

CHAPTER II

THEORY AND LITERATURE REVIEW



2.1 Coal

2.1.1 Lignites and sub-bituminous coals

Lignite is immature coal that is intermediate in composition between peat and bituminous coals. They are of tertiary or late mesozoic age (cretaceous), that is between 10 and 100x10⁶ years old. They often occur in thick seams, varying from a few feet in Pakistan and Borneo to over 1000 ft thick in Victoria, Australia. In Germany and Victoria they are of industrial importance as fuels, including the manufacture of synthesis gas and towns gas. Sub-bituminous coals, which are included in this general class of coals and are harder and mature than lignites and brown coals, occur in the U.S. in Montana. The most immature coals, soft brown coals, cannot be distinguished chemically from mature peats. Some mature lignites, e.g. those in Pakistan, Borneo and Utah possess coking properties.

Table 2.1: Typical ultimate analyses (ash-free-dry basis) [5]

Origin	Description	%C	%H	%O+N+S
Nigeria	Earthy brown lignite	64.5	6.5	29.0
Victoria	Brown lignite	67.4	4.7	27.9
Nigeria	Brown lignite	70.8	6.4	22.8
Wyoming, U.S.A.	Brown lignite	71.9	5.4	22.7
N. Dakota, U.S.A.	Brown lignite	72.9	4.9	22.2

2.1.2 The origin of coal

Coal is a compact, stratified mass of mummified plant debris, interspersed with smaller amounts of inorganic matter and covered by sedimentary rocks. The chemical properties of any coal depend upon the proportion of the different chemical components present in the parent plant debris; the nature and extent of changes which these components have undergone since their deposition; and the nature and quantity of the inorganic matter present.

Peat may be considered to be an immature coal and closely resembles, in composition and properties, the most immature of true coals, viz. Young brown coals.

Agencies causing the change from plant tissues to coal are:

1. Bacteria – as during the formation of peat mainly before the deposit is covered by impervious sedimentary layer.
2. Temperature and time – operating mainly after bacterial action has ceased.
3. Pressure – increasing with increasing depth of burial and accentuated by severe earth movements, e.g. during the folding or buckling of strata.

2.1.3 Rank of coal

The degree of change of chemical composition of coal, within the series of fossil fuels from peat to anthracite, is known as the rank of that coal. The rank of a coal may be measured by several parameters, the most important of which are ultimate and proximate analyses.

2.1.3.1 Mode of formation of coal forming deposits

1. *Drift origin*—the deposition from water of masses of plant debris in

shallow basins, lakes, deltas and estuaries. If the water is fresh or brackish and the deposits are shallow, attacked by aerobic bacteria is mainly oxidizing in character and the resultant coal contains a lower hydrogen/carbon ratio. If seawater is the carving agent, or if the deposit is covered by marine inorganic sediments, reducing conditions occur. The resulting coals are relatively rich in hydrogen and possess coking properties (within certain limits of rank).

2. In situ *origin*---plants grew and died in the same place, under conditions generally similar to those existing in the formation of modern forest-type peat bogs. The growth of the resulting peat bog was arrested by covering with sedimentary inorganic deposits. Conditions of decay during the peat stage were oxidizing or reducing according to the depth in the peat deposit. Flooding by sea water, or cover by marine deposits, favoured reducing conditions. Shallow deposits, or fresh water deposits, favoured oxidizing conditions.[4,6]

2.1.3.2 Cyclic formation of deposits

The cycles of accumulation of plant debris (by either process) and covered by sedimentary deposits were repeated several (or many) times in one area, causing several seams of coal to be formed, each separated by many feet of sedimentary rocks. Such a formation of stratified coal seams and sedimentary rocks is known as a Coal Measure.

2.2 Properties of coals

Coal is a compact, stratified mass of plant matter, the decay of which has been arrested at various stages of completeness and which has been changed in its chemical and physical properties as a result of geological action. The chemical changes involve complex alterations in the compounds making up the plant structures to produce the coal substance, with evolution of moisture, carbon dioxide, and methane. The physical changes include darkening in color of the mass, increases in hardness and in

compactness to mineral like consistencies, and changes in the fracture. Because of its physical character and the nature of the deposits in which it occurs, coal is classed as a rock.

Table 2.2: Changes in composition of wood, peat, coals

Genus	Moisture in raw state, %	Percent on dry, ash-free basis			
		Carbon	Hydrogen	Oxygen	Volatile matter at 900 ^o C (1652 ^o C)
Wood (typical composition)	20	50	6	42.5	75
Peat (typical composition)	90	60	5.5	32.3	65
Brown coal	60-40	60-70	About 5	>25	>50
Lignite	40-20	65-75	About 5	16-25	40-50
Subbituminous	20-10	75-80	4.5-5.5	12-21	About 45
Bituminous	10	75-90	4.5-5.5	5-20	18-40
Semibituminous	Under 5	90-92	4.0-4.5	4-5	18-40
Anthracite	Under 5	92-94	3.0-4.0	3.4	15

Such changes, which may have taken, hundreds of thousands or millions of years, are believed to have converted peat to lignite and progressively, through successively higher ranks of coal, to anthracite. The duration and severity of the conditions to which the former layer of peat was exposed during this period, as well as the nature of the organic deposit, probably determined the rank of coal, which was finally produced. Estimates of the temperatures to which coals have been subjected range from below 100 up to 600^oC (212 to 1112^oF). In deeply buried coal pressures of 1500 atm may have been reached.

