DEVELOPMENT OF ENGINEERING STANDARDS FOR MOST EFFECTIVE CONTACTING OF COAL, CATALYSTS AND REAGENTS IN PROCESSES FOR LIQUEFACTION AND GASIFICATION OF COAL

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PRELUDE

The science of catalysis has progressed at least to the realization that in order to compare the performance of different catalysts we should do so on the basis of specific activity per active site. For a heterogeneous catalyst this basis of comparison often reduces to one based on specific activity per unit surface area, in view of a common assumption of relatively uniform surface densities of active sites. From the purely practical standpoint, however, some better bases of comparison might well be:

A. Specific activity per dollar cost of the catalyst

B. Average activity per dollar cost of the catalyst, where the average is taken over the lifetime of the catalyst

C. Activity per unit mass or per unit volume of the catalyst, a basis that recognizes the relationship between cost and reactor size.

From the fundamental standpoint, it is desireable to measure relative catalytic activities on a unit active site basis in order to compare different catalysts and determine the most intrinsically active catalysts; then those most active catalysts can be used in the proper state of subdivision or supported on a suitably low-cost and properly designed porous carrier in order to get maximum catalytic activity per dollar cost and per unit volume.

The early history of catalytic science is marked by reports of measurements that were not properly designed to determine intrinsic catalytic activity on the basis of the unit active catalytic site or the unit catalytic surface area. The major difficulties in such measurements resulted from failures to eliminate the possible effects of transport resistances, due to slow diffusion rates either within porous solid catalysts or within the fluid phase surrounding solid catalytic particles. The result was that, when the chemical reactions were significantly faster than the rates of diffusion, the experimental techniques employed measured essentially only the rate of diffusion of a reactant to the catalyst or within a porous catalyst, and did not yield information on actual rates of catalytic reaction intrinsic to the actual catalytic sites in question. Catalytic technology has now progressed to the point where we know how to test for the presence of diffusional resistances which might interfere with measurements of reaction rates intrinsic to the active sites. This is possible when the reactants are all in the same fluid phase which is contacted with a solid, porous catalytic pellet. In its essence, the approach calls for: (a) increasing the turbulence of the fluid phase to ascertain whether this, by itself, increases rate of reaction thereby suggesting interference from diffusion in the fluid phase to the external surface of the catalyst pellet, or (b) decreasing the particle size of the pellets to ascertain whether this, by itself, increases rate of reaction thereby suggesting interference from diffusion within the pores of the solid catalyst.

When, however, the reactants as well as the catalyst can occupy more than two separate and distinct phases (as in the case of catalyzed coal gasification or liquefaction) then great difficulties arise in trying to sort out the separate transport effects. When coal gasification is accelerated by a solid catalyst the latter may be in the form of particles distinct from and external to the coal particles - or the catalyst may be impregnated into the porous coal particles. The latter arrangement would appear to be preferable from a recognition of the necessity of bringing together coal molecules and gaseous reactants at active catalytic sites; more catalytic sites can be distributed in close proximity to coal molecules by impregnation within the capillary system of a coal particle than by contact between distinct catalyst particles with the external surfaces of coal particles. From the economic standpoint, however, it may be too costly to pre-impregnate coal with catalyst before gasification; in such cases a mixture of distinct particles of coal and catalyst might be used. Moreover, during a reaction at elevated temperatures, a portion of the catalyst may sublime and enter the pores of the coal as a gas. Whether catalyst is impregnated within coal particles or distinct catalyst particles are mixed with coal particles, it appears that experiments to study and eliminate transport resistances (although possible in principal) could become so complex that they would not ordinarily be carried out due to limitations of time, manpower and other resources. Nevertheless, it appears that at least sufficient experiments should be carried out to permit the establishment or recommendation of certain methodologies for investigating influences of particle sizes and of fluid-phase turbulence or flow rate.

The situation is still more complex in the case of liquefaction of coal slurried in a hydrogen-transfer liquid (one of the more common processing approaches). It appears that the mechanisms involve hydrogenation of coal molecules (perhaps with some hydrocracking); the hydrogenated coal molecules can then detach from the coal particles and enter the liquid phase whence they are transported to catalytic sites for additional reactions, including removal of heteroatoms in the aromatic rings (e.g. hydrodesulfurization using solid cobalt molybdate catalyst as in the case of the Synthoil and the H-Oil processes). There is evidence that there is still further complexity within such processes due to the fact that the rehydrogenation of the liquid which carries the hydrogen to the coal molecules is a process catalyzed by minerals within the coal or by catalysts that can be added separately. Hence, in such processes, there is need to select the size and porosity of coal particles, solvent hydrogenation catalyst (if different from or in addition to natural coal minerals) and hydrodesulfurization catalyst.

