Theory of Carbonization of Coal

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Introduction

Coke making is one of the oldest coal conversion pro-
cesses. The history of the evolution of coke making is traced
from coking in piles to the development of beehive coking to the
modern byproduct coking industry.[1]* The theories of coal to coke
transformation are discussed with reference to the changes that
take place in coal and the products evolved during carboni-
zation. The formation of semi-coke and coke are also discussed
with emphasis on the role of degasification, plasticity, and
solidification. Coking coals possess the unique property of
softening, swelling, fusing, and solidifying to form a coherent
porous structure when carbonized. Only a narrow group of coals in
the lignite to anthracite series possess the properties which
distinguish them as coking coals. Medium volatile bituminous
coals possess the best coking characteristics but these properties
overlap into the high and low volatile bituminous coals. The
macro and microstructures of cokes produced from coals of various
rank are described and the relation of coal petrographic compo-
sition to the coke petrographic characteristics is traced. A
discussion is also presented on what occurs in the coke oven
during carbonization.

History of Coking

The process of carbonization proceeded as an engineering
technological development with very little dependance on under-
standing the mechanism of coal to coke transformation. However,
the process of carbonization has been under investigation for the
past 60 to 70 years even though it is not completely understood
today.

The earliest record of coal carbonization dates to about
1590 when John Tornborough, Dean of York was granted a patent to
purify coal of its offensive smell by coking. In 1656, Sir John
Winters was charring coal to drive off sulfur and arsenic. These
early attempts at coking coal were aimed at making a product from
coal by carbonization that was less objectionable than coal to
burn or use in domestic heating.[2]

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* See References.

Wood charcoal was the accepted fuel for reducing iron ores from prehistoric times till early in the eighteenth century. Coal and/or coke were considered unsuitale for smelting since the excessive carbon and sulfur picked up by the iron from those fuels made it too brittle for use particularly as wrought iron. The scarcity and price of charcoal promoted continued investigations into developing a suitable smelting fuel from coal. In 1735, Abraham Darby designed a blast furnace with a tall stack which permitted more drought so that coke from low sulfur coals could be used to produce sponge iron. In 1784 Cart and Onions discovered puddling for removing carbon from iron by oxidizing with iron-ore. From this point on coke from coal grew as a blast furnace fuel. The blast furnace produced pig iron while the charcoal smelter produced sponge iron.[2]

In USA, uncarbonized anthracite which is a non-coking coal was used as the major blast furnace fuel in the small furnaces operating in the early 19th century. It was not until about 1875 that coke made up more than 50 percent of the blast furnace fuel. However, anthracite continued to be used to some extent until about 1923.[3]

The first coke from coal was produced in charcoal piles in which coal was substituted for wood in the pile. The piles, Figure 1A, were circular domed shaped configurations in which the coal was ignited and the combustion allowed to proceed for a time then the pile was covered with soil or some suitble material to restrict air so that the smoldering coal could coke. Some piles were built with stacks or other means of creating a draft to kindle and ignite and partially combust the pile.

One popular early form of oven was called the beehive, Figure 1B. These dome-shaped structures were built side by side and each chamber had a hole in the top for charging coal. A door in the side served to admit combustion air and for discharging coke. Part of the coal was burnt to coke the coal and no attempt was made to collect the volatile byproducts distilled from coal. Late in the 19th century, coke ovens were developed in Europe to produce coke and recover byproducts. It was the need for coal byproducts for making explosives and a growing demand for coke for an expanding steel industry that resulted in the rapid growth of the byproduct coking industry in the U.S. during and after World War I. A typical byproduct coke oven is shown in Figure 2.

Historic and Modern Theories of Carbonization

Solvent Extraction Theory - One of the earliest theories for explaining the behavior of coking coals employed solvent

extraction studies of coal to prove the "Coking Principle". As early as 1860 systematic solvent extraction experiments were being conducted on coal. Wheeler and Bone, starting in 1910 worked for 25 years on coal extraction studies using pyridine, chloroform, light petroleum, ethyl-ether, and acetone in a soxhlet extraction apparatus. The coal fraction insoluble in pyridine at 115°C was called the alpha fraction (non-coking) or "ulmins"; that part of the pyridine extract which was insoluble in chloroform was called the beta fraction or "carboids"; and the part soluble in chloroform was called gamma fraction (strongly agglutinating which was further subdivided into four gamma compounds by extraction with the remaining solvents.[4]

Fischer and his co-workers used benzene extraction under pressure to obtain a residue called "Restkohle" which was non-coking and a soluble fraction called "Bitumen" which coked. Based on the solvent extraction work, the coal was postulated to consist of extractable coking substances and non coking residues. This theory lost popularity for a time but has recently been resurrected and modified.

Transient Fusion Theories - The "Transient Fusion" theory was suggested by Audibert in 1926 and 1927. He likened coal to $KClO_3$ which melts when heated to form an unstable liquid which decomposes to form a solid as one of the decomposition products. This theory is not considered satisfactory by most coal scientists.[4]

Precursors of Metoplast Theory - Kreulen in 1948 considered coal to be an organosol consisting of an oily dispersion medium (oily phase) and a dispersed phase (micelle phase). The micelle consists of an oleophilic part (protective body) and an oleophobic part (micelle nucleus). The oily phase and protective body consist of bitumens and the micelle nucleus is humins. Coke formation according to Kreulen is not the agglutination of inert material by a binder, but a process shared by the whole system, for which all fractions are responsible.[4]

Hirst 1943 restated by Lahiri (1951) believed the differentiation between dispersed phase and dispersing medium was not chemical but one of size and relative mobility. Houwink (1954) stated that any naturally occurring non-hardening resin may be considered to have three phases at temperatures above the gel point: (1) soluble molecules, freely rotating; (2) soluble molecules fixed by Van der Waal's forces; (3) insoluble molecules fixed by primary bonds (micelles). If the molecules in the system differ only in size then an isogel is formed. The system behaves as insoluble solids below the gel temperature. Lahiri considered

coal as an isogel with micelles, protective colloids and a low
molecular weight medium which becomes mobile at temperatures above
the gel point. Thus coking is a four stage process:[2]

1. Elevate temperature above the gel point.

2. Lower molecular weight fractions become mobile and
    lubricate micelles.

3. Volatization of these fractions forming primary tar,
    followed by solidification.

4. Formation of solid mass due to decomposition through
    loss of side chains and linking through primary
    bonds.

Metaplast Theory[4] - In 1950, Van Krevelen investigated
the kinetics of degasification and divided the pyrolytic decompo-
sition into three types of reaction.

