

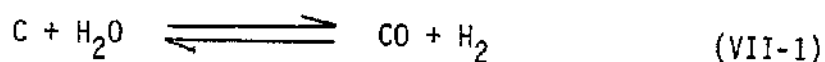
VIII. CATALYTIC GASIFICATION OF COAL OR
LIGNITE TO SYNTHESIS GAS AND/OR SNG

A. INTRODUCTION

Among the various alternative coal conversion processes, gasification is in the most advanced stage of development. Three processes are commercially available (Lurgi, Winkler and Koppers-Totzek). Several others are in the process development stage (e.g. Hygas, Bigas, CO₂ Acceptor, Synthane, Kellog). The common objective of these processes is to convert coal to a gas that can be used as a fuel for power generation or as a feed for a number of possible upgrading operations.

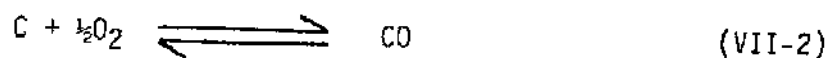
In the most common approach, coal is reacted with oxygen and steam to give a mixture of synthesis gas (CO + H₂), methane, and other products of combustion. Alternate routes include reaction with air and steam to produce a low BTU gas (~ 150-200 BTU/ft³) and reaction with hydrogen (hydrogasification) to maximize the production of CH₄.

In the case of steam gasification, the reaction of carbon with steam



is highly endothermic ($\Delta H_{298k} = 31.4 \text{ Kcal mol}^{-1}$). This places a considerable economic burden on the process. In most cases, the heat requirement is provided by the oxidation of part of the coal

($\Delta H_{298k} = -26.4 \text{ Kcal mol}^{-1}$):



Up to 1/3 of the available energy in the coal is often required. Operation at lower temperatures is therefore desirable, and provides an incentive for the development of catalytic steam gasification processes. The low temperature also favors CH₄ formation, improving the thermal efficiency of the gasification process and increasing the volumetric energy content of the product.

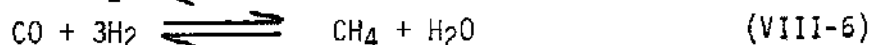
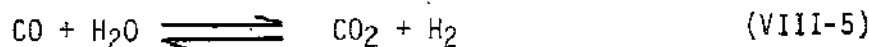
In the present section, the thermodynamic and catalytic constraints of gasification will be discussed first, followed by a review of those concepts and ideas presented in Parts 1 and 2 which are relevant to the development of improved catalytic gasification systems.

B. MAJOR CONSTRAINTS

As indicated above, the gasification of coal has a thermodynamic limitation inherent in the endothermicity of the steam-carbon reaction. This can be seen clearly in Figure VIII-1, a diagram of the standard free energy change of a number of reactions of importance in gasification. In addition to reaction VIII-1, the diagram shows the following reactions of carbon:



as well as the water-gas shift and methanation reactions:



It should be noted that only the gasification reaction (reaction VIII-1) and the reverse Boudouard reaction (reaction VIII-4) are favored by high temperatures. By contrast, the methane producing reactions

