

ADVANCES IN FUEL CHEMISTRY 1961-74

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OUR CHANGING FUEL SUPPLY/USE PATTERNS

The 1961-74 period has been characterized as one of greatly expanding energy use, an increase of over 65 percent occurring in the United States in this period. (Table 1 and Fig. 1) ⁽¹⁾. However, more fundamentally, it has been a period of change, a reversal from abundant, cheap fuels to one of real and impending fuel shortage.

TABLE 1. UNITED STATES TOTAL GROSS CONSUMPTION OF ENERGY RESOURCES BY MAJOR SOURCES, ¹ 1947-70 REVISED, AND 1971 PRELIMINARY ⁽¹⁾ (With Added Data Through 1973)

(Trillion Btu)

Year	Anthracite	Bituminous coal and lignite	Natural gas dry ²	Petroleum ³	Total fossil fuels	Hydro-power ⁴	Nuclear power ⁴	Total gross energy inputs	Percentage change from prior year
1947	1,224	14,600	4,518	11,367	31,709	1,326	—	33,035	—
1948	1,275	13,622	5,033	12,557	32,487	1,393	—	33,880	+2.6
1949	958	11,873	6,289	12,119	30,039	1,449	—	31,488	-7.1
1950	1,013	11,900	6,150	13,489	32,552	1,440	—	33,992	+8.0
1951	940	12,285	7,248	14,848	35,321	1,454	—	36,775	+8.2
1952	897	10,971	7,760	15,334	34,962	1,496	—	36,458	-0.9
1953	711	11,182	8,156	16,098	36,147	1,439	—	37,586	+3.1
1954	683	9,512	8,548	16,132	34,875	1,388	—	36,263	-3.5
1955	599	10,941	9,232	17,524	38,296	1,407	—	39,703	+9.5
1956	610	11,142	9,834	18,627	40,213	1,487	—	41,700	+5.0
1957	628	10,640	10,416	18,570	40,154	1,561	1	41,706	—
1958	483	9,366	10,995	19,214	40,058	1,636	2	41,696	—
1959	478	9,332	11,990	19,747	41,547	1,591	2	43,140	+3.5
1960	447	9,693	12,699	20,067	42,906	1,857	6	44,569	+3.3
1961	404	9,502	13,228	20,487	43,621	1,680	18	45,319	+1.7
1962	363	9,826	14,121	21,267	45,577	1,821	24	47,422	+4.6
1963	361	10,353	14,843	21,950	47,507	1,767	34	49,308	+4.0
1964	365	10,899	15,848	22,386	49,298	1,907	35	51,240	+3.9
1965	328	11,580	16,098	23,241	51,247	2,058	38	53,343	+4.1
1966	290	12,205	17,393	24,394	54,282	2,073	57	56,412	+5.8
1967	274	11,982	18,260	25,335	55,841	2,344	80	58,265	+3.3
1968	258	12,401	19,580	27,052	59,291	2,342	130	61,763	+6.0
1969	224	12,509	21,020	28,421	62,174	2,659	146	64,979	+5.2
1970	210	12,712	22,029	29,814	64,565	2,650	229	67,444	+3.8
1971	186	11,857	22,819	30,570	68,898	2,862	404	68,698	+1.8
1972	150	12,345	23,125	32,966	68,886	2,946	576	72,108	+4.9
1973	140	13,380	23,558	34,689	71,767	2,941	853	75,561	+4.8

¹Gross energy is that contained in all types of commercial energy at the time it is incorporated in the economy, whether the energy is produced domestically or imported. Gross energy comprises inputs of primary fuels (or their derivatives), and outputs of hydropower and nuclear power converted to theoretical energy inputs. Gross energy includes the energy used for the production, processing, and transportation of energy proper.

²Excludes natural gas liquids.

³Petroleum products including still gas, liquefied refinery gas, and natural gas liquids.

⁴Outputs of hydropower (adjusted for net imports or net exports) and nuclear power converted to theoretical energy inputs calculated from national average heat rates for fossil-fueled steam-electric plants provided by the Federal Power Commission. Energy input for nuclear power in 1971 is converted at an average heat rate of 10,660 Btu per net kilowatt-hour based on information from the Atomic Energy Commission. Excludes inputs for power generated by nonutility fuel-burning plants, which are included within the other consuming sectors.

