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A New Round of Coal Chemistry Development

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Abstract

The history of processes for obtaining synthetic fuels by liquefying coals is described. Coal processing technologies are analyzed since the time of F. Bergius up to the present day. Modern hydrogenation processes are described. The basics of single-stage coal liquefaction technologies are described: Kohleoel (Ruhrkohle, Germany), NEDOL (NEDO, Japan), H-Coal (HRI, USA), Exxon Donor Solvent (ExxonMobil, USA), and Solvent Refined Coal (SRC-I and SRC-II, Gulf Oil, USA), as well as two-stage technologies for producing synthetic liquid hydrocarbons from coal: Brown Coal Liquefaction (NEDO, Japan), Catalytic Two-stage Liquefaction (DOE, HTI, USA), Integrated Two-stage liquefaction (Lummus, USA) , Liquid Solvent Extraction (British Coal Corporation, UK), Supercritical Gas Extraction (British Coal Corporation, UK). The scientific foundations of the processes for obtaining biochars from different kinds of biomass by means of hydrothermal carbonization are described. The existing technologies based on this process are indicated. The possibility to upgrade modern coal chemistry in line with "green chemistry" by integrating biomass and the products based on it into coal chemical processes is shown.

Keywords: synthetic fuel, hydrogenization, biomass processing, hydrothermal carbonization

INTRODUCTION

Coal resources are much larger than the resources of oil and gas. In the development of mankind, the turning round to the necessity of involving solid fossil fuels into petrochemical processes and into energy balance in general occurs in cycles.

In particular, before the start of the twentieth century, the almost complete absence of oil fields in Germany possessing vast coal resources had not been an urgent problem. Coal was used to fuel homes, it met the requirements of industry and armed forces. With the appearance of automobiles, lorries, and later planes, Germany turned out to be in the increasing need of liquid motor fuel, so the works aimed at the development of an alternative method to obtain liquid motor fuel were launched. The raw material to obtain synthetic oil was brown coal, which was widespread over German territory. This period of industry is Germany is connected with a brilliant assemblage of outstanding experts in practical chemistry, headed by Friedrich Bergius, Nobel Prize winner, creator of the foundations of berginization and the technology of the production of cellulosic alcohol. In 1913 he developed the method of thermal hydrogenation of coal and heavy oil at high pressure (berginization). He was awarded the Nobel Prize in Chemistry in 1931, together with K. Bosch [1].

FRIDRICH BERGIUS AND COAL PROCESSINGIN GERMANY

The invention of the method of coal hydrogenation by Friedrich Bergius resulted from earlier research [2]:

1. Long-term experience of work with high pressure apparatuses developed by Haber and Le Rossignol for the synthesis of ammonia.

2. Studies in the area of cracking of heavy petroleum oil and residues, which revealed significant improvement of the yield and quality of petrol in the presence of strongly compressed gaseous hydrogen in the system.

3. Development of the technology of coal conversion into hydrogen in the presence of liquid water under high pressure (about 200 atm) and low temperature (300–360 °C).

So, F. Bergius succeeded in solving the major problems encountered by scientists in their attempts to carry out coal hydrogenation: how to work at high pressure, how to obtain higher-quality petrol, and where to take hydrogen necessary for liquefaction. Bergius determined that the addition of a small amount of metal oxides, especially iron oxide, catalyzes coal hydrogenation [3]. He explained this effect through the ability of oxides to prevent polymerization of hydrocarbon fragments formed during coal heating.

Outbreak of the First World War on the 1st of August, 1914, highlighted an acute need for oil in Germany, and attention to obtaining synthetic fuel increased. In 1915, Bergius designed an experimental-industrial continuous-type installation for coal hydrogenation, to be accommodated in Rheinau, not far from Mannheim. However, the war caused a financial crisis, and the construction of the experimental plant was completed only in 1922 (Fig. 1).

