

THE PRODUCTION OF MATERIALS AND CHEMICALS FROM COAL

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Introduction

When coal came to prominence as a fuel during the Industrial Revolution, there developed, in parallel, its use for the production of materials and chemicals. By-product liquids and gases from coal carbonization processes became the basic raw materials for the organic chemical industry, and the production of metallurgical coke from coal was essential to the development of steel manufacture. Coal tar constituents were used for the industrial syntheses of dyes, perfumes, explosives, flavorings, and medicines. Processes were also developed for the conversion of coal to gas and liquid fuels. Gases from coal carbonization and coke production were used for illumination as long ago as the late eighteenth century. By the 1930s direct and indirect liquefaction technologies became available for the substantial conversion of coals to liquid fuels and chemicals. Subsequently, the advent of readily available petroleum and natural gas, and the decline of the steel industry, reduced dependence on coal as a resource for the production of chemicals and materials.

For the last several decades, the availability of coal tar chemicals has depended on the production of metallurgical coke, which in turn is tied to the fortunes of the steel industry. In recent times, coke manufacture has been severely cut back, due to reduced demand for steel, which is facing competition from alternative materials, principally engineering polymers, and to improvements in steel-making technology that have reduced the amount of coke required to produce pig iron. In the US, the coke rate, or tons of coke needed to produce a ton of pig iron, has decreased from 0.75 in 1960, to 0.58 in 1978, while elsewhere rates are as low as 0.4, and new technologies completely obviate the use of coke (Song and Schobert, 1993a). In the 1970s, coal liquefaction processes seemed on the point of commercialization, and would have provided new sources of coal liquids for chemical use, as well as fulfilling the principal intended function of producing alternate fuels. Because of the low price of petroleum crude, this prospect is unlikely to come to fruition in the immediate future, due to the question of economic viability, albeit not technical feasibility. The combination of these and other factors has contributed to sharpening the focus on the use of coal for the production of heat and power, and lessening or eclipsing its possible use as a starting point for other processes. To illustrate this, in the US in 1991, approximately 80 percent of the coal produced was consumed by utilities.

However, coal tars still continue to make an important contribution to the demand for aromatic chemicals. According to Song and Schobert (1993a), metallurgical coke production in 1987 generated 15-17 million tons of coal tar and 5 million tons of benzol as by-products. The worldwide consumption of BTX is about 25 million tons and 5 million tons for two- to four-ring aromatics. Coal liquids accounted for 15-25% of the demand for BTX and about 95% of the demand for polycondensed aromatics and heterocyclics. Other important products of coal tar distillation are phenolics (creosote), feedstocks for carbon black manufacture (Donnet and others, 1993), and pitch that is used as a binder and source for materials such as carbon fibers and needle cokes.

In the US, coal is by far the largest indigenous fossil fuel resource. At the same time, petroleum imports now account for over 50 percent of total consumption, and domestic petroleum and natural gas reserves are limited. Similar situations prevail in other industrialized nations. Consequently, there is a considerable incentive to explore the expanded uses of coal, both as a fuel and as a materials source. In either case, there are also contingent needs and challenges to develop environmentally acceptable manufacturing processes.

Over the last few years, there has been a growing or revived interest in the non-fuel uses of coal, as evidenced by symposia at national meetings, and publications in scientific journals (ACS, 1992; ACS, 1993; Pitts Coal Conf., 1993; EOSS, 1993; Fuel Proc Technology Special Issue, 1993). Optimistically, one would hope that this is driven by a sense of scientific and technical relevance, rather than a new gimmick in the endless quest for research funds. There certainly appear to be some compelling reasons to re-evaluate the utility of coal as a source of non-fuel products. Research and development in Japan has provided a leading example of how this can be accomplished. The development of alternative uses for coal could lead to the diversification of resource use, and new industries. Further, the ability to utilize by-products or process streams for non-fuel applications could also assist the economics of coal utilization processes, and may lead to new materials. [In this context, it must be stressed that the higher the product selling price, the smaller the market, and the quantities of by-product streams that can be realistically utilized may be very limited.] For example, low-rank coals have long provided sources of wax and resin, obtained by solvent extraction (Kirk-Othmer, 1984). It has also been shown that paraffinic waxes, and

some naphthenic compounds, are produced during the liquefaction of subbituminous coals, and that they concentrate in the recycle distillate stream, reaching levels of 15-20 wt% or more. Their presence can adversely affect process solvent quality, while their removal by solvent dewaxing offers a method to improve process performance and recover potentially valuable by-product waxes (Derbyshire and others, 1993).

