

FUELS 1924 - 1940

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ABSTRACT

The period 1924-1940 may be characterized as the flowering era of fuel science and technology. In the field of combustion this period saw the extensive development of the burning of pulverized coal under slagging conditions to generate steam; a greatly improved understanding of the kinetics and mechanism of the combustion of solid fuels. Coal gasification technology was advanced: by the development of gasifiers using oxygen; by operating at elevated pressure, under slagging conditions, and with a fluidized bed; and by demonstrating the feasibility of hydrogasification. During the period the efficient by-product coke oven almost completely replaced the beehive oven for producing metallurgical coke. Coal liquefaction and solvation progressed from the laboratory to the full-scale commercial plant. The Fischer-Tropsch process was discovered just prior to the period under discussion and it too progressed to the commercial stage during this period. Major advances were made in knowledge of the kinetics and mechanism of the oxidation of gaseous fuels and in knowledge of the properties of fuel-air mixtures. Extensive work was done on the chemical constitution of coal and tar and on their physical properties. This latter work led to the establishment of many ASTM standards. These impressive accomplishments in fuel science and technology are discussed in more detail in the paper.

INTRODUCTION

In discussing fuels 1924-1940 we cannot isolate this first period of the symposium from preceding developments in fuel science and technology. Accordingly, an attempt will be made to summarize, briefly, the history of the field prior to 1924. In this way we can give perspective not only to the period under discussion but also we can establish a base on which subsequent developments have been built.

The subject of fuel is so broad, covering as it does solid, liquid and gaseous fuels, that it is obvious that we will have to limit both the scope and depth of our summary.

In the period under discussion, 1924-1940, which we refer to as "our period", the interests of the Fuel Chemistry Division followed the content of the section in Chemical Abstracts then entitled, "Fuels, Gas, Tar and Coke". This then suggests that this be the scope of our discussion insofar as the basic fuels are concerned. Thus petroleum and its products are eliminated from our discussion which is logical not only because petroleum has not been one of the basic concerns of the Division of Fuel Chemistry but also because that fuel is the basic concern of the Division of Petroleum Chemistry.

Insofar as the depth of our discussion is concerned the major emphasis is on carbonization, combustion, gasification and hydrogenation. In these fields key developments are individually referenced. No attempt is made to document all developments by a comprehensive bibliography but rather reference is made to pertinent books and reviews containing such bibliographies. (1-6) One of these contains a comprehensive list of books on fuel science and technology covering the field prior to 1943. (4)

Obviously, to keep our discussion manageable, it was necessary to eliminate many important areas of coal research. These are covered thoroughly by Lowry and include such subjects as : coal petrography; the physical properties of coals; the chemical constitution of coal as determined by reaction with various compounds; the occurrence of sulfur, nitrogen and mineral matter in coal; ash fusion; the action of solvents on coal; and changes in coal during storage. (4) I believe it is clear that meaningful discussion could not be given to such a wide range of topics. For detailed information on developments on these and other related fields in our period, Lowry's book should be consulted.

BRIEF HISTORY OF FUEL SCIENCE AND TECHNOLOGY

In considering the development of fuel science and technology prior to 1924, a logical and identifiable starting point is the year 1350 when coal first became a commercial commodity. Gas was first recognized as a state of matter in 1620 and coal was first distilled in the laboratory to yield gas in 1660.

The carbonization of coal to produce metallurgical coke was known in the late 1600's but was not practiced on a large scale until 1730. Coke was a by-product of another process developed in 1792 in which coal was distilled in an iron retort to produce illuminating gas. These two processes initially were considered basically different and this concept persisted until the early 1900's.

With the increasing use of by-product coke ovens in the early 1900's, it became apparent that it was more efficient and economical to produce gas in the by-product coke oven than in the more labor intensive gas retort. The first by-product coke ovens were constructed in France in 1856. Since then they have gradually replaced beehive ovens which in 1900 accounted for about 95 percent of United States production but less than 5 percent in the late 1930's.

In 1855 Bunsen invented the atmospheric gas burner which opened the way for gas markets to expand from lighting to a wide range of heating applications. A high illuminating power for gas was no longer required after Welsbach invented the incandescent mantle in 1884. This need would have been eliminated anyway in a few years when the incandescent electric light was invented, and the gas lighting load was eventually lost.

The advent of electric lighting opened up a great potential for coal combustion in the generation of steam for power generation. Thus, the combustion of coal went through the stages of burning in open-fireplaces in the early days to burning in the fuel beds of small household furnaces and subsequently large industrial furnaces and finally to burning as pulverized fuel in large central station furnaces. This latter application was first tried in 1876 but was not successful in the United States until the factors affecting proper furnace design were elucidated in 1917.

As the use of coal gas developed, the production of gas for heating purposes was also developing. The first gas producer making low Btu gas was built in 1832. This principle was not widely used until it was applied by the Siemens brothers in connection with their invention of the open-hearth furnace in 1861. The use of producer gas increased from that time, until at the turn of the century it was an important factor for heating furnaces. But subsequent to that time its use has declined and in 1920 there were only 11,000 producers in use in the United States.

