 120°. The mass obtained was ground and sifted to -200 mesh and washed thoroughly to remove contaminats and excess activating agent. The coal required pretreatment by grinding and heating at 400° to remove volatile materials. For the prepn. of granular activated C, tar was used as the agglomerating agent, in addn. to the sawdust, coal, $CaCl_2$, and $ZnCl_2$. The product had a variable particle size (meshes 40, 60, 80).

44.- 98: 217464n **Simultaneous manufacture of wood vinegar and activated carbon.** Kato, Hisayoshi **Jpn. Kokai Tokkyo Koho JP** 57,195,789 [82,196,789] (Cl. C10B53/02), 01 Dec 1982, Appl. 81/80,172, 28 May 1981; 4 pp. In manuf. of wood vinegar and activated carbon by a simultaneous process, wood materials are treated with H_3PO_4 and dry distd. at ~400°. Thus, 100 parts cedar sawdust was dried, treated with 220 parts H_3PO_4, and dry distd. from 350° to 390° to give wood vinegar and activated carbon.

45.- (Utilization of monterey pine (Pinus radiata D. Don) waste for the production of activated charcoal in the 5. Region (Chile)). Aprovechamiento del desecho de pino insigne (Pinus radiata D. Don) para la produccion de carbon activado en la 5 region (Chile).

Yussem Diaz, C.

Universidad de Chile, Santiago Facultad de Ciencias Agrarias, Veterinarias y Forestales. Escuela de Ciencias Forestales.

Es

Santiago (Chile). 1983. 162 p.

Map. scale 1:750.000; 17 ref. Summaries (En, Es) *Biblioteca, Facultad Agronomia, Univ. de Chile, Santiago (Chile). Degree: Tesis (Ing For).

46.- 97: 200251x **Carbonization of organic wastes.** Hokuriku Tanso Kogyo K. K. **Jpn. Kokai Tokkyo Koho JP** 82 96,884 (Cl. C10B53/02), 15 Jun 1982, Appl. 80/172,506, 05 Dec 1980; 4 pp. Sawdust, bark, and other industrial wastes are carbonized continuously without any supplementary fuel in a given system. Thus, a kraft pulp plant sludge was carbonized at 700-800° and then at 1000-1200°. The product had less volatiles than in one obtained by conventional method, and is used as activated C.

47.- 97: 129921h **Activated carbon from Agave residues.** Rubio, M.; Chao, O.; Leon, S.; Cordero, L. E.; Cetina, R. (Inst. Quim., Univ. Nac. Auton. Mexico, Mexico City, Mex.). *Rev. Soc. Quim. Mex.* 1982, 26(2), 69-72 (Span). The use of residues from processing *Agave atrovirens* was studied. The roots of the plant, when activated by using H_3PO_4, gave an activated C with a methylene blue adsorption capacity similar to that of com. activated C.

48.- 97: 111900r **Vertical moving-bed carbon material reactor.** Kuraray Chemical Co., Ltd. **Jpn. Kokai Tokkyo Koho JP** 82 61,609 (Cl. C01B31/10), 14 Apr 1982, Appl. 80/134,558, 26 Sep 1980; 4 pp. In a vertical moving-bed carbon material reactor having a rectangular cross section, several trays and alternate openings on their sides are provided. Several spaces surrounded by the trays and the reactor wall, and a gas flow duct connecting with these spaces, are formed. Air or air-fuel inlets are provided in these spaces or the gas flow duct. A moving bed communicating from the top of the reactor to the bottom and having a rectangular cross section is also formed. Gas passage holes formed by several inclined walls on both sides of the moving bed located in these spaces, and a const.-amt. discharging app. at the bottom of the moving bed are provided. The reactor is used for dry distn., activation, and regeneration of C materials.

49.- 97: 94805u **Activated carbon from rice grains.** Honda Motor Co., Ltd. **Jpn. Kokai Tokkyo Koho JP** 82 61,608 (Cl. C01B31/08), 14 Apr 1982, Appl. 80/136,018, 30 Sep 1980; 4 pp. Rice grains are dry-distd. with addn. of at least one of Na silicate or diatomaceous earth, carbonized, and activated. It is excellent for adsorption of vaporized fuel. Thus, activated carbon from unrefined old rice grains adsorbed methylene blue 22 mg/g compared to 15mg/g from char and 20 mg/g from saw dust.

A. Okuwaki

50._ 97: 94746a **Activated carbon from oil palm (Elaeis guineensis) nut shells.** Chan, K. C.; Goh, S. H.; Toh, H. T.; Tan, W. I.; Tang, T. S. (Dep. Chem., Univ. Malaya, Kuala Lumpur, Malay.). *Malays. J. Sci.* 1980, 6, 131-7 (Eng). The oil palm (*Elaeis guineensis*) nut shells were pyrolyzed at 300-450° to yield charcoal, phenolic tar, pyroligneous acid, and gases. The shell charcoal, when subjected to various methods of activation, provided active C. Best results were obtained by chem. and steam activation.

51._ 96: 183623e **Granular activated carbon.** Sumitomo Bakelite Co., Ltd. **Jpn. Kokai Tokkyo Koho JP 81,160,312** (Cl. C01B31/08), 10 Dec 1981, Appl. 80/63,423, 15 May 1980; 4 pp. A mixt. of an activated C feedstock and an oxide, hydroxide, or salt of an alkali metal or an alk. earth metal is heated and fired at 250-1300° to form a gas contg. H_2O, CO_2, NO_x or SO_y (where *x* is 1-3 and y is 0-3). It is then treated with an acid, an alkali, and/or water. Thus, -320 mesh coconut char (100 parts), -500 mesh $CaCO_3$ (30 parts), and a phenolic resin (RC 30%) (20 parts) were kneaded at room temp. for 30 min, granulated to 1.0 ±0.2 mm diam. spheres, heated at 80° for 30 min, 120° for 30 min, heated in N_2 at 5°/min to 800°, fired and carbonized under the same atm. at the same temp., cooled for 3 h, treated with 6*N* HCl to remove undecomposed $CaCO_3$, washed with H_2O, filtered, and dried at 150° for 3 h. Uric acid adsorption was 84.8% and I_2 adsorption was 1800 mg/g.

52._ 97: 140001d **Manufacture and uses of activated carbon.** Holden, M. J. (Thomas Ness Ltd., Nottingham, UK). *Effluent Water Treat. J.* 1982, 22(1), 27-8, 30-4, 46 (Eng). A review with no refs. see p.37

53._ 96: 71230t **Activated carbon with large specific surface from plant materials.** Berkes, Sandor; Gardos, Gyorgy; Hodossy, Gabor; Jesztl, Mrs. Janos; Kovacs, Miklos; Kun Szabo, Tibor; Pechy, Laszlo; Somogyi, Gyongyi (Veszpremi Vegyipari Egyetem) **Hung. Teljes HU 20,536** (Cl. C01B31/08), 28 Aug 1981, Appl. 77/Pe1013, 10 Jun 1977; 14 pp. Activated C with sp. surface ≥1150 m²/g is manufd. in improved yields from hydrolyzed plant materials by treatment with oleum, H_2SO_4, a waste from H_2SO_4 purifn of petroleum, or $ZnCl_2$ in H_2O, alcs., or halogenated hydrocarbons such as CCl_4, $C_2H_4Cl_2$, and C_2HCl_3, at 50-250°, followed by activation as usual. Thus, a waste material (50 g, dried at 106°) obtained as a product in the manuf. of furfural from corn cobs was refluxed 3 h with 150 g oleum in 500 g CCl_4, the mixt. was evapd., the residue washed, dried, and activated with steam and CO_2 at 900° to give 20.3% C with sp. surface 1320 m²/g. T. Mohacsi

54._ 96: 71193h **High quality adsorbents from tropical plants.** Niikawa, Kazuhiko; Ishibashi, Katsuji; Noda, Yoshio; Hosoda, Hideo (Gov. Ind. Dev. Lab., Sapporo, Japan). *Hokkaido Kogyo Kaihatsu Shikensho Hokoku* 1981, (23), 7-57 (Eng). Fluidized-bed reactors were used to study the manuf. of activated C from tropical woods and wood wastes. The wood specimen initially fed into the reactor at 420° evolved heat by exothermic decompn. so that successively fed specimens could be carbonized without need for an addnl. heat. The fluidized-bed process showed the following advantages for the manuf. of high-quality adsorbents from tropical woods: (*1*) energy consumption was much less than that with externally heated reactors and (2) uniform products were manufd. The Philippine wood species selected for manuf. of good quality granular activated C were ipil-ipil (*Intsia bijuga*) and coconut (*Cocos nucifera*) coir dust. The activated granular char products obtained from ipil-ipil and coir dust would possibly be suited for adsorption of org. solvents, gas adsorption processes, and water treatments. S. Ishihara see p.55

55. **Active carbon** (manufacture, preparation from agricultural and industrial products): a select bibliography (annotated).
Ceylon Inst. of Scientific and Industrial Research, Colombo (Sri Lanka). Technical Library and Information Service.
En
Colombo (Sri Lanka). 1981. 217 p.
831 ref.

56. 96: 24348c **Pyrolysis and gasification of lignocellulosic solid wastes for activated-carbon production.** Mackay, Douglas McDuff (Stanford Univ., Stanford, CA USA). 1981. 232 pp. (Eng). Avail. Univ. Microfilms Int., Order No. 8124106. From *Diss. Abstr. Int. B* 1981, 42(5), 2015–16.

57. 95: 171848y **Preparation and evaluation of active carbon from jute (C. capsularis) seed husks.** Fakharuddin, Mohammed; Mahtab, Rahima; Ahmed, Mahtabuddin; Bhuyan, Abdul Motin (Dep. Chem., Univ. Dacca, Dacca, Bangladesh). *Dacca Univ. Stud., Part B* 1981, 29(1), 1–9 (Eng). Jute (*C. capsularis*) seed husks were activated in the presence of $ZnCl_2$. The C produced at an optimum temp. of 400° using powd. seeds husks/$ZnCl_2$ ratio of 1:3 over an activation period of 2.5 h shows high adsorption of $KMnO_4$ (1693 mg/g C). The C produced from jute seed husks compared well with com. carbons. Physicochem. properties together with decolorization efficiency shows that the C prepd. from jute seed husks is suitable for general application.

58. **Production** of **active carbon** from coffee-making waste by gas- **activation** method.
Goshima, G.; Hirabayashi, K.; Tsuge, H.; Ohashi, K. (Gifu Univ., Kakamigahara (Japan). Faculty of Agriculture).
Ja
Journal of Japanese Society of Food Science and Technology (Japan). ISSN 0029-0394. (Jul 1981). v. 28(7) p. 393-395.
Summary (En).

59. (Obtainment of **activated charcoal** from agricultural **waste**: the optimization of manufacturing conditions (Portugal)). Obtencao de carvao activado a partir de residuos agricolas: Optimizacao das condicoes de fabrico.
Rodrigues, A.E.; Figueiredo, J.L.C.; Orfao, J.J.M.; Lopes, J.C.
Porto Univ. (Portugal). Faculdade de Engenharia.
Pt
(Planning of scientific and technological activities. Programme of research and development contracts/1978. Progress reports. 1. semester (Portugal)). Planeamento das actividades de C e T (Ciencia e Tecnologia): Programa de contratos de investigacao e desenvolvimento/1978. Relatiorios de progresso. 1. semestre. Ministerio das Financas e do Plano, Lisbon (Portugal). Junta Nacional de Investigacao Cientifica e Tecnologica
: Lisboa (Portugal). MFP. Servico de Planeamento e Projectos. 1979. p. 26-37.

60. **95: 152932e Effect of pyrolysis conditions on subsequent gasification of low-temperature lignocellulosic chars.** Mackay, D. M.; Roberts, P. V. (Dep. Civ. Eng., Stanford Univ., Stanford, CA 94305 USA). *Ext. Abstr. Program - Bienn. Conf. Carbon* **1981**, 15th, 220-1 (Eng). The effects of heating rate and final temp. during char prepn. on the yield and porosity of the char after gasification were studied. Char prepn. conditions do not significantly affect the porosity developed for a given mass loss owing to the gasification reactions at 900°. The microporosity of the chars is similar immediately before the onset of the gasification reactions (after repyrolysis or heating to the gasification temp.). The heating rate during pyrolysis at <500° is the crit. factor controlling the mass of char at 900°. For a given pyrolysis heating rate, the temp. attained during the char prepn. at >500° does not significantly affect the final yield of activated C, but the final yield depends on the heating rate during pyrolysis.

61. **95: 121531u The effect of different methods of activation on the porosity of active carbons obtained from agricultural by-products.** Rodriguez-Reinoso, F.; Lopez-Gonzalez, J. de D.; Linares-Solano, A.; Molina-Sabio, M. (Dep. Inorg. Chem., Univ. Granada, Granada, Spain). *Ext. Abstr. Program - Bienn. Conf. Carbon* **1981**, 15th, 230-1 (Eng). Olive stones and almond shells were carbonized and the products were activated by heating in CO_2. The adsorption properties were detd. by adsorbing gases (N, CO_2, n-C_8H_{18}) or indicators (from solns.). Carbons prepd. by reaction in air followed by activation in CO_2 have large adsorption capacities. Carbons prepd. from olive stones are less microporous than those prepd. from almond shells.

62. **95: 34496t Preparation and characterization of active carbons from olive stones.** Lopez-Gonzalez, J. de D.; Martinez-Vilchez, F.; Rodriguez-Reinoso, F. (Dep. Inorg. Chem., Univ. Granada, Granada, Spain). *Carbon* **1980**, 18(6), 413-18 (Eng). Crushed olive stones were carbonized at 700-900° in a flow of N and activated using a CO_2 gas flow at 675-875° or impregnation with $ZnCl_2$. Meso- and macroporosity were detd. by Hg porosity and adsorptive characteristics were detd. by adsorption of N at 77 and 90 K, CO_2 at 195 and 273 K, butane at 273 K, and methylene blue from aq. soln. at 298 K. The activated carbons had large surface areas and highly developed microporosity. Optimal carbonization conditions are discussed. All the carbons had low ash contents and contained no S.

2. AVAILABLE BOOKS AND JOURNALS FOR ACTIVATED CARBON AND RELATED SUBJECTS.

2.1 ACTIVE CARBON
Bansal, et al, 1988
Dekker

2.2 GENERAL PRODUCTS. CHEMICALS SPECIALTIES & END USES PRODUCTS :VOL 15.01, REFRACTORIES; MANUFACTURED CARBON & GRAFITE PRODUCTS; ACTIVATED CARBON
ASTM 1986 , 642 p.

2.3 ADSORPTION, SURFACE AREA AND POROSITY
Gregg & Sing 1987

2.4 CHEMICALS FROM PULP AND WOOD WASTE: PRODUCTION AND APPLICATIONS
N.J.Noyes Data Co. 1978

2.5 ACTIVE CARBON
Smisek, M. and Cerny, S. 1970
Elsevier

2.6 ACTIVATED CARBON
Hassler, J. 1963
Chemical Publishing Co.

2.7 PURIFICATION WITH ACTIVATED CARBON
Hassler, J.W. 1974

2.8 ACTIVATED CARBON TREATMENT : WATER APPLICATIONS (ENVIRONMENTAL SCIENCE & TECHNOLOGY SERVICE)
Wiley, 1988

2.9 AN ENVIRONMENTAL STUDY OF AN ACTIVATED CARBON PLANT
Clayton, P. & Wallin, S.C. 1981
W.Green England

2.10 INTRODUCTION TO INTEGRATED PROCESSING OF COCONUTS
Scarab, Stockholm. 1981, 99p.

2.11 COCONUTS : PRODUCTION, PROCESSING, PRODUCTS
Woodroof. J.G. 2nd.ed. 1979

2.12 COCONUT PALM PRODUCTS : THEIR PROCESSING IN DEVELOPING COUNTRIES
Grimwood B.E. 1976, 261p.

2.13 THE DESIGN, CONSTRUCTION AND OPERATION OF A UNIT FOR THE CARBONIZATION OF COCONUT SHELL WITH RECOVERY OF WASTE HEAT
Breag, G.R. 18p.

2.14 INDUSTRIAL CHARCOAL MAKING
FAO Forestry Department 1985

2.15 COCONUT SHELL PRODUCTS AND OTHER PROCESSES
Part 7 , Asian and Pacific Coconut Community/UNIDO
1980, 57p.

2.16 PHILIPPINE JOURNAL OF COCONUT STUDIES
Philippine Coconut Research and Development Foundation

2.17 COCONIS . COCONUT INFORMATION SERVICE NEWSLETTER
Coconut Research Institute (Sri Lanka)

2.18 INDIAN COCONUT JOURNAL
.Directorate of Coconut Development, Cochin (India)

2.19 COCONUT SITUATION
FAO

Carbon

OTTO VOHLER, FERDINAND VON STURM, ERHARD WEGE, Sigri GmbH, Meitingen, Federal Republic of Germany (Chaps. 1–3)

HARTMUT VON KIENLE, Degussa AG, Zweigniederlassung Wolfgang, Hanau, Federal Republic of Germany (Chap. 4)

MANFRED VOLL, PETER KLEINSCHMIT, Degussa AG, Zweigniederlassung Wolfgang, Hanau, Federal Republic of Germany (Chap. 5)

Book : Ullmann'S Enciclopedia of
Industrial Chemistry
5th.ed. 1985

COCONUT
INDUSTRIES
Quarterly - Number 3 1981

Special Issue: Integrated Processing

Coconuts the modern way

The dream of us all in coconut business is to find a way of using all the parts of the coconut palm in a modern and efficient way. During recent times much work has been done in various locations to find modern workable industrial means for this purpose.

Scarab Development AB, a swedish research company, has now systematized all these efforts and designed a complete integrated plant to increase the revenue from the coconut several times compared to present practices.

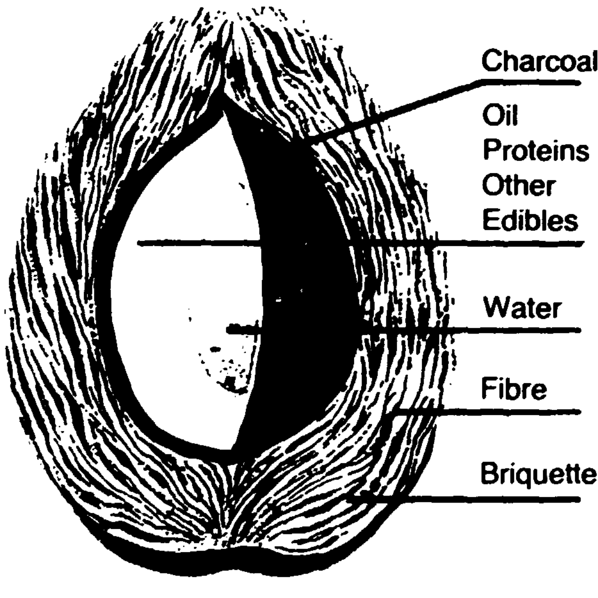
Their work is firmly based on extensive market research for the various products from the coconut palm which ensures the profitability of the process.

The process includes wet-milling of oil from the fresh coconut meat and thereby by-passes the unnecessary copra processing which is a legacy from colonial times when oil-milling was done overseas. The whole nut will be transported to the processing site, but increases in transport costs are more than offset by the reduction in cost for copra making and the increased efficiency of collection.

The reduction of farm labour in copra production is also more than offset by a large increase in employment in by-products processing and farming improvement practices which are now motivated by the increased returns from the crop.

What's a coconut worth?

VALUE OF ONE NUT AFTER BASIC INTEGRATED PROCESSING



	US c
Charcoal	0.9
Oil	9.1
Proteins	2.2
Other Edibles	8.8
Water	1.4
Fibre	5.4
Briquettes	1.7

Total value f.o.b. factory	28.6
Production cost:	2.5
Actual nut prices:	3–7
Minimal added value	21.6

Pages 4 through 8 are based on a report published by Scarab which is a type of pre-feasibility report which convincingly shows the economical and social advantages of what they term Integrated Processing.

Scarab has however refrained from giving a general analysis of the profitability of integrated processing. Their argument is that conditions will vary greatly from place to place and especially the market situation will be different for different areas both in regard to local markets and export markets. Although their general analysis shows that integrated processing no doubt is more profitable than more traditional coconut industry, we know of experience that our readers are very interested in knowing the figures of a particular industry.

We have therefore received permission from Scarab to use some of their background papers and added some figures of our own to find out what a coconut is really worth. We think that the figures we present are fairly correct, but wish to make the reservation that this a purely journalistic excersize and not part of a commercial offer. Our calculations are shown on page 5.

3 WORLDWIDE ACTIVATED CARBON PRODUCERS :

U.S.A

U.S. Producers of Activated Carbon[a]

Company and Plant Location	Annual Capacity as of July 1981 (millions of pounds)	Raw Material[b]	Registered Trade Name	Type of Product	Primary End Uses	Remarks
American Norit Co., Inc. (subsidiary of Norit NV of The Netherlands) Jacksonville, FL	—	Wood, peat	NORIT	Powdered, extruded; granular	Sugar refining, edible oils, electroplating, pharmaceuticals, chemicals, catalyst support, solvent recovery, dry cleaning, water purification	Not currently a domestic producer, but packs, blends, and distributes powdered and granular activated carbons imported from Norit's operations in The Netherlands and subsidiary supply 15-20% of world demand (see INTERNATIONAL section).
Barneby-Cheney Company Columbus, OH	7	Primarily coconut shells, and coal and wood	Adsorbite	Nearly all granular	Primarily gas phase for specialty uses	Formerly a subsidiary of Pennwalt Corporation.
Husky Oil Company (owned by Husky Oil Limited (Canada)) Husky Industries, Inc., subsidiary Romeo, FL	30	Wood	Husky Watercarb	Powdered	Water purification	Reportedly has significant share of the market for odor and taste control in water treatment.
ICI Americas (owned by Imperial Chemical Industries Limited (U.K.)) Specialty Chemicals Division Marshall, TX	85	Lignite, wood, bituminous coal	DARCO	Powdered, granular	Sugar refining, chemical purification, dry cleaning, water purification, electroplating	
Kennecott Corporation Kennecott Development Company, subsidiary Pryor, OK	25	Western subbituminous coal	CARBORUNDUM	Granular	Water purification, wastewater treatment	Kennecott Corporation announced in August 1981, its intention to sell this plant and to withdraw from the activated carbon business.

U.S. Producers of Activated Carbon[a] (continued)

Company and Plant Location	Annual Capacity as of July 1981 (millions of pounds)	Raw Material[b]	Registered Trade Name	Type of Product	Primary End Uses	Remarks
Merck & Co., Inc. Calgon Corporation, subsidiary Catlettsburg, KY Neville Island, PA	100	Bituminous coal, coconut shells	Pittsburgh Filtrasorb, Calgon	Granular	Water purification, industrial gas and liquid phase	Reportedly world's largest producer of granular carbon.
Pacific Carbons, Inc. Blue Lake, CA	8	Redwood sawdust, peach pits	PACarb	Powdered, granular	Water treatment, sugar refining, dry cleaning, mining processing	
Union Carbide Corporation Carbon Products Division Fostoria, OH	5	Petroleum base residues, coconut shells, coal	COLUMBIA	Granular, extruded	Gas purification, catalyst carriers, solvent recovery	Union Carbide Corporation announced in October 1981, the sale of this plant to Witco Chemical Corporation.
Westvaco Corporation Chemical Division Carbon Department Covington, VA	85	Wood, bituminous coal	Nuchar	Powdered, granular	Water purification, sugar refining, pharmaceuticals, fats and oils, packed bed adsorption for liquid- and gas-phase applications	Former capacity based sulfate pulp mill residue (black ash) has been phased out.
Witco Chemical Corporation Inorganic Specialties Division Petrolia, PA	5	Petroleum coke	Witcarb	Granular	Gas-phase applications, catalysts, industrial liquid and water purification.	
Total	352					

---

a. In addition to the companies listed here, the following firms also are involved in the U.S. activated carbon market:

North American Carbon, Inc., Columbus, Ohio, is an importer. The company is known to import activated carbon from France, and granular activated carbon from Hooker Mexicana S.A., Lecheria, Mexico. The latter carbon is used in evaporative loss control devices on automobiles for reduction of hydrocarbon emissions.

Sutcliffe Speakman imports significant quantities of coconut shell-derived material from its manufacturing operation in the United Kingdom.

b. Raw material selection can alter effective capacity significantly due to throughput differences.

SOURCE: CEH estimates and communication with industry.

U.S. PRODUCERS OF ACTIVATED CARBON 1988
SUPPLEMENTARY AND TENTATIVE LIST

COMPANY NAME	ADDRESS
ALDRICH CHEMICAL CO.	940 T-W. ST-PAUL AVE. MILWAUKEE, W 53233, PH 414-273-3850
ALFA PRODUCTS	152-T ANDOVER ST.DANVERS, MA 01923 PH 617-777-1970
ALLIED - SIGNAL INC.	P.O.BOX 2245 R, MORRISTOWN, N.J. 07960
CALIFORNIA CARBON CO	2825-TE. GRANT ST. WILMINGTON CA 90744, PH 213-775-6678
D-MARK,INC.	25712-T D'HONT COURT, MOUNT CLEMENS, MI 48045 PH 313-949-3610
DEGUSSA CORPORATION	RTE 46 AT HOLLISTER RD, TETERBORO RO, N.J. 07608 PH 201-288-6500
GENERAL CLARIFIER CO.	2000 EASTERN PARKWAY BROOKLYN, N.Y. 11233
HARSHAW-FILTROL PARTNERSHIP	30100-T CHAGRIN BLVD. CLEVELAND OH 44124 PH 216-292-9200
INDEPENDENT EQUIPMENT CORP.	THREE BRIDGES N.J.
ION EXCHANGE PRODUCTS, INC.	4834 S. HALSTED STREET, CHICAGO IL 60609 PH 312-254-1300
JONES CHEMICALS, INC.	CALEDONIA N.Y. 14423 PH 716-538-2311
METAL CLADDING INC.	470-T NIAGARA PKY. NORTH TONAWANDA N.Y. 14120 PH 716-693-6205
MOBAY CORPORATION	PITTSBURGH, PA 15205-9741 PH 412-777-4814
NORTH AMERICAN CARBON INC.	432 MC CORMICK BLVD. COLUMBUS, OH 43213
NUCLEAR CONSULTING SERVICES (NUCON)	P.O.BOX -29151-T, COLUMBUS OH 43229 PH 614-846-5710
SUTCLIFFE-CROFTSHAW	1301 YORK RD LUTHERVILLE MD 21093 PH 301-337-2800
THOMPSON HAYWARD CHEMICAL CO.	KANSAS CITY, KS 66106
UNION CHEMICAL DIV. UNION OIL CO OF CALIFORNIA	P.O.BOX 60455, 1231 W. FIFTH ST. LOS ANGELES CALIFORNIA 90068
UNITED CATALYSTS INC.	P.O.BOX 32370, LOUISVILLE K.Y. 40232

EUROPEAN PRODUCERS OF ACTIVATED CARBON 1987

Carbon, activated		Annual Capacity (Thousands of Metric Tons)	Raw Material and Remarks
BELGIUM			
Chemviron Carbon sa	FELUY, (Hainaut)	10	Coal; mostly granular
FRANCE			
CECA SA	PARENTIS EN BORN, (Landes)	12	Wood; granular and powder
J. Laffort & Cie. SA	BORDEAUX, (Gironde)	<1	Regeneration
Pica SA	VIERZON, (Cher)	8	Coconut shells and wood; granular and powder
GERMANY			
Bayer AG	LEVERKUSEN, (Nordrhein-Westfalen)	10	Lignite, peat; granular and powder
Bergwerksverband GmbH	ESSEN 13, (Nordrhein-Westfalen)	3	Coal; granular and powder
Degussa AG Chemicals Sector Inorganic Chemical Products Division	BRILON-WALD, (Nordrhein-Westfalen)	6	Wood and coal
ITALY			
Anticromos SpA	LEGNAGO, (Verona)	3	Wood; powder
Boston SpA	FERRARA, (Ferrara)	<1	Vegetable derived
Norit Italia SpA	RAVENNA, (Ravenna)	na	Regeneration
THE NETHERLANDS			
Norit NV	HEMBRUG-ZAANDAM, (Noord Holland) KLAZIENAVEEN, (Drenthe)	36	Peat; granular and powder
UNITED KINGDOM			
Chemviron Carbon Ltd.	GRAYS, (Essex)	2	Regeneration
Norit (UK) Ltd.	GLASGOW, (Strathclyde) Scotland	10	Wood; powder and granular
Sutcliffe, Speakman PLC	LEIGH, (Manchester, Greater)	5	Coconut shells, coal, lignite, wood
Thomas Ness Ltd.	COEDELY, (Glamorgan, Mid) Wales	2	Coal; on standby.
	ADD TOTAL	<109	

Source: SRI International estimates as of January 1, 1987.

