

CARBON GASIFICATION -- A UBIQUITOUS REACTION OF GREAT IMPORTANCE TO MANKIND

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It is generally not recognized how important the many types of carbon are to our society. Carbon comes in two main crystallographic forms (Figure 1): graphite and diamond. Graphite has trigonal bonding of carbon atoms; diamond has tetrahedral bonding. The carbon artifacts with which we will be concerned will be polycrystalline, their properties determined by their crystallite size (and distribution), degree of crystallite alignment, and extent of defect character within the crystallites (vacancies and dislocations). We will be concerned with carbonaceous solids having trigonal bonding within their crystallites and in some cases, possibly, tetrahedral bonding between crystallites.

There are an infinite number of organic precursors which can be used to produce carbonaceous solids. These precursors contain

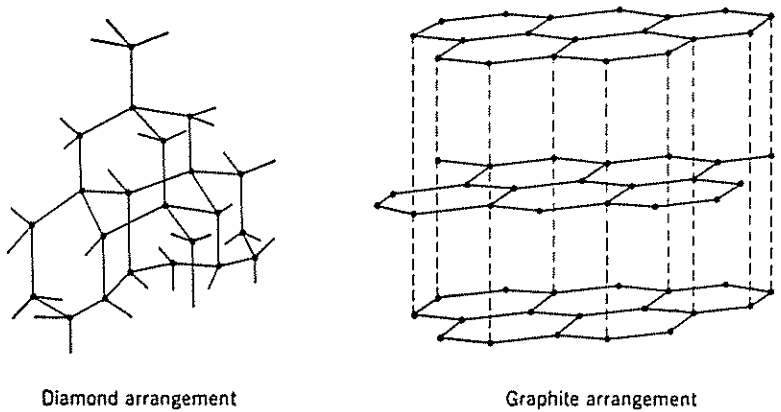


Fig. 1 - The arrangement of carbon atoms in the graphite and diamond lattices.

heteroatoms and possibly inorganic elements in addition to carbon. Upon their thermal treatment at elevated temperatures, they more or less lose their heteroatoms and inorganic elements, yielding a solid higher in carbon content. The structure of the carbonaceous solid produced depends upon the structure or structures of the organic compound(s) in the precursor and the exact thermal treatment to which the precursor is exposed. If part of the thermal treatment consists initially of taking a solid (at room temperature) through a carbonization or charring step in the temperature range from about 400 to 600°C, the nature of the mesophase (or intermediate phase) formed is of overwhelming importance (1,2). If part of the thermal treatment consists initially of pyrolysis of a gaseous or vapor species (the so-called chemical vapor deposition process), the temperature and pressure used is of overwhelming importance (3). The structure of the carbonaceous solid produced and the presence of heteroatoms and inorganic species will determine the ease with which the solid is gasified. In some processes and uses of carbonaceous solids, it is desirable that gasification rates be rapid; in others, it is equally important that gasification rates be very slow.

We will briefly consider the global chemistry of important gasification reactions and then their relevance for particular processes and uses.

1. CARBON GASIFICATION REACTIONS

1.1 C-O₂ Reaction

Arguably, the combustion of carbon to produce heat is the most important chemical reaction available to mankind. However, as we will see shortly, carbon gasification by O₂ is most undesirable when carbon is used as a material. It has been shown that upon the reaction of carbon with O₂, two primary gasification products, CO and CO₂, are formed (4).



Following these reactions, secondary reactions can occur, as follows



1.2 C-H₂O Reaction

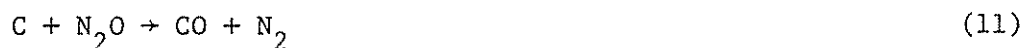
As we will see, carbon gasification by steam is a most important reaction. Like the C-O₂ reaction, there are instances where

the reaction is desirable; there are other instances where it is undesirable. Following the gasification of carbon by steam, other reactions can occur which can be of great importance. Some are listed.



1.3 Gasification of Carbon by Other Reactants

In addition to O_2 , H_2O , CO_2 , and H_2 being important molecular reactants for the gasification of carbon (and the ones which will be considered in detail in later chapters), other reactants should be mentioned. Interaction of several of these reactants with carbon has considerable significance to the air pollution field. For example, oxides of nitrogen formed during the combustion of coal can subsequently react with carbon to produce N_2 -- a highly desirable reaction (5-11).



Sulfur dioxide formed during the combustion of coal can, in turn, react with carbon, giving a number of products (12,13)



The interaction of F_2 with carbon is used to produce a product of commercial interest (14).



Carbon reacts with N_2 at a significant rate above 1400°C to form cyanogen (15)



Gasification of carbon by atomic species (O , H , N) and hydroxyl (OH) radicals is rapid (16,17).

