

DEVELOPMENT OF METHANATION CATALYSTS  
FOR THE SNG PROCESSES

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ABSTRACT

Laboratory work has continued since late 1970 on developing catalysts for commercial methanation of synthesis gas, produced from coal or naphtha gasification, to a high BTU synthetic gas. Over 160 bench-scale tests, involving over 40 different catalysts have been made to determine the most desirable catalysts. Tests were initially made on commercially available catalysts but results indicated a whole new series of catalysts were required for this application. Tests showed the required catalyst loading, operating conditions, effect of particle size, thermal stability, and resistance to poisoning by trace constituents in the feed gas. The literature on the kinetics of the methanation reactors was reviewed in depth to determine the suitability of previous work on the methanation process conditions which are now planned. The initial kinetic system involving CO and CO<sub>2</sub> methanation along with CO shift was revised after analyzing the data utilizing previously published kinetics. A condensed summary of all the tests made to develop a commercial catalyst and an applicable kinetic system are presented.

## DEVELOPMENT OF METHANATION CATALYST FOR SNG PROCESSES

### SUMMARY

In the laboratory studies it was shown that methanation activity increases with increasing nickel content of the catalyst while the activity decreases with increasing catalyst particle size. Increasing steam to gas ratio of the feed gas results in increased carbon monoxide shift conversion but does not influence the rate of methanation.

Trace impurities in the process gas such as  $H_2S$  and  $HCl$  poison the catalyst. The mechanism is different because the sulfur remains on the catalyst while the chloride does not. Hydrocarbons at low concentrations do not affect methanation activity significantly and reform into methane. At higher levels hydrocarbons inhibit methanation and can result in carbon deposition.

A pore diffusion kinetic system was adopted which correlates the laboratory data and defines the rate of reaction.

## INTRODUCTION

In late 1970, Catalysts and Chemicals Inc. began a research and development program on methanation catalysts for the production of a high BTU synthetic natural gas from either coal or naphtha gasification. In 1971, Catalysts and Chemicals Inc. entered into an agreement with the El Paso Natural Gas Company to demonstrate the commercial feasibility of the methanation step in the process for the production of synthetic natural gas from coal. The pilot plant was designed in late 1971 and started up in early 1972. Because of the wide spread interest and concern about the methanation step in the over all production of SNG from coal, this project was opened to other participants in 1972. At that time, the Western Gasification Company and COGAS Development Company decided to participate in the pilot plant program.

This paper is a report on the basic work which was done in the laboratory to develop the catalysts for the methanation of synthesis gas from coal and the development of an applicable kinetic system. This report does not include any of the subsequent pilot plant test work which was carried out.

In the laboratory, over 160 bench-scale tests involving over 40 catalysts have been made to determine the optimum catalysts and process conditions for this application. Tests were initially made on commercially available catalysts but early results indicated that a whole new series of catalysts would be required for this application.

The comprehensive research program included all facets necessary for the development of these catalysts. Laboratory tests were conducted to determine the necessary catalyst loading, the design operating conditions, the effect of particle size, the effect of various trace constituents on catalyst performance and finally, resistance of the catalyst to thermal upsets. In this paper only those results which have direct significance to the kinetic model which was selected will be presented.

The laboratory studies which were particularly important to our development of the most active catalyst and the kinetic model for this new methanation application included the following.

TABLE 1

## LABORATORY STUDIES

Effects on Catalyst Activity by the:

- Nickel Content of the Catalyst
- Particle Size of the Catalyst
- Steam/Gas Ratio in the Process Gas
- Trace Impurities in the Process Gas

In this paper we have included an extensive discussion of the kinetic system we used and the basis for the selection of this system. During our development work, we frequently referred to the literature and the kinetics reported by previous workers. As a part of this program an extensive literature search was made. The complete bibliography of this literature search is presented for future reference by others.

## EFFECT OF NICKEL CONTENT ON CATALYST ACTIVITY

For the methanation reaction, in the process to convert coal to a high BTU gas, various catalyst compositions were evaluated to determine the optimum type catalyst. From this study a series of catalysts were developed to study the effect of nickel content on catalyst activity. This series includes both silica and alumina based catalysts and the nickel content was varied as outlined in Table 2.