In spite of success in scaling coal hydrogenation, in 1921 Bergius almost completed his research in this area, having left two problems unsolved: 1) optimization of catalyst composition; 2) final arrangement of the technological flowchart (thermal dissolution of coal and hydrocracking of the formed heavy petroleum, carried out in one stage, caused the low quality of petrol, which could not be competitive with the petroleum-originating analogue without upgrading).

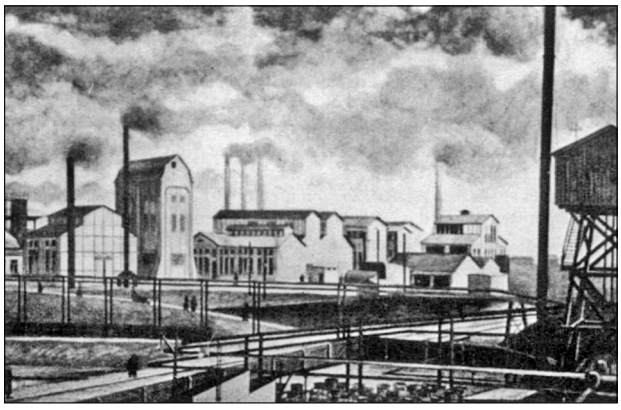

Fig. 1. Experimental coal hydrogenation plant in Rheinau.

In 1925, F. Bergius sold all his rights in the process to BASF company, and in the same year it united with other chemical companies (Bayer, Hoechst, *etc.*) to form a new company I. G. Farben [4]. Karl Bosch, its Director, made commercialization of coal hydrogenation the direction of priority in the development of the company. Due to his efforts, the process developed by F. Bergius (berginization, or direct coal liquefaction under high pressure) became more widespread in Germany in the 1940s than indirect coal liquefaction according to Fischer-Tropsch (coal gasification, followed by obtaining hydrocarbons from carbon oxide and hydrogen).

The personnel of I. G. Farben succeeded in separating the single-stage Bergius process into two stages – thermal liquefaction of coal resulting in the formation of heavy oil, followed by hydrocracking of heavy oil to obtain petrol, - and in developing the catalysts for both stages of the process. It was determined that the most active catalysts for liquid-phase hydrogenation were molybdenum-containing ones, but their limited resources made the manufacturers use better available and cheaper iron-containing analogues.

The first installation of coal hydrogenation with the productive capacity of 2.5 mln barrels of synthetic oil per year was introduced into operation in 1927 in Leun (Germany) [5]. In 1936, according to the four-year plan of the economic development of Germany, I. G. Farben company received almost 73 % of the total finances provided within this programme to create the industry of synthetic fuel. At the peak of development, 12 plants constructed for this purpose were manufacturing more than 25.5 million barrels of synthetic oil. Among this amount, 17 million barrels, after the introduction of the corresponding additives, were high-quality aviation and automobile petrol with octane number 100. During the Second World War, the I. G. Farben plants provided fuel to the major part of the German army.

It should be stressed that the prime cost of the products of coal hydrogenation was high, twice as high as the price of imported petrol. However, Germany did not have any other alternatives during the war and had to use its substantial resources of bituminous and brown coal. The loss of coal hydrogenation plants as a result of the USA air strikes in 1944 became one of the numerous factors that promoted the defeat of Nazi Germany.

So, Germany had created the world's first synthetic fuel industry in 1938–1945, which was actually destroyed at the end of the Second World War by the winners, who prohibited the production of synthetic oil. All plants in Western Germany had been almost immediately restructured for natural oil processing. The plants in Eastern Germany (in the cities of Leun, Bohlen, Zeitz and Brux) continued operation until the 1960s, but then they were also restructured. Four hydrogenation plants were disassembled within reparation and transported into the USA and Russia; their operation in Russia ceased during perestroika.