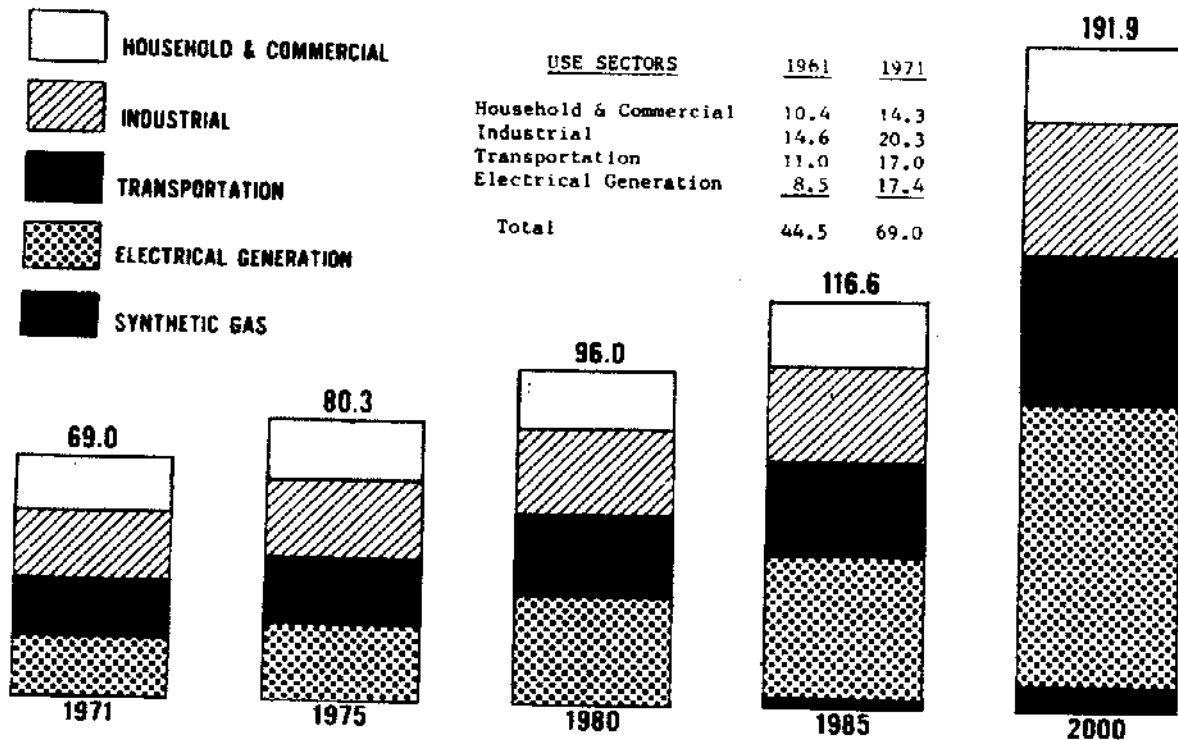


FIGURE 1. UNITED STATES ENERGY CONSUMPTION BY SECTOR
1971 - 2000
(Quadrillion Btu's)

The character of the fuel-use pattern has altered significantly; greatest growth is in use of fuels for transportation and for generation of electricity. A new factor of far-reaching importance has been fuel-use restrictions imposed for prevention of environmental degradation. These restraints have affected the fuel-use pattern: for example, in switching from coal to oil for generation of electricity.

There has also been a change in the fossil-fuel supply pattern. Gas now supplies 33 percent, petroleum 43 percent, and coal 19 percent of our energy needs. A new national feature has been the recognition that coal and oil shale must become major suppliers of energy in the United States in the period 1985-2000 and beyond. A significant activity, therefore, has been the initiation of a greatly expanded effort in coal and oil shale research.

The 1961-74 period is also unusual in the initiation of tar sands exploitation and also of the use of nuclear energy for power use, the latter growing to about 2 percent of our energy spectrum.

The 1961-74 period has been characterized by the spectacular growth in petrochemicals in which many examples of innovative chemistry have contributed to the success of new products and improved processes for chemicals, particularly in the plastics field.

The changing patterns of fuel use and fuel supply have interacted with fuel chemistry, in that new and improved chemical processes have satisfied a need or have provided a means or cause for changes. There have truly been a number of breakthroughs, mostly in petroleum chemistry, no doubt because of the much greater research effort in these areas. It can be confidently expected that synthetic-fuels chemistry will provide breakthroughs in this area in the next few decades.

PETROLEUM CHEMISTRY

The greatly expanded use of petroleum has been reflected in an intensive search for new and improved refining-process technology seeking better products and higher efficiencies. Remarkable improvements have recently been achieved in several refining processes, despite their relative maturity (>25 years) and past research efforts. Thus, means of obtaining greatly improved yields of desired products and suppression of unwanted products have been uncovered for catalytic cracking, reforming, and hydrocracking. Improvements in hydrodesulfurization, although perhaps not as spectacular, are important, especially in the ability to process heavy petroleum residua.

Hydrocarbon Chemistry

Advances in hydrocarbon chemistry were reviewed by Schmerling in 1972 as part of a comprehensive Petroleum Chemistry Symposium.⁽²⁾ He concluded that perhaps the most important advance in theoretical hydrocarbon chemistry during the past 50 years was the postulation that highly reactive intermediates were involved. Such intermediates can be free radicals, carbonium, or carbanion ions or others such as carbenes. Catalytic surface complexes should also be included. Earlier work by Whitmore describing carbonium ions postulated an electron-deficient carbon atom, this deficiency inducing a migration giving rise to a rearranged product. More recently Olah has suggested that two types of positive carbon ions exist: The classical trivalent ion and a pentacoordinated nonclassical ion.⁽³⁾ The pentacoordinated ion is considered to consist of five atoms bound to a carbon atom by three single bonds and a two-electron three-center bond. Postulation of the pentacoordinated ion has many advantages in explanation of reaction mechanisms.

A very interesting catalytic reaction of olefins was described by Banks and Bailey in 1964.⁽⁴⁾ They showed that alkenes undergo disproportionation to homologs of higher and lower molecular weight in the presence of alumina-supported molybdenum oxide, etc., at 100-200 C. Propylene, for example, was disproportionated to ethylene and n-butylenes at 94 percent efficiency at 43 percent conversion. The mechanism of the reaction may be considered to

proceed by a four-center ("quasicyclobutane") intermediate involving the four doubly bonded carbon atoms of two molecules of olefin and catalyst.