TABLE 2  
CATALYST DESIGNATIONS FOR  
VARIOUS NICKEL CONTENT CATALYSTS

<u>Nickel Content</u>	<u>Silica Support</u>	<u>Alumina Support</u>
50%	C150-1-02	C150-1-03
40%	C150-2-02	C150-2-03
30%	C150-3-02	C150-3-03

This study was run in a laboratory bench-scale unit with 3/4" reactor tubes. The catalysts were sized to 10 x 12 mesh and diluted 9 to 1 with SiO<sub>2</sub> to spread the reaction out through the bed and allow for the measurement of temperature profiles, the profile being an excellent indicator of the catalyst activity. The space velocities were also varied in an attempt to move away from equilibrium CO leakages, so the relative activity of the catalysts could be obtained.

The catalysts were reduced with 100 percent hydrogen at 700°F and an inlet space velocity of 1000 hour<sup>-1</sup>. Because of the carbon forming potential of a dry gas recycle composition and the cost of reheating the recycle if the water produced by the methanation reaction is removed, this study was made using a wet gas recycle composition. The catalyst loading gas composition and test conditions for these tests are in Table 3 below.

TABLE 3  
COAL GASIFICATION PRIMARY METHANATION  
TEST CONDITIONS FOR NICKEL CONTENT STUDY

## Catalyst Loading

Volume (cc's)	5.0
Size (mesh)	10 x 12
Bed (L/D)	7.31
Bed Dilution	9/1

## Gas Composition

% CO	3
% CO <sub>2</sub>	4
% H <sub>2</sub>	12
% CH <sub>4</sub>	81
S/G	.35

## Test Conditions

Temperature, °F	500
Pressure (psig)	370
Space Velocity (v/v/hr)	25,000-95,000
Superficial Linear Velocity (ft/sec)	.343-1.302

A brief comparison is given in Table 4.

TABLE 4

NICKEL CONTENT VERSUS H<sub>2</sub> AND CO LEAKAGE

<u>Catalyst</u>	<u>Percent Nickel</u>	<u>Space Velocity (V/V/Hr Outlet Dry Gas)</u>	<u>% CO Leakage</u>	<u>% H<sub>2</sub> Leakage</u>
C150-1-02	50	93,000	0.18	6.93
C150-2-02	40	96,000	0.80	13.10
C150-3-02	30	96,000	3.35	22.30
C150-1-03	50	88,600	0.66	10.70
C150-2-03	40	96,000	0.27	16.88
C150-3-03	30	96,000	1.24	16.40

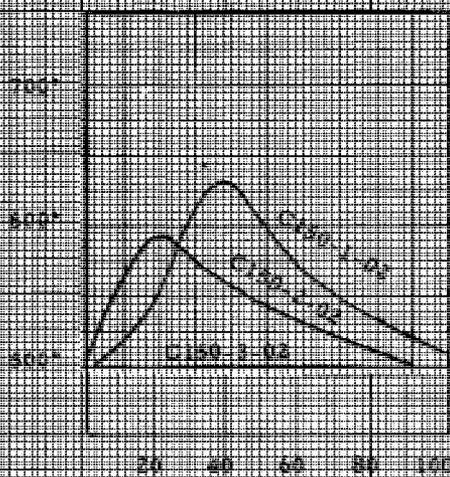
The temperature profiles for each catalyst at two different space velocities are given in Figures 5 and 6.

The lower nickel catalysts demonstrate a reasonable activity but the activity obviously decreases with nickel content. In Figures 5A, 5B, 6A and 6B it can be seen that at approximately 25,000 space velocity the 30% nickel on alumina catalyst uses 50% of the bed to obtain the maximum temperature while at 50% nickel the reaction only uses 30% of the bed. Each of these tests was extended for 300 hours or more. At various times during this study a test condition would be repeated and the percentage of the bed used for reaction indicated the catalyst had not aged.

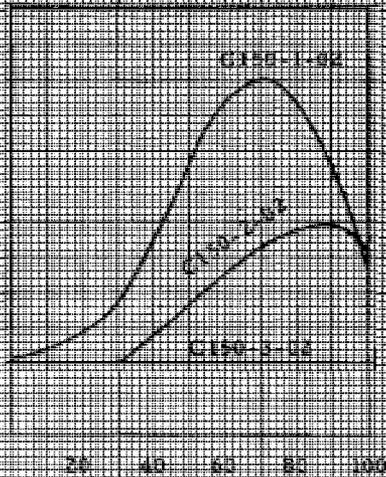
Carbon analysis indicated that no carbon deposition occurred at the conditions of these tests.