EUROPEAN PRODUCERS OF ACTIVATED CARBON 1988
SUPPLEMENTARY AND TENTATIVE LIST

COUNTRY	COMPANY NAME	ADDRESS
BELGIUM	RODESCO	Cockerillplein 3,B-3600
CZECHOSLOVAKIA	CHEMAPOL AG.	KODANSKA 46, CS-100, PRAHA 10
GERMANY (DDR)	CHEMIE-EXPORT-IMPORT	Storkower, Str.133, DDR 1055 Berlin
GERMANY (FDR)	WESTER MINERALIEN A & H WESTER KG.	Heerstr. D-5305 Alfter Witterschlic
	SILICA GEL	Postfach 191120 B.D-100 Berlin 19,Charlottenburg
	IDOS KG.	Richter & Co.Jagerstr. 52-56,D-4000,Dusseldorf 1
	UNION CARBIDE DEUTSCHLAND G.M.B.H.	Postfach 300945, D-4000 Dusseldorf -30
	DEUTSCHE ACTIVEKOHLE GMBH	Gwinnerstr.27/33, D-6000 Frankfurt-60
	RUTGERSWERKE AKTIEN GESELLSCHAFT	Postfach 111541, D-600 Frankfurt-1
	BIESTERFELD & Co.W.	Postfach 100744, D-2000 Hamburg-1
	PROPFE CHEM.FABRIK GMBH. HEINR.	Postfach 81511, D-6800 Mannheim-81
	JAKLE KG. WILHELM	Postfach 840013, D-8500 Nürnberg-80
	NORI ADSORPTION GMBH	Adlerstr.54. D-4000 Dusseldorf 1
ITALY	CECA ITALIANA Spa.	Via G.Galilei, 51-53, I-20096 Pioltello
	FRANKE, Sas.	CP 75, I-10152 Torino
THE NETHERLANDS	WIENTJENS B.V.	Postbus 16, N-6590 DH Milsbeek
	CECA NEDERLAND N.V.	Jufferstraat 238 NL-3011 XL Rotterdam

POLAND	CIECH	Postfach 271, PL-00-950
ROMANIA	CHIMICA	POBOX 3915 R-72209 Bukarest
SWEDEN	AHLSELL MINERAL AB	BOX 81553, S-10482 Stockholm
	PERSTORP AB	S-284 80 Perstorp
	SKOGENS KOL AB	BOX 90, S-82300 Kilafors
	ULTRAMARE AB	BOX 11016, S-16111 Bromma
U.S.S.R.	SOJUSCHIMEXPORT	SMOLENSKAJA-SENNAVA 32/34 SU-121200 Moskau
	GKES TECHNO-EXPORT	Ovchinnikovskayanab 18/1 Moskau

Asian Producers of Activated Carbon - 1980

Producing Company and Plant Location	Annual Capacity as of Year-End 1980 (metric tons)	Raw Material	Trade Name	Type	Primary End Uses
Japan					
Daiichi Tanso Kogyo Co., Ltd. Fukuroi, Shizuoka Prefecture	600 3,500	Sawdust Coconut Shell	KINTAL	Powdered Granular	
Fujisawa Pharmaceutical Co., Ltd. Hiroshima, Hiroshima Prefecture	2,700 1,200	Sawdust Anthracite Coal	FUJITANSO	Powdered Granular	Brewing and food processing
Futamura Chemical Industry Co. Ohgaki, Gifu Prefecture	10,000 600	Sawdust Coconut Shell	TAIKO TAIKO	Powdered Granular	
Hitachi Tanso Kogyo Co., Ltd. Tomobe, Ibaragi Prefecture	2,400 1,000	Sawdust Coconut Shell	NITTAN NITTAN	Powdered Granular	
Hokuetsu Carbon Industry Co., Ltd. Yokohama, Kanagawa Prefecture	1,800 120	Sawdust Coconut Shell	HOKUETSU HOKUETSU	Powdered Granular	
Hokutan Chemical Industries Co., Ltd. Toda, Saitama Prefecture	3,600	Bituminous Coal	S-COAL	Granular	
Kitamura Chemical Co., Ltd. Nara, Nara Prefecture	600	Sawdust	KINTSURU	Powdered	
Kuraray Co., Ltd. Kuraray Chemical Co., Ltd. subsidiary Bizen, Okayama Prefecture	7,800	Coconut Shell	KURARAY	Granular	
Kureha Chemical Industry Co., Ltd.[a] Nishiki, Fukushima Prefecture	3,600	Resinous Pitch	KUREHA BEADS	Granular	Water treatment

cont.

Asian Producers of Activated Carbon - 1980 (continued)

Producing Company and Plant Location	Annual Capacity as of Year-End 1980 (metric tons)	Raw Material	Trade Name	Type	Primary End Uses
Korea, Republic of					
Yoolim Chemical Industrial Co., Ltd. Kimpo	n.a.			n.a.	
Malaysia					
Century Chemical Works Co. (joint venture of Takeda Chemical Industries, Ltd. (25%) (Japan), Tosin Sangyo KK. (20%) (Japan), and Wah Seong Trading Co. (55%) (Malaya)) Prai industrial complex near Penag	2,000	Waste rubber		Powdered	
Philippines					
Cenapro Chemical Corporation (joint venture of Kuraray (Japan), Marubeni Trading Co., (Japan), and Cenapro Group (Philippines)) Mandue, Cebu	5,000	Coconut shell		Granular	
Davao Central Chemical Corporation (joint venture of Takeda Chemical Ind. (Japan), Mitsubishi Corporation (Japan), and local capital in the Philippines)) Davao	2,000	Coconut shell		Granular	
Pacific Activated Carbon Company (joint venture of Daiichi Tanso Kogyo Co., Ltd. (Japan), C. Itoh & Co. (Japan), and H. N. Montenegro & Associates Inc. (Philippines)) Misamis, Mindanao	700	Coconut shell		Granular	

cont.

SOME CANADIAN AND LATINOAMERICAN PRODUCERS :

CANADA	CALGON CANADA ACTIVATED CARBON DIV.	27 Finley Rd. Bramalee , Ont. L6T 1B2
	CARBON & FILTRATION PRODUCTS CO.Div. of Pententar Inc.	9 Brynstor Rd.Islington Ontario M9B 3C5
	PENINSULA WATER TREATMENT INC.	3327 B.Mainway Burlington Ont.L7M 1A6
	SCARBOROUGH & GRANT CO. LTD.	30 Lepage CT.Downsview Ont.M3J 1Z9
	TENNANT CHARLES & CO. (CANADA LTD)	34 Clayson Rd.Weston Ont.
	UNION CARBIDE CANADA LTD.Chem.Div.	123 Eglinton Ave E. Toronto M4P 1J3
ARGENTINA	FACA SA.	J.J.Biesma 1065-68-Cap.
BRAZIL	INDUSTRIAS QUIMICAS CARBOMAFRA SA.	Z.Krosnowski & Co. Ltd
CHILE	FORESTAL S.A.	Ahumada 11 off. 602 Sgo. de Chile
MEXICO	HOOKER MEXICANA S.A.	Lecheria. Mexico
PERU	RAYON Y CELANESE PERUANA S.A. (RAYCEL)	Av. Industrial 491, Casilla 2960. Lima

SOME ASIAN PRODUCERS :

INDONESIA	INTAN PRIMA CARBON INDUSTRI.PT	Jl.P.Jakarta 141 Blk IB/11 Jakarta
MALAYSIA	ALBRIGHT & WILSON (M) Sdn Bhd	42 000 Fort Klang,S.L.
	INDUSTRIAL CARBONS Sdn Bhd	72 000 Kuala Pilah NS

4.. SOME EQUIPMENT SUPPLIERS AND CONSULTANCY SERVICES

COUNTRY	COMPANY NAME	ADDRESS
ARGENTINE	CARBONERA COOK 800	ENRIQUE MARENGO 830 SAN ANDRES PROV. BS.AS.
AUSTRALIA	COMMANDO CHEMLINE	P.O.BOX 34 TORRENSVILLE SA 5031
	LE CARBONE-LORRAINE AUSTRALIA PTY LTD	P.O.BOX 502 CONCORD NSW 2137
	LURGI (AUST) PTY LTD	608 ST KILDA RD MELBOURNE VIC 3004
	PROCESS DESIGN & FABRICATION PTY LTD.	28 LEXTON RD BOX HILL VIC 3129
	WITCO AUSTRALIA PTY LTD	P.O.BOX 444 ROCKDALE NSW 2216
BELGIUM	LAMBIOTTE ET CIE SA	AVENUE BRUGMANN, 290 B-1180 BRUXELLES
FRANCE	CECA	11, AVE MORANE SAULNIER F-78140 VELIZI VILLACOUBLAY
	LA STE LAMBIOTTE POUR	6, LA PLACE DE L'IRIS 92400 COURBEVOIE
GERMANY (FDR)	SEPEX GMBH	DAIMLERSTR. 9 D-7105 LEINGARTEN
	CARBON INTERNATIONAL	BUCHERING 7 D-6078 NEO-ISENBURG
	C. DEILMANN AG-GROUP	P.O.BOX 75 D-4444 BAD BENTHEIM
INDIA	MESSRS GLADWYN & CO.	251, DADABHAI NAOROJI RD BOMBAY-400 009,
	MESSRS ANUP ENGINEERING LIMITED	ANIL ROAD, P.O.BOX 1164 AHMEDABAD-380 002
	M/S. DORR-OLIVER, INDIA LIMITED	16, QUEENS ROAD STATE BOMBAY -400 001

ITALY	LA STE TARBOLTTI	VIA E. FERMI MARTARA, PV
JAPAN	NEGORO CHUO BOEKE GOSHI KAISHA	P.O.BOX 3 IBARAKI CITY OSAKA PREF. 567
	KURARAY CHEMICAL CO LTD.	2-1, KANDASAKUMA-CHO CHIYODA-KU TOKYO 101
	MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.	1048 OAZA KADOMA, KADOMA OSAKA PREF. 571
	MITSUBISHI RESEARCH INSTITUTE INC.	2-36 OTEMACHI CHIYODA-KU 100 TOKYO
SWEDEN	SCARAB	HOVSLAGARGATAN 5 S-11148 STOCKHOLM
SWITZERLAND	ERGO ENERGIE RESOURCES CO. AG.	ZOLLIKOFERSTR.228 CH-8008 ZURICH
U.K.	ALDRED PROCESS PLANT LTD	OAKWOOD CHEMICAL WORKS SANDY LANE WORKSHOP NOTT S 80 34Y
	SIMON CARVES LTD.	STOCKPORT,SK3 ORY CHESHIRE
U.S.A	AEROGLIDE CORPORATION	P.O.BOX AEROGLIDE RALEIGH, N. CAROLINE 27611
	CHARLES LIGHT ENGINEERING ASSOCIATES INC.	POST OFFICE BOX 315 OLYMPIA FIELD, ILLINOIS 60461
	ENERCO INCORPORATED	OLD OXFORD VALLEY RD 1 P.O.BOX 139 A LANGHORNE PENNSYLVANIA 19047
	ENVIROTECH ESP	ONE DAVIS DRIVE BELMONT CA 94002
	NICHOLS ENGINEERING & RESEARCH CO.	HOMESTEAD AND WILLOW RDS. BELLE MEAD, N. J. 08502
	PROCTOR + SCHWARTZ, INC.	7TH. STREET AND TABOR RD. PHILADELPHIA, PENNSYLVANIA 1920
	PROTRAN INC.	P.O.BOX 10764 RALEIGH, NORTH CAROLINA 27605
	RAPHAEL KATZEN ASSOCIATES INTERNATIONAL, INC.	1050 DELTA AVENUE CINCINNATI OH 45208
	[illegible] CONSTRUCTORS & ENGINEERS	P.O.BOX 1528 DOTHAN, ALABAMA 36302FTAB

COCONUT RESEARCH INSTITUTES: A TENTATIVE LIST

COUNTRY	COMPANY NAME AND ADDRESS
BELGIUM	ACTIVATED CARBONS PRODUCERS' ASSOCIATION Avenue louise 250, STE 71, B-1050 Bruxelles
BELIZE	STATION DE RECHERCHES SUR LE COCOTIER Seme-Podji
CEYLON	INDUSTRIAL DEVELOPMENT BOARD OF CEYLON
GERMANY (DDR)	TECHNISCHE UNIVERSITAT DRESDEN Mommenstr. 13, 8027 DRESDEN
INDIA	CENTRAL RESEARCH INSTITUTE FOR DRYLAND AGRICULTURE Santos H. Nagar, Hyderabad-500 659
	COCONUT RESEARCH STATION Veppankulam 614 906, Tamil Nadu
	COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH Rafi Marg, New Delhi 110 003
	INDIAN INSTITUTE OF TECHNOLOGY Madras 600 036
INDONESIAN	ASIAN AND PACIFIC COCONUT COMMUNITY Wisma Bakrie, 3rd. floor Kav. B1 Kuningan-JAKARTA
JAPAN	AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY Kasumigaseki 1-3-1, Chiyoda Ku, Tokyo 100
	GOVERNMENT INDUSTRIAL DEVELOPMENT LABORATORY, HOKKAIDO 2-1, Higashi, 2jo 17-Chome, Tsukisamu Toyohira-ku, 061-01 Sapporo
NEW ZEALAND	DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH (DSIR) Charles Fergusson State Bldg, Bowen Street Wellington 1
PAKISTAN	PAKISTAN COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH (PCSIR) University Road, Peshawar, NWFP.
PHILIPPINES	NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY P.O.BOX 774 Pedro Gil St. Ermita-Manila The
	PHILIPPINE COCONUT RESEARCH AND DEVELOPMENT FOUNDATION, INC. Metro, Manila

PORTUGAL	JUNTA NACIONAL DE INVESTIGACION CIENTIFICA E TECNOLOGICA Av. D.Carlos 1, 126-1, 2-1200 Lisboa
SRI LANKA	COCONUT RESEARCH INSTITUTE Bandiripouwa estate, Lunuwila
SWEDEN	INTERNATIONAL COCONUT DEVELOPMENT ASSOCIATION (ICDA) Box 7605,S-103 94 Stockholm
U.K.	TROPICAL DEVELOPMENT AND RESEARCH INSTITUTE Industrial Development Dpmt. Abingdom Oxfordshire. ox 14 3DA
U.S.A.	STANDFORD RESEARCH INSTITUTE 333 Ravenswood Avenue, Menlo Park, Ca 94025
	AMERICAN SOCIETY OF AGRICULTURAL ENGINEERS P.O.BOX 410, St.Joseph, MI 49085
U.S.S.R.	SIBERIAN TECHNOLOGICAL INSTITUTE All Union Research and Tecnological Institute of Carbon Sorbents

6. BIBLIOGRAPHY

6.1 BOOKS, REPORTS AND JOURNAL ARTICLES :

6.1.1 Mc Graw-Hill Encyclopedia of Science and Technology
6.1.2 Ullmann's Encyclopedia of Industrial Chemistry
5th.ed. 1985
6.1.3 Encyclopedia of Chemical Technology
Kirk & Othmer 3th ed. 1984
6.1.4 Chemical Economics Handbook
SRI International 1982
6.1.5 Coconuts : production, processing, products
Woodroof J.G.1979 2th.ed.
6.1.6 Encyclopedia of Chemical Processing and Design
Mc Ketta 1978
6.1.7 Chemicals Process Industries
Shreve and Brink 1977
6.1.8 Introduction to Integrated Processing of Coconuts
Scarab Development AB 1981
6.1.9 Manufacture and uses of activated carbon
Holden M.J. (see p.37)
6.1.10 Charcoal making in a home and the utilization for activated carbon
Satonaka. Sako 1985 (see p.45)

6.2 ON LINE SEARCHES : 1980-1988

6.2.1 Data Base CA search (Chemical Abstracts)
6.2.2 Data Base AGRIS (FAO)
6.2.3 Data Base IDA (Industrial Development Abstracts, UNIDO)

6.3 DIRECTORIES

6.3.1 ABC Europ Production 1988
6.3.2 CEC 88 (Chemical Engineering Catalog)
6.3.3 SEIBT Industrie Katalog 88
6.3.4 Thomas Register 1988
6.3.5. Kompass catalogs
6.3.6 La Industria Quimica en los paises andinos 1985
6.3.7 Japan Trade Directory 1983-84
6.3.8 Engineering Research Centres 1984

7 RELEVANT TECHNICAL PAPERS (ENCLOSED) :

SUBJECT INDEX

1 Raw material :	46,47,52,53,56,57,62
2 Manufacturing product :	38
2.1 Carbonization	49,50,51,57,58,62,65
2.2 Activation	
2.2.1 Chemical activation	39
2.2.2 Gas activation	39-41,49,50,51,56,62-64,66
2.3 Patents	68,69
3 Equipment :	
3.1 Carbonization	48,49,56,59
3.2 Activation	40,41,49,50,56,61,67,70-72,74-76,78
4 Industrial standards :	79
4.1 Powdered activated carbon	80-82
4.2 Definitions of terms relating to activated carbon	83-86
5 Uses :	41-44,77,78
6 Trade names for activated carbon :	73
7 Coconuts : production costs and returns	87-89
8 Bibliography :	51,53,54,72

* Full documents (73-76,78,79) can be obtained from UNIDO-INTIB

7.2 Manufacture and uses of activated carbon

M J Holden

ACTIVATED carbon is extensively used in a wide variety of applications and yet little is known outside the industry itself of the raw materials and methods of manufacture and also of the qualities which make the product suitable for one use and apparently unsuitable for another. The water industry is a particularly large user of activated carbon and it was felt that a brief, reasonably general introduction might be useful to personnel in the water industry who might come across the product.

Almost all materials that are composed essentially of carbon can be activated. What happens during activation is that the internal surface area of the material (the area accessible to a fluid) becomes vastly expanded, by the controlled oxidation of carbon atoms. 1 gramme of ground anthracite for example, has an internal surface area of about 10sq m and during activation it would acquire an internal surface area of (usually) between 700 and 1,200sq m.

A good activated carbon needs not only a large internal surface area but rapid access to this by means of a well developed pore structure of differing diameters. The pore diameters are usually classified for convenience as micropores, with diameters up to 60Å/100Å, intermediate or mesopores, with diameters up to 600Å/1,000Å, and transport or macropores with diameters larger than this. A significant proportion of all three must be present in a good quality activated carbon. Each individual pore network may be visualised as a hollow tree with a large central pore and a huge network of further pores of progressively reducing diameter.

Surface area is a common, though potentially misleading, indicator of performance. It is usually obtained by use of the Brunauer, Emett, Teller (BET) method which involves use of nitrogen at 77°K and a range of pressures up to saturated vapour pressure, and gives the amount of nitrogen adsorbed assuming monolayer coverage. In practice since adsorption is much greater than monolayer and the molecules encountered in adsorption are larger than nitrogen, the effective area for adsorption is usually considerably less than implied by this value. A more useful criterion is the distribution of pore volume and surface area with pore diameter.

For example, for four commercially available carbons, (see Table I) Carbons 1 to 3 would be used in liquid phase adsorption. Carbon 4 which has a much higher proportion of micropores than the others, would be used in vapour phase adsorption.

The pore size distribution is largely governed by raw material and method of activation. Carbon made by chemically activating sawdust for example, with a high proportion of mesopores, would be ideal for adsorbing high molecular weight bulky molecules of the type encountered in dye stuffs. Carbon made by thermally activating coal or coconut shell, on the other hand, with a high proportion of micropores, would be more suitable for adsorbing low molecular weight molecules such as malodorous substances. Figure 1 illustrates these two extremes.

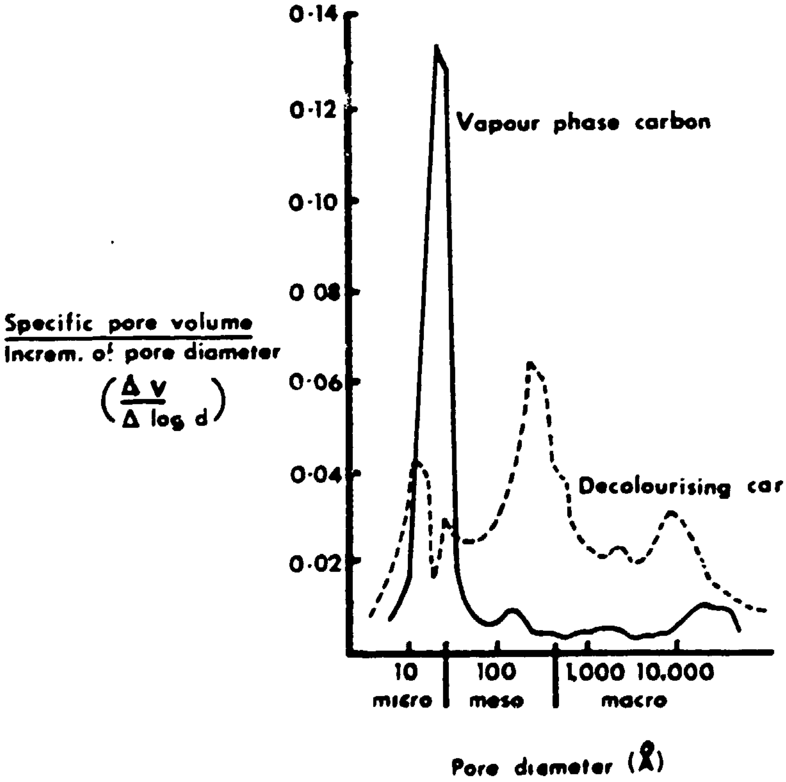


Figure 1

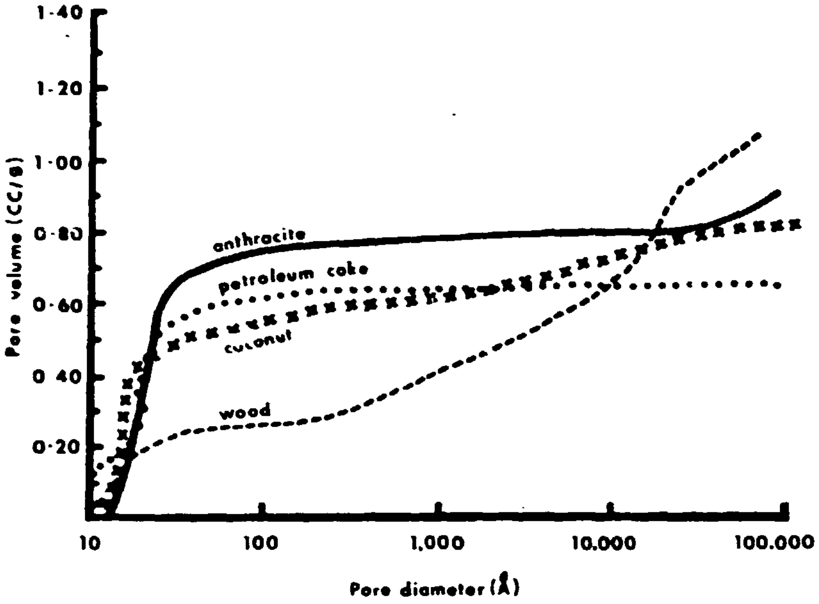


Figure 2

Another way of illustrating this is shown in Figure 2, which indicates pore size distributions for four particular activated carbons made by thermal methods from different raw materials.

An indication of an activated carbon's adsorptive capability can be obtained from its capacity for the standard reference materials used by manufacturers for quality control purposes and given in their commercial literature. The commonest of these are carbon tetrachloride, iodine, benzene, phenol, methylene blue, molasses and alkyl benzene sulphonate (detergent). There is, of course, no substitute for trying the carbon in the specific application under consideration.

Manufacture

It has already been stated that any essentially carbonaceous material can be converted to activated carbon. Just to illustrate this, patents are available, and in some cases carbon adsorbents have been manufactured, from such diverse starting materials as waste tyres, petroleum heavy oil, cellulose, phenol formaldehyde resin, rice husks, pulp mill residue, corn cobs, coffee beans, and bones, and for every one of these, many more could be mentioned. What all these, and the starting materials used in relatively large scale manufacture have in common, apart from carbon content, is ready availability and hence reasonable price.

Some of the commonest raw materials are indicated in Table II.

Statistics are difficult to come by, but from available data and personal knowledge the capacity situation for 1978 is summarised in Table III.

Of the estimated 275,000 tonnes capacity about 30,000 tonnes is probably in pellet form, and the remainder is granular and powder product in roughly equal proportions.

The actual production during the same period is more difficult to assess since in Europe and the USA, in particular, there was over-capacity (which has of course been exacerbated since by recession in the western world), but probably it totalled somewhat in excess of 200,000 tonnes.

The five raw materials given in Table III are predominant, and if the grouping together of materials as diverse as peat, lignite, bituminous coal and anthracite can be accepted (which one might expect individual manufacturers to contest), it can be seen that the coal-based family of raw material takes about 70% of the total. In the western world in fact, the companies which have entered the business in the last decade have tended to concentrate on using bituminous coal and anthracite whereas in the developing world new entrants have concentrated on using coconut shell charcoal.

Since activation takes place by the removal of what may best be termed volatile matter, the economic relationship between price and availability of raw material and of volatile content, is an important one. One of the advantages of using bituminous coal and anthracite for example, is their relatively low volatile content and hence high yield of product. In the developing world a major consideration is the availability

TABLE I: Distribution of pore volume and surface area with pore diameter

	Surface area (m^2/g)		Pore volume (ml/g)	
	Total	In pores > 40 Å diameter	Total	In pores > 40 Å diameter
Carbon 1	665	150	0.95	0.[illegible]3
Carbon 2	900	170	3.24	2.56
Carbon 3	1,335	245	2.33	1.08
Carbon 4	1,055	22	0.59	0.14

TABLE II: Raw materials of more common activated carbons

Material	Carbon content (approx) (%)	Density (approx) (g/ml)
Soft wood	40	0.4
Hard wood	40	0.6
Coconut shell	40	1.3
Lignite	60	1.2
Bituminous coal	75	1.4
Anthracite	90	1.45

TABLE III: Production capacity 1978 (tonnes)

Raw Material	N. America	W. Europe	Others*	Total*
The coal family (including peat, lignite, bituminous coal and anthracite)	104,000	62,000	25,000	191,000
Wood charcoal	28,000	7.000	3,000	38.000
Coconut shell charcoal	4,000	10,500	8,000	22,500
Sawdust	5,500	15,000	—	20,500
Petroleum coke	3,000	—	—	3,000
Totals	144,500	94,500	36,000	275,000

**excluding Eastern Europe and China*

of waste materials such as coconut shell and rice husks, which, despite having very high volatile content and hence giving low yields of activated carbon, are so inexpensive that the economics of using them are unassailable.

As mentioned previously, the methods of manufacture of activated carbons can be grouped into two main types, chemical and thermal, (although this grouping is largely used for convenience since even the chemical methods are carried out at well above ambient temperature).

The main purpose of activation is creation of an internal pore structure, and the two methods achieve this in differing ways. Chemically, porosity is achieved by degradation or dehydration of the (usually cellulosic) structure, or by the action of the oxidising gases generated. Thermally, porosity is achieved by removal of volatiles, and of carbon atoms as gaseous oxides.

Most companies nowadays use thermal methods and two particular processes will be described in some detail. Before doing this however, it would be useful to discuss the chemical route.

Chemical methods

The raw material used in chemical activation is usually sawdust and the most popular activating agent is phosphoric acid, although zinc chloride and sulphuric acid are also well known, and others used in the past include calcium hydroxide, calcium chloride, manganese chloride and sodium hydroxide. All the usual reagents have in common the fact that they are dehydrating agents. Raw material and reagent are mixed into a paste, dried and carbonised in a rotary furnace at about 600°C. Further activation with steam at 7/800°C is sometimes used. When phosphoric acid is the activating agent this carbonised product may be heated for between 2 and 8 hours at temperatures of 800-1,000°C, during which stage some of the carbon present is oxidised by the acid which is itself reduced to phosphorus and hydrides. These vapourised products are discharged to the stack and removed by scrubbing. The reagent is largely recovered by leaching after the carbonisation stage, and converted back to phosphoric acid for re-use. The product is washed with water and then dried.

Activity can be controlled by altering the proportion of raw material to reagent, commonly between the limits 1:0.5 to 1:4. Activity increases with increasing proportion of the reagent. It can also be controlled by the temperautre and residence time in the kiln.

This method produces a range of sizes, but the produce is very soft and is generally ground to powder. Pellets can be produced from this powder. The method also produces carbons with large pore diameters which makes them most suitable for decolourising, but only if pelleted are they hard enough to compare with carbons produced thermally. They generally have relatively high mineral content.

Thermal methods

Peat, lignite, bituminous coal, anthracite and coconut shell charcoal are usually activated thermally, and indeed thermal methods can, and are, used for virtually all raw materials. A variety of methods have been developed, each being appropriate to a particular type of raw material, but all sharing the same principles—carbonisation usually between 500°C and 900°C with simultaneous or subsequent reaction with an activating agent such as steam or CO_2 at 800 900°C. It is possible for the process using steam to be self-sustaining in energy terms, since the overall reaction involving conversion of carbon to carbon dioxide, is exothermic; as shown in Table IV.

The raw material must first be granulated and sized. Soft and high volatile content feedstocks such as lignite and some bituminous coals, because of their coking properties, are usually crushed and then reconstituted by briquetting, extrusion or pelletising, often with addition of a binder to aid the process. Hard and low volatile feedstocks can be carbonised without this step, but reconstitution can be used to increase the proportion of macropores produced.