Another development in the field of gas making stemmed from Fontana's discovery in 1780 of the production of blue gas when steam was passed over incandescent carbon. This discovery was dormant until the period between 1823 and 1859 when additional experimental work was done on the steam carbon reaction. This eventually led to the development of processes for producing blue water gas in the period of 1859 to 1875. The first successful commercial process was developed by Lowe in 1875 when he introduced the carburetted water gas set. The increased use of this gasification technology continued until natural gas supplanted manufactured gas.

The history of coal hydrogenation begins in 1913 when work on the Bergius concept of direct hydrogenation of coal under hydrogen pressure at an elevated temperature was undertaken in Germany. A 31-ton-per-day pilot plant was built in Germany in 1921 and this brings us up to our period.

The possibility of producing liquid hydrocarbons from water gas (Fischer-Tropsch synthesis) was conceived in 1913. The first experimental work on this synthesis which is sometimes referred to as the indirect hydrogenation of coal was published in 1923 just prior to the beginning of our period.

This brief review of the major areas of application of fuel technology - combustion, carbonization, gasification and hydrogenation - presents a broad picture of the status of technology prior to 1924. As each individual area is discussed, more specific details of the status of significant developments are presented.

CARBONIZATION

General

The carbonization of coal involves the interaction of a wide range of chemical and physical properties of the coal itself in a high temperature thermal environment to produce a combustible gas, hydrocarbon liquids or tar and coke. The nature of the tar and its yield as well as the physical properties and reactivity of the coke and its yield are affected by the coal used and by the carbonizing conditions. Thus an understanding of the complex coal carbonization process involves research on: the plastic, agglutinating, agglomerating and swelling properties of coals; dependence of yields of products on type of coal, temperature and rate of heating; the chemical nature of coal tar; and as stated above the physical properties and reactivity of coke.

We cannot go into detail in these areas but we will try to indicate through summaries and selected examples of some of the developments in our period. Also it is only possible to mention here such important related areas as: the properties of coke-oven gas; light oil from coke-oven gas; removal of sulfur compounds and miscellaneous constituents from coke-oven gas; and the treatment of ammoniacal liquors⁽⁴⁾. Finally, the broad field of industrial coal carbonization can only be covered by References 2 and 7 which review the status of the technology up to the end of our period.

The Plastic Properties of Coal

When caking coals are heated they undergo chemical transformation during which gases and condensable vapors are evolved leaving a solid residue consisting predominantly of carbon. During this process the coal

softens, becomes more or less plastic, and forms a bubbly compact mass which swells and then resolidifies leaving a porous solid known as coke.

The characteristics of coal in the plastic state were studied both extensively and intensively and the results of these studies have been summarized in considerable detail by Brewer. (8)

The dilatometer⁽⁹⁻¹³⁾ which measures the variations in the length of a confined coal sample heated at a definite rate gives the most complete information on the behavior of coal in the pre-plastic range⁽¹⁴⁾.

Plastometers measure the fluidity or "viscosity" of coal in the plastic range. The constant torque (Geisler) plastometer⁽¹⁵⁾ gives a better index of fluidity⁽¹⁴⁾ and the variable torque (Davis) plastometer⁽¹⁶⁾ allows the temperature at the softening point and the resolidification point to be determined with a high degree of accuracy.

It was first shown in 1870 that those coals producing the best cokes were capable of incorporating a higher admixture of inert material than those coals producing inferior cokes. (17) This observation led eventually to the development of test methods to measure the agglutinating value of coal. The more important of these were critically reviewed in 1929 by Marshall and Bird who developed an updated method for measuring the agglutinating value of coal. (17) Their work along with that of others^(18, 19) led ultimately to an A.S.T.M. Standard for measuring agglutinating value.

The agglomerating properties of coal indicate the tendency of the particles to stick to one another during heating. Work on this property⁽²¹⁻²³⁾ led eventually to the establishment of standard methods^(24, 25) for determining the free swelling index which is a measure of the agglomerating characteristics of a coal.

The swelling of coal during carbonization, if excessive, can lead to serious damage to the walls of the coke oven. Much work was done in this area⁽⁸⁾ but no standard method was developed in our period for determining this characteristic. Work by the Bureau of Mines on sole-heated ovens⁽²⁶⁾ and vertical-slot ovens⁽²⁷⁾ afforded a satisfactory means for determining the expanding properties of coal⁽¹⁴⁾.

Carbonization Tests

In discussing the experimental carbonization of coals, Reynolds states "A large number of assays for determining the coke- and by-product-making properties of coal have been developed but these methods give little information concerning the quality of products because of the small amount of sample carbonized". (14) In 1929 the Bureau of Mines, in cooperation with the American

Gas Association, developed a carbonization test using charges weighing up to 200 pounds. (28) The yields of coke and by-products from this test are large enough to be tested by standard methods, thereby affording more complete data than are obtainable from tests on a smaller scale. Forty-eight coals have been carbonized by this method at high, medium, and low temperatures, and the qualities of the cokes and by-products determined. Petrographic, agglutinating, plastic, expanding, friability, slacking, and oxidizing properties of these coals have been studied also. The comparison of test results and plant data (available for some coals) is an important part of this work and the agreement has been close enough fully to justify confidence in the method of test. Referring to the results of these investigations, Mulcahy wrote: "Although much work on coal has been regarded as too fundamental or theoretical to be of practical value, the work of the Bureau of Mines in this respect is of tremendous value in indicating the trends we can expect under different carbonizing conditions". (29)

The subject of this section was also reviewed in detail by Davis. (30)

Physical Properties and Reactivity of Coke

The physical properties of coke such as density, size, distribution, and strength as determined by the shatter, tumbler and other tests are significant in relation to the use of coke in fuel beds. Work in this area for our period has been reviewed by Mayers. (31).

