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## THE CHEMISTRY OF COAL LIQUEFACTION

An understanding of the chemistry of coal liquefaction is essential if the processes for converting the carbonaceous matter in coal to environmentally acceptable liquids are to be optimized. Bituminous, subbituminous, and lignitic coals may all be converted to liquids with bituminous coals producing the highest liquid yields. Anthracite tends to produce essentially all gas and is therefore more difficult to liquefy.

The structure of bituminous coal is better understood than that of other types of coal. It consists of clusters of aromatic carbon rings with appreciable amounts of hydroaromatic carbon. An average of 65 to 75 percent of the carbon is aromatic, 15 to 25 percent is hydroaromatic, and 5 to 10 percent is aliphatic. The individual clusters are joined together chemically in layers or lamellae by various types of bonds including short aliphatic bridges (e.g., methylene), ether linkages, sulfide or disulfide linkages, and perhaps biphenyl linkages. The lamellae appear to be held together in more or less parallel layers by physical interactions (e.g., hydrogen bonding or van der Waals forces) in a "graphite-like" structure.

Bituminous coal generally is believed to consist principally of clusters of aromatic carbon rings with appreciable amounts of hydroaromatic carbon. An average of about 65 to 75 percent of the carbon is aromatic, about 15 to 25 percent is hydroaromatic, and about 5 to 10 percent is aliphatic carbon. The individual groups or clusters contain from one to probably not more than five or six rings, an average cluster containing about three rings. The clusters are bound together chemically by various types of bonding such as short aliphatic bridges (e.g., methylene) and oxygen, sulfide, or disulfide, and, perhaps, biphenyl linkages. A schematic representation of the principal types of structural groups in bituminous coal and the manner in which these groups are joined is shown in Figure 1.

Coal appears to consist of layers of more or less parallel lamellae in a "graphite-like" structure. If one considers a single aromatic cluster, the chemical bonds appear to be in one plane (in two dimensions only). The minimum distance in the third dimension has been observed by a modified X-ray technique to be 3.44 angstroms, too long for chemical

