

## FUEL CHEMISTRY 1940-1960

by

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Harlan W. NelsonI. INTRODUCTION

During the period 1940-1960, the study of fuel chemistry was subject to a serious perturbation that persisted for 6-8 years (1945-53), after which research in this field essentially resumed its previous pattern. Dr. Fieldner gave an excellent review of this field in his paper for the ACS Golden Anniversary.

Up to the end of World War II, those doing research in fuel chemistry were concerned to a large extent with coal. The ranking of various coals, the determination of its components, the study of the properties of these components and especially attempts to elucidate the structure of the coal substance were some of the major subjects covered. The elucidation of the coal structure was investigated by studying the products found when various coals or coal fractions were subjected to a fairly wide variety of chemical reagents or treatments.

Those concerned with the utilization of coal were looking primarily for ways to convert it to a smokeless fuel (or at least reduce smoke formation), for ways to determine its coking properties, for ways to use blends as a means of producing a better coke for metallurgical uses, and for ways to reduce the amount of premium medium-volatile coals used so as to use a greater proportion of the less expensive high-volatile coals. The behavior of various coals under the influence of heat and pressure were studied in the laboratory and in a number of experimental ovens. The gas, oil, tar, and pitch resulting from carbonizations were examined and processes were developed for separation of many important chemical products.

The bulk of the research on coal was carried out by a relatively small number of organizations, almost all falling into three classes: the U. S. Bureau of Mines, several of the Schools of Mineral Industry in various universities, and a number of State Geological Surveys or Bureaus of Mineral Industries. This research partook substantially of an academic nature - the research people were in search of knowledge primarily for its own sake, but always with the hope that this knowledge would prove useful in the future.

The large consumers of coke did their research on carbonization primarily in order to develop more efficient, economical processes or to produce a more desirable end product.

The above do not by any means cover the full range of interests of the Fuels Division, but an examination of past programs shows that these subjects were predominant.

Toward the end of World War II, with its shortages and rationing and the expectation of "taking up where we left off", serious concern regarding the country's petroleum futures emerged. It was this situation which gave rise to the perturbation.

To show briefly the situation, Figure 1 shows the U. S. oil proven reserves and production during the years 1935-1944. The reduced rate of discovery and the then fantastic increase in consumption led to serious concern about our oil futures and resulted in the passage of the Synthetic Liquid Fuels Act. For a few years the interests of the Division of Fuel Chemistry were sharply focussed on the problems of producing gasoline from coal and from oil shale.

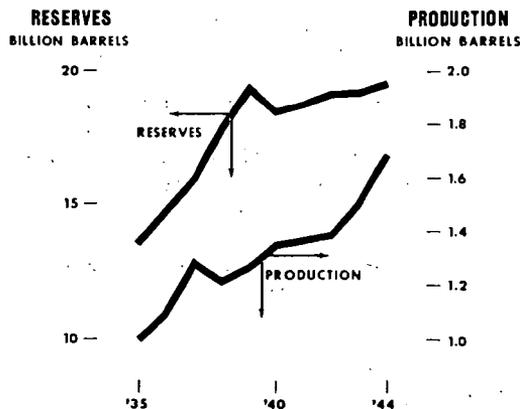


FIGURE 1. CRUDE PRODUCTION AND RESERVES, 1935-1944

Looking back over the programs of the Division meetings, between 1940 and 1960 we find a sharp rise (in many cases from none at all) in papers on coal hydrogenation, coal gasification, coal reactions, and Fischer-Tropsch synthesis. The emphasis was all on liquid fuels; no one thought of natural gas, except as a potential source of hydrogen for coal hydrogenation.

Institutions previously engaged in coal research promptly shifted the emphasis in their work toward the solution of what was generally regarded

as a most pressing problem. In addition, there began to appear papers whose authors worked for companies whose future was tied closely to petroleum or to products made therefrom.