## TEMPERATURE VS PERCENTAGE OF BED DEPTH

## Silica Supported Catalysts

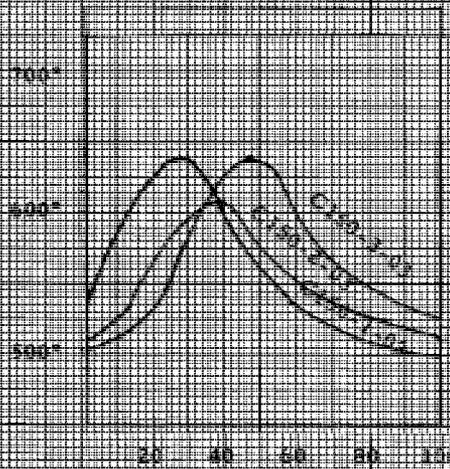


5 A. 25,000 Space Velocity

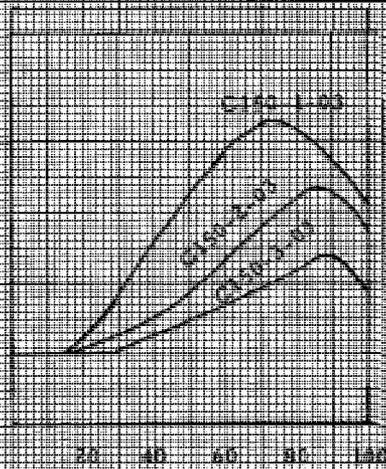


6 A. 25,000 Space Velocity

## Alumina Supported Catalysts



5 B. 25,000 Space Velocity



6 B. 25,000 Space Velocity

## EFFECT OF PARTICLE SIZE ON CATALYST ACTIVITY

The particle size study was made on the C150-1-02 catalyst. The C150-1-02 oxide mixture was tabletted in three different sizes: 1/8" x 1/16", 3/16" x 3/32" and 3/16" x 3/16".

The catalyst was reduced by the procedure described previously and tested at the conditions of the primary wet gas recycle methanation. The catalyst loading, gas composition and test conditions are outlined in Table 7.

TABLE 7

## PARTICLE SIZE STUDY CONDITIONS

## Catalyst Loading:

Type	C150-1-02
Volume, cm <sup>3</sup>	10.0
Form	Tablets
Size, inch	3/16 x 3/16", 3/16 x 3/32", and 1/8 x 3/32"
Bed Length/Diameter	1.46

## Gas Composition:

% CO	5.0
% CO <sub>2</sub>	4.0
% H <sub>2</sub>	23.0
% CH <sub>4</sub>	68.0
S/G	0.35-0.40

## Test Conditions:

Inlet Temp., °F	500-550
Pressure, psig	350
Space Velocity, v/v/hr. (1)	20,000; 40,000; 60,000
Superficial Linear Velocity, ft/sec. (2)	.075-.250

- (1) The space velocity is the volume of outlet dry gas per volume of catalyst per hour.
- (2) The linear velocity is based on 700°F temperature and outlet flow rate.

The results are summarized in Table 8.

TABLE 8

## CATALYST PARTICLE SIZE STUDY

Temperature, °F			Space Velocity V/V/Hr.	Outlet Analyses		Activity Constant Kw CO
Inlet	Hot Spot	Outlet		% CO	% H <sub>2</sub>	
C150-1-02, 3/16" x 3/16"						
558	793	742	20,000	<.03	7.3	40,674
556	740	720	40,000	<.03	10.4	36,659
554	728	680	60,000	<.03	14.8	<u>39,407</u>
Avg.						38,713
C150-1-02, 3/16" x 3/32"						
562	778	735	20,000	<.03	7.3	59,788
563	797	730	40,000	<.03	9.9	<u>51,052</u>
Avg.						55,420
C150-1-02, 1/8" x 1/16"						
564	814	730	20,000	<.03	6.8	78,902
565	785	748	40,000	<.03	8.7	66,045
562	807	755	60,000	<.03	12.2	<u>73,464</u>
Avg						72,804

As the particle size decreases, the hydrogen leakage decreases. Also, the hot spot temperature is higher in the bed as the particle size decreases. Both show that the smaller particle size has greater activity. A kinetic system which defines the reaction in terms of CO and CO<sub>2</sub> methanation and CO shift conversion was used to determine the activity as shown in the last column of the table. The relative activity, based on particle size, is given as follows:

Particle Size	CO Methanation	Kw <sub>x</sub> /Kw <sub>o</sub>
	Kw	
3/16" x 3/16"	38,713	1.00
3/16" x 3/32"	55,420	1.43
1/8" x 1/16"	72,804	1.88

If we assume that the activity is inversely proportional to particle size

$$\frac{Kw_o}{Kw_x} = \left( \frac{D_x}{D_o} \right)^n$$

then n approximately equals 0.9 or Kw is proportional to  $\left( \frac{1}{D} \right)^{0.9}$  where D is the

equivalent sphere diameter. Since the kinetics are based on diffusion control it had been assumed that  $K_w$  was proportional to  $1/D$ . This data gives fairly good agreement since the packing and flow in the small diameter laboratory tubes would also cause some error.

## EFFECT OF STEAM TO GAS RATIO ON CATALYST ACTIVITY

In the various laboratory studies where the outlet gas composition was not at equilibrium, it was observed that the steam to gas ratio significantly affected the hydrogen leakage while the carbon monoxide still remained low.

Assuming that various reactions will proceed at different rates a study was made to determine the effects of the steam to gas ratio on the rate of reaction. The conditions for this test are presented in Table 9. Results of the test are tabulated in Table 10.

In varying the steam/gas ratio from .15 to .40 significant differences were observed. At the lower steam to gas ratios there is no CO shift conversion. At higher steam to gas ratios there is CO shift conversion.

When evaluating the data as summarized in Table 10 and obtaining activity constants for CO and CO<sub>2</sub> methanation and CO shift conversion, the activity for methanation remains the same regardless of the steam to gas ratio. However, with the high steam to gas ratio, shift conversion is occurring at about 25 percent of the rate of CO methanation. At low steam/gas ratios no shift conversion is observed.

TABLE 9

## CONDITIONS FOR STEAM TO GAS RATIO STUDY

## Catalyst Loading:

Type	C150-1-03, C150-4-03
Volume, cm <sup>3</sup>	10.0
Size, inch	3/16 x 3/32"
Bed, Length/Diameter	1.46

## Gas Composition:

% CO	5.0
% CO <sub>2</sub>	4.0
% H <sub>2</sub>	23.0
% CH <sub>4</sub>	68.0
S/G	.15-.40

## Test Conditions:

Temperature, °F	500-850
Pressure, psig	350
Space Velocity, v/v/hr.	20,000
Superficial Linear Velocity, ft./sec.	.078

TABLE 10  
EFFECT OF STEAM TO GAS RATIOS

Catalyst	Hours On Stream	Temperature, °F				Inlet				Outlet				Equilibrium				
		Inlet		Hot		S/G	Inlet	Spot	Outlet	%CO	%CO <sub>2</sub>	%H <sub>2</sub>	%CO	%CO <sub>2</sub>	%H <sub>2</sub>	%CO	%CO <sub>2</sub>	%H <sub>2</sub>
		On Stream	S/G	Inlet	Spot													
C150-1-03 50% Nickel on Alumina	33	.365	498	688	518	4.34	4.13	20.14	.247	5.26	6.45	.007	3.54	2.73				
	79	.368	499	680	518	3.42	6.25	14.60	.183	6.34	4.81	.016	6.50	2.46				
	93	.308	500	637	514	3.12	1.54	14.30	.165	3.01	4.97	.001	.933	2.35				
	35	.15	502	765	512	7.31	4.52	16.90	.459	8.75	2.80	.022	7.21	1.52				
	40	.15	501	773	513	7.31	4.52	16.90	.503	8.50	2.24	.022	7.21	1.52				
	51	.182	502	704	513	4.28	4.26	14.70	.255	6.10	2.34	.020	4.86	2.10				
C150-4-03 60% Nickel on Alumina	58	.02	500	824	518	4.18	5.52	17.70	.167	4.31	1.69	.080	5.44	1.83				
	61	.02	500	804	517	4.18	5.52	17.70	.159	4.43	1.69	.037	5.36	1.25				
	65	.02	500	808	515	4.18	5.52	17.70	.170	4.51	1.82	.061	5.41	1.60				
	33	.365	498	672	514	4.34	4.13	20.14	.223	4.53	4.68	.007	3.54	2.73				
	79	.368	498	666	518	3.42	6.25	14.60	.114	6.10	3.64	.016	6.50	2.46				
	93	.308	499	637	512	3.12	1.54	14.30	.124	2.70	3.36	.001	.933	2.35				
C150-1-03	35	.15	500	731	510	7.31	4.52	16.90	.138	8.77	2.69	.022	7.21	1.52				
	40	.15	499	748	514	7.31	4.52	16.90	.228	8.50	2.27	.022	7.21	1.52				
	51	.182	500	680	512	4.28	4.26	14.70	.139	6.00	1.65	.020	4.86	2.10				
C150-4-03	40	.15	49,564	39,645	29,734	0	0	0	42,336	23,814	0	0	0					
	51	.18	49,564	39,645	29,734	0	0	0	42,336	23,814	0	0	0					
	65	.02	49,564	39,645	29,734	0	0	0	42,336	23,814	0	0	0					
C150-4-03	79	.37	54,520	43,610	39,645	13,011	0	0	51,216	28,809	0	0	0					
	40	.15	49,564	39,645	29,734	0	0	0	51,216	28,809	0	0	0					
	51	.18	49,564	39,645	29,734	0	0	0	51,216	28,809	0	0	0					
C150-4-03	65	.02	49,564	39,645	29,734	0	0	0	51,216	28,809	0	0	0					
	79	.37	54,520	43,610	39,645	13,011	0	0	51,216	28,809	0	0	0					
	40	.15	49,564	39,645	29,734	0	0	0	51,216	28,809	0	0	0					