The "reactivity" of coke is "somewhat loosely used to express the ability of a coke to interact with, usually, oxygen, carbon dioxide or steam". (32) In his review of work on reactivity for our period Mayers points out that it is not necessary to determine reactivities with various agents. By comparing series of cokes of different reactivities, it has been shown that the reactivity with air is parallel to the ignition point⁽³³⁾ and the reactivity to carbon dioxide⁽³⁴⁾ and steam⁽³⁵⁾ is parallel to change in the ignition point; that the reactivity to air, to oxygen, and to carbon dioxide is parallel to changes in the ignition temperature⁽³⁶⁻³⁸⁾; and that reactivities to air, to oxygen, to carbon dioxide, and to steam are all parallel^(39, 40). No attempt is made here to review reactivity tests. Instead certain data from such tests are considered in connection with the discussion of gasification reactions.

Coal Tar

Coal tar is one of the primary products of coal carbonization. It is a complex mixture containing principally aromatic compounds many of which are polynuclear. In our period some 348 compounds were identified as coming from the carbonization of coal. (41) Most of these appeared in the tar.

Reference (41) also contains information on the effect of kind of coal and carbonization temperature on the characteristics and yield of coal tar and more detailed information on certain of the individual chemical constituents of the tar.

COMBUSTION

General

Studies of the combustion of solid fuels have involved experiments: with graphite, coal and wood charcoal; with sizes ranging from less than 200 mesh particles to 1-inch spheres; with individual particles, clouds of particles, filaments; and with both stationary and moving fuel beds. This wide range of conditions can be considered as falling into one of two categories - basic studies and studies of combustion processes. The former includes studies with graphite in filaments or in simple geometric shapes. The latter embraces coal in the more complex systems.

Basic Studies

At the beginning of our period it had been established that CO and CO₂ were produced together in the reaction of carbon with oxygen. (42) The work of Rhead and Wheeler indicated that CO was the primary product at temperatures above 1000 C. (43) Whereas the work of Langmuir and others involving electrically heated filaments at low pressure indicated that CO₂ was the main product. (44-46) Work toward the end of the period showed that low-pressure filament results were not valid because thermions upset the initial equilibrium of the primary reaction. (47) Confirmation of the results of Rhead and Wheeler resulted from high velocity experiments (48) toward the end of the period. Thus in our period we saw the resolution of the primary product of the reaction between carbon and oxygen.

According to Nicholls, "the chemistry of combustion and its physics as regards to temperature, time and diffusion, were well understood in 1840⁽⁵⁰⁾, but such knowledge was not well disseminated". (49) In light of this it is interesting to note that early in our period it was recognized that the rate of combustion reactions was limited by the rate at which oxygen could be transported to the reacting surface. (51-53) This conclusion was supported by experimental work^(54, 55) on the rate of oxidation of spheres of graphite which showed "that the rate of the specific surface reaction depended strongly on the temperature at low temperatures⁽⁵⁵⁾ but less so at high ones^(54, 55); that it was directly proportional to the oxygen concentration in the gas flowing over the carbon surface⁽⁵⁵⁾; that it depended on approximately

the 0.4 power of the mass velocity of the gas at high temperatures(54, 55); and that, for small particles, it was approximately inversely proportional to the diameter of the particle(54). Similar effects were found for the reduction of carbon dioxide and steam(57) in work in which the monotonic effect of increasing gas velocity was used to estimate the absolute reaction rate by increasing the gas flow until no further increase in reaction rate, as measured by gas analysis, was found. "(56)

The dependence of reaction rates on gas velocity could not be accounted for by a pure diffusion process. This led to the application of the concept of the stagnant film to account for this effect. (55, 58) This concept has been an important part of the development of our understanding of general heterogeneous reaction kinetics.

As discussed subsequently the extensive application of the combustion of pulverized coal in large steam boilers occurred in this period. This led to the initiation of studies of burning particles in the size range of pulverized coal.

Tests with 60 to 90-mesh particles dropped through a heated tube showed that some coal particles ignited at about 1100 F but a temperature of about 1300 F was required to ignite the major fraction of the particles. (59) Later tests showed that a temperature of about 1500 F was required to obtain uniform ignition of certain bituminous coals. (60)

Combustion of individual particles of coal is complicated by the formation of cenospheres as a result of simultaneous softening and evolution of volatile matter which when burned shows up as a luminous gas flame in photographic studies. (59) A theoretical analysis indicated that for a given quantity of excess air the burning time of a solid particle is greater than that of a cenosphere containing the same weight of combustible. (61) The magnitude of the difference depends on the ratio of the size of the cenosphere to the size of the original particle. Burning times increase as the quantity of excess air decreases.