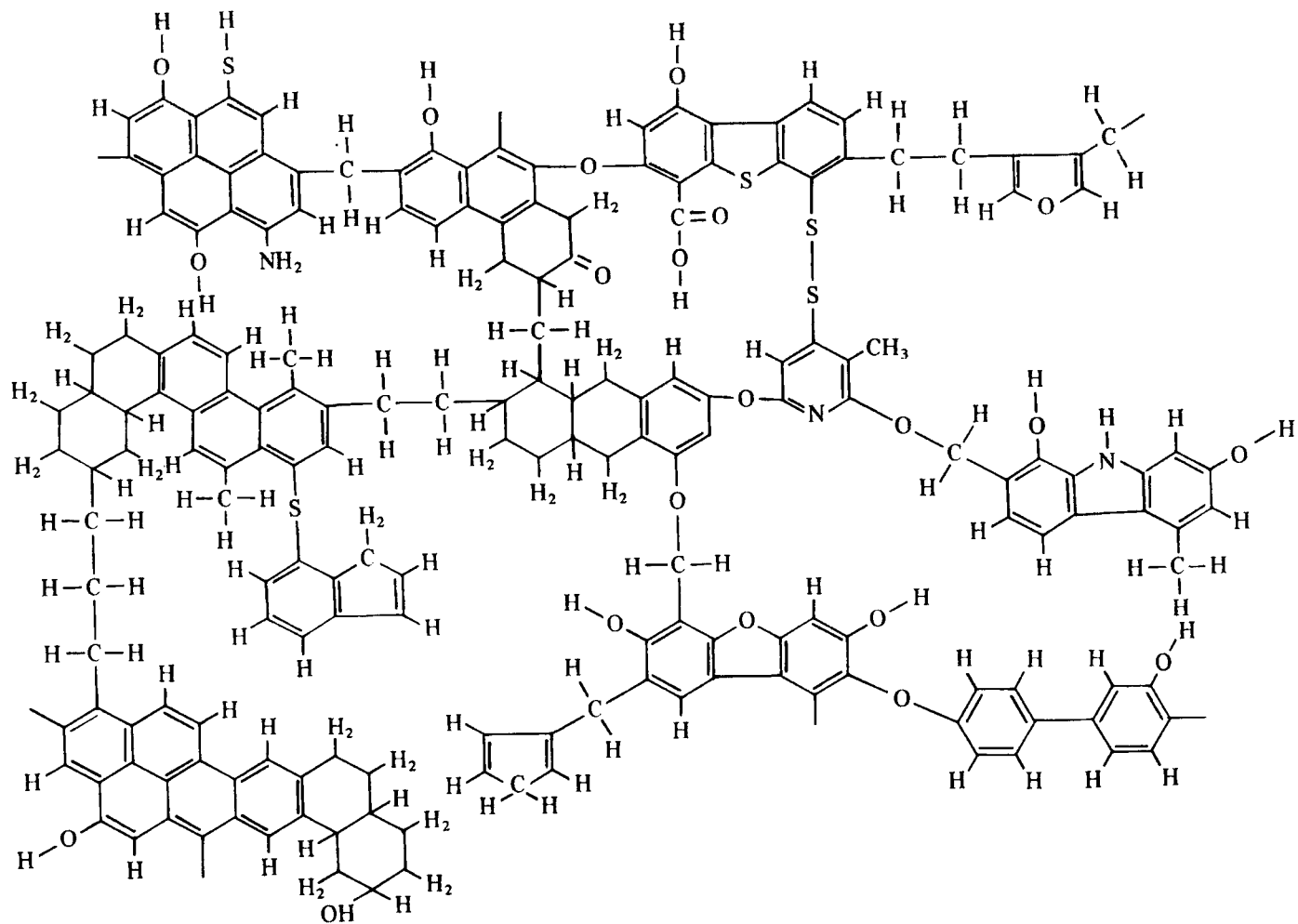


Figure 1 Schematic representation of structural groups and connecting bridges in bituminous coal.

bonds. Clusters appear to be held together in parallel layers by physical interactions (e.g., hydrogen bonding or van der Waals forces). A cluster may be randomly oriented with respect to its nearest neighbor (i.e., it may not necessarily lie in the same plane as its neighbor).

The ratio of atomic hydrogen to carbon in a typical bituminous coal is in the range of 0.8 to 0.9. While the properties of coal vary depending on rank, approximate values of some of the important properties of coal are given in Table 2. One observes the following trends with increasing coal rank: carbon content increases, hydrogen to carbon atomic ratio decreases, oxygen content decreases, aromatic character increases, and the volatile fraction decreases.

The petrographic composition of a coal also strongly influences its liquefaction behavior. If one looks at the face of a coal seam one can see distinct layers--some shiny black, some dull gray, and some exhibiting other visual features. One can examine these various layers under a microscope and note that different material origins are indicated. Various investigators have introduced many terms into the petrographic literature. The thick, shiny layers known as vitrinites originate from undistintegrated woody tissues of tree trunks and branches. They are the most abundant petrographic components in coals suited to liquefaction and can be liquefied quite readily. Exinites, another petrographic component, also are very receptive to liquefaction but are present in only small quantities. Also present are fusinites, which consist of charcoal-like material and are very resistant to hydrogenation.

Bituminous coals in general manifest a phenomenon known as plasticity. When a bituminous coal is heated to between 325 and 350 °C, the coal mass begins to soften or become plastic. When in this state, the coal sticks to almost anything and may plug the reactor or cause other problems that may terminate the liquefaction operation. Gas-fluidized bed operation becomes very difficult or impossible. Much of the liquefaction technology associated with bituminous coals has been directed toward solution of this problem.

The actual physics and chemistry of coal plasticity are not well understood. One group of investigators maintains that the plastic condition represents the formation of a compound that possesses the plastic properties and further decomposes to yield volatile products and a solid residue. Another group maintains that the plastic state is the result of a rather rapid and extensive thermal decomposition of the coal structure yielding a viscous, physical mixture of liquid and gaseous materials in which the yet-undecomposed coal is somewhat mobile. Most theories conclude that the plastic state results from a thermal rupture of the coal's structural bonds, both the physical forces holding the lamellae together and the chemical bonds between clusters within the lamellae. Neither the higher rank coals such as the anthracites nor the lower rank coals such as subbituminous and lignite manifest the plastic

TABLE 2 Approximate Values of Some Coal Properties in Different Rank Ranges

Properties	Lignite	Subbituminous	Bituminous Coal				Anthra- cite	
			High Volatile C	B	A	Medium Volatile		Low Volatile
C (Mineral matter free), %	65-72	72-76	76-78	78-80	80-87	89	90	93
O, %	30	18	13	10	10-4	3-4	3	2
O as COOH, %	13-10	5-2	0	0	0	0	0	0
O as OH, %	15-10	12-10	9	-	7-3	1-2	0-1	0
Aromatic C atoms, % of total C	50	65	-	-	75	80-85	85-90	90-92
Av. number benzene rings/cluster	1-2	←————— 2-3 —————→				5	>25	
Volatile matter, %	40-50	35-50	35-45	-	31-40	31-20	20-10	<10
Density	—————→ increases —————→							

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behavior; however, subjecting the low rank coals to liquefaction temperatures under hydrogen pressure often induces a degree of plasticity with the resultant problems.

