# Friedrich Bergius and the Rise of the German Synthetic Fuel Industry

## By Anthony N. Stranges\*

GERMANY HAS VIRTUALLY NO petroleum deposits. Prior to the twentieth century that lack of a liquid fuel was not a serious problem, because Germany possessed abundant coal reserves. Coal provided for commercial and home heating; it also fulfilled the needs of industry and the military, particularly the navy.

In the first decade of the twentieth century, Germany's energy requirements began to change. Two reasons were especially important. First, Germany became increasingly dependent on gasoline and diesel oil engines. The appearance of automobiles, trucks, and then airplanes made a plentiful supply of gasoline absolutely essential; moreover, ocean-going ships increasingly used diesel oil rather than coal as their energy source. Second, Germany's continuing industrialization and urbanization magnified the shortcomings of coal as an energy source. German scientists and engineers began to replace coal with smokeless liquid fuels, which not only were cleaner burning and more convenient to handle but also had a higher energy content.

Petroleum was clearly the fuel of the future, and to insure that Germany would never be without it, her scientists and engineers created a domestic source of that fuel. From a plentiful natural substance, coal, they synthesized petroleum. Of the several processes the Germans used to convert coal into petroleum, highpressure coal hydrogenation was the most highly advanced. Its history falls into two broad periods: 1910–1925, during which time its inventor, Friedrich Bergius (1884–1949) developed the process through the first stages of industrialization, and 1925–1945, the period of its further commercial development by German industrialists.

This study (which appropriately appears on the hundredth anniversary of Bergius's birth) will concentrate on the first of these periods. It traces the growth of high-pressure coal hydrogenation from a laboratory process to a small factorysize operation and shows the difficulties Bergius faced in making the transformation. The three major problems he confronted and successfully solved were how to work at the high pressures required for converting coal into petroleum; how to provide a sufficient supply of hydrogen gas for the conversion; and how

\* Department of History, Texas A & M University, College Station, Texas 77843.

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Friedrich Bergius, 1884–1949. By permission of Johannes Bergius.

to regulate the reaction's temperature, in as much as the reaction was exothermic and highly sensitive to temperature change.

In spite of Bergius's successes, two important problems remained. Bergius did not investigate the influence of different catalysts on the reaction, nor did he explore alternatives to his process, in which hydrogenation of coal and splitting of the products took place in one step. As a result, relatively less split into gasoline-size molecules. In addition the gasoline was of low quality; without refining it could not compete with gasoline obtained from natural petroleum. In 1925–1926 scientists and engineers at the Badische Anilin- und Soda-Fabrik (BASF) plant in Leuna remedied these defects of Bergius's process and undertook the commercial development of high-pressure coal hydrogenation in Germany.

## I. THE BEGINNING OF HYDROGENATION

Coal hydrogenation or liquefaction is a process that converts different kinds of coal into synthetic petroleum by causing the coal to react with hydrogen gas at high pressure and high temperature. Distilling the petroleum yields its major components.

Marcelin Berthelot (1827–1907) at the Collège de France succeeded in hydrogenating coal for the first time in 1869. He added finely powdered bituminous coal to a saturated hydroiodic acid solution and heated the reactants in a sealed glass tube from ten to twenty hours at 275°C and atmospheric pressure. Berthelot combined the coal with twenty times its weight of acid and obtained a 60 percent conversion to liquid hydrocarbons, mainly saturated compounds such as hexane, dodecane, and cyclohexane, but with some benzene. The other products were a solid residue (33 percent), and gases, chiefly hydrogen (7 percent). Berthelot's coal hydrogenation experiments were only one part of his extensive investigation of the action of hydroiodic acid on organic compounds. He successfully hydrogenated wood and partially carbonized charcoal but failed to hydrogenate pure carbon (graphite), coke, and a completely carbonized charcoal.<sup>1</sup>

Berthelot's experiments showed that hydrogenation occurs only if the carbon of the reactants is part of a compound and not present as the free element. This suggested that coal does not contain elemental carbon and revealed at least one aspect of coal's structure. Hydroiodic acid later became a widely used laboratory reagent for hydrogenating and reducing organic compounds, but because of its high cost Berthelot's "méthode universelle" had no potential industrial value. Indeed, coal hydrogenation was a neglected reaction until the first decades of the twentieth century, when chemists began to study the hydrogenation process extensively.

Two factors contributed to the eventual success of the hydrogenation process: the introduction of metallic catalysts and the application of high pressure. Although a few publications on catalytic hydrogenation had appeared earlier in the nineteenth-century chemical literature, the real breakthrough came with Paul Sabatier's brilliant researches. Sabatier (1854–1941), Berthelot's assistant at the Collège de France and later professor of chemistry at the University of Tou-

<sup>1</sup> Marcelin Berthelot, "Methode universelle pour réduire et saturer d'hydrogène les composés organiques," Bulletin de la Société Chimique de France, 1869, 11:278–286. louse, laid the foundation for the catalytic hydrogenation of organic compounds both in the laboratory and in industry. For fifteen years, beginning in June 1897, Sabatier and his pupils Jean Baptiste Senderens (1856–1936), Alphonse Mailhe, and Marcel Murat demonstrated the ability of finely divided metals, such as nickel, platinum, copper, cobalt, and iron, to act as catalysts in the hydrogenation of unsaturated organic compounds. Working with glass reaction tubes at  $150^{\circ}$ –200°C, they carried out numerous hydrogenations, among them ethylene to ethane, benzene to cyclohexane, phenol to cyclohexanol, and olein to stearin. By the end of 1900 Sabatier had established catalytic hydrogenation as a major new chemical process, and in 1912 he received the Nobel Prize in chemistry for his research with metallic catalysts.<sup>2</sup>

High-pressure hydrogenation began less than a decade after Sabatier initiated his catalytic studies. Working at the Mikhail Artillery Academy in St. Petersburg (Leningrad) from 1903 to 1914, Vladimir Ipatiev (1867–1952) hydrogenated aldehydes, ketones, benzene, and phenol at high pressure. He reduced such compounds as isobutyric aldehyde to the alcohol, acetone to isopropyl alcohol, and naphthalene to tetrahydro- and decahydronaphthalene. Ipatiev used nickel or nickel oxides as catalysts, temperatures of 200–250°C, and pressures of 100–120 atmospheres. Reaction times ran from six hours to three days. His hydrogenating chamber, or autoclave, was a soft malleable steel tube open at one end, with an inside diameter of 2.5 centimeters and a capacity of 25–27 cubic centimeters. Enclosing the other end was a steel cover fitted with a heat-treated red copper gasket and clamped to the tube with three retaining bolts. Two short tubes extended from the cover. One of them led to a pressure gauge, the other allowed gases to enter or exit. The autoclave was heated electrically with nickel resistance wire.<sup>3</sup>

Ipatiev's autoclave, later called the Ipatiev bomb, was a major breakthrough in high-pressure synthesis, for it withstood pressures of 400 atmospheres at 600°C and 1300 atmospheres at low temperatures. Prior to its construction, reaction pressures had never exceeded 20–25 atmospheres. Now chemists were able to use high pressures to investigate reactions that took place very slowly or not at all at atmospheric pressure. This gave further impetus to the search for new and better catalysts.

In 1908, five years after Ipatiev's pioneering high-pressure studies, Walther Nernst (1864–1941) successfully synthesized ammonia by hydrogenating nitrogen gas at high pressure. Working with Fritz Jost (1885–) at the University of Berlin,

<sup>2</sup> Paul Sabatier and J. B. Senderens, "Hydrogénations directes réalisées en presence du nickel réduit: Préparation de l'hexahydrobenzène," *Comptes rendus . . . de l'Academie des Sciences*, 1901, 132:210–212. Sabatier's book *La catalyse en chimie organique* (1913), trans. E. Emmett Reid, *Catalysis in Organic Chemistry* (New York: Van Nostrand, 1922), pp. 125–126, lists numerous references to his publications. See also Paul Sabatier, "The Method of Direct Hydrogenation by Catalysis," Nobel Lecture, 11 Dec. 1912, published in *Nobel Lectures: Chemistry 1901–1921* (New York: Elsevier, 1966), pp. 221–231.

<sup>3</sup> Vladimir Ipatiev, "Catalytic Reductions at High Pressures and Temperatures" (in Russian), Russkoe Fiziko-Kimischeskoe Obshchestvo, 1900–1902, 33:143–154, 496–506, 532–545, 632–643; 1902, 34:182–195, 315–323, 351–356; 1904, 36:786–835; 1906–1907, 38:63–97, 1108–1183; 1907, 39:681–702. German translations of some of Ipatiev's articles appeared in Berichte de deutschen Chemischen Gesellschaft, 1904, 37:2961–3005; 1907, 40:1827–1830; 1908, 41:991–1007; 1909, 42:2089–2102; 1910, 43:3383–3393, 3546–3553. See also Vladimir Ipatiev, Catalytic Reactions at High Pressures and Temperatures (New York: Macmillan, 1936), pp. 31–33, 379–381; and Ipatiev, The Life of a Chemist (Stanford Univ. Press, 1946), pp. 122–125.

Nernst reacted the two gases over a platinum catalyst at 50-70 atmospheres pressure and 685°C, obtaining about a 1 percent (actually 0.896 percent) yield.<sup>4</sup> Nernst was originally investigating the thermodynamic equilibrium of oxides of nitrogen; several factors had led him (as well as many other scientists) to investigate the synthesis of ammonia. In 1898 William Crookes (1832-1919) had warned the British Association for the Advancement of Science that the world faced a serious food shortage unless scientists found a way to fix the atmosphere's nitrogen for fertilizer production. His warning coincided with relevant advances in applied electrical and mechanical engineering and with the advent of the new school of physical chemists, who had begun to investigate gas reactions. Nernst was not the first to synthesize ammonia. In 1902 Adolf Frank (1834-1916) and Nikodem Caro (1871-1935) at the Technische Hochschule in Charlottenburg developed the cyanamide process for ammonia production. In 1903 Kristian Birkeland (1867-1917) at the University of Christiania (Oslo) and Samuel Eyde (1866-1940), the general director of Norsk Hydro in Christiania, invented the Birkeland-Eyde electric arc process. Most significantly, Fritz Haber (1868–1934) in Karlsruhe was working, like Nernst, on a direct synthesis of ammonia from its elements, and in 1904, two years before Nernst, he actually succeeded. But Haber, working with George van Oordt, carried out the reaction at atmospheric pressure (P = 1 atm, T = 1020°C, iron catalyst) and obtained only a 0.012 percent yield.<sup>5</sup>

Although Nernst's high-pressure synthesis was more successful, it was Haber who continued the research that eventually led to commercial production. By 1908 Nernst had all but abandoned ammonia synthesis; the heat theorem had become his major scientific interest. In 1908 Haber and le Rossignol synthesized ammonia in a quartz tube at 30 atmospheres pressure and 980°C, using a platinum foil catalyst. Their 6 percent volume yield showed clearly the advantage of higher pressure on the equilibrium constant. By 1909 Haber and le Rossignol had obtained an 8 percent volume yield of ammonia, 80 grams per hour, and they patented the process.<sup>6</sup> By 1913, working with steel autoclaves similar in