## EFFECT OF TRACE CONSTITUENTS IN THE PROCESS GAS ON CATALYST ACTIVITY

In the process to make SNG from coal the methanation feed gas can contain various trace constituents which could affect performance. The coal can contain various amounts of sulfur, chloride and nitrogen. These will mostly be converted to  $H_2S$ ,  $HCl$ ,  $NO_x$  and  $NH_3$ , the last of which can be scrubbed or condensed out of the gas. These components can then be potential catalyst poisons. In addition to these inorganic compounds, various hydrocarbon compounds will be formed in the gasifier. Most of the heavier components can be separated. However, the  $C_2$  and  $C_3$  hydrocarbons are expected in the methanator feed gas.

Two other components, methanol and benzene, were added to the study. Methanol was included for processes using Rectisol systems for  $CO_2$  removal prior to methanation. Benzene was considered to determine the effect of aromatics on the catalyst activity and potential carbon formation.

In summary, Table 11 shows the components included in this study. The general conditions are tabulated in Table 12.

TABLE 11

### COMPONENTS OF TRACE IMPURITIES STUDY

$H_2S$	$RSH$ and $COS$ were not included since they are expected to hydrogenate to $H_2S$ over the nickel catalyst.
$HCl$	
$NO_x$	$NH_3$ was not included since it can be separated by condensation or scrubbing.
$CH_3OH$	$MeOH$ is included because of anticipated use of a Rectisol System.
$C_2, C_3$	Ethane, ethylene, propane and propylene are the expected light hydrocarbons in the process gas.
Benzene	Benzene was included to study the effect of aromatics on the catalyst in the event of catalytic sulfur removal as opposed to Rectisol.

TABLE 12

## GENERAL CONDITIONS FOR TRACE IMPURITIES STUDY

## Catalyst Loading:

Type	C150-1-03
Volume, cm <sup>3</sup>	10.0
Size	10 x 12 mesh

## Gas Composition:

%CO	5-7
%CO <sub>2</sub>	4-6
%H <sub>2</sub>	20-25
%CH <sub>4</sub>	62-71

## Test Conditions:

Temperature, °F	600
Pressure, psig	350
Space Velocity, V/V/Hr.	10,000
Steam/Gas Ratio	.35

1. Sulfur - Each impurity was added separately to the gas mixture and passed over C150-1-03 to determine its effect on catalyst activity.

These tests were run at the primary methanation conditions, but were run in a small 3/8" tube reactor on sized, 10 x 12 mesh, catalyst. The first test involves the addition of H<sub>2</sub>S in the 1-3 ppm range to the dry feed gas. The effect of the H<sub>2</sub>S on the catalyst activity is summarized in the following table.