The main purpose of carbonisation is to reduce volatile content and thereby convert to a form suitable for activation by (usually) steam. Carbonisation is usually carried out below 900°C with an inert gas such as flue gas.

Carbonisation and activation used to be carried out separately, but increasingly now they are carried out together. A whole variety of furnaces and kilns are used for carbonisation and activation including rotary kilns, fired directly or indirectly, multiple hearth

TABLE IV: Conversion of carbon to carbon dioxide

$C + H_2O$(steam)	$\rightarrow CO + H_2$	—31 kcal
$CO + \frac{1}{2}O_2$	$\rightarrow CO_2$	+67 kcal
$H_2 + \frac{1}{2}O_2$	$\rightarrow H_2O$(steam)	+58 kcal
OVERALL $C + O_2$	$\rightarrow CO_2$	+94 kcal

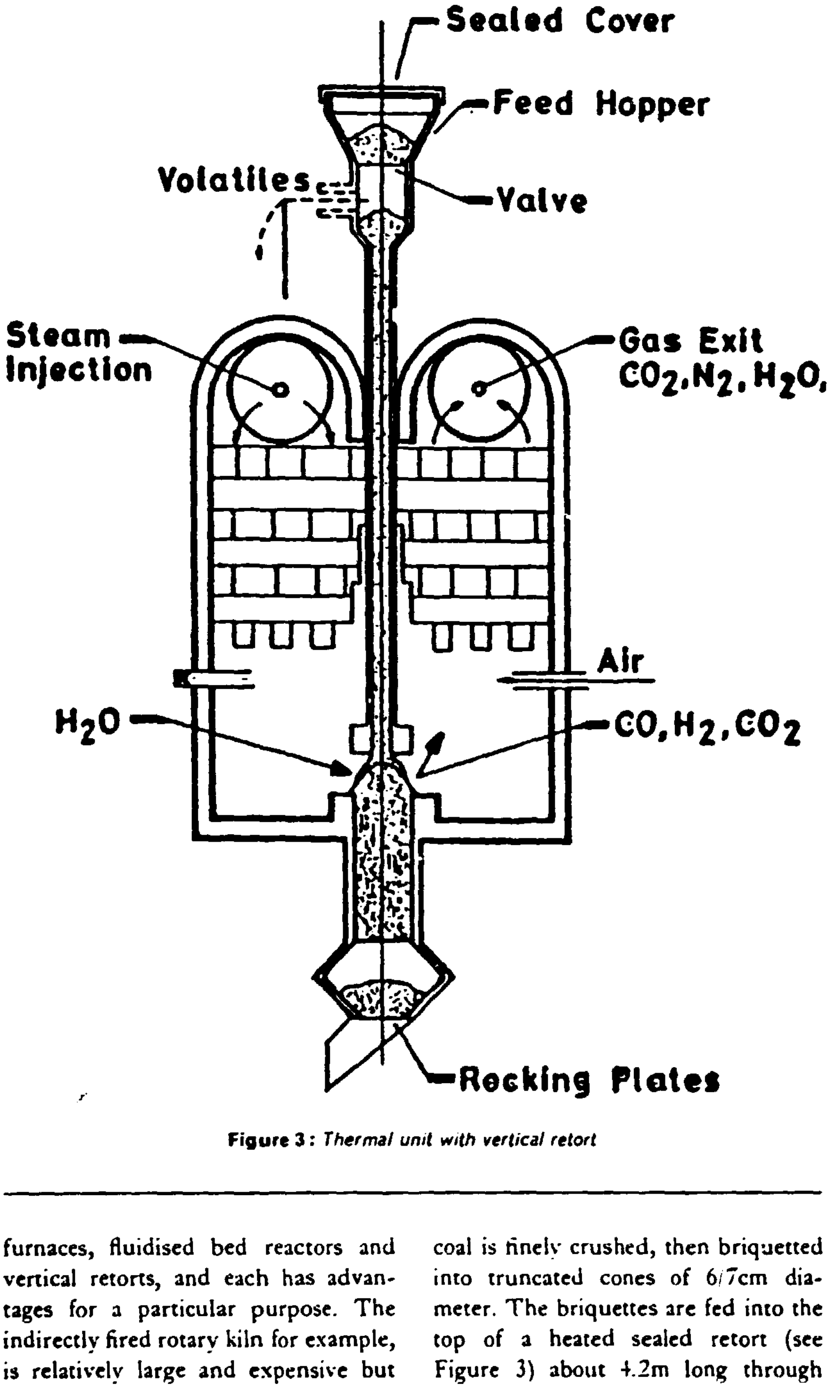


Figure 3 : *Thermal unit with vertical retort*

furnaces, fluidised bed reactors and vertical retorts, and each has advantages for a particular purpose. The indirectly fired rotary kiln for example, is relatively large and expensive but avoids a large discharge of inert gases to the after burner. The fluidised bed reactor is extremely compact but can only be used for the hardest raw materials because of the attrition which can take place during fluidisation.

Of the many thermal processes used two will be described in more detail. Both are UK processes, using coal, one employing a vertical retort and the other a fluidised bed reactor.

The first method uses briquetted bituminous coal as its feedstock, although it is also suitable for some other coals and coconut charcoal. The coal is finely crushed, then briquetted into truncated cones of 6/7cm diameter. The briquettes are fed into the top of a heated sealed retort (see Figure 3) about 4.2m long through which pre-heated steam is passed. As the briquettes move slowly down the retort carbonisation takes place. The rate of movement of briquettes down the retort is controlled by the rocking plates and is dependent on the overall residence time needed to give product of the required activity. Near the bottom of the retort, at a temperature approaching 1000°C, activation takes place. Product, still in briquetted form though by now extremely brittle, is drawn from the bottom. The product gases from the top of the retort are mixed with air and burned in an adjacent one, thereby heating the surrounding brickwork and enabling pre-heating of the steam. Product is cooled before being crushed and graded.

This process has a number of advantages, including close control of activity and high yields of granular carbon. It also enables efficient use of fuel. It would not, however, be suitable for processing low volatile materials such as anthracite which would require very high pressure briquetting before use, nor would it be ideal for coking coals since swelling would damage the retort during carbonisation and give rise to very friable products (this can be avoided to some degree by careful blending of coals or by addition of certain chemicals). The process does, of course, require initial briquetting of feedstock.

The second process described was developed by the National Coal Board at its Coal Research Establishment during the 1960's, and subsequently put into commercial operation by Thomas Ness Limited. It was designed to activate anthracite, because this has intrinsic advantages in being the hardest form of coal and containing the least volatiles. Past attempts to activate anthracite in conventional kilns had not been successful, because no means had been found of allowing sufficient access of heat and steam to individual particles of anthracite to generate formation of an extensive microporous structure. The NCB process achieved this aim by using a fluidised bed to generate movement of anthracite particles. The principle of the fluidised bed involves passage of a gas upwards through a bed of particles at a controlled velocity sufficient to lift them from the reactor base and keep them circulating freely within the bed. This allows uniform treatment of all particles, good heat transfer, and good gas-solids contact.

The process, which operates on the batch principle, is illustrated in Figure 4.

Carefully graded anthracite is fed into the reactor where it is fluidised by superheated steam entering the reactor at about 0.9m/sec velocity and heated up to carbonisation temperature, above 800°C, at a rate of about 50°C/min. Combustion gases are not recovered,

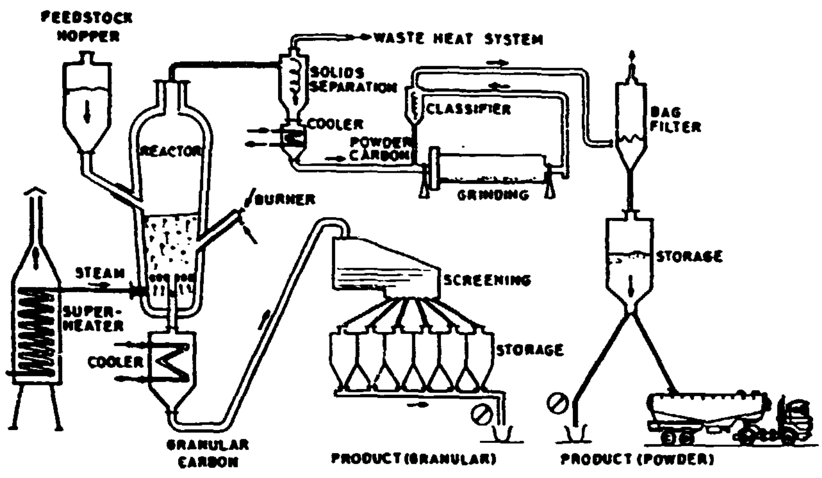


Figure 4

which renders the overall process endothermic. The plant is, however, on a site where excess combustible gas is readily available, and specially designed burners are immersed in the reactor to burn a gas/air mixture which maintains the temperature during activation at 900/950°C. Powder product is taken out of the top of the reactor before being cooled, crushed and packed. Granular product discharged from the bottom of the reactor, is similarly cooled, then graded and packed. Because of the rapid pre-heating and activation stages used in this process, a large number of batches can be processed each day.

The process has two major merits. Firstly, and most importantly, it eliminates the various stages such as crushing, reconstituting and pre-carbonising needed for volatile raw materials, and secondly, being a batch process, the period of activation can simply be lengthened or shortened to achieve the desired product characteristics.

TABLE V: Percentage absorption of various pure compounds on a coal based carbon

Carbon tetrachloride	65%
Perchloroethylene	59%
Nitrobenzene	34%
Aniline	27%
Acrylonitrile	17%
Ethylene glycol	14%
Methanol	6%
Ammonia	1%
Hydrogen sulphide	0.4%

As would be expected, starting with anthracite produces a carbon with a high proportion of micropores, particularly suitable for water treatment and air purification.

This article concentrates, for reasons which will be clear later, on powder and granular forms of carbon since these are by far the most commonly used. There are, however, cases in vapour phase application where these forms are unsuitable and a form is needed which allows rapid passage of gas, ie low pressure drop through a bed. This is achieved by use of pelleted carbon. Pellets usually also have the advantages of hardness and uniform sizing, but are naturally more expensive than granular carbon.

Many different forms of pellet are available but by far the commonest form is the cylinder. Diameters from 1mm to 10mm and lengths from 2mm to 25mm can be obtained for a whole variety of applications, but the vast majority are in the range 1mm to 4mm. It is possible to produce activated carbons in a whole range of shapes such as blocks, rods and bars, by putting the mixture of crushed carbon and resin into moulds and heating until cured.

Usage

Use of activated carbon is generally considered when there is a need to remove small quantities of soluble low and middle molecular weight organic substances from relatively large volumes of fluid. The capability of carbon for adsorbing organic material compared with inorganic in the gaseous phase is illustrated in Table V for a small number of materials. The carbon used for the tests was coal-based, and the figures relate to adsorption of the pure compound at equilibrium at 25°C from an air stream with relative vapour pressure of 0.01.

Performance with some organic materials which would otherwise be poorly adsorbed, can be substantially increased by impregnation of the carbon to allow chemical reaction to take place. An example of this is impregnation of carbon with iodine to aid adsorption of mercaptans, hydrogen sulphide, and other sulphur-containing malodorous substances.

Adsorptive capacity is related to the concentration of a particular substance in a fluid, capacity increasing with increasing concentration of the substance as Figure 5 illustrates.

There is an economic point at which use of activated carbon for purification would not be appropriate because, although greater adsorption takes place at higher levels of concentration, the carbon would naturally become more easily saturated at higher levels and require more frequent replacement. As a rough guide one would generally not consider carbon usage with contaminant concentrations greater than 100 parts per million, and the common level would be between 50 and 100 ppm. At these levels of concentration it would be economically viable to use carbon to take contaminant levels below 10ppm. Carbon is ideally capable of treating fluids with contaminant levels of less than 1 ppm, removing these to less than 0.001 ppm, for example.

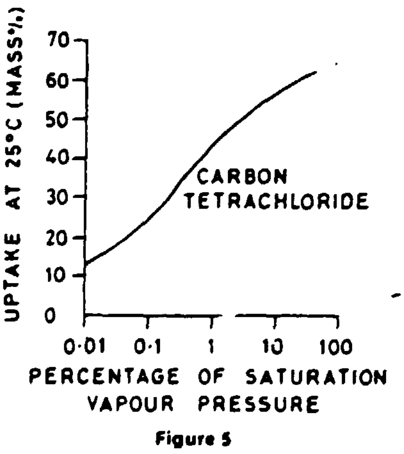


Figure 5

Adsorption

Activated carbon works by adsorption-which may be defined as the preferential accumulation of a dissolved substance, ie solute at an interface. Although the principle is the same both for vapour and liquid phases, it may be easier to understand for the liquid phase and this is appropriate because the other part of this presentation discuses use of the material in this phase.

The solute tends to migrate to the adsorbing interface because of four factors:-

1 Its own hydrophobic nature; 2 Van der Waal's forces; 3 Electrostatic attraction to charged sites at the interface (activated carbon tends to be negatively charged)-and 4 Occasionally, chemisorption takes place.

The one considered most likely to occur is van der Waal's forces, because it is well known that adsorption desorption is taking place continually and adsorbed molecules are free to move around the surface. The molecular attraction is sufficient to allow preferential adsorption to take place but not strong enough to resist the desorption that takes place during relatively mild thermal treatment.

Adsorption isotherm

The effectiveness of an activated carbon in adsorbing a solute may be expressed by producing an adsorption isotherm. The one most frequently used is the Freundlich isotherm and this gives, at a given temperature, the amount adsorbed per gramm of carbon and the equilibrium concentration of the solute.

The Freundlich isotherm is given by

$\frac{x}{m} = kc^{1/n}$ where x is weight of the solute adsorbed.
m is weight of the activated carbon
c is equilibrium residual concention of the solute in solution.
k and n are constants.

Expressed in logarithmic form:-

$\log (x/m) = \log k + 1/n \log c$, and so a graphical plot of $\log (x/m)$, the amount adsorbed per unit weight of carbon against log c should give a straight line.

The example in Figure 6 of p-Nitrophenol adsorption by two different carbons illustrates this, and also suggests limits to the linear relationship.

The relationship given by the Freundlich isotherm is usually linear over a range of concentrations which varies by no more than a factor of 100. The smaller the value of the constant n, the better a carbon will perform in a dilute solution compared to a more concentrated one.

The isotherm also explains one of the fundamental differences between using powder and granular carbon. Powder is used in a batch process, and comes into rapid equilibrium with the relatively low concentration of solute remaining after adsorption has taken place. In a granular carbon column however, the spent carbon at the inlet has to come to equilibrium with the relatively high initial solute concentration and its capacity is therefore more fully utilised.

The capability and performance of a carbon in a particular application is largely dependent on its physical characteristics. Surface area and pore size distribution have already been mentioned, but other important factors include hardness, apparent density and particle size distribution.

Clearly the harder, or more resistant to abrasion, a granular activated carbon is, the more likely it will be to resist breakdown during backwashing, regeneration or other rigorous treatment regimes. The higher the apparent density, the greater will be the weight of granular carbon held in a filter vessel of given volume. This can be considered a disadvantage, since carbon is sold on a weight basis and a greater weight would be required of a denser carbon to fill a given volume, or an advantage, since adsorptive capacity is measured on a weight weight basis and this greater weight of carbon would last for longer before needing replacement. Different views are expressed by different manufacturers depending, of course, on the products they offer! One thing is however beyond dispute, which is that carbons made from anthracite and coconut shell are harder and generally have higher apparent densities than those made from other raw materials, unless these latter are processed further, for example, briquetted. The particle size distribution is important because it governs pressure drop through a filter bed. When particles of widely differing sizes are present a matrix is built up which impedes flow of fluid, whereas a filter containing particles of fairly uniform size will give faster filtration. Good manufacturing practice should lead to saleable grades of relatively uniform sized distribution, as measured by the uniformity coefficient.

Powder and granular

Reference has been made to the

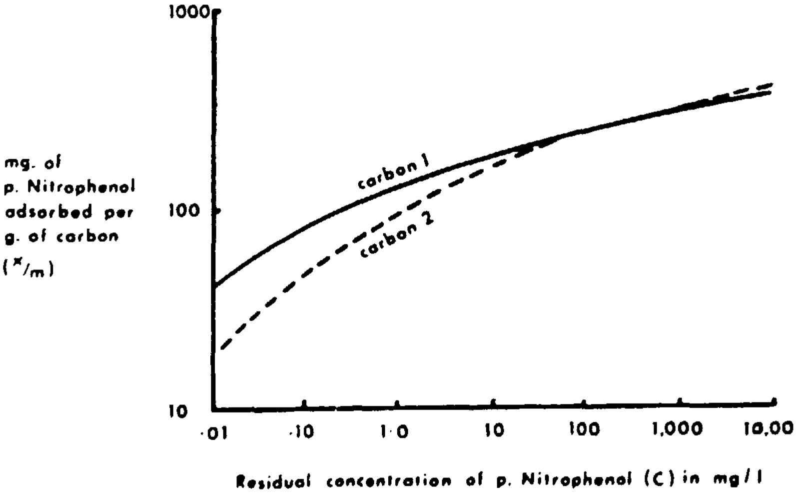


Figure 6

different forms of activated carbon, in particular, powder and granular. Whether they are produced simultaneously, or whether powder is produced by crushing granular material, they are essentially the same product, but they differ considerably in usage.

If the particle size is not large enough to allow an acceptable rate of filtration for a fluid, it is regarded as a powder. Carbon with a particle size of less than about 0.4mm is a poor filtration medium and this material is usually sold as powder after crushing to less than 100 micron. Powder is almost used entirely in liquid phase applications and after thorough mixing with the liquid to allow adsorption to take place to equilibrium, is removed by filtration and then, since recovery is difficult, disposed of.

Granular carbon, on the other hand, is used in filters with downward or upward flow of fluid through the bed, and filters may be arranged in series or parallel for most effective plant operation. Granular carbon, for reasons given when the adsorption isotherm was discussed, adsorbs a greater proportion of solute than the same quantity of equivalent quality powder carbon. It has a further major advantage that, after saturation, it can be regenerated usually by thermal oxidation of adsorbed material and the carbon can then be re-used. Extremely efficient regeneration processes are available with yields sometimes of more than 90 per cent, and the user then needs only to purchase new carbon sufficient to make up losses occurring during regeneration. Virtually all carbon manufacturers have regeneration facilities and these are also increasingly being installed on the sites of large granular carbon users.

Some development work is under way, particularly in the USA, on regeneration of saturated powder carbon. If successful, this may change the relative economics of using the two types of material.

Water treatment

The main use of activated carbon is in treatment of water, both potable and others. Potable water contains organic material which may be considered detrimental and therefore must be removed. Indeed there has been great controversy in the USA because the Carter administration proposed mandatory use of activated carbon in all cities of more than 75,000 population for removal of trace halogenated hydrocarbons from drinking water. Both the scale of the treatment and the implied hazard itself have been contested. The more common use for potable water treatment concerns the tastes and odours which occur at various times of the year because of the breakdoen of algae, and these must be removed for aesthetic reasons. Powder carbon is widely used for taste and odour removal but there is an increasing tendency to use granular carbon which can not only perform this function but, in addition, can effectively reduce the overall level of organics in water. This trend has been particularly noticeable on the Continent and the USA, where potable water is often of poorer quality than in the UK, but interest is increasing also in the UK.

In the industrial world, effluent water often containing toxic or other harmful constituents poses a major problem, and activated carbon is used in its treatment. Removal of trace oil from refinery wastewaters, for example, is a major and increasing use—it is no longer considered acceptable for such waters to be discharged to the sea or inland waterways. Removal of detergents from wastewater at laundries and vehicle washing establishments can be successfully accomplished with activated carbon. Other industries discharging noxious wastes which lend themselves to carbon treatment include the electro-plating industry and those industries manufacturing proprietary insecticides, fungicides and other toxic materials. In addition, activated carbon is starting to be used as a base for nutrient growth in the treatment of sewage by the biologically derived activated sludge process.

Use of granular carbon is widespread in the production of drinks such as beer and soft drinks, where process water is usually super-chlorinated to render it sterile and then the chlorine must be removed before manufacture of the product. Activated carbon effectively removes this chlorine by a process which is essentially one of surface catalysis. The dechlorination carried out in this instance is also valuable where drinking water is in very short supply, for instance, on board ship or on oil drilling platforms. Stored water, initially superchlorinated, is dechlorinated before use.

Decolourising

Small quantities of colour matter are often removed from products for aesthetic reasons. A notable and large scale example of this is in the production of sugar and glucose—activated carbon is extensively used in the production of white sugar. Other examples include the manufacture of edible oils and other foodstuffs, and chemicals such as esters, surfactants and alcohol. Mention of alcohols leads naturally on to the wine industry, where production of off-specification material can occasionally occur, and this may be brought within specification by means of carbon treatment. This is also true in the manufacture of spirits. A further example of this use of activated carbon is in the manufacture of pharmaceuticals where tight control of final product is vital, and where carbon can aid elimination of minute concentrations of contaminants.

Air treatment

The application of carbon in removing trace quantities of noxious contaminants from air streams is vast, and mention of a relatively small number will give an indication of this. Amongst the commonest are the ventilation of areas where large numbers of people congregate, such as theatres, airports and hospitals, and also of areas where relatively high concentrations of noxious smells may be present, such as slaughterhouses, kitchens and sewage treatment plants. Many types of industrial respirators use activated carbon as do all respirators used in combating the gases likely to be encountered in gas warfare, although in this instance the carbon must, of course, be impregnated with a range of chemicals to aid chemisorption of the gases. On a lighter note, use of carbon in cooker hoods is increasing and forms the basis of a large American and West European business. In a similar vein, and resulting from the effectiveness of press and other media advertising, carbon has had an increasing use

(concluded on page 46)

(continued from page 34)

TABLE VI: Estimated carbon use in various industries

Potable water	36%
Other liquid phase applications (including effluent and sewage water and decolourising)	36%
Air purification	14%
Solvent recovery	9%
Others	5%

in the foamed insoles being used to remove foot odour. A more worth while application may be in cigarette filters and in the removal of petrol or car exhaust fumes in motor vehicles. Other examples include vent filters for liquid storage tanks and mobile installations to adsorb the noxious fumes from welding and GRP mould manufacture. A final addition to this lengthy catalogue is the increasing application of activated carbon to the nuclear power industry, which must maintain the very highest safety standards and uses activated carbon installations to eliminate the possibility of radio active isotopes of iodine escaping into the atmosphere.

Solvent recovery

A large and increasing number of industries use hydrocarbon solvents during formulation of products. These include the manufacture of paint, rubber, adhesives, dry-cleaning chemicals, transparent film, printing ink, and plastics. Activated carbons are particualrly effective at adsorbing the reletively low molecular weight organic liquids used as solvents, such as alcohols, ketones and halogenated hydrocarbons, in some cases being capable of adsorbing their own weight of such materials. There is a benefit not only in reducing discharge of solvents but since their recovery can easily be accomplished by steaming an adsorbed bed of carbon, plants can be installed to provide programmed adsorption desorption cycles thereby reducing solvents loss to a minimum. The increasing cost of hydrocarbon solvents has lead to rapid growth of this outlet.

Chemical industry

Many examples already given relate to use by the chemical industry of activated carbon, but there are specific examples of use of carbon by this industry which do not come under the previous categories. The very large surface area encourages the use of carbon as a catalyst carrier, for example in the manufacture of PVC. The recovery of mercury can be accomplished during the alkali manufacturing processes. The vastly increased value of gold has encouraged substantial use of activated carbon in the last year or so in recovery of this metal. Finally, carbon is used in the manufacure of butadiene.

Few published statistics are available to indicate the usage of carbon in particular industries, and the personal estimate given in Table VI is necessarily approximate.

Acknowledgement

My thanks are due to a number of my colleagues and the Coal Research Establishment. The views expressed are my own, and not necessarily those of my company. ■

Mr Holden is with Thomas Ness Ltd at Nottingham.

You write . . .

'Laboratory experiments on the physico-chemical treatment of meat processing effluents'

Sir,

With reference to the very interesting paper by Dr I Tookos, in your November 1981 edition. We would be very pleased as the Alwatech process was mentioned by name, if you would allow us to comment through your correspondence column upon point 9 of Dr Tookos's conclusions.

The precipitate formed by the precipitation of protein with purified lignosulphonates (LS) does not, indeed, separate readily by sedimentation, but forms a stable floc which is readily separable by dissolved air flotation; a process which is employed in all of the full scale LS plants which Alwatech have installed around the world.

This may be a suitable time to remind your readers that this widely used process was first brought to public attention in your Journal in March 1969. Over 20 plants have now been installed and several are under construction.

Yours faithfully,
for Alwatech UK Limited
A P Hopwood
■

Index to Advertisers

7.3 Charcoal-Making in a Home, and the Utilization for Activated Carbon[*]

By

Seiichi SATONAKA[**], Chizuko SAKO[***]
and Kiyoshi KAWASE[**]

家庭製炭と活性炭への利用

里中聖一[**] 迫 千鶴子[***] 川瀬 清[**]

Contents

---

[*] Received June 20, 1964.
A part of this paper was presented at the IUFRO Conference, Madison, Wisconsin, U.S.A., June 1963.

[**] Research Division, College Experiment Forests, Hokkaido University.
北海道大学農学部附属演習林研究部

[***] Laboratory of Chemical Technology of Forest Products, Faculty of Agriculture, Hokkaido University. Present Address: Jasco Co.
北海道大学農学部林産製造学教室（現在 ジャスコ株式会社）

1. Introduction

In Japan, charcoal together with firewood was important energy source in home until 30 years ago. Namely, charcoal was 22%, firewood 12% of the fuel and light expenses a home in 1955.[1] And also, in the total energy supply, that is 56×10^{13} kcal in 1955, firewood occupied 5.4% charcoal 2.6% respectively.[2] But now, the ratio of woody fuel in the supply is only 0.1%.[2] Actually, the amount of charcoal has decreased from 2,170,000 tons in 1957 to 35,000 tons in 1982.[2]

But petroleum, the replacer of them, has some problems that comprise the shortage in future and the steep rise in prices, caused by the "Oil Shocks" that happened in 1973 and 1978. So, the wooden fuel has been noticed again.[3]

Charcoal is necessary and favorite for high grade cooking, tea ceremony, mutton dish named Jinghis Khan and barbecue on the field. Therefore, a simple carbonization in a home to get a small amount of charcoal was planned and practiced in a stove for wooden fuel. There has been reported only one study on stove charcoal by FUKUYAMA and SATONAKA.[4]

This time, the woods of 19 tree species, a *Sasa* bamboo and a densified sawdust fuel (Ogalite) in Hokkaido were carbonized in the laboratory. Next, various activated carbons were prepared by steam activation method which occupies the mainstream in the nowaday industry. The adsorptivity was tested with methylene blue and NSSC spent liquor. As the NSSC spent liquor has lower ~~content of~~ ~~combustible~~ matter, the technical combustion method for the treatment of the spent liquor is expensive.

Now, a paper factory under the strict regulation of effluent quality is practicing the adsorption method with activated carbon.[5,6] With the progress of such regulation, more factories may adopt the same method.

Thanks should be expressed to Miss Yuriko SEZAKI for her much assistance.

2. Experimental

2.1 Raw material

The woods of 19 tree species shown in Table 1 were cut out from Tomakomai Experiment Forest. Nemagaridake, *Sasa kurilensis* was cut out from Uryu Experiment Forest of Hokkaido University. A densified sawdust fuel, Ogalite was purchased from a commerical shop at the price of ¥650 a pack of 14 pieces in October of 1980. And one pack of oak charcoal produced in Iwate Prefecture was also purchased at the price of ¥3600/15 kg in August of 1981. This charcoal was used as a standard raw material for activated carbon.