(i)   Coal complex $\xrightarrow{\text{slow disentegration}}$ primary decomposition
        product and residue;

(ii)   Primary decomposition product $\xrightarrow{\text{rapidly}}$ final decomposi-
        tion gaseous and tarry products;

(iii)   Residue + semicoke + coke. (Secondary decomposition.)

He concluded primary decomposition finished at about 550°C, but
increased with rank. In summary he claims heating coal above
300°C causes thermal cracking with the result that aromatic clus-
ters begins to appear as free radicals. If the aromatic clusters
are sufficiently small and at the same time have a sufficiently
long lifetime, the fragments are mobile, giving the coal a plastic
character. Low-rank coals do not soften because the lifetime of
the radicals is too short while high rank coals do not soften
because the cracking yield is too small and the interaction of the
aromatic clusters too strong.

Fitzgerald believed that plasticity was due to an inter-
mediate component in a consecutive reaction from solid coal to
fluid coal to semicoke with the two rate constants being of about
the same order.

Fitzgerald postulated the following reactions:

(i)   Coking Coal (P) $\xrightarrow{k_1}$ "metoplast (M)
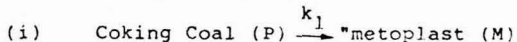
(ii)   Metoplast (M) $\xrightarrow{k_2}$ semicoke (R) + primary gas (G_1)

(iii)   Semicoke (R) $\xrightarrow{k_3}$ coke(s) + secondary gas (G_2)

Reaction (i) is depolymerization forming unstable "meta-plast" which causes plasticity. Reaction (ii) is cracking in which non-aromatic groups are split off producing weight loss. Reaction (iii) is a secondary degasification reaction in which semicoke is welded together with methane and hydrogen evolution and final coke formation.[4]

Thermobitumen Theory[2] - A. P. Oele proposed a "Thermo-bitumen" theory that predates the "Metaplast" theory and the latter bears some relation to the former. However Oele postulated that plastic behavior of coal is due mainly to the formation of a liquid primary product of pyrolysis. Pyrolysis implies extensive decomposition and according to the "Metaplast" theory extensive decomposition is not necessarily the main cause of plasticity in coal.

Liquid Crystal Theory[5] - Coal scientists generally agree that it is the vitrinite in coal that forms coke bond during carbonization. When the polymeric coal substance is heated a metoplaast is formed which peptizes the coal mass producing a plastic state which passes through a liquid crystal state that may or may not produce an ordered mosaic structure as the plastic material is transformed into a semicoke. The semicoke is further-devolatilized to produce final contraction and a coke residue. This latter theory is currently in a state of modification with additional developments.

Liquefaction Theory[6] - Neavel notes that only exinite and vitrinite in bituminous coals have plastic capability. The vitrinite which is a dominant coal maceral consists of packets (micelles) of more-or-less aligned molecular units (lamellae) of variable structures typified by condensed ring systems connected by bridging atoms. Functional groups (=O, -COOH, -OH, $-C_nH_m$) are attached to the ring carbons and some ring carbons may be satu-rated with hydrogen (hydroaromatic structures). Given's model as accepted by Neavel is shown in Figure 3. Different vitrinites depending principally upon rank show variations on this theme. Imperfect packing of the micelles leads to microporosity. Up to about 20 percent of relatively low molecular weight ("bitumen") is extractable by solvents through the pore system

Wendell Wiser, H. R. Brown, P. L. Waters, and R. C. Neavel all recognize the relationship between liquefaction and

plasticity of coking coals. Neavel proposed "that the development of plasticity in coals is essentially a transient, hydrogen-donar liquefaction process in which the solvating and hydrogen-donating "vehicle" is supplied by the coal itself, and it is the pro-gressive reduction of transferable hydrogen inventory which leads to progressive decay of fluidity even at isothermal conditions."

The three conditions cited by Neavel as necessary for the formation of low-moleculalr-weight substances by liquefaction of coals are: (1) the presence in the coal of lamellae bridging structures that can be thermally ruptured, (2) a supply of hydro-aromatic hydrogen, and (3) an initial, intrinsic potential for micellar and lamellar mobility (not related to the rupture of chemical bonds) which provides opportunity for free-radicals formed by bond rupture to contact potentially transferable hydrogen. These conditions appear necessary for the development of coal plasticity which varies with coal rank, type, and pro-cessing conditions. The bitumens are the low melting point (150-180°C) vehicle which solvates the micelles as they become thermally loosened. These hydroaromatic materials serve as mobile hydrogen-donars to stabilize free-radicals produced thermally before plasticity commences. The original bitumen/vehicle decom-poses around 480°C. Without this initial vehicle in coal no plas-ticity would occur and heating would cause polymerization without solvation. Anything that changes the quantity and quality of the vehicle will change the plastic properties of heated coal. Imposed pressures and larger particle size retard vehicle loss and the trapped vapors enhance plasticity. Oxidation of coal retards liquid yield and adversely affects plasticity. The effect on low rank high oxygen coals is most pronounced. Oxygenated substances evolve CO, CO_2, and H_2O and form weak ether links. When such materials crack off from non-mobile coal molecules free radicals are created and in the absence of transferable hydrogen free radicals are stabilized by "polymerization" forming mobility-retarding cross-links.

Tar yields from pyrolysis of coal are directly propor-tional to hydroaromatic hydrogen content and hydrogenation increases tar yeild.

Slow heating of marginally plastic coals destroys plas-ticity. Radicals formed prior to general softening must be stabilized by either hydrogen abstraction or repolymerization. Lack of contact with donor-hydrogen would result in repolymeri-zation.

Neavel summarizes ideal plastic development as follows:

(1) General mobility of micellar units (physical melting) commenced around 350-400°C as Van der Waals forces and hydrogen bonds become weakened, the bitumen serving as a necessary solvating vehicle and hydrogen donor during this phase.

(2) Viscosity decreases progressively as mean molecular size is reduced at a rate which reflects thermal rupture of bridging structures, but only so long as free-radicals thereby formed are stabilized by donor-hydrogen.