The advanced state of transformation typified by Pennsylvania anthracite is probably due to the enormous pressures to which the deposits were subjected when the Appalachian Mountains were formed. The strata containing the vegetal matter seem to have been thrown into immense folds, and very great pressures must have been

developed in the crumpling process. The extent of these forces can be appreciated from the convolutions of the strata, a profile of some of the anthracite structures. The anthracite seams are believed to be extensions of the seams, which contain the bituminous coking coals in central and western Pennsylvania. During the mountain-building era, the greatest pressures and highest temperatures were probably experienced in the eastern portions of the Pennsylvania coal fields. These conditions would likewise account for finding the bituminous coals with the highest free carbons and, in general, the lowest volatile contents in the eastern section of Pennsylvania.

The long period, during which pressure, accompanied by the action of heat, was probably exerted, is termed the "dynamochemical period" of transformation. The conversion of peat to coal is termed "metamorphism," or "coalification."

There is no satisfactory means for computing the rate at which the coal deposits were produced, or the amount of vegetal matter, which made up a deposit. The latter can be estimated only from the rates at which existing deposits have been formed. Studies have indicated that the decomposed mass of vegetation in a swamp shrinks to one-seventh or one-eighth of its volume in the formation of old, compressed peat, and that the latter accumulates at the rate of perhaps 1 ft in 100 years. The rate of formation of coal from the peat is much harder to estimate, but it is possible that about 3 ft of old peat may have been required for the formation of 1 ft of bituminous coal. Thus, roughly 20 to 25 ft of accumulated vegetal matter may have produced 1 ft of coal.

All coal seams contain considerable amounts of inorganic material. Bands or layers of coal are often separated by layers of clay, shale, slate, or other inorganic material. The inorganic layers vary from very small fractions of an inch up to many feet in thickness. The thin layers may represent the soil washed into the swamp by high water in the spring. The thicker layers, which form the dividing lines between successive seams of coal, may represent the effects of alternate elevations and depression of the entire ground area. Inorganic material, including clay, iron pyrites, limestone, sand, and the like, is also distributed throughout the mass of the coal itself in the form of irregular

inclusions, which vary all the way from large masses down to fine particles. Some of these inclusions may have been deposited, either as suspended particles in water or as dust, during formation of the layer of peat. Others possibly resulted from percolation of mineral -bearing waters through the coal seams. Changes have probably occurred in the compositions of some of the inorganic deposits; thus sulfates may have been gradually reduced by reaction with organic matter to form sulfides, such as iron pyrites. Sulfides have possibly also been formed from organic sulfur, which was evolved as hydrogen sulfide during decay of the vegetal matter. Sulfates in turn may have been produced by oxidation of sulfides, a reaction, which can occur slowly when the coal in a seam is exposed to air.

Inorganic elements are combined in organic structures of plants. A large proportion of the inorganic matter so combined will remain in the coal deposit. It represents a second class, termed "inherent" mineral matter, which is, however, usually very small in amount.

Obviously, no two coal deposits can have been produced from exactly like materials, or exposed to the same conditions in the course of their formation. Differences in plant materials and in coalification conditions are true, not only of the various seams of coal but of the parts of an area making up a deposit. They are responsible for the differences in analyses and other properties, which are observed in a coal seam.

Although the theories of coal formation which have just been outlined probably account for the formation of most coals, they do not explain the formation of cannel or boghead coals. Cannel coals contain large proportions of spores and spore extines. Spores are the asexual reproductive organs of lower types of plants, such as liverworts, mosses, and ferns. The outer layer, or extine, is composed largely of waxy and resinous substances, which are very resistant to chemical changes and the actions of microorganisms; consequently they remain unchanged long after the inner, living portion of the spore has disintegrated. The conditions for formation of a peat deposit rich in spores and spore extines may have occurred in a pond in a peat bog. Into it spores and

pollens, together with other fragmentary vegetal debris, were washed by incoming water and collected in large masses. The deposit was subsequently covered with soil, and by a series of coalification transformations, metamorphosed into a coal characterized by a high content of waxy material, cannel coal. [9]

2.2.1 Elementary composition and analysis of coals

The principal elements from which coals are composed are the same ones, which make up wood and other vegetal matter: carbon, hydrogen, and oxygen, together with lesser amounts of sulfur, nitrogen, and other elements characteristic of the inorganic matter. Carbon, hydrogen, oxygen, nitrogen, and a portion of the sulfur are combined in very complex molecules with high molecular weights, which were produced from the original vegetal substances by the coalification reactions. Attempts to isolate individual organic compounds from coal have been almost entirely unsuccessful. No uncombined carbon is present.