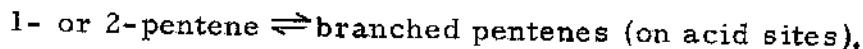
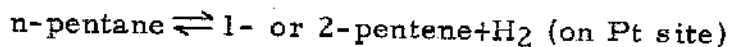
Considerable progress has been made in alkali catalyst hydrocarbon reactions. The behavior of carbon ions is remarkably different from that of carbonium ions. Alkyl groups in the former do not migrate. Primary carbon ions are more stable than secondary ions which are more stable than tertiary ions. The reverse is true with carbonium ions. This leads to much different catalytic products.

Catalytic Reforming

Catalytic reforming of petroleum has taken great strides. The Free-World catalytic reforming capacity totals in excess of seven million barrels per day with about 50 percent of this capacity located within the United States and Canada. The bulk of the U. S. capacity has been built during the past two decades in response to sharply increased demand (beginning about 1952) for high-octane-number gasolines needed to fuel high-compression-ratio, large-displacement engines.

Aromatics (benzene, toluene, and xylenes) are important components of the high-octane reformat. The hydrogen produced as a "by-product" in reforming has become increasingly valuable for use in associated hydrotreating and hydrocracking operations.

A significant advance was the recognition of the dual-function nature (isomerization and hydrogenation) of reforming catalysts. ⁽⁵⁾ The mechanism of hydrocarbon reactions over such dual-function catalysts has been established and is illustrated for the isomerization of n-pentane. ⁽⁶⁾



Branched pentenes + H₂ \rightleftharpoons isopentane (on Pt site). The amount of olefin present in the gas phase is extremely small because of the large excess of hydrogen used in the process and the moderate temperature and high pressure. It is important to recognize that dual-function catalysts can accomplish more than is achieved by passing reactants through two reactors in sequence, each filled with a different single-function catalyst. ⁽⁷⁾

As a result of mechanism studies and an understanding of the catalyst-hydrocarbon interaction, modifications of existing catalysts have been brought about. For example, improved selectivity has been achieved by changing the balance of functions.

Platinum-containing catalysts have dominated the field throughout the 1960's. Late in the 1960's several catalyst suppliers announced new catalysts which have come to be known as bimetallic. The early 1970's continued to show rapid development of additional bimetallic catalysts.

Bimetallic catalysts offer much higher activity and selectivity maintenance. The improved selectivity and activity permits operation at lower pressure and lower gas-recycle ratios and/or higher severity.

The development of reforming catalysts capable of drastically improving performance represents potentially the most far-reaching improvement in catalytic reforming. These recent developments represent a "quantum jump" in catalyst performance. (8)

The addition of rhenium to a platinum reforming catalyst results primarily in improving stability. Figure 2 shows data on Rheniforming a heavy naphtha at lower pressures. (9) It has been suggested that some kind of platinum-rhenium couplet is involved, although it is now known how this complex acts. Other metals and also sulfur are believed to have a beneficial effect. An important point is that platinum-rhenium does not, per se, lead to higher yields. However, higher yields can be achieved because such catalysts can operate at lower pressures where conventional reforming catalysts are not stable but at otherwise equivalent conditions, the initial yields are the same as those obtained with conventional catalysts.

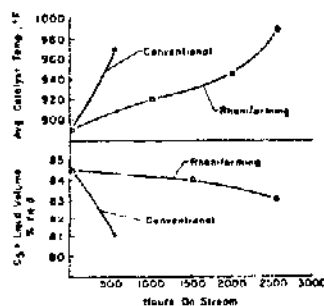


FIGURE 2. RHENIFORMING OF 420 F ISOMAX NAPHTHA

Catalytic Cracking

A "quantum jump" improvement in catalytic cracking has also been achieved by the introduction of so-called crystalline aluminosilicate catalysts. The crystalline aluminosilicate, or zeolitic catalysts, are more active, more stable, and produce considerably more of the desired products, gasoline and

light fuel oil, compared to amorphous silica-alumina catalysts. They also produce considerably less undesirable products, coke and light gas.

The striking improvement in gasoline yield is evident from the following results. (10)

Catalyst:	Yields Volume Percent, fresh feed	
	Durabead(1)	Durabead(5)
	Amorphous	Molecular Sieve
Conversion	54.2	68.0
Heavy fuel	13.9	8.2
Light fuel	31.9	23.8
C ₅ + gasoline	39.9	53.1
Total C ₄ 's	13.3	14.7
Dry gas weight percent	6.7	7.1
Coke weight percent	3.5	4.8

Durabead 5, the first commercial zeolitic cracking catalyst was introduced in March 1962. Since that time a variety of other zeolitic catalysts have developed in both moving bed and fluid form. The zeolite catalysts now are used in over 90 percent of cracking units. The use of x and y zeolites with a pore size of about 10 Å has provided for even further improvements including very high activity. The ion exchanged faujasites can have cracking activities many orders of magnitude greater than silica-alumina. (11) In turn, use of highly active catalysts have enabled process variations including riser cracking.

Crystalline zeolites are molecular sieves which have pores of uniform dimension of molecular size, e.g., 4 Å. Early concepts of molecular sieves as catalysts were to utilize them employing the concept of "shape selective" catalysts with pores which could accommodate molecules of certain molecular dimensions but exclude others, e.g., straight-chain but not branched-chain molecules. Actually, selective reactions were found possible, although later application for catalytic cracking using crystalline zeolites with pores in the 10-Å diameter have become the most significant application. (12) While attention has been given to the unusual electronic charge fields in the pores of the zeolites to which reactant molecules are subject, (13) much of the scientific basis of the catalytic action and selectivity of zeolites has not been resolved (14, 15).