In the following paragraphs the ideas introduced above are discussed within the context of a critical review of some research reports which are particularly relevant.

COAL GASIFICATION

The principal reactions of importance are the slow and endothermic carbon-steam reaction:

I. $C + H_2O_{(g)} \rightarrow CO_{(g)} + H_2 \quad \begin{cases} \Delta F^\circ = +21.9 \text{ kcal} \\ \Delta H^\circ = +31.4 \text{ kcal} \end{cases}$

combustion of coal to supply the enthalpy required by reaction I:

II. $C + O_{2(g)} \rightarrow CO_{2(g)} \quad \begin{cases} \Delta F^\circ = -94.3 \text{ kcal} \\ \Delta H^\circ = -94.1 \text{ kcal} \end{cases}$

and direct hydrogenation of coal which takes place to a significant but minor extent along with equations I and II:

III. $C + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \begin{cases} \Delta F^\circ = -12.1 \text{ kcal} \\ \Delta H^\circ = -17.9 \text{ kcal} \end{cases}$

The thermodynamic quantities cited are for 25°C. The equilibrium for reaction I does not become favorable until the temperature rises above about 800°C; unfortunately, as the temperature rises above about 800°C the thermodynamic equilibrium point for reaction III becomes unfavorable; it is also unfortunate that changing pressure also produces opposing effects on the equilibrium yields of I and III. Other reactions of lesser importance which can take place during gasification of coal by steam and oxygen are:

IV. $C + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \quad \begin{cases} \Delta F^\circ = -32.8 \text{ kcal} \\ \Delta H^\circ = -26.4 \text{ kcal} \end{cases}$

V. $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \quad \begin{cases} \Delta F^\circ = -61.5 \text{ kcal} \\ \Delta H^\circ = -67.7 \text{ kcal} \end{cases}$

VI. $C + CO_{2(g)} \rightarrow 2CO_{(g)} \quad \begin{cases} \Delta H^\circ = +41.3 \text{ kcal} \\ \Delta F^\circ = +28.9 \text{ kcal} \end{cases}$

The water gas produced by reaction I must be shifted to higher hydrogen contents in order to produce the proper stoichiometric mixture ($3H_2/CO$) for production of methane by reaction of CO and H_2. The water gas shift reaction is:

$$\text{VII.}\quad CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \qquad \left\{\begin{array}{l}\Delta H^\circ = -9.9 \text{ kcal} \\ \Delta F^\circ = -6.8 \text{ kcal}\end{array}\right.$$

and the methane production (or methanation) reaction:

$$\text{VIII.}\quad CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)} \qquad \left\{\begin{array}{l}\Delta H^\circ = -49.3 \text{ kcal} \\ \Delta F^\circ = -34.0 \text{ kcal}\end{array}\right.$$

Another possible methanation reaction is:

$$\text{IX.}\quad CO_{(g)} + H_{2(g)} \rightarrow CH_4 + \tfrac{1}{2} CO_2 \qquad \left\{\begin{array}{l}\Delta F^\circ = -26.5 \text{ kcal} \\ \Delta H^\circ = -38.6 \text{ kcal}\end{array}\right.$$

A highly undesireable reaction can take place during methanation to produce coke which deposits on and deactivates the methanation catalyst:

$$\text{X.}\quad 2CO_{(g)} \rightarrow CO_{2(g)} + C \qquad \left\{\begin{array}{l}\Delta F^\circ = -28.7 \text{ kcal} \\ \Delta H^\circ = -41.3 \text{ kcal}\end{array}\right.$$

Different process schemes are in various stages of development for accomplishing gasification. The most conventional approach is to contact coal with a mixture of steam and oxygen or steam and air and thereby cause reactions I through VI to take place in the same reactor. The resulting gas is then purified and may be used as a fuel or feedstock for a neighboring process or combustor. However, if the fuel gas must be pumped to a distant location it should be converted to methane. Such conversion increases the specific energy content (Btu/std ft^3) and thereby reduces pumping costs; to accomplish this, the H_2/CO ratio is adjusted to 3/1 by the shift reaction