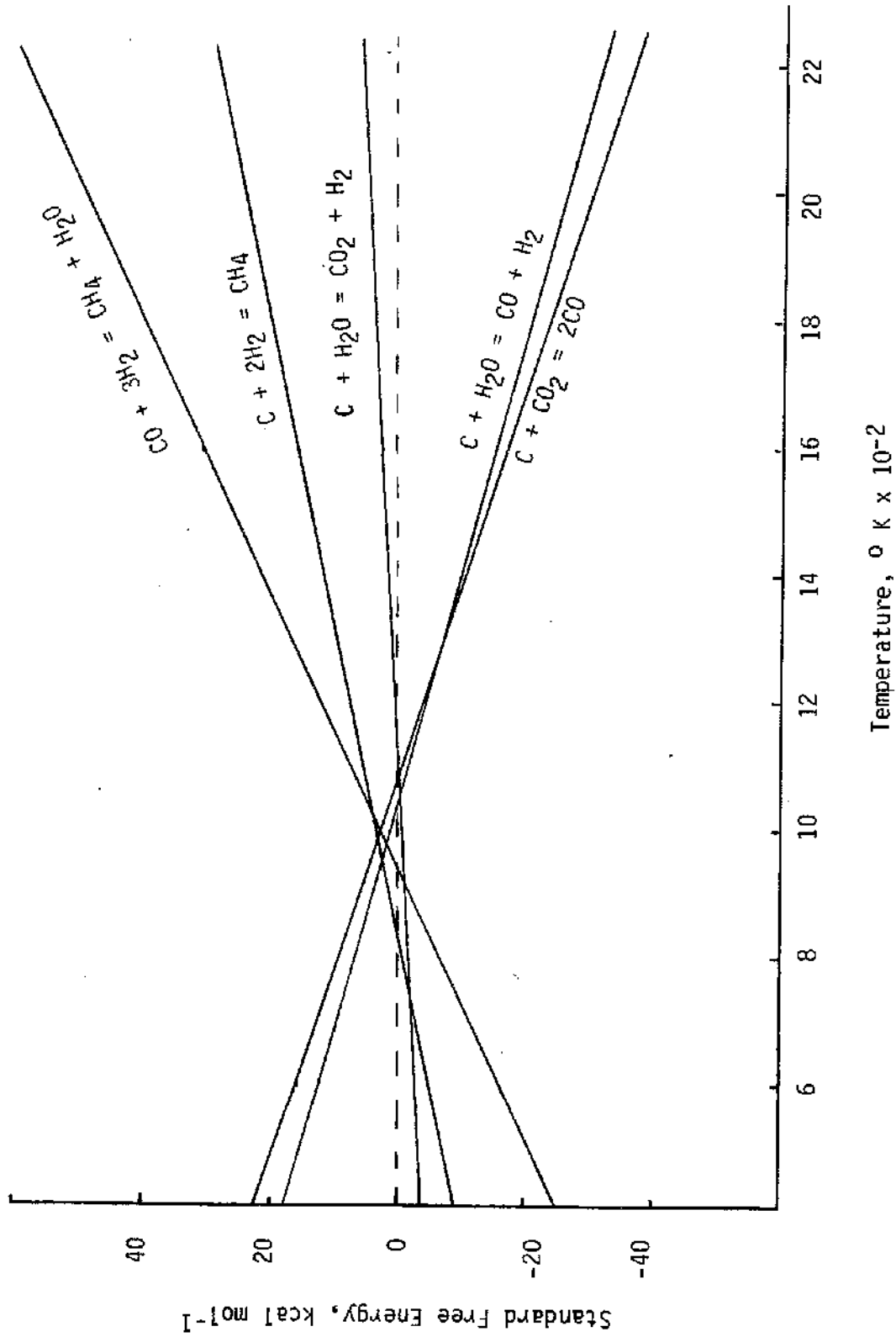


Figure VIII-1. Free Energy Change of Various Gasification Reactions (1)

VIII-3 and VIII-6 are favored by low temperatures, as seen in Figure VIII-2. Unfortunately, Reaction VIII-3 (hydrogasification) is very slow in the absence of a catalyst (3), and while attempts to catalyze the reaction have been made (4), the catalysts that were tried are severely poisoned in the presence of sulfur. Also shown in Figure VIII-2, is the effect of pressure on the methane yield.

In addition to the reaction discussed so far, another reaction that contributes to CH_4 formation during gasification is the initial devolatilization of the coal. As discussed in Part 1 (5), very little is known about the effect of catalysts on the devolatilization even though there are indications that acid catalysts such as SnCl_2 and ZnCl_2 lead to a much larger gas yield in the initial coal conversion stages.

There are a number of major problems which have to be considered in the use of catalysts for the above described gasification reactions. Some of the most severe problems are catalyst-coal contacting, catalyst recovery, and catalyst deactivation and loss due to interaction with sulfur and mineral matter. The most important aspects of these constraints will now be discussed in more detail.

1. CATALYST-COAL CONTACTING

As has been emphasized repeatedly in several parts of this study, the problem of catalyst coal contacting prevails in all of the various schemes for catalytic coal conversion. However, it is most severe in gasification since one deals with a gas-solid rather than a gas-liquid reaction. Current gasification schemes which use catalysts approach this problem by the use of salts which are in the molten state at operation temperatures. Some of the

