Literature Background

Homer Hall
Esso Research and Engineering

This report is a review and analysis of the recent literature on selected priority areas of research in coal catalysis. The interpretation of the literature selected has been limited because independent reports in these areas are being submitted by experts who are thoroughly familiar with the art in their specific field. Accordingly, this is intended more as an overview than as a comprehensive report to examine what the literature is trying to say. Particular attention is made here to possible interactions between different pieces of information rather than to completeness in detail.

The literature background of the application of catalysts to the conversion of coal has undergone profound changes in recent years, with respect both to the process and the technology available for research and development. The application of powerful new tools for hydrocarbon analysis such as high resolution mass spectrometry, electron spin resonance, and proton magnetic resonance which began to appear on a routine basis about 1966, permit the positive identification of individual compounds or transient intermediates in a complex mixture such as coal or coal products. By tracing individual compounds through a process, many of the guesses of the early sixties as the structure and mechanisms can now be confirmed or corrected by direct measurements.

The literature during the late 1940's and 1950's was weighed heavily toward the Fischer-Tropsch process. This has been reported in thoroughly indexed compendiums and analyzed in numerous reference volumes which are well-known to experts in the field. Separate recommendations have been received by Libby Labs on the possibilities of Fischer-Tropsch synthesis using producer gas. No effort has been made, therefore, to go over these grounds in the present review except for Section 7 below.

Aside from Fischer-Tropsch, the literature during the 1950's contains many suggestions for modification of conventional methods for gasification. It also reflects a growing concern over the control of sulfur in combustion stack emissions and the gradual transition from local regulations on Smoke Abatement to a nationwide network of pollution control by the time of the Clean Air Act of 1967. A traditional emphasis on rank as an important factor in the coal economy and, therefore, in studies of its chemistry was blunted as it became clear that the premium market had disappeared for domestic heating.

The studies of the structure of coal which had emphasized differences due to rank, began increasingly in the sixties to recognize that there are basic similarities in the coal molecule of all ranks which shift gradually from one to another during coalification. The first comprehensive examination of the sulfur content of U. S. coal was published by the U. S. Bureau of Mines in 1966. It is only since that time that earlier USDM and USGS surveys of coal as a mineral resource began to emphasize the analysis of typical coals rather than the unusual specimen. The analysis of coal conversion products for emissions of specific elements other than S , N, and ash, which might be catalytic, is reflected only in current research projects which are just beginning to appear in the literature.

The references discussed in this review are addressed primarily to the processes of coal as such and not to the hydro refining of deashed coals, liquids, or cleaned gases.

1. Direct Methanation

Most, if not all, present processes for the manufacture of methane from coal start with coal that has been exposed to air. There is evidence, however, that this exposure to air may have a significant adverse effect. The U. S., Russian, and Japanese literature offer independent leads which indicate that coal and its reactions are changed significantly by the usual exposure to air or oxygen. These changes are rapid, at least partly irreversible, and they are particularly noticeable with coals of low rank. On gasification, half or more of the methane produced is released directly from the coal in a rapid initial stage of the reaction. Most of the oxygen present reacts just as rapidly and at the same time.

The question of whether the effects of oxygen added by exposure to air are chemical, chemisorptive, or catalytic is partly a matter of semantics, and partly a question of data needed which might be answered by techniques now available. Taken together, these lines of evidence suggest that a definite increase in yields of methane from lignite or subbituminous coals might be realized by carrying out all steps of mining, transport, grinding, drying, and initial gasification in the complete absence of air. The importance of this approach has been derived from indications in the literature for various stages of the process, but the combination has not been fully explored:

1.1 Any exposure to air inhibits hydrogenation of coal.

The increase in activity for coals which are freshly ground is well-known, particularly for lignite. A typical set of data by Appell and Wender(1-4)* is as follows:

---

* Numbers refer to Literature Survey in Part 4

Hydrogenation of Lignites at 380°, 1500 psig
Using CO and H_2O

Lignite Sample Ball-Milled	Conversion wt% benzene soluble
Fresh (19% water)	89
4 weeks in air (13% water)	77
105°C, 24 hrs in air ($<$ 1% water)	54
100°C, 0.5 hr in vacuum ($<$ 1% water)	86

An irreversible change occurs in the coal on aging in air, and aged lignites produce less desirable products. The large loss in reactivity indicated on drying in air and the minor decrease on drying under vacuum were taken as evidence that the deactivation is largely a result of oxidation. These data are amply supported by literature on the harmful effects of weathering on coals, of all ranks.

