Problem-Oriented Investigations in Coal Fuel Chemistry and in Chemistry of Carbon Materials

To blessed memory of Victor Samoylovich Kobrin – one of the first researchers at the Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, and my first supervisor in Organic Chemistry

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Abstract

The necessity of broadening and intensification of fundamental research is substantiated for the development of processes which would be the basis of principally new technologies of processing solid fossil fuel to obtain valuable chemical products and materials.

Wide-scale investigations into genesis, structure, composition and properties of solid fossil fuel, exploration of the ways of its use as chemical technological raw material had been launched in the institutions of the Academy of Sciences of the USSR in early 30-ies under the initiative of Prof. I. M. Gubkin. At the end of the year 1934, on the basis of the Sapropel Institute, the Institute of Fossil Fuel of the Academy of Sciences of the USSR was organized and a large complex of fundamental research was launched in the area of chemistry and geochemistry of fossil fuel, lithology, coal and oil prospecting [1].

For the purpose of further development of the fundamental research of solid fossils, another independent institution of the Academy of Sciences was organized, namely, Institute of Coal, SB AS USSR (at present, it is Institute of Coal and Coal Chemistry, SB RAS). During the difficult period of social and economic crisis in Russia, its structure and main directions of its activities have been reformed several times. Now, keeping in mind the essence of the present process in Russia which involves the transition to market economy, it is very important to choose the most rational way in organizing its research activities in the area of materials science studying coal chemistry and chemistry of carbon materials.

The recent crisis of the Russian science and industry was not reduced to only financial and material problems. It touched psychological, social, organizational, manpower, informational and other aspects of the research and industrial activities. Indices of degradation in research teams started to take shape: in professional skills, due to the absence of normal conditions for work; in manpower, due to catastrophic aging of research personnel; psychological, due to a loss of prestige of science in the society; organizational, as a result of worsening of discipline in labour, performance, technology [2]. One of the leaders of modern academic science says that the existing situation [3] “does not leave us the right of free pasturage in the field of fundamental research”. He continues: “today, when applied research in Russia is fulminated almost in literal sense, the burden of reconstruction of industry is heaped on the shoulders of the Academy of Sciences and institutes of RAS". The subject is chemical industry in general and coal chemical branch in particular.

The present paper contains some principal considerations on the market version of the development of research and industrial activities in coal chemistry. These considerations deal with the formation of priority directions of fundamental research in coal chemistry, in personnel training and in preparing projects aimed at revealing physicochemical regularities of the general scale, which is the basis of future high-technology processes of solid fossil fuel processing into valuable chemical products.

First of all, it should be stressed that in the 21st century neither territory nor natural resources but high technologies will be the main source of a country's prosperity [4]. Because of this, it is necessary to rebuild the technological basis through business undertakings in high technologies. The undertaking channel is distinguished by higher operational management and focusing, in comparison with bureaucratic state version. High-technology undertaking includes four stages: academic, which is the birth and development of a scientific idea; technological, which is the implementation of the idea into a specific technology, a prototype of a product; industrial, *i. e.*, the establishment and management of production; commercial, transferring product into profit. Within the state planning system, a special structure was corresponding to each of these stages: academic institution or university; applied-research institute; industrial enterprise, supply and sales agencies. The first three structures received financial resources from the state; their goal was to throw a development out to the neighbouring structure without taking care of whether it would reach the stage of commercial product and profit or not. In the market version, the developer is a participant and interested party at all the stages. In the state planning system, the main consumer of a high-technology product was military industrial branch financed from the state budget. At present, owners of free financial resources are citizens; so, a product should be aimed at meeting their requirements and connected with medicine, food, housing stock, personal automobiles, household devices, *etc.* [5, 6].

Modern coal chemistry still cannot be referred to as a high-technology branch. It continues accumulating the data on origin, composition, structure and properties of solid fossil fuel, which is necessary in order to develop efficient processes and procedures for fossil fuel processing. An obvious lack of developments provided with reliable technical and economical background is observed. However, intensive efforts of researchers in the area of the chemistry of solid fossil fuel should give rise to developments of this kind. Establishment of industrial production on this ground in the countries with the developed market economy will proceed through small high-technology companies forming a structural and industrial basis for larger enterprises. One may assume that this way of realizing the scientific developments will take place also in the coal chemical branch of Russia. However, in this case, it is necessary to intensity the efforts in the fundamental direction [7] understanding that this is the basic cornerstone. From this point of view, the proposal [8] concerning establishment of a state research centre of complex processing of solid fossil fuel cannot be considered at present as a realistic one, even if it is explained by the necessity to solve a fashionable problem of restructuring and diversification of coal branch.