In addition to taking a new look at more traditional uses of coal products, there are a number of emerging technologies for which coal may be the most appropriate resource. Song and Schobert (1993a, 1993b) have discussed, at some length, the growth potential for high performance engineering polymers based on one- to four-ring aromatics, and that many of the aromatic monomers are not readily available from petroleum and could be derived, perhaps more easily, from coal. There is also a host of carbon-based products that can be obtained starting from coal. As can be seen in Table I, these include a high proportion of advanced materials. The connection between coal and high technology materials may serve another useful purpose in dispelling the air of antiquity that is presently associated with coal science, and elevate it to a more respected status.

This paper will address the role of coal as a resource for non-fuel products. Rather than attempt a comprehensive coverage, a few selected materials, electrode coke, activated carbons, and carbon fibers, are reviewed in terms of their production, applications, and existing and future markets.

Electrode Coke

Graphite electrodes for arc-steel furnaces are generally manufactured from needle coke that is produced from selected petroleum feedstocks: one example is decant oils from fluid catalytic cracking. Feedstock properties such as high aromatic carbon content are important. During the process of delayed coking, it is critical to produce a mesophase coke with extended domain structures that will readily graphitize upon subsequent processing. The presence of heteroatoms, for example, can impede mesophase development through crosslinking reactions, resulting in an isotropic coke. The name needle coke arises from the acicular shape of the coke particles that reflects the anisotropic nature of the coke structure. The aromatic character of coals implies that they could present an attractive alternative source for the production of needle coke. In fact, highly aromatic coal tar pitch gives excellent needle cokes with developed anisotropy and low thermal expansion. The high coke yield from coal ~60 wt.% versus ~30% for petroleum makes the coke the principal product of the delayed coking process, although the properties of coal tar, and hence of the coke, are dependent on the coal coking conditions (Mochida and others, Carbon 1989).

Production

During the 1970s, the British Coal Corporation (formerly the National Coal Board) developed a process to produce a suitable substitute needle coke from coal via solvent extraction (Kimber, 1981). In this process, bituminous coal is slurried with about three times its mass of anthracene oil (itself a product of coal tar distillation), and heated to 415°C for 60 min at 0.8 MPa (autogenous pressure), when approximately 70-80% of the coal (dmff) is solubilized. The mineral matter and undissolved coal are then separated by hot pressure filtration to afford a coal extract solution (filtrate) containing around 0.1% ash. The extract is then preheated to ~ 520°C and fed to a delayed coker. The coker overhead is recycled as solvent, and the coke is removed after water quenching the contents of the coker drum.

Laboratory tests showed that cokes with a wide range of properties could be produced, ranging from isotropic to anisotropic, depending on the coal precursor and extraction conditions. Consistent with the above-mentioned influence of heteroatoms on mesophase development, increasing coal rank and/or the severity of extraction were more conducive to the formation of anisotropic cokes (Kimber, 1977). The ability to control the properties of extracts through the selection of the coal and reaction parameters allows considerable latitude in the preparation of precursors for different end-products: as discussed later, the requirements for isotropic and mesophase pitch fibers are quite different.

The coal extraction process was scaled up to construct and operate a pilot plant, which was later used in a project to demonstrate the feasibility of producing quality graphite electrodes from coal. Thirty tonnes of coke were produced from a medium volatile bituminous coal, and used by Anglo Great Lakes Corporation to fabricate graphite electrodes (coal tar pitch binder) that were then tested in a 25 ton steel production furnace by British Steel Corporation (Kimber, 1981).

A comparison of the properties of these electrodes with their petroleum-based equivalents predicted poor furnace performance, based upon the criteria normally considered to be important. However, the results of working trials showed that the coal-based electrodes behaved comparably: this was mainly due to their toughness - although cracks developed relatively quickly, crack propagation was inhibited. While the demonstration project confirmed the potential of coal as a materials source for electrode manufacture, the work was not continued beyond 1979. Because of limited quantities of coke, it was not possible to optimize the steps of electrode fabrication and furnace testing, and potential clearly exists for further improvement.