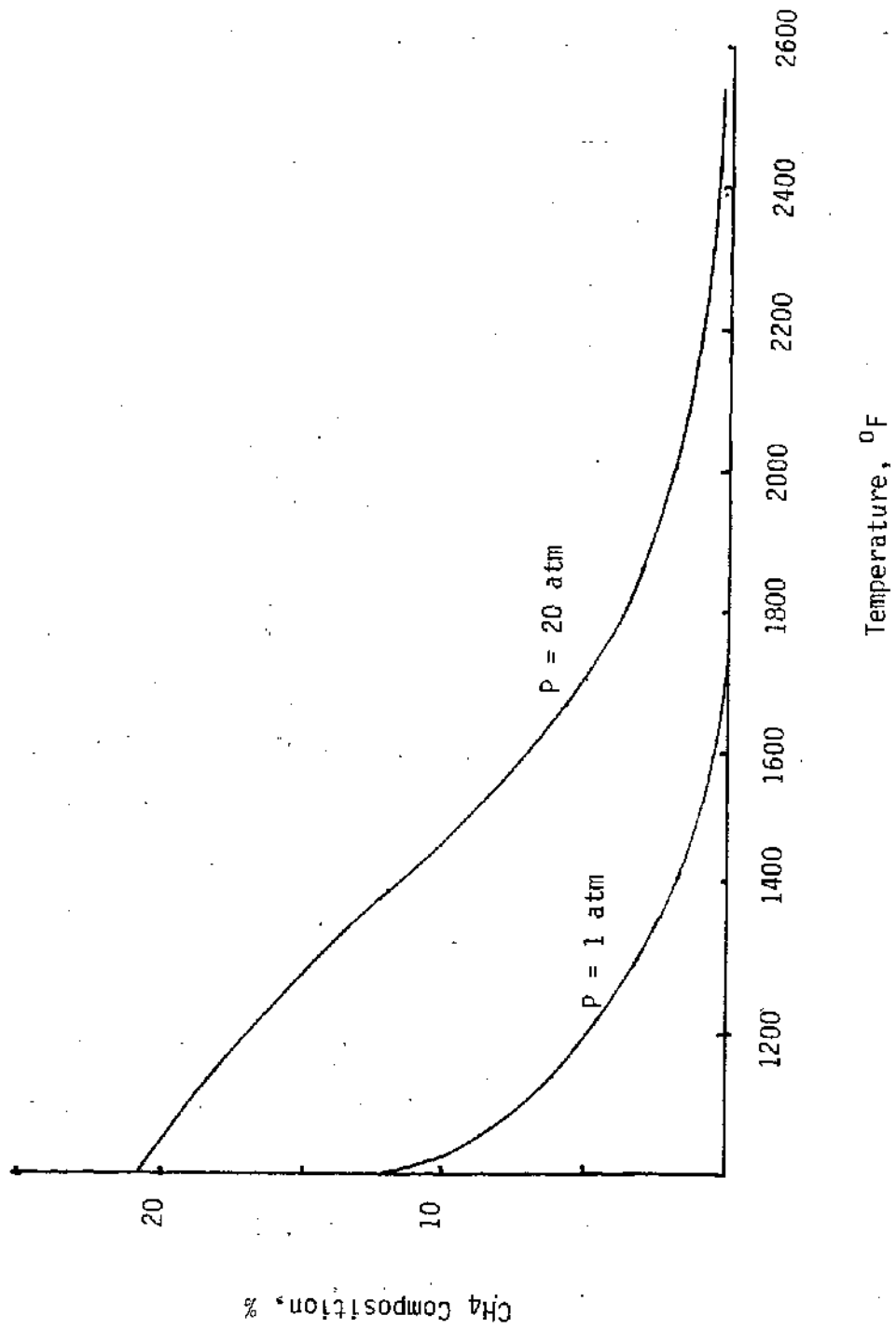


Figure VIII-2. Equilibrium CH₄ Composition of the Carbon-steam System (2)

molten systems that have been tested are KHCO_3 , K_2CO_3 , FeCl_2 , and SnCl_2 (6). In addition to lowering the reaction temperature, these molten salts serve as a heat transfer medium that insures a uniform distribution of the process heat transferred during gasification. The most common salt is K_2CO_3 , which is used in the Kellogg process. As discussed in Part I (6), it is believed to be the most effective catalyst of those tested.

By contrast to the molten salt system, where concentrations on the order of 20% are usually sufficient (7), when metals are used in efforts to increase methane yield by catalyzing the methanation reaction (Reaction VIII-6), the catalyst requirements are significantly higher (6). Catalyst to coal ratio of 1:1 are not uncommon, making such systems unrealistic from an economic standpoint. Part of this high ratio is due to poor catalyst coal contacting. Addition of Ni, for example, can be done using a finely divided metal powder or an aqueous solution of the metal salt. In the latter case, the metal-coal contacting and dispersion of metal is expected to be much better, resulting in an increased catalytic effect. This was found to be the case in a recent atmospheric pressure steam gasification study of low surface area, high purity graphite and several coal chars (8). A negligible catalytic effect was found when 2.4wt% Ni was added as the powder while 2% Ni added by impregnation of the char with an aqueous nitrate solution gave a rate enhancement of about 5. Even impregnation, however, had no catalytic effect when the catalyst was added to the coal before devolatilization (9). This is apparently due to deactivation during the initial pyrolysis step when the coal passes through the plastic phase and either coats

and traps the catalyst or poisons it by contact with sulfur and mineral components.

For successful operation, it is likely that coal gasification catalysts will either be in the liquid state, uniformly impregnated on the coal char before reaction, or ideally, well dispersed and highly mobile, thus maintaining contact with the coal during gasification. In the case of impregnation, the continuously changing catalyst-coal interface may make even an initially uniform impregnation insufficient for good contacting. Such a dynamic system also makes the experimental work complex because of the difficulty in properly defining the catalytic system. However, recent work employing catalytic materials that have some volatility in the gasification environment show a sustained catalytic effect even after a portion of the coal has been reacted (9). This is probably a direct result of maintaining catalyst-coal contact.

2. CATALYST DEACTIVATION

There are two aspects of catalyst deactivation that are important in gasification: the interaction with sulfur and the interaction with mineral matter. Sulfur presents the most severe problem. As discussed in Section II of Part 2 and in more detail elsewhere (10), few materials will survive the high sulfur concentrations of some coals. Certainly none of the transition metals is likely to remain in the metallic state at these conditions. The catalysts that work best for methanation (such as Ni and Ru) will therefore be completely impractical in coal gasification, as has been adequately

demonstrated by work which shows the catalyst deactivation (11, 12). The same applies to catalyst that have been considered for hydrogasification (Reaction VIII-3) such as Ni and Pt (4).