Hydrocracking

The decade of the 1960's witnessed the establishment of modern hydrocracking processes in petroleum refining. From a single demonstration unit of 1000-barrels-per-day capacity in 1960, commercial installations have

grown to over 50 units with a capacity of about 800,000 barrels-per-day total capacity. The demand for gasoline and middle distillates and the availability of low-cost hydrogen have played major roles in their growth. The most significant factor has been the development of superior catalysts having excellent activity and activity maintenance at operating conditions far less severe than those used in the older hydrocracking processes.

Research is making available increasingly active and economical catalysts whose composition can be tailored to meet particular feed and product objectives.

The catalysts are dual-function catalysts having a critical balance. The chemistry of hydrocracking has been discussed and has been reviewed in terms of the balance of catalyst functions.⁽¹⁶⁾ (See also for references.)

The "Paring" reaction is one of the most interesting new reactions discovered. As described, the products of hydrocracking hexamethylbenzene over a dual function catalyst are shown in Figure 3. The principal products are light isoparaffins and C₁₀ and C₁₁ methyl benzene. Essentially no ring cleavage occurs and hydrogenolysis to form methane is small. To account for the formation of isoparaffin products, a process of isomerization leading to side chain growth, followed by cracking of side chains of four or more hydrocarbons is proposed. The mechanism proposed is illustrated in Figure 4. Alkylcycloparaffins also exhibit the Paring reaction.

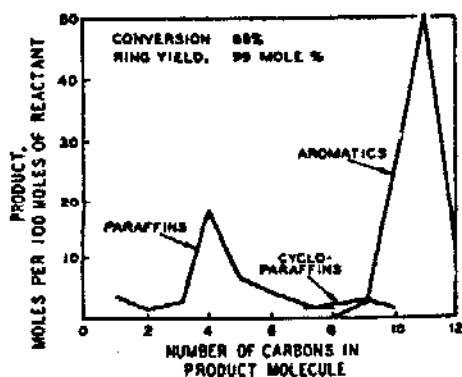


FIGURE 3. PRODUCTS OF HYDROCRACKING HEXAMETHYLBENZENE OVER A DUAL-FUNCTION CATALYST⁽¹⁶⁾

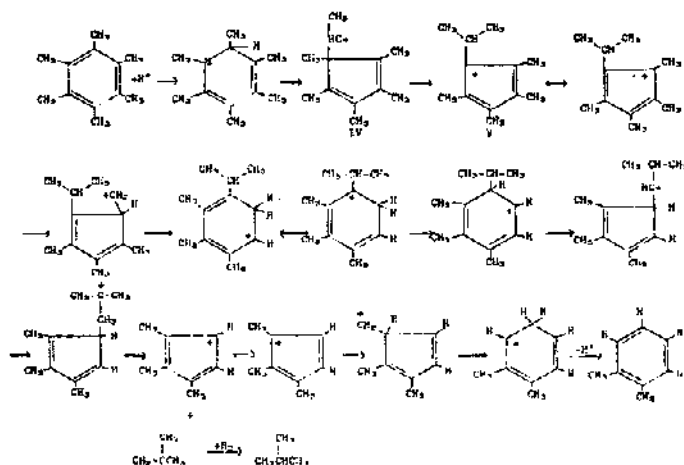


FIGURE 4. PROPOSED MECHANISM FOR
PARING REACTION

Hydrodesulfurization

Desulfurization is one of the most significant petroleum-refining operations. With lighter petroleum fractions, desulfurization is important for subsequent catalytic refining steps (e. g., reforming). A new emphasis on the use of hydrodesulfurization particularly of heavy fuels has been imposed by the strict regulations for low sulfur content of boiler fuels, with an imposition of 0.8 lb SO₂ per million Btu and even more strict regulations for some cities. (17)

In 1960 there were about 2-1/4 million barrels per day of installed hydrotreating and hydrocracking capacity in the United States (about a quarter of the oil processed). In 1971 this has grown to 5-1/2 million BPD or one half the 11 million BPD. Thus, one of the remarkable features of hydrocracking is the rapid growth rate and high capacity reached. A second significant feature of commercial hydrotreating has been its application to heavier fractions including residuals. The tag end of a heavy distillate with a 1050 F end-point may have a molecular weight of 800-900. Much of the sulfur in these cuts is present as substituted benzo and dibenzo thiophenes. (18) Residual fractions contain asphaltenes present as highly dispersed colloidal material with an average molecular weight of roughly 5,000 to 10,000. To remove sulfur from such materials – more difficult because of molecular structure – requires higher severity of hydrodesulfurization. This means raising the temperature, where other bonds will begin to break.

It is of interest to study the asphaltene molecule, where a structure shown in Figure 5 has been postulated. (19) The aromatic sheets are about 14 Å across and there are 4 or 5 sheets per stack. It is structures of this type which must be desulfurized.