Table 1. Raw material used for experiment

Species	Botanical name	D. B. H. (cm)	Height (m)
Todomatsu	*Abies sachalinensis*	10	13.0
Karamatsu	*Larix kaempferi*	10	13.0
		8	9.8
		8	10.7
Shirakanba	*Betula platyphylla* var. *japonica*	11	10.9
Sawashiba	*Carpinus cordata*	8	7.4
Asada	*Ostrya japonica*	10	9.6
Mizunara	*Quercus mongolica* var. *grosseserrata*	10	9.3
Harunire	*Ulmus davidiana* var. *japonica*	6	8.0
Yamaguwa	*Morus bombycis*	7	6.0
Hounoki	*Magnolia obovata*	7	9.3
Noriutsugi	*Hydrangea paniculata*	—	—
Tsuruajisai	*Hydrangea petiolaris*	—	—
Ezoyamazakura	*Prunus sargentii*	13	19.0
Azukinashi	*Sorbus alnifolia*	8	8.7
Itayakaede	*Acer mono*	7	10.0
Yamamomiji	*Acer palmatum* var. *matsumurae*	12	10.3
Shinanoki	*Tilia japonica*	8	9.0
		6	6.7
Koshiabura	*Acanthopanax sciadophylloides*	10	10.4
Harigiri	*Kalopanax septemlobus*	10	8.4
Aodamo	*Fraxinus sieboldiana*	8	10.0

2.2 Preparation of material

At first, the wood was cut at the size of about 5 cm diameter, 8.5 cm long. Two diameters, the longest one, the right-angled one to that, and the two heights that depart from the ends of the longest diameter were measured. The average values were determined as the each diameter and height. The volume was calculated as a column. At that time, in order to obtain the diameter shrinkage

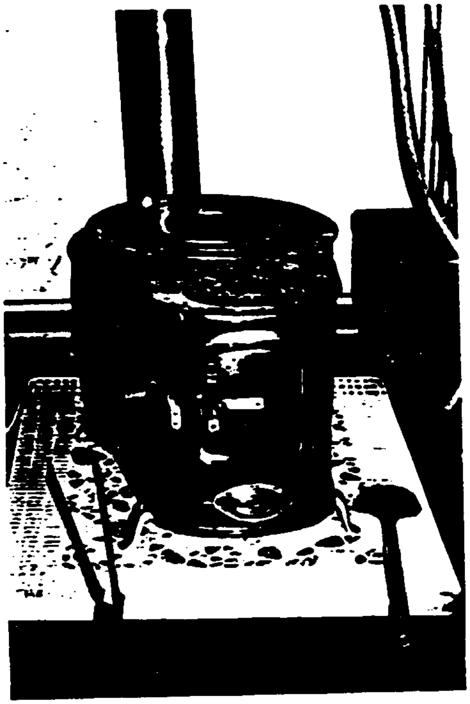


Photo 1. A conventional wood-fuel stove.

Photo 2. A vessel made of iron for carbonization.

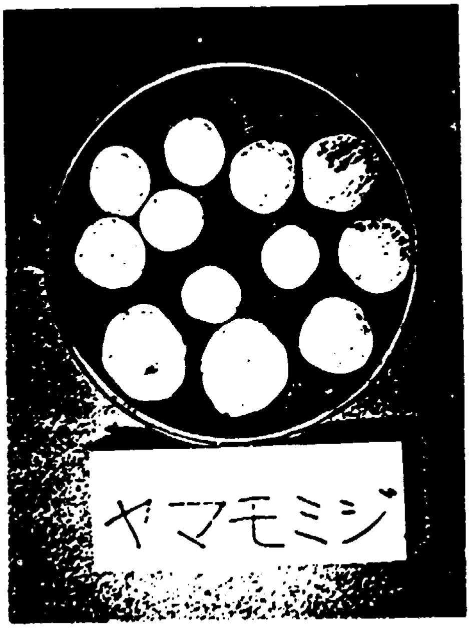


Photo 3. Raw material (*Acer palmatum*) in the vessel.

Photo 4. Charcoal made from *Acer palmatum*.

we hurt a little at an end of the longest diameter. Each specimen was weighed on an upper-dish balance with accuracy of 0.01 g.

2.3 Carbonization

An iron cylindrical lidded vessel in a conventional firewood stove was used. Size of the vessel is 20 cm diameter and 9,5 cm deep. There are three pores of 1 cm diameter through both the round side and the bottom. Through these pores, wood gas and pyroligneous liquor go out, and burn in the stove. This means the efficient utilization of the heat energy comparing with the common charcoal making.

Prepared materials were put into the vessel, the average number in a vessel was 9.7 pieces except *Sasa* bamboo. The lid was put on the vessel, and it was placed in the rear part of the stove, in which a trivet of 10-cm height was put already. With this structure, the heat is transmitted through all of the vessel surface. The combustion of fuel is begun by the ignition of some little pieces of Ogalite. Fuel used was four pieces of Ogalite and the time needed was 3～4 hours. After that, the stove containing charcoals was left through a night. Next morning, the size, volume, weight and moisture content of various charcoals prepared were determined.

2.4 Activation with steam

The charcoals and a commercial charcoal made from oak wood in Iwate Prefecture were crushed and sieved. Each 10～20 mesh fraction was activated with water vapor.

The apparatus for activation is illustrated in Fig. 1. The cylindrical reactor is 5.5 cm inner diameter and 80 cm high. There is a diffusion plate in the center of the reactor. The diffusion plate is tapered down to the center with 30° in angle. And the plate has 64 holes with 2 mm diameter. This electric furnace has the ability of 3.0 kW.

Conditions for activation[7] are as follows:

1) Weight of charcoal charged: OD 10 g
2) Activation temperature: 900 C
3) Activation time: 15 minutes
4) Flow rate of water vapor for activation: 1.5 g min.
5) Flow rate of nitrogen gas for fluidization: 100 m/ min.

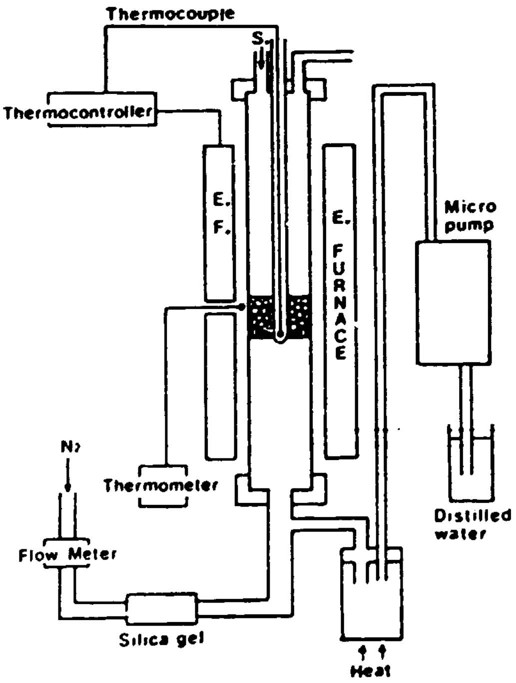


Fig. 1. Apparatus for activation.

coals were obtained from *Ulmus davidiana*, *Abies sachalinensis* and *Kalopanax septemlobus*. Rigid and high density charcoals from Ogalite (densified sawdust fuel), *Acer palmatum* and *Fraxinus sieboldiana* were obtained.

Various activated carbons were prepared from the charcoals by a steam method. In comparison of adsorptivity with commercial activated carbons, there were 10 kinds of activated carbons which were superior to the commercial ones in the methylene blue adsorption test. And also, there were 6 kinds of activated carbons which were superior to the commercial one in the lignin adsorption test. Judging from the total evaluation, it can be said that the excellent activated carbons are produced from *Hydrangea petiolaris* and *Ostrya japonica*.

But, this time, because of the same treatment for all woody materials, the most suitable conditions for each raw material are not yet searched. A new research in future will be able to find the better raw material, charcoal and activated carbon.

5. Summary

People sometimes need a small amount of charcoal for the fine dish such as Jinghis Khan or barbecue in a home. So, a convenient and simpler carbonizer which is composed of a vessel in a conventional wood-fuel stove was developed. Then, people also need an effective "worker" to improve environment, that must be an excellent activated carbon. Several kinds of activated carbon were manufactured by a steam method from the charcoals. The results are as follows:

1) Yield of the charcoal was 28% (min. 25～max. 38%) on basis of oven-dry material.

2) Density of charcoal was 0.29 (0.16 to 0.47), which was lower than 0.50 of kiln-made charcoal.

3) Moisture content of charcoal at the next morning was 2.0% (0.7 to 3.3%).

4) Shrinkage during carbonization was 17% (10 to 24%) in radial direction, 11% (7 to 16%) in longitudinal direction and 38% (22 to 46%) in volume. These data are lower than that in a literature.[10]

5) Adsorption of methylene blue on the charcoal was 36 mg/g (11 to 74 mg/g), these data include some error because of their low values.

6) Yield of activated carbon was 46% (23 to 65%) on basis of charcoal and 13% (8 to 18%) on basis of wood. These data are higher than that in a literature.[11]

7) Adsorption of methylene blue on the activated carbon was 234 mg/g (115 to 345 mg/g), which was a little inferior to a commercial W but was a little superior to commerical K.

8) Adsorption of lignin in NSSC spent liquor on the activated carbon was 38% (5 to 61%). Six kinds of them were superior to a commercial activated carbon W.

9) Total evaluation of activated carbon was calculated by the following way: (Yield of activated carbon on basis of oven-dry wood) × Adsorptivity. As the results,

some excellent activated carbons could be obtained from *Hydrangea petiolaris* and *Ostrya japonica*.

10) Positive and strenuous relation was recognized between the density of wood and that of the charcoal.

11) Negative correlation between the yield of charcoal and both radial and volume shrinkage during carbonization was observed.

12) Negative high correlations between the yield of activated carbon and both the adsorption of methylene blue and lignin were observed.

13) Positive and strong correlation was seen between the adsorption of methylene blue and lignin.

14) Negative correlation was seen between the adsorption of lignin on activated carbon and the density of wood which was used as raw material.

15) Practical combustion test of the charcoal showed the favorable properties such as easy ignition, fast combustion and no smoking.

Literature cited

1) All Japan Fuel Hall: Statistics Material on Charcoal, Firewood and the Other Home Fuel, 230 (1957).
2) Forest Mutual Aid Society: Yearbook of Forestry, 320 (1984).
3) KISHIMOTO, S.: Consideration on Forest Energy, Sohbun (1981).
4) FUKUYAMA, G. and SATONAKA, S.: Properties of carbonized substances, Research Bull. College Experiment Forests, Hokkaido University, 16, 281 (1953).
5) Japan Tappi: Handbook of Pulp and Paper Technology, 577 (1982).
6) Japan Tappi: Measures to Meet Environment, Water for the Industry, 281 (1978).
7) SATO, F., SATONAKA, S. and ISHIBASHI, K.: Production of activated carbon from shavings of a tropical wood, Proceedings of the Hokkaido Branch of the Japan Wood Research Society, No. 8, 47 (1976).
8) Japanese Standards Association: JIS K 1470, Test Method of Powdered Activated Carbon (1978).
9) Forest Products Chemistry Department, University of Tokyo: Textbook of Experimental Forests Products Chemistry, Sangyo Shuppan, 129 (1965).
10) SATONAKA, S.: Fundamental study on wood carbonization, Research Bull. College Experiment Forests, Hokkaido University, 22, 617 (1963).
11) Forestry and Forest Products Research Institute: Handbook of Wood Industry, Maruzen, 898 (1982).
12) SATO, F. and SATONAKA, S.: Preparation of carbon activated with phosphoric acid from NSSC spent liquor, Journal of the Japan Wood Research Society, 24, 101 (1978).

要　　約

家庭で，ジンギスカンまたはバーベキューをおこなう場合には，小量ではあるが，木炭を必要とするときがある．そこで，家庭用普通マキストーブの内部に小型容器を設置して，簡易炭化法により製炭をおこなった．本法は炭化のさいに発生する木ガス・木タールもすべて室内加温の熱エネルギー源として利用するもので，故福山伍郎教授の発案による。

"Present state and future prospects of activated carbon from wastes"

*Lutz-Michael Berger, Vitali Nikolaevič Klušin*¹) und *Anatoli Ivanovič Rodionov*

7.4 Stand und Perspektiven der Nutzung von Abprodukten zur Aktivkohleherstellung

Mitteilung aus dem Moskauer Chemisch-Technologischen Institut „D. I. Mendelejev“, Lehrstuhl für Technologie der Verwertung industrieller Sekundärrohstoffe, Moskau, UdSSR

Abstract

The production of activated carbon from various waste products (byproducts from the pulp and paper industries, sludges from waste water treatment, municipal refuse, waste rubber, plastics and man-made textile fibres) is reviewed. Problems of utilization of these waste products for the production of activated carbon are discussed.

Aktivkohle nimmt unter den industriell hergestellten Adsorbenzien einen führenden Platz ein. Ihre Produktion ist aus sehr vielen Rohstoffen möglich, wobei aus jedem dieser Rohstoffe eine in der Gesamtheit ihrer Eigenschaften spezifische Aktivkohle entsteht [1]. Zu den möglichen Rohstoffen gehören auch Abprodukte verschiedenster Herkunft, die durch ihre ständig wachsende Menge und aus Gründen des Umweltschutzes zu diesem Zweck in Betracht gezogen werden können [2]. Durch bestimmte Carbonisierungs- und Aktivierungsbedingungen ist es möglich, Aktivkohlen zu produzieren, deren Leistungsparameter denen handelsüblicher Sorten nicht nachstehen oder sie gar übertreffen.

Mit diesem Artikel soll das Ziel erreicht werden, den Stand der Aktivkohleherstellung aus einigen Abprodukten zu untersuchen, die dabei auftretenden Probleme zu verdeutlichen und die Perspektiven der Verwendung von Abprodukten einzuschätzen. Durch den äußerst großen Umfang der existierenden periodischen und Patentliteratur ist es nicht möglich, Abprodukte aller Art zu erfassen, die bekanntlich zum Teil zu den „klassischen“ Rohstoffen der Aktivkohleproduktion gehören, wie z. B. Kokosnußschalen oder Fruchtkerne. Bis jetzt existiert zu dieser Thematik lediglich eine Zusammenfassung der japanischen Patentliteratur von 1971 bis 1974 von *Kato* [3]. Gegenstand dieses Artikels sind die in industriell entwickelten Ländern in großen Mengen anfallenden Abprodukte der Celluloseindustrie, die [illegible] bei der Reinigung von Abwässern bildenden Schlämme verschiedener Herkunft, Hausmüll, Gummi- sowie Plast- und Kunstfaserabfälle. Wichtige andere, zur Aktivkohleproduktion genutzte Abprodukte sind landwirtschaftliche Abfälle, Schwefelsäureschlamm als Rückstand der Erdölraffination, andere Rückstände der Erdölverarbeitung, Abprodukte der Braunkohleverarbeitung u. a. Bei der Darstellung wurde hauptsächlich auf die Carbonisierungs- und Aktivierungsbedingungen sowie Besonderheiten der jeweiligen Arbeit Wert gelegt. Auf in den Originalarbeiten angeführte Adsorptionscharakteristiken wurde bewußt verzichtet, da die in den einzelnen Ländern angewendeten, zum Teil standardisierten Methoden von unterschiedlichen Versuchsbedingungen und Vorschriften ausgehen (siehe dazu [1]), so daß ein direkter Vergleich der angeführten Werte nicht möglich ist. In der Mehrzahl der Arbeiten wurden zudem vergleichende Untersuchungen zur Adsorption an handelsüblichen Aktivkohlen durchgeführt und eine qualitative Gleichwertigkeit der aus Abprodukten erhaltenen Adsorbenzien für konkrete Verwendungszwecke registriert. Auf davon abweichende Resultate wird gesondert hingewiesen.

Am Rande sei noch erwähnt, daß die Idee der Nutzung von Abprodukten zur Aktivkohleproduktion bereits sehr alt ist, wovon die in [4] erwähnten Patente zeugen.

Herstellung von Aktivkohle aus Abprodukten der Celluloseindustrie

Grundlage für die Herstellung von Aktivkohle aus Abprodukten der Celluloseindustrie ist die Pyrolyse von Lignincellulosematerialien. Die Abhängigkeit vom Ausgangsstoff, den Pyrolysebedingungen und deren Auswirkungen auf die nachfolgende Aktivierung wurden von *Mackay* und *Roberts* untersucht [5 bis 7]. Dabei wurde festgestellt, daß die Ausbeute vorrangig vom Kohlenstoffgehalt des Ausgangsmaterials abhängt, der bei Lignin 63 % und bei Cellulose 44 % beträgt [5].

Hauptsächlich werden Ablaugen des Kochprozesses und Schlämme, die bei der Abwasserreinigung anfallen, zur Aktivkohleherstellung verwendet.

Hauptbestandteil der Ablaugen der Celluloseindustrie ist das technische Lignin, daß in Abhängigkeit von den am meisten verbreiteten Sulfat- und Sulfitverfahren entweder als Alkalilignin oder Ligninsulfosäure bzw. ihren Salzen, den Ligninsulfonaten, in großen Mengen anfällt. So wurden in der BRD Ende der siebziger Jahre jährlich 780000 t Ablauge (als Trockensubstanz gerechnet) allein als Sulfitablauge erzeugt. 83 % davon wurden verbrannt, d. h. die gesamte organische Substanz also lediglich zur Energiegewinnung genutzt [8]. Der Anteil des verbrannten Alkalilignins liegt noch höher, da die Verbrennung beim Sulfatprozeß Bestandteil der Rückgewinnung der Kochchemikalien ist. Trotzdem ist auch hier eine Verwertung des Verbrennungsrückstandes zur Herstellung von Aktivkohle, auch im industriellen Maßstab, möglich [9].

In [10] wird die ökonomische Zweckmäßigkeit der Aktivkohleherstellung aus Ablaugen bei der Schaffung von geschlossenen Wasserkreisläufen in Zellstoffabriken unterstrichen. Erst die benutzte und erschöpfte Kohle wird zusammen mit den adsorbierten Schadstoffen verbrannt. Gemäß [11 bis 13] ist Aktivkohle eines der Wertprodukte, die durch die komplexe Verwertung von Ablaugen gewonnen werden können.

Ablauge aus dem Sulfitverfahren wurde schon in den zwanziger Jahren zur industriellen Aktivkohleherstellung verwendet. So beschreibt *Kausch* [4] einen technologischen Prozeß der Aktivkohleproduktion aus Calciumsulfitablauge. Nach *Vogel* [14] war allerdings die zu diesem Zweck genutzte Ablaugenmenge Ende der vierziger Jahre, bedingt durch das zu geringe Adsorptionsvermögen der Aktivkohlen, gering.

Einen breiten Raum bei den Versuchen zur Verwertung von Abprodukten der Celluloseindustrie nimmt die Literatur zur chemischen Aktivierung ein. Hydrolyselignin tränkten *Ollila* und *Harva* [15] in verschiedenen Aktivierungsmitteln, erwärmten auf 80 bis 90 °C (1 h) und dekantierten. Das entstandene Produkt wurde bei 120 bis 130 °C (24 h) getrocknet, danach bei 500 °C carbonisiert und nach dem Abkühlen mit konzentrierter HCl bei 70 bis 80 °C nachbehandelt und mit Wasser gespült. Als effektivste Aktivierungsmittel erwiesen sich $ZnCl_2$ und H_3PO_4.

Kutanov und *Udarov* verglichen zunächst die Eigenschaften von aus Lignin mittels Wasserdampf- und $ZnCl_2$-Aktivierung hergestellten Aktivkohlen [16]. Die gleiche Effektivität als Ausgangsstoff besaß ein bei 500 °C durch Pyrolyse erhaltener Ligninkoks, aus dem bereits andere Produkte, wie z. B. Phenole, gewonnen wurden [17]. Danach erfolgte eine Erwärmung des mit $ZnCl_2$ durchtränkten Kokses in einer Retorte innerhalb 0,5 h bis zur Aktivierungstemperatur mit einer Haltezeit von 1 h, das Waschen und die Trocknung. Die Adsorptionskapazität der mit $ZnCl_2$ erhaltenen

---

¹) Korrespondenzautor; Anschrift: Dr.-Ing. *Vitali Nikolaevič Klušin*, Moskovskij chimiko-technologičeskij institut im. D. I. Mendeleeva, kafedra technologii rekuperacii vtoričnych materialov promyšlennosti, Miusskaja ploščad' 9, Moskau A-47, UdSSR-125820.

und die Aktivierung des festen Produkts bei 920 °C mit Wasserdampf. PVC-isolierte Kupferdrähte werden nach [127] zunächst in Luft bis 200 °C und nachfolgend in Stickstoff bis 360 °C erwärmt. Der mit HCl gewaschene Koks wird bei 800 bis 1000 °C mit einem Gemisch aus Stickstoff und Wasserdampf der Aktivierung unterzogen. Einen Zweistufenprozeß schlagen *Yamaguchi* und Mitarbeiter [128] vor. Das bei 500 °C erhaltene PVC-Pyrolyseprodukt mischten sie mit verschiedenen Metallhydroxiden und carbonisierten erneut bei 550 bis 650 °C. Mit Hilfe der Metallhydroxide ließ sich die Porenstruktur regulieren, die Ausbeuten waren aber sehr niedrig. Den Einfluß von Zink- und Calciumstearat auf die Carbonisierung und Aktivierung von PVC-Abfällen untersuchten *Hong* und *Chung* [129, 130]. Die Anwendung von Zinkstearat erwies sich durch die Bildung von $ZnCl_2$ während der Carbonisierung als effektiver. Der Einfluß von Stearaten wird außerdem von *Kasaoka* [121, 122] und *Kitagawa* [140] diskutiert. Die Verwendung eines Gemisches von PVC und NaOH-haltigem Schlamm der Aluminiumproduktion ist Gegenstand von [131]. Die einstufige Wärmebehandlung erfolgt bei 350 bis 450 °C, wobei das NaOH des Schlammes das sich bildende HCl neutralisiert. Aus PVDC-PVC-Copolymerabprodukten (Saran) läßt sich gemäß [132 bis 134] durch Carbonisierung bei 800 °C, Granulierung mit Steinkohlenteer und Sulfitablauge als Bindemittel sowie anschließender Wärmebehandlung bei 600 bis 1000 °C eine Aktivkohle herstellen. Ein bei 800 °C erhaltenes Produkt zeigte Molekularsiebeigenschaften (0,5 nm).

Die Verwertung von Polyacrylnitril(PAN)-Abprodukten erfolgt nach [135 bis 137] zunächst im Luftstrom bei 200 bis 300 °C und danach im Wirbelbett in inerter Atmosphäre bei 800 bis 900 °C. Diese Aktivkohle besaß ein besonders hohes Adsorptionsvermögen für stickstoffhaltige organische Verbindungen.

Im Gegensatz zu der in [121, 122] vertretenen Ansicht können PF-Abprodukte ebenfalls zur Herstellung hochwertiger Aktivkohlen benutzt werden [138 bis 141]. Laut [138 bis 140] besteht die günstigste Variante der Verwertung füllstoffhaltiger PF-Abprodukte in einer Carbonisierung bei 650 °C, der nachfolgenden HCl-Behandlung und Aktivierung mit Wasserdampf bei 850 °C. Die in [141] aus 5 verschiedenen PF-Abprodukten gleichfalls mittels Dampfaktivierung bei 850 °C erhaltene Aktivkohle hatte ähnliche Eigenschaften. Außerdem wird die Möglichkeit der Regenerierung betrachtet.

PC-Abprodukte werden nach [142] bei 250 bis 450 °C (Aufwärmgeschwindigkeit weniger als 0,5 K/min) in der Schmelze carbonisiert, daraufhin bis auf eine Korngröße $\leq$ 5 mm zerkleinert und bei 800 bis 950 °C mit Wasserdampf aktiviert.

Bei der Verwertung von Abprodukten der ABS-Polymerproduktion entsteht bei der optimalen Carbonisierungstemperatur von 700 °C ein Mischadsorbens, das Kohlenstoff und γ-Al_2O_3 enthält und gute mechanische Eigenschaften besitzt [143, 144].

Außer der von *Müller* [123, 124] vorgeschlagenen Methode ist eine Polyamidabproduktverarbeitung nach [145] möglich. Der Depolymerisationsrückstand wird danach mit Holzabfällen vermischt, bei 600 °C carbonisiert, zermahlen, mit Teer als Bindemittel granuliert und einer Wasserdampfaktivierung bei 900 bis 950 °C unterzogen.

Die Erwärmung des Blasenrückstandes der Dimethylterephthalatsynthese erfolgt gemäß [145] mit einer Geschwindigkeit von 5 K/min bis 500 °C und 2 K/min bis 550 °C im Stickstoffstrom mit anschließender Aktivierung durch Wasserdampf bei 830 °C. Die Aktivkohleherstellung aus verbrauchten Ionenaustauscherharzen auf der Basis eines Styren-Divinylbenzen-Copolymers wurde in [147] untersucht. Die höchste Benzenadsorptionskapazität zeigte eine je 1 h bei 600 °C und 750 °C mit Wasserdampf behandelte Probe, während der Schwefelgehalt durch eine Carbonisierung bei 600 °C in einer Wasserstoffatmosphäre mit anschließender Wasserdampfaktivierung bei 750 °C (1 h) bei gleichzeitig hoher Benzenadsorptionskapazität des Produkts am effektivsten gesenkt wird. Durch HCl werden nach [148] verbrauchte Ionenaustauscherharze in die H-Form gebracht, getrocknet, bei 900 °C (5 min) mit begrenztem Luftzutritt carbonisiert sowie bei 1000 °C (20 min) mit Wasserdampf aktiviert.

Ergebnisse und Schlußfolgerungen

Die in den zitierten Quellen angeführten Resultate zeugen davon, daß bei aus Abprodukten hergestellten Aktivkohlen Mesoporen die dominierende Porenart bilden. Nur selten, im Falle der Verwertung von Plast- und Kunstfaserabprodukten sowie Abprodukten der Celluloseindustrie, können Kohlen mit einer Mikroporenstruktur oder mit Molekularsiebeigenschaften entstehen. Daraus folgt, daß die Abwasserreinigung perspektivreichstes Einsatzgebiet derartiger Adsorbenzien ist. Probleme, wie eine mögliche sekundäre Verschmutzung der behandelten Abwässer durch wasserlösliche, in den Kohlen enthaltenen Ionen, werden jedoch häufig vernachlässigt. Die Art der Aktivierung betreffend, wird zumeist der Gas- oder Dampfaktivierung der Vorzug gegeben, da bei einer chemischen Aktivierung technologische Probleme (Oxydation bei der Anwendung von H_3PO_4) und zunehmend Umweltschutzprobleme (Anwendung von $ZnCl_2$ – siehe dazu [1]) auftreten.

Ein bei den meisten aus Abprodukten erhaltenen Aktivkohlen auftretendes Problem ist der hohe Aschegehalt. Übereinstimmend wurde in mehreren Arbeiten [41, 80, 82, 139, 140] für verschiedene Rohstoffe gefunden, daß geringe Aschemengen die Pyrolyse und die Aktivierung katalysieren, jedoch die Adsorptionskapazität für organische Verbindungen, insbesondere bei großen Mengen, beträchtlich herabsetzen. Der Aschegehalt kann in der Regel durch eine HCl-Wäsche vermindert werden, die dabei herausgelösten Metallionen stellen aber ein neues Problem dar, das bis jetzt wenig Beachtung gefunden hat. Gleichzeitig muß bemerkt werden, daß das Vorhandensein von Asche in Aktivkohlen auch als positiver Faktor bei der Entfernung von Schwermetallionen aus Abwässern betrachtet wird [86].

Ökonomische Aspekte des Problems finden sich u. a. in [41, 42, 66, 68, 74, 92, 98]. Die ökonomische Effektivität wird im wesentlichen von folgenden Faktoren bestimmt: von den Kosten für Erfassung der Abprodukte, der Anlage und Produktion, von der Qualität und Menge sowie den Anwendungs- und Verkaufsmöglichkeiten der Aktivkohle sowie von der Verwendbarkeit der bei der Pyrolyse entstehenden gasförmigen und kondensierenden Produkte. Zwar läßt der Umfang etlicher Abprodukte, wie Lignin und Altreifen, eine großtonnagige Produktion zu, derartige Projekte konnten sich aber bis jetzt nicht durchsetzen, da die Produktion aus herkömmlichen Rohstoffen bis heute ökonomisch vorteilhafter ist. Trotzdem müssen Abprodukte aus Gründen ihrer sinnvollen Nutzung, aber auch durch die Verknappung einiger herkömmlicher Rohstoffe, wie z. B. Torf und Holz, stärker in Betracht gezogen werden. Anzustreben sind Prozesse, die von der komplexen Verwertung der Abprodukte ausgehen und bei denen Aktivkohle neben anderen Produkten entsteht. Außerdem verdienen Prozesse Beachtung, in denen verbrauchte Aktivkohle und Abprodukt zusammen als Rohstoff dienen [68, 69].

Literatur

[1] *Von Kienle, H., u. Bäder, E.:* Aktivkohle und ihre industrielle Anwendung. Ferdinand Enke Verlag, Stuttgart 1980.
[2] *Grebe, E., u. Gatichen, D.:* Sekundärrohstoffe: Begriffe, Fakten, Perspektiven. Verlag Die Wirtschaft, Berlin 1985.
[3] *Kato, K.:* Kagaku sōti (Plant and Process) 17 (1975) H. 11, S. 83–87.
[4] *Kausch, O.:* Die aktive Kohle, ihre Herstellung und Verwendung. Verlag Wilhelm Knapp, Halle (Saale) 1928.
[5] *Mackay, D. M., u. Roberts, P. V.:* Carbon 20 (1982) 87–94.
[6] *Mackay, D. M., u. Roberts, P. V.:* Carbon 20 (1982) 95–101.
[7] *Mackay, D. M., u. Roberts, P. V.:* Carbon 20 (1982) 105–111.
[8] Ullmanns Encyklopädie der technischen Chemie, Band 16, 4. Auflage, Verlag Chemie, Weinheim–New York 1978, S. 253–260.

[9] Chem. Engng. 59 (1952) 206 – 209.

[10] Pulp Paper Mag. Canada 71 (1970) H. 13, S. 44 – 45.

[11] *Timpe, W. G.:* US-P. 3762989 (1973).

[12] *Timpe, W. G.:* BRD-OS 2262726 (1973).

