CLEANUP METHANATION FOR HYDROGASIFICATION PROCESS

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INTRODUCTION

Catalytic methanation is the final gas cleanup step in the process for producing a high-Btu pipeline gas from coal being developed at the Institute of Gas Technology. The development project is sponsored jointly by the American Gas Association, Inc., and the U. S. Department of the Interior, Office of Coal Research.

The coal hydrogasification process produces 600-800 Btu/SCF gas consisting primarily of methane, hydrogen, carbon monoxide, and carbon dioxide. Smaller amounts of ethane, hydrogen sulfide, nitrogen, ammonia, and other constituents are also present. Carbon dioxide, sulfur compounds, and nitrogen compounds can be removed rather simply by conventional gas purification methods. However, the final gas should ideally contain less than 0.1 mole percent of carbon monoxide and have a heating value of at least 900 Btu/SCF. Because the raw gas contains rather large amounts of hydrogen, it is not of value to merely shift and scrub to remove carbon monoxide. It seems preferable to first scrub out most of the carbon dioxide and then to methanate the remaining carbon oxides.

Methanation has not been well studied at the pressures (approximately 1000 psig) and feed gas compositions (2 to 10 mole percent CO, 2 mole percent CO_2, and 53 to 87 mole percent CH_4) expected to enter this cleanup step in the IGT process. Based on thermodynamic equilibrium calculations, carbon deposition may be a problem with these feed gases. Moreover, the extent to which CO_2 will be methanated is not definitely known. IGT is therefore obtaining information needed to design large-scale catalytic methanation reactors. Effects of temperature, pressure, and catalyst composition on the process operation are main laboratory study areas.

The first step in the overall methanation study is to find the best commercial catalyst for this cleanup step. The catalyst used must first of all be able to actively catalyze the methanation reaction without catalyzing carbon deposition reactions. It must also be highly active and long-lived at high temperatures. These properties of the catalyst are directly related to chemical events occurring on its surface.

Instead of the commonly used packed-tube reactor, IGT is using a continuous stirred tank catalytic reactor (CSTCR)[3] which permits studying these chemical events without any complicating control of the reaction rate by gas-solid mass or heat transfer. This reactor has several other advantages:

1. The CSTCR operates at conditions where "perfect mixing" prevails, and bulk gas temperature and concentration gradients are eliminated.
2. With sufficient gas velocity at the catalyst surface, temperature and concentration gradients between the bulk gas and the catalyst surface can be minimized.
3. All but the fastest and most exothermic reactions can be studied at nearly isothermal conditions and nearly complete conversion.

4. Because all the catalyst surface "sees" gas of the same composition and temperature, the reaction rate can be calculated by a simple algebraic equation:

$$R = \frac{F_i C_i - F_o C_o}{W} \qquad (1)$$

This procedure is, in general, simpler and more accurate than rate calculation from data obtained with packed-tube reactors.

5. Finally, studies can be made using catalyst pellets of commercial size and shape.

This type of reactor has been used in the past to study solid-catalyzed gaseous reactions. Tajbl, Simons, and Carberry[3] used a CSTCR to study the highly exothermic oxidation of carbon monoxide on a commercial palladium catalyst. Ford and Perlmutter[2] used a CSTCR with a catalytic wall to study sec-butyl alcohol dehydrogenation. In both studies, the authors found data were obtained more easily and accurately with a CSTCR.

This paper deals with:

1. Defining the operating range for "perfect mixing" in the IGT reactor

2. Determining whether gas-solid heat or mass transfer effects were present at the conditions of operation.

3. Preliminary screening of commercial methanation catalysts.

APPARATUS

Figure 1 is a flow diagram of the catalyst testing unit. The gas inlet system and the components operating at elevated temperatures and pressures are stainless steel. Feed gas, stored in high pressure cylinders, is metered by an orifice. Orifice pressure, pressure drop, and temperature are recorded. The feed gas is preheated before it enters the bottom of the reactor. Both the reactor and the preheater are electrically heated.

Exit gas leaves the top of the reactor and passes through a heated line (to avoid condensation of liquids) to a cooler-condenser. Liquid products are collected in a knockout pot and are drained through a solenoid valve actuated by a sonic liquid level controller. A dome-loaded back-pressure regulator controls the reactor pressure and reduces the pressure of the exit gas. The exit gas rate is measured by a wet-test meter. Carbon monoxide and carbon dioxide concentrations in the feed and exit gases are measured by two continuous infrared analyzers and are recorded. Aliquot samples of feed and exit gases are taken during each test period for analysis of all components by mass spectrometer (Consolidated Engineering Model 21-103).