After reviewing basic and applied work on the combustion of pulverized coal Orning concluded "Considering all the data on the mechanism and rate of combustion, it appears that a transition must occur from diffusion to surface reactivity as the controlling factor. Immediately after the zone of ignition and burning of volatile matter, the particle temperature rises very rapidly. In this region the smaller particles burn to a low carbon content within a time proportional to the square of the radius of an equivalent solid sphere and to a function depending upon the influence of coal characteristics and flame conditions upon cenosphere formation.

"The larger particles will still contain a considerable portion of the total carbon after the rate of heat release has passed its peak. Continued rapid combustion of these particles depends upon their ability to maintain themselves above a certain temperature. With the combustion rate, and

hence the heat release, varying as the particle diameter while the rate of loss by radiation is proportional to the surface, the largest particles will have the lowest temperature.

"The reactivity of the original fuel is no indication of the temperature at which the surface reaction begins to control. The high particle temperatures in the early stages of combustion transform the residue into a material whose reactivity is mainly a function of flame conditions. The characteristics of the original fuel appear in their effect on cenosphere formation, in a possible catalysis by ash, and in a hindrance by ash incrustations.

"A complete calculation of burning times must consider the possibility that the surface reaction rate will begin to control beyond a certain degree of combustion. Lack of data on the reactivity and configuration of combustion residues and the dependence of particle temperature upon an equilibrium with furnace surroundings make it inadvisable to attempt a general solution."(61)

Combustion in Fuel Beds

Combustion in fuel beds has been reviewed by Mayers⁽⁵⁶⁾, Nicholls and Barkley⁽⁴⁹⁾, and Haslam and Russell⁽³⁾. This type of combustion encompasses the open grate, the central house-heating furnace, and the various types of mechanical stokers.

At the beginning of our period, extensive research had already been done to improve the convenience and efficiency of the coal fire-place.⁽⁶²⁾ Also extensive tests had been made by the Bureau of Mines and others on the combustion of various coals on a grate in a cylindrical furnace.⁽⁶³⁻⁶⁶⁾ These tests provided information on the effect of rate of firing on gas composition in the fuel bed and on the temperature of the fuel bed. The tests showed conclusively that the quantity of coal burned or the capacity of the furnace depends entirely on the quantity of primary air coming into the furnace under the grate. The Bureau of Mines also studied the combustion of gases over the fuel bed and in this instance demonstrated conclusively that the quantity, distribution, and turbulence of secondary air determines the efficiency of the furnace. Thus at the beginning of the period there existed a significant body of practical knowledge on combustion in fuel beds.

During the period additional work was done on the combustion of various coals in house-heating boilers⁽⁶⁷⁾, on the performance of domestic anthracite stokers⁽⁶⁸⁾, on the fundamentals of combustion in small underfeed stokers⁽⁶⁹⁾, and on burning various coals in domestic overfeed stokers⁽⁷⁰⁾.

Most of the work on various types of stokers during the period involved improvements in mechanical design to secure a high degree of reliability and a high conversion of fuel into heat.⁽⁷¹⁻⁷⁵⁾

Mayers states that "The conditions within the beds of travelling-grate stokers have been determined experimentally(76-78) These investigations show that the layer of coal entering the furnace is ignited at the top of the bed; and that the surface dividing ignited from raw coal moves down as the layer passes through the furnace. The ignition surface reaches the grate ... where the dense flame of volatile matter stops; all the fuel has been ignited and coked at this point, and only the coked residue is burned out beyond it. As this process proceeds, a larger and larger proportion of the bed becomes ashy refuse. The fire should be operated so that all the fuel is burned out of the refuse short of the end of the grate, but the air quantity passing through this end of the grate must be controlled to prevent excessive losses. "(56)

Spreader stokers were a relatively new development in this period. The principles of operation are essentially similar, so far as the fuel bed is concerned, to those obtaining in hand-firing, the stoker being merely a means of producing a continuous flow of small amount of fresh fuel down into it. Description of such units and the results of tests made on them are given by Barkley. (79, 80)

Combustion of Pulverized Coal

The use of pulverized coal in the firing of large steam boilers came into being at the beginning of our period. For example, the boiler heating surface fired with pulverized coal increased from 200,000 sq ft in 1918 to 2,000,000 sq ft in 1925. (44) The progress of this development throughout our period has been detailed by Orning(45), Haslam and Russell(46), and Nicholls and Barkley(49).

The early developments in pulverized coal combustion as well as developments later in our period have been summarized by Nicholls and Barkley as follows:

"In 1917 a report of the Bureau of Mines showed that a long travel of flame was required to give complete combustion unless the air and the combustible were mixed vigorously. (65) When furnaces for pulverized-coal firing were so built they gave satisfactory performance and good efficiencies. (81) The cooperative work of the Bureau of Mines and the Milwaukee Electric Railway and Light Co., resulted in the first successful application of pulverized fuel in the steamboiler field.