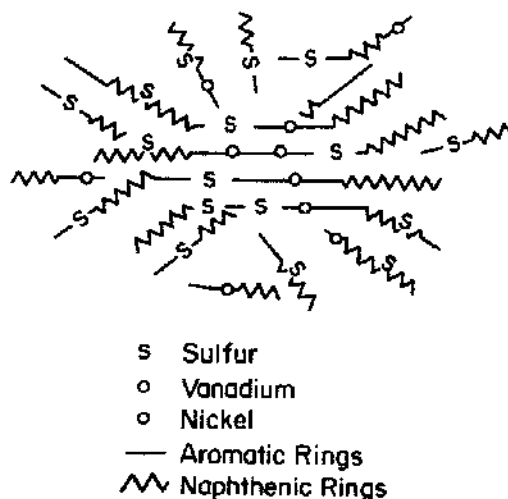


FIGURE 5. MODEL OF AN ASPHALTENE MOLECULE⁽³⁰⁾

The chemistry of hydrodesulfurization is only partially understood. Several excellent reviews have appeared. (20,21,22,23) Most researchers believe that for thiophene the reaction proceeds in two steps, the first producing butylene and hydrogen sulfide, and the second a hydrogenation of butylene to butane. However, it is pointed out that the first step must be complex and proceeds through a butadiene intermediate. Much of the mechanism studies have been published by Beuther and co-workers.

Cobalt molybdate and nickel molybdate catalysts are used extensively. Relatively little is known how they act. In operation, the active components exist as lower valence sulfides. Nickel-tungsten sulfides were used by the Germans. Diffusional effects are important.

The tolerance of catalysts to metals (nickel and vanadium from porphyrins) is important in maintaining catalyst life.

Other Petroleum Processes

Other developments have occurred in hydrocarbon alkylation, polymerization, isomerization, and dehydrogenation. There have been many innovations in the chemistry of petrochemical manufacture. These are outside the scope of this review.

TAR SANDS

An historic event during the 1961-74 period was the initiation of commercial production of oil from the Canadian tar sands. This began in 1967 in a plant designed to produce 45,000 barrels per day. The Athabasca sands cover 12,000 square miles and contain 600 billion barrels of oil in place. The plant built by the Great Canadian Oil Sands Company is based on a four-stage sequence of mining, materials handling, extraction, and heavy oil upgrading. (24) Extraction is by a hot-water system. The heavy oil is processed in delayed coke drums. The overhead is separated into three streams: naphtha, kerosene, and heavy gas oil. These streams are hydrogenated individually and then blended to form a product called synthetic crude. While many unusual mining situations are encountered, the processing of tar is by previously known petroleum-refining techniques applied to an unusual material. The separation of the tar from the sand by hot-water processing has presented an important surface chemical field. A second 80,000 barrel-per-day plant has been proposed with several different process steps, many of them in the mining and conveying. (25)

In clearing the primary oil, a thermal dehydration-cyclone arrangement will take the place of a dilution-centrifuge system. In primary conversion, hydrovisbreaking will replace delayed coking. Again, the innovation is in the application of refining to the tar sands.

The chemical constitution of tar sands has been characterized further using modern analytical tools, including the nature of the sulfur compounds. (26, 27)

OIL SHALE

Oil shale is an important potential source of fossil fuel in the United States, in amount, second only to coal as a resource. The potential estimated from the Green River formation is between 600 (high grade over 25 gallons per ton of rock) and 1,800 (total) billion barrels of oil. Most of the oil shale is on federal lands. An unsuccessful attempt was made in 1968 to lease a few selected tracts. However, events so changed that a second program of leasing in 1973 of four tracts of about 5,000 acres each, has met with highly competitive bidding, the winning bids on the four tracts amounting to nearly \$500,000,000.

Over the years, most technical effort has concerned mining of the oil shale and various mechanical means of retorting it. Retorting of the oil shale has been carried on a fairly large experimental scale of about 1,000 tons per day, employing several different types of retorts. (28) A demonstration plant began operation in Brazil using direct-fired shale calcination. Burning of oil shale for power generation continued in Europe.

The chemical nature of shale oil has been further defined, as shown in the following table of inspection data on typical shale oil crude: (29)

Gravity API	19.8
Pourpoint, F	83.5
N, weight percent	2.1
S, weight percent	0.7
O, weight percent	1.7
C, weight percent	83.9
H, weight percent	11.4
Conradson carbon	4.7
Bromine No.	33.2
Sediment, weight percent	0.04
Ni, ppm	6.4
V, ppm	6.0
Flash, F	108.0
Molecular weight	328.0

Investigations of the structure of kerogen are difficult because kerogen is a large, complex molecule belonging to the multipolymer class, its insolubility, and its inhomogeneity. Colorado oil shale of the Green River formation contains about 16 percent insoluble organic matter called "kerogen." This represents about 4/5 of the organic matter present. The other 1/5 soluble organic matter represents "soluble bitumen." Using a combination of micropyrochromatography separation and mass spectrometry, provided a structure for kerogen shown in Figure 6. X-ray diffraction has also been used for determination of the structure of kerogen. (31)

In situ production of oil shale has shown promise. There are potential advantages both from avoidance of mining costs and a lessening of possible environmental damage. In situ tests at Rock Springs provided a crude shale oil which has been characterized and whose conversion into an oil suitable for refining in a petroleum refinery has been demonstrated. (32,33) Recently, the press has reported tests for in situ shale oil production in which a cavern corresponding to a fraction (e.g., 25 percent of oil shale) is removed, the oil shale above it is fractured to form a permeable rubble, and the whole shaft then calcined to drive off the shale oil with improved economics.

The fracturing of the oil shale with chemical explosives has been described. (34) It was shown that the explosion will propagate in water-filled natural fractures and sand propped, hydraulically induced fractures in oil shale. The shale was fragmented by this method and a successful underground retorting experiment to recover shale oil was performed.