(3) As the limited donor-hydrogen inventory becomes consumed, free radicals that continue to be formed will increasingly "stabilize" by repolymerization, and having reached a minimum, viscosity will then increase progressively as low molecular weight substance volatilize from the metaplast or are "attacked" by the free-radicals.

(4) Repolymerization then becomes the dominant fate of free-radicals and the metaplast sets up as a semi-coke.

Coal Petrography

Coal Petrography has relatively recently helped clarify a number of previously incoherent ideas regarding the nature of coal, its heterogeniety, and the effects of macerals on the process of carbonization. The different macerals or plant derived organic-materials that make up coal behave differently even when they are from the same coal, Figure 3.[7] Exinite is which are highest in hydrogen of all the coal macerals becomes frothy and plastic and highly swollen during carbonization. The coke residue from exinite is small. The exinites lose their distinct characteristics as the coal rank increases. Vitrinites display plastic and swelling properties which vary with coal rank. They are capable of yielding coherent coke residues. Vitrinites are the coke bond forming materials in coking coals. Coal inertinites degasify but otherwise remain relatively inert during carbonization. The vitrinites have the ability to incorporate inerts to form a strong coke agglomerate. The bonding capacity of the vitrinite varies with coal rank.

Rheological Properties of Coal[8]

Coaking coals have the unique property of softening, swelling, agglomerating, and solidifying to form a strong porous coke. The plastic properties of heated coal have been widely investigated as a means of characterizing coking coals. The various methods used to investigate plastic properties include: absolute, agglutinating and free swelling tests, dilation,

torsional, gas flow permeability, extrusion, and penetrometer. These tests are empirical in nature but serve to measure this important property of coal.

One of the most widely used instruments for measuring the plastic properties of coal is the Gieseler plastometer. It is a constant torque plastometer. This instrument is a favorite in the U.S. and Japan. In this test a 5.0 gram sample of minus 40 mesh coal is tightly packed around a rod with rabble arms that has been inserted into a retart crucible. The stirrer at the start of the test is firmly held in the coal so that a 40-gram weight exerting torque through a pulley will not turn the stirrer. When the coal is heated from an initial temperature of 300°C at 3.0°C per minute the coal softens and become plastic and reaches a maximum plasticity then becomes less plastic as the coal is transformed to a semi-coke solid. The stirrer movement is measured throughout the test and the temperatures of initial softening and solidification are recorded together with the maximum fluidity in terms of dial divisions per minute which are the stirrer rotations that are translated through a spool pulley to another pulley with a pointer that is mounted on a dial. Typical Gieseler curves for high, medium, and low volatile coals are shown in Figure 4.

For most coking coals the plastic range which extends from softening to solidification falls within the temperatures of 350 to 550°C.

The Audibert-Arnu dilotometer is another popular rheological test. It is widely used in Europe. In this test a finely ground 2 gram coal sample is moistened and compressed in a mold to form a tapered cylindrical "pencil" that is 60 mm high and 6.5 mm in diameter. The pencil is placed in a metal tube with an inside diameter of 8 mm and a closed bottom. The sample and container are placed in a vertical electric tube furnace. A 7.8 mm diameter rod is placed on top of the sample. The rod is connected to an indicator pointer that moves along a graduated scale to indicate volume changes that take place during pyrolysis at 2°C/minute. The total weight on the sample is 150g. A typical dilatometric curve is shown in Figure 5. The softening is point, O_s; maximum contraction temperature, O_c, or initial swelling point; final swelling temperature O_e; contraction, C: dilotation, d: swelling, $S = c + d$ where c, d, and s are in percentages of initial sample heights. The plasticity index is $C/O_c - O_s)$ which is mean shape of the descending branch of the curve.[9]

The free-swelling test is another commonly used procedure to determine the agglomerating and swelling characteristics

of coal. A 1 gram sample of minus 60 mesh is placed in a covered
crucible and heated 820°C in 2-1/2 minutes the height of the
button produced is graded from the lowest button of 1 to that
which fills the cricible which is 9. Agglutinating tests, such as
Roga Test, mixes inerts with coal and then measure the strength of
the agglomerate on heating.

Sopozhikhov has developed a pentrometer which measures
the strength and thickness of the plastic layer developed during
carbonization. This instrument is widely used in easten Europe.
Reportedly there are correlations between the thickness of the
plastic layer, coal type and volatile matter.

Coking Process

To further examine the process of carbonization, we can
consider what happens in a single coal particle when heated,
Figure 6. The poorly conducting angular coal particle loses
surface moisture and in the temperature range below 200°C, the
occluded gases such as water, carbon dioxide, oxygen, nitrogen,
and methane are evolved while the particle becomes rounded. At
the first critical temperature level (350-450°C) there is a marked
evolution of high-molecular weight hydrocarbons (tars and oils
where the coal softens and develops internal pores. As the tem-
perature increases between 350-500°C, the force of entrapped gas
in the pores causes the softened coal to become deformable. The
evolved gases within the plastic particle lead to vacuole develop-
ment and swelling. At 400 to 600°C, the plastic mass solidifies
into semi-coke with liberation of additional high molecular weight
liquids and gases. At 600-700°C, the lower molecular weight
liquids and gases are evolved. From 700 to 1000°C is the second
critical temperature where low molecular weight gases stop and
large amounts of hydrogen are released. However hydrogen gas is
present after the coal softens. The semi-coke is transformed to
the final cellular structure of high temperature coke. The
amounts and temperature of release of volatiles are related mainly
to the rank and also the petrographic makeup of the coal. The
rate of degasification of different coals is shown in Figure 7.
As noted, the amount and rate of degasification is important to
the overall coking process in that it affects the behavior of the
plastic mass and the formation of pore structure of the coke as
the cells are formed.

The properties of the plastic mass that includes its
permeability to gases is another major factor in the coking pro-
cess. The fluidity of coal as measured in the Gieseler Plasto-
meter in relation to the rank of coal is illustrated in
Figure 8.

Coals below the rank of high volatile B or C produce thermally unstable metaplast that tends to decompose below the softening temperature of the coal and are not available to plasticize the micelle. These coals tend to produce incoherent coke or only sinter at the contacts between particles, Figure 9. The areas between particles may make up a significant portion of the sintered coke structure.