"In the earlier designs successful removal of the ash required that the particles be deposited in a dry or unmolten state. These dry-bottom furnaces were not so successful with coals having low-fusion ashes. The problem was solved by going to the other extreme of maintaining the ash in

a liquid state and tapping it intermittently or continuously; the wet-bottom furnace was the outcome.

"Operation of these furnaces depends largely on the properties of the coal ash and its slag. As relatively few data were available, the Bureau of Mines initiated in 1929 a study on the ash factor in such furnaces and the properties of coal-ash slags in general(82)."(65)

The initiation of the systematic study of coal-ash slags followed closely the first successful application of the slagging-type furnace(83) and the first studies on slagging conditions in full-scale furnaces(84). Other studies of conditions of temperature and gas composition in full-scale furnaces were directed toward the explanation of the striking difference in refractory service conditions in two similar furnaces(85) and toward the effect of different burner and heat absorption configurations(86).

HYDROGENATION

Coal hydrogenation was practiced for the first time on a large scale in Germany in 1925 and subsequently in France, Great Britain, Japan and the United States.(87) In commenting on these early developments Storch states:

"Except for a relatively small amount of research published by the British Fuel Research Laboratory, little information on the fundamentals of coal hydrogenation is available, despite the voluminous patent literature, which is often more confusing than informative. Unquestionably much more is known by industrial interests, particularly in Germany and Great Britain, than appears in print. However, a study of the development of coal hydrogenation in these countries reveals that the intensive drive made during the past decade to achieve large-scale production has left little, if any, time and funds for fundamental research."(88)

The literature on coal hydrogenation prior to 1931 was reviewed by Skinner and Zerbe(89,90) and between 1931 and 1938 by Fieldner(91). These reviews along with two books by Berthelot and Hot(92) and reviews by Storch(88) and Wu and Storch(87) cover the basic work on coal and tar hydrogenation in our period.

Studies of the hydrogenation of a number of British coals in small bombs showed that the yield of oil boiling below 360 C at atmospheric pressure increased approximately linearly with the carbon content of the coal.(93) As a corollary, the reactivity of the coals to hydrogenation was approximately inversely proportional to their carbon content.

Similar studies on the hydrogenation of the mechanically separable constituents of American coals showed that the translucent constituents (spores, resins, oil algae, translucent attritus, and anthraxylon) are liquefied completely. The opaque constituents (fusain and opaque attritus) contain about 75 to 95 percent and 20 to 60 percent, respectively, of materials resistant to hydrogenation.

On the basis of the foregoing results, it was suggested that "petrographic analysis would be a desirable, although only semiquantitative, tool for predicting liquefaction yield upon hydrogenation." (94-96) This was confirmed by work done in the Bureau of Mines' experimental plant which showed fair agreement between petrographic estimates of organic residue yield and yields obtained in the continuous operation of the plant. (97) These tests were made on nine coals ranging in rank from lignite to bituminous A.

Laboratory work on the effect of hydrogenating coal in the presence of a catalyst (stannous oxide), with and without a vehicle, showed that these two variables are not independent of each other. (98, 99) For example with small amounts of catalyst (less than 0.1 percent of charge) the addition of a vehicle results in an appreciably greater yield of volatile products. With higher concentrations (more than 0.5 percent) the effect is small and may even become negative.

The extensive work done in our period on the effect of catalysts on the liquid phase hydrogenation of coal has been reviewed in considerable detail by Storch. (88)

In laboratory studies, the catalytic effect of the walls of the converter cannot be neglected. (100) This effect is less important in large-diameter industrial reactors although it may be of considerable importance in engineering development work involving the use of small-diameter tubes. (101-103)

The effect of the halogens in enhancing the activity of stannous oxide, stannous hydroxide, ammonium molybdate, and nickel sesquioxide as liquid-phase hydrogenation catalysts was demonstrated by the British (104, 105) and Japanese (106, 107). Results obtained with various catalysts on the liquid-phase hydrogenation of coal are generally applicable to the liquid-phase hydrogenation of tar. (108)

The preparation and performance of catalysts for the vapor-phase hydrogenation of low temperature tar and middle oil has been discussed by Storch. (88) Information on such catalysts as supported molybdenum oxide, pelleted molybdenum or tungsten disulfide, as well as on many others, is also presented.

Tests on the effect of pressure on the liquid-phase hydrogenation of coal showed little effect on the capacity of a small-scale plant in the range of 180 to 250 atmospheres.⁽¹⁰⁹⁾ However, Pier stated: "The conversion of old coals or of asphalts of high molecular weight, which goes but slowly at 200 to 300 atmospheres, proceeds without difficulty and at a satisfactory rate for large-scale production at considerably higher pressures, e. g., 700 atmospheres or more."⁽¹¹⁰⁾

An increase in temperature in the range of 420 to 460 C increases the yield of crude gasoline, middle oil and hydrocarbon gas, and decreases the yield of heavy oil (boiling at 300 C) and solid organic residue.^(111, 112) The hydrogen absorbed also increases with increasing temperature. The effect of temperature and contact time are analogous in that higher temperatures are equivalent to a longer contact time.⁽¹¹¹⁾