The emphasis in research again shifted with the later advent of the Middle East oil at prices that were extremely attractive, and with the estimated reserves in the Middle East that seemed almost unlimited. Interest in liquid fuels from coal subsided very rapidly, the Office of Synthetic Fuels was eliminated, and many of the academic research workers (or their successors) returned to the study of coal as a substance - looking for an increase in knowledge that would contribute in the future to the advancement of science.

Rarely, if ever, has such a severe dislocation in a field of research been experienced, and rarely has interest in a particular area of science and technology disappeared so rapidly.

This is the period that we will attempt to explore. We will concentrate to some extent on the production of liquid fuels from coal, partly because it caused the perturbation and partly because of its present interest.

In order to supply some background we will review the fuels situation worldwide and in the U. S. during the period 1940-1960.

Because of its importance at the time and because of its relevance today we devote a fair amount of time to the production of synthetic liquids from coal, and the production of synthesis gas and hydrogen, also from coal. From some years these occupied the attention of many of those concerned with coal chemistry.

The history of the demise of that effort and a brief summary of the situation in 1960 will complete our story.

## II. REVIEW OF FUELS SITUATION - 1940-1960

In the United States in 1940, there was little reason for concern regarding domestic energy sources. Coal, petroleum, and natural gas (locally) were all in abundant supply. Reserves, if considered at all, were judged to be ample for the foreseeable future. As a matter of fact, one concern was the persistent displacement of coal as a source of energy by petroleum and its derivatives and the consequent reduction of coal mining. Much natural gas was being flared or used for the production of carbon black, and the by-products were wasted to the air.

The distribution of our various sources of energy is shown in Figure 2 from 1940 to 1960. At the beginning of the period, coal supplied about half of our needs, but lost ground steadily; first to petroleum then after the advent of gas pipelines, to natural gas. By 1960 coal was supplying only about one-fourth of our energy needs. These needs had increased significantly during the postwar years. Petroleum, whose situation was so disturbing during the immediate postwar years, had increased its share of the total energy consumption to about 42 percent by virtue of almost doubled production during the 20 years.

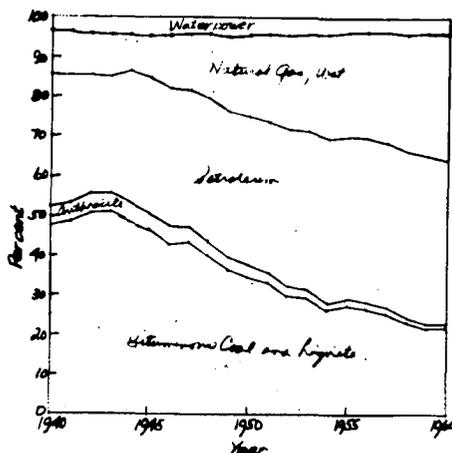


FIGURE 2. CONSUMPTION OF MINERAL FUELS AND WATER POWER IN U. S., 1940-1960

Natural gas, until the long gas pipelines were built, held quite steady at around 10 percent of the total. However, once there were means to distribute this gas, its convenience, cleanliness, and above all its low price led to remarkable gains. By 1960 gas was supplying almost one-third of our total energy consumption. Annual production rose from something under 4 trillion cubic feet in 1940 to 13 trillion cubic feet in 1960, a more than threefold increase. As we all know, this increase continued almost unabated for the next decade and led in large part to our present situation.

This then has been the pattern of the distribution of the energy load among our principal sources. It will perhaps be worthwhile to look at the situation for each one.

Figure 3 shows the story for coal production. No figure for reserves is shown because there are such wide variations depending on the basis for

the estimate. We have been assured by one of the power companies that we have more coal in the ground than the Arabs have oil. If this does not reassure us, then estimates ranging from 200 to 1000 years' supply should give some comfort.