The use of nuclear detonation has also been proposed. An interesting proposal is the bioleaching of oil shale, and experiments have shown promise. (35)

The hydrogasification of oil shale has been described. It was shown that the presence of hydrogen, even low pressure, significantly increases the organic carbon deposit compared with hydrogen-free retorting. (36)

Studies on the chemical nature of kerogen showed the feasibility of using kerogen as a natural raw material for the synthesis of monomers, not by traditional pyrolytic methods, but by direct chemical processing resulting in the scission of native polymethylene chains, structural elements of the natural polymer, in the form of monoacid and preferably dicarboxylic acids. (37) Conventional industrial oxidants have been found to be suitable for direct oxidative destruction of the kerogen to saturated dicarboxylic acids. Kerogen treated with nitric acid and molecular oxygen yields 55 percent of C₄ - C₁₀ dicarboxylic acids.

In certain oil shale zones, the rock contains appreciable percentages of potentially valuable saline minerals. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$), associated with oil shale, occurs in vast quantities in Wyoming's Green River basin. In Colorado nahcolite (NaHCO_3) and dawsonite ($\text{NaAl}(\text{CO}_3)(\text{OH})_2$) have been discovered in a zone 700 feet thick, also associated with oil shale.

Environmental protection and water usage continue to be of great concern in oil shale processing. Spent shale has been found to have properties similar to low-quality cement, enhancing its disposal in compact fills. It can also be made to support vegetation. Disposal areas must be designed to prevent leaching of soluble minerals.

COAL

During the period 1961-74, science progressed further in elucidating the structure of coal (using modern instrumentation) and in establishing the factors involved in chemical reactivity of coal. On the applied side, major efforts were made in developing chemical processes to remove sulfur dioxide from products of coal combustion (stack-gas scrubbing). Over \$200 million has been spent for such installations in power plants in what must still be regarded as an experimental program.

Coal Gasification (38-42)

For the most part, the gasification processes under development are closely related to the technology developed in the 1930's. In general, the chemistry of high-temperature gasification reactions remains the same for all processes. Mechanical and engineering variations characterize the processes, particularly those features for supplying heat for the endothermic $C+H_2O$ reaction.

The required heat can be furnished by any of several methods: partial combustion of coal with oxygen, by electrical energy, by inert heat carrier by heat released by reacting CO_2 with metal oxide, or by nuclear heat. Four large coal-gasification pilot plants are in operation or under construction in the United States. Each involves fluid bed operation in contrast to the so-called fixed-bed design of the Lurgi process which is in use in Europe. These four processes involve certain novel chemical features. In the IGT Hygas process (hydrogasification), char formed in the process is reacted with steam using electrical energy as the heat source. The gas so formed, rich in H_2 and low in CO_2 , is reacted with pretreated coal to produce a gas with high methane content. Since the hydrogen content of coal (averaging about 5 weight percent) is very low compared to that of methane (25 percent), coal gasification consists chemically of adding hydrogen to coal. In addition, sulfur, nitrogen, and oxygen constituents are converted to H_2S , NH_3 and H_2O , respectively. The Hydrane process also converts coal to methane by hydrogasification.

Perhaps the most novel process in pilot-plant stage is the CO_2 acceptor process. This process utilizes the reaction between hot lime (CaO) and CO_2

to furnish the required gasification heat. Through use of a separate regeneration vessel, air is used instead of oxygen as in the Synthane or Bigas process.

One unique feature of the Synthane process is the use of a "tube-wall" reactor for methanation. The catalyst is a Raney nickel applied to heat-exchange tubes by a flame-spraying technique. This provides for a highly effective heat-transfer system. Another unusual methanation technique is provided by a liquid-phase catalysis system.

The ideal gasification reaction for gasification of carbon is $C + 2H_2O \rightleftharpoons CH_4 + CO_2$, which is balanced chemically and nearly so calorimetrically. However, because the steam-carbon reaction does not proceed fast enough at lower temperatures, the reaction is carried out at 900 C or above. Attempts to operate at lower temperatures by catalyzing the carbon-steam reaction have met partial success. One intriguing fact is the known capability of microorganisms to convert cellulose to $CO_2 + CH_4$ at ambient temperature. While cellulose is somewhat different from coal, lignite can have an oxygen content of more than 20 percent.

The use of nuclear heat for coal gasification has been of considerable interest and is being actively investigated in Germany.

The in-situ gasification of coal is once again being tested experimentally in the United States since it offers many potential advantages.

Other novel coal gasification processes are in the research stage. The molten salt process and self-agglomerating process are further examples.

Interest has increased tremendously in coal gasification in recent years. The symposia reference provide detailed information. ⁽⁴²⁾ Also, research needs have been critically analyzed. ⁽⁴³⁾

Coal Liquefaction

Coal can be converted to liquids by four generic procedures:

- (1) pyrolysis to produce a gas, liquid, and char
- (2) "solvent refining" - actually involving the transfer of hydrogen from a hydrogen "donor" organic molecule with some additional hydrogenation catalyzed by coal-ash constituents
- (3) Fischer - Tropsch synthesis in which coal is converted to

$\text{CO} + \text{H}_2$ which are then reacted to form hydrocarbon and alcohols

(4) Direct catalytic hydrogenation.

Several large pilot plants have been constructed recently in the United States to test new technology and several more are planned.

Pyrolysis

At the present time, the FMC Corp., under sponsorship of the Office of Coal Research, is operating a large COED (Coal Oil Energy Development) pilot plant with fluid bed pyrolysis. (44) Powdered coal is subjected to increased temperatures in four successive fluid beds. Volatile liquid products are withdrawn at each stage and hence not subjected to the highest temperature where further cracking would occur. In this way maximum liquid yields are obtained.