<sup>4</sup> Walther Nernst, "Über die Berechnung chemischer Gleichgewichte aus thermischen Messungen," Zeitschrift für Elektrochemie, 1906, 12:738–743; Walther Nernst and Fritz Jost, "Über das Ammoniakgleichgewicht," Z. Elektrochem., 1907, 13:521–524; Fritz Jost, "Über das Ammoniakgleichgewicht," Zeitschrift für anorganische Chemie, 1908, 57:414–430. See also Erwin Hiebert, "Walther Nernst," Dictionary of Scientific Biography, 14 vols. (New York: Scribners, 1970–1980), Vol. XV, pp. 432–453. Alfred von Nagel, Stickstoff (Schriftenreihe des Firmenarchivs des BASF, 3) (Ludwigshafen: BASF, 1969) gives a good discussion of Nernst's work on the ammonia synthesis. <sup>5</sup> Kristian Birkeland, French patent 335,692, 18 Sept. 1903; U.S. patent 772,862, 18 Oct. 1904;

<sup>5</sup> Kristian Birkeland, French patent 335,692, 18 Sept. 1903; U.S. patent 772,862, 18 Oct. 1904; Samuel Eyde, "Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway," Industrial and Engineering Chemistry, 1912, 4:771–774, and Chemical and Metallurgical Engineering, 1912, 10:617–619 (the Birkeland-Eyde process required 65,000 kilowatt-hours per ton of nitrogen fixed); Adolph Frank, "Über die direkte Verwertung des Stickstoffs der Atmosphäre zur Gewinnung von Düngmitteln und anderen chemischen Produktion," Zeitschrift für angewandte Chemie, 1906, 19:1835–840; Nikodem Caro, "Über einheimische Stickstoffquellen," Z. angew. Chem., 1906, 19:1569–1581; 1909, 22:1178–1182; Caro, "Industrien des Kalkstickstoffs und verwandter Verfahren," Z. angew. Chem., 1909, 22:1178–1182; Fritz Haber, Thermodynamik technischer Gasreaktionen (Munich: Oldenbourg, 1905), p. 187; Fritz Haber and G. van Oordt, "Über Bildung von Ammoniak aus den Elementen," Z. anorg. Chem., 1905, 43:111–115; 1905, 44:341–378; 1905, 47:42–44.

<sup>6</sup> Fritz Haber and Robert le Rossignol, "Über das Ammoniakgleichgewichte," *Ber. deut. Chem. Gesell.*, 1907, 40:2144–2154; Haber and le Rossignol, "Bestimmung des Ammoniakgleichgewichtes unter Druck," *Z. Elecktrochem.*, 1908, 14:181–196, 513–514; Haber and le Rossignol, German

design to Ipatiev's at 200 atmospheres pressure, 500°C, and with a variety of metallic catalysts (iron, tungsten, osmium), Haber and le Rossignol had more than doubled the yield.<sup>7</sup>

### **II. THE FIRST COMMERCIAL APPLICATION OF HIGH-PRESSURE HYDROGENATION**

Haber had been working as a consultant for BASF, and during 1909–1913 BASF's chairman of the board, the chemist Carl Bosch (1874–1940) successfully transformed Haber's gas-phase ammonia synthesis from a laboratory process to a commercial industry. Bosch's success came after three crucial problems were solved: finding effective, inexpensive catalysts; constructing large, hydrogenresistant converters for the hydrogenation reaction; and producing the two reacting gases, hydrogen and nitrogen, economically. Another BASF chemist, Alwin Mittasch (1869–1953) solved the catalyst problem. For three years, 1909– 1912, Mittasch and his research assistants tested 2500 substances in about 6500 experiments. The experiments included testing metals such as iron, cobalt, and nickel combined with the oxides of aluminum, magnesium, and potassium, or with other metals such as molybdenum, tungsten, and calcium. Iron activated with aluminum oxide or other metallic oxides was the best catalyst.<sup>8</sup>

In the spring of 1910 Bosch began work on the converters for the reacting gases, nitrogen and hydrogen, in a small experimental plant in Ludwigshafen. Haber's original converter was small, only 0.75 meters high and 2 to 3 centimeters wide, and it was susceptible to corrosion from hydrogen gas. Bosch and his engineering group successfully increased the converter's height to 2 meters, then to 4 meters, and in 1911 they solved the problem of constructing a converter that resisted hydrogen attack by the introduction of double-tubing. The new converter consisted of an inner tube of low carbon steel or wrought iron enclosed in a tightly fitting outer tube of ordinary steel that contained a large number of small holes. At high pressures some of the hydrogen gas diffused through the inner tube, but it did little damage because there was little carbon in the steel with which it could react. When it came in contact with the outer tube, its pressure had fallen to atmospheric pressure, and at this low value hydrogen could not react with and thus embrittle the carbon steel. It passed harmlessly through the outer tube's many small holes. When BASF's first industrialscale synthetic ammonia plant at nearby Oppau opened on 9 September 1913, less than a year before the outbreak of World War I, it had a hydrogen-resistant

patent 235,421, 13 Oct. 1908; U.S. patent 971,501, 27 Sept. 1910. Haber also received German patents 229,126, 29 Nov. 1910 (filed 15 June 1909), and 238,450, 28 Sept. 1911 (filed 14 Sept. 1909). See also Haber, "Über die Darstellung des Ammoniaks aus Stickstoff und Wasserstoff," Z. Elektrochem., 1910, 16:244–246.

<sup>&</sup>lt;sup>7</sup> Fritz Haber, "The Synthesis of Ammonia from its Elements," Nobel lecture, 2 June 1920, in *Nobel Lectures: Chemistry 1901–1921* (cit. n. 2), pp. 327–340; Fritz Haber and Robert le Rossignol, "Über die technische Darstellung von Ammoniak aus den Elementen," Z. Elektrochem., 1913, 19:53–72, on p. 55.

<sup>&</sup>lt;sup>8</sup> BASF, German patents 249,447, 23 July 1912; 254,344, 2 Dec. 1912; 254,437, 3 Dec. 1912; Alwin Mittasch, Geschichte der Ammoniaksynthese (Weinheim: Verlag Chemie, 1951), pp. 93–116; A. Mittasch and W. Frankenburger, "Zur geschichtlichen Entwicklung und zur Theorie der Ammoniakkatlyse," Z. Elektrochem., 1929, 35:920–927; L. F. Haber, The Chemical Industry 1900–1930 (Oxford: Clarendon Press, 1971), pp. 93–95; Eduard Farber, "From Chemistry to Philosophy: The Way of Alwin Mittasch," Chymia, 1966, 11:157–178.

converter 8 meters high and 45 centimeters wide, weighing 8<sup>1</sup>/<sub>2</sub> metric tons.<sup>9</sup>

An air-liquefaction unit that Carl von Linde developed in 1895 supplied the nitrogen gas required for the synthesis. To produce hydrogen gas BASF at first used the Linde-Frank-Caro process (see Section V below), though by 1916 Bosch's group had perfected a new method for hydrogen's production, the catalytic decomposition of water gas, or Bosch-Wild process. In this process steam reacted with water gas (a mixture of hydrogen and carbon monoxide gases) in the presence of an iron oxide or other metallic oxide catalyst to form carbon dioxide and hydrogen.

$$H_2 + CO + H_2O \rightarrow CO_2 + 2H_2$$

Washing the products with water in scrubbing towers removed carbon dioxide; compressing the gaseous mixture at 200 atmospheres and then dissolving it in solutions first of tetrammine copper (II) formate and then of sodium hydroxide removed carbon monoxide, leaving 97–98 percent pure hydrogen gas.<sup>10</sup>

The following year, in April 1917, BASF completed construction of its second synthetic ammonia plant at Leuna, near Merseburg. At this time Bosch introduced an improved process for producing the reacting gases. Instead of first separating hydrogen from the water gas mixture and then having it react with nitrogen, Bosch prepared a cheaper form of water gas known as producer gas. This gas consisted essentially of hydrogen, carbon monoxide, carbon dioxide, and nitrogen and resulted from heating incandescent coke with a mixture of air and steam. By adjusting the temperature and volume of air added, employing a catalyst such as iron oxide, and removing the carbon dioxide present, Bosch obtained a nitrogen-hydrogen mixture in the correct proportion for synthesizing ammonia.<sup>11</sup> As a result of BASF's scientific and technological breakthroughs, Oppau and Leuna had a combined capacity of 620 metric tons of ammonia per day before World War I ended in November 1918.<sup>12</sup> Germany maintained her leadership in high-pressure technology throughout the 1920s, largely because of Bosch's efforts.

The successful high-pressure synthesis of ammonia, achieved on a commercial scale by 1913, marked the start of industrial high-pressure reactions. Soon after, in 1912–1913, Friedrich Bergius began to apply high-pressure technology to a

<sup>9</sup> BASF, German patent 254,571, 6 Dec. 1912; Carl Bosch, U.S. patent 1,188,530, 27 June 1916 (filed 5 Feb. 1912); Haber, *The Chemical Industry*, p. 94; Farber, "From Chemistry to Philosophy," p. 165; Walter Witschakowski, *Hochdrucktechnik* (Schriftenreihe des Firmenarchivs des BASF, 12) (Ludwigshafen: BASF, 1974), pp. 10–15.

<sup>10</sup> Bosch and Wild, U.S. patents 1,113,096 and 1,113,097, 6 Oct. 1914; Badische Co., French patent 459,918, 2 July 1913; German patent 297,258, 11 Sept. 1914; J. R. Partington and L. H. Parker, *The Nitrogen Industry* (London: Constable, 1922), pp. 160–167; T. P. Hilditch, *Catalytic Processes in Applied Chemistry* (New York: Van Nostrand, 1931), pp. 77–83. Another name for the Bosch-Wild Process is the BAMAG Process (Berlin Anhaltischer Maschinenbau Aktien-Gesellschaft), after the firm that built the equipment used in the process.

<sup>11</sup> Bosch, "The Procedure of the Synthesis of Ammonia," *Chemical Age*, 1921, 29:451–456; Bosch, "Wo ein Wille ist, ist auch ein Weg," *The Industrial Chemist*, 1934, 10:90–94; Nagel, *Stick-stoff* (cit. n. 4), pp. 41–44; Hilditch, *Catalytic Processes in Applied Chemistry*, p. 77; Fritz ter Meer, *Die I. G. Farben* (Düsseldorf: Econ-Verlag GMBH, 1953), p. 26; Gerhart Wolf, *BASF: De-velopment of a World-Wide Enterprise* (Schriftenreihe des Firmenarchivs BASF, 6) (Ludwigshafen: BASF, 1970), pp. 32–37; 43.