2. RELEVANCE OF CARBON GASIFICATION FOR PARTICULAR PROCESSES AND USES

2.1 Coal and Coal Char Combustion

Along with escalating oil prices and the advent of synfuels, there has been accelerated interest in the combustion of coal and coal chars. Fine pulverized fuel (pf) particles (< 0.2 mm in size) are used in many power generating plants. At the high particle temperatures achieved during combustion in air (1500-2000°C), particle burn-out times are short; and combustion rates are determined to a large extent (or completely) by the rate at which O₂ can diffuse to the exterior surface of the particles (18-20). We recently studied the reactivity of 60-80 μm particles of five coal chars, obtained as residues from various synfuel processes (21), to air. Three of the chars had particle densities of about 0.90 g/cc (high porosity chars); two of the chars had particle densities of about 1.50 g/cc (low porosity chars). At low temperatures (Figure 2) where combustion rates were determined by the intrinsic reactivity of chars, there was a 60-fold difference in mass reactivities, depending upon the rank of the starting coals and their thermal history in the particular synfuel process (21). At elevated temperatures (Figure 3), similar to those found in pf combustion, mass reactivities were inversely proportional to particle density, which

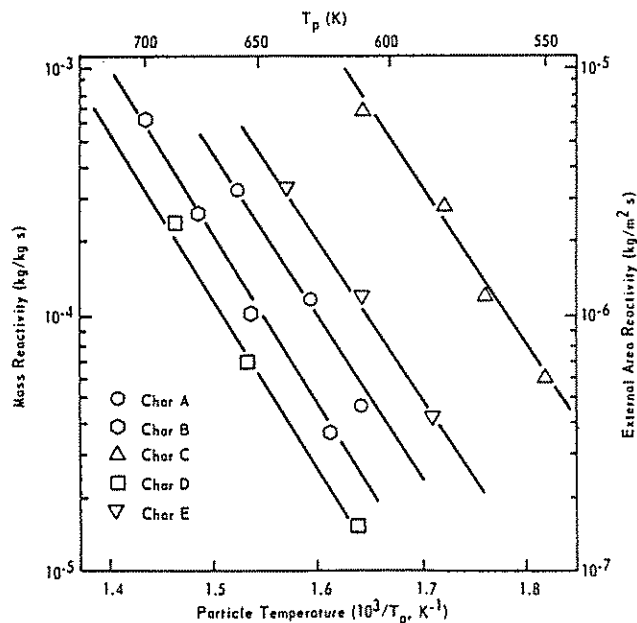


Fig. 2 - Reactivities of residual chars from coal conversion processes in air at low temperatures.
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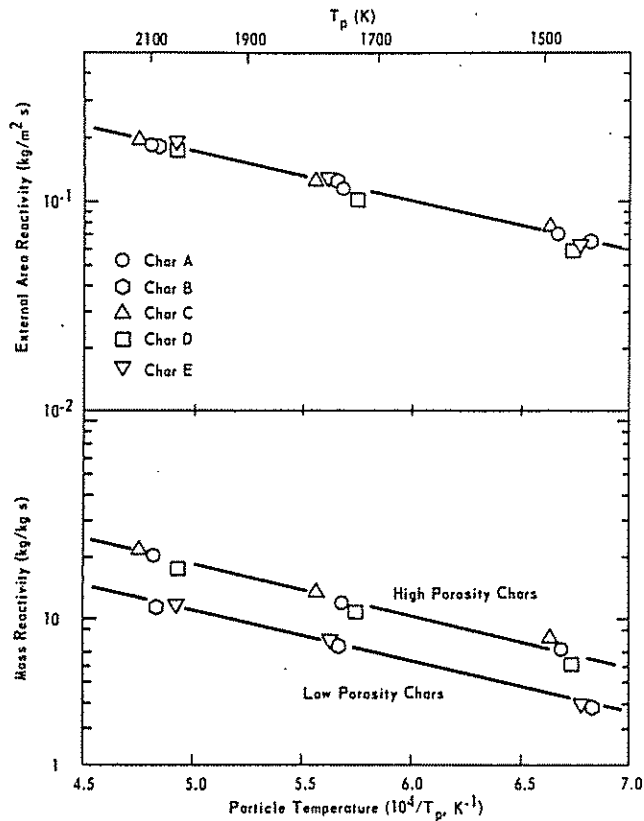


Fig. 3 - Reactivities of residual chars from coal conversion processes in air at high temperatures (22).

was expected for chars of similar particle sizes (22). Further, external area reactivities were independent of intrinsic char reactivities, again as expected.

2.2 Production of Hydrogen and/or Carbon Monoxide

The production of H_2 and/or CO via coke or char gasification is now an important commercial process and promises to become of much greater importance in the future. As seen in Figure 4, if a product H_2/CO mixture is desired, a blend of coal (or other carbonaceous solid), steam, and O_2 is fed into the gasifier. The exact ratio of these reactants charged depends on reactivity of the carbonaceous solid, whether the gasifier is to be operated in a slagging or nonslagging mode, and the composition of product gas desired. The higher the maximum temperature at which the gasifier is to be operated the lower is the feed H_2O/O_2 ratio. In the limit as the ratio approaches zero, the gasifier operates at a very high temperature yielding primarily CO as the product gas. The product gas is frequently passed through a CO -shift converter [reaction (6)] to produce a final desired H_2/CO ratio. The desired ratio depends upon