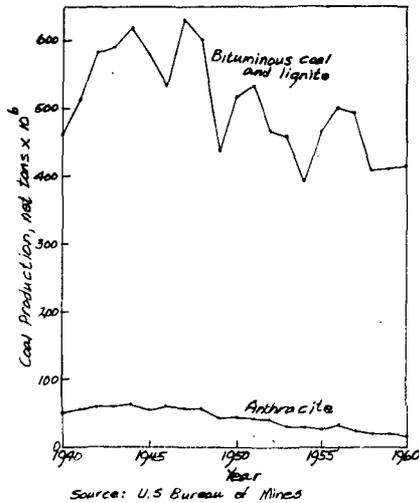


FIGURE 3. COAL PRODUCTION, 1940 TO 1960

The war and its aftermath gave some impetus to coal production, but the inroads of oil and gas began to show their effect and production of coal had decreased by almost one-third by 1960.

Figure 4 shows data on crude petroleum production. On this scale the sharp increase during the war is overshadowed by the continuing increase over the rest of the decade. World production, however, about 1950 began to show a tremendous rate of growth, doubling from 1950 to 1960. The U. S. share of world production dropped from over two-thirds to one-third.

Figure 5 shows the changes in world and U. S. reserves.

Known reserves in the U. S. showed a modest but steady growth throughout the period, but since production rose much more rapidly than new reserves, there was a significant decline in the reserves-to-production ratio.

The Middle East discoveries starting in 1950 began to grow at an almost unbelievable rate. From a little over 20 billion barrels in 1950, the estimated reserves rose to almost 200 billion barrels by 1960, a ten-fold increase in 10 years! After about 1957 reserves in other parts of the world began to increase also and the total world reserves rose to about 270 billion barrels.