The problem of the interaction of sulfur in the case of salts such as Na_2CO_3 and K_2CO_3 is not as severe as with metals. In effect, several schemes attempt to take advantage of the interaction to achieve some sulfur removal during the gasification process (13). In general, at the reducing conditions of gasification, these salts form the sulfide, which could then be regenerated or discarded. However, to date there has not been much success with the regeneration of such sulfide species. Interest in this problem is related to current work in fluidized bed combustion of coal where dolomite and limestone are used to remove SO_2 during combustion by the formation of CaSO_4 (14). Discarding of the sulfide or sulfate may lead to severe environmental problems which, in the long run, may be even less desirable than the air pollution problems solved by removal of SO_2 (15).

The other deactivation problem is the interaction of the catalyst with the mineral matter in the coal. A typical composition of this mineral matter is shown in Table VIII-1. The higher concentration components such as Na, Fe, SiO_2 and Al_2O_3 are likely to be of greatest concern, in particular SiO_2 . This is best illustrated by the phase diagrams of the $\text{Na}_2\text{O} - \text{SiO}_2$ and the $\text{K}_2\text{O} - \text{SiO}_2$ systems (17). Both systems have a number of low melting eutectics: 846°C at 37.9% Na_2O , 793°C at 26.1% Na_2O , 767°C at 26.4% K_2O , 769°C at 27.5% K_2O , 742°C at 32.4% K_2O and 780°C at 54.5% K_2O .

TABLE VIII-1

TYPICAL COMPOSITION OF MINERAL MATTER IN BITUMINOUS COALS (16)

<u>Constituent</u>	<u>Percent of Ash</u>
SiO ₂	20 - 60
Al ₂ O ₃	10 - 35
Fe ₂ O ₃	5 - 35
CuO	1 - 20
MgO	0.3 - 4
TiO ₂	0.5 - 2.5
Na ₂ O + K ₂ O	1 - 4

In the presence of catalysts containing these alkali metals, these eutectics would lead to catalyst loss which would be difficult to recover or regenerate. The problem may not be as severe in the reducing environment of gasification. However, it certainly would preclude oxidation regeneration of the catalyst if this were required.

3. CATALYST RECOVERY

This problem is closely related with the problem discussed above, namely the ash-catalyst interaction. Intimate chemical and physical mixtures of the catalyst and the mineral matter of the coal will lead to catalyst loss during gasification and create separation problems which are likely to make regeneration impractical.

C. IMPORTANT RESEARCH DEVELOPMENTS

In view of the constraints discussed above, it is expected that only inexpensive, readily available materials will be practical as catalysts for coal gasification. Since they are likely to be used only on a once-through basis, their disposal will have to be environmentally acceptable. In view of the large quantities of coal to be gasified, this implies a low level of added catalytic material or an ash-catalyst combination of a highly useful nature. Any alternative to this approach is likely to require the discovery and development of a completely new concept, a process that within the the context of this analysis is considered long range.

With this perspective, and in view of the limited amount of work that has been done in coal gasification catalysis to date, the discussion of important research programs will emphasize the short term need to develop an inexpensive, disposable catalyst. Longer term research ideas will only be discussed briefly and will include a discussion of the advantages to be gained from a mobile and highly dispersed catalytic phase.

1. SHORT TERM PROGRAMS

A review of the steam gasification literature shows that little is known about the nature of the catalytic phenomena in this process. Most studies have concentrated on screening of catalysts (6), without much emphasis on the understanding of the catalyzed reaction. This has limited the discovery of new catalyst systems.

A number of the concepts and ideas discussed in Parts 1 and 2 are likely to be important in the development of improved catalytic gasification processes. They will be divided into four areas: testing procedures, possible new catalytic materials, the effect of coal treatment procedures, and the understanding of the mechanism of the catalytic reactions.

a. Testing

One of the challenges of a development program is the choice of a laboratory reactor which provides representative information about the reactions that are important on a commercial scale. In Part 2, this question was discussed extensively in relation to a number of coal conversion processes (8). A system that is of particular interest to coal gasification is the thermogravimetric

balance (19). The technique, which has been used in a number of investigations of the reactivity of graphite (20), and the combustion of coal (14) consists of monitoring the loss of sample weight at controlled temperature, pressure and flow conditions. The high sensitivity of currently available balances permits study of very low reaction rates where mass transfer limitations are minimized. Both low and high pressure thermobalances have been described in the literature (13) and have been used recently in coal gasification experiments (21, 22).

Gravimetric techniques allow the study of gasification reaction at a broad range of temperatures and pressures. The high pressure thermobalance, for example, can be operated up to 1000°C and 2000 psi (22). In spite of this flexibility, however, the data obtained from these gravimetric studies cannot be related to other experimental work unless the samples tested are carefully characterized before and after testing. This is clearly shown by the recent work of Otto and Shelef using atmospheric pressure balance (8, 21). In a comparison of a number of different coals and chars with graphite, they find considerable differences in the gasification rate of a given weight of sample. Some samples gasified up to 2×10^3 times faster than graphite. However, when this rate was corrected for the surface area of the coal or graphite sample, the difference was found to be less than one order of magnitude. This illustrates the importance of characterization in the interpretation of the results. In particular in the case of coal, it emphasizes the importance of determining the sample surface area.