The processes of direct coal liquefaction, developed in Germany, were economically ineffective and required very high pressure and high temperature, but they were of interest for the production of synthetic oil from alternative raw material sources. However, with the discovery of large deposits of cheap natural oil in Near East in the 1950s, developments in the area of the direct liquefaction of coal were suspended.

MODERN COAL LIQUEFACTION PROCESSES

The oil crises of 1973 and 1978 caused an outbreak of attention to the alternative methods of the production of liquid hydrocarbon fuel, in particular to CTL processes (coal to liquid). Since, then, a number of technologies have been developed for the direct coal liquefaction, including single- and two-stage processes [6]. Single-stage processes allow obtaining distillates in one reactor or a cascade of reactors arranged in series, operating under identical conditions. These technologies include the following processes: Kohleoel (Ruhrkohle, Germany), NEDOL (NEDO, Japan), H-Coal (HRI, USA), Exxon Donor Solvent (ExxonMobil, USA) and Solvent Refined Coal (SRC-I and SRC-II, Gulf Oil, USA).

Two-step technology of direct coal liquefaction allows one to obtain liquid products using two steps of reactors operating under different conditions. The first step involves thermal dissolution of coal in the presence of (most frequently) single-use iron catalyst with low activity. Thus obtained heavy hydrocarbon liquids are subjected at the second stage to hydrocracking and hydropurification in the presence of a more active, though also more expensive catalyst. The technologies of this type include the following processes: Brown Coal Liquefaction (NEDO, Japan), Catalytic Two-stage Liquefaction (DOE, HTI, USA), Integrated Two-stage Liquefaction (Lummus, USA), Liquid Solvent Extraction (British Coal Corporation, UK), Supercritical Gas Extraction (British Coal Corporation, UK).

The data [7, 8] allowing a comparison between single- and two-stage technologies of direct coal liquefaction are presented in Table 1. Among the considered single-stage processes, the most promising one is H-Coal technology. Though its economics cannot be called attractive at present, however, some developments allow expecting a decrease in expenses. These developments include a new catalyst with bimodal pore size distribution, which allows enhancing the yield of distillates, as well as the possibility to decrease hydrogen consumption and the use of a reactor with a fluidized-bed catalyst.

Attention to two-stage coal liquefaction is due to the fact that the optimal conditions for coal dissolution differ from those for upgrading the liquid products obtained at the first stage. It is rather improbable that a catalyst providing a number of functions necessary for the selective transformation of coal into distillates in one stage might be found ever. In comparison with the single-stage H-Coal process, the use of two-step liquefaction technology (CTSL) enhances selectivity with respect to the formation of distillates with low heteroatom content. However, in spite of evident potential, these technologies (except CTSL technology) were not commercialized because of the low price of oil, which was set since middle 1990s.

The only commercial plant for direct coal liquefaction after the Second World War was constructed by Shenhua group in Inner Mongolia (China) [9]. It was put into operation in 2008 and annually produces 780 thousand t of liquid fuel, 230 thousand t of naphtha and about 100 thousand t of liquefied gas.

INTEGRATION OF BIOMASS PROCESSING TECHNOLOGIES INTO MODERN COAL CHEMISTRY

At present, power engineering is actively revised in view of ecological problems. Intense work aimed at the formation of modern legislation to provide carbon emission control and to stimulate decrease in emissions is carried out in Russia. This strategy foresees an unambiguous transformation of modern coal chemistry, from the point of view of enhancement of technological efficiency and the

TABLE 1

Comparison of single- and two-stage technologies of the direct liquefaction of coal