Kimber and Gray (1976) also showed that there are other advantages in using coal-derived electrode coke. The evolution of heteroatoms, when carbonized coal extracts are subjected to graphitizing conditions, is quite different to that for petroleum cokes. In particular, sulfur evolution from petroleum cokes continues to elevated temperatures, when it causes expansion and cracking of the artefact (puffing). This does not occur with coal extract cokes, presumably as the organic sulfur is in a different form, leading to a stronger, denser carbon product, and eliminating the need to add iron oxide as a puffing inhibitor.

Recent work by Zondlo and others (1993) has confirmed these earlier results, showing that different graphitic products can be obtained from the same coal, depending on the conditions of extraction. Extracts obtained under hydrogenation conditions were more anisotropic than those obtained by non-hydrogenative solvent extraction. It is supposed that the former have a lower content of heteroatoms, which would reduce the propensity for crosslinking reactions upon carbonization, and allow more extensive mesophase development.

Markets

The global capacity for coke production of all types in 1992 was about 21 million tons. Needle coke production in 1992 was 1.3 million tons per annum of which approximately 10% was produced from pretreated coal tar after the removal of free carbons (quinoline insoluble substances) by anti-solvent techniques. The production of anode coke for aluminum manufacture was around 10 million tons, and the remaining coke was used as fuel, where the sulfur content allowed.

The consumption of carbon in arc-steel making is about 3.5 kg per ton of steel, and the principal criteria for needle coke quality are the carbon structure, impurity content (nitrogen and sulfur), and CTE (Coefficient of Thermal Expansion). The selling price of needle coke is about \$500 per ton.

For anode coke, carbon consumption is 0.5 tons per ton of aluminum, the higher consumption because the carbon serves as a reductant. In this case, a low content of metal impurities is desired, especially of metals such as Fe, Na. The cost of anode coke corresponds to its fuel value and is around \$100 per ton.

Activated Carbons

Activated carbons are materials with highly developed internal surface area and pore volume, and hence have a large capacity for adsorbing chemicals from gases or liquids. The extensive industrial use of activated carbons is related to their unique properties and low cost compared to that of possible competitive adsorbents (Baker, 1992; Derbyshire and others, 1993; Bansal and others, 1988)

Activated carbons can be synthesized from almost any carbonaceous precursor, naturally occurring or synthetic. An essential criterion is that the starting material is thermosetting, or can be so rendered during processing. Common commercial feedstocks are biomass materials such as wood, coconutshell, and nut kernels, and degraded or coalified plant matter - peat, lignite, and all ranks of coal. The properties of activated carbons can be very diverse. While they are influenced to some extent by the process route and conditions, they are predominantly determined by the precursor structure. Generally, microporous carbons (pore diameter <2 nm) are synthesised from high rank coals, or coconutshell precursors. Carbons with larger pore sizes (mesopores with 2nm <d <50nm) are synthesised from wood, peat, lignite and lower rank coals. In 1988, coals accounted for almost 30% of the raw materials for activated carbon manufacture, lignite 14%, peat, 10%, with wood at 35% and coconut shell, 10% (Bansal and others, 1988).

Production

Activated carbons are produced in the form of powders, granules, and shaped products (pellets and extrudates). Activated carbons have also been produced in fibrous form from cellulose (Audley, 1989) and pitch (see later section). There are two main routes for the synthesis of activated carbons, thermal activation or chemical activation. Thermal activation is a two-step process where the precursor is first carbonized in an inert atmosphere at temperatures from 500-700°C to produce a low surface area char. Subsequent controlled gasification or activation at 800-1000°C in steam or CO₂ greatly increases the pore volume and surface area, through volatile loss and carbon burn-off. Coconut shell, anthracite, and certain woods can be carbonized in granular form to produce hard carbons. Precursors that tend to form soft carbons must be reconstituted at some stage using a binder if strong shaped carbons are required. Bituminous coals are first pulverized and then reconstituted by briquetting under pressure, optionally with added binder. Thermoplasticity is eliminated by the promotion of crosslinking reactions, either by air oxidation, or the use of additives.

Chemical activation is normally used for lignocellulosic precursors, and consists of mixing the precursor with a chemical reagent such as H₃PO₄ or ZnCl₂ and heat treating in a single stage at

temperatures between 400-700°C. The reagent is then recovered in a leaching step to recover the reagent for recycle. Porosity is developed as a consequence of dehydration reactions occurring at low temperatures. Recent studies of the phosphoric acid activation of hardwood have revealed that reaction with the acid first causes shrinkage at temperatures around 150°C, which is attributed to the promotion of dehydration reactions, and there then follows a dilation of the structure, corresponding to the development of porosity (Jagtøyen and Derbyshire, 1993).