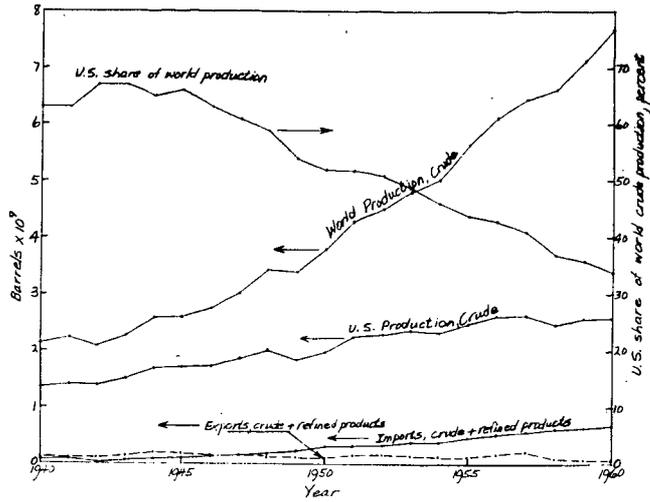


FIGURE 4. CRUDE PETROLEUM PRODUCTION

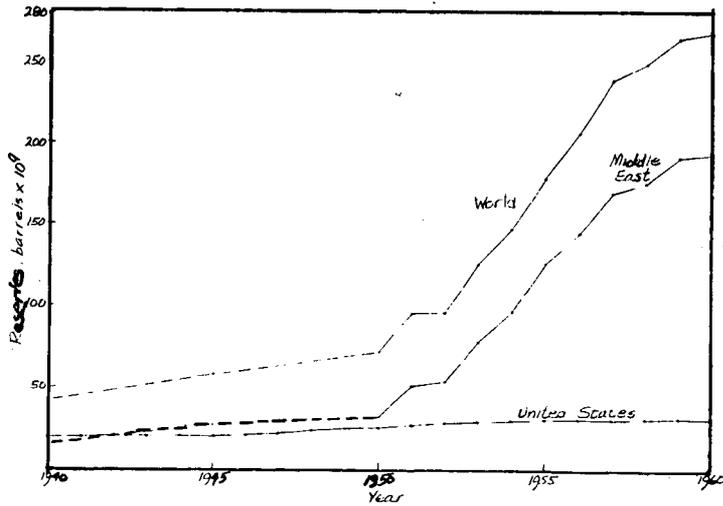


FIGURE 5. PETROLEUM RESERVES: FREE WORLD TOTAL, MIDDLE EAST, AND THE UNITED STATES, 1940 TO 1960

Figure 6 shows the history of gas during this period. In 1946 production was about 5 trillion cubic feet and by 1960 had risen to over 15 trillion cubic feet. However, for a number of reasons, the development of new reserves failed to keep pace with increases in production. In 1945 the ratio of reserves to annual production was over 30. By 1960 this had dropped to 20!

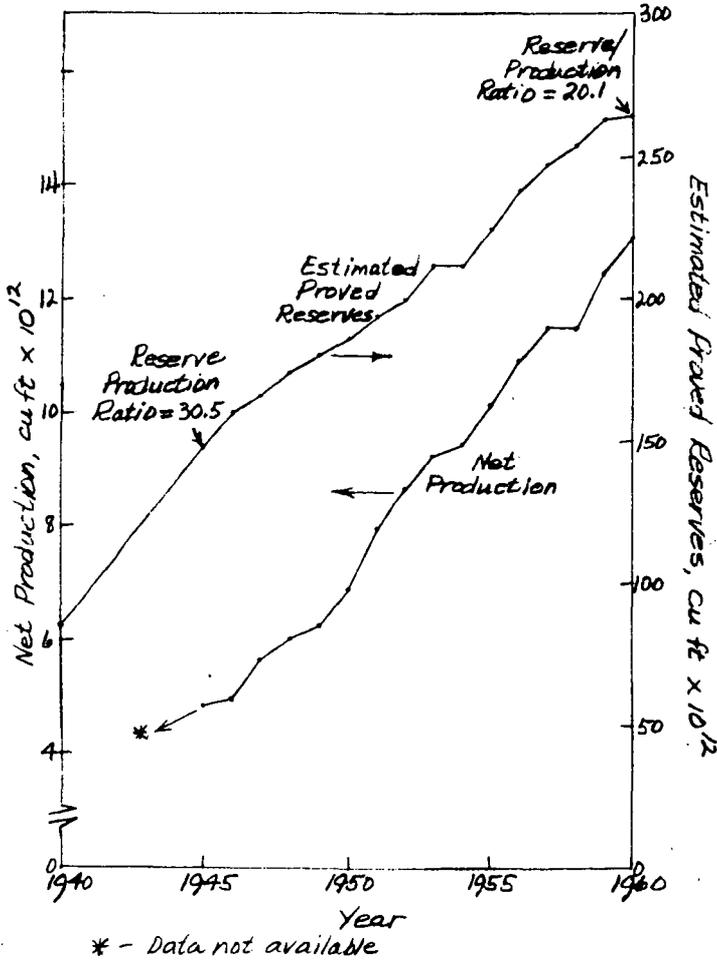


FIGURE 6. NATURAL GAS ESTIMATED PROVED RESERVES AND NET PRODUCTION, 1940 TO 1960

### III. PRODUCTION OF LIQUID FUELS FROM COAL (1946-1953)

As noted above, the strong worry about postwar fuel supplies led to an almost complete dedication to solutions of the problems of producing synthetic fuel.

Not only was it necessary to develop coal hydrogenation processes, but also to develop the Fischer-Tropsch synthesis, the production of hydrogen and synthesis gas from coal, and finally the purification of those gases.

#### A. Coal Hydrogenation

In what seemed to be an emergency, the research and development work in the U. S. drew very heavily at the beginning on the information regarding German war-time activities. In the closing days of the war, British and U. S. Technical Oil Missions followed hard on the heels of the advancing armies, collecting documents, drawings, and intelligence concerning the top German men in the field who might be available for information and advice concerning the work in the U. S. and Great Britain. A considerable number of these men left Germany for England and the United States. Their contribution was significant.