[13] St. Regis Paper Co.: Franz.-P. 2171581 (1973).

[14] *Vogel, H.:* Sulfitzellstoff-Ablaugen. Wepf & Co., Basel 1948.

[15] *Ollila, O.,* u. *Harva, O.:* Suomen kemistilehti [Finnische Chemiker-Ztg.] 21 (1948) H. 1 – 2, S. A 42-A 53.

[16] *Kutanov, I. P.,* u. *Uluzov, B. G.:* Vesci AN BSSR, Seryja Fizika-techničnych Navuk [Nachr. Akad. Wiss. Beloruss. SSR, Ser. physik.-techn. Wiss.] (1964) H. 1, S. 44 – 48.

[17] *Kutanov, I. P.,* u. *Uluzov, B. G.:* Vesci AN BSSR, Seryja Chimičnych Navuk [Nachr. Akad. Wiss. Beloruss. SSR, Ser. chem. Wiss.] (1965) H. 4, S. 112 – 114.

[18] *Koerlin, A. D.,* u. *Goluber, V. N.:* Uglerodnye adsorbenty i ich primenenie v promyšlennosti, č. 1 [Aktivkohlen und ihre Anwendung in der Industrie]. Konferenzmaterialien, Perm, 1969, S. 179 – 192.

[19] *Bauer, R.,* u. a.: DDR-P. 91600 (1972).

[20] *Shimada, U., Miura, K.,* u. *Takeuchi, Y.:* Patentanmeldung Japan 50-126594 (1975).

[21] *Kishimoto, S.,* u. *Mori, K.:* Kami-pa gikyoshi [J. Jap. Assoc. Pulp Paper Ind.] 23 (1969) 80 – 81.

[22] *Satomoto, S., Isobe, T.,* u. *Kayama, T.:* Enshurin kenkyu hokoku (Hokkaido daigaku nogakubu) [Res. Bull. Coll. Exp. Forests, Hokkaido Univ.] 41 (1984) 551 – 562.

[23] *Tomita, K.,* u. *Hayashi, J.:* Kami-pa gikyoshi [J. Jap. Assoc. Pulp Paper Ind.] 29 (1975) 316 – 323.

[24] *Watanabe, S.:* Japan.-Patentanmeldung 48-67189 (1973).

[25] *Watanabe, S.:* Japan.-Patentanmeldung 49-191 (1974).

[26] *Tomita, K., Suzuki, E.,* u. *Hayashi, J.:* Asahi garasu kogyo gijutsu shoreikai kenkyu hokoku [The Asahi Glass Foundation for the Contribution to Industrial Technology, Annual Report] 35 (1979) 251 – 265.

[27] *Kobayashi, Y., Ozawa, Y.,* u. *Tanabe, H.:* Japan.-Patentanmeldung 49-34194 (1974).

[28] *Kobayashi, Y., Ozawa, Y.,* u. *Tanabe, H.:* Japan.-Patentanmeldung 49-72193 (1974).

[29] *Kuneno, T., Marakami, H.,* u. *Aono, Y.:* Japan.-Patentanmeldung 51-14195 (1976).

[30] *Ramteke, D. S.,* u. a.: Indian Pulp Paper 37 (1983) H. 7, S. 6 – 13.

[31] *Vekšegonov, F. Ja.,* u. *Kozlov, V. N.:* Trudy Ural'skogo Lesotechničeskogo Instituta [Arb. Uraler Forsttechn. Inst.] 18 (1962) 84 – 91.

[32] *Vekšegonov, F. Ja.,* u. *Kozlov, V. N.:* Izvestija Vysšich Učebnych Zavedenij. Lesnoj Žurnal [Hochschulnachr. Forst-J.] 8 (1965) H. 3, S. 134 – 140.

[33] *Ryk, V. A., Achmina, E. I.,* u. *Guseva, V. I.:* Sbornik Trudov Vsesojuznogo NII Gidroliza Rastitel'nych Materialov [Gesammelte Arb. Allunionsforschungsinst. Hydrolyse pflanzlicher Materialien] 28 (1978) 119 – 123.

[34] *Mühlberg, L.,* u. *Erhard, K.:* Zellstoff u. Papier 33 (1984) 214 – 218.

[35] *Mühlberg, L.,* u. *Erhard, K.:* DDR-P. 160570 (1983).

[36] *Mühlberg, L.,* u. *Erhard, K.:* DDR-P. 160592 (1983).

[37] *Nagaya, K., Maeda, N.,* u. *Nakata, T.:* Hitachi Zosen giho [The Hitachi Zosen Technical Review] 35 (1974) H. 2, S. 90 – 95.

[38] *Masaki, M.:* Hokkaidoritsu kogyo shikenjo hokoku [Reports Hokkaido Ind. Res. Inst.] 1964/65 (Publ. 1967), S. 8 – 13.

[39] *Masunaga, K.,* u. *Echigo, T.:* Japan.-Patentanmeldung 54-71097 (1979).

[40] *Prahacs, S.:* Fuel Gasification. Advances in Chemistry Series, Vol. 69. American Chemical Society, Washington 1967, S. 230 – 252.

[41] *Barclay, H. G.,* u. *Prahacs, S.:* Pulp Paper Mag. Canada 72 (1971) H. 2, S. 51 – 64.

[42] *Prahacs, S., Barclay, H. G.,* u. *Bhatia, S. P.:* A.I.Ch.E. Sympos. Ser. 69 (1973) H. 133, S. 11 – 19.

[43] *Prahacs, S., Barclay, H. G.,* u. *Gravel, J. J. O.:* US-P. 3595806 (1971).

[44] Japan. Patentanmeldung 57-96084 (1982).

[45] *Medvedev, M. I., Maksimova, V. P.,* u. *Panasevič, A. A.:* Chimija i Technologija Vody [Chemie u. Technol. Wasser] 3 (1981) 215 – 220.

[46] *Andrianov, S. F., Semenov, V. P.,* u. *Dondukovskaja, M. N.:* Soveršenstvovanie sistem vodopol'zovanija i metodov obezvreživanija promyšlennych vybrosov predprijatij CBP [Vervollkommnung der Wassernutzung und Methoden der Entsorgung von Emissionen der Cellulose- und Papierindustrie]. Allunionsinstitut der Cellulose- und Papierindustrie, Leningrad 1982, S. 60 – 62.

[47] *Andrianov, S. F.,* u. a.: Očistka stočnych vod i gazopylevych vybrosov celljulozno-bumažnych predprijatij [Reinigung von Abwässern und Gas-Staub-Emissionen von Cellulose- und Papierfabriken]. Lesnaja promyšlennost', Moskau 1981, S. 30 – 35.

[48] *Honbe, Y.,* u. *Kunimasa, H.:* Japan. Patentanmeldung 52-117892 (1977).

[49] *Suzuki, M.:* Kankyo kagaku tokubetsu kenkyu, kenkyu hokokusho [Research Reports on Environmental Sciences, Special Report] (1981) B 89-R 34, S. 125 – 128.

[50] *Panasjuk, V. G.:* Žurnal Prikladnoi Chimii [J. angew. Chemie] 30 (1957) 813 – 816.

[51] *Norita, T.,* u. a.: Japan. Patentanmeldung 50-62990 (1975).

[52] *Čubarova, T. F.,* u. a.: Handschrift 3275-82, deponiert VINITI (Allunionsinstitut für wissenschaftliche und technische Information), Moskau (UdSSR) 1982.

[53] *Fal'kuk, V. M.,* u. *Platonov, T. G.:* Uglerodnye adsorbenty i ich primenenie v promyšlennosti, č. 1 [Aktivkohlen und ihre Anwendung in der Industrie, Teil 1]. Konferenzmaterialien, Perm 1969, S. 83 – 96.

[54] *Fal'kuk, V. M.,* u. *Platonov, T. G.:* Žurnal Prikladnoj Chimii [J. angew. Chemie] 42 (1969) 715 – 717.

[55] *Uchijima, H.:* Japan. Patentanmeldung 53-8906 (1978).

[56] *Ohno, S., Ohta, M.,* u. *Sano, S.:* Japan. Patentanmeldung 51-52856 (1976).

[57] *Echigo, T.:* Fukui-ken kogyo shikenjo nenpo [Annual Report of Fukui Prefecture Industrial Research Institute] 51 (1976) 47 – 51.

[58] *Echigo, T.:* Kogai [Pollution Control] 15 (1980) H. 2, S. 87 – 96.

[59] *Masamoto, K.,* u. *Kasinoto, T.:* Japan. Patentanmeldung 55-121908 (1980).

[60] *Matsuda, Y.:* Japan. P. 49-26838 (1974).

[61] *Hassler, J. W.,* u. *McMinn, W. E.:* US-P. 2632738 (1953).

[62] *Suarez Duran, A.:* Memorias de la Conferencia Anual ATAC (Asociacion de Tecnicos Azucareros de Cuba) [Memoiren der Jahreskonferenz der Zuckerhersteller Kubas] 38 (1968, Publ. 1981) 884 – 900.

[63] *Panasjuk, V. G.,* u. *Maksimenko, N. S.:* Gidroliznaja i Lesochimičeskaja Promyšlennost' [Hydrolysen- u. holzchem. Ind.] 9 (1956) 13 – 14.

[64] *Weber, H. H.:* Chemie-Ing.-Techn. 44 (1972) 659 – 662.

[65] *Beeckmans, J. M.,* u. *Ng, P. C.:* Environ. Sci. Technol. 5 (1971) 69 – 71.

[66] *Davis, D. A., Vigil, S. A.,* u. *Tchobanoglous, G.:* Biotechnol. Bioeng. Sympos. (1981) H. 11, S. 214 – 224.

[67] *Boeck, H., Kleerebezem, G. J.,* u. *Mars, P.:* J. Water Pollut. Control Federat. 48 (1976) 551 – 561.

[68] *Sider, J. E.:* Solid Wastes and Residues: Conversion by Advanced Thermal Processes. ACS Sympos. Ser., Vol. 76. American Chemical Society, Washington 1978, S. 241 – 251.

[69] Water Pollut. Control 114 (1976) H. 1, S. 31.

[70] *Satapathy, B. K.,* u. *Ramana Rao, D. V.:* J. Institn. Chemists (India) 54 (1982) 125 – 129.

[71] *Jakovlev, S. V.,* u. a.: Vodosnabženie i Sanitarnaja Technika [Wasserversorg. sanit. Techn.] (1978) H. 4, S. 19 – 22.

[72] *Faudi, V., Guzzelum, G.,* u. *Ondrin, M.:* La rivista dei Combustibili 38 (1984) H. 1, S. 7 – 14.

[73] *Mitchell, M.,* u. a.: Bull. Environ. Contamination Toxicology 19 (1978) 307 – 311.

[74] *Ogurcov, A. V.,* u. a.: Vodosnabženie i Sanitarnaja Technika [Wasserversorg. sanit. Techn.] (1978) H. 5, S. 10 – 11.

[75] *Ogurcov, A. V., Bobrova, V. N.,* u. *Korolev, L. P.:* Torfjanaja Promyšlennost' [Torf-Ind.] (1985) H. 10, S. 21 – 24.

[76] *Ogurcov, A. V.,* u. a.: UdSSR-P. 1096210 (1984).

[77] *Ito, Y., Ukai, N.,* u. *Iriyama, H.:* Japan.-P. 53-27716 (1978).

[78] *Bauer, O.,* u. *Bauer, S.:* BRD-OS 2260616 (1974).

[79] *Higashide, T.:* Japan. Patentanmeldung 57-150097 (1982).

[80] *Brunner, P. H.:* Dissertation, ETH Zürich 1976.

[81] *Brunner, P.:* Ingegneria ambientale: inquinamento e depurazione 9 (1980) H. 1, S. 27 – 34.

[82] *Roberts, P. V., Leckie, J. O.,* u. *Brunner, P. H.:* Solid Wastes and Residues: Conversion by Advanced Thermal Processes. ACS Sympos. Ser., Vol. 76. American Chemical Society, Washington 1978, S. 392 – 410.

[83] *Spil'fogel', P. V.,* u. a.: Ekologičeskaja technologija i očistka promyšlennych vybrosov [Ökologische Technologie und Reinigung industrieller Emissionen]. Technologisches Institut „Lensovet", Leningrad 1980, S. 137 – 141.

[84] *Petrova, L. A.,* u. a.: Ekologičeskaja technologija i očistka promyšlennych vybrosov [Ökologische Technologie und Reinigung industrieller Emissionen]. Technologisches Institut „Lensovet", Leningrad 1979, S. 134 bis 140.

[85] *Galutkina, K. A.,* u. a.: Ekologičeskaja technologija i očistka promyšlennych vybrosov [Ökologische Technologie und Reinigung industrieller Emissionen]. Technologisches Institut „Lensovet", Leningrad 1980, S. 106 – 109.

[86] *Petrova, L. A.,* u. a.: Ekologičeskaja technologija i očistka promyšlennych vybrosov [Ökologische Technologie und Reinigung industrieller Emissionen]. Technologisches Institut „Lensovet", Leningrad 1980, S. 142 – 147.

[87] *Petrova, L. A.:* Ekologičeskaja technologija i očistka promyšlennych vybrosov [Ökologische Technologie und Reinigung industrieller Emissionen]. Technologisches Institut „Lensovet", Leningrad 1982, S. 122 – 126.

[88] *Petrova, L. A.,* u. a.: Žurnal Prikladnoj Chimii [J. angew. Chemie] 56 (1983) 911 – 914.

[89] *Ishibashi, K.:* Sangyo kogai [Ind. Pollut. Control] 19 (1983) 136 – 140.

[90] *Ishibashi, K.,* u. *Shikata, N.:* Japan. Patentanmeldung 53-108086 (1978).

[91] *Makarov, V. M.,* u. *Drozdovskij, V. F.:* Ispol'zovanie amortizovannych šin i otchodov proizvodstva rezinovych izdelij [Verwendung von amortisierten Reifen und Abprodukten der Gummiproduktion]. Verlag Chimija, Leningrad 1986.

[92] *Saeki, Y.,* u. *Suzuki, G.:* Rubber Age 108 (1976) H. 2, S. 33 – 40.

[93] *Komarov, V. S., Jaceraskaja, M. I.,* u. *Artemova, T. A.:* Doklady AN BSSR [Ber. Akad. Wiss. Beloruss. SSR] 26 (1982) 712 – 715.

[94] *Jaceraskaja, M. I., Komarov, V. S.,* u. *Artemova, T. A.:* Doklady AN BSSR [Ber. Akad. Wiss. Beloruss. SSR] 27 (1983) 343 – 345.

[95] *Komarov, V. S., Jaceraskaja, M. I.,* u. *Artemova, T. A.:* Vesci AN BSSR, Seryja Chimičnych Navuk [Nachr. Akad. Wiss. Beloruss. SSR, Ser. chem. Wiss.] (1984) H. 4, S. 3 – 5.

[96] *Jaceraskaja, M. I.,* u. a.: Vodosnabženie i Sanitarnaja Technika [Wasserversorg. sanit. Tech.] (1985) H. 11, S. 7 – 8.

[97] *Bilitewski, B.:* Chem. Rdsch. 32 (1979) H. 50, S. 7, 16.

[98] *Bilitewski, B.:* Korr. Abwasser 28 (1981) 75 – 78.

[99] *Foit, J., Walopt, E.,* u. *Skorzkowski, K.:* Koks, Smola, Gaz [Koks – Teer – Gas] 24 (1979) 222 – 224.

[100] *Foit, J.,* u. a.: Pol. P. 99349 (1978).

[101] *Lacchia, A.,* u. *Matchio, G.:* Conserv. Recycling 6 (1983) 85 – 90.

[102] *Garavini, C.:* Fuel 64 (1985) 1331 – 1332.

[103] *Tocikai, N., Meguro, T.,* u. *Kawaguchi, Y.:* Nippon kagaku kaishi [J. chem. Soc. Japan, Chem. Ind. Chem.] (1979) 782 – 787.

[104] *Toshiai, N., Meguro, T.,* u. *Nakamura, Y.:* Nippon kagaku kaishi [J. chem. Soc. Japan, Chem. Ind. Chem.] (1979) 1604 – 1608.

[105] *Nakano, K.,* u. a.: Japan. P. 50-35920 (1975).

[106] *Jo, Y.,* u. *Yoda, K.:* Japan. Patentanmeldung 49-102595 (1974).

[107] *Yoda, K.:* Japan. Patentanmeldung 50-115283 (1975).

[108] *Delewski, Z.,* u. *Plata, L.:* Pol. P. 107057 (1980).

[109] *Sampi, Y.:* US-P. 3875077 (1975).

[110] *Sampi, Y.:* BRD-OS 2328400 (1974).

[111] *Hosomura, K., Wakamatsu, K.,* u. *Furukawa, T.:* Japan. Patentanmeldung 51-1109 (1976).

[112] *Nakahara, T., Watanabe, Y.,* u. *Miyajima, T.:* Japan. P. 53-10054 (1978).

[113] *Inoue, K., Matsuda, Y.,* u. *Ogawa, K.:* Japan. Patentanmeldung 51-33796 (1976).

[114] *Watanabe, Y.,* u. *Miyajima, T.:* Japan. Patentanmeldung 51-[illegible] (1976).

[115] *Inoue, I.,* u. a.: Japan. Patentanmeldung 51-98653 (1976).

[116] *Plata, L.,* u. a.: Pol. P. 90164 (1977).

7.5 PRODUCTION OF HIGH QUALITY ADSORBENTS FROM TROPICAL PLANTS

TABLE OF CONTENTS

I. Production of Powdered Activated Carbon

A series of basic experiments on the production of activated carbon from tropical woods including a wood waste was carried out using fluidized bed reactors. The raw materials selected by NIST, the counter part institute, from the view point of utilization of unutilized woods and wood wastes consist of 12 species of woods and a coconut's waste (Coir-Dust). The production process employed includes (1)preparation of samples, (2) carbonization of samples, and (3) activation of the chars under an atmosphere of super heat steam. The screened raw materials of particle size ranging from 0.25mm to 2.0mm were used for the tests. The sample which was initialy fed into an inner heat type reactor in which temperature was held at approximetely 420°C with an electric heater began to evolve heat by the exothermic decomposition so that successively fed sample could be carbonized with the heat without any other heat source. All of the chars were activated batch wise in an external heat type reactor to know the characteristics of the reaction and of the activated products. A comparative activation test was carried out in an inner heat type reactor using a selected char. The adsorptive capacities of the activated products from both reactors attained maximum values at the yield rate of approximetely 30% under temperature ranging from 800°C to 900°C. These values, which are as high as commercialized carbons were as follows: internal surface area, 1000-1500m^2/g; methylene blue adsorptive value, 270-370 mg M.B./g products; iodine adsorptive value, 1000-1200mg/g. It was found from the results of the study that the fluidized bed process showed the following advantages for the production of high quality adosorbents from tropical woods: (1) The successful carbonization in the inner heat type reactor indicates that considerable saving in energy consumption could be realized as with other external heat type reactors. (2) The methylene blue adsorptive value for the different particle sizes of the activated products are almost the same. This indicates that the fluidized bed can produce more uniform products. (3) The chars and the activated products were both obtained within 45 minutes using the respective fluidized bed reactors. Other existing processes, rotary kiln for example, require at least several hours for each products. Thus, the fluidized bed offers great advantages however, further research and development on a pilot scale should be done for the practical application of the results.

Part 1. Carbonization Step

Kazuhiko NIIKAWA, Hideo HOSODA

1 1 Raw Materials

The raw materials were selected by NIST and consist of 12 wood species including coconut's waste (Coir-Dust) as listed in Table 1.

1 2 Analytical Procedure

The analytical methods employed were in accordance with the Japan Industrial Standard (JIS) procedure or with slight modification thereof.

1) Proximate analysis :

Moisture and ash content, volatile combustible materials and fix carbon in the raw materials, chars and activated carbon products were determined.

Table 1. Wood Species

Common names	Botanical names
Apitong	Dipterocarpus grandiflorus Blanco
Mayapis	Shorea squamata (Turez) Dyer.
Tangile	Shorea polysperma (Blanco) Merr.
Palosapis	Anisoptea thurifera (Blanco) Vid.
Bagtikan	Parashorea plicate Brandis
Yakal	Shorea astylosa Foxw.
Malabayabas	Tristania decorticate Merr.
Kaatoan Baugkal	Anthocephalus chinensis Lamk
Bakauan	Rhizophara
Ipil-Ipil	Istsia bejuga (Coleber.) O. Ktze.
KaKauate	-
Coconut	Cocus hucitera

Sample Preparation

All raw materials were chipped, crushed and screened to obtain small particle sizes ranging from 0.25mm to 2.0mm, the optimum particle size range for fluidizing bed. The screened samples were dried in a drying oven at 105°C for 24 hours.

Carbonization Process

Carbonization of the dried samples was carried out in a continuous fluidized bed reactor as shown in the schematic diagram in Figure 1.

The reactor, made of stainless steel with 155mm diameter and 750 mm in height has a screw feeder which can control feed velocity of the sample automatically to keep constant temperature in the reactor and an agitator at a rotation speed of 16 rpm.

Air is fed into the reactor with a blower which can control feed velocity automatically and flows up through a perforated plate with a perforation ratio of 0.5% located just below the screw feeder. In the beginning of the carbonization, suitable amount of sample was perviously fed into the reactor to make a fixed bed with a height nearly double that of the bed's diameter and then is heated with an electric heater fixed at the external surface of the reactor. When the temperature of the bed rises to nearly 400°C, sample begins to decompose and reacts rapidly with oxygen in the air to produce heat enough to carbonize the sample without any other heat source, so carbonization proceeds continuously at an almost constant temperature by varying feed rate of sample.

Table 2. Proximate Analysis of Wood Materials

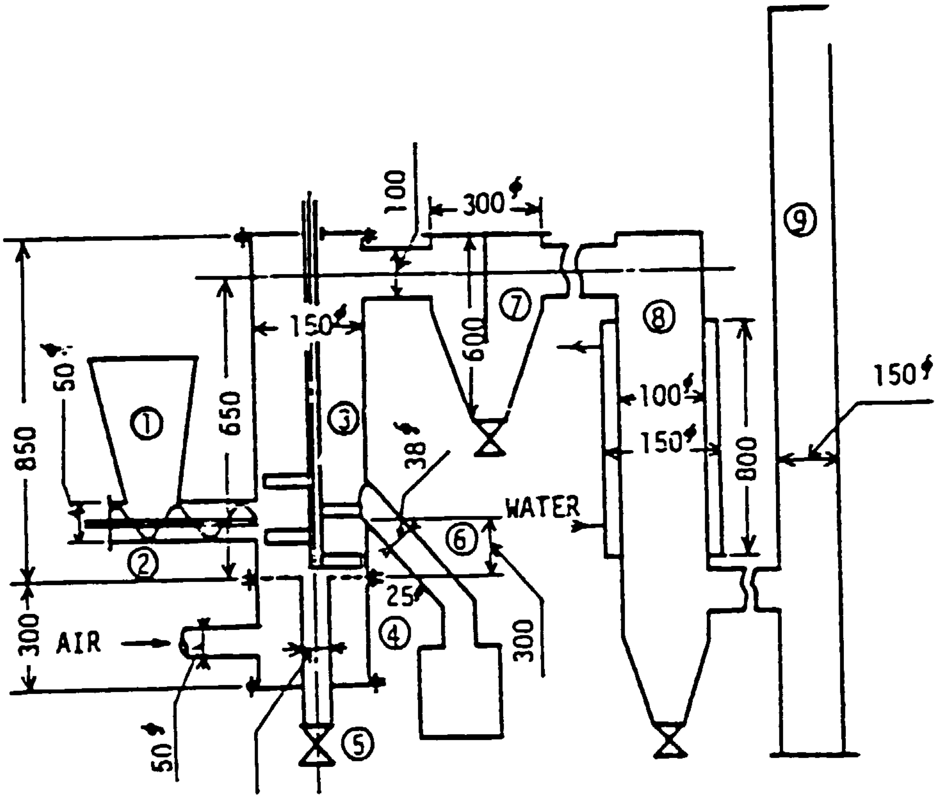
Sample Spicies	Moisture (wt.%)	Ash (wt.%)	VCM (wt.%)	FC (wt.%)
Malabayabas	11.16	0.41	77.72	10.72
Kakauate	10.72	0.87	75.92	12.49
Bakauan	10.66	1.12	74.30	13.92
Coir-Dust	15.93	6.44	53.97	23.66
Ipil-ipil	21.07	0.28	71.18	7.47
Mayapis	12.48	0.03	80.10	7.39
K. Bangkal	11.68	0.76	77.18	10.37
Apitong	7.41	3.69	23.94	66.96
Kakauate	6.88	6.08	20.45	66.59
Palosapis	7.28	3.87	18.75	70.10
Tangile	9.42	1.46	24.90	64.22

VCM : Volatile Combustible Matter   FC : Fixed Carbon

EXPERIMENTAL RESULTS AND DISCUSSION

1·5 Characteristics of Raw Materials

Table 2 shows the result of proximate analysis of the prepared raw materials. Most of the samples showed common characteristics as in other wooden materials; low ash and fixed carbon contents and high volatile matter and moisture contents.



1 - Hopper
2 - Screw feeder
3 - Stirred fluidized bed
4 - Perforated plate
5 - Char take-off valve
6 - Over flow pipe of char
7 - Dust collector
8 - Heat exchanger
9 - Stack

Fig. 1. Inner Heat type Continuous flow Reactor for Carbonization

Part 2. Activation Step

K.Ishibashi, Y.Noda

Apparatus

The reactor employed is called external heat type batch reactor of which schmatic diagram is showen in Fig 1

Analytical procedure

1) Methylene blue value [MB]

The methylene blue value was measured by spectrpohtometry: 0.2g of sample was placed in a glass flask and 50ml of standard methylene blue apueous solution was added. The operation is repeated until the blue color of the solution persists. The concentration of the remaining methylene blue was measured.

The methylene blue balue is expressed as mg of methylene blue per gram of sample.

2) Iodine value [I] :

Iodine value was determined by volumetric titration with $Na_2S_2O_3$ solution. Iodine solution was prepared by dissolving 12.7g of I_2 and KI into 1 liter of biffer solution and was standardized against 0.1N $Na_2S_2O_3$ solution.

The value is expressed as mg I_2 per g AC.

3) Intermal surface area [S]

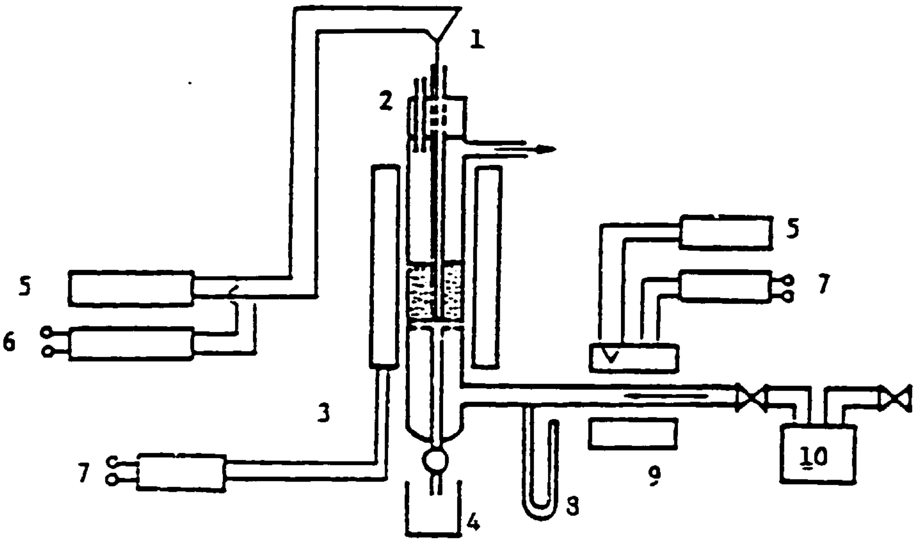
Internal surface area of activated carbon was measured by BET method, expressed as m^2/g.

4) Pore distribution analysis:

Pore distribution in unit weight of activated chars were analyzed (1) terms of the range of pore's radii from 5A to 100A, calculated by C.I. method from isothermal adsorption curve of liquid nitrogen.

Experimental Procedure

The obtained chars were activated in a batch type fluidized bed reactor under the atmosphere of super heated steam.



1. Thermocouple
2. Sample inlet
3. Electric furnace
4. Vessel
5. Temperature indicator
6. Temperature controller
7. Electric transformer
8. Manometer
9. Superheater
10. Boiler

Fig. 1 Schematic Diagram of Activation Apparatus with Batchwise Fluidized Bed.

A 100ml portion of char was taken for every experimental run. The reactor was heated up to operating temperature and nitrogen was brown into it before charging of char.

Nitrogen was switched to steam immediately after charging so that activation could be proceeded in the atmosphere of complete steam.

The activated carbon products were taken out at various reaction time to examine yields and adsorptive capacities.