TABLE 13  
EFFECT OF SULFUR POISONING

	Initial %-CO Conv.	Initial Kw-CO Meth.	Final %-CO Conv.	Final Kw-CO Meth.	% S Added to Catalyst	Ppm S in Feed	Calculated Inlet Sulfur ppm
Test 1	99.8	81,500	6.4	1,000	0.295	2-3	3.1
Test 2	98.6	65,500	85.5	25,500	0.274	0	0.93
Test 3	98.2	65,000	84.3	25,000	0.125	0	0.26

Tests 2 and 3 were made in the same reactor as Test 1. The catalyst was started up with no sulfur addition to confirm the initial activity. As can be seen from the table in the second and third tests, the catalysts picked up sulfur in both tests and deactivated even though no sulfur was added to the feed indicating that sulfur had remained in the reactor after Test 1. This is a common problem working with sulfur in laboratory test reactors. The sulfur will react with the steel walls of the reactor. Then even though sulfur is removed from the feed sulfur will evolve from the walls of the reactor and either be picked up by the catalyst or appear in the effluent from the reactor. With continuous addition of sulfur the CO leakage continues to increase.

In Test 1 with 3 ppm sulfur in the feed gas the catalyst showed continuous deactivation; it did not maintain some intermediate level of activity. For Tests 2 and 3, the calculated inlet sulfur concentration is shown and this value is calculated based upon the amount of sulfur found on the catalyst and the time on stream. With .13 to .30 percent sulfur on the catalyst, 60-90 percent of the activity was lost. Although Tests 2 and 3 were never conducted as originally planned, feeding 1 ppm sulfur in the feed gas, it was felt that the results of Tests 2 and 3 satisfactorily proved the severe poisoning effect of sulfur on C150-1-03.

RSH or COS as the source of sulfur was not studied because at the conditions of the test they are expected to hydrolyze or hydrogenate to H<sub>2</sub>S and poison the catalyst the same as if they were H<sub>2</sub>S.

2. Chloride - C150-1-03 was tested at primary wet gas conditions to determine the effect of chloride on catalyst performance. Chloride was expected to be very detrimental to catalyst activity, but the manner of deactivation was uncertain. The chloride was added to the system as hydrogen chloride in the feed water, up to 14 ppm, dry gas basis.

The test was conducted in a single reactor unit with an electric furnace heater. The feed water served as the source of steam and chloride for this test.

Table 13 provides a synopsis of test results as the chloride level was changed. Table 14 shows the change in the hot spot location caused by increased chloride levels.

Analysis of the discharged catalyst is presented in Table 15. New catalyst analyzed less than 0.01 percent chloride.

The chloride level was raised to greater than 5 ppm in the feed gas because the hot spot had moved down to the 69 percent level and remained there. Note that the percent conversion changed significantly only when the hot spot had reached the bottom of the bed. When the chloride was removed, neither the hot spot location nor the percent conversion improved.

Hydrogen chloride is a permanent irreversible poison to the methanation activity of C150-1-03 even though the majority of it is not picked up by the catalyst and is observed in the effluent gas. Only 0.02-0.04 percent was found on the discharged catalyst, but any amount of chloride in the feed gas is detrimental to catalyst activity.

TABLE 13

## CHLORIDE POISON TEST

Days		
1 - 5	No Chloride added.	Steady 99.1% conversion of CO with constant hot spot location 31% into the bed.
6 - 21	0.52 ppm Cl added on dry gas basis.	Seemed to be a slight decrease in percent conversion (Avg. = 98.7%). Hot spot moved down into bed to 69% level.
22 - 29	2-4 ppm Cl added on dry gas basis.	The overall average percent conversion was 98.5 during this period. The hot spot remained at the 69% level.
30 - 33	All chlorides were removed from feed.	The conversion did not change when chlorides were removed (98.6%). The hot spot also remained unchanged.
34 - 47	11-14 ppm Cl added on dry gas basis.	The percent conversion steadily decreased during this period of high chloride levels until on the 47th day the conversion was only 84.0%. The hot spot also decreased down into the bed at the 94% level. On the 37th day, the unit had to be shut down to repair a leak on the inlet to the reactor. The catalyst was kept under CO <sub>2</sub> during this period.
48 - 51	All chlorides were removed from feed again.	The percent conversion continued to decrease. On the 51st day the conversion was 75.8% when the test was stopped. The hot spot remained at the 94% level, nearly at the very bottom of the bed. (See Figure 1)