German Practice. Germany used a variety of carbonaceous feedstocks in seven major plants. Detailed descriptions of these plants will not be attempted because of time limitations.

In general the coal was pulverized and made into a paste (50 percent coal) with a recycle heavy oil; catalyst was added and the paste preheated in the presence of some hydrogen as shown in Figure 7. The heated mixture passed through a series of three converters usually operating in the neighborhood of 900 F and 10,000 psi. By stepwise pressure letdown at the outlet, oil and gaseous product were separated and sent to the distillation system for recovery. The residue (ash, catalyst, unconverted coal, and the heaviest oil) was diluted with heavy oil, and centrifuged to recover as much oil as possible. The centrifuge residue was sent to coking kilns where additional oil was recovered and the solid residue was discarded.

The high-boiling portions of the product oil were vaporized and hydrogenated further over catalyst contained in a series of baskets in the vapor-phase converter as shown in Figure 8.\* The character of the final products was determined by the amount of recycle and by the amount of hydrogen used. Any reasonable product mix was possible, but the lighter the product, the smaller the plant output and the greater the hydrogen consumption.

\* At lower temperatures.

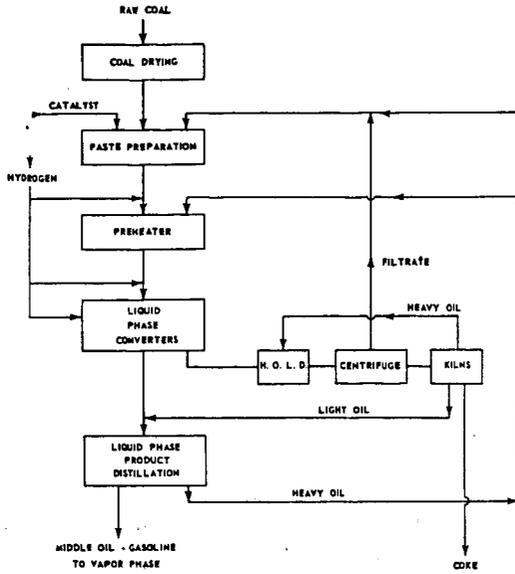


FIGURE 7. GENERAL SCHEME, LIQUID PHASE

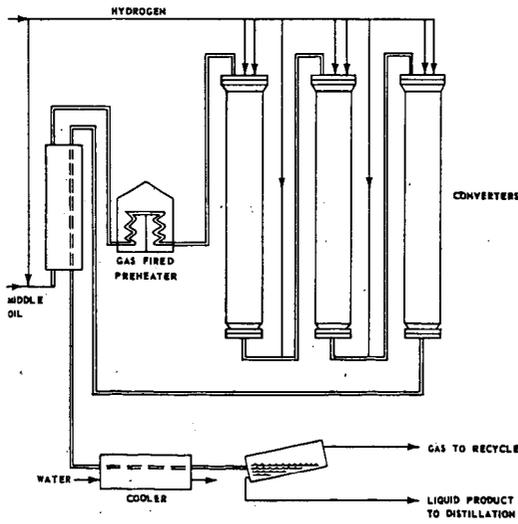


FIGURE 8. FLOW DIAGRAM, VAPOR PHASE

It should be borne in mind that although Germany produced over one-third of its total requirements by synthesis, this amounted to only 100,000 barrels per day. This may be compared with the 1973 consumption of 16-17 million barrels per day in the U. S.

U. S. Bureau of Mines Demonstration Plant. The construction of this plant was authorized by the Synthetic Liquid Fuels Act. The basis for the design was patterned after the German operations at Lutzkendorff and Welheim. The design was developed with the aim of applying modern U. S. engineering practices whenever such applications showed promise of increasing throughput or efficiency, promoting safety, or decreasing the cost of the gasoline product. The converters (2 liquid phase, one vapor phase) were 39 feet long and approximately 20 inches inside diameter. The plant was designed to charge just under 2 tons of coal per hour and to produce about 200 barrels per day. When the operations terminated in 1953, 2000 to 4000 tons each of four bituminous coals, one sub-bituminous coal, and one lignite had been processed.