VII and the mixture is then reacted to form methane by reactions VIII and IX. Alternative variations call for the combustion of coal [reaction II] in a separate reactor to produce the heat necessary to drive reaction I in another reactor. In the process proposed by Kellogg (1), for example, the heat is transferred between reactors by molten salt and, in the CONSOL CO_2-acceptor (2) process, the needed enthalpy is transferred by circulation of a mixture of dolomite and char. Other schemes include processes proposed by Lurgi (3) IGT (HYGAS) (4), BCR (BI-GAS) (5) and BOM (Synthane) (6), but it is beyond the scope of this document to devote further space to these process variations. One interesting variation is the BOM HYDRANE process (7) in which methane is produced by reacting hydrogen directly with coal according to equation III; of course the hydrogen must be produced in a separate system where gasification reactions I and II are carried out, followed by the water-gas shift reaction VII to poise the equilibrium in favor of hydrogen.

Further research on the combination of gasification and methanation in the same reactor has been reported by Hoffman et al (8) who observed that reactions I and IX can be carried out in the same reactor using K_2CO_3 and Na_2CO_3 as catalysts for I and Ni as the catalyst for IX. The Ni catalyst was stratified and isolated from the coal and alkali-metal catalyst mixture. Hoffman et al (8) do not report further on the physical form and particle size of the coal, the gasification catalysts and the methanation catalysts in their reacting system but this would appear to be a potential direction for fruitful further research, especially because the overall result given by combining equations I and IX is:

$$\text{XI.} \quad C + H_2O \rightarrow \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \qquad \begin{cases} \Delta F^\circ = 4.5 \text{ kcal} \\ \Delta H^\circ = +6.3 \text{ kcal} \end{cases}$$

In this overall scheme the exothermic heat of methanation (IX) supplies the endothermic requirement of gasification (I) with the result that overall reaction (XI) is only slightly endothermic and very little external heat must be supplied; the necessary heat might be added to the reactants before injection into the catalytic reactor.

The important effect of catalyst particle size has been clearly demonstrated by Walker et al (9) who studied the catalysis of graphite gasification by reaction VI using Ni, Co and Fe as catalysts; they mixed iron particles with graphite particles, the former in sizes ranging from submicron up to about 20 μm; the small particles were far more effective catalysts. These workers also studied the oxygen-graphite reaction and the CO_2-sugar char reaction; they also used colloidal iron, impregnation by solutions of iron and dispersions of metals in carbon prepared from organic polymers containing metal salts.

Walker et al (9) also review much published work on catalytic gasification of carbon and, in this context, point out how strongly the results depend on parameters and conditions other than the catalyst itself, viz. size and porosity of catalyst particles (and consequently catalytic surface area), intimacy of contact between catalyst and carbon surface and location of the catalyst relative to basal and prismatic planes of the carbon crystallites. Because carbon by itself is a well known catalyst for a variety of reactions, including oxidations and hydrogenations, it also appears that the potential importance of the carbon surface area, particle size and porosity has been overlooked in many such gasification studies. The catalytic behavior of carbon has been reviewed by Coughlin (10).

There appears, therefore, to be additional need for experiments in catalyzed coal gasification in which the porous structures and particle sizes of the coal and of the catalyst are varied and comparisons made between situations in which the catalyst is outside the coal particles as compared to within the pores of the coal particles. Such work should be carried out systematically for all the reactions of importance in coal gasification using various catalysts and coals of well defined properties. Results of such work would be twofold: (1) practical improvement in methods of contacting coal reagents and catalysts and (2) development of standards of optimum contacting to be employed in designing experiments for comparing the effects of various catalysts. Investigation of all possible such permutations of coals, reactions, catalysts, particles sizes, porosities, impregnation techniques etc. might appear to be an effort of almost overwhelming proportions; a suitable experimental program of reasonable size, however, could probably be designed by introducing constraints based on practical economics and feasibility for commercial-size gasification reactions. For example, expensive catalysts would not be employed in schemes that would preclude catalyst recovery and re-use and there would also be practical limits on coal particle size, impregnation techniques, etc.; moreover it should be possible to choose a range of coals for which results might be extrapolatable to other coals.

Forney (10) has reported that limestone, hydrated lime, CaO and lignite ash are good gasification catalysts in that these additives increase carbon conversion, increase yield of CO, H_2 and CH_4 and increase steam decomposition; these increases are the greater the greater the ratio of catalytic additive to coal. However Forney (10) made no mention of particle sizes or porosities.