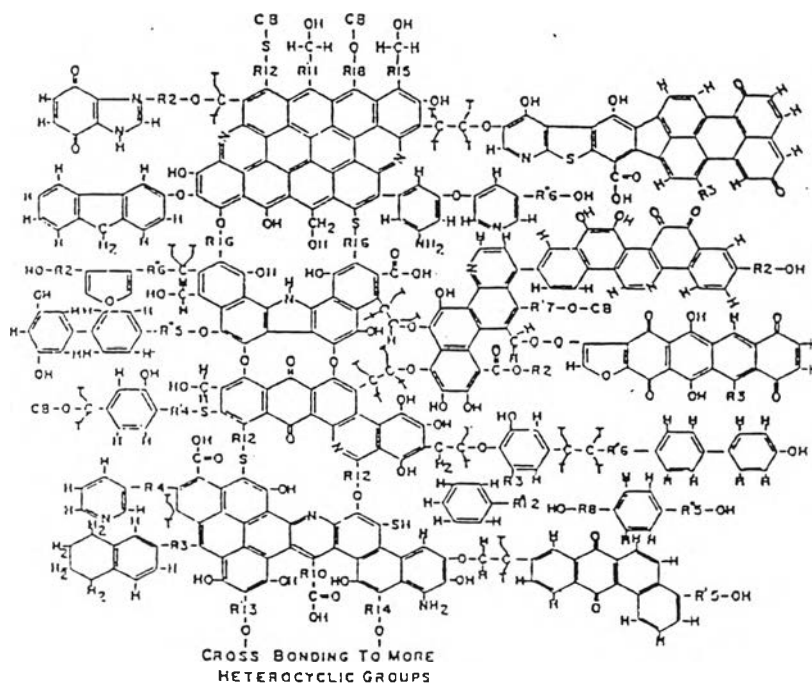


Figure 2.1: Possible chemical structure of coal

The primary methods for the analysis of coals are the proximate analysis and the ultimate analysis. These methods are of value only when they are based on representative samples of the coal. Too much attention cannot be paid to the selection of a sample, which properly represents the average composition of the coal to be tested and in the preparation of the sample for analysis. American Society for Testing Materials (ASTM) Specifications should be followed in sampling, in preparation of the laboratory sample, and in the proximate and ultimate analyses.

2.2.1.1 Proximate Analysis.

The proximate analysis comprises determinations of moisture, volatile matter, ash, and fixed carbon (the last by difference). With it is usually included a determination of sulfur, and sometimes phosphorus. The proximate analysis is the most widely used method for analyzing coals. It is relatively quick, easily carried out in the average laboratory, and for most applications furnishes a satisfactory indication of the quality of a coal. The results, except moisture, are usually expressed on the basis of percentages by weight of dry coal.

Moisture. Moisture is determined by drying a weighed sample of the coal at a temperature between 104 and 110 °C (219 to 230 °F). The moisture content varies with such factors as the mine from which the coal was removed, the coal seam, and the extent to which the coal has been exposed to the weather. In some cases, as a result of air drying, atmospheric exposure decreases the moisture; in others, rain or snow materially increases it. In order to ensure that the moisture determination is significant, particular care is necessary in sampling.

In general, the moisture contents of coals as mined from some of the principal fields range as follows:

	<i>Percent by weight</i>
Eastern Appalachian bituminous coals	1-4
Western Appalachian and Ohio bituminous coals	2-8

Indiana, Illinois, Iowa, and Missouri bituminous coals	8-17
Subbituminous coals	12-30
Lignite	20-45

Moisture, particularly a high percentage, is naturally undesirable to the purchaser of a coal because a portion of the heat of combustion of the coal is consumed in its evaporation.

Volatile Matter. The volatile matter represents that portion of a coal which is converted into volatile products when the coal is heated in the absence of air. Because the proportion thus vaporized varies with temperature and time of heating, for comparative results the conditions of the test are standardized and are rigidly adhered to. A 1-g sample of the dry coal in a weighed, covered platinum crucible is heated for exactly 7 min at $950 \pm 20^\circ\text{C}$ ($1742 \pm 36^\circ\text{F}$). The loss in weight times 100 equals the percentage of volatile matter.

The concentration of volatile matter ranges from about 2 to 8 percent in anthracites, and up to over 40 percent in some American bituminous coal. It is a very important value to consumers of coal. High-volatile coals, for instance, tend to burn with a long flame and may give much smoke. In order to secure maximum thermal efficiency during combustion, the volatile matter must be completely burned; the coal, therefore, requires careful firing or is burned on grates designed for its combustion. Steam coals containing a relatively low volatile content, 15 percent, have often been preferred because they tend to give less smoke. Powdered coal for boiler firing is preferably high in volatile matter, although low-volatile coals have also been used satisfactorily in this form. The gases evolved from the powdered coal aid in rapid combustion. On account of the high yields of gas obtainable from high-volatile coals, they are preferred for the manufacture of coal gas. The importance of the volatile matter in byproduct coking

Ash. The ash is determined by complete combustion in excess air of a weighed sample of the coal. From the weight of noncombustible residue the percentage of ash is

calculated. The following figures show the range in ash content of the coals from three important bituminous fields in the United States:

	<i>Percent by weight</i>
Pennsylvania	5-12
Illinois, Indiana	7-17
Oklahoma	6-11

Coal ash is derived from clay, iron pyrites, limestone, sand, and other mineral matter, all in a more or less finely divided form distributed throughout the coal in the seam; clay, shale, or slate from the floor, the roof of the seam, or veins in the coal mass; and the inherent inorganic matter chemically combined with the organic matter of the coal. Although the ash in coals in the United States varies widely in chemical composition, it usually comes within typical percentage limits, as follows:

Silica, SiO_2	20- 60
Aluminum oxide, Al_2O_3	10- 35
Ferric oxide, Fe_2O_3	5- 35
Calcium oxide, CaO	1- 20
Magnesium oxide, MgO	0.3- 4
Titanium oxide, TiO_2	0.5- 2.5
Alkalies, $\text{Na}_2\text{O} + \text{K}_2\text{O}$	1- 4
Sulfur trioxide, SO_3	0.1- 12

Fixed Carbon. The fixed carbon is obtained by subtracting from 100 the sum of the percentages of volatile matter and ash in the dry coal.