Liquefaction of bituminous coal involves passing through the plastic state because the rate of liquefaction is too slow at temperatures below the initiation of the plastic state. Viable liquefaction processes operate between 400 and 550 °C. Temperatures above 550 °C cause extensive cracking that results in high gas yields.

When bituminous coal is heated to a suitable liquefaction temperature the following changes occur: (1) rupture of the physical bonds (van der Waals forces and hydrogen bonds) between the layers (lamellae) in the coal and formation of smaller organic fragments; (2) rupture of a sufficient number of the chemical bonds linking clusters together to free these clusters and at the same time form free radicals; and (3) stabilization of the free radical fragments. The production of a significant yield to liquids requires stabilization of these fragments as small entities to inhibit polymerization that would form a less reactive mass. The various approaches to liquefaction of coal involve alternative techniques for stabilizing these free radicals.

Pyrolysis, as defined in this report, involves heating coal to a temperature of between 400 and 550 °C in the absence of air or oxygen. Stabilization of the thermally produced fragments must occur by abstraction of hydrogen or interaction with other small radicals from within the coal structure. An example of such stabilization could be the abstraction of hydrogen from a hydroaromatic structure in the coal. When the limited hydrogen-donor inventory (e.g., hydroaromatic hydrogen) of the coal becomes consumed, the free radicals that continue to form undergo repolymerization resulting in char formation. The hydrogen present in the coal is redistributed via the donor-hydrogen transfer process to form a volatile fraction that has a hydrogen-to-carbon atomic order of approximately 1.5 to 1.8 (as compared with 0.8 to 0.9 in the original coal) and a more hydrogen-deficient char residue. The lower molecular weight material boils off and the mass sets up, forming coke. A limited extent of liquefaction can occur in this case.

When a solvent with hydrogen donor capability is present in the system (a condition associated with most coal liquefaction processes), the free radicals may abstract hydrogen from the solvent and thereby achieve stabilization. Repolymerization is inhibited because the free radicals formed can continue to be stabilized by hydrogen transfer from the hydroaromatic hydrogen-donor solvent molecules.

If molecular hydrogen and an appropriate catalyst are added to the system, dissociative chemisorption of the hydrogen on the catalyst can yield active hydrogen that can stabilize the free radicals.\* In addition,

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\*It is also possible for molecular hydrogen alone to stabilize free radicals in the absence of catalyst or donor solvent but at slower reaction rates.

the introduction of the catalyst and hydrogen can promote hydrogenation of a ring on a multi-ringed cluster followed by ring opening and scission, thereby reducing the size of large clusters.

The addition of a CO-steam mixture to coal under liquefaction conditions seems to yield "active hydrogen," evidently by a process related to the water-gas shift mechanism, that can stabilize the thermally produced free radicals. Figure 2 shows the action of a hydroaromatic-donor solvent in the stabilization of thermally produced free radicals in coal.

With increasing temperature the extent of bond breaking via thermal rupture of relatively weak chemical bonds increases (depolymerization of the coal). This continued bond rupture further reduces viscosity by reducing the mean molecular size of the product; however, it usually results in the production of more gases, with a consequent increase in hydrogen consumption. It should be noted that thermal cracking of aliphatic hydrocarbons of the size desired in a liquid product becomes quite extensive in the 450 to 550 °C temperature range and that aliphatic side chains on aromatic rings crack readily. The aromatic rings themselves do not crack and open in this temperature range. Extended residence times at these temperatures can result in increased aromatization and coke formation. Since coal liquefaction occurs on the temperature threshold for cracking of aliphatic hydrocarbons, it is important that these materials not be held at those temperatures very long. If one wishes to maximize the yield of liquids, it is advantageous to operate with rapid heating, a short residence time in the reactor, and rapid cooling.

Most coal liquefaction processes involve the addition of a coal-derived solvent to the coal prior to heating the coal to the high temperature zone. This is done to facilitate the feeding of the coal into a high-pressure region and to avoid the sticking problems. When the coal particles are surrounded by liquid near ambient temperature, several minutes are required to bring the particle to reaction temperature (i.e., 400 to 500 °C), and residence times in the preheater and the reactor in these processes are usually from 15 minutes to 1 hour. The use of dry coal particles (e.g., 40 to 60 mesh) with hydrogen gas in turbulent flow can shorten heat-up times to a few seconds, thus requiring residence times in the preheater and reactor of only about 10 to 15 seconds. With bituminous coals, the absence of a solvent with donor capabilities requires the presence of an appropriate catalyst together with an atmosphere of sufficient hydrogen under partial pressure to permit rapid hydrogenation of the thermally produced free radicals.