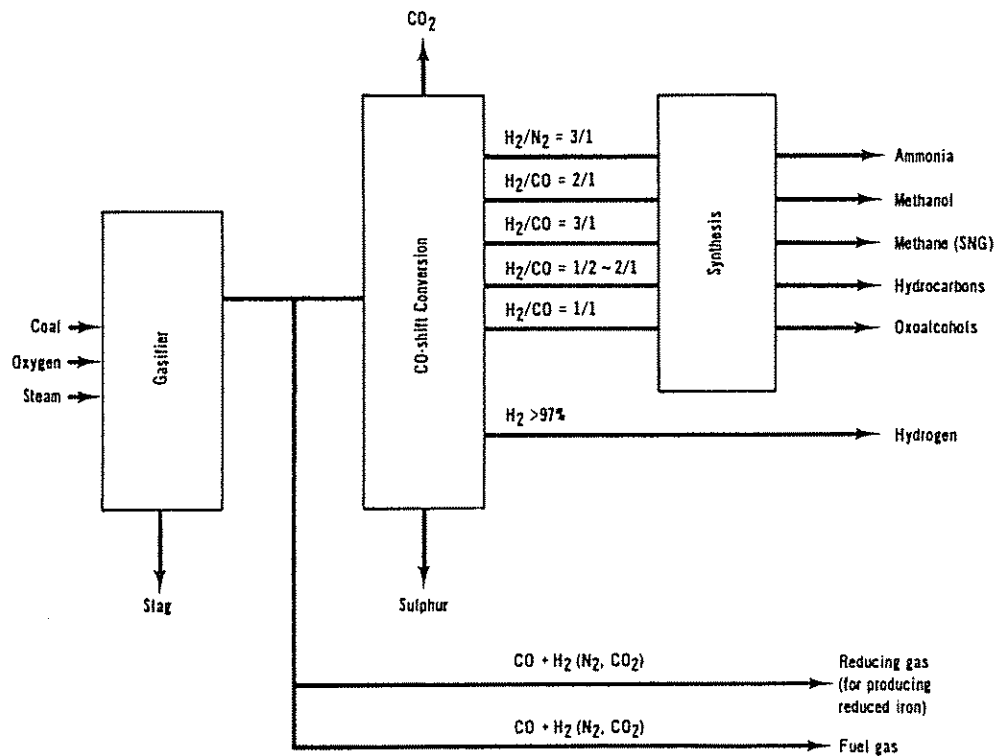


Fig. 4 - Production of CO and H₂ by coal gasification.

the ultimate use to be made of the synthesis gas, as seen in Figure 4. Fundamentals of coal gasification and description of various gasification processes are well covered elsewhere (23,24).

Gasifiers can be classified as operating essentially in one of three modes: fixed bed, fluid bed or entrained flow. It appears that, commercially, gasifiers increasingly operate in either a fixed bed (for example, the Lurgi) or entrained flow (for example, the Texaco or Koppers-Totzek) mode. The four main reaction zones in a nonslagging fixed bed gasifier are shown in Figure 5. The nonslagging gasifier suffers from the basic disadvantages that (i) a large stoichiometric excess of steam is required to moderate the combustion zone temperature above the grate and thereby prevent ash clinkering and fusion and (ii) relatively large amounts of aqueous liquor are produced. By decreasing the H₂O/O₂ ratio from about 9 to 1.3, the gasifier can operate in a slagging mode, thereby increasing thermal efficiency, lowering liquor production, and increasing CO production at the expense of CO₂.

Entrained-flow gasifiers use pulverized fuel, which is introduced into the gasifier either in a dry mode (Koppers-Totzek) using high gas velocities or in a wet mode (Texaco) as a solid-water slurry. Figure 6 shows the Koppers-Totzek two headed gasifier,

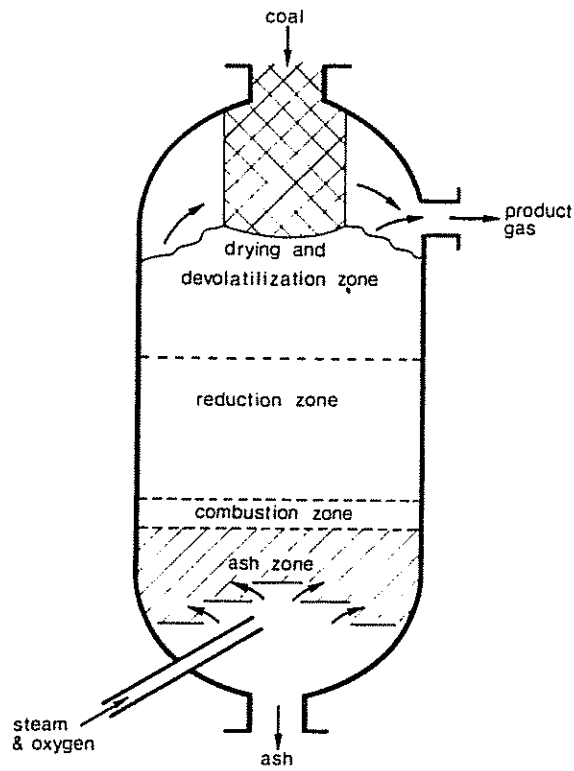


Fig. 5 - Four main reaction zones in a nonslagging fixed bed gasifier.
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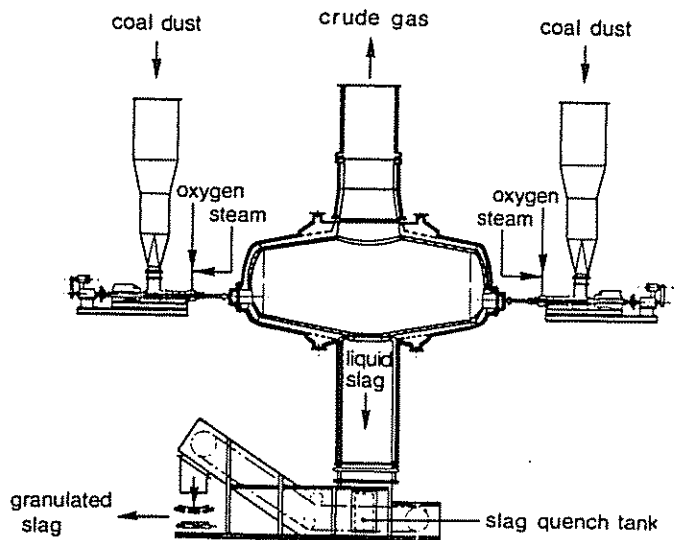