Sulfur. Sulfur usually occurs in coal in the form of inorganic and organic compounds. The Inorganic forms are pyritic sulfur, FeS_2 , and sulfate sulfur, CaSO_4 and $\text{Fe}_2(\text{SO}_4)_3$. Pyrites occur as particles or masses which range from microscopic size to coarse lumps, distributed through the coal. They also occur as bands in the coal. In fresh coal the sulfate sulfur is low, but it increases as the coal weathers. Organic sulfur is combined in complex coal molecules and is almost uniformly distributed through the

pure coal substance. The sulfur contents of coals vary from a fraction of 1 percent to 10 percent or more. In the American coals now utilized in industry it usually ranges between 0.5 and 3 percent, although it may run to 5 percent in some western coals. The distribution of the sulfur forms in certain samples of typical coals is shown in Table 2.3

Table 2.3: Distribution of sulfur forms in certain samples of typical coals [6]

Source of sample, bed, and state	Total S, %	Pyritic S, %	Organic S, %	Sulfate S, %
Pocahontas No. 3 (L.V.), W. Va.	0.56	0.08	0.47	0.01
Beckley (L.V.), W. Va.	0.81	0.22	0.58	0.01
Pittsburgh, Pa.	1.08	0.41	0.64	0.03
Upper Freeport, Pa.	1.21	0.47	0.67	0.07
Pittsburgh, Pa.	1.41	0.61	0.80	0.00
No. 6, Ill.	3.28	2.03	1.10	0.15

Sulfur is determined by oxidation to sulfur dioxide and sulfur trioxide, absorption of the oxides with an alkali to form the corresponding sulfite and sulfate, oxidation of the sulfite to sulfate, and finally conversion of all the sulfate to insoluble barium sulfate. From the weight of barium sulfate produced, the percentage of sulfur in the coal is calculated. The commonest objection to a high- sulfur content in a coal is the correspondingly large proportion of sulfur dioxide formed when the coal or its products are burned.

Phosphorus. Phosphorus occurs in coal both as phosphates and as organic phosphorus compounds. On combustion of the coal all the phosphorus enters the ash, and the amount is determined by analysis of the ash. Phosphorus is not important in combustion; but in evaluating coal for the production of metallurgical coke, the determination is frequently important

2.2.1.2 Ultimate Analysis.

In an ultimate analysis is determined the percentages of the principal elements in a coal, carbon, hydrogen, and oxygen, together with the so-called "minor" constituents, nitrogen and sulfur. The carbon and hydrogen are determined by burning the coal in oxygen in a combustion tube under controlled conditions. The carbon dioxide from the carbon and the water formed from the hydrogen are removed from the combustion gases in absorption tubes containing known weights of suitable absorbing materials. From the weights of the carbon dioxide and water absorbed, respectively, the percentages of carbon and hydrogen are calculated.

The nitrogen is determined by the Kjeldahl method. A small sample of the coal is completely oxidized by boiling with a mixture of concentrated sulfuric acid, potassium sulfate, and a little mercury. After the mercury is precipitated, sodium hydroxide is added in excess; and the ammonia formed during the oxidation is distilled off and determined by standard analytical methods. The amount of ammonia is used to calculate the percentage of nitrogen in the coal. The nitrogen contents of American coals usually range between 1 and 2 percent. The nitrogen is apparently linked in the organic molecules.

The method for determining sulfur has been described in the proximate analysis. No satisfactory method has been developed for the determination of oxygen. It is calculated by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, sulfur, and ash in the dry coal from 100. This procedure has the disadvantage of throwing the accumulated errors onto the oxygen.

The ultimate analysis takes much longer to perform than the proximate analysis and requires considerable technical skill. Although the information, which it furnishes, is useful, it is not essential as a rule in plant operation. Consequently, ultimate analyses of coals are seldom made in industrial analytical laboratories. [10]

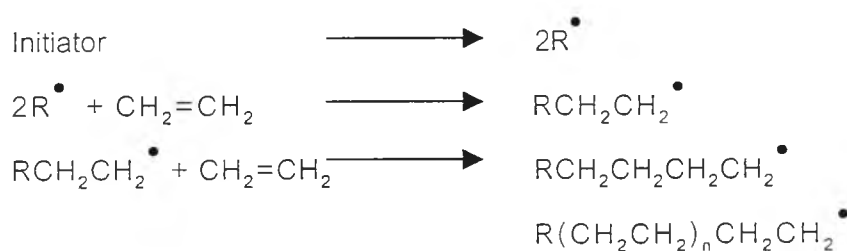


2.3 Polyethylene

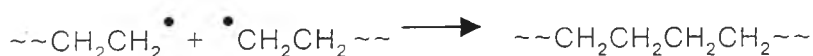
The manufacture of polyethylene is the most important outlet for ethylene, accounting for about 50% of consumption in the USA, and rather more than that in Western Europe. Polyethylene is the largest tonnage polymer made. US capacity is about 7.6 million tons per annum.

There are three distinct types of polyethylene. The original types, now called low density polyethylene was discovered by workers at ICI in the UK 1933, and was first produced commercially in 1938. It is a relatively soft, flexible plastic, probably most familiar as clear wrapping film. High-density polyethylene or HDPE, a harder, more rigid plastic, typically used for articles like buckets and washing-up bowls, was introduced in the mid-1950s. Linear low-density polyethylene, which has similar properties and uses to low density polyethylene, was introduced towards the end of the 1970s. This group of products provides an interesting example of the effects of process chemistry on polymer structure, and hence on polymer properties and applications.[11]

Low-density polyethylene is made by free radical polymerization. The reaction is carried out at temperatures from 80 to 300°C and pressures in the range 1000 to 3000 atm. Either oxygen or organic peroxide is used as the initiator. Initiation and propagation occur as follows:

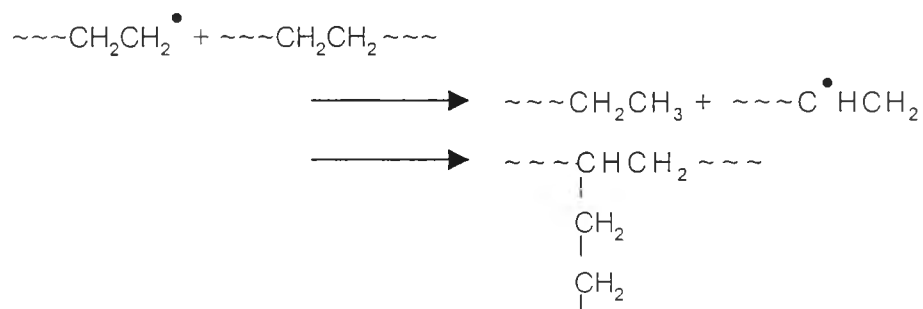


Termination occurs by coupling and disproportionation of free radicals:

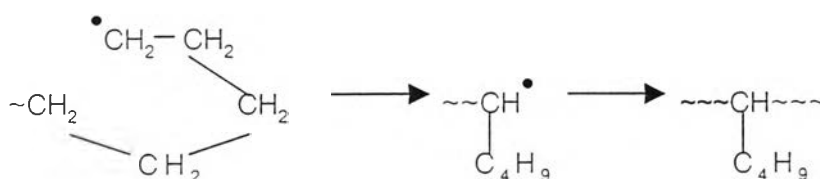




If the above reactions were the only one to occur during the polymerization, the product would be linear polyethylene, with the structure $[-\text{CH}_2\text{CH}_2-]_n$. In fact, low density polyethylene does not have this structure. Its molecules, far from being linear, are quite highly branched. Branches of up to five carbon atoms result from chain transfer reactions, in which hydrogen atom abstraction results in the active center being transferred from one position to another. In intermolecular chain transfer, the free radical site is transferred from the growing radical to a finished polymer molecule. This leads to the formation of a long branch:



In intramolecular chain transfer, the radical site is moved from one position on the radical to another a few carbon atoms away, resulting in the formation of a short branch:



As we will see shortly, the branching has a profound effect on the properties of the polymer.

The pressures used in the manufacture of low-density polyethylene are exceptionally high for a chemical process. Since the use of such pressures is expensive

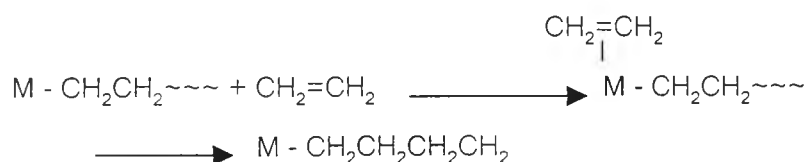
both in terms of capital costs and of operating cost, the question arises as to why they are used. The reason is that it is only at very high pressures, i.e. at high ethylene concentrations, that the propagation reactions are fast enough for high molecular weight polymer to be formed.

High-density polyethylene is made by an entirely different type of process, called *co-ordination* or Ziegler polymerisation. This was discovered by Karl Ziegler in 1953, and the first commercial production of HDPE was about two years after that.

The catalyst systems developed by Ziegler consist of complexes formed from aluminium alkyls and transition metal halides, typically triethylaluminium and titanium tetrachloride. In the presence of such catalysts, polymerization of ethylene occurs at about 100°C and at moderate pressures. Originally the reaction was carried out in an inert solvent such as hexane, but now it is also carried out in the gas phase. Quite separately from Ziegler, other workers developed metal oxide catalysts.

The mechanism of co-ordination polymerization is complicated. We will simply consider it in outline.

The polymer chain grows at active metal sites on the catalyst, molecules of ethylene being first co-ordinated to the site, and then inserted between it and the growing chain:



Chain transfer to polymer does not occur, and the polymer obtained is linear. It is this fact that accounts for the difference between its properties and those of low-density polyethylene.

One of the reasons why polymers have useful mechanical properties is that there are large attractive forces between the very big polymer molecules. In non-polar polymers like polyethylene the attractions are due to van der Waal's forces. In other polymers, dipole-dipole interactions or hydrogen bonding may be involved. It can be appreciated that the more closely and regularly the polymer molecules can pack together, the stronger will be the forces between them. In high density polyethylene, with its regular linear structure, the molecules can pack together very closely in orderly arrays, called *crystalline regions*, for most of their lengths. In low density polyethylene the branches tend to get in the way, and a much smaller proportion of the total length of the molecules is in close packed ordered regions. This results in the polymer being softer, less strong, and having a lower melting point than the linear polymer, and also, as is indicated by the name, in its having a lower density.

The two products have different ranges of applications, reflecting their different properties and also the fact that low density polyethylene has traditionally been cheaper than high density polyethylene. This price relationship may seem strange in view of the costs associated with the operating pressure in the low-density polyethylene process. The cost of making and handling the catalyst in the polymer, more than outweighed the cost of high pressure operation. With modern high activity catalysts this is probably no longer the case, and the price differential probably reflects the fact for many applications high-density polyethylene is the superior product. [12,13]

2.4 Physical and chemical properties

The most important property of polyethylene is its molecular weight and its distribution within a sample. Methods used to determine molecular weights are numerous. A widely used one is viscosity and the melt flow index, MFI, measure the extent of polymerization. A polymer with a high melt flow index has a low melt tensile strength.

Polyethylene is to some extent permeable to most gases. The higher density polymers are less permeable than the lower density ones. Polyethylene has a low degree of water absorption and is not attacked by dilute acids and alkalis. However, concentrated acids attack it. Its overall chemical resistance is excellent. Hydrocarbons and chlorinated hydrocarbons and swell slowly in these solvents affect polyethylene. Tensile strength of polyethylene is relatively low, but impact resistance is high. The use of polyethylene in insulation is due to its excellent electrical resistance properties.[14]

Table 2.4: Typical Properties of Polyethylene [13]

Polymer	Melting point range °C	Density g/cm ³	Degree of crystallinity %	Stiffness module psi x 10 ³
Branched,				
Low density	107~121	0.92	60~65	25~30
Medium density	0.935	75	60~65
Linear, High density				
Ziegler type	125~132	0.95	85	90~110
Phillips type	0.96	91	130~150

2.5 Thermal cracking

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which crack, by a β -scission mechanism.