Catalysis of the steam-carbon reaction was further investigated by Haynes et al (11) at 850°C and 300 psig in which they passed steam over pretreated bituminous coal to which was admixed 5% (by weight) of various potential catalysts with results as follows:

CH_4	H_2	CO	Carbon Gasified
Li_2CO_3 - 21	K_2CO_3 - 83	K_2CO_3 - 91	K_2CO_3 - 62
Pb_3O_4 - 20	Li_2CO_3 - 55	Li_2CO_3 - 72	Li_2CO_3 - 40
Fe_3O_4 - 18	Pb_3O_4 - 39	Fe_3O_4 - 60	Pb_3O_4 - 30
MgO - 17	CaO - 37	Cr_2O_3 - 55	Cr_2O_3 - 26
Cn_2O_3 - 16	MgO - 35	Pb_3O_4 - 52	MgO - 26
CuO - 15	Fe_3O_4 - 33	CuO - 49	Fe_3O_4 - 23
Al_2O_3 - 14	Al_2O_3 - 33	Al_2O_3 - 45	CuO - 22
K_2CO_3 - 6	Cr_2O_3 - 25	MgO - 28	Al_2O_3 - 22

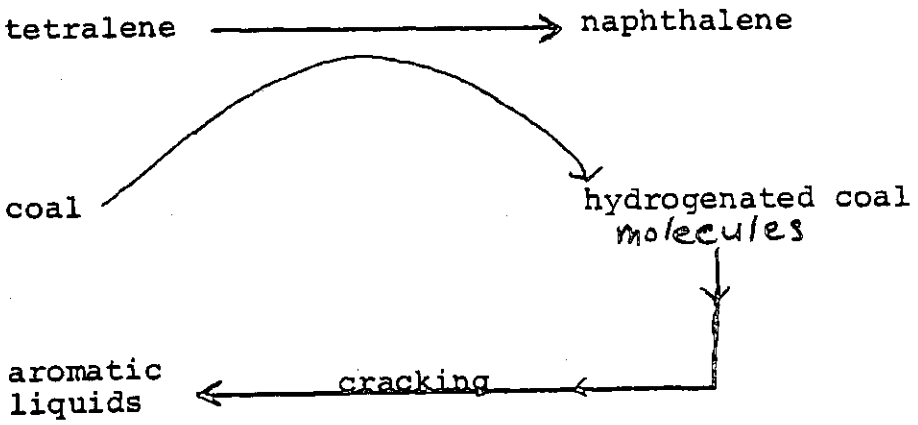
These results, which have also been reported by Mills (7,12), show the percentage increase in yield of CH_4, H_2, CO or of carbon gasified upon addition of 5% of the salts shown; it is clear from these data that appropriate additives can significantly increase the production of methane and hydrogen in the gasification process. Haynes et al also found that still greater increases in methane production occurred when a Raney nickel catalyst was inserted as a probe into the reacting mixture. It appears that this work was not directed toward studying the effect of particle sizes, porosities or of methods of contacting coal, reagent gases and catalyst; such investigations are further suggested by the experimental results, however.

Catalysis of reaction III is the subject of a vast literature dating from the discoveries of Bergius early in the 20th Century. Most of this work has been reviewed by workers at the Bureau of Mines (29-34); early work in English has been published by Dent (14). Weller (15) studied coal hydrogenation catalysis by NiO_2, $SnCl_2$ and $(NH_4)_2MoO_4$; he also found (15) that $FeSO_4$ significantly increased the hydrogasification of coal particles but powdered $FeSO_4$ merely admixed with coal particles had almost no effect. It appears that Weller et al (15) were motivated to investigate the relative efficacies of impregnation, simple admixture and ball milling of coal and catalyst by a knowledge that earlier large scale industrial coal hydrogenation was practiced by mixing coal and tin oxalate in the finely divided state at the ICI Billingham Plant whereas the German plants at Pölitz, Blechhammer and Gelsenberg used $FeSO_4$ impregnated into the coal from aqueous solution. Although Weller et al aimed their experiments toward hydrogenation to liquid products primarily (rather than hydrogasification), the implications regarding the modus operandi of catalyst contacting appear equally valid in either instance. Friedman et al (16) have also reported on the ability of various materials to catalyze the hydrogenation of coal. Gardner (17) studied the hydrogasification of coal chars impregnated with $KHCO_3$, K_2CO_3 and $ZnCl_2$; the potassium compounds were found to be effective catalysts of about equal activity whereas the $ZnCl_2$ was slightly less active in Gardner's experiments.