Figure 2 shows the construction of the reactor, built by Autoclave Engineers, Inc. It was constructed of Type 316 stainless steel so that it could be used in the future to test the effects of elevated temperatures on catalyst stability. A magnetic drive rotates the stirrer shaft. The reactor has an inside depth of 12 in. and an inside

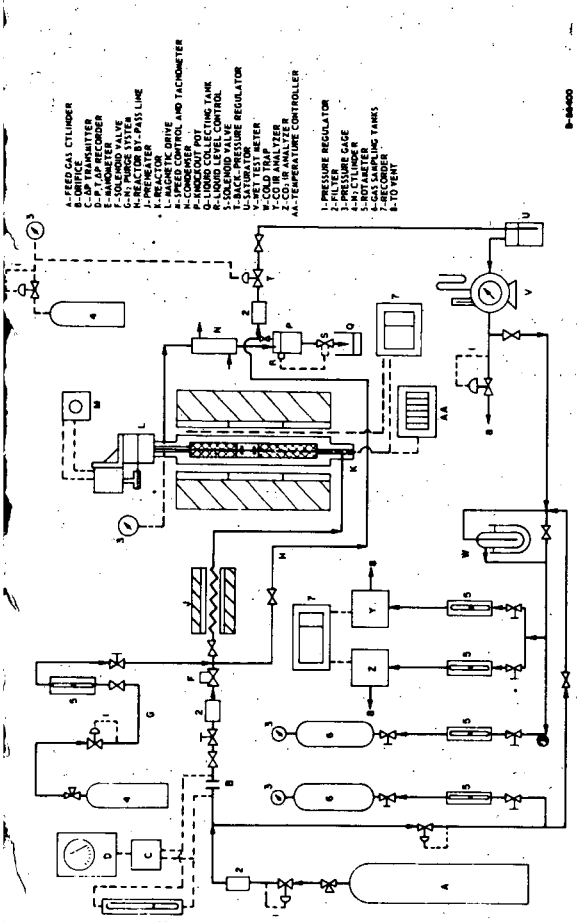

Figure 1. CATALYST TESTING UNIT

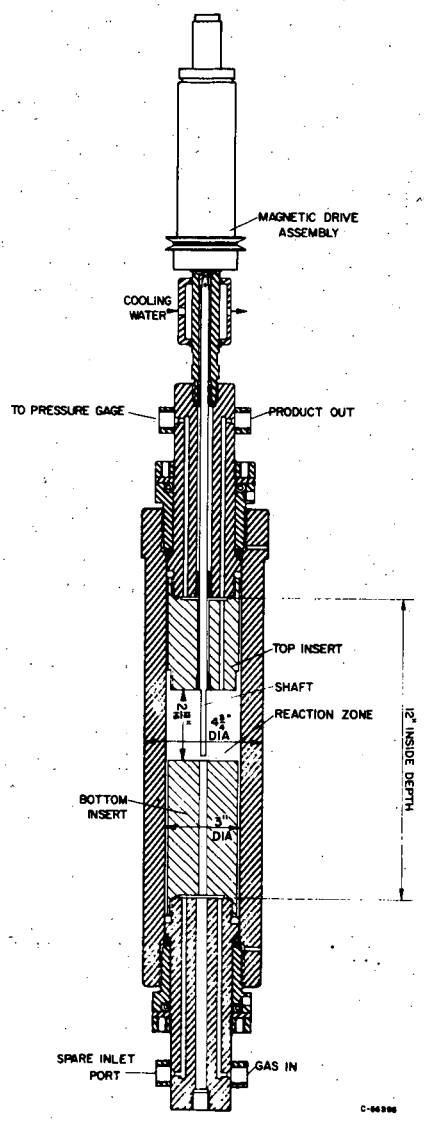

Figure 2. CONTINUOUS STIRRED TANK CATALYTIC REACTOR

diameter of 3 in. For CSTCR operation, two inserts are installed which reduce the inside depth to 2-13/16 in.

Two methods of catalyst mounting are employed. Catalyst can be placed in an annular basket or in a paddle-basket arrangement as sho in Figure 3. When the paddle basket is used it replaces the radial impeller which is used only with the annular basket. For either arrangement the propellers remain in place. The cylindrical wall and the top and bottom of the reactor each have four 1/8-in.-wide baffles. The wall baffles extend along the total height of the stirred chamber; the top a bottom baffles extend radially to the cylindrical wall.