Fig. 6 - The Koppers-Totzek entrained flow gasifier.
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which operates in a slagging mode at essentially atmospheric pressure. Two burners are positioned directly opposed to improve turbulence and to ensure continuous ignition. Because of rapid heating, devolatilization of coal takes place so rapidly that agglomeration of bituminous coal particles during their plastic stage does not occur; therefore, any coal can be gasified irrespective of coking properties, ash content, or ash fusion temperature. Further, since the gasifier can operate at very high temperatures (when the H_2O/O_2 ratio becomes small), unreactive fuels such as anthracite and petroleum coke can be readily gasified. Shell is now developing a pressurized version of the Koppers-Totzek gasifier, which is thought to hold great promise (23).

It is thought that, at present, the only commercially available entrained-flow gasifier is the Texaco unit. It operates at elevated pressures. Recently Eastman Kodak's Chemical Division unveiled its chemicals from coal plant, using the Texaco gasifier to produce synthesis gas for the production of acetic anhydride (25). More recently the Cool Water coal gasification-combined-cycle power plant was brought on-line, using the Texaco gasifier (26). The gasifier is followed by a gas (combustion) turbine and then a steam turbine. It has been said that "this plant is the first fundamentally new technology for making electricity from coal since the 1920s." Since coal is fed to the gasifier in slurry form, it means that a high H_2O /coal input ratio is required (particularly for low rank coals which adsorb considerable H_2O into their pore system). The resultant additional heat requirement is reflected in a high O_2 demand.

It is most advantageous to have the reaction(s) of H_2 and CO produce the desired gaseous fuels or chemicals, to as great an extent as possible, within the gasifier. Since synthesis reactions are highly exothermic, their occurrence in the gasifier helps supply the heat required for the endothermic $C-H_2O$ reaction and thereby reduces or eliminates the need for O_2 . Entrained flow gasifiers produce little hydrocarbons since they operate at high temperatures (producing equilibrium restrictions) and short residence times (producing kinetic limitations). Fixed bed reactors, operating at lower temperatures and longer residence times, produce some hydrocarbons. Exxon, through its pioneering Catalytic Coal Gasification Process, has demonstrated the possibility of producing CH_4 entirely within a fluid bed gasifier (27). Figure 7 presents a schematic of the process. All product CO and H_2 leaving the gasifier is recycled. The sum of the following reactions are involved to make the process essentially thermo neutral:

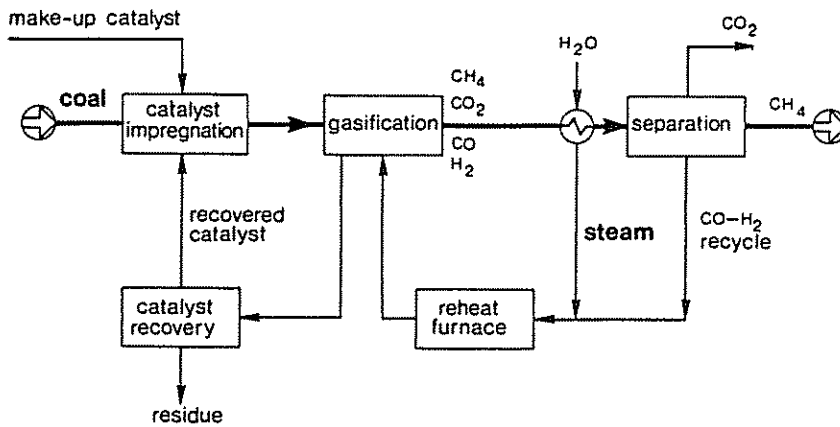


Fig. 7 - Schematic flow plan for the Exxon catalytic coal gasification process.
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Since reduction in temperature favors the formation of CH_4 (at equilibrium), a potassium catalyst is introduced to accelerate the gasification rate such that reaction (5) goes at a suitable speed at $600^\circ C$ and 3.5 MPa pressure. Fortunately, potassium is also found to be a reasonably good catalyst for the methanation reaction and, perhaps even more important, is not strongly poisoned by H_2S produced during gasification (28).

2.3 Metallurgical Processes

2.3.1 The blast furnace. In many ways, the blast furnace resembles the air blown fixed bed gasifier. Air introduced through the tuyeres towards the bottom of the furnace reacts rapidly with coke producing CO which is in turn rapidly oxidized to CO_2 producing a temperature of about $1800^\circ C$. At this temperature, the CO_2 then reacts rapidly with coke to produce CO . The CO in turn reduces iron ore passing down the furnace, again producing CO_2 . The CO/CO_2 ratio leaving the top of the blast furnace depends upon the reactivity of the coke to CO_2 and the ease with which CO reduces a particular iron ore. A coke of high reactivity to CO_2 can be beneficial or detrimental depending upon the thermal and chemical requirements of the process (29). Cokes of intermediate reactivity to CO_2 are generally desired. Coke reactivity to CO_2 decreases the higher

the coking temperature and rank of bituminous coal from which the coke is made (30).

Because of a shortage of good coking coals in some parts of the world, there recently has been an interest in form coke -- a composite made from a filler char and binder pitch coke obtained from low temperature coal carbonization (31). Here it is important that the binder coke is not more reactive to CO₂ than is the filler char. If it is more reactive, serious loss of strength and disintegration of the form coke occurs, leading to fines formation and restriction of gas flow up through the blast furnace. To achieve a low reactivity in the binder carbon, it is imperative that the metals content in the pitch precursor be low so that catalyzed carbon gasification be held to a minimum.