The emphasis was on operability and, although, not all of the problems were successfully eliminated, a remarkable amount of progress had been made.

Bureau of Mines Pilot and Research Efforts. Research on coal hydrogenation started in the Bureau in 1936 and with the advent of the Synthetic Fuels Program a new laboratory was built at Bruceton, Pennsylvania. The bench-scale and pilot-plant research carried on here made a large contribution to the construction and operation of the demonstration plant. Studies were performed on new catalysts, catalyst preparation, effects of process variables, reaction mechanism, and other significant elements.

Activities in England. England had a commercial coal hydrogenation plant in operation in 1937. When war came, because of the bomb hazards, coal operations were terminated and the plant was used at lower pressures for the hydrogenation of creosote oils. Undoubtedly some research and development were carried on but references in the literature are scarce.

Union Carbide Company. The Union Carbide Company announced in 1952 the operation of its coal-hydrogenation plant at South Charleston, West Virginia. It was stated that the process would be aimed at the production of chemical raw materials and intermediates rather than liquid fuels from coal. Pressures were lower (6,000 psi maximum), temperatures lower, throughputs higher, and hydrogen consumption lower than in conventional liquid- and vapor-phase operations. A substantial part of the coal was liquefied to asphalt, and the announced intention was to feed this

to a unit for the production of metallurgical or specialty coke. The lighter products were to be processed to separate chemicals or classes of chemicals for sale or use as such. The unit was stated to have a design capacity of 300 tons of coal per day with the expectation that this could be increased as operating experience was gained.

Since operating conditions differed so widely from those actually required for gasoline production, this operation is not of direct interest in connection with synthetic fuels.

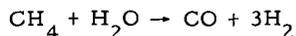
### B. Fischer-Tropsch Synthesis

Work on the Fischer-Tropsch Synthesis had been carried out for many years in Germany and had been brought to commercial production, although on a limited scale.

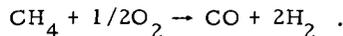
With the prospects of petroleum shortages in the U. S., interest in the process became widespread. In general, there were two basic approaches.

One was a high-temperature fluid bed synthesis aimed primarily at the production of gasoline. This was the path followed by the petroleum companies. Such a synthesis required a high ratio of hydrogen to carbon monoxide, to minimize deposition of carbon on the catalyst. In cases where cheap methane was available, the decomposition of methane with steam or oxygen was used as a source of synthesis gas.

The methane was reformed with steam:



or partial combustion with oxygen:



The hydrogen-to-carbon monoxide ratio was adjusted by water-gas shift if necessary to give the desired feed to the synthesis unit.

Construction of two commercial plants was started and one of these was put in operation. Little was published on the results except that the operation was not economically competitive at that time with gasoline from petroleum.

The second approach to liquid fuels from coal by the Fischer-Tropsch reaction was generally a compromise between the German operations and those contemplated by the oil companies. The coal was to be gasified as described below, the deleterious sulfur compounds removed, and the H<sub>2</sub> to CO ratio adjusted by the water-gas shift reaction, to produce the desired

feed to the synthesis unit. There were a goodly number of variations proposed each with its own advocates. Also, there was required a substantial study of the theoretical aspects of the process. The thermodynamics and kinetics of the various schemes were explored, and the work required was multiplied by the possibility of hot and cold gas recycle, additions of carbon dioxide or water to the feed, and a wide variety of means to remove the heat of reaction and to control temperatures. The search for new and improved catalysts also was pursued vigorously.

Undoubtedly much of the research and development related to the Fischer-Tropsch processes has never been reported, but the publications that did issue bear ample evidence of the large amounts of work that was done.