The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the "RK-theory" as follows to explain the cracking of normal paraffin:

The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approaches each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary secondary primary free radical. [15]

Cracking of either the original or isomerized radical then take place at carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an alpha olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect to the carbon skeleton.

The primary radical derived from this step may immediately re crack at the β position to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived from cracking reaction of normal paraffin; primary radicals are derived from cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive re cracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction. [11]

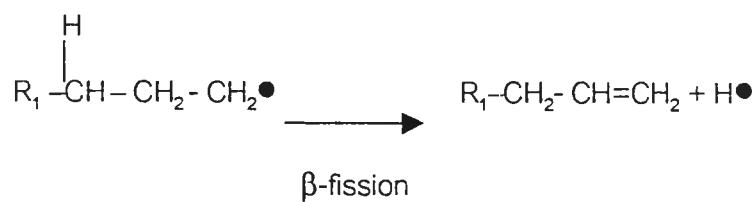
A schematic representation of polyethylene cracking is as follows;

1. Initiation Step



2. Propagation Step

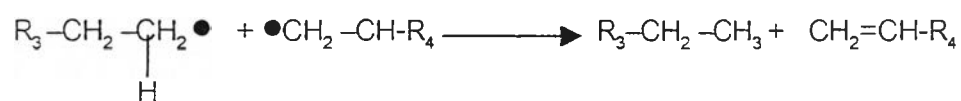
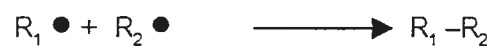
2.1 β -fission



2.2 Chain transfer



3. Termination Step



2.6 Catalytic cracking

Catalytic cracking is the most important and widely used refinery process for converting heavy oil into more valuable gasoline and lighter product. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced

thermal cracking because of more gasoline having a higher octane and less heavy oil and unsaturated gases are produced.

Commercial cracking catalysts can be divided into three classes:

1. Acid-treated natural aluminosilicates
2. Amorphous synthetic silica-alumina
3. Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

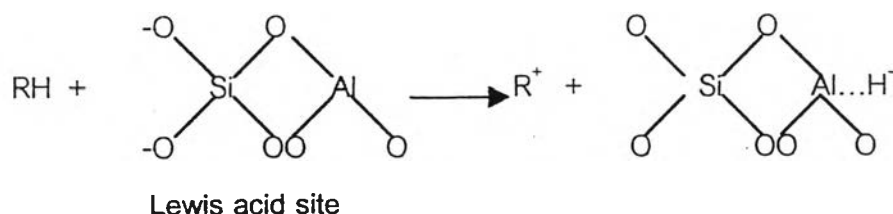
Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are:

1. Higher activity
2. Higher gasoline yields at a given conversion
3. Product of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield
5. Increased isobutane production

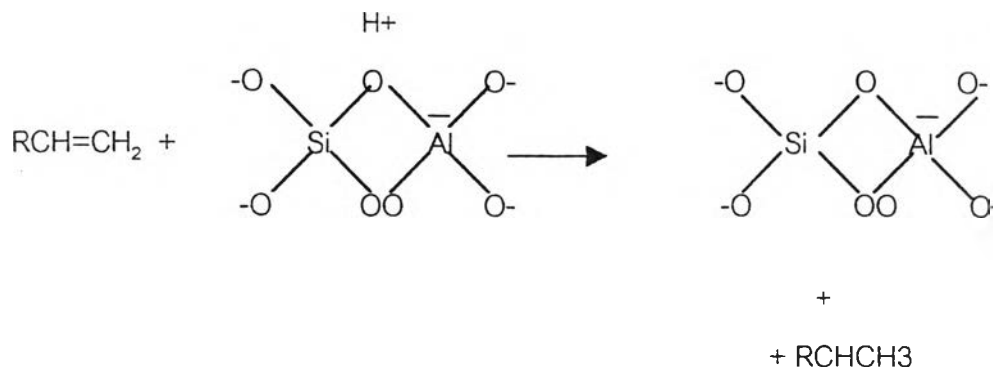
A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer-lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions. The following illustrates the different ways by which carbonium ions may be generated in the reactor.

[17,19]

1. Abstraction of a hydride ion by a lewis acid site from a hydrocarbon



2. Reaction between a Bronsted acid site (H^+) and an olefin



3. Reaction of a carbonium ion formed from step 1 or 2 with another hydrocarbon by abstraction of a hydride ion



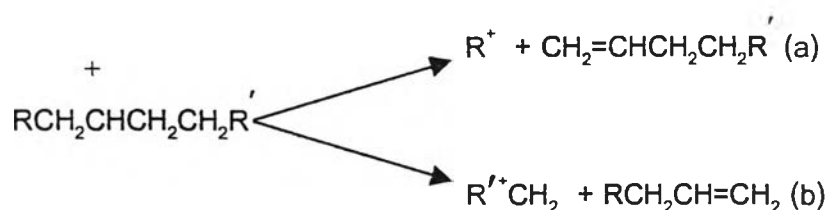
Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming. This isomerization reaction is responsible for a high ratio of branched isomers in the products.

