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PRODUCTION OF METHANE FROM COAL

We have been asked to comment and make recommendations on the Proceedings of the EPRI Conference on "Coal Catalysis" as summarized by the W. F. Libby Laboratories. The report of this conference indicates areas of high priority and the area assigned to us is that covered in item 2.1 "Combination Catalyst for Direct Coal-Water Reaction to Methane".

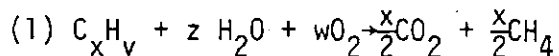
After a number of discussions, between us and with others including Dr. Libby, of the various possibilities we have concluded that there are two main directions that research should take in an endeavor to discover means for the direct conversion of coal to methane. These will be described and summarized in the following paragraphs.

Catalyst for Direct Coal-Water Reaction to Methane

Converting coal to high BTU gas now involves a number of steps:
preparation of synthesis gas by coal gasification by oxygen and steam, purification of the gas stream, adjustment of the CO/H_2 ratio by water gas shift, followed by methanation.

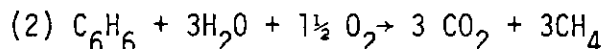
The most difficult of these steps is the first, that is the gasification of coal by steam and oxygen. Generally, the step is non-catalytic except for the Kellogg molten salt process. In this case, the melted carbonate-sulfate medium appears to catalyze the steam-hydrocarbon-carbon reaction. Other evidence to substantiate the fact that alkali metal carbonates catalyze the steam-hydrocarbon-carbon reaction is found in the literature indicating that alkali metals as carbonates, silicates, etc., have a profound effect on carbon deposition on nickel reforming catalysts in the steam reforming of hydrocarbons. In fact, commercial catalysts used in the steam reforming of naphthas are nickel promoted with alkali metal as the carbonate or other compounds that are easily converted to the carbonate in the presence of CO_2 formed during steam reforming. These results indicate that catalyst composition plays a significant role in synthesis gas formation from steam and hydrocarbons. If this is the case, it should be possible theoretically to devise a catalyst system that would bring about the gasification, shift and methanation all in one step. Both shift and methanation proceed at

temperatures between 250° - 450° over transition metal catalysts while the same catalysts are effective for steam-hydrocarbon reactions at somewhat higher temperatures, 500°-800°C. We can ask ourselves the theoretical question : can the reaction



be made to occur?

The free energy of this reaction is probably favorable at low to intermediate temperatures. Consider the reaction:



This reaction is highly favorable at all temperatures, enough so that we can safely conclude that reaction 1 is favorable. Temperature limitations are likely those at which methane would begin to decompose, that is about 650°C. Hence we should conclude that temperatures in the range of about 550°C should not be exceeded in our attempts to bring about reaction 1.

Two big problems loom as we look at possibilities for reaction 1.

1. Transport difficulties in bringing together the coal and the catalyst or catalysts.
2. Sensitivity of likely catalysts to sulfur poisoning.

In solving these two main problems a sulfur insensitive catalyst must be developed or ways to capture sulfur in the presence of active transition metal conventional catalysts must be developed and techniques must be generated to overcome the transport problems.

The main thrusts for solutions should initially be fundamental research on the following generalized reactions:

1. Carbon and steam,
2. Carbon and steam and oxygen,
3. Aromatics and steam,
4. Aromatics and steam and oxygen,
5. Carbon and steam as modified by presence of CO and H₂,
6. Aromatics and steam as modified by presence of CO and H₂.

This would involve comprehensive studies of catalyst systems which are likely to work in these reactions.

We recommend that exploratory research to develop likely catalyst systems for the reactions indicated be carried out and after such systems have been indicated that basic research follow on the system to determine the mechanism of reactions. The objective is to gain understanding of the reactions between coal, steam and possibly oxygen. Only then will practical possibilities emerge.

Catalysts for Direct Hydrogenation of Coal to Methane

An alternative, although not quite so direct, path to high methane yield from coal is believed to be worthy of consideration. This second path depends upon an economically attractive approach to hydrogen production, probably from char and steam. Development of coal liquefaction technology depends heavily upon an economical hydrogen source, and such development is expected, indeed is well underway. Coal gasification technology should be prepared to benefit from the anticipated hydrogen production technology.

All well-advanced schemes for production of high methane yield from coal utilize to a significant degree the water gas-shift-methanation sequence mentioned above. This sequence takes coal from a (C-H) reduced state to a (C-O) oxidized state at high temperature (e.g. 900°C) followed subsequently by a return to the (C-H) reduced state at low temperature (e.g. 400-500°C). The highly endothermic reaction between coal and steam is conducted in one stage, while the exothermic reactions of the water gas shift and methanation occur in different stages.

It is envisaged that one could catalytically hydrogenate a slurry of coal and an appropriate catalyst in a coal-derived liquid, in the temperature range 350-450°C, to produce a liquid, perhaps similar to the liquid of the Synthoil process of the U. S. Bureau of Mines. By combination of thermal and catalytic hydrogenolysis this liquid could be hydrogenated to a high-methane gas.

The parameters requiring definition and optimization would include

1. Temperature
2. Catalyst types
3. Pressures
4. Coal/oil/catalyst ratios in slurry

A follow-on program for research would be directed at discerning the mechanisms of the various reactions to enable and ensure optimization of the process.