1.2 Deactivation due to oxidation penetrates coal beds to a considerable depth.

Data on this by Terpogosova (USSR)(1-1) were obtained on samples of coal taken from a mine face which had been exposed for several months, and also from a fresh cut. The further away from the wall surface, the less deactivation. The effect was attributed to the protective action of methane in the unmined coal to exclude oxygen, and the differences observed were still detectable at a depth of 1.0 - 1.2 meters. This observation is supported qualitatively by other references which indicate that larger yields have been obtained in low temperature gasification by increasing the grain size of coal. There are other indications, however, that in high temperature reactions such as the oxidation of anthracite by CO_2 or pyrolisis to acetylene, particle size does not have the same effect.

1.3 Unexposed coal develops new structures on exposure to air.

ESR studies by Ohuchi(1-2,-3) show new active spin centers developed on the exposure of coals, and this is not reversible on subsequent evacuation. The increment was greater for coals of lower rank, and linear in intensity with the sum of volatile matter and moisture in the original coal. Ohuchi concludes that air oxidation forms free radicals in proportion to the aliphatic/alicyclic content of the unreacted molecule. Other evidence suggests that this might include the addition of oxygen at a point of rupture(1-36,-37). The exact nature of the neutral oxygen compounds removed during initial degradation of coal has been the subject of intensive study. The present consensus is that they consist largely of ether bridges and an unreactive carbonyl grouping which may be chelated to a neighboring hydroxyl(1-7,-10,-15,5-24).

Since this attack by molecular oxygen takes place most aggressively with lignites, it is entirely possible that the most reactive methane-forming sites are the first to be lost to any O_2 present. Pertinent data may be available from current research at the U. S. Geological Survey (Project 00448).

Earlier studies both by chemical methods and by infrared have suggested that CO_2 formed in the oxidation of lignites is derived from methylene structures, either in bridged rings or in longer alkyls. These are considered a significant source of methane on hydrogenolysis, and thus of the larger amounts of methane that might be derived from lignite.

On this basis, any oxidation of lignite alkyl groups by molecular oxygen could lead to an increase in CO_2 with a corresponding decrease in preformed CH_4. Evidence in this direction has been found by the exposure of coal to O^{18} followed by high temperature pyrolysis, where 60% of the combined O^{18} appeared in the volatile fraction. No report was made in these experiments of the particular type of oxygen bonds enriched in the remaining part of the coal macromolecule. Oxygen bridges established at this point would represent a type of condensation polymerization between adjacent rings, with a corresponding loss in volatility.

The necessity of grinding certain lignites either in an inert atmosphere or before complete drying is commonly recognized. The loss of water from lignites includes both free and combined HOH even at 105°C, and at 110°C carbon dioxide begins to be evolved by the decomposition of carboxyl groups. This decarboxylation can be promoted by cations present, particularly Ca, and is apparently related to their tendency to form hydrates in aqueous solution. The loss of this combined

CO_2 and HOH both create active sites in the molecule and, at the time when this occurs, the coal would be particularly susceptible to re-attack by atmospheric oxygen. Drying in the complete absence of air is possible. One method which might be suitable is a thermal dewatering process for brown coal recommended by Murray, using liquid phase separation under pressure at 150-300°C. Liquid water recoverable by this means could have a significant value.