This is confirmed in the determination of the gasification rate at various stages of gasification (8). Thus, in spite of a four-fold change in surface area, the gasification rate per unit area was found to be constant in the gasification range tested (0-15% reaction).

Characterization of the coal is particularly important in catalytic studies, since it allows discrimination between physical and chemical effects. The occurrence of both types of effects have been suggested in recent gasification work (23), as will be discussed later in this section. It should be noted, however, that the determination of surface area of carbons and coal is not simple. It varies considerably with the pretreatment of the sample, including the level of pyrolysis and devolatilization. Furthermore, even after devolatilization, the measurements are complicated by extensive microporosity which can account for up to about 80% of the pore volume of a high ranking coal (24). Some of the pores are as small as 5 to 8 Å, leading to severe diffusion limitations during the adsorption of gases used for surface area determination. This is particularly the case at the temperature of -196°C used for characterization by N_2 and rare gas adsorption. The use of these gases can, therefore, lead to a low value of the surface area compared to the measurement using adsorption of other gases at higher temperatures. The use of CO_2 at -79°C , for example, was found to be the preferred method in the work of Shelef et al. discussed above (21).

b. New Catalytic Materials

As mentioned earlier, the contacting problem in gasification has been surmounted in processes currently under development by

the use of molten salts. The most common salts are K_2CO_3 and Na_2CO_3 . Their low melting points ($891^\circ C$ and $851^\circ C$, respectively) and low cost (Na_2CO_3 sells for \sim \$30/Ton), make these salts excellent candidates for disposable gasification catalysts. Their effect on the combustibility of carbon has been known for more than fifty years (25, 26) and the use of basic materials to enhance the reactivity of steam with carbon is practiced extensively in the petrochemical industry. For example, in steam reforming of hydrocarbons, alkali and alkaline earth oxides are used as catalyst promoters to minimize coking (27). Potassium is considered one of the best promoters for this purpose.

In the search for new catalytic materials for gasification, two factors mentioned earlier have to be considered: cost and catalyst-coal contacting. Melts serve the latter purpose very effectively, in addition to providing a good heat transfer medium. However, for both of these functions large amounts of molten salt are required. Two alternative possibilities are the uniform impregnation of catalysts on the coal and the use of catalytic materials that have sufficient volatility at conditions of operation to achieve continuous catalyst redistribution. Before these alternatives are examined, it is worth noting that there are a large number of naturally occurring minerals which may be of interest as inexpensive gasification catalysts. Many of these are constituents of the mineral matter in coal as illustrated by the work of Haynes et. al (7). It is confirmed by the results of Shelef and Otto who have examined the gasification of a variety of coals (8, 21). Expressed on a unit surface area basis,

the non-catalytic gasification of these coals and of graphite differs only by one order of magnitude. Within this range, one coal stands out as having the highest rate: Braunkohle lignite. Upon further examination, the Ford workers find that when the mineral matter of this coal is extracted and mixed with other less reactive coals, a considerable enhancement is observed (28). This suggests that compounds in this particular mineral mixture are active in the gasification. A comparison of the composition of the mineral matter in Braunkohle and other coals shows low levels of Si, Al, K and Ti, and a very high level of Ca. Whether this suggests that a Ca compound is the gasification catalyst is not clear. There are indications that Ca is not an effective additive to prevent C deposition in steam reforming, in particular when compared to K (28). Calcium has, nevertheless, been used successfully by Battelle in combination with sodium in their impregnation process (23), and has been claimed in several patents to be a gasification catalyst (29).

There are many minerals that contain Na and K and are used as sources of pure salts of these compounds. The need for purification in an application such as coal gasification may be minimal, and the use of raw materials should be considered. For example, brines such as those from Searles Lake (30), which are used as sources for the production of potassium, contain considerable amounts of Na_2CO_3 and other Na salts which do not have to be removed for gasification applications.

The alternative of impregnating coal with salts to insure better catalyst-coal contacting has been tested by Battelle (23).

Enhanced gasification is observed in this work upon impregnation of the coal with sodium and potassium salts. Part of the observed effect is considered to be physical, and the impregnation procedure itself may have an important effect on the reactivity of the coal.

Finally, the possibility of a catalyst with sufficient volatility to continuously re-disperse as the coal is consumed should be explored. It is particularly interesting in the steam-coal system since steam is an effective vapor transport agent for many compounds, including alkali metals (31).

c. Preparative Procedures

Impregnation of a catalyst on coal was mentioned above as a method to maximize catalyst-coal contacting. In principle, this is the same objective as the preparation of supported catalysts, where maximum dispersion of the active species on the high surface area support is desired. As described in detail in Part 1 (32), many factors affect the preparation of such high surface area materials. They include the pH of the impregnating solution, the nature of the salt, the concentration of the solution and the mode of impregnation. There are many different impregnation techniques, some of which may be especially suited for impregnation of coal. Because of the extensive microporosity of the coal, for example, the use of vacuum impregnation may be very effective. In this technique, the coal is evacuated slightly and the impregnating solution admitted at higher pressure. The pressure differential results in much better penetration than if the solution has to displace the air and gases in the coal at ambient conditions. However, the gain in reaction rate or the

Lowering of the required reaction temperature must be substantial to justify such a complicated coal treatment procedure. Changes in pH of the impregnating solution may also be very important in view of the acid-base nature of coal (33).