<sup>12</sup> Witschakowski, *Hochdrucktechnik*, pp. 10–12; Partington and Parker, *The Nitrogen Industry*, p. 154.

new hydrogen addition reaction, the hydrogenation of coal to produce synthetic petroleum.

## III. FRIEDRICH BERGIUS: BACKGROUND TO HIGH-PRESSURE COAL HYDROGENATION

Friedrich Bergius was born in Goldschmieden, near Breslau, in 1884. His father was the owner of a small alumina-producing plant, so that Bergius was exposed to the chemical industry at an early age. After Bergius completed his studies at the *Realgymnasium*, his father sent him to Mülheim in the Ruhr district for six months to observe the operation of a large metallurgical plant. In 1903, following his stay in Mülheim, Bergius decided to enter the University of Breslau, where he studied with Richard Abegg (1869–1910). Later he went to Leipzig to study under Arthur Hantzsch (1857–1935); there he obtained the Ph.D. in chemistry in 1907 with a dissertation on the solvent properties of absolute sulfuric acid. Bergius then spent a year with Walther Nernst in Berlin and six months with Fritz Haber in Karlsruhe.<sup>13</sup>

With Nernst and Haber, Bergius worked on the synthesis of ammonia and its equilibrium at high pressures. At this time, 1909, chemists were just beginning to recognize the influence of pressure on reaction rates, in particular how pressure influenced a reaction's equilibrium point. With Nernst's heat theorem and several experimental determinations of the equilibrium point at different temperatures and pressures, they could calculate an equilibrium mixture's composition over a broad temperature and pressure range.

Describing his eighteen-month association with Nernst and Haber, at that time world leaders in high-pressure theory and application, Bergius said that he tried his hand "in these laboratories at syntheses by high-pressure techniques, with the then imperfect apparatuses, and with little success." Yet the time he spent with Nernst and Haber provided the impetus for his later investigations. Indeed, by 1909 Bergius had already decided to work "in this new field which appeared promising . . . on a wider scale." That year he left Karlsruhe to take a teaching position in Max Bodenstein's Institute of Physical Chemistry at the Technische Hochschule in Hanover, where he wrote his *Habilitationsschrift*, published as a monograph in 1913. The theme of Bergius's foreword was faith in new methods and instruments: here and elsewhere Bergius argued that introducing new experimental methods and new instruments to the laboratory—in this case, high-pressure apparatus—often led to progress in chemistry.<sup>14</sup>

Bergius's high-pressure research program at Bodenstein's Institute began with a detailed study of the equilibrium of calcium peroxide. He investigated the compound's dissociation pressure at high temperatures, 300–400°C, calculated its

<sup>13</sup> "The Career of Dr. Bergius," Journal of the Institute of Fuel, 1934, 8:73-79; Edgar von Schmidt-Pauli, Friedrich Bergius (Berlin: Mittler & Sohn, 1943), pp. 14-30; Friedrich Bergius, "Chemical Reactions under High Pressure," Nobel Lecture, 21 May 1932, in Nobel Lectures: Chemistry 1922-1941 (New York: Elsevier, 1966), pp. 244-276; oral interview with Johannes Bergius, Bonn, Germany, 4 July 1981.

<sup>14</sup> Friedrich Bergius, Die Anwendung hoher Drucke bei chemische Vorgangen und eine Nachbildung des Entstehungsprozesses der Steinkohle (Halle: Wilhelm Knapp, 1913), p. 1; cf. Friedrich Bergius, "Production of Hydrogen from Water and Coal from Cellulose at High Temperatures and Pressures," Journal of the Society of Chemistry Industry, 1913, 32:462–467, on p. 462. Bergius was a Privatdozent teaching physical and industrial chemistry; see Bergius, "Chemical Reactions," p. 244; Schmidt-Pauli, Friedrich Bergius, p. 31. heat of formation using Nernst's heat theorem, and compared this value with his experimentally determined value. Bergius made the study at high temperatures because the reaction's velocity increased enough to make accurate measurement possible. At the Institute Bergius also began to work on improved designs for high-pressure autoclaves, which he had first encountered in Haber's Karlsruhe laboratory, constructing apparatus for pressures up to 300 atmospheres.<sup>15</sup>

Because the Institute's facilities did not permit expansion of his research program, however, Bergius left in 1910 and established a well-equipped private laboratory, also in Hanover, that gradually grew to include several workshops and plants. With the assistance of Kurt Meyer, Richard Tillman, John Billwiller, Paul Kalnin, Stephan Löffler, Arnold Debo, and Hugo Specht, Bergius continued his program of theoretical and applied high-pressure research. Among the initial investigations were those of liquid behavior at 200 atmospheres and at temperatures well above the liquid's normal boiling point (at which temperatures the liquids normally reacted as gases). They included the reaction of superheated water with coal to give hydrogen gas and with iron to produce a purer hydrogen gas and the saponification of organic chlorides such as chlorobenzene and ethylene chloride with sodium hydroxide solution to give products like phenol or ethylene glycol.<sup>16</sup> Bergius and his assistants also examined the high-pressure hydrogenation of unsaturated fats and oils.<sup>17</sup>

Three aspects of the early research at the Hanover laboratory contributed to the invention of high-pressure coal hydrogenation in the years 1912–1913. First, Bergius gained extensive experience with high-pressure apparatus. He took the autoclave design that Haber and le Rossignol first used in their ammonia synthesis, and by 1910 he was working with pressures of 300 atmospheres and temperatures as high as 450°C. Haber and le Rossignol had constructed their airtight autoclaves by designing the autoclave cover to fit within the autoclave's cone-shaped chamber. The two parts were clamped along their line of contact and forced together by a screw. Heating produced no gas leakage because chamber and cover, constructed of the same metal, usually steel, expanded equally. The autoclave design was so reliable that Bergius remarked that he could work with high-pressure apparatus almost as conveniently as with ordinary test tubes and flasks.<sup>18</sup>

The second factor was the incentive provided by Bergius's colleague Ludwig Landsberg, director of the Aktiengesellschaft für Petroleumindustrie (AGP) in Nürnberg. In 1910 Landsberg encouraged Bergius to study the cracking of heavy petroleum oils and oil residues into gasoline and provided financial support from AGP for two years, from 1912 to 1914.<sup>19</sup> Landsberg had noted economic forecasts that the dramatically expanding automobile industry would ensure a con-

<sup>16</sup> Friedrich Bergius, German patent 254,593, 9 Dec. 1912; French patent 447,000, 9 Aug. 1912; Friedrich Bergius, "Untersuchungen über chemische Vorgänge bei hohen Drucken," Zeit. angew. Chem., 1912, 25:1171–1173.

<sup>17</sup> Bergius, "Chemical Reactions," pp. 245, 253-254.

<sup>18</sup> Bergius, *Anwendung*, pp. 4–8, and "Unterschungen über chemische Vorgänge," pp. 1171–1173; see Haber and le Rossignol, "Bestimmung des Ammoniakgleichgewichtes," diagrams follow p. 184; and Haber and le Rossignol, "Über die technische Darstellung von Ammoniak," on pp. 58–59, 61.

<sup>&</sup>lt;sup>15</sup> Bergius, Anwendung, pp. 5–8, 28–29. For descriptions of Haber's high-pressure autoclave, see Haber and le Rossignol, "Bestimmung des Ammoniakgleichgewichtes," pp. 181–196 (diagrams follow p. 184); and Haber and le Rossignol, "Über die technische Darstellung von Ammoniak aus den Elementen," Z. Elektrochem., 1913, 19:53–108, on pp. 58–59, 61.

siderable increase in gasoline consumption worldwide. In 1909 Henry Ford had begun mass production of automobiles in the United States, and as a result the number of cars rose from slightly more than a hundred thousand in 1905 to about nine million in 1920, only ten years after Landsberg's prediction.<sup>20</sup> Petroleum production rose to meet the increased demand for gasoline. It took forty-one years for the United States, then the world's leading petroleum producer, to extract its first billion barrels of petroleum after its first substantial strike, but only eight years for its next billion; by the seventh billion, extraction time was only one year and seven months. Crude petroleum production increased from slightly less than two hundred million barrels in 1908 to more than a billion barrels in 1929.<sup>21</sup>

Once Bergius began to study petroleum cracking, he was soon convinced that the extreme inefficiency and high cost of producing gasoline resulted from large losses of hydrogen as methane gas and unsaturated hydrocarbons, and from coke deposits forming on the reaction container's walls. By May 1913 he discovered that he could eliminate these problems, which invariably gave an unsaturated gasoline of poor quality, by adding highly compressed hydrogen gas to replace the hydrogen removed in cracking. In effect, Bergius cracked the molecular structure of high-boiling heavy petroleum oils and added highly compressed hydrogen gas to form lower-boiling–saturated-gasoline hydrocarbons and other light oils. The reaction also eliminated formation of the hydrogendeficient products that caused coking. Because the autoclave's steel walls undoubtedly catalyzed the reaction, Bergius's process was essentially the same as the catalytic hydrocracking process introduced to the petroleum industry in the 1930s and 1940s.<sup>22</sup>

The third development that led to Bergius's invention of high-pressure coal hydrogenation occurred during his experiments on the water gas reaction, a well-known process used to produce hydrogen gas  $C + H_2O \rightarrow CO + H_2$ . Bergius believed that at high pressure (200 atm) he could run the reaction at a much lower temperature (300-600°C rather than 900°C). This would shift the equilibrium point to favor the production of carbon dioxide and hydrogen, eliminating entirely the formation of carbon monoxide and thus the problem of separating it from hydrogen. In an experiment conducted in 1911, Bergius substituted peat, a cellulose-containing plant substance, as the carbon source. When heated under water at 340°C and 100 atmospheres the reaction liberated large amounts of carbon dioxide and left in the autoclave a dark residue that resembled a soft natural coal.<sup>23</sup>

<sup>19</sup> Friedrich Bergius, "An Historical Account of Hydrogenation," *Proceedings of the World Petroleum Congress*, Vol. II (London: Office of the Congress, 1934), 282–289, on p. 282.

<sup>21</sup> Arno C. Fieldner and R. L. Brown, "Future Trends in Automotive Fuels," *Industrial and Engineering Chemistry*, 1926, 18:1009–1014, on p. 1009; R. Wigginton, "Notes on Developments in Fuel Technology," *Fuel*, 1925, 4:95; Howard W. Sheldon, "Twenty-Five Years of Progress in Petroleum Refining," in *Twenty-Five Years of Chemical Engineering Progress*, ed. Sidney K. Kirkpatrick (New York: American Institute of Chemical Engineers, 1933), pp. 52–76.

<sup>22</sup> Bergius, German patent 301,231, 9 Aug. 1913; see W. H. Hoffert and G. Claxton, *Motor Benzole: Its Production and Use* (2nd ed., London: The National Benzole Association, 1938), pp. 94–96.