Another type of process begins by treating coal with a hydrogen-donor solvent. There are several promising processes of this type under development in the United States. (45) Broadly speaking, two categories are possible, those in which liquid extraction is carried out in a separate first step, and those in which extraction is carried out in the presence of a catalyst and under hydrogen pressure. The operation at Cresap by Consolidation Coal Company, and sponsored by OCR is of the first category; the hydrogen-donor solvent is hydrogenated in a separate step so as to regenerate its solvent capabilities. (44)

Solvent-Refined Coal

The dissolution of coal by organic agents under elevated pressure and temperature has long been known. German chemists Pott and Broche found a mixture of tetralin, phenol, and naphthalene to be the most satisfactory for bituminous coal. A key feature is that tetralin is a hydroaromatic "donor" able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism that is not accelerated by the pressure, or hydrofining, or cracking catalysts.

A pilot plant processing 6 tons of coal per day built by industry began operating in 1974 using a solvent refining process. The PAMCO solvent-refined coal process developed by Pittsburgh and Midway Coal Mining Company consists of mixing pulverized coal with a coal-derived solvent having a 500-800 F boiling range, passing the mixture with hydrogen through a preheater and reactor at about 1000 psi, separating the hydrogen plus hydrogen sulfide and light hydrocarbons formed, filtering the solution, flash evaporating the solvent, and recovering the solidified-coal product. The chemical analysis of charge and product is shown below. During the reaction phase, hydrogen reacts with part of the organic sulfur compounds forming the

hydrogen sulfide. The hydrogen also stabilizes the solubilized coal products. The pyritic sulfur leaves the process in the filtration step, as do the other ash components.

	Kentucky No. 11 coal	Refined coal
Ash	6.9	0.1
C	71.3	89.2
H	5.3	5.0
N	0.9	1.3
S	3.3	1.0
O	12.3	4.4
Btu/lb	13,978	15,956
Melting point degrees C	-	128

Under the sponsorship of OCR a large pilot plant has been authorized for construction and operation in the State of Washington. This plant to start in 1974 not only will test scale-up factors, but also will produce sufficient product for larger scale testing of its combustion characteristics. Scientists at the Bureau of Mines discovered that a mixture of (CO+H₂O), or (CO+H₂O+H₂) is even more effective than H₂ alone for hydrogenation. The mechanism is related to the shift reaction (CO+H₂O \rightleftharpoons H₂+CO₂) during which the hydrogen at an intermediate stage, possibly as the formate ion, is in a particularly reactive state. It should be possible to test the use of synthesis gas plus steam as an improvement in the solvent refined coal process.

H-Coal Process

The H-Coal process utilizes an ebullated bed reactor system developed by Hydrocarbon Research Inc. A unique feature of this reactor system is the ability to operate a catalyst system continuously with a feed consisting of solids, liquids, and gases. The upward flow of the feed maintains the catalysts in a state of rapid motion and permits the continuous passage of unconverted coal and ash from the reactor. Catalyst can be added and removed from the reactor during operation.

The production of low-sulfur fuel oil from coal by the H-Coal process has been discussed. (47) It is stated that processing conditions can be varied to attain 1.5 to 1.0 percent sulfur without ash removal, 0.5 percent with ash removal and increased conversion severity, and 0.25 percent with secondary treatment of part of the product.

For example, in processing an Illinois No. 6 bituminous coal, 3.6 bbl of C₄ + liquids were made per ton dry coal at 93 percent coal conversion. The sulfur content of the coal was 3.4 percent and of the liquids was 0.5 percent.

Turbulent Catalytic Reaction

In experiments conducted at the Bureau of Mines, a high-sulfur bituminous coal suspended in oil derived from coal was converted to a low-sulfur fuel oil by continuous processing through a fixed bed of pelletized cobalt molybdate alumina catalyst, under conditions of highly turbulent flow of hydrogen to prevent obstruction of the flow and to promote catalytic contact. (48) From coal having 3.0 percent sulfur and 9.4 percent ash, the totally coal-derived centrifuged synthetic fuel oil, produced at 2000 psi and 850 F had 0.31 percent sulfur and 1.3 percent ash. The data indicated that more selective separation of unconverted residual coal would provide fuel oils with sulfur content as low as 0.1 percent sulfur because the bulk of the sulfur is in the benzene-insoluble fraction of the product oil.

The new catalytic concepts for direct hydrogenation has been reviewed. (45, 49) References are detailed.

NEW HYDROGENATION CATALYTIC SYSTEMS

A list of the systems is given below.

"Nascent"-active hydrogen generated in situ

Complexes of transition metals

Massive amounts of halide and catalysts

Organic hydrogen donor solvents

Alkali metals

- (a) With H_2
- (b) With amines
- (c) Electrocatalytic

Reductive alkylation

Miscellaneous.

Active Hydrogen Generated in Situ. A combination of carbon monoxide and steam can hydrogenate coal more rapidly and to a greater degree than can hydrogen itself under the same conditions of temperature and pressure. The suggestion has been made that hydrogen, generated in situ by the water gas shift reaction between CO and H_2O , is in an activated form. It has also been suggested that the mechanism is via a formate ion.