Some catalytic properties in connection with coal liquefaction reactions have been attributed to the inorganic matter (ash) within the coal. Coals generally contain 5 to 15 weight percent ash material. A wide variety of elements and compounds occurs in the inorganic portions of coals, some of which are known to possess catalytic properties in

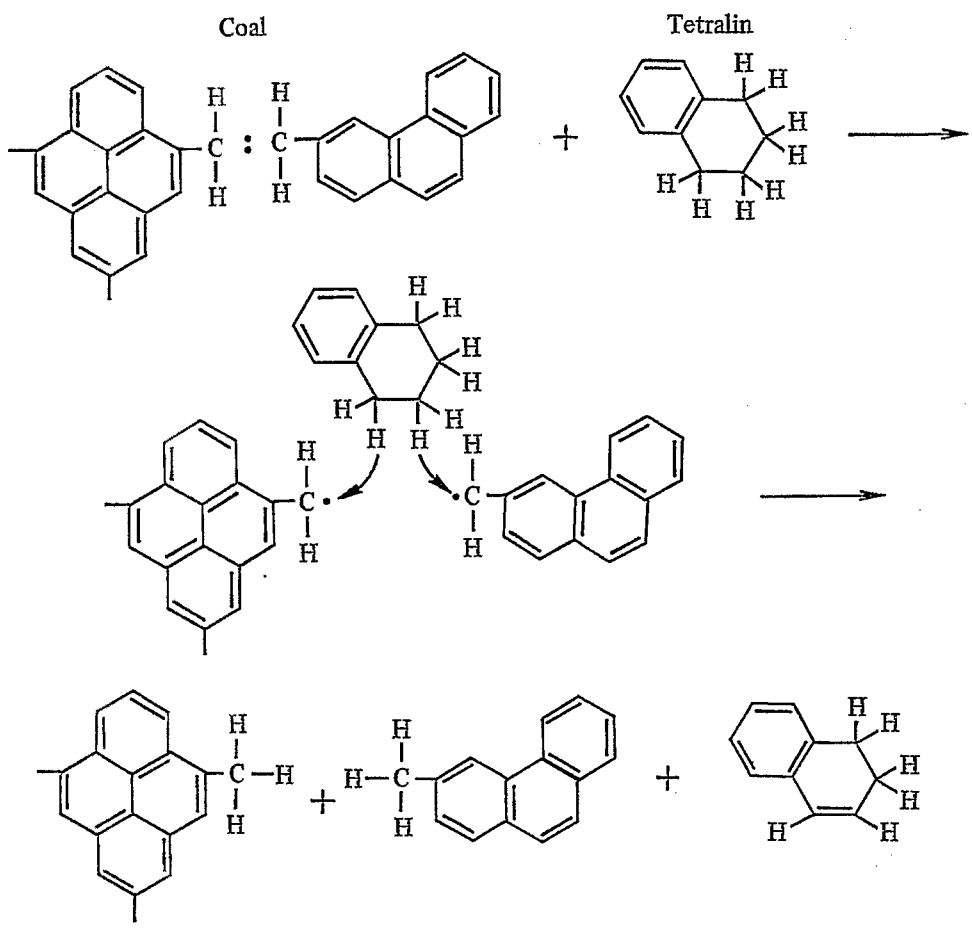


Figure 2 Schematic representation of the donor action involving pyrolytic rupture of an ethylene bond in the coal structure followed by hydrogen transfer from tetralin to form stable hydrocarbon fragments.

certain coal liquefaction reactions. While some coals do not react appreciably within a hydrogen atmosphere in the absence of an external catalyst, others do, possibly because of the catalytic nature of the inorganic matter. The quantity and degree of dispersion of the inorganic matter in the coal may be an important factor in these cases. Although very little work concerning the nature of this catalytic activity has been reported, it should be noted that some of the materials in the inorganic matter also act as catalyst poisons.

The fundamental mechanisms of the various approaches to coal liquefaction are not well understood. It is believed that considerable research activity could well be directed to an understanding of the basic principles of these processes in order to optimize coal liquefaction technology.