<sup>23</sup> Bergius, "Production of Hydrogen from Water and Coal from Cellulose," pp. 463-467; Bergius,

<sup>&</sup>lt;sup>20</sup> John Cadman, "British Fuel Problem: Oil," *Chemistry and Industry*, 1931, 50:908–912, on p. 909. The rise was more dramatic in the next ten years, increasing to 35 million automobiles at the end of 1930.

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In the decade before Bergius's high-pressure experiments, investigators had often run the water gas reaction at high temperatures in trying to convert plant substances such as cellulose and wood into coal. They had not succeeded because the reaction always released a large quantity of heat and left hydrogendeficient coke instead of coal.<sup>24</sup> By working at high pressure, Bergius at last solved the overheating problem. Water remained in the liquid state instead of vaporizing, and not only did it serve as a reactant, but, because of its high heat capacity, it absorbed and distributed the heat produced, thus preventing overheating. Analysis of the artificial coal showed that it had the formula  $C_{21}H_{16}O_2$  and contained 74.3–85.2 percent carbon and 4.5–5.2 percent hydrogen, which compared well with natural bituminous coal of 75–90 percent carbon and 4.5–5.0 percent hydrogen. The equation below represents Bergius's "coalification" or *Inkohlung* (end coal) reaction.

$$4C_6H_{10}O_5 \rightarrow C_{21}H_{16}O_2 + 3CO_2 + 12H_2O \quad \Delta H = -70 \text{ kcal/mole } C_6H_{10}O_5$$

Bergius's investigation also showed that the percentage of carbon in his artificial coal increased with temperature and time of heating but reached a maximum value of about 84 percent; even after prolonged heating (about 64 hours) it did not increase. A coal of 84 percent carbon thus represented the reaction's stable end product. Indeed, Bergius argued that the amount of carbon in natural coals formed from decaying vegetable matter reached 84 percent and rose above that value only when new external factors entered, namely extremely high temperatures and pressures.<sup>25</sup> Artificial or natural coals containing 84 percent carbon, according to his estimate, were about eight million years old, a figure in good agreement with the geologists' calculations.<sup>26</sup> Largely as a result of the success of his coalification reaction, which converted plant substances into artificial coal, Bergius began further study of the chemical constitution of coal.

## IV. EARLY STUDIES ON THE COMPOSITION OF COAL

In 1911 chemists knew very little about the composition and molecular structure of coal. Many believed that coal was merely carbon mixed with hydrogen-

<sup>25</sup> See references in note 23 above.

<sup>&</sup>quot;Die Anwendung von hohen Drucken bei chemischen und chemisch-technischen Vorgängen," Z. Elektrochem., 1912, 18:660–662; and Bergius, Anwendung, pp. 41–58. Bergius reported his later results on the cellulose to coal process in "Contributions to Knowledge of the Transformation of Cellulose and Lignin into Coal," Proceedings of the Second International Conference on Bituminous Coal, 1928, Vol. II (Pittsburgh: Carnegie Institute of Technology, 1929), pp. 48–53.

<sup>&</sup>lt;sup>24</sup> Georg Paul Alexander Petzholdt, *Beitrag zur Kenntnis der Steinkohlenbildung nebst Kritik des Werkes von P. F. Reinsch* (Leipzig: Weigel, 1882); S. Stein, "Beitrag zur Kenntnis der Bildung von fossilen Kohlen," *Chemisches Zentralblatt*, 1901, 2:950–951; Peter Klason, Gustav von Heidenstam, and Evert Norlin, "Untersuchungen zur Holzverkohlung, I: Die trockene Destillation der Cellulose," *Z. angew. Chem.*, 1909, 22:1205–1214, and "II: Die trockene Destillation des Holzes von Keifer, Fichte, Birke and Buche," *ibid.*, 1910, 23:1252–1257.

<sup>&</sup>lt;sup>26</sup> See, e.g., Henry Potonić, *Die Enstehung der Steinkohle* (Berlin: Gebrüder Borntraeger, 1910). In this study Bergius found that the time required to reach the same point in the reaction doubled when he reduced the temperature by 10 degrees. This was in agreement with the approximate rule of chemical kinetics. Later he changed the reaction equation to read  $2C_6H_{10}O_5 \rightarrow 2CO_2 + 5H_2O + C_{10}H_{10}O$ : Bergius, "Neue Methode zur Verarbeitung von Mineralöl und Kohle," *Z. angew. Chem.*, 1921, *34*:341–347.

containing impurities.<sup>27</sup> The two methods of coal analysis used at that time, destructive distillation and solvent extraction (reacting the coal with different solvents), showed only that a typical ash-free dry coal contained about 85 percent carbon, with hydrogen, oxygen, nitrogen, and sulfur the other major constituents. Inorganic compounds such as aluminum and silicon oxides constituted the ash. Distillation always produced gases, water, and tar. Of the gases liberated, hydrogen was the chief component, though ammonia, carbon monoxide and dioxide, benzene, and other hydrocarbon vapors were present. Redistilling the tar gave a high-boiling pitch, which consisted almost entirely of polynuclear aromatic compounds, and a variety of lower-boiling compounds that included ethylene-like hydrocarbons, naphthenes ( $C_nH_{2n}$ ), phenols, and aromatic compounds (homologues of naphthalene), and a small amount of a solid paraffin whose molecular weight indicated the formula  $C_{26}H_{54}$  or  $C_{27}H_{56}$ .<sup>28</sup>

Richard V. Wheeler and his associates at the Imperial College of Science and Technology in London carried out some of the earliest and most extensive investigations on coal's structure, beginning around 1910. They found that coal contained two types of compounds that differed in their ease of decomposition: a more stable type that decomposed with greater difficulty to give paraffin hydrocarbons and hydrogen gas, and an unstable type that gave paraffin hydrocarbons and no hydrogen gas on decomposition. The "paraffin-yielding" compounds were the degradation products of resinous substances originally present in the coal plants, while the "hydrogen-yielding" compounds resulted from the plant's cellulose degradation. Léo Vignon's studies on French coals in 1912 confirmed Wheeler's results but those of other investigators differed, sometimes significantly, from Wheeler's.<sup>29</sup>

Bergius's researches on artificial and natural coal in 1910–1913 led him to conclude that natural coals and lignite contain two kinds of chemical compounds; his findings therefore supported Wheeler's work. The first, the carbonaceous compounds, came from the decayed plant's cellulose and lignite; the second, the bituminous compounds, derived from the albuminous material, resins,

<sup>29</sup> Burgess and Wheeler, "The Volatile Constituents of Coal, Part II," pp. 649–667; Arthur Herbert Clark and Richard Vernon Wheeler, "The Volatile Constituents of Coal, Part III," J. Chem. Soc., 1913, 103:1704–1715; Léo Vignon, "Distillation fractionée de la houille," Compt. rend. Acad. Sci., 1912, 155:1514–1517; V. B. Lewes, The Carbonisation of Coal (London: Allan & Co., 1912), pp. 24, 215; and Amé Pictet and Maurice Bouvier, "Sur la distillation de la houille sous pression réduite," Compt. rend. Acad. Sci., 1913, 157:779–781. Progress on the structure of coal did not really occur until the 1920s. For discussion of later coal research see William A. Bone and Godrey W. Himus, Coal: Its Constitution and Uses (London: Longmans, Green & Co., 1936), Ch. 9–11, and numerous papers in Fuel and J. Inst. Fuel, 1922–1932.

 <sup>&</sup>lt;sup>27</sup> Friedrich Bergius, "The Transformation of Coal into Oil by Means of Hydrogenation," *Proceedings of the International Conference on Bituminous Coal, 1926* (Pittsburgh: Carnegie Institute of Technology, 1927), pp. 102–131, on pp. 105–106.
 <sup>28</sup> Maurice John Burgess and Richard Vernon Wheeler, "The Volatile Constituents of Coal,"

<sup>&</sup>lt;sup>28</sup> Maurice John Burgess and Richard Vernon Wheeler, "The Volatile Constituents of Coal," Journal of the Chemical Society, 1910, 97:1917-1935; Horace C. Porter and F. K. Ovitz, "Nature of Volatile Matter of Coal as Evolved Under Different Conditions," Journal of Gas Lighting, 1908, 104:343-348; Horace C. Porter and G. B. Taylor, "The Mode of Decomposition of Coal by Heat," Proceedings of the American Gas Institute, Part I, 1914, 9:234-288; and David Trevor Jones and Richard Vernon Wheeler, "The Composition of Coal," J. Chem. Soc., 1914, 105:140-151. Phillips P. Bedson invented the pyridine extraction method in 1899; see Bedson, "Notes on the Proximate Constituents of Coal," J. Soc. Chem. Ind., 1908, 27:147-150. Wheeler and associates added the chloroform extraction; see Maurice John Burgess and Richard Vernon Wheeler, "The Volatile Constituents of Coal, Part II," J. Chem. Soc., 1911, 99:649-667.

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waxes, fats, and other substances in the plants. Carbon, hydrogen, and oxygen were present in the carbonaceous compounds; the bituminous compounds contained the same three elements but more hydrogen and less oxygen. Bergius suggested that structurally coal resembled a group of unsaturated hydrocarbons called terpenes with molecular formula  $C_{10}H_{16}$  or some higher multiple; these hydrocarbons were either open-chained or cyclic with one or more benzenoid groups. Coal, therefore, could add hydrogen and approach in composition the heavy petroleum oils, hydrocarbons with about twenty-three carbon atoms and a molecular weight of 300. It could then separate into medium and light hydrocarbons of fifteen or fewer carbon atoms and molecular weights of less than 200.

Bergius reported his conclusions to the International Congress of Applied Chemistry in New York in 1912.<sup>30</sup> But the benzenoid structure of coal was not confirmed until 1925, as a result of coal-extraction and oxidation studies that William Bone and his research team conducted at the Imperial College in London. The benzene tri-, tetra-, and other higher carboxylic acids they obtained as oxidation products of lignite, bituminous, and anthracite coals showed that these substances had a preponderance of aromatic structures with three, four, and five fused benzene rings, as well as some structures with a single benzene ring. The simplest benzene-like structures contained eight or ten carbon atoms, while the fused-ring structures consisted of fifteen or twenty carbon atoms.<sup>31</sup>

## V. A NEW METHOD FOR PRODUCING HYDROGEN GAS

From the very beginning of his hydrogenation experiments, Bergius, like Haber, Bosch, and others working on hydrogen-addition reactions, recognized the need for an inexpensive and reliable source of pure hydrogen gas. Because the hydrogenation of petroleum involved two independent steps, the destruction or cracking of heavy petroleum hydrocarbons and the addition of hydrogen atoms to the cracked fragments, the process required sufficient gas to ensure equal rates of cracking and hydrogen addition. In other words, the process had to provide a sufficient number of hydrogen atoms for addition to the cracked hydrocarbon molecules.