High Volatile A rank bituminous coals tend to produce more stable metaplast (thermobitumens) which plasticize the micelle and form coke but due to their high volatile content tend to shrink excessively and produce fissured relatively weak coke. These coals frequently become highly plastic during carbonization and the coal particles interact to destroy the interparticle porosity and the initial charge voidage is replaced by a new porous structure formed by gas moving through the low viscosity permeability mass. The bond between particles is a chemical bond Figure 9.

Medium volatile coals product the most thermally stable metaplast and produce the best coke since the particles fuse and destroy charge porosity without becoming frothy, Figure 9. The pressures (driving force) developed in the plastic layer of intermediate viscosity and permeability permits molding of the coke structure in the confined mass. Low volatile coals produce the least amount and the most thermally stable metaplast. The highly viscous particles entrap gas and the expanding gas creates significant driving force which tends to force particles to fuse together under pressure, Figure 9. These coals produce viscous low permeability plastic layers. The plastic envelope formed in the coking process entraps the gas and the expanding gas pressure is translated to the oven walls through the competent solid coke and plastic layer. These pressures can damage coke oven walls.

Coke fissure development is probably the most important feature affecting coke strength and fissures are probably due to shrinkage of the semi-coke which takes place above the upper limit of plastic range or solidification temperature.

The shrinkage is not evenly distributed throughout the solid mass because of the uneven distribution of temperature and because of the final cellular structure that forms from the semi-coke. As a result internal stresses occur to cause cracks or fissures.[10,11)

The agglomeration of the particles resulting from the softening and swelling of the particles allows the formation of a mass that is hard, cohesive and of an open structure. This phenomena mainly dictates the abradability of the coke and to a

certain extent its typical strength. However, the fissuring
determines the size of the pieces of coke and also affects the
impact strength of the coke.

The tendency of coke to fissure has been measured by the
average distance between the fissures. Experimental studies by
CHERCHAR[1,2] have shown that the distance between fissures is
proportional to the coefficient of shrinkage of coke at its
resolidification temperature. This coefficient of shrinkage has
been measured by using the Chevenard-Joussier dilatometer. A
typical shrinkage curve is shown in Figure 10. In addition to the
shrinkage determined by thermal gradients in coke ovens, the rank
and type of coal have an affect on the coefficient of shrinkage or
contraction. High-volatile coals have higher coefficients of
shrinkage in the solidification state as well as lower solidi-
fication temperature than low-volatile coals. Thus the con-
traction peaks can be reduced by addition of low- and medium-
volatile coal or antifissunats such as coke dust, petroleum coke,
etc. to the coal blend. (See Figure 10 for the effect of coke
dust to high-volatile coal.) Coking factors can also affect this
coefficient of shrinkage. For example, fast coking rates increase
the thermal gradients to cause more fissures than those from slow
coking rates and therefore fast coking rates result in small coke
of lower impact strength (stability).

In the final high temperature coke the coal maceral
composition and vitrinoid reflectance determine the carbon forms
and a portion of the microstructure in the product coke. The
organic inerts in coal with the possible exception of micrinoids
retain their identity in the coke and the inorganics in the coke
can be traced to their mineral equivalent in the coal, Fig-
ure 11. In addition, as the coal vitrinoid reflectance increases
the anisotropism of the bond carbon phase in the coke increases,
Figure 12. Marginal-coking high-volatile coals produce isotropic
carbon. As the volatile content of the coal decreases the virti-
noid reflectance increases and also the size of the anisotropic
domains and the degree of anisotropism increase and coke strength
generally increases, but peaks between medium and low-volatile
rank coal. In addition, the pore and wall microstructures in coke
show rank related changes provided the coal maceral compositions
and carbonization conditions are similar, Figure 13. Marginal
coking high-volatile coals produce a small pored thin to thick
walled poorly fused coke structure. The better coking high-
volatile coals produce thin to thick walled cokes with hetero-
geneous small to large size pores. Medium-volatile coals have
more uniform medium sized pores and walls while low-volatile coals
have an abundance of uniform small pores with thin walls.
Marginal coking high- and low-volatile coals do not fit the
general rules.

Relationships to a Coke Oven

        A similar phenomenon to that described for carbonization
of a coal particle takes place in a coke oven, Figure 14. In
conventional ovens, the temperature of the inner surface of the
chamber wall is about 2000°F. Within a few moments of charging an
ordinary blend, the coal immediately adjacent to the hot wall
begins to soften and decompose. As the process continues, the
rate of softening and decomposition increases and there is an
active evolution of gases from the plastic mass. The plastic
stage is a transient one, resolidification soon sets in, and a
layer of coke begins to form at the wall. The plastic zone may be
conceived as a vertical layer a few centimeters thick, essentially
plane, bounded on one side by coke and on the other by untrans-
formed coal. Two such layers are formed, one parallel to each
wall. Similar layers, but horizontal, begin to form at the top
and bottom of the charge and may be visualized as joining with the
vertical layers to form a continuous region often referred to as
the "plastic envelope" (Figure 14). However, there are conditions
such as at very low bulk densities where the plastic envelope is
not completely formed.

        The origin of coking pressure, is in the vertical
plastic layers and is related to the internal gas pressure. The
gas pressure arises because of the resistance to gas flow out of
the plastic zone. The magnitude of the pressure is clearly a
function of the permeability of the plastic layer and the rate of
gas evolution. The permeability of the plastic mass is related to
the plastic properties which are influenced by the ranks and type
of coal and the coking conditions used. If the plastic layer is
thick and impermeable, internal gas and wall pressures develop.
If the plastic layer is more fluid and permeable a frothier,
weaker coke develops. Increasing the resistance to gas release
from the plastic layer improves coke. The greater part of the
gases escapes through the coke toward the hot wall; only a major
portion passes into the cold coal. Measurements at this stage
have shown that gas pressures, both in the coke and in the uncon-
verted coal, are much smaller than gas pressures in the plastic
layers. Since the process is confined in a chamber, the net
result is that some part of the developed pressure is transmitted
through the coke as a lateral thrust on the wall.