Chloride Poison Study: TABLE 14  
Hot Spot Location Vs. Days on Stream

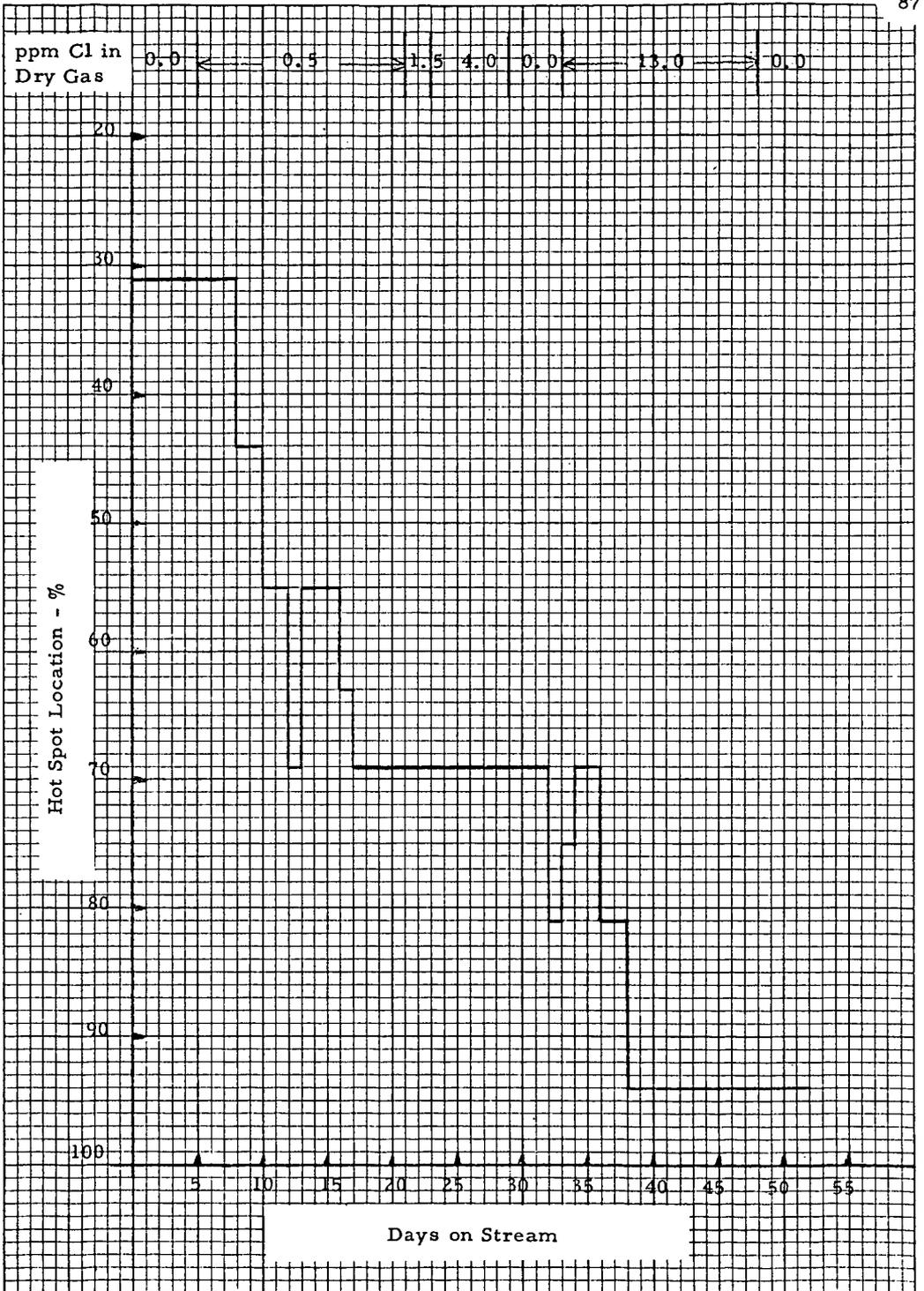


TABLE 15

## ANALYSIS OF DISCHARGED CATALYST

	Wt. % Chloride	
	<u>Wet Method</u>	<u>XRF Method</u>
Top 1/3	0.051	0.04
Middle 1/3	0.039	0.02
Bottom 1/3	<u>0.039</u>	<u>&lt;0.01</u>
Average	0.043	0.023

3. Nitrogen Dioxide - Nitrogen dioxide can be formed in the gasifier from the nitrogen present in the coal. Since it is an acid gas it was included in the study as a potential poison. This study was conducted with C150-1-03 in the electrical furnace reactor unit. The catalyst was tested at primary wet gas conditions with up to 8 ppm nitrogen dioxide in the dry feed gas. Table 16 provides a synopsis of test results as the NO<sub>2</sub> level was changed.