Storch points out that "coal is usually hydrogenated for the single purpose of producing hydrocarbon fuels. Consequently, there has been little incentive to study the characteristics of intermediate products such as the "middle" oil (boiling range 210 to 330 C) from liquid-phase coal hydrogenation. As a source of organic chemicals, however, this intermediate product is most interesting and merits examination. The middle oils from liquid-phase coal hydrogenation contain benzene, toluene, xylene, cyclohexane, methylcyclohexane, about 20 percent of tar acids (phenol, aerosols, xylenols), and 2 to 5 percent of nitrogen bases." In addition "several patents mention the isolation of many polynuclear aromatic compounds of high molecular weight from coal-hydrogenation products. Sometimes the actual isolation is preceded by dehydrogenation. Products of this kind include pyrene, chrysene, retene, fluoranthene, carbazole, methyl- and dimethylpyrenes, 1,12-benzoperylene, coronene, picene, fluorene, methylanthracene, and naphthalene."⁽⁸⁸⁾

"The products of the hydrogenation of coal are largely aromatic and naphthenic in nature, whereas appreciable yields (about 12 percent) of the paraffin hydrocarbons have been reported in the hydrogenation of German brown coals."⁽⁸⁸⁾

Tar may be hydrogenated under the same conditions as coal except that no solid materials other than a small quantity of catalyst powder in the case of high temperature tar must be introduced or removed from high-pressure vessels. Low-temperature tar may be processed directly by mixing with recycle oil and hydrogen and passing the mixture over a fixed catalyst bed in a high-pressure vessel.

The effect of process variables on the yield and distribution of products are essentially the same as those shown for coal in Storch's review⁽¹²⁴⁾ of tar hydrogenation covering our period. This review also shows that this similarity also exists in the nature of the products obtained from the two feedstocks.

SYNTHESIS OF HYDROCARBONS FROM MIXTURES OF
CARBON MONOXIDE AND HYDROGEN

The catalytic conversion of mixtures of carbon monoxide and hydrogen to hydrocarbons which is referred to as the Fischer-Tropsch synthesis or the gas-synthesis process was developed and commercialized in our period. The details of laboratory research and industrial development have been reviewed by Storch, (113) A more comprehensive treatise on the Fischer-Tropsch and related syntheses was published in 1951. (114) The vast amount of work done on the Fischer-Tropsch synthesis in Germany, Great Britain, Japan and the United States cannot be presented here. Instead, we will quote the excellent brief summary of developments in our period given in the book by Storch, et al. (114)

"The Fischer-Tropsch synthesis had its origin in an observation made in 1923 by Franz Fischer and Hans Tropsch that alkalized iron turnings at 100-150 atm of hydrogen plus carbon monoxide and 400-450 C catalyzed the production of 'synthol'. This product consisted chiefly of oxygenated compounds and a very small quantity of hydrocarbons. At 7 atm and, later, at 1 atm, Fischer found that the distribution of oxygenated and hydrocarbon products was reversed. The first Fischer-Tropsch catalyst was an iron-zinc oxide preparation which was reported by Fischer in 1925. It was tested at atmospheric pressure with a mixture containing 3 volumes of hydrogen and 1 volume of carbon monoxide, and at a temperature of 370 C. However, development of iron catalysts was unsuccessful until 1937, which was several years after the Fischer-Tropsch process was in commercial operation with a cobalt catalyst.

"An important advance in the development of Fischer-Tropsch catalysts was the precipitation of nickel-thoria on kieselguhr in 1931. This catalyst was followed in 1932 by the corresponding cobalt catalyst, 100 Co:18 ThO₂:100 kieselguhr, parts by weight, which was the starting point in the development of the Ruhrchemie commercial catalyst. Subsequent changes in catalyst composition, concomitant with process development, resulted in a standard composition in 1937 of 100 Co:18 ThO₂:200 kieselguhr and in 1938 of 100 Co:5 ThO₂:8 MgO:200 kieselguhr.

"The advantages of iron over cobalt, in being easily available from many sources and in imparting flexibility to the process, stimulated continuous research on iron catalysts. In 1937, alkalized precipitated iron catalysts were successfully operated on a laboratory scale by the Kaiser Wilhelm Institut für Kohlenforschung at 15 atm of water gas at temperatures of 235-250 C ...

"In the Fischer-Tropsch process as developed commercially by the Ruhrchemie A. G. in Germany in 1935-1940, synthesis gas containing 2 volumes of hydrogen per volume of carbon monoxide was compressed to about 7 atm and passed through a granular bed of cobalt catalyst at 185-205 C.

The major products of the synthesis were wax, oil, water, gaseous hydrocarbons, and a minor amount of carbon dioxide. The hydrocarbons were largely straight-chain paraffins. The olefin content varied with pressure, contact time, and temperature. Improved modifications of the Ruhrchemie process involved the recycling of exit gas from the reactor and the use of iron to replace cobalt in catalyst preparation. These changes increased the olefin content of the product and the flexibility of the process, particularly in the control of the proportions of gasoline, diesel oil, and alcohols."