COAL LIQUEFACTION

Perhaps the most significant parameter which marks the conversion of coal to a liquid oil is hydrogen content. Hydrogen contents of coals range from about 2 - 6% whereas crude petroleum contains hydrogen to the extent of about 11 - 14%. Liquefaction of coal can, therefore, be described phenomenologically in terms of hydrogenation. From the molecular standpoint the structure of coal may be thought of as layers of polynuclear aromatic or hydroaromatic structures joined together in two dimensions by short (1-4 carbon atoms) aliphatic groups, ether linkages, sulfide and disulfide bonds and biphenyl-type linkages. The aromatic moities range in size from one to several condensed rings, with a typical such structure containing about three such rings; these are probably arranged on average more in the phenanthrene-type structure than the anthracene-type structure (18). About 70% of all carbon atoms are in aromatic rings, but only about 23% of all coal hydrogen atoms are attached to aromatic carbon atoms as the aromatic structure is highly substituted (19

For coal to assume liquid form its molecules must be transformed so that they contain very little 3-ring clusters and almost no clusters of 4 or more rings. Liquefaction processes must rupture not only the aliphatic links connecting the aromatic moities but must also reduce the size of the aromatic structures themselves. Extensive rupture of aromatic rings by thermal processes is not likely without catalysts at the temperatures (400-500°C) usually employed for liquefaction. It appears that most processes which treat a slurry of coal in recycle oil or aromatic solvent operate by hydrogen transfer from a hydroaromatic solvent to the aromatic portions of the coal. The resulting hydroaromatic clusters in the coal then crack to products containing fewer condensed rings, thereby entering the liquid phase. For example:



There is evidence that the rehydrogenation of the solvent (e.g. naphthalene to tetralene) may be catalyzed by coal minerals or by externally added catalysts although there is evidence that catalysts are not necessary for the transfer of hydrogen from the solvent to the coal (20). Furthermore, the cracking of the hydrogenated coal molecules may also be accelerated by catalysts, and hydrodesulfurization catalysts appear especially appropriate for this as they also promote removal of sulfur as H_2S and produce a low-sulfur liquid oil. The initial hydrogenation of the aromatic portions of the coal molecules cause the planar polynuclear aromatic moities to buckle as they become hydrogenated and it appears that this "buckling" leads to exfoliation of the hydrogenated clusters from the solid phase, whence they enter solution in the hydrogen-transferring oil. For example, Hill (21) reports that, for dissolution of coal in tetralin at degrees of solubilization ranging from 5% to 10% dissolved, the kinetic rate constants for dissolution rate display a shift in Arrhenius pre-exponential factor (entropy of activation change) corresponding to enormous increases in surface area; the coal then might be viewed as exfoliating into platelets of about 100 $Å^2$ by 10 Å thick during the dissolution process. Thus it appears that liquefaction of coal in slurries takes place by the following series of steps:

A.) A hydroaromatic solvent molecule travels to a coal molecule.

B.) The solvent molecule transfers hydrogen to the coal molecule.

C.) The partially hydrogenated coal molecule exfoliates from the coal and dissolves in the solvent.

D.) The hydrogenated coal molecule cracks, either thermally in the solvent, or catalytically with the aid of a heterogeneous catalyst such as cobalt molybdate.

In this conceptual sequence, which is substantially in agreement with the views of Mills (22), there would appear to be much opportunity for fruitful further investigations based on promoting the transport processes in steps A, C and D above. Such effects will depend on the particle size and porosity of the coal and of the external catalyst as well as on the viscosity of the hydrogenating solvent, among other parameters. Hopefully engineering standards for contacting coal and catalyst can be evolved to promote favorable transport rates. Promotion of transport via turbulence in the solvent oil appears to be one of the advantages of the BOM Synthoil process (to be discussed below).