The Bureau of Mines Laboratories at Bruceton did much bench-scale and pilot-plant experimentation, and a demonstration plant was constructed and operated at Louisiana, Missouri. There still remained unsolved problems when the plant was shut down in 1953, but it is reasonable to believe that a reliable, sustained operation of this process could be achieved.

### C. Coal Gasification

Whether coal hydrogenation or Fischer-Tropsch were used to make liquid fuels, hydrogen or synthesis gas would be needed in great quantities.

Petroleum consumption in the United States was in 1946 about 5 million barrels a day; if synthetic fuels were to make a significant contribution, outputs of 1/2 million barrels a day certainly could be visualized. Coal hydrogenation required about 8,000 cubic feet of hydrogen per barrel of liquid product, and the Fischer-Tropsch process required around 30,000 cubic feet of synthesis gas per barrel. Gas requirements then could range from 4 to 15 billion cubic feet per day, or 1.5 to 5 trillion cubic feet per year. On a volume basis, that is of the same order as the total natural gas production of the United States at that time.

Although it was proposed in some cases to make hydrogen or synthesis gas by reaction of methane with steam or oxygen, even in those days it was practical only if for some special reason methane was extremely low in price.

For most of the country, the source of synthesis gas or hydrogen must be coal, and the gasification of coal became the subject of very extensive investigation. If synthetic fuels were to be used widely, they must be produced in almost every part of the country and, if possible they must use coals locally available. This meant that the preferred gasification step should be one in which almost any coal was suitable. As is known today, this puts some very stringent restrictions on the gasification process.

Lignite seemed favorable because of its suspected higher reactivity, but the higher moisture and ash content, and the location of most of the lignite deposits did not make it attractive as the universal feed.

Much of the bituminous coal available in the heavily industrialized regions of the country was moderately or strongly caking, which difficulty would have to be overcome. In any case most of the coal-gasification process development work was aimed at a process that could use any coal as a feed.

Some processes operated at atmospheric pressure, but most were designed for operation at pressures that would permit gas purification and Fischer-Tropsch operations without further compression. For coal hydrogenation, compression costs would be substantially reduced with hydrogen at 300-400 psi instead of at atmospheric pressure.

Substantially all of the processes under investigation used oxygen and steam to gasify the coal. In the few attempts that were made to eliminate or minimize the use of oxygen, analyses showed that the economics were not favorable.

The surge of interest in this field can be illustrated by the United States patents granted on gasification processes. The following tabulation shows the number of patents granted whose application dates fall in the period indicated.

	<u>Number</u>
1930-1944 (avg/yr = 5.5)	77
1945	13
1946	25
1947	29
1948	28
1949	31

These figures apply only to United States patents.

It is not possible to discuss each of these many approaches. There are many literature references that describe them in detail and judging by the publications, many of the members of the Fuel Division at that time were heavily preoccupied with the problems of coal gasification. Except for the Bureau of Mines Synthetic Fuels Plant, and the Du Pont Company at Belle, West Virginia, most did not progress beyond a throughput of 100 to 500 pounds of coal per hour.

At Louisiana, Missouri, the Bureau was able to obtain a Linde-Franke oxygen plant with a production of 25 tons per day and the gasification section was designed on that basis. Coal was pulverized to about 80 percent through 200 mesh and transported by the oxygen to a Koppers-Totsek gasifier. Steam was preheated to about 2000 F in a pebble heater fired by natural gas.

The unit was a horizontal cylinder with steam, coal, and oxygen fed at each end and a gas offtake near the top center. After a waste heat boiler, the product was water scrubbed, passed through an electrostatic precipitator, and sent to the compressor or to atmospheric pressure storage.

The 2000 F steam superheat was to promote reaction and to reduce the oxygen demand. It was found that this was not economical and later operations in another unit used steam at 1000 F. The operation of these units was primarily experimental, and almost all of the gas supplied to the Fischer-Tropsch unit was made from coke in a Kerpely producer with steam-oxygen blast. (Operation of this process had been practiced for some years for the production of ammonia synthesis gas.)