Catalyst temperatures are measured easily in the annular bask Since the catalyst is stationary, a thermocouple is simply inserted in hole drilled into the center of a catalyst pellet.

For either basket arrangement, the gas temperature is measure with a 0.025-in.-OD magnesium-oxide-insulated thermocouple made of Chro mel-Alumel with a swaged stainless steel sheath.

DISCUSSION

Mixing Theory

Several tracer techniques can be used to check for perfect mi ing. These consist of measuring the response in the reactor effluent t either:

1. The injection of a very small amount of tracer into the reactor ove a very short time (pulse test); or
2. The instantaneous switching from a steady flow of inert gas to a steady flow of tracer (step test) or vice versa (purge test).

After the tracer concentration reaches a maximum value, the response for any of these tests is an exponential decay of tracer concen tration with time. For the pulse test the response is:

$$\frac{C}{C_M} = e^{-tF/V} \qquad (2)$$

where C_M is the gas concentration in the reactor at the instant the puls enters, and — in actual tests — the maximum gas concentration measured i the effluent.

For the step test the response is:

$$1 - \frac{C}{C_S} = e^{-tF/V} \qquad (3)$$

where C_S is the steady-state tracer concentration. For the purge test the response is the same as Equation 2 except that $C_S = C_M$. A plot of line C/C_M versus tF/V yielding a straight line of slope -1 indicates "perfect mixing."

Mixing Test

All of these techniques were used in our mixing studies. Because of the difficulty of injecting a perfect pulse of tracer, the step or purge tests were easier to carry out. In spite of this, the pulse tests have an advantage because of the small amount of tracer used. In step or purge tests an allowance must be made for transfer of tracer (or purge) contained in the reactor dead volume before switching, i.e., in the lines to the pressure gages, etc. This, in effect, increases the volume to be purged and affects the slope of the line C/C_M versus tF/V plot.

Of the three tracer tests, then, the pulse test is most accurate in systems with extensive dead volumes.

CO or CO_2 was used as tracer with nitrogen as the inert gas in these tests. A switching valve served to inject the pulse of tracer or to change from tracer to inert. Flow rates ranged from 1 to 40 SCF/hr. Measured at flowing conditions, this flow range is about that used in the Najbl-Simons-Carberry reactor. Shaft speed was varied from 0 to 2500 rpm. Tracer response was measured by the in-line infrared analyzers. A typical response to a pulse test is shown in Figure 4.

Typical test results are plotted in Figure 5. The data at 200 rpm indicate imperfect mixing. As the shaft velocity is increased, perfect mixing is realized for high and low flows and at high and low pressures. Above 1500 rpm perfect mixing is ensured for the range of flows studied. Changing temperature or tracer gas had no effect. The purge and step tests also gave linear semilog plots of C/C_S versus tF/V, but the slope was not -1 because of the reactor dead volume previously noted.

Interphase Transport

Transport phenomena between the catalyst surface and the bulk gas may control the reaction rate for very fast – or very exothermic or endothermic – reactions. To study chemical events on the catalyst surface these transport effects must be minimized. It is simple to check for the influence of transport effects in a CSTCR. In the case of catalyst mounted in a stationary basket, the stirrer speed is varied while all other variables are held constant. Changes in conversion with varying stirrer speeds indicate the presence of transport effects. A temperature gradient between the gas and the catalyst will exist if the reaction is heat-transfer limited. Both gas and catalyst temperatures can be easily measured with the stationary catalyst mounting.

Mass transfer was found not to control above about 750 rpm at 415°F with a 10.2% CO-31.2% H_2 feed, and nickel catalyst in the annular basket. Of course, a check should be made for mass transfer at each run temperature. Since the rate constant increases with increased temperature, mass transfer should be more important at higher temperatures.

Commercial Catalyst Comparison

A variety of products can be produced catalytically from hydrogen and carbon oxides. The type of products depend upon the catalyst composition, temperature, pressure, and the hydrogen/carbon oxides ratio. Nickel catalysts produce mainly methane at almost all useful operating conditions. Iron, ruthenium, and cobalt catalyze the Fischer-Tropsch synthesis, producing higher hydrocarbons. Iron and ruthenium catalysts were nevertheless considered since higher hydrocarbon formation would