In discussing several important processes for coal liquefaction we shall neglect pyrolysis which is based on thermal rupture of bonds in the coal molecule and does not appear amenable to improvement by catalysis, nor does pyrolysis produce maximum quantities of liquid or gas as the free radicals formed by bond rupture can repolymerize to form char; liquid yields in pyrolysis are on the order of about 1-2 bbl/ton compared to about 3 bbl/ton for some of the other liquefaction processes. We shall also neglect the Fischer-Tropsch process in which hydrocarbons are synthesized from CO and H_2 produced by coal gasification; Wiser advises that Fischer-Tropsch schemes do not appear economically feasible for use in the United States at this time (23). The PAMCO process (24,25) is essentially one in which coal is hydrogenated by a solvent without added catalyst at 500-800°F and 1000 psi to produce a meltable product; some sulfur is removed by this process and ash is filtered from the molten product. It appears that the natural minerals present in the coal may act as catalysts for rehydrogenation of the aromatic solvent during this process. The PAMCO process then might be considered a special case of the Synthoil (26,27) and H-Coal (28) processes which we discuss in the next paragraph.

Both the Synthoil and the H-Coal processes appear to rely on essentially the same chemistry; in these processes a hydrogen-transfer solvent hydrogenates and liquefies the coal molecules which then migrate from the coal particles, through the liquid phase, to catalyst pellets where the following processes take place: hydrocracking, hydrodesulfurization and probably some hydrodealkylation. The catalysts employed are closely related to commercial hydrodesulfurization catalysts such as cobalt molybdate and tungsten sulfide. Presumably cracking can take place at various stages during the hydrogenation process, depending on temperature and degree of hydrogenation. Reviews of various mechanistic viewpoints and bibliographies of thousands of literature references and patents on coal hydrogenation (much of the work dating from pre-World War II German technology) have been published by workers at the Bureau of Mines (29-34). In the H-Coal process an oil slurry of finely particulate coal flows together with hydrogen through an ebullating or suspended bed (partially fluidized) of granular hydrodesulfurization catalyst (28,35). The Bureau of Mines Synthoil Process (26,27) is substantially the same with the important differences being that the Synthoil process employs a fixed bed of commercial hydrodesulfurization (cobalt molybdate) catalyst pellets, and rapid turbulent flow of coal, oil and hydrogen through the fixed bed promotes turbulence with lower chance of catalyst attrition. Moreover, the hydrogenation appears to be less extensive in the Synthoil process, thereby producing a liquid fuel of lower hydrogen content and with lower attendant hydrogen consumption than for the H-Coal Process.

One of the major features of both the H-Oil and the Synthoil processes is good removal of sulfur (as H_2S) via catalyzed hydrodesulfurization. It is instructive, therefore, to examine some of the literature on catalytic hydrodesulfurization which has been reviewed recently by Schuit et al (36) and Schuman et al (37). One interesting aspect of the mechanism of these reactions was elucidated by Givens and Venuto (38) who worked with benzothiophenes and were able to rule out desulfurization reactions involving breaking of C-C bonds over cobalt molybdate catalysts; they also deduced that saturation of the aromatic rings was not necessary before breaking of bonds between sulfur and aromatic carbon. More interesting from the standpoint of catalyst particle size are reports that there is often significant mass-transfer resistance with catalyst pores for feeds ranging from residua to light distillates; for example, effectiveness factors for hydrodesulfurization were estimated from experimental data as follows: EF = 0.6 for 3.2×10^{-3}m diameter pellets (39) and EF = 0.4 - 0.8 for 1.6×10^{-3}m cylinders (40,41). On the other hand, Wan and Crynes (42), in their studies of hydrodesulfurization of anthracene oil, found no significant advantage in using a catalyst of large pore volume and pore size (bi dispersed distribution with macropores) as compared to a catalyst with smaller pores, although they attributed this behavior to a possible non-uniform structure of the catalyst of bidispersed pore size distribution (i.e. small pores on the outside).

In view of the complexity of coal liquefaction using hydrogen-transfer solvents together with hydrodesulfurization catalysts, in view of evidence that mass transfer within these latter catalysts is often a significantly controlling step, in view of the possibilities for additional catalytic reactions of coal hydrogenation and rehydrogenation of the hydrogen transfer solvent (whether by intrinsic coal minerals or by other catalysts added to the system), it appears that great possibilities exist for improving the performance of such systems by research aimed at developing standards related to particle size and porous structure of coal and of catalysts. Such work should lead to improved engineering rationales and approaches for achieving best contacting of coal, solvent, hydrogen and catalysts.