        As the process of carbonization proceeds, the vertical
plastic zones move toward the center of the oven at a slowly
decreasing rate.[4] The rate at which the plastic layer moves is
related to the bulk density and heating rate. The thermal
gradient controls fissuration and is in turn related to bulk

density and heating rate. Some of the relatively high-boiling products of decomposition may condense in the cold coal and may be slowly driven forward through a mechanism of continual redistillation and condensation. The internal volume of unconverted coal steadily becomes smaller. Eventually none is left and the two plastic layers coalesce at or near the center line. At this time, the rate of gas evolution increases sharply, frequently accompanied by a sharply increased value of the gas pressure, and a maximum or peak value of the force transmitted to the wall. Some blends exhibit only slight increases in gas pressure at the time of coalescence and no accompanying maximum in wall thrust. The phenomena may not develop in classical form if the plastic zone is of high permeability or has been modified by condensed material or if much shrinkage of the charge away from the walls has taken place.[4] The final coke breaks into elongate fingers[1] that represent half oven widths. The end near the walls is called the cauliflower while that near the middle is the sponge end, Figure 15. Thus, all stages of coking are occurring in a coke oven until the entire charge is coked out.

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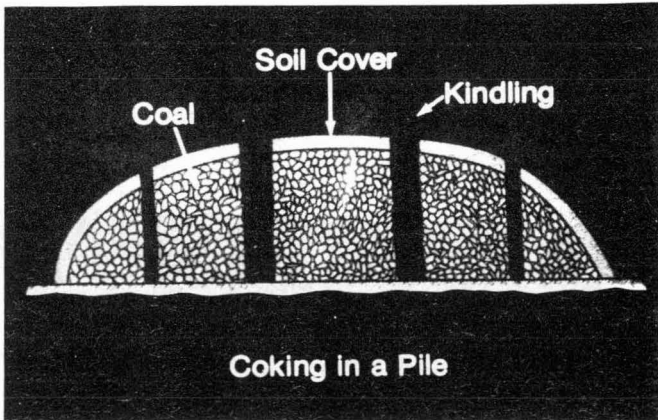
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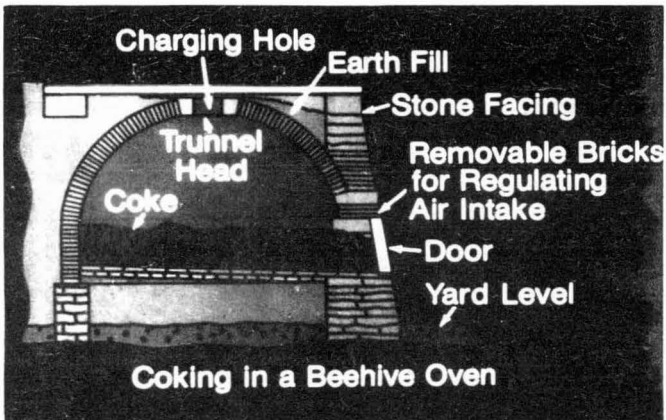
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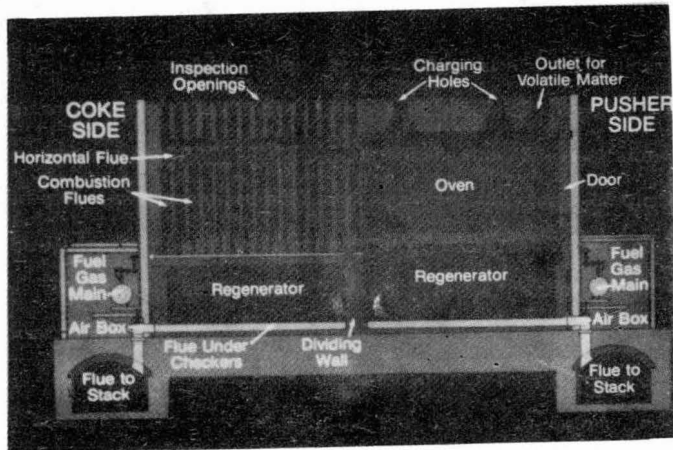
Figure 2. MODERN BY-PRODUCT COKE OVEN
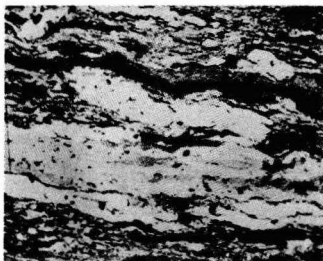
Figure 3A. Entities remain
unchanged, 553 F.
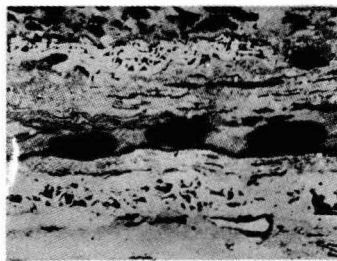
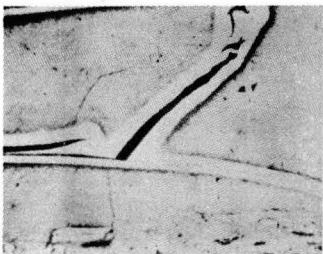Figure 3B. Resinite volatilizes,
626 F.

Figure 3C. Dark bordered
cracks, 626 F.

Figure 3D. Fusiform vacuoles
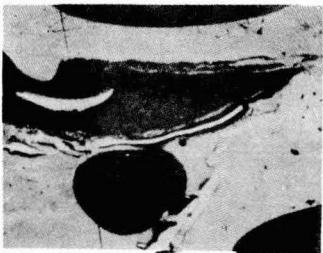in attrital vitrinite, 626 F.

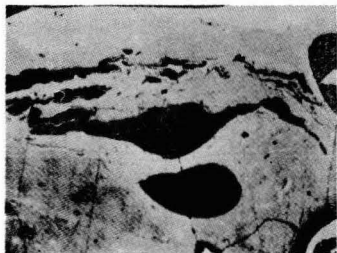Figure 3E. Exinite partially
volatilized, 685 F.

Figure 3F. Exinite partially
volatilized, 685 F.

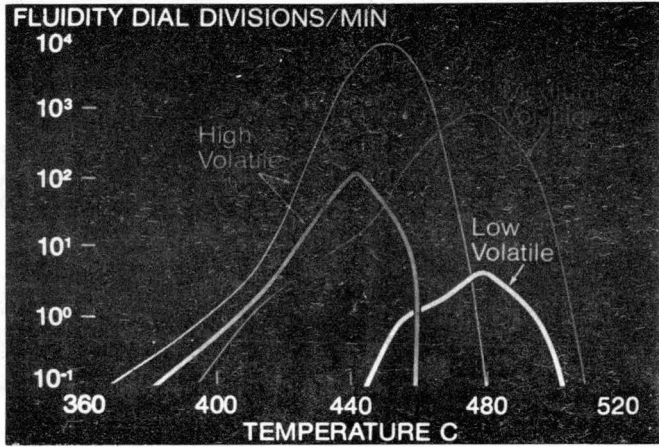Figure 3. PHOTOMICROGRAPHS SHOW CHANGES IN COAL AT INDICATED
TEMPERATURE. REFLECTED LIGHT. X175.