2.3.2 The electric furnace. Increasingly, the electric furnace is being used for the smelting of ores and the production of alloys. For example, in the United States, approximately 30% of the steel is produced in electric furnaces using graphite electrodes. Part of the electrode close to the top of the steel bath is at a sufficiently elevated temperature to undergo slow gasification in air. Roughly, 1 kg of electrode is consumed for each 200 kg of steel produced, with loss primarily being due to carbon gasification in air. The rate of electrode gasification in air decreases with increasing crystallite alignment in the synthetic graphite (32) and decreasing metals content, particularly Ca and V.

2.3.3 The Hall cell for aluminum production. Aluminum is produced in a cell consisting of an electrolyte of Al₂O₃ dissolved in cryolite operating at about 960°C. Carbon anodes are used both to carry current to the cell and to serve as a reductant of Al₂O₃. Important reactions to be considered are:



Or adding reactions (16) and (4)



At equilibrium for these reactions at the anode, the gaseous product would be about 99% CO. It is generally agreed that the primary anodic product, at the current densities used in practice, is close to 100% CO₂ (33,34). For this case, essentially 0.33 kg of carbon anode would be consumed per kg of Al produced through reaction (16). In practice, carbon consumption is higher, or about 0.5 kg of anode per kg of Al produced (35). This is attributed, in part, to the secondary carbon gasification reaction (4). The fact that this reaction is relatively slow, however, means that equilibrium is not

attained and that, fortuitously, carbon consumption is less than that which would exist at equilibrium.

2.4 Production of Activated Carbon

Activated carbon is used extensively for the cleaning up of air and water. Thermosetting precursors like coal, wood, coconut hulls, acid sludge coke, and olive pits are pyrolyzed at about 800-900°C, liberating volatile matter, and producing a porous char containing a significant open and closed (to He) micropore volume. Either concurrent with or following the pyrolysis step, the char is gasified (usually in steam or a steam/CO₂ mixture) to enlarge the average size of open micropores and open micropores which are closed.

Figures 8-10 summarize pertinent results for the production of activated carbon from an anthracite coal (36). The anthracite was first devolatilized in N₂ at 950°C, and then the 230 μm particle size was gasified in 0.1 MPa of CO₂ to different extents of burn-off at both 850°C and 950°C. As seen in Figure 8, as the amount of carbon gasified increases, the apparent density of the particle (ρ_a), as measured by Hg displacement, decreases essentially linearly; and the He density (ρ_{He}) increases. The decrease in ρ_a is due to the continuous removal of carbon atoms from the interior of the particle. The increase in ρ_{He} is due to the opening up of closed pore volume.

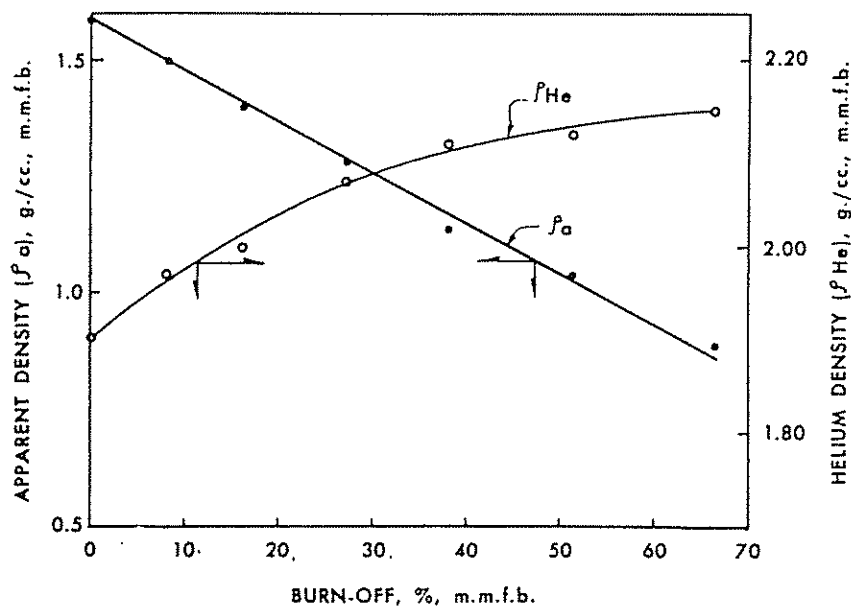


Fig. 8 - Variation of densities with burn-off of anthracite char in CO₂ at 850°C.

