

Introduction to Hydrocarbon Conversion Science and Achievements of Professor Isao Mochida

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Background to the studies of I. Mochida

Fossil fuels, such as coal, petroleum and natural gas (methane), although used dominantly as fuels, either by direct combustion, or to power engines, have other significant uses. Coal is carbonized, directly, to produce metallurgical coke and coal-tar from which is derived coal-tar pitch, this material being a precursor to several carbon artifacts. Further, coal can be 'liquefied' to produce acceptable fuels, although the economics for this, currently, are far from favorable. Each of these conversion processes has been studied extensively by Mochida, to produce industrially acceptable materials, and to be able to use, more effectively, raw materials or feedstocks with less and less acceptable specifications, and to improve the overall economy of the conversion processes.

Likewise, it is with petroleum. Crude petroleum is processed by thermal and vacuum distillation, including catalytic systems, to produce a variety of liquid fuels, for gasoline, diesel and aircraft engines, and for space heating. Not all of the barrel can be converted to such high value products. There exists a variety of 'pitch residues' from the conversion processes. Mid-century, these residues would be used either as a fuel, or would be converted to a solid in the so-called 'delayed cokers', the solid 'delayed coke' being itself used as a fuel or disposed of in land-fill operations. Mid-century onwards, after W.W. II, saw a tremendous increase in the use of petroleum, with associated increases in the tonnage of 'pitch residues' which required disposal. However, during this growth process it was realized that these 'pitch residues' could have commercial application, and that their status could be raised to that of a 'by-product'. Thus, the 'delayed coker' became more than a disposal unit, it became specialized equipment to produce the required 'sponge' (or 'regular') cokes and 'needle' cokes. Mochida undertook a massive programme of research into the workings of delayed cokers, and improvements in quality of delayed cokes. Delayed cokes find an irreplaceable use in the manufacture of carbon anodes which are used in the Hall-Héroult cells of the aluminum industry, and the large electrodes of the steel industry, used to transmit electrical energy into the crucibles of steel production.

Personal notes: I. Mochida

Professor Isao Mochida, born in 1944, took his B. Eng. in the University of Tokyo in 1963, with a M. Eng. also from the University of Tokyo, specializing in Linear Free Energy Relationships in Heterogeneous Catalysis. He joined the University of Kyushu in 1968, and currently has the title of Professor: Institute of Advanced Material Study. During these years in Kyushu, Professor Mochida has published 485 Technical Papers, has written 10 Books and has 25 Patents. He spent one year with Professor Harry Marsh, 1977-1978, in the University of Newcastle upon Tyne, U.K. The scientific community has recognized the massive contribution he has already made to the sciences associated with coal and petroleum, and their many derivatives, in the form of eight Awards from Societies both within Japan and abroad. Trained initially in catalysis, he has applied this discipline successfully in his studies associated with carbon science and with coal and petroleum refining. There is more. At the time when relation-

ships between Universities in Japan and Industry needed to be strengthened (and this was a world-wide problem) Mochida worked intensely to build-up a research school, and to relate the findings of this research to the problems which industry was experiencing. Further, this period of time saw a significant growth in the size of research teams from the occasional two or three, to numbers approaching about twenty. And other changes were taking place. These research teams were now including students from outside Japan, and students from Japan were being offered opportunities to study in Universities, worldwide. At the centre of these activities Mochida operated with an apparent limitless energy, with the welfare of his students very much at the fore-front of his thinking. So, simultaneously, massive contributions were made to the sciences of hydrocarbon conversions, and young people were being highly trained to take their place in industrial and academic societies.

New materials: I. Mochida

Mochida has the ability, also, to be extremely innovative. Taking a look at recent issues of the journal *Carbon*, e.g., *Carbon* 1996, Mochida has, with his co-authors, studied the axial nano-scale microstructures in graphitized fibers inherited from liquid crystal mesophase. Limitations to thermal conductance, thermal capacity, tensile strength and Young's modulus of fibre materials, and hence limitations in applications, ultimately depend on the continuity of crystal alignments in such fibres. Such studies are to the fore-front of research into the applications of fibres and are both timely and relevant. Also, Mochida has recently looked at the carbonization properties of the fullerenes C_{60} and C_{70} . Further, in the area of new carbon forms, he has studied the mechanical properties of binderless carbon moulds prepared from heat-treated mesophase pitch of controlled grain size. A similar, but quite distinct problem is that of gas separations. Molecular sieve carbons, similar in behaviour to the microporous zeolites, have been known for some years now. Mochida has applied these approaches to the separation of carbon dioxide from coal-bed methane, a mixture of these two gases, usually heavily contaminated with water vapour. Such a separation requires not only a carbon with the appropriate microporosity, but with this contained between surfaces which are of a hydrophobic nature. The coal-bed methane needs to be of a suitable purity for use in homes and industry.

The mesophase story: I. Mochida

During his career, Mochida has applied his earlier training in catalysis to reactions associated with the formation of carbons, of diverse properties, from various original, aromatic feedstocks. Studies have been published of catalytic syntheses of 'mesophase' pitch from aromatic hydrocarbons, such processes allowing the molecular design of carbon precursors. Synthetic methods have been developed for the creation of pitches from pure aromatic hydrocarbons using such Lewis acids as HF/BF_3 or $AlCl_3$ as catalysts. The preparation of nitrogen-containing pitches, from quinoline and isoquinoline, is an attempt to understand how differences in locations of nitrogen atoms, within the ring structures of the graphene layer of graphitizable carbons, influences the carbonization properties of the starting materials and the properties of the derived carbons.