1.4 Same portions of the macromolecule give rise to CH_4, CO_2, or C_2-C_4 hydrocarbons on initial degradation.

While pictures of the molecular structure of coal continue to change with additional data and more refined methods of analysis, there is general agreement that the changes between ranks during coalification correspond to gradual shifts in ring saturation and substituent groups in macromolecules which are similar for all ranks(1-10,-14,-15,-18). The basic unit in configuration apparently has about 3-4 rings plus substituents, and a molecular weight of about 300-500. In coals of the lowest rank, only one of these rings may be aromatic and others either hydroaromatic or carbocyclic, derived from humic acid or carbohydrate structures which are still rich in combined oxygen. Humic acid structures include a high proportion of C_6 rings which have not been reduced to hydrocarbons.

The alkyl groups present are predominantly methyl in coals of all ranks, but the lignites include a significant amount of longer methylene chains. Gasification of lignites under very mild conditions can give a small amount of C_2 and C_3 olefins and parafins, but their amount is reported as inversely related to the yield of CH_4 from a given coal. No significant amounts of hydrocarbons above C_3/C_4 are reported from such treatment in the absence of hydrogenation sufficient to rupture a hydroaromatic ring. This suggests that the alkyl chains as well as carbocyclic rings may be derived in part by the reduction of cellulose residues which have been bonded into the initial macromolecule during coalification. Residues of this type would explain centers of high chemical activity formed by mild heating and degradation.

These lines of evidence reinforce each other in the suggestion that completely "anaerobic" mining of lignite or subbituminous coal may be worth careful evaluation, from a closed pit mine all the way into the initial rapid stage of gasification and methane formation. This may be as short as one second or less, depending on the temperature, and it requires only a mild pressure of hydrogen of 600 psig or less for maximum CH_4 yield. Low initial temperatures in the range of 300-400°C are recommended in processes now under development, such as BiGas and Hydrane. This helps minimize unnecessary hydrocracking of C_2= and C_3= to CH_4, which consumes more hydrogen for a given product BTU. Additional data on the effects of the exclusion of air would be useful at a number of points, and the use of isotope tracing, coupled with magnetic resonance measurements, are promising tools for their investigation.

2. Catalytic Effects of Ash Constituents

Ash is a major nuisance in the catalytic processing of coal because it dilutes the catalyst and complicates or prevents the economic recovery of catalyst for re-use or regeneration. It usually includes a large proportion of fine particles that are so small, they can plug the pores of a high-surface area catalyst. In addition, it frequently has a high content of reactive alkali or alkaline earth ions which can form fusible slag by reaction with the carrier, or by reaction with other ash components which can then coat the catalyst. One way of counteracting such deactivation is to use large catalyst particles moving in suspension, which continually abrades or attrits off any ash coating on the surface. Ash suspended in product fuels is also undesirable, since it comes through as dirt or deposits on combustion. These negative effects are so strong that coal conversion processes regularly include preliminary deashing as an important step, and processes such as coal liquefaction cite deashing as a primary benefit.

2.1 Elements Present in Ash

The major components of coal ash are the common elements of rocks and soils present as mineral intrusions in the coal. They are combined in widely varying proportions, as in ordinary are high, and only a few elements such as manganese are low. Anomalous amounts of specific elements may be found in beds contiguous to mineral ore bodies of the same element. This is regularly the case for coals having a mercury, lead, zinc, or uranium content higher than the usual range, and may be equally true for other elements including copper, tin, and arsenic.

The selection of coal samples for analysis has an important bearing on the results, and for many years, the analysis of coals for elements such as mercury, tin, or lead, has been used as a guide to valuable ores nearby. Considerable care must be used in interpreting analyses made on samples selected as mineral specimens, to avoid confusing them with results obtained on typical or average coals. The best analyses for many years were those obtained by the U. S. Geological Survey in mineral resource surveys, and the U. S. Bureau of Mines on delivered commercial coals.