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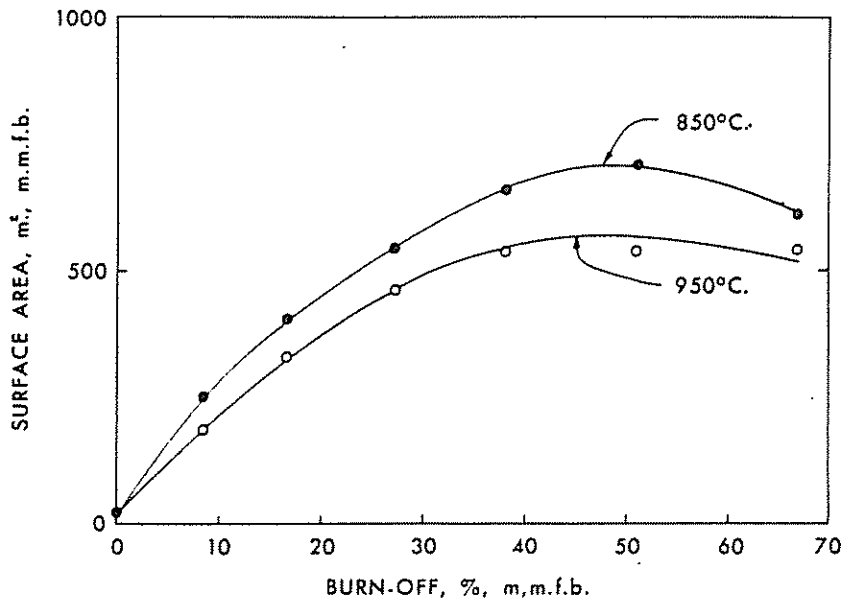


Fig. 9 - Variation of surface area with burn-off of 1 g of anthracite char in CO_2 .
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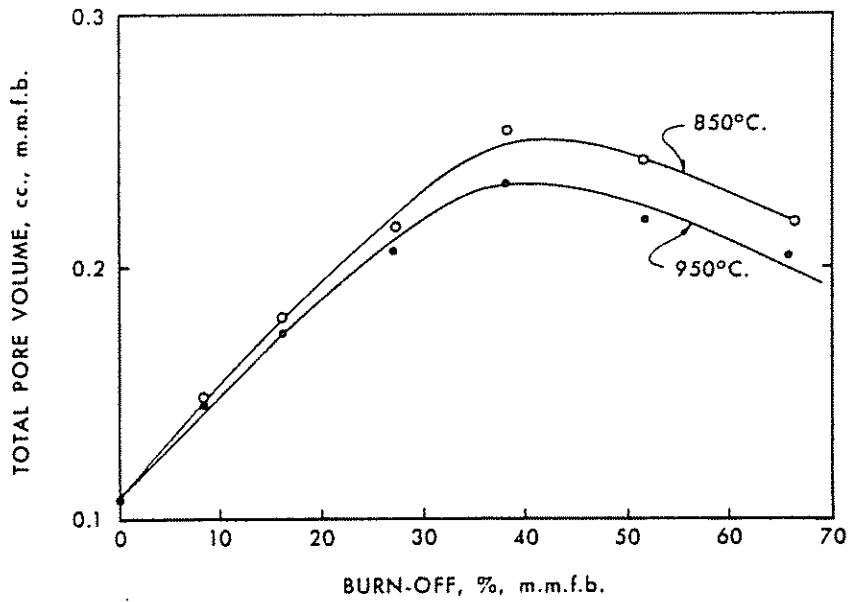


Fig. 10 - Variation of total open pore volume with burn-off of 1 g of anthracite char in CO_2 .
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At high carbon burn-offs, the ρ_{He} approaches closely the true density of the carbon crystallite.

In both Figures 9 and 10, activation was started with 1 g of anthracite char. Surface area was measured by N_2 adsorption at 77 K, and total pore volume (accessible to He) was calculated from values of ρ_a and ρ_{He} (37). It is seen that surface area and pore volume, remaining, initially increase with extent of carbon gasified. Both parameters go through maxima at about 40-50% burn-off and then decrease. However, the extent of surface area and pore volume development is seen to increase with decreasing temperature used for activation. This is attributed to a balance between the rate of gasification and the rate of diffusion of reactant into the interior porosity of the char. The lower the gasification temperature, the less the concentration gradient of CO_2 in the radial direction of the particle and, as a consequence, the more uniform is the extent of activation through the particle. Producers of activated carbon optimize their process by deciding what total burn-off to give the char and at what temperature to activate. The higher the temperature they use the greater is the rate of throughput in the reactor but the less area and pore volume produced per unit of burn-off.

Recently, there has been interest in the production of molecular sieves from microporous carbons to be used for the separation of molecules. In this case, the extent of carbon gasification is kept relatively low so that the micropores remain small -- comparable to the sizes of molecules to be separated. Figure 11 summarizes results for the production of a molecular sieve carbon from an anthracite char (38). Small differences in amounts of burn-off drastically change the accessibility of CH_4 into the char particles, as measured by the diffusion parameter and its change with temperature.

2.5 Regeneration of Catalysts

In typical refinery operations for the upgrading of petroleum feedstocks, catalyst deactivation, as a result of coke deposition in the pores of the catalyst, is a continuing problem. The problem has become of increasing seriousness as feedstocks of higher molecular weights and aromaticities and catalysts of increasing Lewis acidities are used (39,40). Catalysts are intermittently regenerated by gasifying away the coke deposits using air, air/ H_2O , or air/ CO_2 as reactants (41). Intrinsic reactivities of the coke deposits are expected to vary markedly depending upon their structure and amount of heteroatoms present, which in turn depend upon the nature of the feedstock, temperature at which the coke was deposited (or reacted off the catalyst if it is higher), and nature of the catalyst surface on which coke deposition occurred. If the catalyst is regenerated at sufficiently low temperatures in air (Zone I kinetics are