Figure 4. RELATION OF INDIVIDUAL GIESELER PLASTICITY CURVES FOR HIGH, MEDIUM, AND LOW-VOLATILE COAL
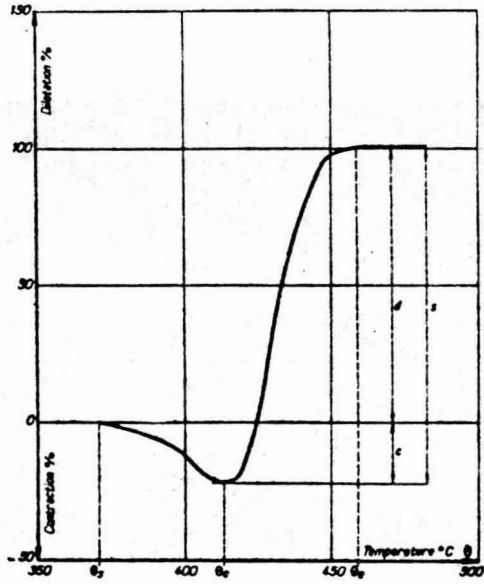
Figure 5. AUDIBERT-ARNU DILATOMETER HEATING RATE
2°C/MINUTE DILATOMETRIC CURVE
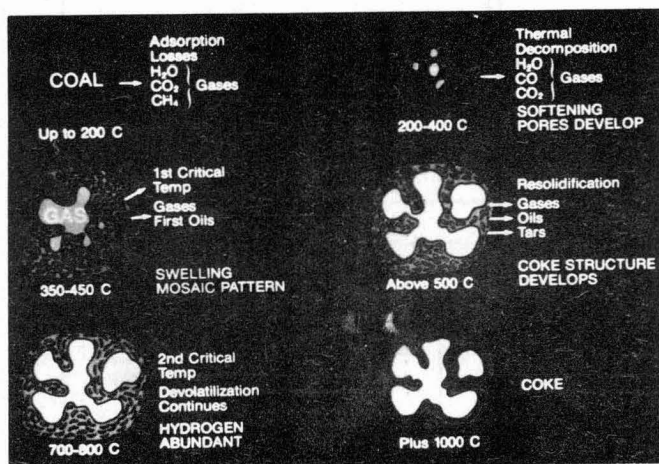
Figure 6. THE STEPS IN COKING OF AN INDIVIDUAL UNCONFINED
COAL PARTICLE
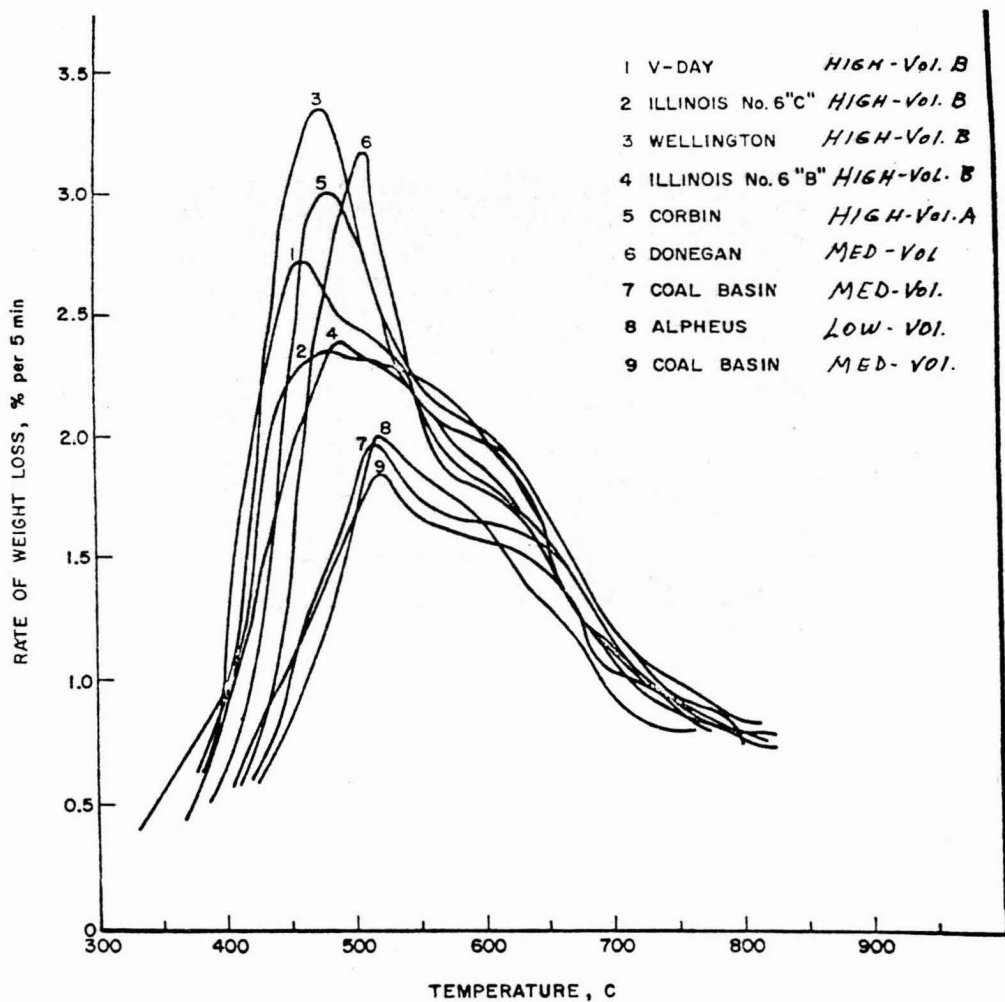
Figure 7. DIFFERENTIAL PYROLYSES CURVES OF VITRINOIDS