The most important cracking reaction, however, is the carbon-carbon beta bond scission. A bond at a position beta to the positively charged carbon breaks heterolytically, yielding an olefin and another carbonium ion. This can be represented by the following example:



The carbon-carbon beta scission may occur on either side of the carbonium

ion, with the smallest fragment usually containing at least three carbon atoms. For example, cracking a secondary carbonium ion formed from long chain paraffin could be represented as follows:



If $\text{R} = \text{H}$ in the above example, then according to the beta scission rule (an empirical rule) only route b becomes possible, and propylene would be a product:



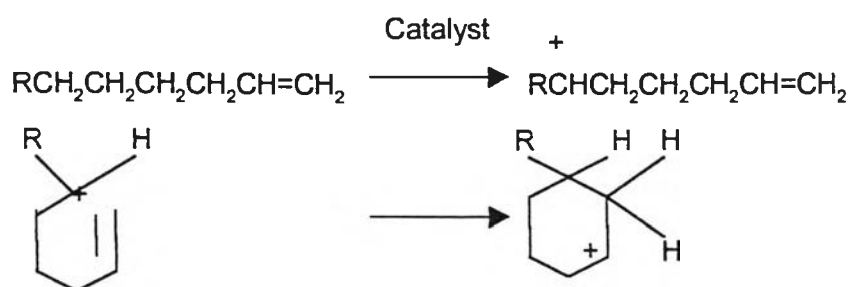
The propene may be protonated to an isopropyl carbonium ion :



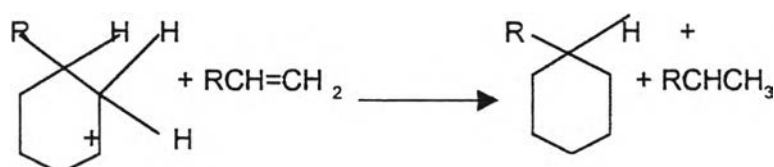
An isopropyl carbonium ion cannot experience a beta fission (no C-C bond beta to the carbon with the positive charge). It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propene by eliminating a proton. This could explain the relatively higher yield of propane from catalytic cracking units than from thermal cracking units. [12,13]

Aromatization of paraffins can occur through a dehydrocyclization reaction.

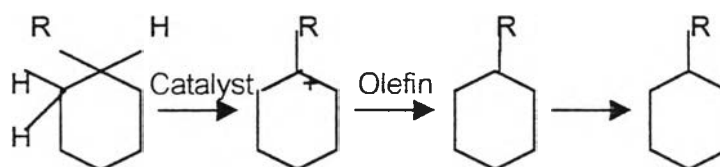
Olefinic compounds formed by the beta scission can form a carbonium ion intermediate with the configuration conducive to cyclization. For example, if a carbonium ion such as that shown below is formed (by any of the methods mentioned earlier), cyclization is likely to occur.



Once cyclization has occurred, the formed carbonium ion can lose a proton, and a cyclohexene derivative is obtained. This reaction is aided by the presence of an olefin in the vicinity ($\text{R}-\text{CH}=\text{CH}_2$).



The next step is the abstraction of a hydride ion by a Lewis acid site from the catalyst surface to form the more stable allylic carbonium ion. This is again followed by a proton elimination to form a cyclohexadiene intermediate. The same sequence is followed until the ring is completely aromatized.



During the cracking process, fragmentation of complex polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins. These compounds can be a source of C_6 , C_7 , and C_8 aromatics through isomerization and hydrogen transfer reactions.

Coke formed on the catalyst surface is thought to be due to polycondensation of aromatic nuclei. The reaction can also occur through a carbonium ion intermediate of the benzene ring. The polynuclear aromatic structure has a high C/H ratio. [11]

2.7 Hydrocracking Processing

Hydrocracking is essentially catalytic cracking in the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks. Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene. The process can also use feeds with high aromatic content.

Products from hydrocracking processes lack olefinic hydrocarbons. The product slate ranges from light hydrocarbon gases to gasolines to residues. Depending on the operation variables, the process could be adapted for maximizing gasoline, jet fuel, or diesel production. [18,19]

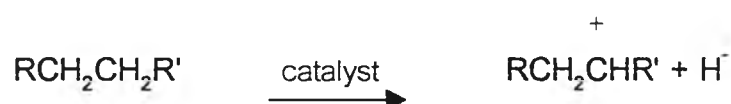
Table 2.5: Analysis of feed and products from hydrocracking process. [20]

Yields: Typical form various feeds:				
Feed	Naphtha	LCCO	VGO	VGO
Catalyst stages	1	2	2	2
Gravity, ° API	72.5	24.6	25.8	21.6
Aniline pt, ° F	145	92	180	180
ASTM 10% EP, ° F	154/290	478/632	740/1,050	740/1,100
Sulfur, wt%	0.005	0.6	1.0	2.5
Nitrogen, ppm	0.1	500	1,000	900
Yields, vol%				
Propane	55	3.4	-	-
Iso-Butane	29	9.1	3.0	2.5
n-Butane	19	4.5	3.0	2.5
Light naphtha	23	30.0	11.9	7.0
Heavy naphtha	-	78.7	14.2	7.0
Kerosine	-	-	86.8	48.0

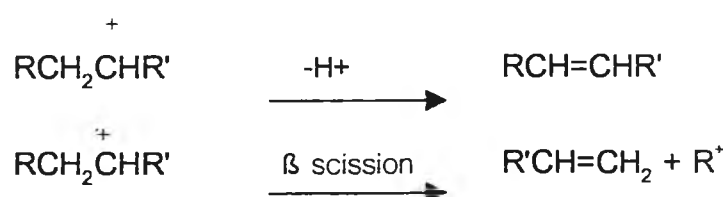
Yields: Typical from various feeds:

Feed	Naphtha	LCCO	VGO	VGO
Lt. Naphtha RON cl	85	76	77	76
Hv. Naphtha RON cl	-	65	61	61
Kerosine freeze pt, ° F	-	-	-65	-75
Diesel pour pt, ° F	-	-	-	-10

The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. Amorphous silica-alumina, zeolites, or mixture of them promote carbonium ion formation. Catalysts with strong acidic activity promote isomerization, leading to a high iso/normal ratios. The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements. As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst surface. The main hydrocracking reaction could be illustrated by the first step formation of a carbonium ion over the catalyst surface:



The carbonium ion may rearrange, eliminate a proton to produce an olefin, or crack at a beta position to yield to an olefin and a new carbonium ion. Under an atmosphere of hydrogen and in the presence of a catalyst with hydrogenation-dehydrogenation activity, the olefins are hydrogenated to paraffinic compounds. This reaction sequence could be represented as follows:





As can be anticipated, most products from hydrocracking are saturated. For this reason, gasoline from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation activity. Products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feedstock.

Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds.

Hydrocracking reaction conditions vary widely, depending on the feed and the required products. Temperature and pressure range from 400 to 480°C and 35 to 170 atmospheres, respectively. Space velocities in the range of 0.5 to 2.0 hr⁻¹ are applied.

[11]

2.8 Literature review

Hyun and Christine,[1] studied effect of reaction time on the coprocessing of low-density polyethylene with coal and petroleum. The effect of reaction time on the reactivity, conversion and product distribution of coprocessing reactions in systems containing LDPE, coal and heavy petroleum resid was evaluated by performing reactions for 30-360 min. LDPE reactions with reaction times that increased from 60 to 360 min resulted in conversion, in which increased from 39.5% at 60 min to 90.2% at 300 min. After 300 min the conversion decreased to 70.9%. Similar results were obtained with the LDPE and coal reactions; increased reaction time resulted in increased LDPE conversion as well as increased overall conversion. The conversions and hexane soluble products produced for ternary systems also increased with increased reaction time.

Hyun and Christine,[3] studied catalytic coprocessing of plastics with coal and petroleum resid using NiMo/Al₂O₃. The objective of their study was to determine the feasibility of coprocessing three different materials together: coal, petroleum resid, and waste plastics. The effect of using the ternary combination of coal, resid, and plastics on the conversion of solids to tetrahydrofuran (THF) soluble and the product distribution in terms of solubility in THF, toluene, and hexane was determined and compared to that obtained in binary and individual systems. Three systems, the individual species, binary combination, and ternary combination were reacted at conditions of 430°C and 8.7 MPa of H₂ introduced at ambient temperature for 60 min of reaction time. Presulfided NiMo/Al₂O₃ was used as the catalyst, typically at 1 wt % loading. PET reacted readily, while LDPE was difficult to convert. Binary reactions with resids resulted in high conversions of ~ 94% from PS and PET, while the reactions with LDPE yielded somewhat less conversion of ~ 72%. By contrast, reaction of plastics with coal converted substantially less, ranging from 70.2% for polystyrene and coal to 39.9% for LDPE and coal. Ternary reactions with coal, plastic, and resid resulted in high conversion for all systems (~ 89-95%) except those with LDPE (~77-81%).

Mingsheng and Christine,[15] studied thermal and catalytic coprocessing of Illinois no.6 coal with model and comingled waste plastics. Reactions were performed with individual model polymers including polyisoprene, polystyrene, high and low density polyethylene with coal alone in the presence and absence of a hydrogen donor solvent and catalysts at 400°C and of an initial H₂ pressure of 5.6 MPa. The conversion to THF solubles and product distribution from coprocessing reactions with coal and each polymer performed at the same reaction conditions were compared to those obtained with individual polymers. The coprocessing reactions with polyisoprene and polystyrene yielded thermal and catalytic conversions in the range of 62.3 to 95.5% while the coprocessing reactions with HDPE or LDPE yielded low conversion in the range of 20.2 to 43.2%.

Nakamura and Fujimoto,[16] studied development of new disposable catalyst for waste plastic treatment for high quality transportation fuel. An iron supported coal-

derived active carbon catalyst showed excellent activity for liquefaction of polypropylene at low reaction temperature (380°C) to give colorless distillates selectively (98 wt%) in the presence of small amount of H_2S . Free radical on active carbon should initiate a cracking reaction by hydrogen abstraction to form a hydrocarbon radical. H_2S and HS should promote radical transfer from the hydrocarbon radical to large size hydrocarbon molecule to suppress consecutive cracking of the hydrocarbon radical and to promote cracking of the large size molecule, which cannot contact with solid catalyst.

Paul and Elizabeth,[2] studied interaction of plastics in mixed-plastic pyrolysis. The interaction of the main plastic types in plastic mixtures is significant in predicting the likely yield and composition of products from different plastic mixtures. The six main plastics in municipal solid waste are high-density polyethylene, low-density polyethylene, polypropylene, polystyrene, poly(vinyl chloride) and poly(ethylene-terephthalate). Each of the plastics was pyrolyzed individually in a fixed-bed reactor heater at $25^{\circ}\text{C min}^{-1}$ to a final temperature of 700°C . The yield and composition of the derived oil/wax and gases was determined. The main gases produced from the individual plastics were hydrogen, methane, ethane, ethene, propane, butane and butene. Analysis of the oil/wax showed that the polyalkene plastics, HDPE, LDPE and PP, gave a mainly aliphatic composition consisting of a series of alkanes, alkenes and alkadienes. PVC gave a mainly aromatic oil, PS and PET, which have aromatic groups in their structures, also showed a more aromatic composition.