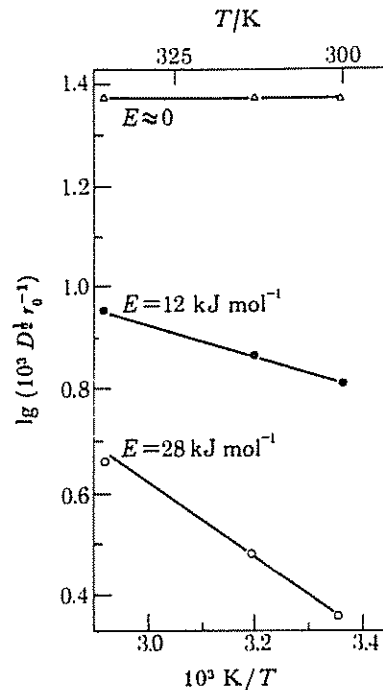


Fig. 11 - Effect of burn-off of an anthracite char on ease of diffusion of CH_4 into the micropores. Burn-offs (%): \circ , 6.9; \bullet , 8.0; Δ , 9.1. Reprinted from Ref. 38 by courtesy of the Royal Society (London).

observed (42)), regeneration time (t) is determined by the following parameters.

$$t \sim C_c / knC_{O_2}^m$$

where C_c is coke concentration on the catalyst, k is intrinsic coke reactivity, n is the atoms of carbon gasified per molecule of O_2 consumed, C_{O_2} is the O_2 concentration at the exterior of the granule, and m is the order of reaction. If the catalyst is regenerated at higher temperatures, the combustion process in a porous catalyst granule may assume a shell-progressive model (43). In this case regeneration time is independent of intrinsic coke reactivity and is determined by the following parameters (43):

$$t \sim R^2 C_c / nDC_{O_2}$$

where R is the granule radius and D is the effective diffusivity of the porous granule for O_2 . Usually regeneration is conducted at as

high a temperature as possible, consistent with negligible catalyst deactivation caused by sintering.

Recently there has been interest in carbon as a catalyst support for metals (44), due in some cases to its low activity for promoting coke formation, compared to alumina for example (45). Obviously, if carbon is to be used as a support, its rate of gasification either during production runs or during catalyst regeneration must be small. The former is true in the case of most reactions involving H_2 , both because the C- H_2 reaction inherently proceeds at a slow rate (42) and one or more of the reactants or products inhibits the gasification rate. For example, CO inhibits carbon support gasification when H_2/CO mixtures are used in methanation or Fischer-Tropsch synthesis. Likewise H_2S , produced during hydrocarbon desulfurization in H_2 , is an inhibitor of carbon gasification. The minimization of gasification of the carbon support in air, during catalyst regeneration to remove deposited coke, is still a challenge to researchers.

2.6 Graphite Nozzles for Rocket Motors

Because of its strength at high temperatures, good thermal shock resistance, and low density, carbon is the preferred nozzle material in rocket motors. Upon the firing of a typical propellant consisting of 75% ammonium perchlorate (oxidizer), 10% hydroxy terminated polybutadiene (binder), and 15% aluminum powder (fuel), a complex mixture of propellant combustion species is produced. This combustion gas enters the nozzle throat at a velocity of about 1000 m/s, a pressure of 4.5 MPa, and temperature of 3100°C. Of major concern is the extent to which the combustion gases remove carbon from the nozzle by gasification, causing throat recession. Throat recession affects motor performance by reducing the delivered specific impulse and by altering the thermostructural behavior of the nozzle. The ability to predict the amount of recession a nozzle will experience as a function of graphite used and operating conditions is highly desirable. For the typical propellant described above, the major reactant which causes graphite gasification (recession) is steam (mole fraction of about 0.23 in combustion products). The major products which are expected to inhibit carbon gasification in steam are H_2 , Cl_2 , and HCl (42,46). Inhibition is caused by the strong chemisorption of H and Cl atoms on carbon active sites, thereby blocking these sites from attack by steam.

Recently reactivities in H_2O and H_2O/H_2 mixtures of carbon composites and bulk graphite used as nozzle materials have been studied (47). It was found that composites made of PAN (polyacrylonitrile) fibers were more reactive than those made of petroleum pitch fibers. It was concluded that carbon consumption under nozzle conditions was in the regime between Zones II and III (42), where carbon gasification occurs in a thin layer close to the exterior surface of the

nozzle. Consumption of carbon in this layer reduces graphite density and can lead to reduction in strength and modulus, resulting in mechanical erosion of carbon from the nozzle under the high velocity conditions encountered. For example, Figure 12 presents data for the loss of modulus in a PAN fiber-based composite as weight loss due to gasification occurs (48).

The importance of understanding gasification of graphite rocket nozzles was brought out dramatically during a recent mission of the space shuttle, Challenger. The launching of two communication satellites went awry because of the failure of the small rocket that was to loft them into proper orbit in space. They ceased firing after only a few seconds rather than the intended 88 s burn. Experts suspect that the nozzle, consisting of a carbon fiber composite, burned through prematurely.

2.7. Graphite in Nuclear Reactors

Graphite is used in gas-cooled (CO_2 or He is used) nuclear reactors both as a moderator of fast neutrons and a structural material. It is important that the graphite does not gasify away. Unfortunately, the presence of fast neutrons and gamma radiation in the reactor promotes carbon gasification. Collision of fast neutrons with