PRODUCTION OF HIGH QUALITY ADSORBENTS FROM TROPICAL PLANTS: II. Production of Granulated Activated Carbon

Part 1. Granulation of chars using molasses as binder.

by

K. Ishibashi. Y. Noda.

K. Niikawa. H. Hosoda.

From a total of 12 Philippine wood species, two were selected for the production of good quality granulated activated carbon, namely ipil-ipil and coconut coir dust. Fluidization method was used in the study. The conditions for the granulation of the carbonized chars using molasses as binder was studied. An optimum ratio of 1:0.5 and 1:0.8 (char: binder) was used in the granulation process for ipil-ipil and coir dust, respectively. The carbonization was done at a gradually increasing temperature of 3°C/min at 600°C. Carbonized granules with particle size ranging from 0.5 - 2.0 mm were used for the activation study. The produced granules were activated using an external heat type stainless steel reactor according to the procedure discussed in the previous report. Steam was used as the activating agent at the rate of 2.5 mlH_2O per minute at an activation temperature of 850°C and 900°C, respectively. Maximum value for methylene blue adsorption and internal surface area obtained for ipil-ipil are 290 mg/gAC and 1200 m^2/gAC at 900°C; for coir dust, 390 mg/gAC and 1000 m^2/gAC at 850°C. The gas adsorption test done for both ipil-ipil and coir dust showed that both exhibited maximum adsorbability at 900°C. Maximum value of 40-50% (by wt.) was observed for both benzene and acetone; while 70-90 % (by wt.) was obtained for carbon tetrachloride. Results of the study indicated that the activated granular char products obtained from both ipil-ipil and coir dust would possibly be suited for adsorption of organic solvents, gas adsorption processes and water treatment, among others.

coal at the desired temperature and reaction time.

Activation of the granulated chars were done at 850°C and 900°C, respectively with varying reaction time from 10 to 60 minutes.

Determination and Evaluation of Adsorptive Properties of Activated Carbon

The bulk density, internal surface area and pore destribution of the activated carbon products obtained at various reaction time were measured by the respective methods described in the previous report.

The adsorptive capacity of the obtained products were evaluated by methylene blue adsorption [MB] test as discussed in the previous report.

RESULTS AND DISCUSSION

Effect of activation time on product yield

Correlation of the yield of activated char granules with activation time shows that there was significant loss in weight of product as activation time proceeded. More pronounced decrease in yield was noted with increasing temperature as shown in Fig. 3. Higher weight loss which resulted to lower yield was observed in coir dust as compared to that of ipil-ipil.

In the activation process, the reaction rate of charcoal with steam in terms of weight loss was calculated as discussed in the previous report. The value of k (apparent constant) for coir dust was twice the k obtained for ipil-ipil as shown below:

Activation Temp.	k	
t (°C)	Coir dust	Ipil-ipil
850	$57.5\text{x}10^{-3}$ min^{-1}	$29.48\text{x}10^{-3}\text{min}^{-1}$
900	$92.0\text{x}10^{-3}$ min^{-1}	$35.93\text{x}10^{-3}\text{min}^{-1}$

The above data show that coir dust can be activated faster than ipil-ipil, thus the former required shorter time for activation.

Correlation of Methylene blue [MB] Adsorptive Capacity and Internal Surface Area [S] with Reaction Time (θ)

Figures 4 & 5 show the correlation of reaction time with [MB] and [S] respectively. A gradual increase in [MB] adsorbability was noted with increasing reaction time. For coir dust, activation was more effective at lower temperature. Maximum value of 390 mg/g AC was obtained at 850°C and 30 minutes. Beyond this point, [MB] value tended to decrease. For ipil-ipil, longer reaction time (60 min.) was needed to attain the maximum value of 300 mg/g AC at 850°C.

The results of the internal surface area [S] determination also gave the same increasing trend of results with reaction time until a saturation point was reached. Beyond this point, an abrupt decrease in the surface area was noted. Development of internal surface area for ipil-ipil was more effective at higher temperature. Thus higher [S] of 1,200 m^2/g AC was obtained at 900°C for ipil-ipil while 1,000 m^2/g AC at 850°C was obtained for coir dust.

Correlation of [MB] Value an' [S]

Fig. 6 indicates that the [MB] value is directly proportional to the [S] for both coir dust and ipil-ipil. Linear lines with the same slopes which indicate good inference was obtained. At [MB] = 0, the intercept gave values of 380m^2/g AC and 450 m^2/g AC. From the slope, the area occupied by individual molecule on the activated products was determined at a value of 150$Å^2$ for both samples. An accessible area of 192$Å^2$ was obtained for Graphon (a non porous carbon)[3]. This nearly similar values is an indication that adsorption of MB on the obtained products is physical adsorption.

Correlation Between Bulk Density and Reaction Time

Finally, the bulk density of each of the activated products obtained with particle sizes ranging between 0.5 - 2.0 mm were compared with the commercial activated carbon of the same particle size range. Comparative results as shown in Fig. 7 indicates that the bulk density of the activated granular char products compare favorably or is even higher than that of the commercial product.

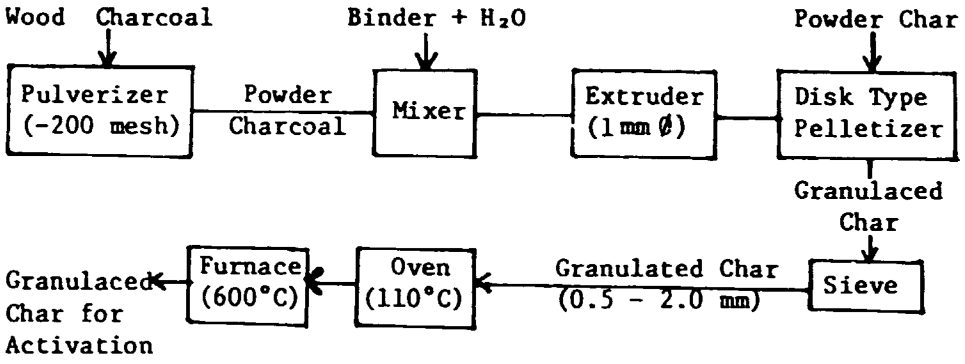


Fig. 1. Schematic Diagram of Granulation Process for Powder Char

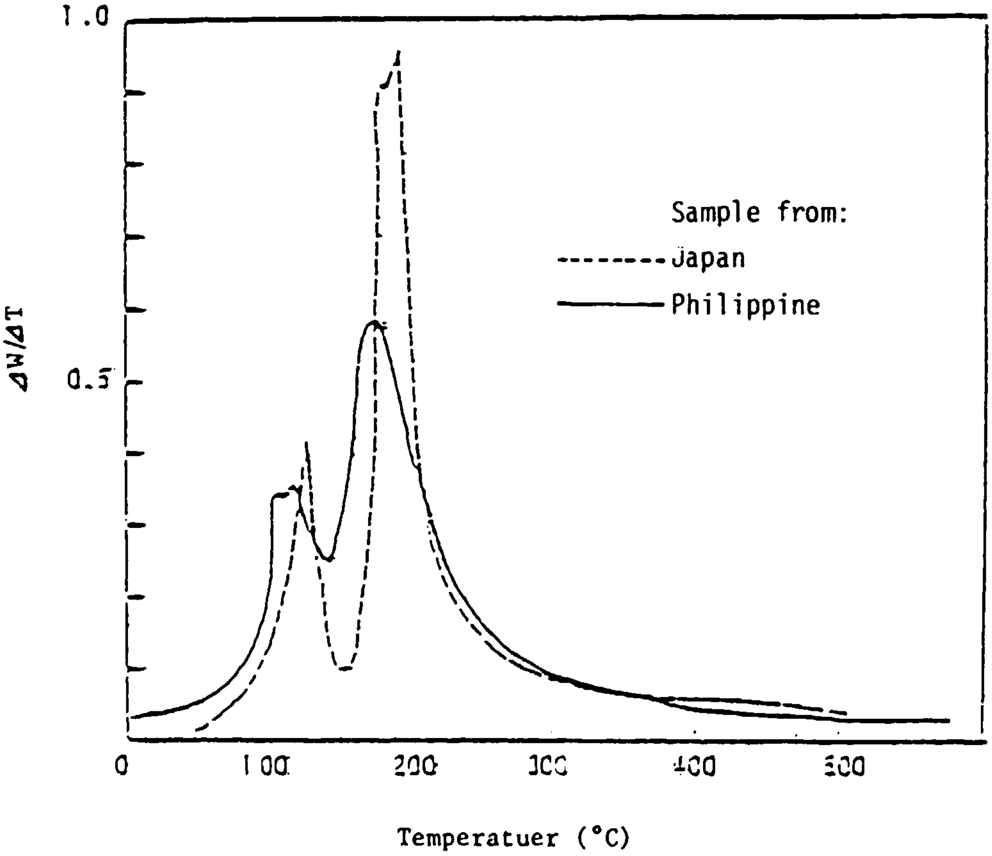


Fig. 2. Thermogravimetric Curve of Molasses.

III Steam activation of chars by the use of an inner heat type fluidized bed reactor.

by
Hideo Hosoda, Kazuhiko Niikawa,
Katsuji Ishibasi, Yoshio Noda

In the previour works, as described in part I and 2 in this report, we obtained basic data and parameters about production of activated carbon from tropical plants using an external heat type batch reactor.

It is known, however. that the reactor is not beneficial for practical use because of it's high energy consumption.

The present work was done to evaluate activation of chars using an inner heat type fluidized bed reactor to explore practical process for the production of activated carbon from tropical plants.

Experimental

Sample preparation

IPIL-IPIL and Coir-Dust were selcted as raw materials, and were carbonized using the procedures described before. The powder and the granulated chars prepared by the previous method were used as sample.

Apparatus

A flow sheet of the inner heat type fluidized bed reactor is shown in Fig. 1.

The reactor, 160cm long, made of stain-less steel was shaped as seen in the figure: upper part was step wise expanded by two different sizes of diameter so that the small particles of sample could be retained longer in the reactor.

Sample was fed into the reactor by a screw feeder fixed at just above level of a perforated plate. The activated carbon products were taken out from a take off pipe by opening a valve fixed at it's inlet located at the opposite side of the screw feeder.

A propane gas burner connected with an air pipe was located at just below the perforated plate. Steam was fed into the bottom side of the reactor from a water boiler through a steam heater with which steam was heated to 650°C. The feed rates of the fuel gas, air and steam were measured by gas flow meters, weighing loss of water in the boiler respectively. Temperatures in the reactor were measured, recorded by thermometers located at six point of it.

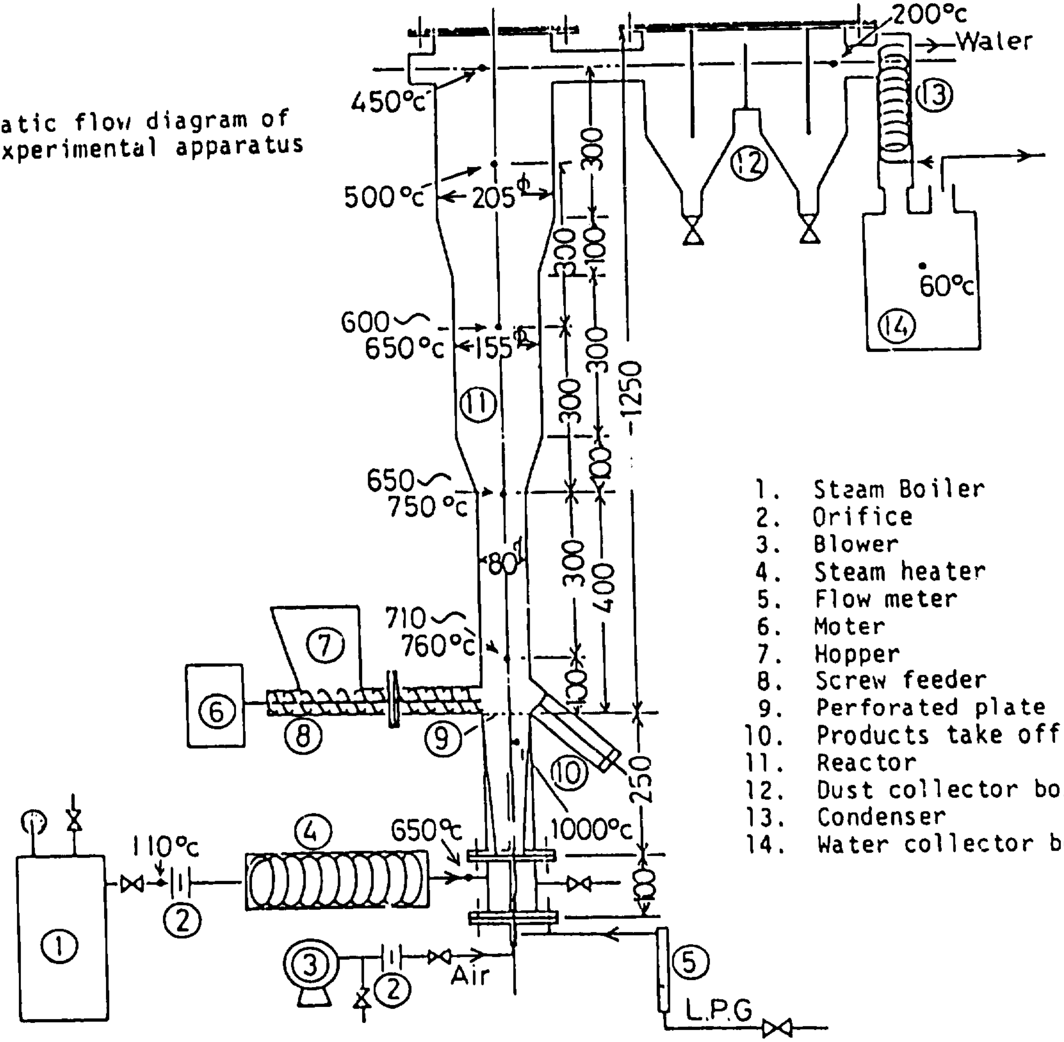
The exhausted gas passed through a dust collector box was led into a condender in which steam was condensed and removed, then purged from an outlet of the water collector box.

Analytical procedure

Gas analysis was done in terms of O_2, CO_2, CO, H_2, and CH_4, in the exhasted gas by gas chromatography.

The methelene blue adsorptive valve, iodine number, internal surface areas and pored distribution of the activated carbon products were measured by the methods described in previous paper.

Fig. 1. Schematic flow diagram of the experimental apparatus



1. Steam Boiler
2. Orifice
3. Blower
4. Steam heater
5. Flow meter
6. Moter
7. Hopper
8. Screw feeder
9. Perforated plate
10. Products take off pipe
11. Reactor
12. Dust collector box
13. Condenser
14. Water collector box

7.6 WOOD PRODUCTS

Source : 2.4

ACTIVATED CARBON

Sugar, Tar and Activated Carbon

H.F. Funk and P.M. Sarten; U.S. Patent 3,523,911; August 11, 1970 describe a continuous process by which cellulosic material including lignin and hemicellulose may be treated so that the raw sugars may be removed in a low temperature range and recovered with condensate. The tars may be removed in a higher temperature range and recovered as a condensate. The remaining material may be converted into highly activated carbon in a still higher temperature range, with the production of acids and inert gases which can be utilized in the removal of the sugar and tars.

The method may be applied to various types of the cellulosic materials including particularly woods such as birch, hard and soft maple, beech, and the like and mixtures of one or more of those woods. The cellulosic material to be treated should be in finely divided form such as sawdust, small chips or broken and partly pulverized bark.

Dilute aqueous acids are preferably employed in the extraction part of the method. The amount of sugar recovered without the use of any acid is quite small and is ordinarily considered as being noncommercial. The acid should be 0.5 to 6%. This range is quite economical since it recovers most of the sugar of the hemicellulose without breaking down any substantial amount of the cellulose and prepares the residue for ready activation to a high degree.

Many organic and inorganic acids may be used in this method, such as hydrochloric, sulfuric, nitric, hydrofluoric, hydrobromic, formic, acetic, and pyroligneous acid. It is preferable to add the organic acids when the method is being initiated, although such acids are generated throughout the extraction phase and can be recycled after separation from the sugars. Such recycled acids increase the amount of sugar recovered as contrasted with the extraction performed in the absence of an acid solution. The inorganic acids reduce the ash content of the final carbon and promote hydrolysis at an increased rate. Acid solutions which have been used consisted of (1) 2% of acetic acid, 1% of formic acid and 0.6% of hydrochloric acid and (2) 2% of acetic acid and 1% of formic acid.

Example 1: A charge consisting of 500 g of finely divided wood containing 132 g of moisture and made up of equal parts of birch and hard maple was placed in an acid mixture consisting of 14.7 g of acetic acid, 7.4 g of formic acid, 4.5 g of hydrochloric acid, and 604 g of distilled water. The percentages of raw sugar recovered, based on the wood charged, was 12.12%, 9.70%, 1.55%, 0.43% and 0.34% for the first to fifth lots of 500 cc of condensate collected, respectively. These percentages expressed in grams were 61.0, 43.7, 7.6, 2.36 and 0.2 grams, respectively.

The acid present in the first four of those lots of condensate required 9.33, 7.34, 0.71 and 0.09 cc of N/10 NaOH to titrate. When 113.5 g of the material residue from the above example was heated for about nine hours below 400°C and for one hour at 800°C while steam was being injected, 148.14 g of tar and water were recovered. About 24.75 g of activated carbon, that is, 21.8% of the material subjected to activation, was found to have a MBT value of 12 and a BET value of 985 m^2/g.

The MBT value was determined by mixing 0.1 g of activated carbon and 10 cc of 0.15% methylene blue solution at a temperature of about 20°C and stirring until the color disappeared. Additional 10 cc quantities of the solution were added until the blue color persisted. The MBT value was the quantity of the solution which was discolored by the carbon. The BET value expressed in square meters per gram was determined by measuring the adsorption of nitrogen by the activated surfaces of the carbon in a stream of helium at -190°C, employing a sorptometer.

Example 2: A charge consisting of 510 g of the wood mixture as prepared for Example 1 and containing 135 g of moisture was placed in an acid mixture consisting of 15.0 g of acetic acid, 7.5 g of formic acid, and 615 g of distilled water. This charge was heated to 120°C for four hours and was then extracted with steam at 125°C for two hours. The percentages of sugar recovered, based on the wood charged, for the first, second, third, fourth and fifth lots of condensate were 1.20%, 2.13%, 5.07%, 5.18% and 4.52%, respectively. The weight of the raw sugar represented by these percentages was 0.75, 9.60, 12.90, 14.50 and 20.20 g, respectively.

The acid present in each of those lots of condensate required, respectively, 5.30, 5.16, 4.42, 2.25 and 0.79 cc of N/10 NaOH to titrate. 70.2 g of the material residue from Example 2 was heated for two hours to 450°C without steam injection, and then for three hours to 850°C while steam was being injected. 3.38 g of tar and water were recovered before the steam was admitted and 75.85 grams of tar and water were recovered during the time steam was being injected. The activated carbon obtained weighed 13.8 g, that is, 19.65% of the material from the No. 2 example and had a MBT value of 8 and a BET value of 665 m^2/g.

The activated carbon produced by this method is characterized by unusually high activation as is indicated by MBT values of 8 to 15 and a BET value of 665 and 1085 m^2/g. This result is believed to be traceable to the more complete removal of substances from the pores of the wood or by an increase in the number of pores.

Submerged Combustion Carbonization

According to *H.L. Barnebey; U.S. Patent 3,525,674; August 25, 1970; assigned to Barnebey-Cheney Co.* carbonization is effected in a pile of carbonizable particles while, preferably, the particles move continuously through a relatively stationary combustion zone. The combustible gases evolved as a result of carbonization are not removed from the pile but, rather, are burned in the combustion zone, as they evolve, by the introduction of air therein. Stabilization of the combustion zone is maintained, when heating is necessary, by introducing air and combustible fluids into the combustion zone from outside the pile; and, when cooling is necessary, by introducing water into the zone. The process permits of a single step production of activated carbon.

Drying, carbonization, and activation can be carried out in a single furnace, or single pile without requiring the use of expensive materials for furnace construction, without requiring the use of fuel gas, and without requiring the use of steam. Similarly, when a chemically impregnated material is added to the pile, there is a relatively smaller proportion of volatiles evolved as compared to nonimpregnated materials.

The use of such materials usually requires the introduction of some fluid fuel into the carbonization zone. Although corrosive vapors are generated in the carbonization zone in this latter case the outer, and relatively colder portions of the pile act as a scrubber and prevent the vapors from entering the atmosphere. The absence of a container during the use of corrosive chemicals leads to very significant savings in operating costs.

HCl or HBr Carbonization

A. Shindo, I. Souma and Y. Nakanishi; U.S. Patent 3,557,020; January 19, 1971; assigned to Agency of Industrial Science and Techn[illegible] Japan describe a method of producing activated carbon of superior adsorption activity by carbonizing a vegetable material having nonuniform shape such as a shapeless particle powder, flaky powder or chip in an acidic atmosphere containing vapor or gas of hydrochloric or hydrobromic acid or acid anhydride. The adsorption activity of such activated carbon is improved by subjecting it further to an activation treatment in an atmosphere containing an oxidizing gas such as carbon dioxide gas, steam, air or in an inert atmosphere.

Materials which are utilized as the starting materials include cellulose, starch, sucrose, molasses and lignin, or materials containing these, for example, cereals, wood, shells, straw, chaff, strained lees of white potato, sweet potato or beet molasses, and the cob and stalk of corn. As the cellulose, use may be made of pulp, nitrocellulose, or microcrystalline cellulose. Also, granular materials produced from the above-mentioned materials with molasses, alcohol, sucrose, etc. can be used as caking agents.

In practice, an atmosphere containing hydrochloric acid gas is most preferable. The temperature at which the raw material is carbonized is 80° to 1200°C, desirably 200° to 1000°C, most preferably 300° to 900°C. The temperature may be elevated either continuously or stagewise.

The time of carbonizing in an acidic atmosphere is 10 minutes to 10 hours but, in some cases, it may be made longer. For example, when an inert atmosphere containing less than 5% by volume of vapor of acid is used, the carbonizing time must be made long. The carbonization treatment may be effectively carried out by circulating or refluxing the acidic atmosphere in a furnace, or by continuously feeding in a fresh acidic atmosphere, during the carbonizing of raw material.

As stated above, it is possible, by carbonizing raw material in a nonoxidizing acidic atmosphere, to produce activated carbon of superior adsorption activity in high yields. For example, by carbonizing cellulose, starch, sucrose and lignin each in a hydrochloric acid atmosphere at 800°C, it was possible to obtain activated carbons in the respective yields 30%, 40%, 55% and 25% higher than in the case where each of the materials was carbonized under the same conditions but in an inert atmosphere.

However, it was found that, if the activated carbon obtained by carbonizing in an acidic atmosphere is further subjected to an activation treatment in an atmosphere containing an oxidizing gas such as steam, carbon dioxide gas or air, the adsorption activity of the carbon would be improved.

In a steam containing atmosphere, the activation treatment is carried out for 30 minutes to 10 hours at 600° to 1000°C, but, in an atmosphere containing carbon dioxide gas, 700° to 900°C is effective, and, in an air-containing atmosphere, 500° to 800°C is effective. This activation treatment, at 500° to 1000°C, may be carried out continuously by replacing the acidic atmosphere with an oxidizing gas-containing atmosphere while carbonizing raw material in the acidic atmosphere.

It was further confirmed that, when the activated carbon obtained by carbonizing in an acidic atmosphere at 200° to 600°C was heated further in an inert atmosphere at a temperature higher than said temperature but below 1200°C, the adsorption activity of the carbon was improved.

Example 1: Lauan saw-dust was carbonized in a hydrochloric acid gas atmosphere under one atmosphere pressure at a temperature elevation rate of 120°C per hour from 100° to 250°C. The material was reduced in weight by about 30%, and activated carbon of superior adsorption activity was obtained.

Example 2: In a nitrogen atmosphere containing 20% by volume of hydrochloric acid gas, a particle powder sucrose was carbonized for two hours by continuously elevating the temperature from 80° to 500°C. Activated carbon of superior adsorption activity was obtained in a yield of about 60%.

Example 3: Wood meal was carbonized in a hydrochloric acid gas atmosphere by elevating the temperature from 100° to 700°C. After carbonizing for 20 minutes at 700°C, the hydrochloric acid gas was expelled by nitrogen gas, then steam was fed in, and the material was heated for 30 minutes at 800°C to obtain activated carbon of superior adsorption activity.

Example 4: In a nitrogen gas atmosphere containing 60% by volume of hydrochloric acid gas, strained lees of sweet potato were carbonized by continuously elevating the temperature from 100° to 400°C in one hour and from 400° to 750°C in one hour. Thereafter, at 750°C, while feeding in carbonic acid gas, the material was heated for 40 minutes to obtain activated carbon of superior adsorption activity.

7.7 Modified Stationary Furnace for the Manufacture of Activated Carbons from Coconut Shells and Pine Wood

M. Aslam Ali, *B. Sc., B. E., M. S., M. I. A. W. S., Research Scholar,*
—Department of Chemical Engineering.
Indian Institute of Technology, Madars-600036.

Introduction

The work carried out at the Forest Research Laboratory, Bangalore by me revealed that the furnace has to be modified further to get better yields on the most economical basis. My main interest was to go into such processes by which we can get activated carbons having uniformity and high activity. The approach I had made is a practical one based on the study of actual units engaged in the manufacture of activated carbons in India. It includes commercial, financial and technical features of such units.

Technically speaking the existing furnaces have a number of defects which include the low yield, high fuel cost, short duration of brick lining, handling of material, manual operations, mechanical breakdowns etc. For the detailed study, the readers are requested to go through the author's paper entitled *'Activated Carbon'* published in Indian Chemical Manufacturer, April 1970 issue and *'Activating Furnace'*, paper presented at the Convention of Cemists, 1971 at the Institute of Science, Bombay University. Some of these defects may be eliminated by the use of modern technology but the economical factors does not permit to do so. It is therefore necessary to think of two alternatives—either to develop the existing rotary furnace or to develop such furnaces which are more economical than the rotary furnaces. I preferred the latter way and eliminated successfully.

Any kind of charcoal when treated with air and steam at at a temperature of about 900-1000°C gives activated carbon but the quality of charcoal depends largely on the type of charcoal we use, for example, pine charcoal, take charcoal, euclyptus charcoal, sandal charcoal, and shell charcoal yields superior grades of activated carbons. For the commercial exploitation, pine charcoal and shell charcoal seems to be most favourable. If we use pine charcoal we get such activated carbons which are useful in liquid phase adsorption while the use of shell charcoal yields activated carbons which are used in gaseous phase adsorption. Since we are dealing with the manufacturing process the industrial applications of activated carbons are therefore not included in this paper.

Rotary Furnace

In this the principal of steam activation has been utilised in the process of treating the charcoal to open an enormous number of pours at definite conditions. In other words, the process of activation is a selective oxidation of the base carbon with steam. Here the carbon so produced possesses a large surface area the ability to accumulate or concentrate substances at this surface. Actually what we do is we release the absorptive forces by burning out the hydro-carbon obtained from the carbonization and that are strongly absorbed by the carbon: experiments showed that the above phenomena, in other words activity depends to a considerable extent not only on the startin material but on the way by which it was prepared. It is therefore absolutely necessary to have a proce which has its own advantages.

Modified Furnace:

The basic principle adopted in the design of t furnace under consideration, is the steam activati and gravity. It overcomes all the disadvantages the rotary furnace. The constructional details of su a furnace are given in the accompanied sketches. T materials required include as those of rotary furnace except the rotating parts such as motor, gear, pinion, etc. Here the cylindrical vessel kept vertical and is stationary one. It is designed in such a way that it should work as a continuons process, the material will come out of the furnace only when it has attained a certain activity. Otherwise it will stay in the furnace itself till it attains such a value. The feeding mechanism adopted is a mechanical one and works effectively to produce the desired product. Preheating mechanism is also provided to heat the charcoal before heating. Provision is made to utilise alternative feeding mechanisms (Mechanical and Steam).

Equipments and Constructional Details:

A mild steel cylindrical vessel lined inside with fire bricks, brick chamber, oxidising chamber, steam and air pipe lines, blower, boiler, feed hopper, mechanical bucket conveyer, vibratory feeder, crusher etc.

The unit consists of one long cylindrical vessel made out of mild steel. It is lined inside with fire bricks. Outside a chamber of bricks is constructed all around the furnace. At the bottom an oxidising chamber is attached and at the top it is closed with a plate having capillary holes above which is constructed a chimney with a damper. Steam and air connections are made at the bottom of the oxidising chamber. Just above the bottom of furnace of the main vessel a feed hopper is connected at one side. To the feed hopper conveyer and the crusher arrangements are made in such a way that the required quantity of charcoal should enter the furnace at the required interval of time. Arrangements are made in such a way that the pieces weighing between 0.8 and 1 gram should enter the furnace when the feeding arrangment is made to operate.

One more steam connection is provided at the top at an inclined angle. This is to facilitate to remove the activated carbon easily and at the same time continuously, from the furnace.

So according to this, the furnace comprises of a chamber, a steam supply, automatic feeder system and a preheater arrangement. Arrangement being such that the unactivated charcoal should reach the bottom and after some time should move to the middle portion then to the top where it is driven out of the chamber by the top steam supply.