Hydrogen obtained from the electrolysis of water was of high purity and by far the best for hydrogenation, because it contained no catalyst poisons such as

he congress. For the results of Bergius's research, therefore, i have rended on ins 1920 and 1935 papers and his papers of 1912 and 1913 that deal with the artificial production of coal. <sup>31</sup> See William A. Bone et al., "Researches on the Chemistry of Coal: Part I," *Proceedings of the Royal Society*, Series A, 1919, 96:119–136; "Part II," 1922, 100:582–598; "Part III," 1924, 105:608– 625; "Part IV," 1926, 110:537–542; "Part V," 1928, 120:523–545; "Part VI," 1930, 127:480–510; "Part VII," 1934, 147:58–67; "Part VIII," 1935, 148:492–522. Bone and Himus, *Coal: Its Constitution and Uses*, pp. 191–192, have diagrams of the benzene-like structures found in coal.

<sup>&</sup>lt;sup>30</sup> Bergius mentioned in several publications that he reported the results of his research before the International Congress of Applied Chemistry, New York, Sept. 1912: see Bergius, "The Transformation of Coal into Oil," p. 106, and "An Historical Account of Hydrogenation," p. 284. But I have examined the 29 volumes published by the congress and found no paper by Bergius (see "Papers Presented," Vol. 29, pp. 19–71). He attended the congress and is listed under "Membership List, Germany," in Vol. 29, p. 378. A brief summary of his paper, entitled "Artificial Production of Coal: A Pretty Application of the Law of Reaction Velocity," appeared in *Chemical and Metallurgical Engineering*, 1912, 10:616; this issue contains abstracts of many of the papers presented at the Congress. For the results of Bergius's research, therefore, I have relied on his 1926 and 1933 papers and his papers of 1912 and 1913 that deal with the artificial production of coal.

sulfur compounds or carbon monoxide derivatives. Electrolytic hydrogen found considerable application where the cheap cost of electricity from hydropower made its production practicable, as in the large De-No-Fa hydrogenation factory in Fredrikstad, Norway, and in northern Italian and Swiss factories. But for most of Europe, including Germany, which lacked hydropower, electrolytic hydrogen was entirely uneconomical. An alternative hydrogen source was a process that Carl von Linde (1842–1935), Adolf Frank (1834–1916), and Nikodem Caro (1871–1935) had developed by 1911.<sup>32</sup> The Linde-Frank-Caro process separated the products of the water gas reaction, hydrogen and carbon monoxide, by liquefying the carbon monoxide; it yielded hydrogen gas of 97–99 percent purity.

While certainly cheaper than the electrolytic process, water gas production followed by liquefaction of the carbon monoxide had two very serious disadvantages, as Bergius was aware. The water gas reaction produced hydrogen only at a rather high temperature, 900°C, and the liquefaction required expensive equipment to cool and compress the carbon monoxide for separation. Nevertheless, Bergius believed that he could improve the process by eliminating carbon monoxide formation from the water gas reaction. He planned to run the reaction at a much lower temperature, 300–360°C, but at a high pressure of 200 atmospheres in a steel autoclave with a capacity of 80 liters. This modification decreased carbon monoxide formation slightly by oxidizing it to carbon dioxide, which was then removed through absorption in lime. Further, Bergius unexpectedly found that dissolved metallic salts, particularly thallium (III) chloride, catalyzed the reaction sufficiently to give pure hydrogen gas at a maximum daily production of 5 cubic meters. He patented his catalytic process in June 1911.<sup>33</sup>

A second unexpected result occurred in the course of the water gas investigation. Bergius discovered that water, which remained liquid under the reaction conditions employed, attacked the autoclave's walls, liberating hydrogen gas. According to Bergius, the liberation resulted because liquid water at high temperature and high pressure behaved as an acid and therefore reacted with active metals. Bergius in fact demonstrated that under these conditions finely divided iron, or iron filings, reacted extremely rapidly and liberated hydrogen gas quantitatively. Further, he could reduce the iron oxide formed in the reaction with coal or carbon monoxide at 1000°C and use it again for hydrogen production.

> $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$  $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

Because his process produced a much purer gas without any additional purification cost, eliminated compression cost since the liberated hydrogen gas was already compressed, and used cheaper and more compact apparatus, Bergius

<sup>33</sup> Bergius, German patent 259,030, 24 June 1911. For diagrams of Bergius's apparatus see Anwendung, pp. 6, 39; for discussion of his results, *ibid.*, pp. 33–41.

<sup>&</sup>lt;sup>32</sup> See Carl von Linde's description of the production of hydrogen by liquefaction in *Proceedings* of the Third International Congress of Refrigeration, 1913; and Linde, Lowest Temperatures in Industry (Munich: Gesellschaft für Lindes Eismaschinen, A.G., 1912); see also Linde, French patent 427,983, 31 Mar. 1911; U.S. patents 1,020,102 and 1,020,103, 12 Mar. 1912; 1,027,862 and 1,027,863, 28 May 1912.

believed that it represented a definite improvement over water gas liquefaction. The total energy cost was only 60 percent of the Linde-Frank-Caro process; the actual hydrogen cost, about two cents a cubic meter.<sup>34</sup>

By 1913 Bergius had enlarged his hydrogenating operation to the point where it had outgrown his private laboratory and required the facilities of a small factory in a Hanover suburb. There he set up six hydrogen generators, each with about 40 liters capacity, that produced hydrogen gas at the rate of 28,000 liters an hour. The gas passed directly into steel cylinders for storage at pressures as high as 200 atmospheres. In the Hanover plant as in his laboratory, Bergius located the hydrogen gas removal, separating them by a thick concrete wall. Bergius carried out much of the research on hydrogen gas production for the Chemische Fabrik A.G. (formerly Moritz Milch and Company) in Posen. By late 1913 he had several joint patents with the company.<sup>35</sup>

## VI. EARLY EXPERIMENTS ON COAL HYDROGENATION

During this same period Bergius began the high-pressure hydrogenation of naturally occurring heavy oils. Working with Paul Kalnin and Kurt Meyer and with financial support from the AGP, he hydrogenated various gas oils and crude heavy oils, some of which came from oilfields in Galicia and Rumania. In these early experiments Bergius, Kalnin, and Meyer used a stationary autoclave and did not stir the reactants. They achieved three important results: when cracked, heavy oils reacted with hydrogen gas; the resulting lighter oils were more saturated after hydrogenation, and no coke formation occurred during the reaction. The success of these experiments in May 1913 led Bergius to file his first patent on the high-pressure hydrogenation of heavy oils.<sup>36</sup>

Other significant improvements in the process followed quickly. To ensure a more thorough mixing of the heavy oil and hydrogen gas, Bergius, Kalnin, and Meyer introduced a rotating autoclave (Fig. 1). They also discovered that adding metals and metallic oxides, such as ferric oxide, enhanced hydrogenation; they patented this process in August 1913. Converting the process from a batch to a continuous flow operation marked another major advance: hydrogen gas entered the autoclave at one end and low-molecular-weight hydrogenation products such as gasoline passed continuously out the other. The conversion required a return to a stationary autoclave but one now equipped with a mechanical stirrer.<sup>37</sup>

By the beginning of 1914 the high-pressure hydrogenation of heavy oils had

<sup>34</sup> Bergius, "Production of Hydrogen from Water and Coal from Cellulose," p. 463; German patents 254,593, 9 Dec. 1912; 277,501, 30 Nov. 1913; U.S. patent 1,059,818, 22 Apr. 1913. Bergius, "Eine neue Methode zur technischen Herstellung reinen, hochkomprimierten Wasserstoffs: Die Zersetzung flüssigen Wassers durch Eisen," Z. angew. Chem., 1913, 26:517–518.

<sup>36</sup> Bergius, German patent 304,348, 17 Sept. 1919 (filed 6 May 1913); U.S. patent 1,344,671, 29 June 1920.

 $^{37}$  Bergius, German patent 301,231, 9 Aug. 1913; British patents 4,574, 21 Feb. 1914; 18,232, 1 Aug. 1914; French patent 470,551, 6 Apr. 1914; German patent 303,272, 25 Dec. 1914. See also Bergius, "An Historical Account of Hydrogenation," p. 282.

<sup>&</sup>lt;sup>35</sup> Bergius, "The Transformation of Coal into Oil," pp. 102–131; Bergius, "An Historical Account of Hydrogenation," pp. 282–289; Bergius, German patents 202,831, 23 July 1913; 286,691, 21 Nov. 1913; 277,501, 30 Nov. 1913.

progressed sufficiently to permit Bergius, Kalnin, and Meyer to carry out reactions in 40-liter autoclaves heated externally to 430°C and held at 120 atmospheres pressure. They avoided coke formation, a long-time problem of petroleum cracking, by adding and mixing sufficient hydrogen gas with the heavy oil. The hydrogen also removed any sulfur contained in the oil by reacting with it to form hydrogen sulfide gas, though adding ferric oxide to the autoclave worked equally well. The process gave about a 50 percent conversion of crude petroleum to a highly saturated gasoline.<sup>38</sup>

Bergius was simultaneously conducting experiments with Hugo Specht and John Billwiller to test whether they could hydrogenate the unsaturated artificial coal they had produced from peat (see the end of Section III, above). Bergius, Specht, and Billwiller also wanted to learn whether their coal, like the heavy



**Figure 1.** Rotary autoclave developed by Bergius and his associates in 1912. From Nobel Lectures: Chemistry 1922–1941 (New York: Elsevier, 1966), by permission of the Nobel Prize Committee.

petroleum oils, broke down when hydrogenated into medium- and low-molecular-weight hydrocarbons. The experiments, conducted in the summer of 1913, were a success. Reacting two- and three-gram samples with hydrogen gas at about 150 atmospheres pressure and temperatures of 400–430°C, the team converted 80 percent of the coal into gaseous, liquid, and solid products soluble in benzene. Encouraged by the successful hydrogenation of artificial coal, Bergius, Specht, and Billwiller proceeded to experiment with natural coal. They obtained practically the same results, showing for the first time that the hydrogenation of natural coal yielded solid, liquid, and gaseous products. In the autumn of 1913 Bergius filed the first patent on the high-pressure hydrogenation of coal.<sup>39</sup>

Bergius carried out the research on coal hydrogenation, like that on heavy oil hydrogenation, in steel autoclaves, rotating and stationary, though these autoclaves were of much larger capacity—400 liters. All experiments were batch operations at 400°C and a hydrogen pressure of 200 atmospheres. In a typical experiment Bergius mixed 150 kilograms of powdered coal with an equal weight of a heavy oil solvent, such as a commercial grade of benzene, to form a paste. He then added about 5 kilograms of hydrogen gas to the autoclave and after twelve hours stopped the reaction. Inspection of the products showed 85 percent of the coal had liquefied and dissolved in the benzene solvent and only 15 percent remained as a dark residue that contained the ash. Bergius also discovered as a result of these experiments that the solvent, by dissolving the products, shortened the reaction time and thus significantly increased the yield. Distillation separated the hydrogenated products, which consisted of phenol, phenollike derivatives, and petroleum hydrocarbons, from the solvent.<sup>40</sup>

<sup>&</sup>lt;sup>38</sup> Bergius, German patent 290,563, 30 Nov. 1913.