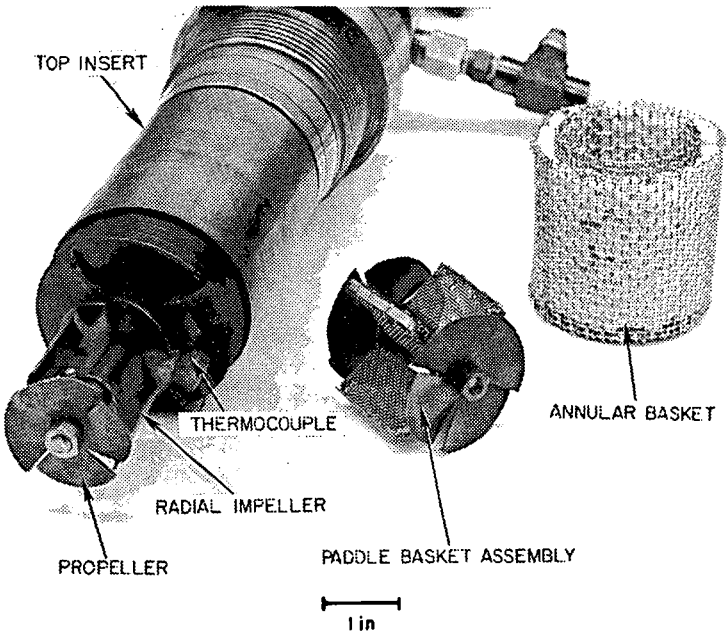

Figure 3. CATALYST BASKETS

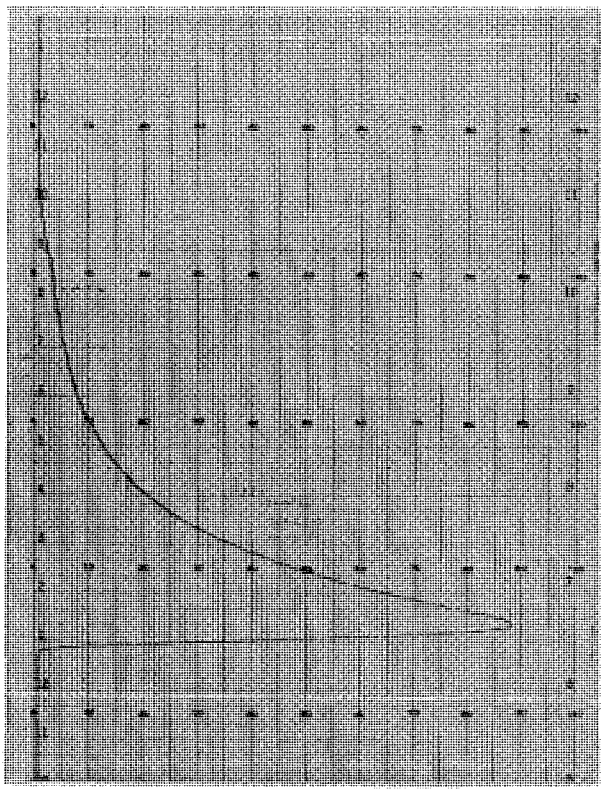

Figure 4. TYPICAL PULST TEST RESPONSES

/e the final gas a higher heating value. Cobalt catalysts were not con-
iered because they operate best at lower pressures (1-10 atm).[1]

Catalysts were compared by measuring their rate of carbon monox-
e conversion. Test variables were temperature, feed gas composition,
i the feed rate/catalyst weight ratio. All tests were made at 1000 psig.
ree feed gases, covering a range of compositions typical of projected
thanation feeds, were selected.

Table 1. COMPOSITIONS OF FEED GASES

ed	High CO	Intermediate CO	Low CO
mposition, mole %			
arbon Monoxide	10.0	7.0	2.4
arbon Dioxide	2.1	2.1	2.0
ydrogen	34.5	26.1	13.5
ethane	53.4	64.8	82.1
Total	100.0	100.0	100.0

Nickel Catalysts

The nickel catalysts studied were:

Catalyst A: Nickel on kieselguhr
Catalyst B: Nickel on alumina
Catalyst C: Nickel on alumina

talyst A is more active than catalysts B and C. For comparable feed
te/catalyst weight ratios and the same low-CO feed gas, catalyst A
nverts more carbon monoxide at 560°F than catalyst B at 700°F (Figure
. This also holds true for other feed gases. Figure 7 shows typical
ta for catalyst A in isothermal runs with low-CO feed gas.

Iron Catalyst

An ammonia-synthesis catalyst was studied. Much lower feed rate/
talyst weight ratios must be used with this catalyst to obtain conver-
ons approaching those of catalyst A (Table 2).