Thus in accordance with this, the steam supply should be at the bottom and also at the top at an inclined angle, here the steam acts as a lifter or driver and also as an agent of activation. This arrangement enables us to produce uniform quality of activated carbon. The feeder should also be attached at an inclined angle. The chamber being heated internally. The top outlet (small capillary holes) for steam also facilitates to remove waste gases produced inside the chamber. The opening provided at the top to remove the finished product finally leads the product to a pulvoniser. It has to be noted that the outlet opening of the steam from the chamber should always have smaller holes than the diameter of the steam pipes. It is obvious that further modifications can be made within the ambit and scope of this modified method.

Operational Procedure:

The preheated charcoal pieces which are having uniform size and weight are fed in the main chamber. They are heated to about 1115°C by passing the hot gases inside the chamber through the oxidising chamber. When once the furnace attains the temparature, i.e. 1115°C. steam valve is operated. Temperature inside the chamber by passing the desired proportion of the flue gases and steam. After some time we observe that there will be some loss in the charcoal pieces. This loss in the weight enables to lift the charcoal pieces upwards. Now the pressure inside the chamber is maintained in such a way that the charcoal pieces which have lost about 30 of their weight should remain at the middle of the furnace. Once again we find that after some time these pieces move further upwards. Now the pressure inside the furnace is adjusted in such a way that these pieces should be at the top of the furnace when their weight is further reduced to 30.. that is, now pieces which are at the top have totally lost about 60 of their weight. Then the steam supply on the top is operated to remove these pieces which are activated by this time. It has to be noted that the proportion of flue gases and air should be maintained at a constant rate. The temperature should not be below 900°C and above 1115°C. Only selected charcoal pieces should be fed inside the chamber. The pressure of the steam is adjusted in such a way that only highly activated carbon pieces should reach the top of the chamber where they will be driven out automatically with the help of top steam supply. The quality of the activated carbon can be controlled by adjusting the pressure inside the chamber.

The above phenomena, may will be illustrated in the following way. First the steam pressure—that is the pressure inside the main chamber is adjusted in such a way that the unactivated or newly fed charcoal pieces weighing say 0.55 gram to 1 gram should remain at the bottom when they loose their weight of about 30 say when they weight 0.55 gram to 0.7 gram they should move upwards and remain almost at the middle of the furnace. Again as time posses when the charcoal pieces loose again 30 that is when their actual weight is about 0.3 to 0.4 gram they should be at the top of the chamber where they will be driven out the chamber by additional steam supply. Here uniformity can be attained throughout the operation by keeping the steam pressure at a constant value. It should however be noted that charcoal pieces will now remain or concentrate in one place as a slight change in weight will shift their places which finally bring to a state in which the charcoal pieces can be en impinging one another and almost every time one or the other pieces will be reaching the surface and at the same time will be driven out immediately and hence the furnace can be regarded as a continuous one. In this furnace we can get the finished product without any kind of interuption or handling.

Advantages:

1. Temperature can be maintained uniformly and accurate measurements could be made very easily.
2. Desired quality of activated carbons could be obtained. Uniformity can also be obtained.
3. During the production we observe that no handling of the product is required.
4. It overcomes all the difficulties of the existing furnaces.
5. The fuel cost will be very less when compared to that of the existing processes.
6. No stoppages during the production. Ex.-mechnical etc.
7. Saving in price. In this furnace about 40 by weight of raw material of highly activated carbon could be produced as far as other charges are concerned, it costs almost the same as that of the existing rotary furnaces.
8. *Shell Activated Carbon:*

   It is possible for us to produce coconut shell activated carbon with the same arrangement.

Disadvantages:

It is very difficult to standardise this kind of furnace as it mainly depends upon the type of raw material used in the production of activated carbons. Since standardisation of the furnace depends upon the weight, shape, size of the charcoal used, we find it extremely difficult to list common standardising factors of the furnace. Hence depeding upon the type of the charcoal used, we have to fix the height of the furnace, pressure of steam, rate of feeding etc.

Discussion

The furnace is stationery one, continuous type of furnace. Internally fired one. As far as the rotary furnace is concerned it has got similarities except the rotary part of it. Here removing of the finished product is quite different from that of the rotary one. The yield will be more when compared to the rotary furnace of the same capicity. Even the fuel costs will also be less The life of the furnace will be more than that of a similar size and type of rotary furnace. The initial investments will also be slightly less than that of a similar type of rotary furnace Here in this furnace, almost all the operations are mechanical and are automatic.

References

1. Aslam Ali, M.—*Ind. Chem. Ment.* Vol. VIII, No. 4 Pp 22-25, 1970.
2. Parry, R. H.—Thesis, Pennsylvania State Univ., Dec. 1961.
3. Deitz, V. R.—Bibliography of Solid Adsorbents. United States Cane Sugar Refineries and Bone Manufacturers and the National Bureau of Standards. Washington, D. C., 1944. Supplementary volume published in 1956
4. Hassler, J. W.—Proceedings of the Anthracite Conference, Pennsylvania State University, Oct 18, 1956.
5. Hassler, J. W., Westly, Oren A. and Filicky, Joseph, J.—U. S. Patent 2,894,914.
6. British Patent 213,195.
7. U. S. Patents 1,547,037.
8. Krczil, F.—Kolloid, Z., 67 : 253, 1934.
9. Holmes, J. H. and Emmett, P. H.—*J. Phys. Colloid Chem.*, 51 : 1276, 1947.
10. Scott, G. S.—*Ind. Engg. Chem.*, 33 : 1279, 1941.

Table 12. Trade names for activated carbon

Trade name	Type of carbon*	Application	Manufacturer Supplier
Acticarbone	P, G, Pel	decolorization, gas purification, water purification	Ceca S.A. (F)
Anthrasorb	P, G	water purification	Thomas Ness (GB)
Benzorbon	Pel	solvent recovery	Bayer (Lurgi) (FRG)
Brilonit	P	decolorization	Degussa (Lurgi) (FRG)
Carboraffin	P	decolorization	Bayer (Lurgi) (FRG)
Darco	P	decolorization	American Norit (USA)
DeguSorb	P, G, Pel	decolorization, gas purification, solvent recovery, catalysis	Degussa (FRG)
Filtrasorb	G	water purification	Calgon Carbon Corp. (USA), Chemviron (B)
Hydraffin	G	water purification	Bayer and Degussa (Lurgi) (FRG)
Kuraraycoal	G	gas purification	Kuraray Chemical Co. (Japan)
Kureha	Pel	gas purification	Kureha Chemical Ind. (Japan)
Le Carbon	G	gold extraction	Pica (F)
Norit	P, G, Pel	decolorization, gas purification, water purification	Norit (NL, GB, and USA)
Nuchar	P, G	water purification, air purification	Westvaco Corp. (USA)
Nusorb	G	gas purification	(Nucon) (USA)
Picactif	G	catalysis, water purification	Pica (F)
Shirasagi	P, G, Pel	various	Takeda (Japan)
Solvosorbon	Pel	solvent recovery	Bayer (Lurgi) (FRG)
Sorbonorit	Pel	solvent recovery	Norit (NL)
Supersorbon	Pel	solvent recovery	Bayer and Degussa (Lurgi) (FRG)
Sutcliffe	G	gas purification	Sutcliffe Speakman & Co. (GB)
Taiko	P, G, Pel	various	Futumura Chem. Ind. (Japan)
Tsurumicoal	P, G, Pel	various	Tsurumicoal Co. (Japan)
Watercarb	P	water purification	Husky Ind. (USA)

* P = powdered carbon; G = granular carbon; Pel = pelletized carbon.

[263]. If other volatile substances are present, the moisture content can be determined by the xylene method [263], [264].

The ash content is usually determined as the residue after ignition, e.g., at 650 ± 25 C [265]. Frequently only the water-soluble or acid-soluble part of the ash is determined [266], since the total ash content is often unimportant. In cases where certain cations or anions have an adverse effect on the products, they can be determined by first extracting with hydrochloric acid, nitric acid, or water in a prescribed way, and then analyzing this extract. Arsenic, cyanide, and sulfide must be determined by experiments on the activated carbon itself. Determination of acid or alkali content can be carried out by boiling an aqueous suspension and finding the pH of the filtered or decanted aqueous extract. Working with the unfiltered suspension or with the carbon itself would give a misleading result due to the effect of the carbon surface on the pH.

Mechanical Properties. To determine the apparent density of activated carbon, the filling or compaction procedure must be specified so as to obtain reproducibility, e.g., in accordance with [267]–[269]. Dry material is used. Grain size distribution is determined by using standard sieves and motor-driven sieving apparatus. The fineness of powdered carbons may be determined by elutriation or by laser-beam scattering (e.g., Microtrac). Equipment such as the Coulter counter or sedimentation tests lead to incorrect results because the single particles of activated carbon vary in electrical conductivity and density. The hardness of granules of activated carbon may be

Source : 6.1.2

---

determined by mea
and the impact
strength. There ar
available, which do
however. The resist
gases has a practic
to the filtration re
There is a linear re
and pressure drop

Adsorption Mea
mon method of mea
of activated carbon
the BET surface, e.
However, the nume
only a limited pract
practical situation.
usually to large to r
very small pores d
molecules, whereas
gen isotherm [270]
using mercury vapor
into the pore structu
porosity by measuri
cyclohexane vapor a
at 20 °C and at a ra
difference between
isotherm represents
limiting values of po
An example of the
determination of the
tivity according to A
Carbons for gas
the breakthrough tir
times), which are d
test substances such
For many pract
gas-phase adsorptio
pacity is of minor int
adsorption capacity
cases, the "working c
of adsorption and de
For the characte
properties in the liqu
termined with a num
as iodine, phenol, or

4.5. Uses

4.5.1. Gas Phase

Activated carbon
ly for the removal of

these values [250]. The high-carbon materials graphite and anthracite are very difficult to activate. Bituminous coals with high oxygen and hydrogen contents can have troublesome sticking and swelling properties. In these cases, a preoxidation is usually carried out before gas activation [251], [252]. This is done with air or oxygen-containing gases at temperatures between 150 and 350 C. This causes 5-30% oxygen to be taken up. The optimum temperature is 220-250 C. This procedure is carried out as long as necessary to cause complete disappearance of the swelling and sticking properties; as much as 5 h may be required. The reaction time may be reduced by addition of catalytic amounts of nitrogen oxides.

Bituminous coal may be more easily activated after addition of mineral acids such as phosphoric acid. For this purpose, the raw material is finely ground and mixed with a few percent of acid before being formed into shapes. This process, which was developed by Carborundum [253], is operated in the United States by Ceca. It uses a combination of chemical and gas activation. In some types of bituminous coal, the quality of the activated product is adversely affected by the high ash content; however, a small ash content that includes potassium compounds, for example, can have a catalytic effect and, when the material is preoxidized, can lead to intensive gasification of the coal. In these cases the ash content of the raw material can be reduced by grinding and flotation. The preoxidation can be carried out on the powder or after granulation. Following are some companies which activate bituminous coal: the Calgon Carbon Corp. (United States), Ceca (United States), Sutcliffe Speakman (United Kingdom), Thomas Ness (United Kingdom), and the Bergwerksverband (Federal Republic of Germany).

Brown coals and the related lignites offer an inexpensive and readily activated starting material for the production of activated carbons. Their relatively high ash and sulfur contents are detrimental. Therefore, methods have been developed for removing ash from brown coal before coking, e.g., by treatment with an oil-water mixture. The ash goes into the aqueous phase, while the coal remains in the oil phase. By this means the ash content can be reduced by 80-90%. Lignite is activated in high tonnages by Norit in the United States according to a process by ICI United States [254].

In recent years a large number of publications and patents have been concerned with activated carbon from *mineral oil products*, asphalt, and tar. Liquid petroleum fractions and residues are used by the Witco Chemical Co. Inc. (United States) as starting materials for the manufacture of granulated and shaped activated carbons. Calcined petroleum coke practically cannot be activated. Green petroleum coke can be activated after pretreatment (preoxidation) with concentrated nitric acid. In Japan, the Kureha Kakagu Kogyo Co. produces activated carbon in the form of spheres by low-temperature carbonization and subsequent activation of emulsified petroleum droplets [255]. Petroleum sludges and the acidic resin cokes produced from these contain a high proportion of sulfuric or sulfonic acids and can be activated by steam. There have been many discussions in the literature in recent years concerning the use of waste materials such as fly ash, old tires, domestic refuse, or sewage sludge as raw materials for activated carbon [256]. These materials have not attained practical importance because of the high proportion of uncarbonizable accompanying materials.

4.2.3. Activating Furnaces

Shaft furnaces originally consisted of simple vertical chambers with smooth walls made of refractory bricks. Heating is external. As the process was developed, the mixing of the feed materials was improved and, consequently, so was the reaction with the activating gas. This was done by installing ceramic attachments in the form of gratings or replaceable louvers which can control the direction and velocity of the gas stream within the furnace. The reaction gases (hydrogen and carbon monoxide) can be removed at various levels. The temperature of the furnace, usually 5-8 m high, can be controlled by means of a number of burners or afterburners (Fig. 22) [257]. Shaft furnaces can be used for the reactivation of exhausted activated carbon (see Chap. 4.6) [258]. They are used for manufacturing activated carbon by the following companies: Ceca (France), Degussa (Federal Republic of Germany), and Sutcliffe Speakman (United Kingdom).

Rotary kilns are the most commonly used activating furnaces. Due to the length of the kiln and the high temperatures necessary for gas acti-

number of publica-
n concerned with acti-
l *oil products*, asphalt,
fractions and residues
nical Co. Inc. (United
s for the manufacture
d activated carbons.
practically cannot be
m coke can be acti-
(preoxidation) with
n Japan, the Kureha
ces activated carbon
low-temperature car-
t activation of emul-
ts [255]. Petroleum
cokes produced from
ortion of sulfuric or
ac[illegible]ed by steam.
cussions in the litera-
ning the use of waste
. old tires, domestic
raw materials for acti-
naterials have not at-
because of the high
able accompanying

s

consisted of simple
oth walls made of re-
external. As the pro-
ing of the feed mate-
sequently, so was the
gas. This was done
ments in the form of
rs which can control
[illegible]gas stream with-
gases (hydrogen and
removed at various
the furnace, usually
lled by means of a
terburners (Fig. 22)
e used for the reac-
ivated carbon (see
sed for manufactur-
ollowing companies:
ederal Republic of
Speakman (United

commonly used ac-
e length of the kiln
cessary for gas acti-

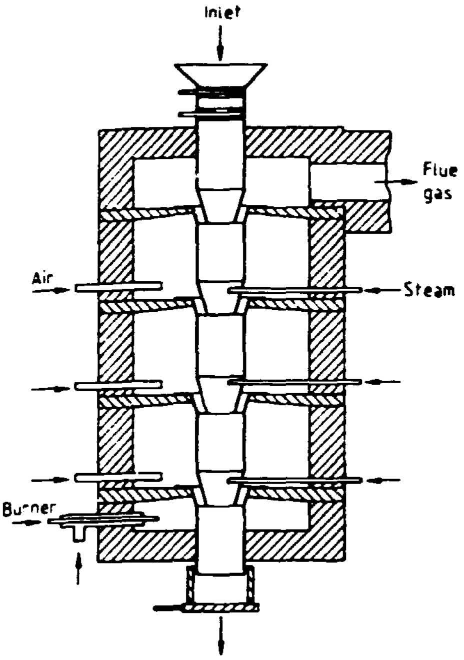


Figure 22. Shaft furnace

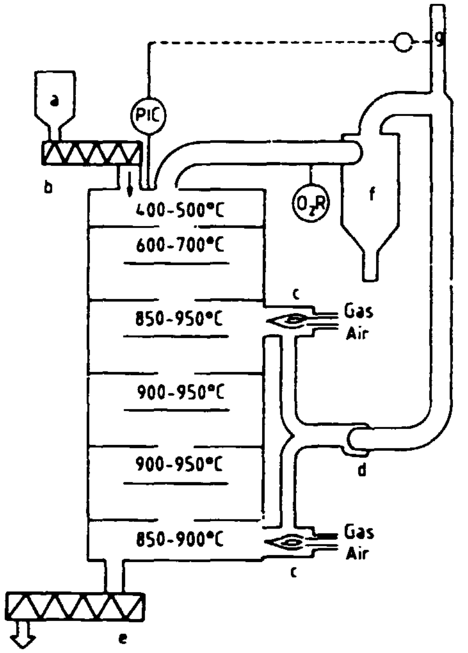


Figure 24. Multiple hearth furnace
a) Raw material silo; b) Inlet; c) Burner; d) Off-gas suction; e) Outlet for activated carbon; f) Dust collector; g) Off-gas stack

vation, direct heating is the only feasible method when the materials of construction of the kiln are considered. To be able to control gas composition and temperature throughout the entire length of the kiln, several burners and gas supply lines are distributed along and around the kiln casing, e.g., in the American Norit furnace. Figure 23 shows an arrangement including lifters to give improved mixing of the feed material. By means of steam injection at a rate which can be varied, the water vapor content and, therefore, the activation rate can be further controlled.

Multiple hearth furnaces (Fig. 24) with rotating arms and stationary floors on each stage are

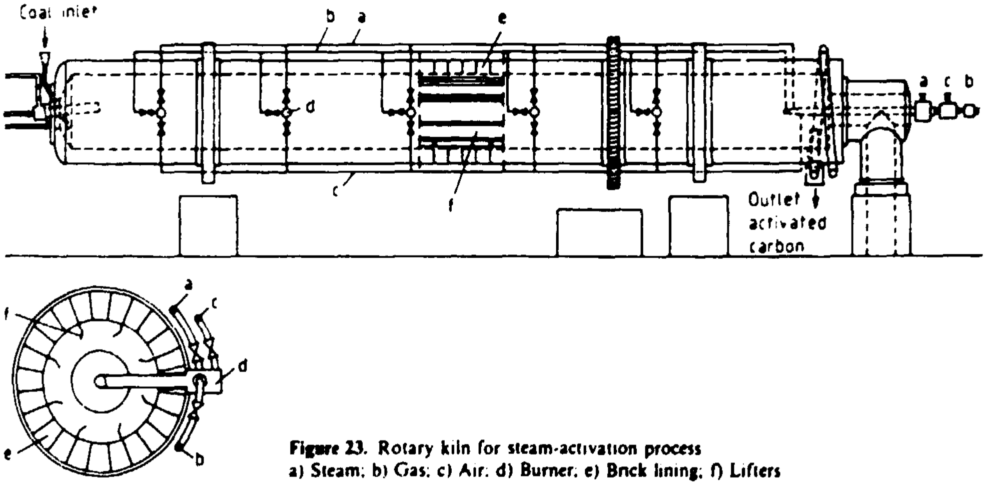


Figure 23. Rotary kiln for steam-activation process
a) Steam; b) Gas; c) Air; d) Burner; e) Brick lining; f) Lifters

used by several firms such as Calgon in the United States and Belgium. This type of furnace is also operated for the purpose of reactivation, e.g., by Windhoek Municipality (Republic of South-West Africa).

Fluidized-bed furnaces offer the advantage of extremely intensive heat and mass transfer. This means not only that the activating gases are quickly brought into contact with the raw material, but also that the waste gases are just as quickly removed. In recent years furnaces have been developed which are operated continuously (Fig. 25) and in which several fluidized beds are run in series. The activating gases may be introduced into the spaces between the fluidized layers and also into the circulatory system. Thus, it is possible to achieve a preoxidation in the first stage with oxygen-containing gas and then to carry out the actual activation with oxygen-free gases in a second stage. The activation in the fluidized bed is so intensive that usually only fragile products with poor resistance to abrasion are obtained, which are processed to give decolorizing carbon in powder form. By maintaining certain conditions, in particular by keeping the water vapor content of the gas below 0.6 kg/m³ and by maintaining a neutral or slightly reducing atmosphere, it is possible to produce abrasion-resistant granules.

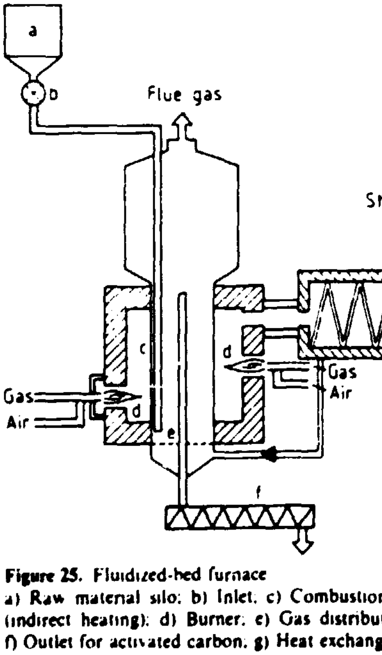


Figure 25. Fluidized-bed furnace
a) Raw material silo; b) Inlet; c) Combustion chamber (indirect heating); d) Burner; e) Gas distribution plate; f) Outlet for activated carbon; g) Heat exchanger

4.2.4. Methods of Activation

4.2.4.1. Chemical Activation

In addition to the classical zinc chloride process for the chemical activation of carbonaceous materials on a large scale, phosphoric acid is also largely used.

Zinc chloride [*7646-85-7*] is used by Ceca in Italy, by Takeda Chemical Industries in Japan, and in Czechoslovakia. In this process, 0.4 - 5.0 parts of zinc chloride as a concentrated solution are mixed with 1 part peat or sawdust. The mixture is then dried and heated to 600 - 700 °C in a rotary kiln. The product is washed with acid and water, and the zinc salts are recovered. In some cases, chemical activation is followed by steam activation to obtain additional fine pores.

Activation with zinc chloride alone gives large pores. In spite of the efficiency and simplicity of the process, it is in decline because of the problems of environmental contamination with zinc compounds.

Phosphoric acid [*7664-38-2*] can be used to treat either uncarbonized or carbonized raw materials, and the process is operated by Bayer (Federal Republic of Germany), Ceca (France), Hooker (Mexico), and Norit (United Kingdom and United States). Finely ground raw material such as sawdust is mixed with a phosphoric acid solution, forming a pulp. This is dried and heated to 400 - 600 °C in a furnace such as a rotary kiln. The phosphoric acid is then extracted, sometimes after neutralizing it to give phosphate salts, and the material is dried, giving an activated carbon which usually has finer pores than the zinc chloride product. Activation using a combination of phosphoric acid and steam is also possible.

As with zinc chloride activation, a highly active decolorizing carbon is obtained by a rapid process in high yield and at a relatively low reaction temperature. However, the cost of recovering the activating chemicals is high. Activation by phosphoric acid has become more popular in recent years, and there is no doubt that improved methods of phosphoric acid recovery have contributed to this. These innovations have hardly been reported in the literature; the "know-how" is not divulged by the producers.

There have been reports in the literature of many chemicals which can be used to activate carbonaceous raw materials:

Aluminum chloride [*7446-70-0*]

Ammonium chloride [
Borates
Boric acid [*10043-35-3*
Calcium chloride [*100*
Calcium hydroxide [*13*
Chlorine [*7782-50-5*]
Hydrogen chloride [*76*
Iron salts
Nickel salts
Nitric acid [*7697-37-2*]
Nitrous gases
Phosphorus pentoxide
Potassium metal [*7440*
Potassium hydr[illegible]de [
Potassium per[illegible]ana
Potassium sulfide [*131*
Sodium metal [*7440-23*
Sodium hydroxide [*131*
Sodium oxide [*1313-59*
Sulfur dioxide [*7446-09*
Sulfuric acid [*7664-93-9*

Of these, only sulfu
attained any commerci
tion with sulfuric acid
properties, while potas
and fine pores. Neither

A Standard Oil
cial position. The
carbonaceous mate
potassium hydroxid
yields an activated
porosity, the speci
3000 m²/g. The pro
commercial scale by
Michigan (United S

4.2.4.2. Gas Activa

In gas activatio
treated at elevated
gases, the most co
dioxide, and mixture
using graphite have
locities: steam has
reactive as carbon
as mild oxidizing a
being several simult

$H_2O + C \longrightarrow CO + H_2$
$2\,H_2O + C \longrightarrow CO_2 + 2$
$CO_2 + C \longrightarrow 2\,CO$

Due to the endo
reactions, the carbo
into intimate contact
must be hotter than
perature; otherwise,

t. for specialty applications (e.g..

nm diameter) and carcass grade
gnated according to a three-digit
› the particle diameter range. as
(super abrasive furnace) black
meter. while the former FEF-LS
ting a particle diameter of 40 to
out based on natural gas as feed-
· capable of reproducing all gas

cell batteries and for imparting
ced by acetylene decomposition
process. This material (of about
e level than furnace and chan-

dsorbent in gas masks in World
om[illegible]on of wood can remove
he first commercial application
l filters were used in a British
ctivated carbons can be divided
. for which a granular material
or which a powdered material

e for all purposes (Table 8.2).
nd pore volume. is hundreds of
one black. It is estimated that
mount of material adsorbed by
a quarter to an equal weight of
ibstances can be *recovered and*
upon surface area and pore
be adsorbed. and the surface
ed. assuming suitable molecu-

h as the cleanup of cane. beet.
ı water supplies. vegetable and
icals. The recovery of strepto-
[illegible]liquids.
[illegible]tary gas masks because of
mployed in both military and

TABLE 8.2 *Applications of Activated Carbon*

Adsorbing gases or vapors (gas-adsorbent carbon)

1. Adsorbent in military and industrial gas masks and other devices.
2. Recovery of gasoline from natural gas.
3. Recovery of benzol from manufactured gas.
4. Recovery of solvents vaporized in industrial processes such as manufacture of rayon. rubber products. artificial leather. transparent wrappings. film. smokeless powder. and plastics. and in rotogravure printing. dry cleaning of fabrics. degreasing of metals. solvent extraction. fermentation. etc.
5. Removing impurities from gases such as hydrogen. nitrogen. helium. acetylene. ammonia. carbon dioxide. and carbon monoxide.
6. Removing organic sulfur compounds. H_2S. and other impurities from manufactured and synthesis gas (usually impregnated with either Fe or Cu salts).
7. Removing odors from air in air conditioning. stench abatement. etc.
8. Absorbing radio-active emanations from nucleonic reactors for the time sufficient so that the decay is completed while still trapped in the activated carbon bed.

Decolorizing and purifying liquids (decolorizing carbon)

1. Refining of cane sugar. beet sugar. glucose. and other sirups.
2. Refining oils. fats. and waxes such as cottonseed oil. coconut oil.
3. Removing impurities from food products such as gelatin. vinegar. cocoa butter. pectin. fruit juices. and alcoholic beverages.
4. Removing impurities from pharmaceutical and other chemical products. including acids.
5. Water purification—removal of taste. odor. and color.
6. Removing impurities from used oils. dry-cleaning solvents. electroplating solutions. sirups. etc.
7. Removal of metals from solution—silver. gold. etc.

Catalyst and catalyst support (gas-adsorbent carbon)

1. Support for $HgCl_2$ catalyst for manufacture of vinyl chloride.
2. Support for zinc acetate catalyst in the manufacture of vinyl acetate.
3. Manufacture of phosgene.
4. Carrier for hydrogenation catalysts. etc.

Medicine

1. Internal medicine for adsorption of gases. toxins. and poisons.
2. Administering adsorbent medicinals.
3. External adsorbent for odors from ulcers and wounds.

Source: Carbon Products Div.. Union Carbide.

industrial gas masks. Activated carbon is used in air conditioning systems to control odors in large restaurants. auditoriums. and airport concourses. An important field of application is the industrial recovery and control of vapors (Fig. 8.4). The recovery of such vapors amounts to billions of pounds per year. with a recovered value of several hundred million dollars. Activated carbon is able to adsorb practically any organic solvent at about 100°F and release it when heated to 250°F or higher for organic solvents. Activated carbon can now be made in an extruded form. which in vapor adsorbing presents only about half the air resistance of the older granulated heterogeneous powder. The pressure drop through carbon. whether pelleted or granular. depends primarily on the average particle size. Pelleted material ensures more uniform packing. hence more even distribution of air flow.

MANUFACTURE Many carbonaceous materials. such as petroleum coke. sawdust. lignite. coal. peat. wood. charcoal. nutshells. and fruit pits. may be used for the manufacture of activated carbon. but the properties of the finished material are governed not only by the raw material but by the method of activation used. Decolorizing activated carbons are usually employed as powders. Thus the raw materials for this type are either structureless or have a weak structure. Sawdust and

Source : 6.1.7

Exchange.
962): Fornwalt and Hutchins. Purifying
w Water-cleanup Roles for Powdered
d Carbon Processes for Liquids. *Chem.*
. *Chem. Eng. Prog.* 67(11). 45 (1971).

Activated coconut shell carbon also for water treatment

Traditionally activated coconut shell carbon is mainly used for recovery of solvants and for gas purification. A much larger market would however be purification of municipal and industrial water, for which purpose today normally cheaper grades of activated carbon are used based on coal or biowastes, if cleaning with activated carbon is used at all.

A few municipal water authorities do however use activated coconut shell carbon. One of them is the Gothenburg water and sewage works in Sweden. They have used activated carbon for water purification for the last ten years and are now buying coconut shell carbon for that purpose.