<sup>&</sup>lt;sup>39</sup> Bergius, German patents 304,348, 17 Sept. 1919; 301,231, 9 Aug. 1913; British patents 18,232, 1 Aug. 1914; 5,021, 31 Mar. 1915. See also Bergius, "Chemical Reactions" (cit. n. 15).

<sup>&</sup>lt;sup>40</sup> Bergius, U.S. patent 1,251,954, 1 Jan. 1918 (filed 3 Aug. 1914); British patent 18,232, 1 Aug. 1914; German patent 301,231, 9 Aug. 1913.

By 1914, after a large number of trials in his Hanover factory, Bergius had reached several important conclusions about high-pressure coal hydrogenation. Of all the coals tested, the younger brown coals and lignites were most suitable for hydrogenation. They had a carbon content of less than 85 percent in the ash-free coal, and on liquefying, their hydrogen content rose from about 6 percent to almost 15 percent. However, Bergius could not hydrogenate anthracite or any coals that were low in hydrogen and had an ash-free carbon content exceeding 85 percent. The reaction always produced methane gas, and any oxygen, nitrogen, or sulfur present in the coal reacted to form water, ammonia, and hydrogen sulfide respectively. Most of the carbon appeared in the light, medium, and heavy oils, though anywhere from 1 to 20 percent remained in the ash residue.<sup>41</sup>

Bergius's trials also demonstrated that adding small amounts of metallic oxides, especially ferric oxide, to the reactants catalyzed the hydrogenation of coal.<sup>42</sup> He attributed this effect to the oxides' ability to prevent polymerization of the hydrocarbon fragments produced when the coal was heated. However, in his Hanover factory Bergius had neither experts skilled in catalysis nor the funds to investigate catalytic influence on the reaction rate systematically. He attempted to perfect the hydrogenation of coal without catalysts, in a sense using high pressure to compensate for the lack of a catalyst.

One serious difficulty quickly became apparent when Bergius expanded from his small laboratory-scale operation to the bigger factory. Especially when scaled up, the hydrogenation of coal emitted a considerable quantity of heat, producing large amounts of coke rather than liquids. Because the solids and gases present in the autoclave could not distribute the heat of the reaction effectively, the reaction temperature increased so much that the coal rapidly decomposed and then distilled to give coke. Once again it became necessary to introduce a heavy oil solvent, which absorbed and distributed the heat produced in the reaction, thus preventing any overheating. Moreover, the high temperature cracked the oily solvent so that it too reacted with hydrogen gas.

Bergius's ultimate objective was to transform his small-scale coal conversion process into an industrial-scale operation. The introduction of a solvent to dissolve the reaction's products and to eliminate coking was certainly an important improvement. But the key to industrializing coal hydrogenation was to convert it from a batch process to a continuous-flow operation. By 1914 Bergius had succeeded.<sup>43</sup> Mixing the heavy oil solvent with powdered coal had produced a paste that he could pump continuously into the high-pressure reactor while simultaneously removing and collecting the liquid and gaseous products in a condenser.

The hydrogenation experiments at the Hanover factory enabled Bergius to arrive at a mechanism for coal hydrogenation. They showed clearly that the process consisted of two separate reactions: conversion of the coal into heavy

<sup>&</sup>lt;sup>41</sup> *Ibid*.

<sup>&</sup>lt;sup>42</sup> Bergius, German patent 290,563, 30 Nov. 1913.

<sup>&</sup>lt;sup>43</sup> Bergius, "Neue Methode zur Verarbeitung" (cit. n. 26), pp. 341–347. Because of the outbreak of World War I and perhaps because of the delay in his receiving patents on coal hydrogenation, Bergius published nothing on his process until 1921. This is the first article—along with U.S. patents 1,342,790, 8 June 1920 (filed 18 Apr. 1916), and 1,391,664, 27 Sept. 1921 (filed 18 Apr. 1916)—in which Bergius discussed the continuous process and temperature control.

pitch-like petroleum hydrocarbons as the result of adding hydrogen atoms at temperatures of 300-400°C and pressures of 200 atmospheres, and cracking or splitting of the heavy pitch-like hydrocarbons into lighter liquid hydrocarbons at about 450°C. In other words, coal hydrogenation was both an addition and a cracking reaction.

Before the outbreak of World War I in 1914, Germany had been exporting coal while importing practically all of her petroleum. In 1913 she imported 1.75 million tons of petroleum valued at 170 million marks. World demand for petroleum increased significantly at this time, rising from about 45 million tons in 1910 to 55 million tons in 1913.<sup>44</sup> The mass production of automobiles signaled an even more dramatic increase in petroleum consumption. Germany's only domestic source of petroleum was the destructive distillation of coal, heating coal in the absence of air to produce coke, gases, and liquids. But the yield of liquid products from a ton of coal never exceeded 3 percent. Thus Bergius saw a bright future for commercial high-pressure coal hydrogenation. It would be the way to decrease or perhaps eliminate Germany's dependence on imported petroleum.<sup>45</sup>

## VII. THE MOVES TO ESSEN AND RHEINAU: WORLD WAR I

At the Bunsen Society's 1911 meeting in Heidelberg, Bergius read a paper in which he discussed the results of his high-pressure research program in Hanover. His program so impressed Karl Goldschmidt, director of Theodore Goldschmidt A.G., a petroleum refining company in Essen, that he approached Bergius with an offer of financial support. Bergius accepted Goldschmidt's offer, but because he had already planned to move from his private laboratory to a small factory, he and Goldschmidt agreed to continue the research in Hanover and not relocate it in Essen. But by late 1913 Bergius, who wanted to expand his operations, was finding it increasingly difficult to finance his program, and at the beginning of 1914, when his current agreement with Goldschmidt ended, he and his assistants moved to Essen, where he became director of Goldschmidt's newly constructed research laboratory.<sup>46</sup>

Shortly afterwards the start of World War I revealed Germany's critical need for petroleum. When hostilities began on 1 August 1914, the German general staff counted on a quick military victory but soon realized that the war was going to last longer than expected. Commitment to a swift victory was the basic war philosophy of the late Count Alfried von Schlieffen (1833–1913), chief of the general staff from 1895 to 1906. From the time of Germany's quick victory over France in 1870–1871 the general staff had reworked and refined the Schlieffen Plan. In the current war against Britain, France, and Russia the plan entailed launching a tremendous assault on France and retaining only a minimal force to

<sup>46</sup> Bergius, "Die Anwendung von hohen Drucken," pp. 660–662; Schmidt-Pauli, *Friedrich Bergius*, p. 62.

<sup>&</sup>lt;sup>44</sup> Heinrich Brückmann, "Coal Liquefaction and Its Importance in World Economy," *The Mining Journal*, 28 Jan. 1928, *160*:69–70; 4 Feb. 1928, *160*:94; 11 Feb. 1928, *160*:116; Carleton Ellis, *Hydrogenation of Organic Substances*, 3rd ed. (New York: Van Nostrand, 1930), p. 552.

<sup>&</sup>lt;sup>45</sup> Franz Fischer and Hans Tropsch in Germany did not develop their process for the production of liquid and gaseous hydrocarbons from coal until after World War I. See Fischer and Tropsch, "Die Erdölsynthese bei Gewöhnlichen Druck aus den Vergasungsprodukten der Kohlen," *Brennstoff-Chemie*, 1926, 7:97–104; Fischer, "Liquid Fuels from Water Gas," *Ind. Eng. Chem.*, 1925, 17:574–576.

hold off the Russians. With the defeat of France, the German army's full force would easily prevail over Russia. Britain, now alone, would have no choice but to surrender.<sup>47</sup>

The Schlieffen Plan almost worked. But at the Battle of the Marne during the second week of September 1914, an unexpected French counterattack halted the German army's rapid advance to Paris. German industry had up to this time played no part in the Schlieffen Plan. Now, with all hope for a quick victory banished, the German high command was forced to contemplate the grim prospects of fighting a war with limited supplies of such strategic materials as sodium nitrate and petroleum.

Carl Bosch and Alwin Mittasch of BASF eliminated the nitrate shortage that occurred after the British sea blockade effectively cut off the nitrate supply from Chile. By May 1915 they had successfully developed an industrial-scale process for oxidizing ammonia at the Oppau plant. Their process converted the large quantities of synthetic ammonia produced by the Haber process to nitric acid and other nitrates that were essential for fertilizers and explosives.<sup>48</sup>

Bergius's effort to establish an industrial-scale coal hydrogenation process for the production of synthetic petroleum was not as successful. In 1915, with Goldschmidt's financial backing, he had begun to construct an industrial-scale apparatus for a continuous-flow plant in Rheinau near Mannheim. The entire operation-the feeding, mixing, reaction, and product removal-would be continuous, just as in his smaller Hanover plant.<sup>49</sup>

By 1916 Bergius needed substantial additional funding to continue his research and complete construction of the plant. Finally, on 10 May 1918, in conjunction with Goldschmidt, Heinrich Brückmann, Robert Friedlander, and several other German industrialists and financiers, Bergius established the Konsortium für Kohlenchemie, which in July became the Erdöl- und Kohleverwertung A.G. (EVAG), Berlin. Under the general direction of Bergius and Brückmann, EVAG spent thirty million marks to construct and about eighteen million marks to operate the Rheinau plant, where operating expenses averaged about fifty thousand marks per month.<sup>50</sup> Bergius did not solve the major operating problems until long after the war ended, however. Development also languished, particularly during the later stages of the war, when Germany obtained access to Rumanian oil fields and the conversion of coal to petroleum became of minor importance.<sup>51</sup> In fact Bergius did not resume active research at Rheinau until 1919, first with the hydrogenation of crude oil and later with coal; EVAG completed construction of the plant only in 1924.

Bergius faced two major technical problems at Rheinau: how to make the

<sup>49</sup> Bergius, "Neue Methode zur Verarbeitung," pp. 341–347. See also Bergius, U.S. patents 1,342,790, 8 June 1920, and 1,391,664, 27 Sept. 1921.

<sup>50</sup> Brückmann, "Coal Liquefaction," p. 69.
 <sup>51</sup> "Early Difficulties of Hydrogenation," The Iron and Coal Trades Review, 3 Dec. 1937, 135:937.

<sup>&</sup>lt;sup>47</sup> Gerhard Ritter, The Schlieffen Plan: Critique of a Myth (New York: Praeger Press, 1958); Alfried Graf von Schlieffen, Gesammlte Werke, 2 vols. (Berlin: Mittler, 1913).