A different chemical activation process has been developed that uses KOH to produce exceptionally high surface area carbons from precursors such as bituminous coals and petroleum coke (Wennerberg and Grady, 1978; Jagtøyen and others, 1993). Activation with KOH can also be used to produce high surface area, hard extruded carbons from low-rank coals (Guy and others, 1989) or preoxidized bituminous coals (Verheyen and others, 1993). The chemical activation of viscose with Lewis acids (e.g. aluminum chloride, ferric chloride or zinc chloride) has been used to produce activates in the form of fibers or cloth (Baker, 1992).

Applications

Activated carbons are used in both liquid and gas phase applications for purification, environmental applications, chemical recovery, and catalysis. Liquid phase applications require carbons with a higher proportion of wide pores (macro- and mesoporosity) than gas phase applications, in order to reduce diffusional restrictions on the adsorption of impurities. The presence of wide pores (mesopores) also allows adsorption of large molecules such as color bodies and humic acids. Liquid phase carbons are used in both powder (typically 15 - 25 µm) and granular or shaped (0.3 - 3.0 mm) forms. Powdered carbons are normally used on a once-through basis. Their advantage over larger particles is their lower diffusional resistance to adsorption. Granular or shaped carbons are more desirable for continuous or cyclic processes, and can be removed for regeneration.

In 1987, liquid phase applications accounted for about 80% of the total activated carbon use in the USA (Goin and others, 1989). The principal uses are in potable water treatment (24%), industrial waste water treatment (17%), and the removal of color from sugars and foods (21%). Other applications include the refining of foods, beverages and cooking oils, gold recovery from low-grade ores, medical applications such as the recovery of antibiotics, vitamins and steroids from fermentation broths, the removal of blood toxins, and as catalyst supports (Goin and others, 1989, The Economics of Activated Carbon, 1990, Hassler, 1974).

Activated carbons for gas phase applications are mostly microporous and usually in a shaped or granular form. They are used for solvent recovery (26%), gasoline emission control in Evaporative Loss Control Devices (24%), air purification to remove toxic constituents and odors (18%), gas separation by pressure swing adsorption (6%), and catalysis (16%). [Percentages are figures for the USA in 1990, Chemical Economics Handbook, 1993]

Market

The world annual production of activated carbons was estimated to be in the region of 375,000 tonnes in 1990 (Baker, 1992), excluding Eastern Europe and China. About 55% of production is in powder form, 35% as granules, and the remainder as shaped carbons. The highest production capacity is in the US (40%), followed by Western Europe (30%), and Japan (20%).

The approximate selling price for granular or shaped carbons is in the region of \$4.50 - 5.50/kg, while for powdered carbons it is closer to \$2.00/kg. The actual price depends upon the adsorption capacity (typical surface areas fall in the range 800 to 1500 m²g⁻¹), hardness, and whether impregnants have been added to enhance performance. Speciality carbons can be much more expensive.

Consumption is increasing by about 5 - 7% per year (Baker, 1992, Irving-Monshaw, 1990). Growth will be primarily in areas affected by environmental regulations for the improvement of air and water quality.

Isotropic and Mesophase Pitch-Based Carbon Fibers

Carbon fibers can be divided into four main types based upon polymers, rayon and polyacrylonitrile (PAN), upon pitch, or are vapor-grown, Singer (1992). The focus here is on fibers that can be produced from pitch: petroleum and coal tar pitches are used industrially (Okuda, 1982; Matsumura, 1987; Thwaites, 1992). Fibers have also been produced from coal extracts (Jorro and Ladner, 1974), and recent work has shown that continuous filaments of isotropic carbon fibers and activated carbon fibers can be produced from coal liquefaction products (Fei and others, 1993). Appropriate precursor materials could be produced from coal by several methods: solvent extraction; carbonization; hydrolysis; and coal liquefaction. Pitch-derived fibers can be divided into those produced from isotropic precursors, and those derived from pitch that has been pretreated to introduce a high concentration of carbonaceous mesophase. The former are low-

performance, general purpose fibers while the latter are high performance products that can be produced with high tensile strength and very high modulus. An extensive discussion of the synthesis and applications of isotropic pitch-based and mesophase pitch-based carbon fibers has been given by Edie (1990).