Complexes of Transition Metals. Certainly one of the most, if not the most, significant development in the field of catalysis in recent years has been the discovery of a variety of new, and often unusual, catalytic reactions of transition metals and coordination complexes. The catalytic properties depend upon the central ion and the number and character of ligands. Some of these catalysts are soluble and have therefore been called homogeneous catalysts. Knowledge of their electronic structure has enabled the establishing of catalytic mechanisms on a molecular basis.

The capability of such metal-ligands complexes to react with hydrogen to form active species and the existence of coordinatively unsaturated metal complexes are fundamental to the mechanism of their reactivity.

One of the earliest and most important examples of their type of catalysts is cobalt carbonyl which, in the presence of $\text{CO} + \text{H}_2$, is capable of hydroformylating olefins. Cobalt carbonyl is also active in hydrogenating certain aromatic compounds and coal. Dicobalt octacarbonyl, in the presence of carbon monoxide and hydrogen, functions as a selective homogeneous hydrogenation catalyst for polynuclear aromatic hydrocarbons.

Coal was also treated with $\text{CO} + \text{H}_2$ in the presence of dicobalt octacarbonyl at the same temperature, 200 C. Both H_2 and CO were added to coal under these conditions. Thus, this is one of the most active catalytic systems ever observed for coal hydrogenation.

Massive Amounts of Halide Catalysts. The use of halide catalysts in amounts comparable to the coal or polynuclear hydrocarbons used has given some unusual hydrocracking results. Comparison of a SnCl_2 /coal ratio of 0.01 and 1.0 illustrates that while about 85 percent of the coal was converted to benzene solubles in each instance, the asphaltene conversion – the difficult step – was nearly completed with the larger amount of catalyst. Similarly, large amounts of zinc chloride were effective, and this compound was superior to conventional hydrocracking catalysts for coal or coal extract. Zinc chloride gave more rapid reaction, more complete conversion, than conventional catalysts, and a very high octane without reforming.

Compared with conventional catalysts, molten zinc chloride more than doubled the conversion and hydrogen consumption when using a hydrocracking residue as feed stock, even though a lower temperature was used. Noteworthy also, is the high selectivity of the process for production of gasoline and the high ratio of isoparaffins to normal paraffins.

Hydrogen Donor. The solution of coal by extraction using organic agents under pressure has long been known, and a vast literature exists. The German chemists, Pott and Broche, found that a mixture of tetralin, phenol, and naphthalene was the most satisfactory solvent for bituminous coal. A key

feature is the presence of tetralin which is a hydroaromatic "donor", able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism. The structure of the donor is important. The function of the phenol is apparently to assist in pulling the hydrogenated coal into solution. This combination effect is demonstrated in the table below where, it is seen, the synergistic effect can be built into a single molecule, o-cyclohexylphenol. The process mechanism is complicated. For example, much of the oxygen is eliminated in making the coal soluble.

In liquefaction of bituminous coal by hydrogen donor solvent for 6.5 hr at 400 C we find:

<u>Vehicle</u>	<u>Liquefaction, percent</u>
Naphthalene	25
Cresol	32
Tetralin	50
o-Cyclohexylphenol	82

Alkali metals. The alkali metals can act in hydrogenation of coal in several related ways: (a) as a direct hydrogenation catalyst (with molecular H_2), (b) with amines, and (c) in a catalytic electrochemical reduction.

Reductive Alkylation. The formation of aromatic hydrocarbon anions is made possible by reaction with alkali metals. For example, naphthalene, dissolved in hexamethylphosphoramide*, reacts with one or two moles of lithium to form the mono- or dianion. In turn, the dianion can react with CH_3I to give 9, 10-dimethyl 9, 10-dihydroanthracene. This is called reductive alkylation, since one of the aromatic nuclei is converted to an alkylated dihydrobenzene.

Reductive alkylation can also be carried out with coal substance. Although only 3 percent soluble in HMPA, coal became 90 percent soluble on addition of lithium to a suspension of coal in HMPA. Alkylation of coal with ethyl iodide yielded an ethylated coal which was 35 percent soluble in benzene at room temperature. It was estimated that the alkylation corresponds to 1 alkyl to 5 carbon atoms. Reductive alkylation is also a means of adding hydrogen, in that H/C of coal is increased. This alkylation method is much more effective in causing solubility of coal than addition of an equal number of hydrogen atoms. Moreover, a degree of benzene solubility is achieved which is not possible by hydrogenation.

The alkylation of coal was not restricted to use of HMPA. Coal can be readily alkylated in tetrahydrofuran, provided a small amount of naphthalene is added which acts as an electron-transfer agent.

*HMPA.

Other Novel Hydrogenation Systems. There are a number of other novel hydrogenation systems. These include volatile catalysts such as iodine, dehydrogenation of coal to form hydrogen ($9000 \text{ ft}^3/\text{ton}$) which possibly could be combined in a dehydrogenation-hydrogenation disproportionation process, use of molecular sieves containing metals to bring about hydrogenation of selected molecules, high-energy modification of coal or catalysts, use of ultrasonics to increase coal solubilization.

Combustion

Space does not permit the review of advances in the chemistry of combustion. Important new knowledge relates to combustion control for prevention of pollution. Thus it is possible to control combustion in a manner which minimizes NO_x formation — of particular importance in coal combustion. Likewise, the use of limestone addition in combustion for removal of SO_2 may become of major practical importance in developing fluid bed combustion. The chemical removal of SO_2 from stack gases is an alternative to synthetic fuels from coal in many large installations. (50) The competition between synthetic fuels and stack gas scrubbing promises to become even more important, and both processes are economically dependent on future advances in their respective technology. (51)



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