Under the conditions existing in Russia, the efforts of academic institutions aimed directly at the industrial coal chemical enterprises have no prospects from the strategic viewpoint. Even those industrial works which had their research laboratories are forced to reduce the staff or to close them. An example may be the Coal Semi-coking Plant in Leninsk-Kuznetskiy of the Kemerovo Region. Academic institutions trying to interact with the Plant come across problems connected, on the one hand, with the absence of ready scientific developments, and on the other hand, with unwillingness to finance these developments by contract basis. At the same time, followers of the state planning version of the sustainable development aim at persistent asking of additional cash grants from the Government and the Region Administration for supporting inefficiently operating academic institutions through the declared cooperation with a plant (so-called research and industrial centre). At the same time, they perform reorganization of the basic research sub-units, which is expressed by actual decrease in the amount and worsening of the quality of fundamental research. Meanwhile, fundamental research in coal chemistry are necessary for market; market is necessary for attracting attention to the problem, in order to find financial resources for solving it, choosing the best versions of solution, and obtaining positive results which involve organizing high-technology business in the coal chemical branch.

The ways of development of coal chemistry and personnel training are directly dependent on the essence which is attributed to the subject of this branch of science at the present stage of its development as a phenomenon of natural history [7, 9]. At present, coal chemistry is the branch of knowledge which embraces physicochemical regularities of the formation and changes (natural, industry-borne, and technological) of the organic matter (OM) of carbonaceous sedimentary rocks (coal, shale oil, rocks with scattered or weakly concentrated OM). Recently we have also defined general specific investigation methods of modern coal chemistry: a) physicochemical instrumental analysis of OM and products of its transformations; b) physicochemical calculations of kinetic and thermodynamic parameters of transformations of the compounds modeling the structural fragments of OM; c) experimental modeling of the promising technological and organic geochemical processes with reconstruction of physicochemical conditions as close to those observed in nature as possible; d) theoretical physicochemical modeling of processes of formation and changes of OM.

So, the formation of new directions of investigations in coal chemistry and personnel training should be based on modern data in physical organic chemistry, chemistry of high-molecular compounds (HMC), geochemistry of organic matter, and geochemistry of HMC. This approach differs substantially from the traditional one [10] which is mainly based on the data of catalysis and synthesis methods in organic chemistry.

It is necessary to adjust conventional notions concerning the priority directions of the development of coal chemistry and personnel training for this branch, taking into account principally important goal of an academic institution, namely, activation of its role in the development of fundamental research of the OM of coal and other carbonaceous sedimentary rocks.

In spite of the existence of numerous data on the chemical mechanism of the formation of the organic constituent of carbonaceous sedimentary rocks (fossil fuel), enormous experimental material has been insufficiently and simplistically examined from the physicochemical viewpoint. This is clearly observed, for instance, in analyzing the contradictions between theory and facts reported in the monograph by N. D. Rus'yanova [11] (this can be read in our review [12]).

In addition, physicochemical direction often plays only subsidiary role in studying high-molecular organic matter of coal and other sedimentary rocks, refining and supplementing outdated scientific and technical solutions. Not without reason, one of the experts of highest authority in coal chemistry of the 20th century I. V. Kalechits following the German specialists had come to a conclusion that coal chemistry could not reappear on the basis of the known processes, and "perspectives of the transfer of chemical industry to coal raw material would depend on new developments" [10, p. 156].

Interpretation of the results of many thorough experimental works that involve physicochemical investigation methods is very formal. The reason is that the general notions about the origin and evolution of the fossil high-molecular OM have not been yet translated into the terms of physical organic chemistry [7]. Due to the complexity of natural processes, the analysis of structural changes in the fossil organic matter (kerogen) from the viewpoint of physical organic chemistry often turns out to be unsuccessful. In the general case, the problem connected with structural transformations of high-molecular OM into oil-like fluids has not been yet solved even theoretically because of the variety of molecular forms of fossils. Very simple models (individual organic compounds) are not very suitable for investigating chemical transformations of high polymers of carbon under the conditions characteristic of natural phenomena and technogenic processes; the creation of synthetic polymeric kerogen molecules of humite carbonaceous rocks has not yet lead to structures that satisfactorily depict the properties of real fossil matter.