The trace elements considered in this review as "Potential Pollutants in Fossil Fuels" are divided into three groups:

Trace Elements in Coal
(about 0.1% or less, on ash)

Considered Hazardous	Others Analyzed in Coal (USGS)	Analyzed in Ash (USBM)
Beryllium	Boron	Lithium
Fluorine	Vanadium	Scandium
Arsenic	Chromium	Manganese
Selenium	Cobalt	Strontium
Cadmium	Nickel	Zironcium
Mercury	Copper	Barium
Lead	Zinc	Ytterbium
	Gallium	Bismuth
	Germanium	
	Tin	
	Yttrium	
	Lanthanum	
	Uranium	

The seven elements commonly considered as hazardous are volatile themselves or as stable organic compounds. The analytical data for most of those are poor, and new methods of analysis are now being developed. Several of them can act as serious poisons for noble metal catalysts, but they have not been important themselves as catalysts for the conversion of coal. Many active catalysts are included in the list of elements analyzed for as mineral resources, but their concentration in the average coal is low and fairly uniform.

The relationship of coal composition to catalytic activity has not usually been discussed in terms of trace elements, and most references to the catalytic activity of ash are talking only about sintered or fused alumino-silicates of alkalis and alkaline earths. The weight per cent of most trace elements dirt, and the effects they may have as catalysts or surface active agents will vary accordingly. The petrographic examination of coals to determine which clays or other minerals are present requires a major effort (Penn State), and unless this has been done, there is no reason to assume that the ash from one coal will be the same as another.

There are eight inorganic elements which are commonly present to the extent of 1% or more on ash: sodium, magnesium, aluminum, silicon, potassium, calcium, titanium, and iron. Sulfur is present primarily as pyrites which is found as part of the coal and not as a mineral inclusion. Presumably, the amount of pyrites precipitated under reducing conditions in the coal-forming process depends on the amount of sulfur present, since swamp water normally contains an excess of iron. The origin of the organic sulfur in coal is less certain: its amount is seldom above 1% and the rest of the sulfur is present as pyrites. The nitrogen in coal is primarily, if not exclusively, organic. The question of whether there may be a small amount of nitrate in some lignites is still under discussion.

Other inorganic elements in coal are present in trace amounts only of the order of 0.1% or less on ash. A critical review of the data on the occurrence and distributions of these trace elements in U. S. coals has been submitted as background for this search(PB). The usual amount of some 20 elements present is about 5-10 ppm, in the range 1-100 ppm. B and F are higher, about 50-200 ppm, and Hg is lower, about .04-.4 ppm. Trace element concentration, as a whole, correlates only moderately with geographical location, and not at all with coal rank. Boron, which is high in lignites and lower in high rank coals, is an exception.

The amount of some trace elements is commonly highest in the top and bottom few inches of a bed, and the edges of a coal basin (Ge, Be, Ga, and B at bottom only). These variations are frequently greater than the differences between the averages for different beds. Other elements (Cu, Ni, Co) show no such correlation. Those elements which tend to be concentrated in coals (S, Ge, Be, B, Ga) are associated primarily with the organic portion of the coal. They also show the largest variance in average concentrations between different major producing areas: e.g., for germanium, which is high in Illinois. As would be expected from long association over geological periods of time, these elements are not considered catalysts in the conversion of coals.

Most trace elements are present in concentrations which fall within a narrow range, varying by a factor of 3 or less in the averages for different basins or areas. This range is close to their average crustal abundance, which usually lies between the concentration of the elements in coal and its concentration in ash. On this basis, boron and germanium in coal on ash is of the order of 0.005 to 0.05. Exceptions to this are barium and strontium enriched up to 0.5% in the ash of some western lignites, which may go as high as 52% of CaO. Lithium values as high as 0.1% appear in some Appalachian coals. Of the well-known catalytic metals, nickel contents are somewhat higher at 0.03 to 0.07% in Illinois coals than in other regions which are all below this. Tin is below 0.005 except for a few mineral specimens which may go as high as 0.2%. This is enough to show definite hydrogenation activity, but the amount of such coals would be very small and in strictly limited locations. The nearest to a real exception is zinc, which has many values of 0.1% on ash and ranges between 0.02 and 0.13% in average for various states. It is true, of course, that cumulative amounts of many elements may have a synergistic effect. This is true of any clay or rock, however, and is not limited to coal ash.