Parameter	Single-stage technology				Two-stage technology		
	NEDOL	H-Coal	EDS	Kohleoel	BCL	CTSL	LSE
Productive capacity, t/day	150	200	250	200	50	1 mln t/year	2.5
Development level	Pilot	Pilot	Pilot	Pilot	Pilot	Commercial	Pilot
Reactor/catalyst	2–4 % Fe	Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3	Нет	Fe (red mud)	I stage: Fe slurry, II stage: Ca–Ni–Mo	I stage: Fe Gelcat, II stage: fluidized-bed reactor, Ni–Mo/Al_2O_3	I stage: no, II stage: fluidized-bed reactor
Temperature, °C	435–465	435–465	425–450	470	427–448, 360–400	430, 435–440	410–440, 400–440
Pressure, atm	150–200	200	175	300	150–200	170	10–20 200
Yield, %							
Hydrocarbon gases	16.9	10.5	5	19	13.6	--	15.4
Light distillates (fraction C_5–200 °C)	28.8	13.3	14	25.3	36.7	60–65	49.9
Medium distillates (fraction 200–325 °C)	19.3	19.7	10	32.6	15.1	--	12.4
Unreacted coal and coke	18.8	37.1	48	22.1	8.1	7–22	24.7

principles of green chemistry and maintenance of environment.

At present, biomass is considered mainly as a reproducible raw material for the production of thermal and electric energy. This thesis is especially relevant when so-called distributed power engineering is considered. This concept implies the construction of additional sources of electric energy in the direct vicinity of consumers. The power level of these sources is chosen on the basis of expected consumer power taking into account the existing limitations (technological, ecological, *etc.*) and may be varied within a broad range. The experience of western countries shows that distributed power engineering is a new mainstream. During the recent two years, small-scale distributed power engineering has become one of the centres of discussions in the area of energy policy [10]. It is known that the biomass, similarly to fossil coal, is a solid energy-producing fuel. Biomass is an available, CO_2-neutral energy resource, and it is counted upon in view of the development of distributed power engineering in Russia.

However, the application areas of natural coal are not limited to power engineering. Before the beginning of the petroleum era in the middle of the past century, coal had been almost the only source from which organic substances including liquid motor fuel, could be obtained. Unfortunately, the presence of large amounts of water and oxygen in biomass worsens the quality of products and thus holds back the use of this resource in the majority of coal chemical processes. However, thermal treatment of biomass, in particular hydrothermal carbonization, allows one to obtain biochar and to approach the properties of fossil analogues. So, the application of biochar may be expanded substantially in the direction of processes that are traditionally used in fossil coal processing: to obtain liquid hydrocarbon products, artificial combustible gases and valuable chemical compounds. In this case, biomass will be the raw material, and the process of biochar formation may be represented as the stage of raw material upgrading.

An implicit advantage of biochar processing technologies in comparison with similar processes used for fossil coal is the possibility to modify the properties of biochar according to the requirements of subsequent processing stages. Attention to the production of biochar is due to a number of advantageous characteristics of biochar in comparison with initial biomass, for example, higher

heating capacity, the possibility of long-term storage and transportation over long distances. Similarly to biomass, biochar is a CO_2-neutral energy fuel. These facts make biochar a promising energy source for distributed power engineering. The production of biochar as energy fuel is a self-consistent chemical process in which biochar is a commercial product and may successfully compete with the natural analogue by occupying its own economic niche.

Hydrothermal carbonization of biomass is the process of obtaining biochar, which forms a new round of the development of modern coal chemistry; a historical example which may be used to consider the dialectic spiral-like development: investigation of the conversion of organic raw material under high pressure in the presence of liquid water enabled F. Bergius to discover coalification method, which was later on named hydrothermal carbonization.