GASIFICATION

General

As for combustion, research and development work on coal gasification in our period can be divided into basic studies and studies of and development of gasification processes. Work in the latter areas can be considered in three categories: (a) processes for making low-Btu or producer gas; (b) continuous processes for making intermediate-heating-value gas; and, (c) intermittent processes for making blue-water gas and carburetted water gas.

Basic Studies

In all gasification processes the endotherm of the steam-carbon reaction must be supplied by the combustion of some of the fuel with air or oxygen. Accordingly, the results of much of the basic work on combustion of carbon are also applicable to the gasification of carbon. However, gasification also involves the reaction of carbon dioxide with carbon and of steam with carbon.

Prior to our period, considerable work had been done on the reaction of carbon dioxide with carbon to form carbon monoxide. This reaction is referred to as the "Boudouard reaction" because Boudouard was the first to study its equilibrium. (115) The reversal of the above reaction can occur in the gas space above the fuel bed and is referred to as the "Neumann reversal" because Neumann was the first to direct attention to the possibility of its occurrence. (116) The carbon dioxide-carbon reaction as well as the steam-carbon reaction were studied extensively by Clement and co-workers (117) and by Rhead and Wheeler (43, 118). The former study presented data on the effect of temperature and time of contact on carbon dioxide or steam conversion. The latter study presented data on reaction rate constants and advanced the concept of a carbon surface covered with an adsorbed film of oxygen referred to as the "carbon-oxygen complex". During our period,

evidence was presented of the existence of the "carbon-oxygen complex"(46, 119-121) and on its role in the mechanism of gasification reactions.

Basic studies of gasification prior to and during our period have been thoroughly reviewed by Mayers(56, 122), Orning(61), and Haslam and Russell(3). In addition to reviewing such studies, van der Hoeven(123) has reviewed developments in the production of producer gas, and Morgan(124) has reviewed developments in the production of blue water gas. Work on the gasification reactions done prior to 1933 has been reviewed by Logan(125) and Elliott(126) who subsequently reviewed developments in the gasification field prior to 1940(127).

As stated earlier the reactivity of carbon to air, to oxygen, to steam and to carbon dioxide are all parallel, (31) Therefore relative rates of reaction determined with one reactant are generally the same with one or the other of the above reactants.

Blakely and Cobb studied the effect of contact time at two different temperatures on the rate of reaction of carbon dioxide with a variety of cokes and other forms of carbon and also the effect of temperature at constant time of contact. (128) Reactivity decreased with an increase in contact time because the more reactive parts of the surfaces had already been consumed. Similar effects would be expected with steam.

In a study of the influence of coke reactivity on the formation of water gas Bunte and Giessen observed that in the case of the more reactive cokes a large fraction of the steam was decomposed by the reaction forming one mole of carbon monoxide and one mole of hydrogen per mole of carbon. (35) They pointed out that the value obtained for the quantity of steam decomposed was not characteristic of the actual conditions in the fuel bed but was influenced by the subsequent establishment of water gas shift equilibrium in the gas phase.

P. Dolch(129) analyzed the data of Bunte and Giessen(35) and of M. Dolch(130) and concluded that there is no experimental evidence that the reaction of steam with carbon to form carbon dioxide and hydrogen occurs but that the reaction forming carbon monoxide and hydrogen with the subsequent water gas shift reaction are of primary importance. In the experiments analyzed, water gas equilibrium was obtained at a temperature of 800 C with reactive carbon materials such as lignite coke and wood charcoal. With less reactive cokes, such as gas coke, water gas equilibrium was not attained until temperatures approached 1000 C.

In earlier studies of the steam carbon reaction the catalytic effect of ash on the water gas reaction was observed. (131, 132) The first studies on the magnitude of the effect of catalyzing the steam carbon reaction were made by Taylor and Neville in 1921 just prior to our period. (133) They found that potassium and sodium carbonates were the most effective catalysts of all

those investigated, and they clearly demonstrated that their effect was indeed catalytic. They believed that the catalysts accelerated the decomposition of the surface complex of carbon and oxygen suggested by Rhead and Wheeler⁽⁴³⁾, thereby exposing a clean carbon surface which was reactive to carbon dioxide. Carbon dioxide produced in the water gas shift reaction would then interact with this carbon to form additional carbon monoxide which in the presence of excess steam would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net increase of gas from the steam-carbon reaction.

Marson and Cobb found that sodium carbonate was the most effective additive in gasifying laboratory coke at 1000 C.⁽¹³⁴⁾ It was found that additions of potassium carbonate and sodium sulfate were just as effective in catalyzing the steam-carbon reaction as was sodium carbonate. In this same investigation it was observed that those additives which produced a maximum effect on the steam-carbon reaction exhibited an analogous effect on the reduction of carbon dioxide by carbon.