2.2 Total Ash as Catalyst

A few references describe beneficial effects of coal ash as a catalyst. Soviet research describes improvements in the caking properties of coals due to the presence or addition of specific clays or minerals, and attributes this effect to their cracking action to liberate small amounts of volatile tars within the coal. Several patents to Gatsis describe catalytic ash for use in hydrocracking heavy hydrocarbons or coal extracts, but no analysis is given for the ash employed. The H-Coal process which is being actively developed uses as a contact mass large particles which are derived from the ash of coal and renewed as required.

Many earlier references refer to the use of sifted coal ash as a guard bed or contact surface for the pretreatment of dusty or dirty feed stocks, but the action in these cases is only vaguely catalytic at best.

2.3 Soluble Alkali or Alkaline Earths

The alkalis and alkaline earths are water-soluble as the hydroxides or carbonates and easily enriched by the leaching of ashes. The best known of these are potash, soda ash, and lime. These materials in coal ash have a considerable value as chemical reagents to remove and retain SO_2 in the combustion gas. This is particularly true for lignite ash, which has a very high content of alkaline earths, and, in this case, much of the sulfur in the coal appears as gypsum in the ash. A number of processes are under active development which involve the use of lime or dolomite as chemical reagents for desulfurizing flue gas or coal, but the reagent in this reaction is consumed and not properly considered as a catalyst. Related processes in which coal is desulfurized by partial oxidation in the presence of ash benefit from being able to avoid added chemicals, but this will be limited to the analysis of the specific coal.

The use of potash and lime as definite catalytic agents has been important in the Fischer-Tropsch process. Early work by Tropsch(2-21) seeks to discredit still earlier references to the effect of calcium in producing methane from lime, steam, and coke alone, and with the addition of other oxides, including Fe and Al, but the fact remains that these ended up in his preferred catalysts. In hydrocarbon conversion catalysts, the neutralization of acid sites may be desirable to limit or control the cracking activity of silicates or other acid contact surfaces. The presence of sodium is frequently undesirable to avoid the formation of fusible silicate or alumino-silicate slags. Potassium, calcium, and magnesium undergo the same reactions but are less harmful in this respect. The extent to which cracking reactions can cause the degradation of methane to hydrogen in coal gasification is determined by temperatures.

Slagging reactions at higher temperatures are a severe limitation on the usefulness of alkaline ash components to limit surface acidity, and other approaches are preferred. At lower temperatures or in the absence of an active catalyst, these alkalis may be valuable for their chemical content. One such possibility is to add a leachate of lignite ash to fresh lignite by using it as water for hydraulic mining, or at some other stage of pretreatment before initial gasification. Any alkali recovered or insolubilized by such processing means less loss to potential water pollution.

3. Model Compounds

There is now general agreement that the basic structural units of coal consist of three or four rings of which one at least is aromatic and the others are progressively changing with coalification from unreduced carbocyclics in lignite to fused ring hydroaromatics in low-rank bituminous to completely aromatic in anthracites. Both phenanthrene and anthracene arrangements are present, with more phenanthrene than anthracene and much less of the peri structures such as acenaphthenes. Five-membered fused rings account for most of the organic sulfur and some nitrogen, but less so for hydrocarbons. There is very little evidence for single methylene bridges between aromatic rings, and what little there is may be limited to fluorene types and dihydroanthracenes.

Methyl groups account for at least half of the aliphatic carbon, and much more than half on taking into consideration the carbon number of the C_2 to C_4 groups present. Few, if any, of the original alkyl groups are longer than C_4, and it appears that longer alkyls found on hydrogenation are formed by the rupture of hydroaromatic rings. In fused rings such as naphthalene or tetralin, there is a better than 60% preference for the beta position and close to a statistical average distribution of all possible isomers in the dimethyl homologues. While this determination has been made on volatile products which may have been equilibrated by thermal exposure, the same trend would be expected in coals over geologic times.

The lignites contain large amounts of oxygen combined as hydroxyl groups and carboxyls, much of which are present as the salts of alkaline earths. There are also carbonyl groups in ring structures which are partly quinones and partly another grouping not clearly identified, but assumed to be chelated with a neighboring hydroxyl. The phenols liberated on initial degradation may be partly formed by the interaction of aromatic groups from any bond rupture with free or combined water in the coal.