Wright and Severson (20) showed very clearly the catalytic role of coal minerals in the hydrogenation of coal slurried in aromatic oils and they even found that, without the presence of coal insolubles, an aromatic coal-derived anthracene oil solvent could not be hydrogenated at 425°C and 1000 psi. This was true whether hydrogen itself or mixtures of CO and H_2O were used for hydrogenation. [More will be said below about the use of CO and H_2O.] Wright et al (20) attributed the catalytic hydrogenation to FeS in coal and Ca ions in lignite and also found that externally added $NaHCO_3$ and Na_2CO_3 also served as catalysts. Most important for the development of standards for contacting catalysts and coal, they found that when the Na^+ in lignite (presumably bound as a counter ion to polymeric acids) was exchanged for Ca^{++}, catalytic hydrogenation decreased; similar results were obtained by washing with HCl. This suggests that ion exchange may be a facile and feasible approach for adding catalytic agents to coal minerals; This may be what happens during impregnation and such phenomena deserve further study.

Another catalytic approach has been to hydrocrack the coal by using large amounts of catalysts such as $ZnCl_2$ or $SnCl_2$ which, of course, must be regenerated, recovered and reused. $ZnCl_2$ appears to provide advantages such as rapid reaction, extensive conversion and high selectivity toward high octane of the cracked products (high isoparaffin to normal paraffin ratio) which are largely in the distillate range. Much of this work has been carried out at

Consolidation Coal Company by Gorin, Zielke and coworkers (43,44, 45) who focused primarily on molten $ZnCl_2$ as a catalyst; continuing work is aimed at perfecting techniques of recovering and recycling $ZnCl_2$. Another interesting approach using $ZnCl_2$ is underway at the University of Utah according to Wiser (23). This approach uses coal impregnated with $ZnCl_2$ for direct hydrogenation. Deposition of $ZnCl_2$ in the porous structure of the coal gives much better results than mixing the dry coal with the catalyst powder (unless the temperature is very high, and thereby facilitates the penetration of catalyst vapors into the coal); in the Utah process it appears that hydrogen is readily transported to the active sites deposited within the coal. The latter variation in the use of $ZnCl_2$ also appears to produce a more highly cracked product as in the case of the Consol schemes using $ZnCl_2$. These recent variations in ways to contact coal and $ZnCl_2$ catalyst, as well as related earlier work by Weller et al (15,46,47,48) emphasize the variations that are possible in contacting catalyst, coal and reagents and demonstrate the need for further research into such questions aimed at the development of rational standards for methods of contacting in experiments aimed at comparing the relative efficacies of different catalysts.

Another important scheme for hydrogenating coal involves the use of CO and H_2O instead of hydrogen as practiced by Appell, Wender et al (49-52). It appears that this technique can provide more rapid hydrogenation and is attributed to the formation of hydrogen (perhaps in "nascent" form) within the porous structure of the coal by the water-gas shift reaction VII. Appell et al found that the reaction proceeds with lignites and coals of higher rank, either with or without a solvent, and is catalyzed by alkali metal carbonates. York (53) reports that iron oxides and sodium content also appear to exert catalytic activity for such reaction. Again, for coal hydrogenation by CO and H_2O it also appears that much work remains to be done regarding porosities and particle sizes of coal and catalyst and the general development of standards for contacting coal, catalyst and reagents.

MODEL COMPOUNDS

One of the very important requirements in converting coal to liquid and gaseous fuels is the removal of sulfur and nitrogen (in the case of liquid fuels). Since oxygen is removed in liquefaction processes that also remove organic sulfur and nitrogen, it is common to speak about the simultaneous removal of these three elements. The removal of sulfur and nitrogen from locations as heteroatoms in aromatic rings appears to be most difficult and this suggests as model compounds thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes. Forney (10) has stated that thiophene formation is a problem even in coal gasification in that it is not easily removed by scrubbing processes which can remove sulfides and mercaptans from the gases. The experiments of Given and Venuto (38) and Amberg and coworkers (54-57) represent notable attempts at using such model compounds in studies of hydrodesulfurization.

There appears to be less experience in using model compounds to study the removal of nitrogen from aromatic rings and it appears that nitrogen may be more difficult to remove than sulfur. Notable work is that of Flinn et al (58) and McIlvried (59) using carbazole and pyridine compounds. Other important nitrogen compounds are quinolines and pyrroles (23)(also indole and acridine).