Additives were effective in the range of concentrations from 0.5 to 5.0 percent. Sutcliffe and Cobb studied the effect of temperature on coke containing 5 percent additives of various constituents.⁽¹³⁵⁾ The accelerated effect was considerably greater at 600 C than at 1000 C. Similar studies were made by other investigators.⁽¹³⁶⁾

Studies of the mechanism of the catalysis of the carbon gasification reactions showed that the acceleration is brought about by the alternate reduction and reformation of the alkali carbonate in the following manner: The sodium carbonate first reacts with carbon yielding carbon monoxide and sodium in a mol ratio 3:2. The sodium thus transported into the gaseous phase is at liberty to react with carbon dioxide with the subsequent formation of carbon monoxide and sodium oxide. The sodium oxide may then further react with carbon dioxide to form sodium carbonate which is deposited on the carbon surface and is therefore capable of further reaction.^(136, 137)

The steam-carbon reaction may also be catalyzed when carbon is deposited on a refractory impregnated with a sodium-containing salt.⁽¹²⁶⁾

Toward the end of our period, Dent and co-workers laid the foundation for the hydrogasification of coal in studies of the kinetics of methane formation in the reaction of cokes and coals with hydrogen at elevated temperatures and at pressures ranging from 1 to 100 atmospheres.⁽¹³⁸⁾

Producer Gas

Several investigators studied the reactions occurring in the fuel bed of a gas producer.^(3, 139) The zones designated from top to bottom are: ash

zone; oxidation zone; primary reduction in which the steam-carbon and carbon-dioxide-carbon reactions occur; the secondary reduction zone in which the water gas shift and carbon dioxide reduction reactions occur; distillation zone in which the volatile matter in the fuel is added to the gas; and, finally, the gas space in which a decrease in heating value may occur as a result of the so-called "Neumann reversal" of the Boudouard reaction. (3)

The effect of steam in the air blast of a producer was well known prior to our period. (140) Additional work in our period established that the efficiency of the producer reached a maximum between 0.3 and 0.4 lb of steam per lb of coal. (141, 142) However this range may have to be exceeded in practice to avoid clinker formation.

Work on the performance of full-scale producers done during our period was summarized. (3, 123) Reference (123) discusses a variety of theoretical, thermodynamic, and stoichiometric analyses of the producer gas process.

Development work on the slagging gas producer was done prior to our period. (123) Data from tests on these producers (123, 143) made in our period and on some of their further developments and operating characteristics are described in Reference (144).

Continuous Production of Intermediate Heating Value Gas

The use of oxygen in the blast of a producer was advocated just prior to the beginning of our period. (145-147) Experimental work done first at atmospheric pressure led eventually to the development of the Lurgi process which operated at 20 atmospheres. (148) Data on the effect of pressure in increasing the heating value of gas from the Lurgi process was presented by Hubmann (149) and Danulat (150).

The Lurgi process commercialized in 1936 made possible the continuous production of gas having a heating value as high as 450 Btu per cu ft.

The Winkler generator which used oxygen or oxygen-enriched air and steam to gasify lignite or semicoke was developed and used commercially in our period. (150, 151) In this process a fluidized bed was used for the first time in gasifying solid fuel.

Carburetted Water Gas

The production of carburetted water gas reached a peak in 1926 when it represented about 60 percent of the total manufactured gas in the United States. (124) To put this into perspective, the energy in this quantity of gas

represents about 0.5 percent of the energy in the natural gas produced in 1973. Today (1974) carburetted water gas is not being produced in the United States. In view of this, developments in our period are mentioned only briefly. These have been discussed and include the application of automatic controls; the use of mechanical grates; the substitution of heavy oil for gas oil; the application of the back-run process; reforming of refinery and natural gas in water gas generators; and, the production of high-Btu gas that could be mixed with or even substituted for natural gas. (124, 127)

SUMMARY

In the period 1924-1940, we saw many developments in fuel science and technology that were innovative and of lasting importance. Methods for classifying coals and their petrographic constituents were developed. Many tests for determining the properties of coals and cokes were standardized. In the United States a standard method for carbonizing coal was developed to determine yields of coke, gas, and tar, and to evaluate the utility of these products.

In the field of combustion we advanced our understanding of the basic combustion reactions and of combustion of coal in fuel beds as well as in pulverized form. This latter development is, until now, the most widely applied advance of any in our period.

In the area of gasification we also advanced our understanding of basic gasification reactions. But most importantly we saw many innovations such as the use of oxygen; gasification at elevated pressures; the use of fluidized beds in gasification reactors; the direct gasification of coal and coke with hydrogen; and the improvement of slagging gasifiers.

The period 1924-1940 saw the development and commercialization of technology for producing liquid fuels directly from coal and indirectly by the catalytic conversion of carbon monoxide and hydrogen produced from coal. Commercial synthetic-liquid-fuel plants were important to Germany in World War II but such processes are not generally economical today. However modifications of this technology may be economic in the near future.

The advances in gasification and production of synthetic hydrocarbons have not yet had a major impact on the field of energy conversion, but they most certainly will in the future.

It is apparent that the period 1924-1940 was most productive in developing fuel science and technology that has given us energy-conversion technology that has made possible the widespread use of coal and other fuels in the generation of electricity today. In the emerging era of producing synthetic

gaseous and liquid hydrocarbons from fossil fuels we will certainly draw heavily on the advances in gasification and hydrogenation made in the 1924-1940 period. Let us hope that the next 50 years of research and development on fuel science and technology and on other sources of energy will be as productive of useful technology as the first part of the past 50-year period.

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