The coal structure is three-dimensional, with both chemical bonding and physical interlocking between folded planes. One possibility which the literature both proposes and denies is that a part of this bonding occurs as neutral oxygen ether bridges between separate units of the macromolecule. Such bonds may or may not be artifacts formed during dewatering of the original coal. An increase in density occurs with increasing cyclization and aromatization from lignites to bituminous coal. This is followed by a decrease in density and increased porosity as further coalification leads to the formation of much larger assemblies of fused rings, which are so large that they are unable to pack closely together in the solid.

If these hypotheses are accepted, a model compounds or a standard mixture for test purposes should contain both phenanthrene and anthracene structures, either separately or combined as in 1,2 benzanthracene. This could be partly methylated by a suitably standardized process, nonselective as to position. The same molecule or mixture could be partly or more fully hydrogenated as desired. Since some of the reactions on which more information is desired involve differences between the behavior of anthracene and phenanthrene (as coal solvents or hydrogen donor diluents), a simple but standardized mixture of these compounds and their methyl derivatives might be preferred.

Dibenzothiophene or one of its methyl derivatives is a satisfactory model for the ring sulfur compounds in coal. The choice or synthesis of a suitable model compound for lignite is not so simple. An alternate route which might be feasible is to isolate a standard preparation of a humic acid-type material from lignite by a relatively nondestructive method such as extraction by water or methanol under pressure, with further processing in the absence of air, such as a possible separation by preparative GC. This is a research problem which has not yet been solved.

There are statements in the literature that para substitutions in a single aromatic ring are not typical of coal. It is also said that biphenyl compounds are absent in raw coal and probably formed as artifacts in pyrolysis. This may be in line with the ease with which one ring of biphenyl is destroyed by hydrogen transfer. These statements are interesting if true, and might be investigated to advantage.

Meanwhile, they should be kept in mind in considering model compounds.

4. Bridged Ring Cracking

The methylene bridges present in coal or formed by simple hydrogen transfer reactions are largely of the type of dihydro-anthracene or dihydro-phenanthrene, with very little if any other diarylmethane except fluorenes. There is very little evidence for diphenyls. This may mean that phenanthrenes once hydrogenated proceed to the complete hydrogenation and rupture of one ring, rather than stabilizing as a biphenyl residue. Since there is evidence that anthracene is better than phenanthrene for recycling as a hydrogen donor solvent oil (Krichko)[5-10,-11,-17,-23,-26,-32,-33], studies on the preferential hydrogenolysis of phenanthrene rather than anthracene would provide useful data not now available.

5. Solvent/Catalyst Interactions

Solvent oil for coal conversion is much more effective if it is catalytically hydrogenated. This can be accomplished either in direct contact our outside the coal conversion zone. In either case, a heavy aromatic fraction in the range of anthracene oil is preferred, both for its solvent action and as a hydrogen donor. Anthracene oil is a complex mixture of many compounds. With improved methods of analysis, it has become easier to distinguish between hydrocarbon types in this range, both before and after use. Analyses of this type by Krichko have indicated that anthracene is better than phenanthrene as a solvent oil, even though phenanthrene is usually present in a greater amount. This effect is attributed to the ability of hydrogenated anthracene to penetrate more readily into the coal molecule and, in part, to its ability to inhibit the repolymerization of molecular fragments formed during degradation. Both of these tricyclic compounds are superior to naphthalene/tetralin or their alkyl derivatives, which have been employed less and less in the literature in recent years.

The good quality of anthracene as a solvent oil is supported by many references. Comparisons between the effectiveness of different solvents have frequently been based on Prausnitz solubility parameters. The Japanese literature suggests that this is only partly responsible and that an important independent factor is the fluidity of the solvent/coal slurry which improves mass transfer. It appears that both factors might be combined to advantage.