The Du Pont Company installed a commercial-sized atmospheric coal-gasification unit in the plant at Belle, West Virginia, primarily for the production of hydrogen for ammonia synthesis. The design used was an outgrowth of their own development work, plus that of the Babcock and Wilcox Company in cooperation with the Bureau of Mines at Morgantown, West Virginia. The unit was designed for the production of 25 million cubic feet per day and is reported to have operated satisfactorily. No data have been published. After more than 2 years of use, operations were terminated in favor of the use of natural gas as a raw material.

Theoretical Studies. At the same time that the process development work was in progress, there was a large amount of research and development devoted to the thermodynamics and the kinetics of steam-coal-oxygen-synthesis gas systems. This work was essential to the design of the various gasifiers, it led to new gasifier concepts, and it led to means of increasing coal conversion and decreasing oxygen requirements.

#### D. Synthesis Gas Purification

The Fischer-Tropsch catalysts under investigation were in general very sensitive to sulfur poisoning, and much effort was devoted to purification of the synthesis gas from coal. Many commercial processes existed, but it was felt that further work would result in more efficient and economical processes. Except for that at Louisiana, Missouri, none of these newer approaches were placed in operation on a significant scale, but from the standpoint of fuel chemistry research and development, a considerable effort was expended.

#### IV. ADVENT OF INCREASED FOREIGN OIL SUPPLIES

Even as the United States was engaged in a major effort to develop oil supplies for our anticipated demand, the development began of new oil reserves in the Middle East and in Africa.

In 1951, the U. S. had a consumption of a little over 2 billion barrels per year and proven reserves of only 25 million barrels. Even at this low figure, only the Middle East showed more reserves, at about 50 billion barrels. World reserves were only 103 billion barrels.

By the end of 1961, proven U. S. reserves had increased to about 38 billion barrels and consumption had risen to over 3-1/2 billion barrels per year. Elsewhere, however, the situation was vastly different. The Middle East reserves had increased to almost 200 billion barrels, Russia's proven reserves were about equivalent to those of the U. S. Africa was beginning to be developed, as were other eastern hemisphere sources. New additions to reserves were being made in Canada, and in the Carribbean countries. World reserves had risen to 305 billion barrels in the face of rising consumption in the U. S. and in the rest of the world.

The increase in world reserves cast increasing doubt on the wisdom of continuing the urgent U. S. effort to develop synthetic liquid fuels. A change of administration in the U. S. added impetus to the movement to abandon this effort, and the Office of Synthetic Liquid Fuels was eliminated in 1953. The Demonstration Plants were shut down, laboratory staffs were reduced, and the research emphasis for those remaining was shifted to other lines of endeavor.

The programs of the Fuel Chemistry Division for the remainder of the decade reflected this change very quickly. Papers describing work on synthetic fuels almost disappeared, and other subjects began to replace them.

#### V. SITUATION IN 1960

At the end of 1960 then, we find the research in fuels chemistry focussed on much the same fields as in 1940. The upset occasioned by the effort on synthetic fuels had largely subsided and pressures associated with it had largely been relieved.

There were evidences of increasing concern regarding our diminishing domestic resources, especially with respect to natural gas. Some efforts

were being restarted on the gasification of coal and on the synthesis of pipeline-quality gas - but these were not extensive. Discussing this aspect further would probably carry this paper over into the realm of the following one.

Although the fields of fuels research generally were comparable to those in 1940, it does not mean that no progress was made during the 20 years. In spite of the war interruption, much fruitful work was done and our knowledge of the constitution, character, and utilization of fossil fuels had been advanced significantly.

#### ACKNOWLEDGEMENT

Preparation of this paper was made possible by a grant from the Energy Program of the Battelle Memorial Institute of Columbus, Ohio.