It is necessary to note that high-molecular OM of carbonaceous rocks is an extremely difficult object for investigation by means of the chemistry of organic synthesis. V. I. Zabavin [13] compared the situation in this methodic approach with the situation in the chemistry of high-molecular compounds, in which synthesis methods were used in addition to the destructive ones in order to study chemical composition and structure of natural high-molecular compounds, such as cellulose and caoutchouc. For example, at first the models of these compounds were synthesized (polyoxymethylene and polystyrene); after that, the features of the structure of natural polymers were revealed by examining the synthesis products differing in complexity.

Encouraging examples of the synthesis of compounds modeling kerogen of sapropelite carbonaceous rocks are already available [14, 15]. It turned out that it is possible to synthesize kerogen-like polymers not only from polyene aliphatic acids, which are characteristic of algal fat, but also from phospholipid liposomes, which are the closest analogues of biomembranes of microorganisms. The addition of clays to the initial substances had no noticeable effect on synthesis but caused the formation of mechanically stronger material.

From the geochemical point of view, very important results are those obtained in experiments on the synthesis of model sapropelite kerogen; these results indicate that the major part of chemical reactions occur at relatively early stages of diagenesis. These reactions cause an increase in the number of cross bonds and the formation of basis chemical structure, while only the degree of chemical maturity increases during geological sedimentation process [16].

What are the trends of the development of the academic research subdivisions oriented at coal chemistry? Answering this question may be helpful in better understanding the directions of fundamental research and modern approach to personnel training in coal chemistry. The main changes in the composition of laboratories in the division of academic institute in Kemerovo within about 15 recent years are shown in Fig. 1.

The most urgent problem in the Institute of Coal and Coal Chemistry is connected with the organization of research in the area of chemistry of humolite coal and carbon materials obtained on its basis. Our experience in investigating sapropelite coal and products obtained from them is unique in many aspects, which is usual in fundamental research. However, this experience makes us think that similar problems in fundamental research should be put forward and solved in the chemistry of humolite solid fuel.

The fundamental research problem of coal chemistry at which the projects in the Laboratory of chemistry of sapropelite coals are aimed involves obtaining new information on physicochemical nature of formation and hydrothermal transformation of the polymeric lipid substance which comprises the major organic part of sapropelite fossil fuel.

The application of methods of physicochemical instrumental analysis, physicochemical calculations, experimental and theoretical modeling allows us drawing more and more definite conclusions concerning the composition and structure of kerogen macromolecules (algaenanes) and oil-like substances (primary naphthoids). Formulation of the concept of the formation of carbon-carbon bridging (cross-linking) bonds in algaenanes [17] has been important stage in solving the problem of the origin of sapropelite kerogen. This concept, allowing us to predict the composition and structure of the products of primary hydrothermal changes of sapropelite kerogen has not only eliminated some contradictions that existed for considering only polymethylene, oxygen and sul-