Table 2. RESULTS WITH IRON CATALYST

mp, °F	Fi/w, SCF/hr-g catalyst	Feed Gas	CO Conv,%	Dry Prod Gas Content, mole % CH_4	C_2+
509	0.036	Int. CO	13.0	68.2	0.8
604	0.027	Int. CO	55.7	73.4	1.3
700	0.026	Int. CO	62.2	74.7	1.3
800	0.026	Int. CO	66.3	76.2	1.4

hger-chained hydrocarbon formation is much lower than expected. This
presumably because of the high hydrogen/carbon monoxide ratio of the
ed gas and the high pressure. Bond[1] cites both these conditions as
voring hydrogenolysis.

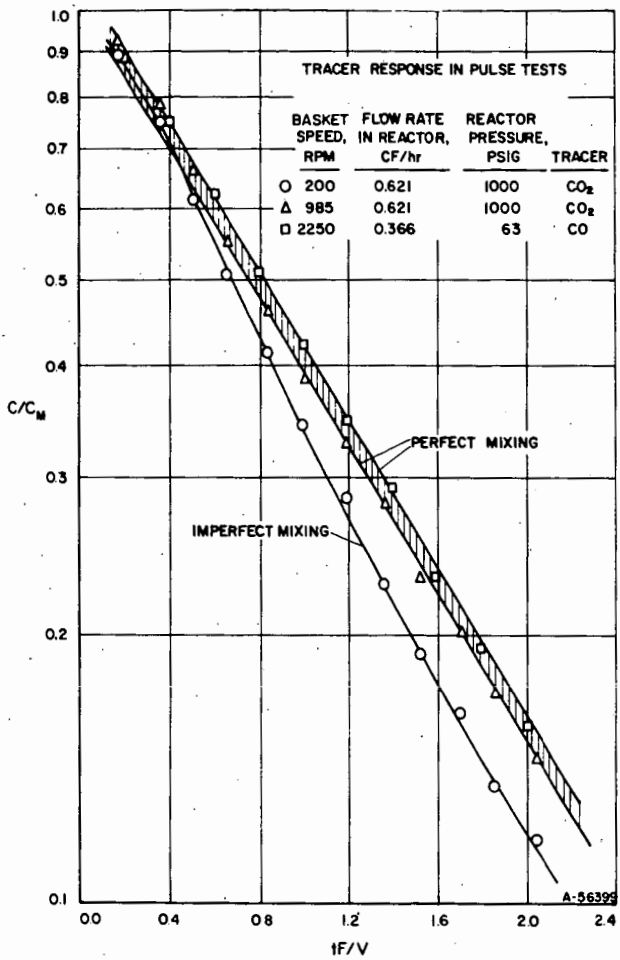

Figure 5. TYPICAL PULSE TEST RESULTS

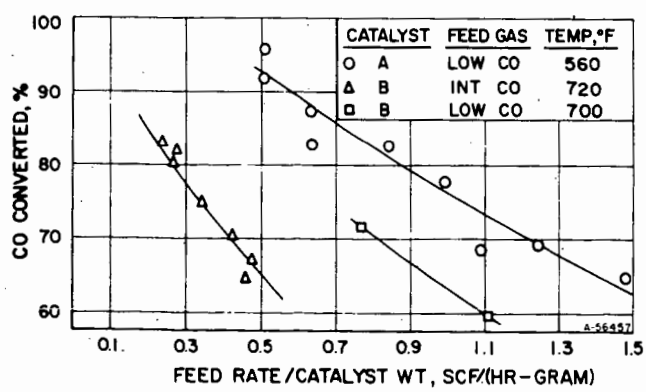

Figure 6. COMPARISON OF ACTIVITY OF NICKEL CATALYSTS A AND B

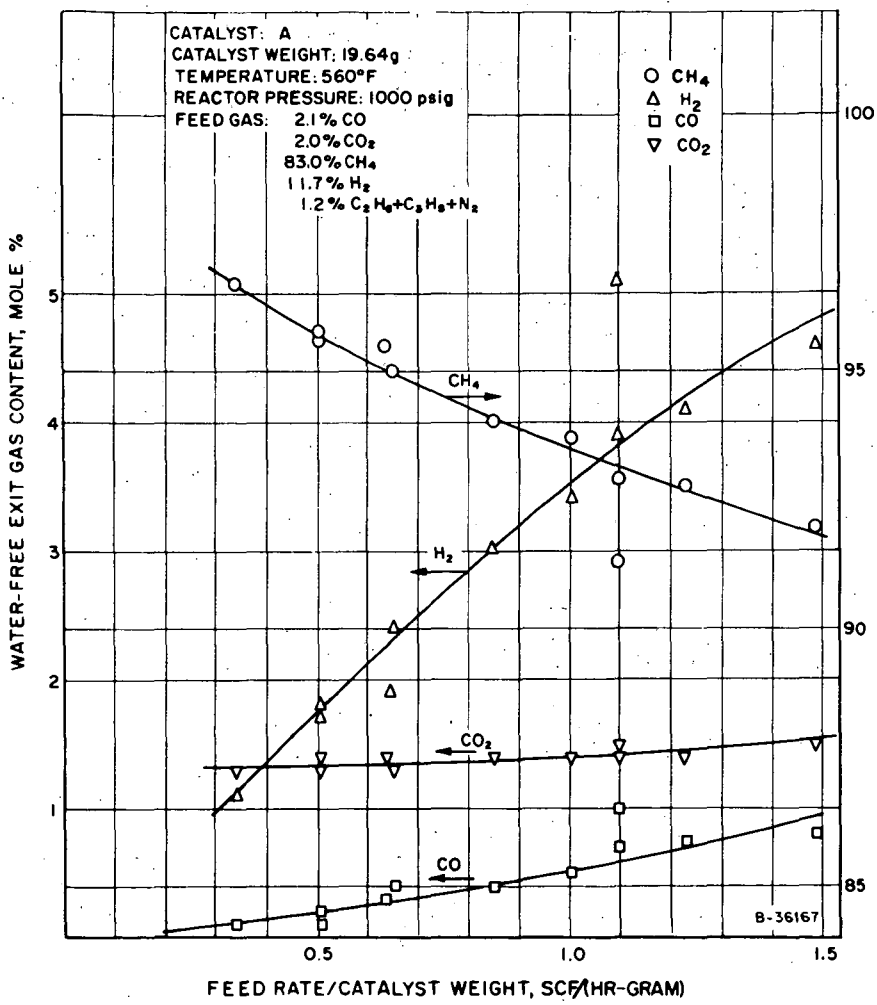

Figure 7. METHANATION PRODUCT GAS COMPOSITIONS AS A FUNCTION OF STIRRED REACTOR SPACE VELOCITIES

Ruthenium Catalyst

The ruthenium catalyst studied was 0.5% ruthenium on alumina. Data in Table 3 show that at low temperatures and low feed rate/catalyst weight ratios. this catalyst is an effective methanation catalyst. Higher hydrocarbon formation is, again, lower than expected, possibly due to hydrogenolysis. Trace yields of oils containing paraffins, olefins, and aromatics were obtained.

Table 3. RESULTS WITH RUTHENIUM CATALYST

Temp, °F	Fi/w SCF/hr-g Catalyst	Feed Gas	CO Conv,%	Dry Prod Gas Content, mole % CH_4	C_2+
210	0.059	Int. CO	5.5	66.6	0.9
290	0.058	Int. CO	6.0	67.7	0.9