6. Lewis Acids and Bases

The use of metal halides as catalysts for the industrial conversion of heavy hydrocarbons has been attempted repeatedly over the past 60 years, but it has never been a commercial success. The Gulf Oil Company studied the process intensively for 20 years, seeking to develop large-scale uses for the halides, but they were never able to overcome the two problems of corrosion and the loss of catalyst to sludge. Their patents to McAfee and others recommend the chlorides of aluminum, iron, or zinc. Aluminum was preferred, and used at temperatures starting about 150°F for plant scale experiments. Even though Al was the cheapest, the loss of as much as 5 to 10% of the catalyst per cycle was considered too expensive to be practical.

The literature contains numerous indications that interesting results can be obtained by the use of these same catalysts in the conversion of coal. The conditions employed are at least as severe as those used by McAfee, however. No published evidence was found in this review which indicates that the chronic problems of corrosion and catalyst loss have yet to be solved.

The use of milder reagents such as phenol plus toluene sulfonic acid has been studied extensively in Japan. This is an effective combination for the depolymerization of coal, and it suggests that Lewis acids much less corrosive than the metal halides might be used to advantage. Ample supplies of SO_2 and SO_3 could be provided at any coal conversion plant, and there are numerous possibilities of interaction with aromatics or phenolic compounds available. H_2S has been recommended, both as an acid solvent and as a source of H(6-6).

The chemical or electrolytic reduction of coal molecules with Lewis bases such as alkali metals in ammine solution shows that this combination is also a powerful reagent, but too expensive for industrial use. Catalytic effects where the alkali metal is not necessarily consumed have been observed in the high temperature reaction of mixed alkali carbonates with hot char. The presence of a free alkali metal with the carbonate of a different one has been shown to give the effect of both free metals. This would be useful only in the absence of oxygen or free H_2O, or at very high temperatures where the free metal can exist in the presence of oxygen.

7. CO Reactions

Gasification processes often inject oxygen and CO_2 in the initial stages even though this is not essential. Experiments under a vacuum indicate that some carrier gas is desirable, apparently as a quenching agent to assist in the release of methane during degradation. Other references indicate that CO in synthesis gas is as desirable a reducing agent as hydrogen. Its use as a carrier gas for heat transfer and gasification has the potential advantage of avoiding the degradation of reactive sitesin coals which have not otherwise been exposed to oxygen, and which can go either to CO_2 or CH_4 , depending on what gas sees them first. The presence of excess water also has an oxidizing action at high temperatures, releasing hydrogen and carbon oxides instead of methane. While it is not practical to avoid water entirely, there is no need to employ it in excess, and hot synthesis gas made from steam and char should lead to more CH_4 and less H_2 than any steam injection in the initial gasification.

The question of catalysts for the methanation of CO and H_2 in the initial gasification involves catalyst poisoning effects due both to sulfur and ash. This is commonly handled by using a gas cleaned to remove both sulfur compounds and particulates. Useful review of the art on this process are available from Richardson and from OCR.

7.1 Modified Fischer-Tropsch

Producer gas has been traditionally considered as the cheapest source of CO and H_2, because air is cheaper than oxygen. This shows in a major part of the literature on coal gasification, and it leads to the suggestion that producer gas might be used in a modified process for the synthesis of hydrocarbons. The basic assumption is not necessarily true, however, and the breakeven point depends on opposing effects in plant costs. The presence of 50% N_2 in the feed gas will double the gas volume to be processed for a given product yield, and since vessels for F-T are now at their maximum size (for heat control), this would mean twice the number of vessels and roughly twice the cost. To the extent that the oxygen plant required costs less than half of the investment for other facilities, therefore, it would be cheaper to use oxygen than such a producer gas, even if the catalyst to process it were available.

On this basis, a significant savings in cost might be realized by developing an active catalyst for use at much lower pressures, which would decrease the penalty for equipment construction and simplify the use of larger vessels. This is an aim which has been apparent for 50 years and the subject of intensive research (see USBM Bulletins 544 and 585) which has continued at a lower rate in recent years. The literature on this subject has been considered by other experts who are consultants under the EPRI contract, and it has not been critically reviewed in this report.