BEHAVIOR OF NICKEL METHANATION CATALYSTS IN COAL-STEAM REACTIONS

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Introduction

The principal objective of the investigation is the direct conversion of coal-steam systems on to hydrocarbons in a single-stage reactor using multiple catalysts. The work has been described at a previous ACS symposium (1), and is sponsored by the Office of Coal Research of the United States Department of the Interior by contract with the University of Wyoming.

Depending upon catalysts and conditions, either gaseous or liquid hydrocarbon products predominate. In the case of gasification using nickel catalyst, methane is the principal hydrocarbon product. Excess steam rates will yield hydrogen, principally. In this reporting, however, gasification to produce methane will be the overriding consideration.

A potential advantage to the overall reaction is that the production of methane and carbon dioxide tends to be autothermal. The large heat requirement for gasification to only carbon monoxide and hydrogen could be avoided. The relatively small amount of heat needed to sustain the reaction would possibly be added to the reactants prior to injection into the catalyst bed proper.

In addition to the conversion of coal and lignite, other carboniferous materials have been gasified. These include waste paper, tire rubber, polyethylene plastic, and even manure and sewage sludge.

Description of Reactions

While the exact, step-wise sequence may not yet be known, observations on intermediate products obtained by operating the overall reaction in stages indicate two possibilities:

$$\begin{array}{rcl} C + H_2O & = & CO + H_2 \\ CO + H_2 & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \\ \hline C + H_2O & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \end{array}$$

or

$$\begin{array}{rcl} C + H_2O & = & CO + H_2 \\ CO + H_2O & = & CO_2 + H_2 \\ \tfrac{1}{2}CO_2 + 2H_2 & = & \tfrac{1}{2}CH_4 + H_2O \\ \hline C + H_2O & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \end{array}$$

The initiation reaction between coal and steam will occur at lower temperatures in the presence of alkali materials, chiefly potassium or sodium carbonate. The sequence is carried to completion by use of nickel catalysts. Various commercial nickel catalysts have been found to work. These catalysts in the active form are partially reduced oxides on various support materials, which are related to catalyst durability.

Experimental Systems

Studies on the integrated coal-steam-catalysts systems have been carried out in a one-inch diameter, semi-continuous flow reactor described previously (1). Superheated steam at reactor conditions is introduced continuously into a charge of coal and catalysts. Provision is also made for stratification or isolation of the nickel catalyst from the coal and alkali.

Studies on nickel catalyst behavior alone have been carried out in a half-inch diameter flow reactor. Provision is made for introducing various gases as reactants, chiefly CO, H_2, CO_2, and H_2S in varying combinations.

In all cases, reactor pressure is maintained by back-pressure regulators, and reaction temperature may be varied by tubular heaters. Pressures from atmospheric to 800 psi have been used, and temperatures up to 1500°F. The overall reaction is largely independent of pressure, but methane production quickly falls off above 1400°F.

Catalyst Behavior

Normally, nickel methanation catalysts are effective on streams of CO and H_2 at temperatures in the neighborhood of 700°F and are easily poisoned by sulfur. The H_2/CO ratio must be kept up to avoid carbonization and breakdown of the catalyst -- and may be resolved by the addition of steam.

In the integrated system, however, with all reactants mixed, operating temperatures of 1300°F can be maintained with no catalyst breakdown. Furthermore, at the higher temperature, equilibrium is away from the formation of sulfur compounds with the catalyst (2).

Hence, as a result, the effect of sulfur from the low-sulfur coals generally used has been nil. The sulfur content of the spent catalyst has been detected at 0.3%, of the same order as initially present.

As an additional benefit, the presence of sulfur may allay decarbonization of the catalyst (3,4). This has been found to be true in our own work.

The low-sulfur Wyoming coals have been found to retain much of their sulfur in the ash at these reaction conditions (possibly due in part to sulfur occuring as the sulfate).

The mechanical strength of the catalyst is of some concern at this point of the investigation. It is anticipated that a fluidized or ebullating bed will be utilized, and a high degree of strength is needed. Toward this end, techniques are being followed for depositing nickel on spheres of various materials. Perhaps ceramic supports will be required ultimately.

Experimental Results

The ultimate objective of most recent work on coal gasification is the production of a high-Btu gas. For a product of the order of 900 Btu/SCF, no modification of existing burners and jets would be required. The technology of CO_2-removal is already well-developed. Hence, on a CO_2-free basis, any product which is largely methane could be used as a full substitute for natural gas. With this in mind, a selected group of results are presented in Table I.

Table I

GASIFICATION OF COAL STEAM SYSTEMS

Run Number	274	361	312	356
Coal	Glenrock	Reynolds	Consol	Minnkota
Rank	Sub-bit	Sub-bit	Lignite	Lignite
Catalyst	Ni-0104	Ni-0104	G-65RS	Ni-0104
Pressure (psi)	250	250	250	250
Temperature (°F)	1200°	1400°	1350°	1400°
Gas Comp.				
CO_2	48.0	46.9	44.2	44.9
CO	--	--	--	--
H_2	1.8	3.1	8.7	5.1
C_1	50.4	50.0	47.1	50.0
SCF H_2/ton	562	855	2,733	1,689
SCF Hydroc/ton	15,725	13,783	14,795	16,556
Theo. C_1 yield	16,600	16,100	15,900	18,400
Btu/SCF (CO_2-free)	977	962	899	939

The coals, as used, were air dried from 25-30% moisture to about 5-20%. Yields are reported on an "as used" basis.

A different comparison is presented in Table II on average representative yields from various organic materials.

Table II

YIELD OF HIGH BTU GAS
(Standard Cu. Ft. per Ton)

	Actual	Theoretical
COAL	15,000	18,000
PAPER (RAW)	12,000	--
(CHAR)	20,000	--
TIRE RUBBER	24,000	25,600
POLYETH. PLASTIC	24,000	27,100
MANURE (CHAR)	14,000	--
SEWAGE SLUDGE		
(TREATED)	6,000	7,000
(CHAR)	7,000	9,000

In addition, various coal-derived chars and tars have been gasified, and also oil shale.

Conclusions

The investigations so far indicate without a doubt that it is chemically possible to convert coal and other carbonaceous materials with steam to directly yield hydrocarbons. It is a question now of demonstrating that this can be done feasibly in a fully-continuous system, with heat added only to the reactants. Toward this end, the detailed engineering design is underway for fabrication of a fully-continuous unit with a 6-inch diameter, fluidized reactor. Various ways of introducing the pulverized-coal feed will also be investigated with this unit.

LITERATURE CITED

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