The pretreatment of the coal is expected to be another important parameter in catalyst impregnation. It is likely to influence not only the possible interaction of the catalyst with the coal, but the rate of gasification as well, by changing the pore structure and internal surface area of the coal. As indicated earlier, measurement of gasification rates at various gasification levels (21) has shown that while the coal surface area increases with increased gasification, so does the gasification rate per unit weight. When the rate is normalized to the surface area, the change with degree of gasification is minimal. From the surface area measurements in these experiments, it can be concluded that the pore structure of the coal changes with the progress of the reaction, at least during the initial stages. This is illustrated in Figure VIII-3 by a plot of the degree of gasification as a function of the ratio of surface areas determined by adsorption of CO_2 at -79°C and Ar at -196°C . As the gasification progresses, the ratio approaches unity from an initial value of six. This is explained in terms of the recognized diffusion limitation of molecules into coal at low temperatures (24, 34). Argon at -196°C does not reach part of the coal microstructure while CO_2 at -79°C does, the difference being a function of the adsorption temperature and not the molecular size. Therefore, CO_2 measures a higher surface area. As the gasification

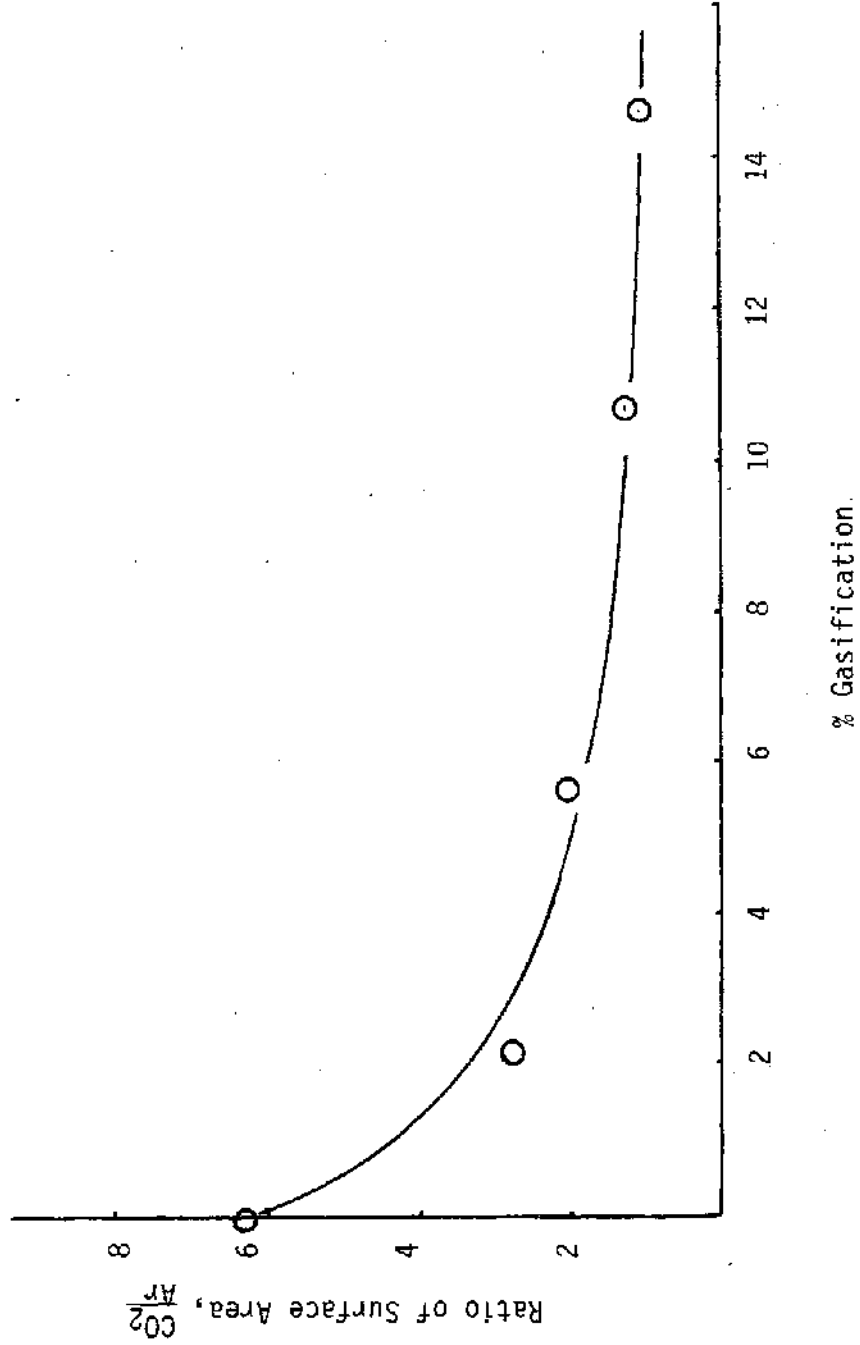


Figure VIII-3. Change in Pore Structure With Gasification: Difference in Surface Area Measurement by CO_2 and Ar (21)

proceeds, the microstructure of the coal opens up until it is equally accessible to both gases.