Production

The steps involved in the synthesis of both types of fibers are illustrated in Figure 1. In each case, care must be taken in the selection and preparation of the starting material, although the requirements are quite different, and the pretreatment required to produce mesophase fibers is much more extensive. Accurate control of process conditions is also critical to the production of isotropic and mesophase fibers. However, the end-uses of isotropic fibers also allow them to be produced by melt-blowing, which produces short blown fibers and is relatively inexpensive, while the applications of high performance fibers necessitate the production of continuous filaments.

Whether produced from mesophase or isotropic pitch, the as-formed, "green" fibers require to be stabilized to render them thermosetting before carbonization. Stabilization is normally accomplished by air oxidation, although other methods may be used (Otani, 1971). Oxidation must be initiated at temperatures below the softening point of the fibers. As this temperature is lower for isotropic fibers than mesophase fibers, the process of oxidative stabilization is much slower in the former case.

For the development of tensile strength, the fibers are carbonized at temperatures up to 1700°C, or graphitized by heat treatment at temperatures approaching 3000°C. The final fiber properties are determined by the degree of orientation of layer planes along the fiber axis, and the size and perfection of individual crystallites. The lack of orientation in the structure of isotropic fibers causes their modulus to be about 1/20 of that of mesophase fibers, while their tensile strength is around 1/3. While there is little improvement in the properties of isotropic fibers on graphitization, graphitized mesophase fibers develop very high modulus. Compared to carbonized or graphitized PAN fibers, they have higher modulus and lower tensile strength, giving advantages in applications requiring high stiffness, high electrical and thermal conductivity, low thermal expansion, and high temperature oxidation resistance, while the former are employed where high strength is required.

Applications

The costs of PAN, isotropic pitch and mesophase pitch fibers are in the region of \$60, \$22, and \$90 per kg. The low precursor cost, lower processing costs and higher carbon yields contribute to isotropic pitch fibers being much cheaper than PAN fibers. For mesophase fibers, the additional step of mesophase formation, and higher complexity of other processing steps result in a much higher fiber price.

Low cost makes isotropic pitch fibers attractive for applications where high tensile strength or stiffness are not required. Examples include: enhancing the properties of composite friction materials for brake pads and clutches; the reinforcement of engineering plastics; ablation and thermal insulating materials; electrically conductive fillers for polymers; filter media; paper and panels; the production of hybrid yarns with other fibers; reinforcing concrete to improve flexural strength and other properties (Okuda, 1992; Soroushian and others, 1991); and as potential replacements for asbestos.

Because of their high modulus, mesophase fibers are used in aerospace structures, and the very high thermal conductivity of more recently developed fibers has opened applications for heat dissipation in areas such as high speed machinery, aircraft structures, and electronics. The cost of some of these specialized, ultra high performance fibers can be many hundreds of dollars per kg. Even for the lower cost products, their use is only readily justified in military and commercial aircraft applications and aerospace, where they can be used in materials that have performance characteristics unobtainable elsewhere. Reductions in the cost of mesophase fibers would substantially expand their applications into areas such as automotive structures.

Market

The worldwide production of all types of carbon fiber is in the region of 9000 tonnes (1993). The largest growth is in general purpose fibers which accounted for about 2500 tonnes in 1992, representing a threefold increase since 1989: projections for 1994 are over 5000 tonnes, and by the year 2000, one estimate predicts 40,000 tonnes.

In 1989-90, approximately 25% of pitch-based fibers were produced from coal tar pitch, and the remainder from petroleum pitch. At that time, the production capacity for mesophase pitch fibers was 800 tonnes, about 65% from coal tar pitch and 35% from petroleum pitch.

Activated Carbon Fibers from Pitch

In recent years, interest has developed in the activated forms of isotropic carbon fibers, where high surface areas can be produced by partial gasification in steam or other oxidizing gas (Thwaites and others, 1993, Suzuki, 1993). Carbon fibers have only been commercially available since the 1960s, and the development of activated carbon fibers has been a direct consequence of this technology.