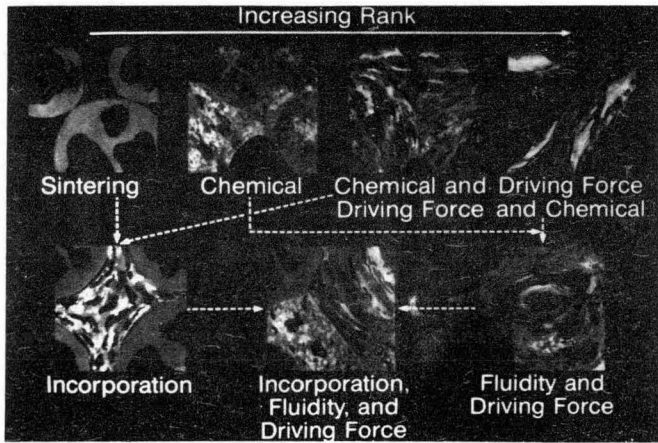
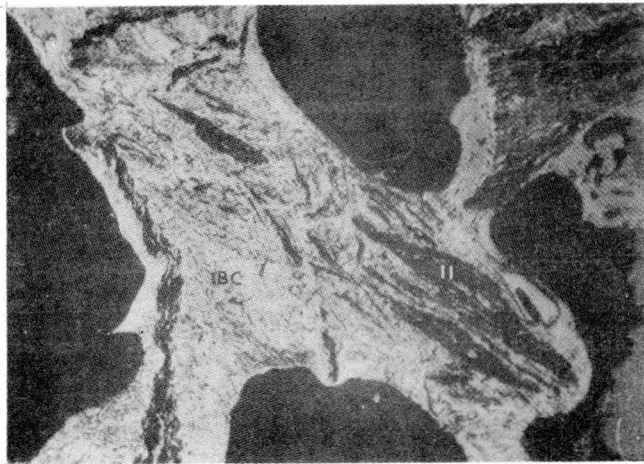Figure 9. RELATION OF COKING MECHANISM TO COAL RANK
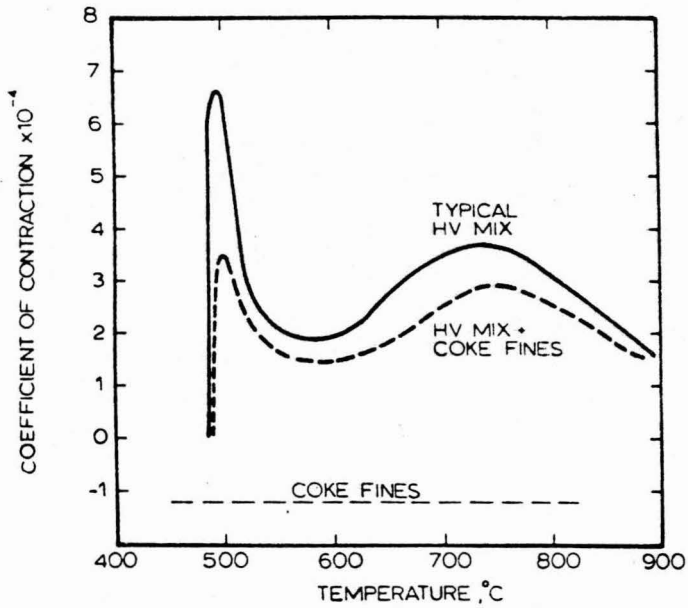
Figure 10. INFLUENCE OF COKE FINES ON THE COEFFICIENT
OF CONTRACTION OF A HIGH-VOLATILE MIX
SEMI-COKE
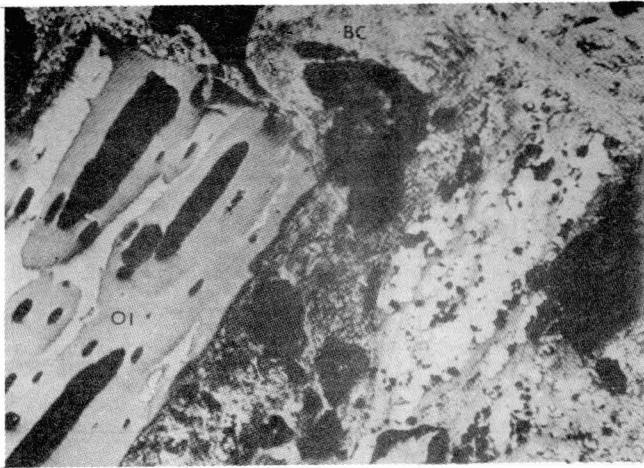
Figure 11A. ORGANIC INERTS (OI) IN COKE MICROSTRUCTURE
(BINDER COKE BC) 400X