For a substance to catalyze a chemical reaction, at least one of the reactants must interact chemically with the catalyst (e.g., chemisorption of a reactant on the surface of a solid catalyst). In the hydrogenation of olefins, hydrogen has been observed to chemisorb on the catalyst, the hydrogen adsorbing as atoms rather than as diatomic molecules (called dissociative chemisorption). If the olefin molecule adsorbs near one of these hydrogen atoms, it can very readily react with it while under the same conditions it cannot react with molecular hydrogen from the gas phase.

If a material is to catalyze the direct interaction of molecular hydrogen with coal to stabilize a thermally produced free radical, the catalyst, the hydrogen, and the free radical must be brought together simultaneously. Since a coal particle and a catalyst particle, each of many microns diameter, cannot establish intimate contact, either the coal must be subdivided into particles of dimensions of a few angstroms and given mobility to enter the pores of the catalyst (dissolving the coal in a solvent prior to contact with the catalyst) or the catalyst must be subdivided to essentially a molecular scale and given mobility to enter the pores of the coal (impregnating from a liquid solution or diffusion as a vapor). The molecular hydrogen then diffuses to the reaction site and in either of the above cases all three components are present when the temperature is reached for the reaction. If this operation is carefully accomplished, polymerization of the free radical fragments is inhibited and stabilization as small molecules is maximized.

In the presence of the hydrogen-donor solvent it may be easier for the donor solvent itself to stabilize the free radicals from the coal with the catalyst, if present, and hydrogen acting to regenerate the donor capability of the solvent. However, these processes are not well understood and require additional investigation. Synthetic crude yields from reactions involving the hydrogen-donor solvent can contain 60 to 75 percent of the carbon in the coal, and similar yields can be obtained in processes involving an appropriate catalyst and molecular hydrogen.



The removal of heteroatoms (i.e., oxygen, sulfur, and nitrogen) represents an important part of coal liquefaction technology. While most of the oxygen and sulfur in coals do not occupy positions within aromatic rings, much of the nitrogen does. In the temperature range required for coal liquefaction those heteroatoms that do not occupy ring positions may be removed to a great extent through noncatalytic processes yielding water and H<sub>2</sub>S, but very little nitrogen is removed under these conditions. The removal of sulfur and nitrogen from ring positions requires catalytic hydrogenation of the ring and subsequent ring opening. These heteroatoms then are removed as H<sub>2</sub>S and NH<sub>3</sub>. It is generally observed that younger, lower rank coals (e.g., subbituminous and lignite) are easier to hydrogenate (require lower pressures and retention time as well as less active catalysts) than older, higher rank bituminous coals. The younger coals contain more volatile matter and oxygen and represent a structure less consolidated into ring clusters and more amenable to disintegration by heat and hydrogen transfer than the highly metamorphosed older coals. However, the bituminous coals usually give higher liquid yields with lower gas yields than the younger coals.

Maximizing the liquid yield requires a careful balance between temperature, pressure, heat-up time, residence time at elevated temperature, and the addition of an appropriate catalyst. In general, short residence time in the heated zone is favorable to higher liquid yield if the other conditions are satisfactory.

The major factors that affect the liquefaction of coal are:

1. Reactivity of Coal--Anthracite cannot be hydrogenated to liquids. High rank bituminous coals require more severe conditions than lower rank coals. Younger, lower rank subbituminous coals or lignites liquefy most readily but give lower yields and lower ratios of liquids to gases than bituminous coals.

2. Rate of Heating and Liquefaction Temperature--Rate of heating to liquefaction temperature should be as rapid as possible to prevent re-polymerization of reactive fragments formed from the rupture of the weakest bonds in the coal at temperatures lower than those for which hydrogen transfer becomes rapid. Temperatures to produce liquids range from 400 to 550 °C.

3. Catalysts--Many metals act as catalysts in coal liquefaction and are especially effective in the temperature range in which liquids are formed; similarly, the ash present in the coal probably has catalytic capabilities.

4. Pressure--Required pressures for liquids production by hydrogenation range from about 500 to 4,000 psi. Rank of coal, liquefaction scheme, desired end product, mineral matter and added catalyst present, and extent of conversion determine the optimum pressure. Lower rank coals can be liquefied at lower pressures.

5. Contact Time--Mixtures of coal and vehicle oil require from about 20 minutes to 1 hour at pressure and temperature for as much as 3 barrels of liquids per ton of coal in most hydrogen-donor solvent schemes. Evidence indicates that comparable conversion can be achieved in a much shorter time (i.e., 10 to 15 seconds) if the coal particles are heated rapidly in a hydrogen gas atmosphere (usually also requiring a catalyst).