347	0.058	Int. CO	20.3	69.5	1.1
405	0.056	Int. CO	27.7	71.1	0.7
470	0.056	Int. CO	86.2	84.1	1.6
547	0.055	High CO	90.0	85.2	1.3
600	0.503	Int. CO	44.0	76.7	0.8
670	0.503	Int. CO	89.3	89.2	0.7

CONCLUSIONS

Conditions for "perfect mixing" were determined in a continuous stirred tank catalytic reactor operated at 1000 psig. "Perfect mixing" was obtained at stirring speeds above 1500 rpm over the flow range used in this study.

Neither gas-solid heat nor mass transfer effects were found in this methanation study of typical feed gases produced from coal hydrogasification.

Evaluation of commercial catalysts showed that nickel-on-kieselguhr catalyst is more active than nickel-on-alumina, iron, and ruthenium catalysts for cleanup of CO in IGT's hydrogasification process. Longer-chained hydrocarbon formation is much less than expected for tests with iron and ruthenium catalysts.

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NOMENCLATURE

C = concentration, lb moles/cu ft

C_M = maximum concentration of tracer in pulse test, lb moles/cu ft

C_S = steady-state tracer concentration in purge or step test, lb moles/cu ft

F = flow rate, SCF/hr

R = reaction rate, lb moles/hr-g

t = time, hr

V = reactor volume, cu ft

w = catalyst weight, g

Subscripts

i refers to gas entering reactor

o refers to gas leaving reactor

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