Once the effect of pretreatment and surface area on the gasification rate is recognized, it should be considered how the coal can be treated to maximize the effect. The effect of rapid devolatilization, the degree and rate of pyrolysis, and, in general, the history of the coal before gasification may be important. Increase in surface area may be obtained, for example, by rapid heating of high vapor pressure liquids that are preadsorbed on the coal. If the gases are expanding faster than the diffusion rate out of the microstructure, it will result in break-up of the coal matrix. In the most dramatic example of this phenomenon, molecules that are intercalated within the planes of layered compounds open the structure to such a degree that there is a macroscopic change in the compound. The effect, known as exfoliation is used commercially for clays such as vermiculite to achieve a very open structure. It has also been observed for graphite, which has a layered structure as described later in this section. The possibility to take advantage of this effect, in the case of coal, should be explored, since all coal structure models show some graphite-like layered arrangement. Since the gasification rate is proportional to surface area, an increase in area by exfoliation would have a significant effect on the gasification process.

d. Mechanism of Gasification Reactions

As mentioned earlier, there is only limited information about the detailed mechanism of the catalytic reaction between H_2O and coal. By contrast, considerable work has been done in understanding the effect of metals on the reaction of oxygen with carbon, in particular with graphite (20, 35, 36). In this system, it has been shown that the rate is critically dependent on the structure of the sample, the edges of the hexagonal planes of graphite being the most reactive (20). The role of the metal is to provide a surface that facilitates O_2 dissociation and thus becomes a source of the reactive oxygen atoms. As gasification proceeds, certain metal particles become mobile due to the consumption of the carbon in contact with the catalyst. This has been shown in a number of studies, including recent work of Baker et. al. (37) which showed that the mobility of the particles is a function of the environment.

The catalyst mobility and the continuously changing catalyst-coal interface in all gasification reactions present problems in the interpretation of gasification data. The dynamic nature of the system has to be incorporated in any model of the gasification reaction, and should also be included in the consideration of improved catalyst systems. This was suggested earlier in the discussion of new materials. Difference in mobility may be responsible for some of the differences observed in the catalytic activity of various compounds. In the complex balance between redispersion and agglomeration of catalytic particles, those that tend to redisperse at the conditions of gasification are likely to be more effective catalysts.

Because of the mobility of the catalyst and the effect of surface area and pore size on gasification activity, measurement of the physical properties of the coal at different stages of gasification may be an effective means to monitor the reactivity of various materials. This should be combined with information on the properties of the catalyst, in particular the basicity of the catalyst surface. The latter is likely to be important in determining the interaction of water with the catalyst and the coal as well as possibly influencing the reactivity of coal itself. The mechanism of catalysis of the steam gasification by metals may be similar to that established for oxidation of graphite, that is, the metal oxide being a source of dissociated oxygen. However, the action of other materials such as K_2CO_3 may be very different and both systems should be examined.

In summary, the study of the mechanism of coal gasification is considered an important supporting investigation to programs in the area of catalytic coal gasification. Aspects that should be included are the effect of the catalyst on the physical properties of the coal, the possibility of pretreatment to increase coal reactivity, the effect of catalysts on coal devolatilization and the general study of catalyst properties that may determine catalyst activity for the reactions of interest.

2. LONG TERM RESEARCH AREAS

In the first part of this section, it was stressed that catalysts for the gasification of coal have to meet a number of constraints such as the interaction of mineral matter with the catalyst, catalyst deactivation due to the presence of sulfur, high temperature, and the

problems of catalyst recovery and regeneration. The short term research areas discussed above therefore have concentrated on the development of inexpensive, disposable catalysts. In this section, two ideas for the development of new catalytic gasification systems will be discussed: the intercalation of layered structures and the use of volatile catalysts.

a. Intercalation

Because of the high levels of sulfur present in many coals, the use of effective gasification catalysts such as Ni and other group VIII metals is unrealistic even if economic methods were devised to recover these more expensive materials completely. Sulfide formation would lead to very short life for these metals. It is, therefore, questionable whether a research effort in this direction is warranted. However, there is one aspect of the interaction of metals with carbon which merits examination: the intercalation of metals and other elements and compounds into the structure of graphite. This will be explored briefly in this section. The direct relationship between the ability of graphite to intercalate molecules and the behavior of coal is not clear, and for this reason such an investigation is considered to be a long term effort. However, the dramatic effect of intercalation on the properties of graphite may well be an indication of the type of modifications one may expect with coal.