Activated carbon fibers have novel properties that make them more attractive than other, more conventional forms (powder or large-size carbons) for certain applications (Suzuki, 1993). While porosity could be generated in most types of carbon fiber, low-modulus, isotropic pitch fibers are particularly well-suited for activation due to their unique structure in which the random packing of small crystallites allows the development of an extensive pore structure. A growing and completely different array of applications exists for the activated forms of isotropic carbon fibers (Suzuki, 1993; Mochida and others, 1991 and 1992; Foster and others, 1992; Economy and others, 1992).

High surface areas can be produced and most commercially produced fibers are microporous (< 2nm diameter pores). The narrow fiber diameter essentially eliminates mass transfer limitations, and adsorption and desorption rates are very rapid, roughly two orders of magnitude higher than for granular carbons. The fibrous form facilitates incorporation into woven and non-woven fabrics, felt, paper, and specific formed shapes. Among the possible applications, activated carbon fibers are of interest for the adsorption and recovery of organic vapors (Suzuki, 1993, Foster and others, 1992), removal of SO_x and NO_x from flue gas (Mochida and others, 1991, 1992), and for water treatment (Suzuki, 1991).

Despite the singular attributes of carbon fibers and activated carbon fibers from isotropic pitches, the potential of these materials has not yet been realized: in 1992, only 200 tons were produced in Japan (Suzuki, 1993). One reason is that production costs are still too high to attract widespread use and hence economies of scale. Lowering production costs through technological advances would help to reverse this situation, increasing the volume of sales and providing the incentive for larger scale production which would, in turn, effect further economies - a pattern that has already been realized for high performance carbon fibers. The high material costs and low yield for polymer derived fibers makes pitch a viable alternative with greater potential for reducing processing costs.

Literature

American Chemical Society (1992), Preprints Fuel Science Division, "Symposium on High Value Materials from Fossil Fuels", San Francisco, CA, April 5-10, 37, No. 2, p. 497-619.

American Chemical Society (1993), Preprints Fuel Science Division, "Symposium on Alternate Uses for Fossil Fuels", Denver, CO, March 28-April 4, 38, No. 2, p.400-468.

Audley, G. J.(1989), European Patent 0312 395 A2.

Baker, F. S. (1992), Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 4th. Ed., 4.

Bansal, R. C., Donnet, J. B. and Stoekli, F. (1988), Active Carbon, Marcel Dekker, New York.

Chemical Economics Handbook (1993)-SRI International, Menlo Park, Calif.

Derbyshire, F., Jagtoyen, M. and Thwaites, M. (1993), Active Carbons-Production and Applications, in book to be published by Butterworths.

Donnet, J. B., Bansal, R. C. and Wang, M. J. (1993), Carbon Black, Second Edition, Marcel Dekker, Inc.

Economy, J., Foster, K., Andreopoulos, A., and Jung, H. (1992), Chemtech, October, 597-603.

Edie, D. D.(1990), Carbon Fibers Filaments and Composites, Kluwer Academic Publishers, Netherlands, p. 43-72.

Eastern Oil Shale Symposium (1993), Papers presented in "Symposium on New Products and Uses of Oil Shales and Oil Sands", Lexington, KY, Nov. 17-19, 1993.

Fei, Y. Q., Derbyshire, F., Jagtoyen, M. and Mochida, I.(1993), Paper presented at 1993 Eastern Oil Shale Symposium, Lexington, KY, Nov. 17-19.

Foster, K. L., Fuerman, R. G., Economy, J., Larson, S. M., and Rood, M. J.(1992.),

Chem. Mater., 4, p.1068-1073.

Fuel Processing Technology (1993), Special Issue: High Value Materials from Coal, 34 (2).

Goin, J., von Schuller-Goetzburg, V. and Sakuma, Y.(1989), Chemical Economics Handbook-SRI International, Menlo Park, Calif.

Guy, P.J. , Verheyen, T. V. , Heng, S., Felber, M. D. and Perry, G. J.(1989), Proc. Int. Conf. Coal. Sci., p. 23.

Hassler, J. W.(1974), in Purification with Activated Carbon, 3rd. ed., Chemical Publishing Company, Inc., New York, p. 353.

Irving-Monshaw, S.(1990), Chemical Engineering, Feb., p. 43.

Jagtoyen, M. and Derbyshire, F. J. (1993),Carbon, 31(7), p.1185.

Jagtoyen, M., Toles, C. and Derbyshire, F.(1993), Preprints Fuel Science Division, ACS meetingDenver, CO, March 28 - April 4, 38, No.2, p. 400.