We have asked Mr Tibor Nemeth who is chief of laboratories to tell us a little about his experiences with coconut shell activated carbon, because if others were to follow his example, an entirely new enormous market would open up for coconut producers.

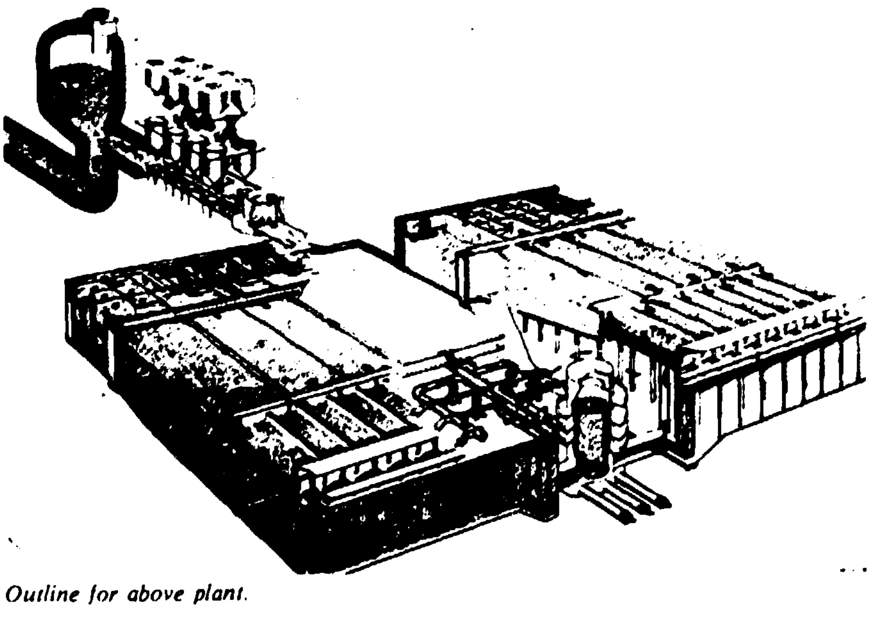
Sewage treatment plant for 150.000 m^3/day, contains 400 MT of coconut shell activated carbon.

"The reason we are buying coconut she activated carbon is that this type carbon is superior in quality to othe alternatives and our experience is tha high quality costs more, but also pa more. With other less expensive carbon you will find that some particles ar undersized and are immediately washe away. You may loose up to ten percen of the carbon you buy this way. Ther will also be oversized particles whic may cause disturbancies in the functioning of the purification equipment, at cost which is hard to estimate, but whic is certainly high. The greatest advantag of coconut carbon is its even quality. Therefore none of the two problem above have been encountered with ou carbon during the ten ears we have used it and we are very satisfied with the performance.

In contrast with industrial applications where the type of pollution is well known in advance, we at the municipal water side have to be prepared for a[illegible] type of contamination in the water. We never know what industry, or nature, has in store for us. For this reason we are not too much concerned with specifications on the adsorbtive capacity for various specified chemical substances tested in laboratory at extremly high concentration. What we need is an all-round reliable adsorber and we have found coconut carbon to fulfil this task. Compared to the coal based activated carbons that we have also used, coconut carbon has a much larger absorbtive area and a more even particle size and is thus much more efficient. Coal based carbon also has a much higher pore size and tends to take up also large organic molecules which do not affect the taste and smell of the water and are completely harmless. This will unnecessarily clog up the coal based carbon, and since this does not happen to the coconut

The most recent order from Gothenborg water and sewage works was placed for activated coconut shell carbon from the Philippines.

Now, if europeans will buy this produce from the other side of the globe in order to purify their water, it is evident that the same stuff should also be used in the coconut growing countriest themselves and in neighbouring countries where today millions of childen die from unsafe drinking water. This it seemes would be a most important consideration for local and state governments and for the United Nations.



Outline for above plant.

7.8 STANDARDS FOR ACTIVATED CARBON

7.8.1 ASTM : American Chemical Society for Testing Materials

- (D-2854)30 : Ash content, test
- (D-3467)30 : Carbon tetrachloride test
- (D-2652)30 : Standards definitions of terms relating to activated carbon (see p.83)

7.8.2 IS : Indian Standard Institution

- IS:2752-1978 : Activated carbon, granular
- IS:8366-1977 : Activated carbon, powdered
- IS:877-1977 : Methods of sampling and test for activated carbon, powdered and granular

7.8.3 JIS : Japanese Industrial Standard

- K-1470 : Testing method for powdered activated carbon (p.80)
- K-1474 : Testing method for granular activated carbon

UDC 661.183.2:543.8:66.067.72

JIS

JAPANESE INDUSTRIAL STANDARD

Testing Method for Powdered Activated Carbon

JIS K 1470-1967

Translated and Published

by

Japanese Standards Association

19 JUN. 1975

Printed in Japan

Price ¥300

UDC 661.183.2:543.8:66.067.72

JAPANESE INDUSTRIAL STANDARD

JIS K 1470-1967

Testing Method for Powdered Activated Carbon

1. Scope

This standard specifies the testing method for powdered activated carbon for use as decolourizing and refining agent.

2. Test Articles

The test shall be made on the articles given below:

(1) Caramel Decolourizing Power
(2) Methylene Blue Decolourizing Power
(3) Loss on Drying
(4) Chloride
(5) Iron
(6) Residue on Ignition
(7) pH

Reference Standards:

JIS K 0050-General Considerations for Chemical Analysis
JIS K 0115-General Rules for Absorptiometric Analysis
JIS K 1306-Testing Method for Refined Sulfuric Acid
JIS K 8005-Primary Standard Substances for Volumetric Determination
JIS K 8150-Sodium Chloride (Reagent)
JIS K 8180-Hydrochloric Acid (Reagent)
JIS K 8201-Hydroxylamine Hydrochloride (Reagent)
JIS K 8359-Ammonium Acetate (Reagent)
JIS K 8486-α, α'-Dipyridyl (Reagent)
JIS K 8541-Nitric Acid (Reagent)
JIS K 8550-Silver Nitrate (Reagent)
JIS K 8576-Sodium Hydroxide (Reagent)
JIS K 8897-Methylene Blue (Reagent)
JIS K 8951-Sulfuric Acid (Reagent)
JIS K 8979-Ferrous Ammonium Sulfate (Mohr's Salt) (Reagent)
JIS K 9007-Potassium Phosphate, Monobasic (Reagent)
JIS K 9019-Sodium Phosphate, Dibasic, 12 Hydrate (Reagent)
JIS P 3801-Filter Paper (for Chemical Analysis)
JIS R 1301-Porcelain Crucibles for Chemical Analysis
JIS R 3503-Glass Apparatus for Chemical Analysis
JIS R 3505-Glass Volumenometer for Chemical Use
JIS Z 8802-Methods for Determination of pH of Aqueous Solutions

3. General Descriptions on Analysis

The general descriptions common to the chemical analysis shall be referred to JIS K 0050-General Considerations for Chemical Analysis.

4. Method of Sampling

Two containers shall be drawn at random from each manufacturing unit, such as lot or batch, date of manufacture or others. In case the manufacturing unit is not designated, two containers containing 500 kg or its fractions in acceptance weight shall be drawn. Then suitable amount of the sample representative of the whole shall be taken, mixed thoroughly and stored in a tightly stoppered container.

5. Method of Test

5.1 Caramel Decolourizing Power

5.1.1 Principle Caramel test solution is added to the sample, shaken by means of the shaker and filtered and the decolourizing power is calculated from the absorbancies of the filtrate and caramel test solution.

5.1.2 Reagents

(1) 36.8 w/v % Sulfuric Acid Assay the purity in accordance with 2.2 of JIS K 1306-Testing Method for Refined Sulfuric Acid and prepare in the concentration 36.8 w/v % as H_2SO_4.

(2) Sulfuric Acid (1 + 10)

(3) 20.0 w/v % Sodium Hydroxide Solution Assay the purity in accordance with 4. (1) (o) of JIS K 8576-Sodium Hydroxide (Reagent) and prepare in the concentration 20.0 w/v % as NaOH.

(4) Sodium Hydroxide Solution (10 w/v %)

(5) Colour Standard Solution Pulverize proper amount of potassium dichromate (primary standard substance) in an agate mortar and place in an oven maintained at 100 to 110 °C for 3 to 4 hours. After cooling in a H_2SO_4-desiccator, weigh 0.310 g of potassium dichromate and dissolve in water. Transfer the solution to a 1000 ml volumetric flask and dilute with water to the mark to prepare the colour standard solution.

The absorbancy of the solution shall be measured by means of a photoelectric photometer or spectrophotometer in accordance with JIS K 0115-General Rules for Absorptiometric Analysis at a wavelength of 420 to 430 mμ and this value shall be taken as the standard absorbancy of caramel test solution.

(6) Preparation of Caramel Stock Solution Dry proper amount of granular sugar in a silica gel-desiccator for at least 24 hours to remove water.

Weigh 60.0 g of the dehydrated sugar into a 500 ml Erlenmeyer flask. Add 240 ml of water and stir thoroughly at room temperature to dissolve. Add exactly 25 ml of 36.8 w/v % sulfuric acid and place the flask in a water bath kept at 80 ± 1 °C until the solution attains 80 °C and keep this temperature for 30 minutes.

AMERICAN NATIONAL STANDARD **ASTM D 2652 - 76**

Standard Definitions of Terms Relating to
ACTIVATED CARBON[1]

This Standard is issued under the fixed designation D 2652; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

abrasion resistance the property of activated carbon to resist attrition or wearing away by friction.

absorption—a process in which fluid molecules are taken up by a liquid or solid and distributed throughout the body of that liquid or solid.

accelerated adsorption tests—adsorption tests in which the end point is hastened by testing at conditions more severe than those anticipated in service.

accelerated service life—the elapsed time until the end point is reached in an accelerated adsorption test.

acid-extractable material—substances dissolved from an activated carbon by an acid under specified conditions.

activated carbon—a family of carbonaceous substances manufactured by processes that develop adsorptive properties.

activation—any process whereby a substance is treated to develop adsorptive properties.

activity—a generic term used to describe the capacity to adsorb in general; also, the adsorptive capacity of an activated carbon as measured by a standard test.

adsorbate—any substance that is or can be adsorbed.

adsorbent any solid having the ability to concentrate significant quantities of other substances on its surface.

adsorption—a process in which fluid molecules are concentrated on a surface by chemical or physical forces, or both.

adsorption wave—see **mass transfer zone.**

adsorption zone— see **mass transfer zone.**

ash—residue after the combustion of an activated carbon under specified conditions.

as is basis as received.

breakpoint—the first appearance in the effluent of an adsorbate of interest under specified conditions.

channeling—the greater flow of fluid through passages of lower resistance which can occur in fixed beds or columns of activated carbon due to nonuniform packing, irregular sizes and shapes of the particles, gas pockets, wall effects, and other causes.

chemical adsorption—see **chemisorption.**

chemisorption (chemical adsorption)—the binding of an adsorbate to the surface of a solid by forces whose energy levels approximate those of a chemical bond.

coadsorption—the adsorption of two or more components on activated carbon, each affecting the adsorbability of the other.

contact batch operation—an adsorption process in which an activated carbon is dispersed in a fluid to be treated and then separated when practical equilibrium is attained.

continuous moving bed—an adsorption process characterized by flow of a fluid through a continuously moving bed of granular activated carbon with continuous withdrawal of spent carbon and continuous addition of reprocessed or virgin carbon.

countercurrent adsorption an adsorption process in which the flow of fluid is in a direction opposite to the movement of the activated carbon.

critical bed depth—the minimum depth of an adsorbent bed required to contain the mass transfer zone.

crushing strength—the property of an activated carbon to resist physical breakdown when contained and subjected to a slowly increasing continuously applied force.

degassing removal of gases.

density, absolute or true—the weight under specified conditions of a unit volume of an activated carbon excluding its pore volume

---

[1] These definitions are under the jurisdiction of ASTM Committee D-28 on Activated Carbon and are the direct responsibility of Subcommittee D28.02 on Liquid Phase Evaluation Tests.

Current edition approved Oct. 29, 1976. Published December 1976. Originally published as D 2652 - 67. Last previous edition D 2652 - 74.

and inter-particle voids.

density, apparent (density, bulk)—the weight under specified conditions of a unit volume of an activated carbon including its pore volume and inter-particle voids.

density, block—see **density, particle.**

density, bulk—see **density, apparent.**

density, particle (density, block)—the weight under specified conditions of a unit volume of an activated carbon including its pore volume but excluding inter-particle voids.

desorption—the separation of an adsorbate as such from activated carbon.

differential heat of adsorption—the heat evolved during the adsorption of an incremental quantity of adsorbate at a given level of adsorption.

dosage the quantity of substance applied per unit weight or volume of the fluid being treated.

dry basis exclusive of any moisture which may be present.

dust—an imprecise term referring to particulates capable of temporary suspension in air or other gases; also, particles smaller than an arbitrarily selected size.

dynamic adsorptive capacity—the quantity of a given component adsorbed per unit of activated carbon from a fluid, or fluid mixture moving through a fixed bed at the breakpoint for that component.

electrical conductivity of a particulate substance the current flowing through a unit cross section for an imposed unit potential gradient under specified conditions of packing.

electrophoresis migration of dispersed solid, liquid or gaseous material to one of two electrodes under the influence of an impressed direct-current voltage.

end point—the occurrence in the effluent of the maximum permissible concentration of an adsorbate of interest.

equilibrium adsorptive capacity—the quantity of a given component adsorbed per unit of activated carbon from a fluid or fluid mixture at equilibrium temperature and concentration, or pressure.

expanded bed—a bed of granular activated carbon through which a fluid flows upward at a rate sufficient to slightly elevate and separate the particles without changing their relative positions.

filterability—the rate at which an activated carbon can be separated from a slurry by means of a permeable medium under specified conditions.

fines—particles smaller than the smallest nominal specification particle size.

fixed bed—a bed of granular activated carbon through which a fluid flows without causing substantial movement of the bed.

fluidized bed—a bed of granular activated carbon in which the fluid flows upward at a rate sufficient to suspend the particles completely and randomly in the fluid phase.

Freundlich adsorption isotherm—a logarithmic plot of quantity of component adsorbed per unit of activated carbon *versus* concentration of that component at equilibrium and at constant temperature, which approximates the straight line postulated by the Freundlich adsorption equation

$$X/M = kC^n$$

where:

X = quantity adsorbed,

M = quantity of activated carbon,

C = concentration,

k and n = constants.

granular activated carbon—activated carbon in particle sizes predominantly greater than 80 mesh.

hardness—a generic term referring to the resistance of an activated carbon to breakdown as measured by specific tests.

heat of adsorption—the heat evolved during adsorption.

hydrolytic adsorption—the adsorption of a weakly ionized acid or base formed by the hydrolysis of some types of salts in aqueous solution.

hysteresis loop—the divergence between the paths of the adsorption and desorption isotherms.

ignition temperature (kindling point) the lowest temperature at which combustion will occur spontaneously under specified conditions.

impact strength—the property of an activated carbon to resist physical breakdown when subjected to a rapidly increasing applied force.

integral heat of adsorption—the sum of the differential heats of adsorption from zero to a given level of adsorption.

intermittent moving bed (pulse, slug)—an adsorption process characterized by upward flow of a fluid through a fixed bed of granular activated carbon with periodic withdrawal of spent carbon from the bottom of the bed and additions of reprocessed or virgin carbon to the top of the bed.

irreversible adsorption—adsorption in which the desorption isotherm is displaced toward higher equilibrium adsorption capacities from the adsorption isotherm.

isobar—a plot of quantity adsorbed per unit of activated carbon against equilibrium temperature when concentration or pressure is held constant.

isostere—a plot of equilibrium concentration or pressure against temperature when the quantity adsorbed per unit of activated carbon is held constant.

isotherm—a plot of quantity adsorbed per unit of activated carbon against equilibrium concentration, or pressure, when temperature is held constant.

Langmuir isotherm a plot of isothermal adsorption data which to a reasonable degree fit the Langmuir adsorption equation.

Langmuir adsorption theory the surface of an adsorbent has only uniform energy sites and adsorption is limited to a monomolecular layer.

macropore—a pore in activated carbon having a diameter greater than 5000 Å.

mass transfer zone (adsorption wave) (adsorption zone)—the region in which the concentration of the adsorbate of interest in the fluid decreases from influent concentration to the lowest detectable concentration.

micropore—a pore in activated carbon having a diameter less than 40 Å.

moisture content the water content of a substance as measured under specified conditions.

monomolecular layer—an adsorbed film, one molecule thick.

multimolecular layer—an adsorbed film more than one molecule thick.

oven drying loss the reduction in weight resulting when a substance is heated in an oven under specified conditions.

physical adsorption (van der Waals adsorption)—the binding of an adsorbate to the surface of a solid by forces whose energy levels approximate those of condensation.

pore diameter—the diameter of a pore in a model in which the pores in activated carbon are assumed to be cylindrical in shape and which is calculated from data obtained by a specified procedure.

pores—the complex network of channels in the interior of a particle of activated carbon.

pore volume volume of the pores in a unit weight of activated carbon.

pore volume distribution—the distribution of pore volume among pores of different size or diameter.

powdered activated carbon—activated carbon in particle sizes predominantly smaller than 80 mesh.

preferential adsorption adsorption in which a certain component or certain components are adsorbed to a much greater extent than others.

reactivation (revivification)—oxidation processes for restoring the adsorptive properties of a spent activated carbon.

regeneration—distillation or elution-type processes for restoring the adsorptive properties of a spent activated carbon.

relative efficiency—the rating of the adsorptive capacity of an activated carbon based on a comparison of its performance with that of a reference carbon in a defined test.

retentivity—the ability of an activated carbon to resist desorption of an adsorbate.

reversible adsorption—adsorption in which the desorption isotherm approximates the adsorption isotherm.

revivification—see **reactivation.**

service life (service time)—the elapsed time until the end point is reached in an adsorption process.

service time see **service life.**

sorption—a process in which fluid molecules are taken up by absorption and adsorption.

split feed—a liquid-phase adsorption process in which a powdered activated carbon is added to the solution to be treated in two or more steps, with or without intermediate separation of the carbon.

surface area (B.E.T.) the total surface area of a solid calculated by the B.E.T. (Brunauer, Emmett, Teller) equation, from nitrogen adsorption or desorption data obtained under specified conditions.

surface area distribution—the distribution of surface area according to some parameter such as pores of different size or diameter.

surface oxides oxygen containing compounds and complexes formed at the surface of activated carbon.

synthetic test solution a solution of two or more components prepared under specified conditions for use in evaluation of adsorbents.

threshold concentration—the minimum concentration at which a substance can be detected by the taste or odor test method employed.

threshold odor test a method of evaluating the odor level in a fluid by dilution under specified conditions with an odor-free fluid.

transitional pore—a pore in activated carbon having a diameter between 40 and 5000 Å.

van der Waals adsorption—see **physical adsorption.**

water-extractable material—substances dissolved from an activated carbon by water under specified conditions.

wettability—the rate at which an activated carbon can be made wet under specified conditions.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.

7.9 Production Costs and Returns of Coconut Cultivar East Coast Tall in Tamil Nadu

G. NALLATHAMBI[1], T. S. RAVEENDRAN[2]
AND
T. RAMANATHAN[3]

ABSTRACT

The estimated cost for establishing one hectare of coconut plantation was worked out to Rs. 23,804 and Rs. 35,254 for rainfed and irrigated conditions respectively for the initial seven year period excluding the interest on investment. The annual maintenance cost for the subsequent crop years was Rs. 4,233 for the rainfed and Rs. 5,483 for the irrigated gardens per year per ha. The production cost of coconut both under rainfed and irrigated conditions in Tamil Nadu was estimated at Rs. 1.18 and 1.10 per nut respectively, under 1984 - 85 factor costs without considering the land value. The net return under rainfed condition from nut yield alone was Rs. 3,990 per ha per annum whereas it was Rs. 6,825 under irrigation. Further the income from other axillary produces was estimated at Rs. 1,207 per ha per annum for rainfed and Rs. 1,452 per ha per annnm for irrigated gardens. The annual net return from one hectare of rainfed coconut plantation was Rs. 5,197. The corresponding revenue from irrigated garden was Rs. 8,277 per ha. The study indicated the profitability of large scale coconut cultivation in Tamil Nadu under good management and pure-cropped conditions.

INTRODUCTION

Coconut is one of the main sources of edible oil and is grown in an area of 143 thousand hectares and the production is 1450 million nuts in Tamil Nadu (Ramanathan. 1987). The mean annual nut yield per palm in Tamil Nadu is 40 and 60 nuts respectively under rainfed and irrigated conditions, which is higher than the all-India average of 30 nuts. Of late, the productivity of this crop in Tamil Nadu shows an increasing trend due to adoption of improved technologies and research findings by the farmers of this State. The objective of the present study is to estimate the cultivation expenses for establishment and maintenance of one hectare of coconut plantation both under irrigation and rainfed cropping systems and the return on the investment under Tamil Nadu conditions.

MATERIALS AND METHODS

In this study two populations of 175 palms of cultivar East Coast Tall planted with a spacing of 7.5m x 7.5m and maintained under rainfed and irrigation separately were considered for estimating cultivation expenses and returns per hectre of coconut as a monocrop. The labour utilisation for each operation was calculated separately under rainfed as well as under irrigation for the initial seven years (establishment period) and the next 8-60 years (maintenance period). The cost of labour for different operations was estimated based on the rate of wages that prevailed during 1984-85 in Thanjavur district where coconut is grown in an extensive area. The various input requirements were calculated based on the package of practices recommended by the Coconut Research Station, Veppankulam. The prices of different inputs were

• (M) - Municipality

---

[1] Assistant Professor, [2] Associate Professor [3] Professor, Coconut Research Station, Veppankulam-614 906, Tamil Nadu

also based on the rates that prevailed in Tamil Nadu during 1984-85 A period of seven years has been taken as the pre-bearing period followed by another seven years as the early bearing period for assessment of production costs. The economic life of East Cost Tall coconut in Tamil Nadu was considered as 60 years.

The labour requirement, considering 7 hrs of work as one man-day was calcuated for establishing one hectare of coconut plantation and found to be 184, 55, 56 man days for rainfed plantation and 334, 205, 206 for the irrigated plantation for the first, second and third years respectively (Table 1). For the subsequent four years, the labour requirement remained 52 for rainfed cropping and 127 for irrigated condition. This was 76 and 196 man days per year for the maintenance period of 8 to 60 years under rainfed and irrigated conditions respectively. The various inputs such as seedlings, shading materials, manures and plant protection appliances were assessed for the initial period of seven years and for the subsequent years for maintenance, separately (Table 2). A total of 201 seedlings would be required for establishing 175 palms after allowing a margin of 26 seedlings for the mortality etc. over a period of three years. For shading and protection of seedlings 1400 thatched coconut leaves and 1050 small bamboo / casuarina poles were estimated to be adequate for the first year. The quantities of farmyard manure required for the first, second, third and fourth years were 1750kg (10kg/palm), 3500 kg (20kg/palm), 5250 kg (30 kg/palm) and 8750kg (50kg/palm) par hectare. For the subsequent years also, 8750 kg per ha will be required. The inorganic manurial requirement was 600g $N+320g\ P_2O_5+1200g\ K_2O$ per palm per annum from fourth year which was limited to one-fourth, half and three - fourth for the first, second and third years repectively. A full dose of fertilisers in terms of urea, superphosphate and muriate of potash comprises 228 kg, 350 kg and 350 kg per ha per annum from fourth year onwards. Application of neem cake at the rate of 5 kg per palm along with normal fertilizers since fourth year of planting, is a recommended practice and quantity of neem cake for one hectare works out to 1050 kg for these years. However, the use of these inputs was restricted to one-fourth, half and three-fourth of the full dose for the first, second and third years respectively. In this study, the use of plant protection chemicals was limited to prophylactic measures like application of BHC 10% for rhinoceros beetle, stem injection with monocrotophos at the rate of 5ml per palm and fumigation with celphos tablets @ two per palm in the case infected trees for the control of red palm weevil. For the control of diseases, spraying fytolan 2g per tree against bud rot and soil drenching 1% Boredeaux mixture for the control of bud and collar rots were considered. A contingency grant of Rs. 200 per year for the non bearing period and Rs. 250 per year for the bearing period was provided to meet any unforseen expenditure for the both the systems of cropping.

RESULTS AND DISCUSSION

Taking into consideration all inputs, the establishment cost was worked out at Rs. 23,804 and Rs. 35,254 per hectare for rainfed and irrigated systems respectively (Table 3). In the first year, the expenditure was the highest for both rainfed (Rs. 5018/ha) and irrigated plantation (Rs. 7168/ha). This is quite obvious due to the special expenses incurred on clearing the site, levelling, cost of planting materials and planting. On the contrary it was the lowest in the second year (Rs. 2,189/ha for rainfed, Rs. 4,339/ha for irrigated) as the important operations include only interculture, manuring and plant protection. The expenditure increased in the third year and remained more or less constant from fourth year to seventh year (Rs. 3,446/ha/annum and Rs. 4696/ha/annum). The expenditure since eighth year for maintenance and harvesting was Rs. 4,233 per ha for rainfed and Rs. 5,483 per ha for irrigated conditions.

The yield per palm varied from year to year in the initial period of bearing and stabilised yield could be obtained only from fifteenth year after planting. The stabilised average yield was 40 and 60 nuts per palm per year for the rainfed and irrigated crops respectively, which remained the same throughout the economic bearing period. This results in an annual output of 7000 nuts and 10,500 nuts per ha per annum both under rainfed and irrigated gardens. For estimating cost of production per nut, the establishment and maintenance costs are the two major components to be

conside
plantati
period
investm
interest
in addit
tenance
The tot
seven y
compou
been rec
bearing
the inve
calculat
(Das,

A

P =
r =
n =

The a
this stu
for rainf
for irrig
added o
ance
for rain
annum f
Rs. 8,49
being th
tenance

Das, P. K

Das, P. K

Ramanath

considered The return from the plantation during its yielding period should cover the entire investment and also a fair rate of interest (10%) on the investment in addition to the annual maintenance cost in the bearing stage. The total investment for the initial seven years' expenditure and the compound interest thereon have been reduced to an annuity value bearing 10 per cent interest on the investment. The annuity was calculated by using the formula (Das, 1984).

$$A = \frac{P}{\sum_{i=1}^{n} \frac{1}{(1+r)^i}}$$

Where A = annuity value

P = total investment

r = rate of interest and

n = economic bearing period.

The annuity value calculated in this study was Rs. 4,260 per ha for rainfed and Rs. 6,371 per ha for irrigated cropping. It was added on to the annual maintenance cost (Rs. 4,233/ha/annum for rainfed and Rs. 5,483/ha/annum for irrigated) to arrive at Rs. 8,493 and Rs. 11,854 per ha being the overall annual maintenance cost per hectare for rainfed and irrigated conditions. From this amount, the income from dry leaves and petioles was deducted. The amount so arrived at viz., Rs. 8,293 (rainfed) and Rs. 11,554 per ha (irrigated) was divided by the number of nuts that could be realised after stabilisation. Accordingly the cost of production per nut works out to Rs. 1.18 under rainfed and Rs. 1.10 under irrigated conditions (Table 4). The corresponding cost for producing one nut in Kerala under rainfed condition was reported by Das (1984) as Rs. 1.10. For estimating production cost, the value of land was not included taken into account as the land value always shows an increasing trend, the rate of appreciation of which is higher than the interest rates paid by banks.

The returns were calculated based on the prices that prevailed during 1984-85 in Tamil Nadu. The mean selling price of coconut for 1984-85 was Rs. 1.75 per nut. Considering this price and the production cost of Rs. 1.18 (rainfed) and Rs. 1.10 (irrigated) the net return from nuts alone was Rs. 3990 per ha for rainfed and Rs. 6 825 per ha for irrigated plantations (Table 5). Besides, the annual revenue from one ha from other axillary produces such as spathes, spadices, coconut leaves and petioles was estimated and arrived at Rs. 1,207 and Rs. 1,452 for rainfed and irrigated cropping systems respectively. The total annual net return on the investment from one hectare of rainfed coconut plantation was Rs. 5197 and irrigated garden was Rs. 8277. This is a modest estimate based on the average annual yield per palm of 40 nuts (rainfed) and 60 nuts (irrigated) which is the State average and also under coconut monocropping. However, a much higher return could be expected from well maintained gardens recording average yield of 80 nuts and above per tree. Intercropping with banana or other suitable crops will also add to the profit from unit area.

The above discussions go to show that coconut cultivation is a profitable enterprise for expanding the financial worth of Tamil Nadu farmers.

ACKNOWLEDGEMENT

The authors express their thanks to Dr. S. Chelliah, Director, Tamil Nadu Rice Research Institute, Aduthurai for constant encouragement.

REFERENCES

Das, P. K. 1984 Estimating production costs and returns for coconut in Kerala. *J. Plant. Crops.* 12 (2): 152-159.

Das, P. K. 1984. Trends in coconut production and trade in the world. *Oleagineux.* 39.

Ramanathan, T. (1987). Technology for increasing coconut production in Tamil Nadu. *Indian Coconut J.* 17 (10) : 3-8.