Figure 11B. INORGANIC INERTS (II) IN COKE MICROSTRUCTURE
(BINDER COKE BC) 400X
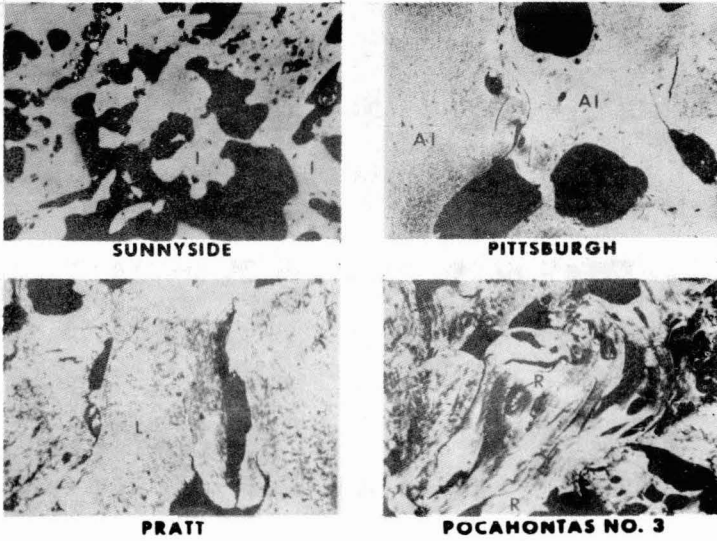
Figure 12. CARBON FORMS IN COKES OF DIFFERENT RANK RANGING FROM ISOTROPIC (I), INCIPIENT ANISOTROPY (AI), LENTICULAR (L), TO RIBBONY ANISOTROPY (R). 200X
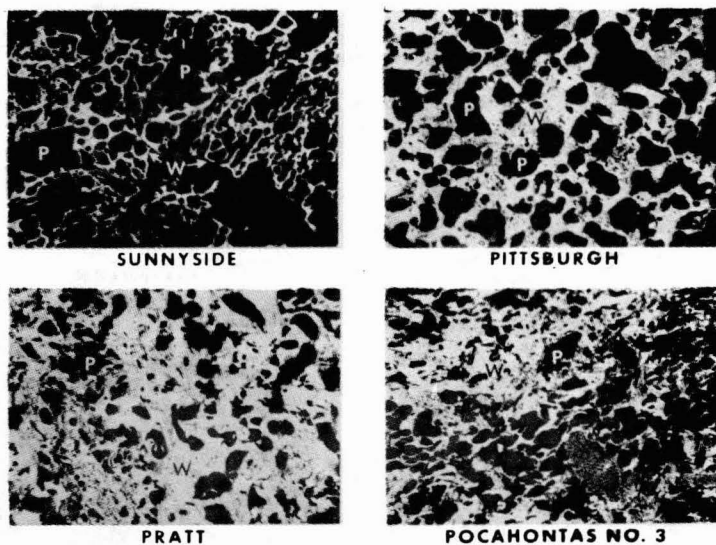
Figure 13. VARIATIONS IN COKE PORE (P) AND WALL (W)
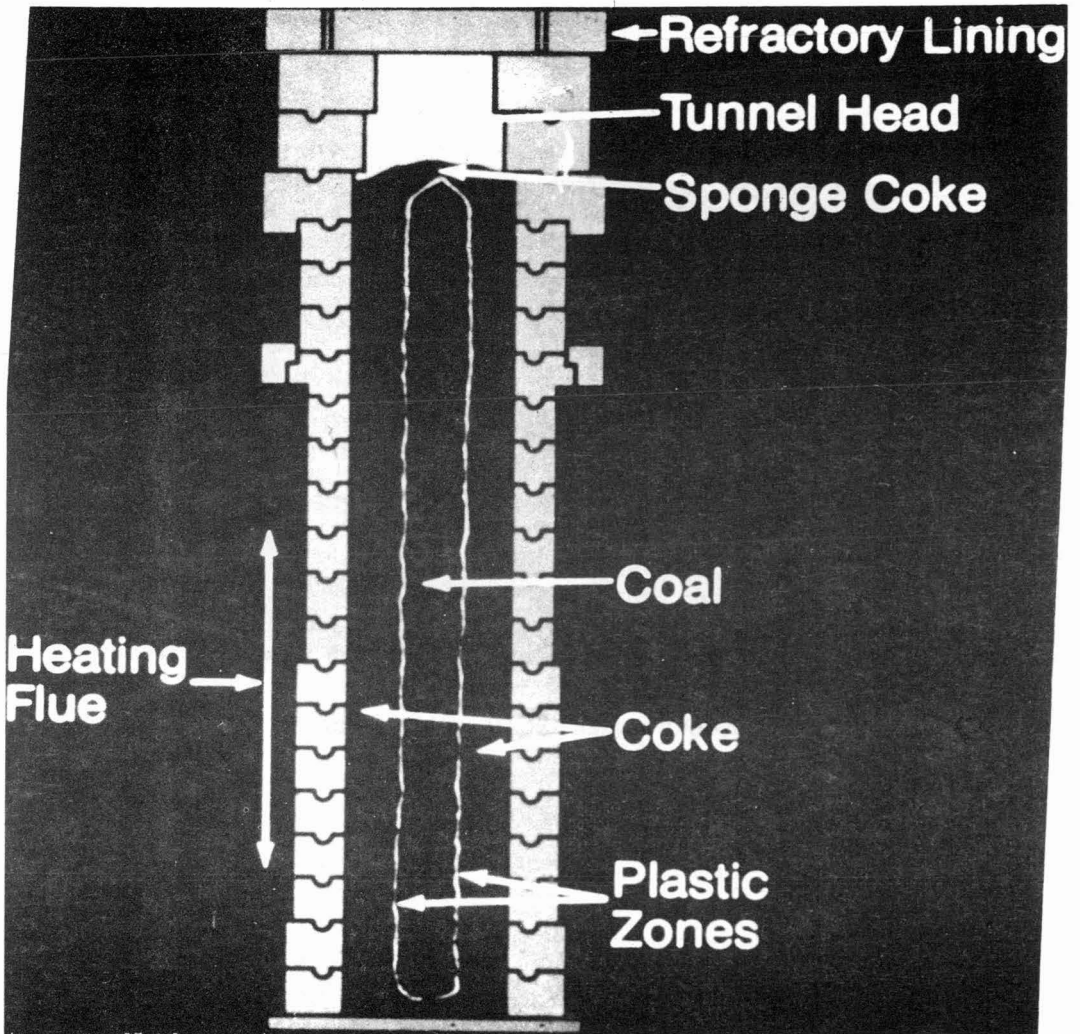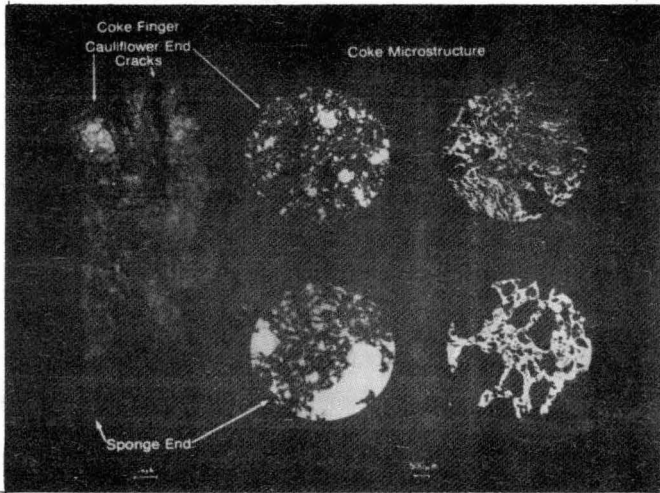STRUCTURES WITH RANK. 23X

Figure 14. CROSS-SECTION THROUGH THE SHORT DIMENSION
OF A COKE OVEN

Figure 15. A COKE FINGER AND ITS MICROSTRUCTURE