<sup>&</sup>lt;sup>48</sup> BASF, German patents 249,447, 23 July 1912; 254,344, 2 Dec. 1912; 254,437, 3 Dec. 1912; 254,571, 6 Dec. 1912; Bosch, "The Procedure of the Synthesis of Ammonia," pp. 451-456; Bosch, "Wo ein Wille ist," pp. 90-94; Bosch, "The Development of the Chemical High Pressure Method," in Nobel Lectures: Chemistry 1922-1941, pp. 197-235; Mittasch, Geschichte der Ammoniaksynthese, pp. 93-116; Mittasch and Frankenburger, "Zur Geschichtlichen Entwicklung," pp. 920-927.

industrial-scale hydrogenation process a continuous-flow operation, and how to design heating apparatus that permitted temperature control to within 5 or 10 degrees of the hydrogenation temperature. After many trials Bergius, Löffler, Tillman, and Debo finally achieved a continuous flow operation in 1921. As in the smaller Hanover plant, they first ground the coal into pieces of about 2 millimeters in diameter, then mixed it with one-half its weight of a heavy petroleum oil to form a thick paste. The oil was obtained from a previous hydrogenation or from crude petroleum. Specially designed hydraulically operated pistons pushed the paste, after preheating, into the first of two horizontally arranged reactors, each 8 meters in length and 1 meter in diameter. Finally, the preheated hydrogen gas was pumped into the reactor, where it mixed with the paste.<sup>52</sup>

Pitch was formed in the first reactor, and from there the entire mass passed to the second reactor for the addition of more hydrogen gas. An outlet at the bottom of this reactor permitted removal of the products, which consisted of gas, liquefied coal, untransformed coal, and ash, at the reaction's completion. After the mixture was cooled and the pressure reduced to one atmosphere through the release of the gaseous products through valves, the gases, mainly hydrogen, separated from the liquid and solid products. Bergius and his assistants operated the coal hydrogenation process at 400–500°C and 150–200 atmospheres pressure. They used a heat engine to recover the heat energy of the compressed gas.<sup>53</sup>

The second technical problem facing Bergius and his assistants, to design heating apparatus that permitted accurate temperature control, was important because of the reaction's sensitivity to temperature change. At very high temperatures coke formed, whereas low temperatures led to a slow reaction rate. The new temperature-control apparatus, which was in operation at the Rheinau plant by 1921, used the heat-exchange principle, with relatively unreactive nitrogen or carbon dioxide gas as the heat-exchange medium. The apparatus required enclosing each reactor in a steel container or jacket, heating and compressing the heat-exchange gas to the pressure inside the reactor, and then circulating the gas in the space between the reactor and jacket. Equalizing the two pressures was important, for the strength of the autoclave's wrought-iron or pressed-steel walls decreased considerably at the working temperature, 400-500°C. Applying exterior pressure permitted construction of a reactor with relatively thin walls, because only the outer jacket's walls had to withstand the high pressure. A water column, one end connected by a pipe to the reactor, the other end to the jacket space, indicated any pressure difference. This indirect heating arrangement, according to Bergius, permitted very accurate temperature control and was highly economic, for it recovered all the heat exchanged in the process.<sup>54</sup>

Over a three-year period at Rheinau, 1922-1925, Bergius's research group

118. <sup>54</sup> Bergius, U.S. patent 1,592,772, 13 July 1926 (filed 30 Aug. 1921); Bergius and Stephan Löffler, British patents 192,849 and 192,850, 8 Mar. 1923 (filed 30 Nov. 1921).

<sup>&</sup>lt;sup>52</sup> Bergius, "Neue Methode zur Verarbeitung," pp. 341–347; Friedrich Bergius, "The Transformation of Coal into Oil by Means of Hydrogenation," *Canadian Chemistry and Metallurgy*, 1926, 10:275–279. See also Richard Tillman, German patent 307,853, 29 February 1916; and Bergius, U.S. patents 1,342,790, 8 June 1920, and 1,391,664, 27 Sept. 1921.

 $<sup>^{53}</sup>$  Bergius, U.S. patent 1,391,664, 27 Sept. 1921; Bergius, "Transformation of Coal into Oil," p. 118.

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tested more than two hundred different kinds of coal. Starting on a relatively small scale, they eventually hydrogenated quantities as large as 1000 kilograms (one metric ton). A typical reaction run contained 100 kilograms of powdered coal mixed with 40 kilograms of a heavy oil, 5 kilograms of hydrogen gas, and 5 kilograms of ferric oxide to remove any sulfur present in the coal. The reaction yielded 20 kilograms of gas, consisting of excess hydrogen and such low-molecular-weight hydrocarbons as methane and ethane, and about 128 kilograms of oil and solids. Distilling the oil produced 20 kilograms of gasoline with boiling points to 230°C, 10 kilograms of liquid with a boiling-point range 230–330°C, and 51 kilograms of heavy oils boiling above 330°C. The heavy oils contained all other constituents present in the coal and amounted to 10 percent of the coal consumed (see Fig. 2).<sup>55</sup>



Expanding the coal hydrogenation program forced Bergius to seek a larger and more economical supply of hydrogen gas than that provided by the reaction of iron with superheated water. Bergius recognized that the economic success of coal hydrogenation depended on a cheap and convenient supply of hydrogen gas. At the Rheinau plant he therefore decided to experiment once more with the well-known water gas reaction, hoping to improve its efficiency and yield by making two modifications: using methane and ethane, which were present in high concentrations in the gaseous products, as starting materials and carrying out the reaction in two steps. Bergius first heated methane or ethane in the presence of steam ( $T = 1100^{\circ}$ C) to give carbon monoxide and hydrogen; he then treated the gaseous mixture with additional steam ( $T = 700^{\circ}$ C) and a catalyst, so that the reaction yielded carbon dioxide and more hydrogen.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

<sup>55</sup> Bergius, "Transformation of Coal into Oil," p. 123; Bergius, "An Historical Account of Hydrogenation," p. 287.

This content downloaded from 139.184.014.159 on October 12, 2016 18:36:08 PM All use subject to University of Chicago Press Terms and Conditions (http://www.journals.uchicago.edu/t-and-c). The net result of these modifications was that one volume of methane gas supplied four volumes of hydrogen gas, whereas in the standard water gas reaction the reactant yielded only one volume of the product. Compressing the two gases and then dissolving the carbon dioxide in water under pressure permitted their easy separation.<sup>56</sup>

At the Rheinau plant, one metric ton of coal produced 490–650 kilograms of liquids at a cost of 71 marks. These products—gasoline, diesel oil, and lubricating oil—had a combined value of 141 marks, giving a profit of 70 marks per ton of hydrogenated coal. As EVAG's codirector Brückmann pointed out, since Germany imported annually 2,500,000 tons of petroleum costing 500,000,000 marks, development of a synthetic petroleum industry would be enormously beneficial for her balance of trade.<sup>57</sup>

#### **VIII. INTERNATIONAL DEVELOPMENT OF THE BERGIUS PROCESS**

The obstacles that stood in the way of Bergius's promising research on coal hydrogenation were not only technical. Obtaining sufficient research funds proved such a serious problem in postwar, inflation-plagued Germany that by 1920 EVAG had exhausted its entire capital. To secure the necessary funds, Bergius and Brückmann decided to license the foreign rights to the coal hydrogenation process. In October of that year they established a new company, the Deberg company in the Hague, which controlled all rights outside of Germany.

The licensing arrangements were rather complicated. They led to the Royal Dutch Shell Oil Company's acquiring 50 percent ownership of Deberg through one of its divisions, the Bataafsche Company; the licensing also brought two entirely new corporations into existence: the Makot Company and the International Bergin Company (IBC). First EVAG, which owned 100 percent of Deberg, transferred that ownership to Makot, a corporation that it also owned outright and had organized for this purpose. Makot then sold 50 percent of its stock to Bataafsche on 10 September 1921; these two then established IBC, which then owned 100 percent of Deberg and was itself owned 50 percent by Bataafsche and 50 percent by Makot. Makot (or EVAG) had only the patents and Bergius's expertise to offer, while Bataafsche provided the required capital.<sup>58</sup> By 1923 Bataafsche's president, Sir Henry Deterding, reported that his company had contributed 9,700,000 marks toward developing high-pressure coal hydrogenation at Rheinau.<sup>59</sup>

Bergius and Brückmann had of course welcomed Bataafsche's investment in IBC, but they also feared that without renewed German investment, foreign control of the process was inevitable. In 1925 Bergius and Brückmann were able to reduce considerably their financial dependence on Bataafsche,<sup>60</sup> when BASF

<sup>&</sup>lt;sup>56</sup> Bergius, "Production of Hydrogen from Water and Coal from Cellulose," p. 463; Bergius, German patents 254,593, 9 Dec. 1912; 277,501, 30 Nov. 1913; U.S. patent 1,059,818, 22 Apr. 1913; Bergius, "Transformation of Coal into Oil," pp. 123–124; Bergius "An Historical Account of Hydrogenation," p. 289.

<sup>&</sup>lt;sup>57</sup> Brückmann, "Coal Liquefaction," p. 116.

<sup>&</sup>lt;sup>58</sup> Bergius-Verträge, Summary Survey, pp. 1–8, Bergius Papers, BASF Archives, Ludwigshafen, Germany.

 <sup>&</sup>lt;sup>59</sup> "Zur Geschichte des Bergin-Verfahrens," Erdöl und Teer, 7 Oct. 1926, 40:630–632.
 <sup>60</sup> Ibid.



Figure 3. The plant at Rheinau. By permission of Johannes Bergius.

invested in IBC. In the 1920s BASF had expanded its high-pressure synthesis of ammonia and methanol to include brown coal hydrogenation. The success of this program led BASF to believe that high-pressure coal hydrogenation was ready for commercial development, and on 26 May 1925 it acquired, for 2,850,000 marks, a controlling interest in IBC.<sup>61</sup>

The establishment of IBC and the licensing of rights in 1920 actually led to the formation of only one foreign subsidiary. In 1924 a group of British investors in London organized the British Bergius Syndicate to experiment with the hydrogenation of British coals and (if successful) to develop the process within the British Empire. The British group also acquired a 20 percent interest in Makot. Once BASF and the British Bergius Syndicate became shareholders in IBC, its organization broke down as follows: Bataafsche, 20 percent; BASF, 30 percent; and Makot, 50 percent, with Makot's ownership breaking down as BASF, 40 percent; Bergius, 40 percent; and the British Bergius Syndicate, 20 percent.<sup>62</sup>

Sir James Calder of London, a board member of IBC, was chairman of the British Bergius Syndicate, which comprised fifteen leading British industries, among them Brunner Mond and Company, South Metropolitan Gas Company, United Steel Companies, and International Sugar and Alcohol Company. The syndicate worked closely with the Department of Scientific and Industrial Research, which conducted the early studies on the hydrogenation of British coals at the government's London Fuel Research Station. The success of these experiments resulted in the government's providing financial support to the syndicate in 1926. William R. Ormandy, C. H. Lander, and other members of the Fuel Research Station actively participated in the research at Bergius's Rheinau

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<sup>&</sup>lt;sup>61</sup> Company report of 6 June 1941 to Maria Höring, Höring Papers, BASF Archives, Ludwigshafen.