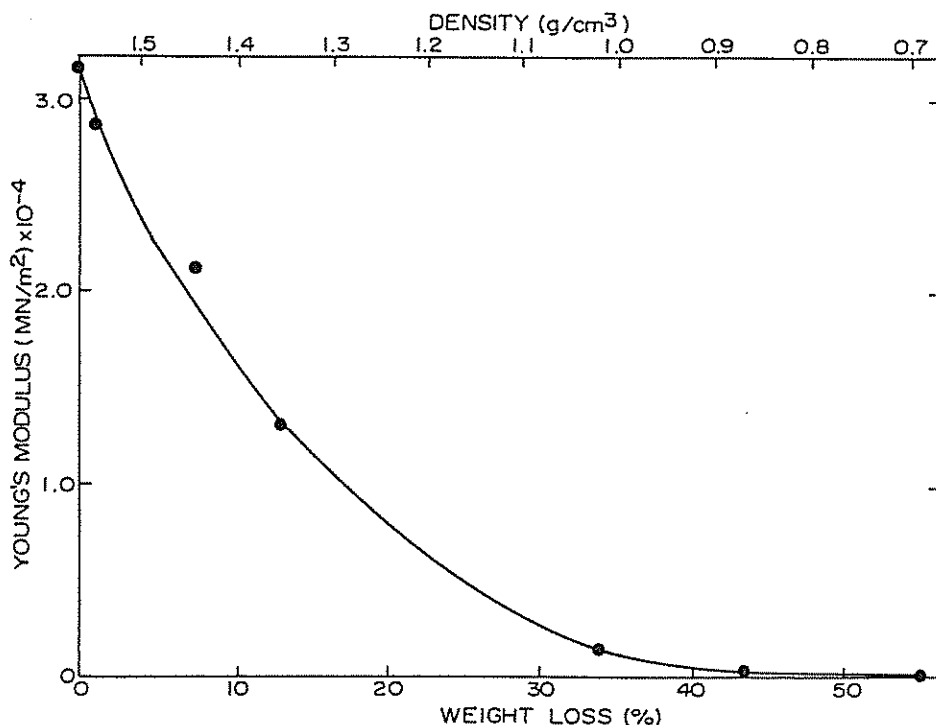


Fig. 12 - Effect of carbon gasification on Young's modulus of PAN fiber-based composite (48).

the graphite produces damage in the form of vacancies and interstitials (49). Gamma radiation of CO₂ or of trace impurities in the He coolant produces reactive free radical and ionic species (50). Figure 13 presents results for the gasification of graphite in air at 300°C (51). Damage to the graphite and gamma radiation produce an additive effect on graphite gasification rates -- in the case shown the rate is increased some 20 times over the base case.

The problem of gasification of moderator graphite by trace amounts of H₂O found in the He stream in the high temperature region of the nuclear reactor is compounded by the existence of the Boudouard reaction over steel heat exchanger tubes in the cooler part of the reactor (50). Enhanced rates of carbon transport from the warmer to the cooler part of the reactor occur as the concentration of CO builds up in the reactor, as follows:

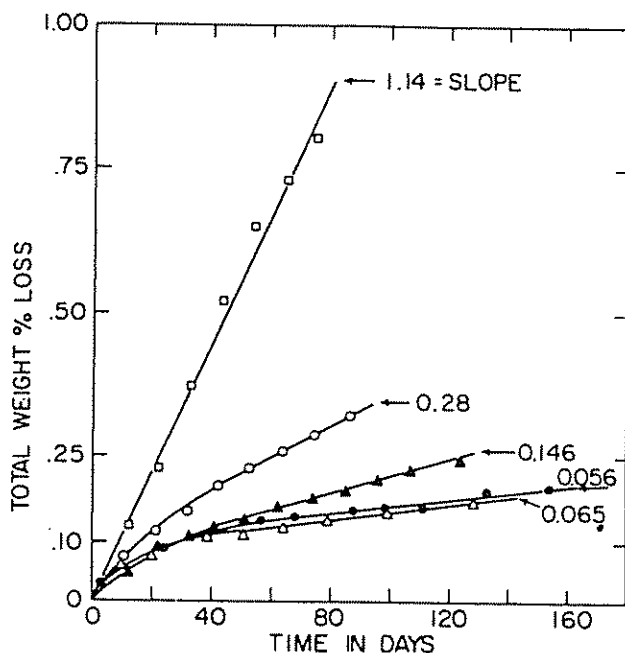


Fig. 13 - Gasification of nuclear graphite in air at 300°C under different conditions. Slopes give % loss in 100 days.
 ●, Unirradiated sample, oxidized in absence of radiation; ○, irradiated sample, oxidized in absence of radiation; △, unirradiated sample, oxidized in 2x10⁵ r/h gamma flux; □, irradiated sample, oxidized in 2x10⁵ r/h gamma flux; ▲, unirradiated sample, oxidized in 6.1x10⁵ r/h gamma flux.



3. CONCLUSIONS

The gasification of carbon is a most important process in our society. In some cases, it is a highly desirable reaction which we want to proceed at a maximum rate. In other cases, it is a highly undesirable reaction, which we want to proceed at a negligible rate. In both cases, understanding the fundamentals of carbon gasification is vital to our making the desired technological advances.

In this chapter, we have considered some of the main cases where carbon gasification is of prime importance. However, in fact, the number of cases which we would have considered is almost endless. The following is a partial list of additional areas of importance:

(i) Carbon in batteries, fuel cells, and industrial electrolysis (in addition to its use in aluminum production) where carbon corrosion in acidic and basic electrolytes is of concern (52).

(ii) Carbon oxidation when used as a refractory (53).

(iii) Carbon oxidation when used as a thermal insulator.

(iv) Carbon oxidation when used in aerospace applications (in addition to its use as a nozzle).

(v) Carbon fiber etching to roughen its surface (54).

(vi) Carbon oxidation when used as bearings and seals.

(vii) Gasification of carbons in various oxidizing media to analyze for amounts of various structural components (55).

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