Before F. Bergius' experiments at high pressure, researchers often carried out steam conversion at high temperature trying to gasify plant raw material, for example cellulose and wood. However, the high exothermal effect of the reaction caused overheating of the system, pyrolysis was intensified, and coal became the major reaction product. Bergius made attempts to cope with excessive heat evolution. In the process developed by him, not steam but water was used, which remained in the liquid state at the working temperature. It served not only as a reagent but also, due to its high heat capacity, it absorbed and distributed the released heat, thus preventing overheating. In 1911, this method was used by Bergius for thermal treatment of peat for the purpose of obtaining hydrogen: at 340 °C and 100 atm, reaction products were a gas containing hydrogen with a significant admixture of CO_2, and a dark precipitate resembling soft natural coal [11]. Thus obtained artificial coal (termed today as biochar) contained carbon 74–85 % and hydrogen about 5 %, that is, it was an analogue of natural bituminous coal. Though Bergius' studies were directed to obtaining hydrogen, he unintentionally succeeded in discovering the method of biomass coalification. This disruptive discovery was followed by studies carried out by other scientists. Different kinds of biomass were subjected to carbonization, which allowed researchers to generalize and systematize the existing knowledge on the origin of coal [12, 13], and to determine the effect of pH value on reaction course and on the yield of the product [14]. Hydrothermal carbonization has also found industrial application in the processes of brown coal drying according to Fleissner's method [15] and in improving the heat-producing properties of peat [16]. However, these processes did not become noticeably widespread.

Revival of hydrothermal carbonization took place in the early 2000s, when studies of low-temperature hydrothermal synthesis of biochar from sugar or glucose were reported [17, 18]. By this time, the instrumental possibilities of investigation into the chemical transformations of substances broadened significantly, and understanding of hydrothermal carbonization passed up to the new step. From the viewpoint of modern science, hydrothermal carbonization (HTC), or cold coaling, is the process of biochar (or hydro-coal) formation at a temperature of 180–220 °C and pressure up to 25 atm in the presence of water without air access and with the addition of a catalyst [19]. During the process (usually for 16 h) the biomass is dehydrated and carbonized. As a result, a dense suspension composed of powdered coal and water is formed. The process is distinguished by almost 100 % carbon efficiency, that is, almost the whole amount of carbon from the raw material remains in the target product, and a minimal amount of carbon-containing gases is formed (mainly carbon dioxide or methane). Hydrothermal carbonization has another important advantage over other methods of obtaining biochar: the process is exothermal. In addition, mineral substances that are present in plants, for example, salts containing phosphorus, potassium and ammonium, remain dissolved in water and may be isolated, and then used as fertilizers.

As the first approximation, hydrothermal carbonization (in application to glucose) may be expressed as follows [20]:

$$[C_6H_{12}O_6]_n \rightarrow n\,[C_6H_2O + 5H_2O] + \sim 950\ \text{kJ/mol}.$$

Depending on the degree of reaction progress, each carbohydrate releases four or five water molecules. At the first glance, water removal seems improbable in the presence of water; however, the possibility for the reaction to proceed is to a high extent explained by an increase in entropy (due to an increase in the number of molecules and degrees of freedom) and exothermal effect of the transformation.

According to modern notions, the first step of HTC is hydrolysis: water enters the interaction with hemicellulose or cellulose and breaks ether and ester bonds (mainly beta-(1-4)glycoside bonds). According to the available data, pure

hemicellulose starts to be hydrolyzed at a temperature above 180 °C, and hydrolysis of pure cellulose proceeds at a temperature above 230 °C [21]. As a result, many products are formed, including soluble oligomers. Lignin mainly remains unchanged. Additives, such as acids or bases, catalyze hydrolysis and may affect the yield and composition of the formed products.

The process technology has been developed not long ago, and several private companies launched the production of biochar from biomass. In 2012, AVA-CO_2 Schweiz AG company (Switzerland) put into operation an industrial installation on hydrothermal carbonization of biomass. Since 2016, TerraNova Energy GmbH company (Denmark) possesses an operating plant manufacturing biochar in the territory of China. In 2013, Ingelia company (Spain) put into operation the first plant for biomass processing by means of hydrothermal carbonization, and at present three plants are functioning. One plant more is at the stage of construction in Great Britain.

So, hydrothermal carbonization is a process that may be defined by the phrase: "New is well forgotten old". This reaction causes much enthusiasm of researchers working in various areas, including solid fuel modification for the purpose of improving their storage conditions and energy characteristics, the synthesis of active coal and carbon-containing materials with unique adsorption properties, preparation of efficient carbon-containing catalysts, *etc*. This allows us to assume that hydrothermal carbonization may launch the beginning of the entire branch of targeted synthesis of carbon materials and carbon-containing composites with various characteristics.