<sup>62 &</sup>quot;British Interests in Bergius Coal-Oil," Chemical Age, 7 Aug. 1926, 15:150; Bergius-Verträge, p. 2.

plant, and in February 1927 the British government completed construction on a similar plant, which processed one ton of coal per day.<sup>63</sup>

By late 1926 another British concern, Imperial Chemical Industries (ICI), considered the process ready for commercial development, and in February 1927 it bought control of the British Bergius Syndicate. ICI also entered into an agreement with the Department of Scientific and Industrial Research and IBC that called for the Fuel Research Station to do basic research on coal hydrogenation and ICI to proceed with the commercial development. Consequently, in October 1935 ICI completed a plant at Billingham in northeast England that produced 100,000 tons of gasoline per year. The Billingham plant provided high-quality synthetic gasoline for the British Air Force in World War II, but economic conditions forced ICI to end its coal hydrogenation program in 1958.<sup>64</sup>

## IX. THE I. G. FARBEN PROCESS AND ITS COMMERCIALIZATION IN GERMANY

In 1927 Bergius brought his coal hydrogenation program to a successful conclusion. In the Rheinau factory, where he had spent millions of marks in research and employed 150 men, Bergius had demonstrated the commercial potential of coal hydrogenation. But two problems remained. First, Bergius had not studied the influence of different catalysts on the reaction. Second, in his process the hydrogenation and decomposition of coal into petroleum took place in one step. As a consequence the yield was smaller than expected and the gasoline was of low quality; unless refined it could not compete with gasoline obtained from natural petroleum.<sup>65</sup>

BASF in Leuna solved these problems. In 1925 BASF reached an agreement with Bergius, who withdrew from further experimental work on coal hydrogenation. Carl Bosch, who had successfully built up BASF's commercial ammonia operations during 1909–1913, now made the commercialization of coal hydrogenation his personal crusade. Despite considerable opposition on the grounds of cost from his company's executive directors, Bosch succeeded.<sup>66</sup> In the process he ensured Germany's developing the Bergius high-pressure coal liquefaction rather than a second coal-conversion process, Franz Fischer and Hans Tropsch's indirect synthesis of petroleum from carbon monoxide and hydrogen.<sup>67</sup>

<sup>63</sup> "Early Difficulties of Hydrogenation" (cit. n. 51), p. 937; "Report of the Fuel Research Board," *Chemical Age*, 6 Oct. 1928, *19*:318–319. For a complete description of the coal hydrogenation research done at Fuel Research Station, see the Fuel Research Board, Department of Scientific and Industrial Research, *Annual Reports* and *Technical Papers*, for the 1930s.

<sup>64</sup> William J. Reader, *Imperial Chemical Industries: A History*, Vol. II (London: Oxford Univ. Press, 1975), pp. 164, 180–181, 265; on the agreement see also "The Hydrogenation of Coal," *Chemical Age*, 6 Oct. 1928, 19:310; D. J. Payton-Smith, *Oil* (London: Her Majesty's Stationery Office, 1971), p. 20.

<sup>65</sup> Bergius, "An Historical Account of Hydrogenation," p. 289.

<sup>66</sup> Joseph Borkin, *The Crime and Punishment of I. G. Farben* (New York: The Free Press, 1978), p. 48–50; Thomas Parke Hughes, "Technological Momentum in History: Hydrogenation in Germany 1898–1923," *Past and Present*, 1969, 44:106–132.

<sup>67</sup> Franz Fischer and Hans Tropsch, "Über die Reduktion des Kohlenoxyds zu Methan am Eisenkontakt unter Druck," *Brennstoff-Chemie*, 1923, 4:193–197; Fischer and Tropsch, "Über die Herstellung synthetischer Ölgemische (Synthol) durch Aufbau aus Kohlenoxyd und Wasserstoff," *ibid.*, pp. 276–285; Fischer and Tropsch, "Methanol und Synthol aus Kohlenoxyds als Motorbetreibstoff," *ibid.*, 1925, 6:233–234; and Fischer, "Liquid Fuels from Water Gas," pp. 574–576; Fischer and Tropsch, "Die Erdölsynthese bei Gewöhnlichem Druck," pp. 97–104 (both cit. n. 45). On 9 December 1925 BASF merged with seven other German chemical companies to form the industrial giant I. G. Farben. By 1926, Matthias Pier (1882– 1965), now I. G. Farben's director of research, succeeded in separating Bergius's one-stage operation into two stages: hydrogenation of coal to a heavy oil in the first or liquid phase, decomposition of the heavy oil to gasoline-size molecules in the second or vapor phase. Pier also directed the successful search for catalysts that accelerated each phase of the process; he discovered that metallic sulfides were insensitive to sulfur, one of the worst catalyst poisons and one almost always present in coal.<sup>68</sup>

In I. G. Farben's two-stage process, the liquid phase required grinding the coal, suspending it in a heavy oil and adding a catalyst, heating the coal paste to 300°C, and then pumping it into converters where the paste combined with hydrogen gas at 230 atmospheres pressure. The liquid-phase products consisted of 10–20 percent gases, 5–10 percent solids, 50–55 percent heavy oils, and 20–30 percent medium-weight oils such as kerosene, diesel oil, and heating oil. Molybdenum catalysts performed very well in liquid-phase hydrogenation, but their limited supply compelled I. G. Farben to use low-cost iron catalysts. In the vapor phase, the medium-weight oils produced in the liquid phase reacted with hydrogen gas over fixed-bed catalysts at a temperature of 400°C and pressure of 200–300 atmospheres. The catalysts were usually tungsten sulfide carried in terrana earth or activated alumina. The second-stage hydrogenation yielded 50–70 percent gasoline with a boiling range of up to  $165^{\circ}C.^{69}$ 

From the first coal-hydrogenation plant constructed in April 1927 at Leuna, which by 1931 had the capacity to produce 300,000 metric tons (2.5 million barrels) of synthetic petroleum per year, the German coal hydrogenation industry grew to comprise twelve large plants in 1944 (Böhlen, Scholven, Magdeburg, Welheim, Lützkendorf, Gelsenberg, Wesseling, Leuna, Zeitz, Brüx, Pölitz, and Blechhammer). At their peak in 1944, Germany's twelve plants produced over three million metric tons (25.5 million barrels) of synthetic petroleum; of this, after lead was added, two million metric tons (17 million barrels) were high-quality 100-octane aviation and motor gasoline. In World War II these plants provided most of the German military's fuel.<sup>70</sup>

The cost of hydrogenating coal was high, 190 marks per metric ton. This was equivalent to 24 cents per U.S. gallon of gasoline<sup>71</sup> and more than double the price of imported gasoline. But for Germany, with only a limited supply of nat-

<sup>69</sup> Ministry of Fuel and Power, *Report on the Petroleum and Synthetic Oil Industry of Germany* (London: His Majesty's Stationery Office, 1947), pp. 46–69.

<sup>70</sup> *Ibid.*, pp. 46–48, 1–2, 50.

 $^{71}$  Prewar rate of exchange: RM = \$.25; from *Statistical Abstract of the United States*, 1939 (Washington, D.C.: GPO, 1939), p. 208. To convert tons of petroleum to barrels of petroleum: 1 ton equals 7.3 barrels, 1 barrel equals 42 U.S. gallons.

<sup>&</sup>lt;sup>68</sup> High-Pressure Hydrogenation at Ludwigshafen-Heidelberg, FIAT Final Report No. 1317, Vol. I (Dayton, Ohio: published for Joint Intelligence Objectives Agency by Central Air Documents Office, 1951) pp. 24–26, 32; Matthias Pier, "The Hydrogenation of Bituminous Coal," Fuel, 1935, 14:136–146; Alfred von Nagel, Methanol Treibstoffe (Schriftenreihe des Firmenarchivs des BASF, 5) (Ludwigshafen: BASF, 1970), pp. 41–47; Matthias Pier, U.S. patent 1,955,829, 24 Apr. 1934 (filed 27 Aug. 1930); Matthias Pier and Karl Winkler, U.S. patent 1,946,108, 6 Feb. 1934 (filed 3 Jan. 1929); E. E. Donath and Maria Höring, "Early Coal Hydrogenation Catalysis," Fuel Processing Technology, 1977; 1:3–20; Donath and Höring, "Kohle- und Ölhydrierung," Ullmanns Encyklopädie der technischen Chemie, 3rd ed. (Munich: Urban & Schwarzenberg, 1958), Vol. X, pp. 483–569, on pp. 486–535.

ural petroleum, there was no alternative during the war to the construction of coal hydrogenation plants. In this way she utilized her abundant supplies of bituminous and brown coal.

#### X. CONCLUSION

Clearly, Germany, which produced 128 million barrels in the period 1938–1945, had the first successful synthetic petroleum industry. German industry did not continue with coal liquefaction after World War II, however, because the Potsdam (Babelsberg) Conference of 16 July 1945 prohibited it.<sup>72</sup> Four years later, on 14 April 1949, the Frankfort (Frankfurt) Agreement ordered all coal conversion plants dismantled, but a new agreement, the Petersburg (Bonn) Agreement of 22 November 1949, quickly halted the dismantling process.<sup>73</sup> The West German government completely removed the ban on coal hydrogenation in 1951, though by this time the plants in West Germany had been modified so as to refine natural petroleum rather than hydrogenate coal.<sup>74</sup>

The Russians dismantled four of the hydrogenation plants located in their zone at Pölitz, Magdeburg, Blechhammer, and Auschwitz, and reassembled them in Siberia for the production of aviation fuel from coal. The plants at Leuna, Böhlen, Zeitz, and Brüx continued with coal and coal-tar hydrogenation into the early 1960s, but they also have since been modified to refine natural petroleum. Thus today possibly four of Germany's twelve World War II coal hydrogenation plants continue to convert coal into petroleum.<sup>75</sup>

<sup>72</sup> "Principles to Govern the Treatment of Germany in the Initial Control Period," No. 848, The Conference of Berlin (The Potsdam Conference), 1945, Foreign Relations of the United States, Diplomatic Papers, Vol. II (Washington, D.C.: GPO, 1960), pp. 750-753, on p. 752.

<sup>73</sup> "Multilateral: German Industries," United States Treaties and Other International Agreements, Volume II, Part I, 1951 (Washington, D.C.: GPO, 1952), pp. 902-972, on p. 963; "Multilateral: Incorporation of Germany into European Community of Nations," ibid., Vol. III, Part II, 1952 (Washington, D.C.: GPO, 1954), pp. 2714-2722, on p. 2716.

Wolfgang Birkenfeld, Der synthetische Treibstoff, 1933-1945 (Göttingen: Muster-Schmidt-Verlag, 1964), pp. 213-215; E. E. Donath, "Hydrogenation of Coal and Tar," in Chemistry of Coal Utilization, Supplementary Volume, ed. H. H. Lowry (New York: Wiley, 1963), pp. 1041-1080, on pp. 1042–1044. <sup>75</sup> Donath, "Hydrogenation of Coal and Tar," pp. 1042–1044.