However, very significant contributions of Mochida are with the conversions of coal and petroleum to carbons and further derived materials. These two sources or feedstocks have two aspects in common. Both are very complex organic materials which require careful structural and chemical analyses, and both, on pyrolysis and carbonization, when in the fluid state, are able to form liquid-crystal systems, that is, the so-called mesophase. In simple terms, there are

many 'mesophases' which give the diverse structures to graphitizable carbons. Mesophases are generated from molecules (mesogens), size $\gg 1,000$ u, formed during carbonizations of coals and pitches. Mesogens, themselves, possess a wide range of chemical reactivity, and it is this variation which results in liquid crystal formation of differing size and ability to coalesce. Herein lies another long story. It is the 'crystallinity' of these liquid-crystals which is carried over into the solid phase of the carbon or coke, and which imparts the associated properties of anisotropy and graphitizability. By way of comparison, if wood material or a phenolic resin is carbonized, without passing through a fluid phase, then the resultant carbon, although not amorphous, is of limited structural order, is isotropic, and certainly is non-graphitizable.

Coal carbonization: I. Mochida

As far as coal is concerned it has to be recognized that 'coal materials' exhibit a wide range of chemical and physical properties, called 'coal rank'. The youngest of coals, the lignites and brown coals, with their internal co-valent bonding, do not fuse on carbonization, but produce carbons (or chars) which are meso- and micro-porous and hence have the properties of an adsorbent. As the rank range is traversed, the co-valent bonding is progressively replaced by hydrogen bonding and Van der Waals bonding, this enabling the coals to fuse on carbonization. The structure of the coal also becomes progressively more aromatic in content. With a further increase in rank, it is found that this fusibility, or softening or plasticity reaches a maximum to descend to zero in the semi-anthracites and anthracites, where the weak hydrogen bonding is replaced by carbon to carbon co-valent bonding. It is the coals with descending fusibility which have coking ability. However, the making of metallurgical coke no longer depends upon the use of a single coal being fed to the coking ovens. Rather, quite often, more than ten coals are previously blended and it is the blend which is charged to the coke ovens to be subsequently carbonized. Each of the ten or more coals, on their own, would not make a metallurgical coke. Procedures involving co-carbonizations of the coal (coal blend) with additives of high solubility parameters and hydrogen transfer ability were developed. It is this theory of the carbonization process, the interactions within the mixed fused states, and the formation of liquid-crystal systems and the fusing of these liquid-crystals, which has enabled the technology of coke-making to advance in the way it has done.

Coal, essentially, and considering the vitrinite macerals, is an organic, macromolecular system, containing microporosity. The ability of the coal to fuse (depolymerize) is a function of the strength of bonding within the macromolecular networks. Pyrolysis of coal produces molecular degradation to form the plastic (liquid) system. Subsequent carbonization brings about dehydrogenative polymerization of the dominantly aromatic molecules within plastic coal such that when the molecular size is about 1,000 u, formation of liquid crystals occurs and coke structure is established. Depolymerization of higher activation energies is favoured at higher temperatures, with rapid heating to prevent the retrogressive reactions at lower temperatures. Rapid heating under pressure is favorable with the use of additives in co-carbonizations because they have an enhanced facility for dissolution in the coal and reaction at higher temperatures. Mochida has submitted a proposal to the Ministry of International Trade and Industry and Japanese Association of Iron and Steel Making, which outlines coke-making procedures to be adopted in the next decade. The proposal includes coal pretreatment, rapid heating to enhance the fusibility for coke strength, by lower temperature of calcination, and potential for anisotropic development, hot moulding, and carbonization at controlled heating rates. The application of such a scheme would widen the range of usable coals, would make coke making less energy intensive, improving quality and productivity, and suggesting the possibility of a continuous rather than a batch process of coke making.

Coal liquefaction: I. Mochida

A thorough understanding of the macromolecular structures of coal, of bondings within and between these macromolecules, as well as the microporosity (so enabling reactive molecules to enter into coal structure) has enabled Mochida to improve the process of coal liquefaction. Early on, he demonstrated the importance of coal liquefaction solvents in terms of their boiling range, their dissolving ability and capacity as well as the reactivity of hydrogen donating molecules. Hydrogen donors not only stabilize radicals from coal pyrolysis but also lead to bond fissure of the rather more stable bridges, so achieving larger extents of depolymerization and hence of oil yield. In the area of liquefaction catalysts, the contribution of Mochida is with the design, the recovery and regeneration of catalysts, proposing the use of TiO_2 and carbon. He has advanced integrated schemes which include coal pretreatment, coal dissolution using donors at high temperatures, with two or three steps for the catalytic upgrading, such as hydro-desulfurization and hydro-denitrification.

Activated cokes (carbons): I. Mochida

Professor Mochida applied his combined understanding of coal chemistry and structure, as well as surface chemistry and heterogeneous catalysis to the production of activated carbons from coal, with the viewpoint of efficient removal of oxides of nitrogen and sulfur from combustion gases. Using a bituminous coal, he produced an activated carbon of higher performance characteristics than that of Bergbau Forschung (now DMT). He found (a) that the activity of the carbon for NO_x reduction, using ammonia, is intimately related to the oxygen functionality associated with the oxidatively adsorbed SO_2 , (b) that nitrogen functional groups introduced into the carbon, during the stage of the $\text{NH}_3\text{-NO}$ reaction, enhance the NO_x reduction, and (c) that the regeneration of SO_2 adsorption activity, after SO_2 recovery, relates to extents of surface oxygen complexes contained on carbon surfaces. Removal of SO_x and NO_x using activated coke (from coal) is now commercialized in Japan. The same principles have been applied to activated carbon fibers from PAN (polyacrylonitrile).