Jorro, M. A. A. and Ladner, W.R.(1974), Proc., 4th Int. Carbon-Graphite Conference, London, Sept, p. 287-303.

Kimber, G. M. , Brown, A. and Kirk, J. N.(1981), High Temperatures-High Pressures, 13, p. 133-137.

Kimber, G. M., Proceedings 13th Carbon Conference, Irvine, CA, 1977.

Kimber, G. M. and Gray, M. D. (1976), in Petroleum Derived Carbons, 31, p. 444-450.

Kirk-Othmer (1984), Encyclopedia of Chemical Technology, John Wiley & Sons.,3rd. ed, 24, p. 472.

Matsumura, Y.(1987), Seikiyu Gakaishi, 30(5), p. 291.

Mochida, I., Hirayama, T., Kisamori, S., Kawano, S., and Fijitsu, H.(1992), Langmuir, 8 (9), p. 2290-94.

Mochida, I., Sun, Y-N., Fijitsu, H., Kisamori, S., and Kawano, S. (1991), Nippon Kagaku Kaishi (J.Chemical Society of Japan), 6, p. 885-890.

Mochida, I., Fei, Y.Q., Korai, Y. and Fujimoto, K.(1989), Carbon, 27 (3), p. 375.

Otani, S. (1971), U.S. Patent # 3,629,379.

Okuda, K.(1992), TANSO, 155, p. 426.

Okuda, K.(1982), Petrotech, 5(1), p. 37.

Pittsburgh Coal Conference (1993), Session on "Non-Fuel Use of Coal", Proceedings, September 20-24, p. 379-416.

Singer, L. S.(1992), Proc. Eighth Annual Conference on Materials Technology: Structural Carbons, Sept. 1-2, 1992, Southern Illinois University at Carbondale, Carbondale, IL 2901, USA, p. 3-32.

Song, C. and Schobert, H.H (1993a), Fuel Processing Technology, 34, p. 157-196.

Song, C. and Schobert, H.H (1993b), Proceedings, 10th Internatl. Pittsburgh Coal Conference, September 20-24, p. 384.

Soroshian, P., Aouadi, F. and Nagi, M.(1991), ACI Materials Journal, 88, No. 1, p. 11-18.

Suzuki, M.(1993.), Proc. 21st Biennial Carbon Conference, Buffalo, June 13 to 18.

Suzuki, M.(1991), Water Science technology, 23, p. 1649.

The Economics of Activated Carbon (1990), 3rd. Ed., Roskill Information Services Ltd., London, p.8,9.

Thwaites, M.W., Stewart, M. L., McNeese, B. E., and Sumner, M. B.(1993), Fuel Proc. Tech., 34, p. 137-145.

Verheyen, V., Rathbone, R., Jagtoyen, M. and Derbyshire, F. (1993), paper submitted to Carbon.

Wennerberg, A. N, Grady, T. M.(1978), United States Patent 4 082 694 .

Zondlo, J., Stansberry, P. and Stiller, A.(1993), Proceedings, 10th Pittsburgh Coal Conference, September 20-24, p. 379.

Table 1: Carbon materials based on coal-derived feedstocks (adapted from Song and Schobert, 1993a)

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| <ul style="list-style-type: none">* Pitch-based carbon fibers* Mesophase-based carbon fibers* Carbon fiber reinforced plastic* Carbon whiskers or filament* Graphite and graphite-based materials* Electrodes* Composite materials* Molecular sieving carbons* Mesocarbon microbeads | <ul style="list-style-type: none">* Activated carbons* Activated carbon fibers* Metallurgical cokes* Carbon blacks* Intercalation materials* Elastic carbons* Fullerenes or "bucky-balls"* Diamond-like films |
|--|--|

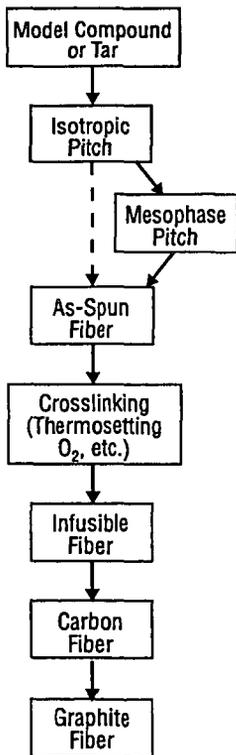


Figure 1: Preparation of isotropic and mesophase pitch carbon fibers