Another important use of model compounds is in seeking the mechanism and testing potential catalysts for splitting polynuclear aromatic compounds into simpler structures. In particular, as Wiser (23) has pointed out, it should be possible, at least in principle, to improve the yield of aromatic liquid product by splitting anthrocenic or phenanthenic structures at the central ring (thereby obtaining two single-ring compounds) instead of the sequence of removing one outer ring at a time which does not take full advantage of the potential of a polynuclear aromatic molecule to produce aromatic, high-octane, liquid product. Some of the work done in unravelling these mechanisms has been reported by Flinn et al (60), Sullivan et al (61) Quader and Hill (62) and Friedman et al (16). This work has been based on model compounds such as naphthalene, anthracene, phenanthrene, naphthacene, chrysene, triphenylene, pyrene, perylene, fluorene, biphenyl, o - and p - terphenyl and 1,3,5 - triphenylbenzene.

CONCLUSIONS AND RECOMMENDATIONS

Engineering standards for the most effective contacting of coal, reagents and catalysts should be developed:

Coal Gasification

A) Experimental program to evaluate effects of particle sizes of coal and admixed catalyst particles.

suggested funding level: $50,000/year for 3 years

B) Experimental program to evaluate relative effectiveness of impregnating as compared to admixing catalysts.

suggested funding level: $40,000/year for 3 years

C) Theoretical and computational program to model the combined transport and chemical reaction processes of (A) and (B) above and to develop practical approaches, possibly as extensions of Thiele modulus and effectiveness factor concepts; such practical approaches should result in useful techniques for easy and simple correlation of experimental results to elucidate best system design.

suggested funding level: $30,000/year for 3 years

D) Review and Assessment Program to review the results of (A), (B) and (C) above, unify the viewpoints in report form and make recommendations of engineering standards for contacting coal, reagents and catalysts in gasification as well as make final recommendations of best ways to design experiments and correlate results.

suggested funding: $20,000 for 1 year

Coal Liquefaction

A) Experimental program to evaluate effects of particle size of coal and hydrodesulfurization catalyst; this work should include achieving an understanding of molecular transport from the coal to and within the hydrodesulfurization catalyst; pore structure of the latter is of course an important consideration.

suggested funding level: $80,000/year for 3 years

B) Experimental studies of catalysis of the rehydrogenation of the hydrogen-transfer solvent. Work should focus not only on the catalytic effect of intrinsic coal minerals but also on the possibilities for externally added catalysts; such external catalysts for solvent rehydrogenation might be mixed into the hydrodesulfurization catalyst in the H-Oil and Synthoil Processes. Particle size and pore structure will be important parameters for study. An important part of the work should focus on transport of hydrogen and methods of contacting hydrogen with the coal-oil-catalyst system.

suggested funding level: $80,000/year for 3 years

C) Theoretical and computational program to model the complex interrelationships of transport and reaction kinetics in coal liquefaction. Results should provide a practical framework for correlating experimental results based on combinations of different catalysts for different functions and include effects of coal and catalyst particle size and porosity. Such work should also include consideration of hydrogen transport and different methods of contacting hydrogen with the coal-oil-catalyst system.

suggested funding level: $40,000/year for 3 years

D) Develop an assessment and instructional report to evaluate and summarize the work of (A), (B) and (C) above. This should result in instructions and rational procedures for correlating, evaluating, interpreting and using experimental results, with a view toward setting standards of contacting for experimental work in coal liquefaction.

suggested funding: $20,000 for one year

<u>Model Compounds</u>

A) Experiments should continue into catalytic hydrodesulfurization as it takes place in coal liquefaction using model compounds such as thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes.

suggested funding: $25,000/year for 3 years

B) Far less is known about the removal of heteronitrogen atoms than sulfur atoms. Experimental programs should be expanded to study nitrogen removal during coal liquefaction using model compounds such as carbazoles, pyridenes, quinolines, gsyrroles and amines.

suggested funding: $50,000/year for 3 years

C) The potential for higher yields of aromatics in coal liquefaction underlies the need for continuing experimental studies of catalytic cracking and scission of polynuclear aromatic molecules. Such investigations should be aimed at improvements over what is apparently the predominant pathway with present catalysts and systems: sequential hydrogenation and scission of individual outer rings of polynuclear aromatic compounds. Primary attack on the inner rings would appear to hold promise for higher aromatic yields in liquefaction.

suggested funding: $80,000/year for 3 years

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