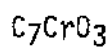
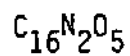
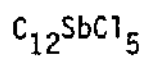
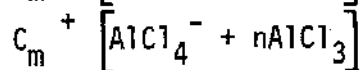
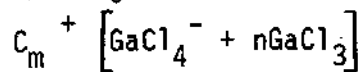
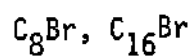
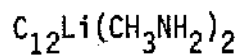
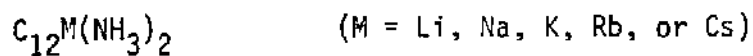
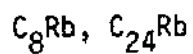
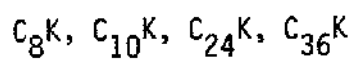
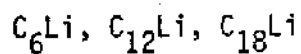
To understand the phenomenon of intercalation, it is useful to refer to the structure of graphite. A graphite crystal is composed of layers of hexagonal carbon networks. The carbon-carbon distance within these networks is 1.42 Å. The distance between layers is much larger (3.35 Å) and indicates that the interlayer forces are very weak.

These weak forces allow one layer to slide over the other, and are responsible for the unique lubricating properties of graphite. They are also responsible for the ability of graphite to intercalate a number of molecules. These molecules penetrate the inter-layer space and interact strongly with the layer. This phenomenon is seen with a number of other layered compounds such as micas and, in particular, transition metal chalcogenides (sulfides, selenides and tellurides). Graphite is unique, however, in its ability to intercalate both electron donors, such as potassium and electron acceptors, such as bromine.

Intercalation occurs only with molecules that interact with the layer. Examples are shown in Table VIII-2. The strength of the interaction varies with the nature of the intercalating species and the stoichiometry. It can be substantial, as in the case of the potassium-graphite system where the heat of intercalation ranges from 7 to 18 kcal (mole)⁻¹. This strong interaction results in changes in the properties of the graphite. For example, upon potassium intercalation, the conductivity changes by a factor of 10 (38). The lattice expands to 5.40 Å (39). The expansion can be as high as 9.45 Å for the case of C_nFeCl₃, and in other layered compounds such as TaS₂, expansions to interlayer spacings as high as 50 Å have been observed (40).

As expected from the changes in interlayer spacing, the adsorption properties of the graphite change as well. The compound C₂₄K, for example, adsorbs large volumes of hydrogen until the stoichiometry C₂₄KH is reached (41). This compound, as well as a number of other graphite intercalates, exhibit catalytic activity

TABLE VIII-2
SELECTED INTERCALATION COMPOUNDS OF GRAPHITE



in a variety of reactions including low temperature ammonia synthesis (42), hydrogenation of unsaturated hydrocarbons (43) and several other reactions that have been reviewed recently (39). From these examples, it is clear that the properties of the carbon layers are changed substantially from those of the original graphite. It is likely that the reactivity of graphite is changed as well. Intercalation may, therefore, be an effective way to overcome the catalyst-carbon contacting problem in reactions such as gasification. The challenge is to find an intercalated system that will remain stable at the high gasification temperatures and inert to the sulfur and ash compounds of coal.

b. Volatile Catalysts

A second area that is of interest for long term research is the use of volatile materials that are catalytic at the conditions of gasification. This has been discussed briefly with respect to catalyst coal contacting, which represents its most significant advantage. Recent work with coal chars (28) shows that Ru, which possesses a volatile oxide, retains its catalytic activity for the gasification of coal much longer than other transition metals. This same volatility could be used to remove the catalyst from the ash and retain it in the reacting coal bed. The high cost of Ru and the sulfur poisoning problems discussed earlier makes this an impractical catalyst. However, the concept should be established and other more realistic systems tested.

D. CONCLUSIONS

The catalytic gasification of coal faces a number of constraints which restrict the choice of catalysts for this system. They include

the difficulty in obtaining good catalyst-coal contacting, catalyst deactivation due to sulfur or mineral matter and the problems of catalyst recovery and regeneration. Because of these severe constraints, the most likely catalysts for coal gasification are inexpensive, disposable materials that will be used on a once-through basis.

Because of the limited amount of information that is available concerning the role of the catalyst and the nature of its activity, the major effort in this area is short term. Effective testing programs using thermogravimetric techniques can lead to a better understanding of the mechanism of the catalytic reaction and the determination of properties of the catalyst which are important for activity. Characterization of the coal before and during reaction is crucial for this purpose. The gasification rate is a function of coal surface area and, therefore, measurements of the area of the sample have to be included in any data analysis. These measurements can be done conveniently in situ with the thermogravimetric system.

The pretreatment of the coal is likely to effect the gasification rate. It is, therefore, a parameter that should be included in an investigation of coal gasification. It can affect the reactivity of coal by changing the porosity or surface area, and it may also affect the interaction of the catalyst with the coal. The latter is particularly important when impregnation of the coal is considered as a means to achieve good catalyst-coal contacting.

Impregnation has been shown by the Battelle work to be effective in preparing the catalyst coal system. Since the objective is the same as practiced in the preparation of high surface area supported catalysts, many of the techniques developed in catalysis over the years may be applicable to coal gasification. Research in this area should be pursued.

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