However, it should be stressed that, in spite of the old age, hydrothermal carbonization remains poorly investigated yet. First of all, this is due to the complicated nature of the raw material involved in the process, which is plant biomass. Biomass is a set of natural polymers noticeably different from each other in polymerization degree and in composition. In addition, fractionary behaviour is exhibited by cellulose and hemicellulose in the reactions of monomer links: either all functional groups or only some of them may participate in chemical reactions. The reactivity is affected by the energy of intermolecular interactions between separate macromolecules, their conformations and inhomogeneities. This brings about substantial hindrance in the studies of hydrothermal transformations of biomass and requires much time for detailed investigation.

Returning to Friedrich Bergius, classical coal chemistry and coal liquefaction processes that are described in the first part of the present review, a natural question arises: is it possible to apply the flowchart finding of the chemical processing of native coal to synthetic coal obtained by means of hydrothermal carbonization? Is this approach necessary in principle? Combination of the processes of classical petro-, coal and gas chemistry with biomass processing is increasingly frequently discussed in the scientific literature [22–24]. Some authors suppose that the future of the green chemical industry belongs to these processes, and a combination of the methods used for processing fossil and renewable raw materials is a modern scientific trend. In addition, it has been proved that biochar is close in its nature, morphology and composition to native coal (the data of Van Krevelen diagrams). Therefore, eh flowchart findings in biochar processing may be quite relevant for the technological approaches in classical coal chemistry, for example, they may be applied in thermal dissolution processes. This process is traditionally aimed at achieving deep destruction of the organic mass of coal to obtain light hydrocarbon fractions for use as fuel [25, 26]. It is stressed in [27–29] that thermal dissolution of fossil fuels may be carried out in the presence of organic solvents, which are hydrogen donors, such as tetralin or N-methyl-2-pyrrolidone (NMP). Modern research in the area of liquefaction [30] demonstrates the possibility to use biochar as a replacement for fossils in thermal dissolution processes. In particular, it is known [31] that biochar obtained through hydrothermal carbonization of biomass may be subjected to thermal dissolution in tetralin at 350 °C in the presence of Ni/TiO_2 catalyst. This process leads to the formation of synthetic oil at a yield of 42 %. Higher yield of synthetic oil (>80 %) is achieved through thermal dissolution of biochar obtained by HTC of cellulose at 230 °C. It has also been noted in [32] that variation of the first stage of cellulose processing, namely hydrothermal carbonization, may affect the conversion and yield of hydrocarbons.

CONCLUSION

Thus, further integrative development of hydrothermal carbonization as an example of so-called biorefining, and modern classical coal chemistry, the foundations of which had been paved by F. Bergius, and understanding of the

possibilities of this interaction are already outlined but have not been implemented in practice yet. While the driving force for Bergius' research was the solution of the applied tasks underlined by aggressive political motifs, at present the alternative technologies under development are mostly an instrument to sustain ecological stability over the world. This is indirect evidence of the transition from technogenic civilization to new views toward science. The scientific worldview in technogenic civilization was directing humans to transformation of nature in relationship with technologies, while the forefront idea in modern culture is a harmonic integrated human-to-nature relation. According to the ideas described in [33], a dialogue with nature as initiated by classical science, in which nature is considered as an automated device, gave birth to quite different view on nature investigation, in which the active questioning of the nature is an inalienable part of its internal activity. Transferring this approach to the heritage of Friedrich Bergius, one may observe how his ideas had been implemented in the construction of the world's first industry of synthetic fuel during the Second World War, and then, in early 2000s, they have led to the development of hydrothermal carbonization of biomass and continue developing in biochar processing with the formation of valuable chemical compounds.

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