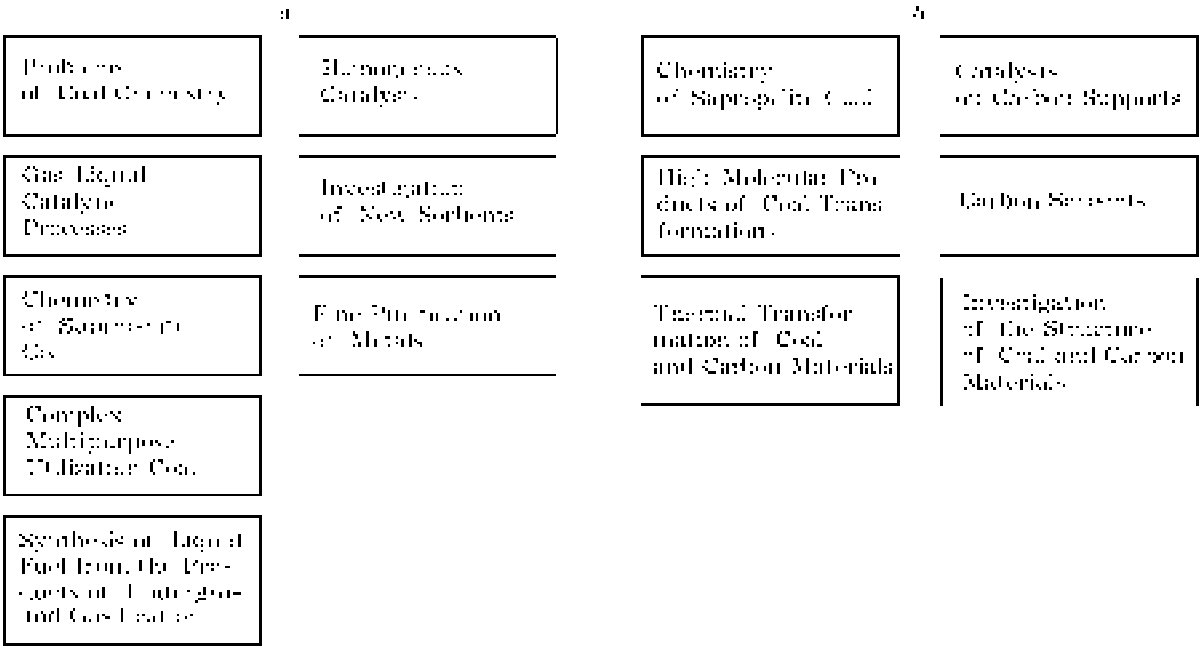

Fig. 1. Basic research subdivisions in the Department of Physical Chemistry and Coal Chemistry of the Institute of Coal, SB AS USSR (1988) (*a*) and Department of Coal Chemistry of the Institute of Coal and Coal Chemistry, SB RAS (2002) (*b*).

phide bridges, but has also become the starting point for the creation of a large research area, namely, chemistry of algenanes, multicomponent polymeric lipid systems and hydrothermal decomposition of sapropelite carbonaceous rocks [7, 18, 19]. The development of this direction allows one to understand better composition and structure of high-molecular OM of sapropelite carbonaceous rocks. In turn, these results are important for the development of new methods of processing sapropelite solid fossil fuel into synthetic oil-chemical raw materials. Our works in this area stimulate the development of hydrothermal coal chemistry, including chemistry of hydrothermal decomposition of sapropelite carbonaceous rocks [20, 21].

The essence of projects under implementation is the combination of the hydrothermal decomposition of sapropelites (a method developed by us) with radiation chemistry. With relatively small dose rate of natural ionizing radiation of any nature (1–2 W/kg), the saturated carbon frame of high-molecular fragments of kerogen does not change. At the same time, radiation-induced dehydrogenation of the saturated hydrocarbon fragments occurs along with the formation of unsaturated and oxygen-containing structural elements, which are extremely reactive under the conditions of hydrothermal decomposition. So, with the help of radiation, it will be possible to govern the transformations of structural elements of OM during hydrothermal decomposition. Such a combination of hydrothermal and radiation action is likely to allow us to perform hydrothermal decomposition of sapropelite coal and shale at relatively low temperature and pressure in the absence of chemical initiators and catalysts.

At the Laboratory of Chemistry of Sapropelite Coal, the research problem is being developed which is connected with obtaining new information on physicochemical regularities of changes in absorption properties of carbon material, which are products of pyrolytic transformation of the fossil organic matter of the sapropelite nature. Researchers succeeded in obtaining nano-structured carbon material with good adsorption properties from the products of pyrolysis of coal and oil. Preliminary tests indicated that this material is able to absorb methane (150 mg/g) at room temperature and pressure up to 40 atm; this material is very promising as an adsorbent for methane storage and transportation. At the

Institute of Catalysis, they called this material *kemerit* because of its unusual useful properties [22].

There is no necessity to give strict recommendations but it would be not out of place to stress that coal chemistry, as one of the most practically important areas of chemistry, is directed to the development of efficient processing of solid fossil fuel into valuable chemical products and materials. Because of this, we believe that under the modern conditions our fundamental works in the area of coal chemistry are to build up ideology and structure of this branch of science, provide the necessary theoretical foundations [7] for the technological development. A programme in coal chemistry at an academic institution should be a set of projects aimed at solving specific problems, united in order to solve a prominent fundamental problem, such as obtaining new information on physicochemical nature of the formation and changes (natural, technogenic, technological) in the fossil high-molecular organic matter, which is the main component of solid fossil fuel (coal, shale oil) and at the same time the most important source of oil and gas.

Problem-oriented investigations at the competitive expert basis comprise the route for the development of the fundamental research in coal chemistry and chemistry of carbon materials which is necessary for the elaboration of scientific foundations of a new coal chemical branch of industry: high-technological methods and processes of processing solid fossil fuel into valuable chemical products and materials.

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