TABLE 16

RESULTS OF NO<sub>2</sub> ON CATALYST ACTIVITY

<u>Days</u>	<u>Condition</u>	<u>Result</u>
1-8	No NO <sub>2</sub> Added	Average 99.1% conversion of CO with hot spot location between 31-44% into bed.
9-13	1-2 ppmv NO <sub>2</sub> Added	Average 99.1% conversion with hot spot location at steady 31%. No change.
14-28	2-7 ppmv NO <sub>2</sub> Added	Average 99.2% conversion with hot spot location between 31-44% into bed.

Nitrogen dioxide up to 8 ppmv concentration in the inlet gas did not poison C150-1-03 catalyst.

The location of the hot spot fluctuated between 31 and 44 percent levels during this test. The hot spot did not drop sharply down into the catalyst bed as did previous poisoning studies with H<sub>2</sub>S and HCl.

4. Alkanes and Alkenes - For this study, C150-1-01 and C150-1-03 were tested at primary wet gas conditions with ethylene, ethane, propylene and propane added to the feed gas. The purpose in testing these hydrocarbons as a possible catalyst poison was to determine whether they would deposit carbon on the catalyst, reform, or pass through without reaction. The test was conducted using the dual-reactor heat sink unit and a water pump and vaporizer as the source of steam. All gas analyses were performed by gas chromatography. The test was stopped with the poisons still in the feed gas in order to preserve any carbon buildup which may have occurred on the catalysts.

The gas analyses, Table 17, show that the catalysts are not visibly affected by these alkanes or alkenes. The CO and H<sub>2</sub> leakages remained low throughout the test, rising slightly after hour 181 when the jacket temperature was raised. The disappearance of the ethane, ethylene, propane and propylene is attributed to reforming reactions taking place, even though a continuous trace ethane leakage was observed. Reforming of such small amounts of hydrocarbons would not create a discernible difference in the gas analyses. There was no downward movement of the hot spot during the test, and carbon deposition did not occur. These observations support our conclusion that ethylene, ethane, propylene and propane undergo reaction over the catalyst but do not poison it.

5. Methanol - In another series of tests, the effect of methanol, which can be carried over from the Rectisol scrubber system, on catalyst activity was determined by adding methanol to the water before vaporizing into the unit. The methanol was added to give .01% to 1.0% on a dry gas basis. Methanol up to 1000 ppm had no effect on activity as evidenced by no change in the H<sub>2</sub> and CO leakages. On increasing the methanol to 1% the temperature profile moved down through the bed but with no noticeable effect on H<sub>2</sub> and CO leakage. On removing the methanol the hot spot returned to its original location in the catalyst bed. The effluent H<sub>2</sub>O showed no methanol during the test, indicating that the methanol has reformed to methane.
6. Benzene - Although benzene would ordinarily be scrubbed out by a Rectisol system before the methanators, the possibility of a different H<sub>2</sub>S removal system resulted in the inclusion of benzene with our poison study. Benzene could pass through the system, hydrogenate, plug up the catalyst pores or reform.

C150-1-03 and C150-4-03 were loaded into the small dual-tube reactor. The unit was equipped with inlet saturators used as the source of benzene, of which poison levels of 0-5 percent were tested. The results are summarized in Table 18.

The test results show that benzene at low levels had no noticeable effect on activity and was reforming to methane, carbon oxides and hydrogen. At higher levels, greater than 0.5 percent, the activity of the catalyst declined which is demonstrated by the hot spot moving down the catalyst bed and the increase in CO and H<sub>2</sub> leakage. In addition, benzene and cyclohexane were observed in the effluent. At very high levels carbon formation was observed over the C150-1-03 catalyst.

Although benzene is not a poison in the sense that H<sub>2</sub>S and HCl are, it is depressing activity by reforming and adsorption on the catalyst, and at high levels can produce carbon.

Poisons not taken into account in kinetics system.

TABLE 17

## EFFECT OF LIGHT HYDROCARBONS ON CATALYST ACTIVITY

INLET	Outlet S/G	Temperature of, °C		% of Catalyst Bed Above Hot Spot	GAS COMPOSITION																	
		Top	Bottom		INLET, %				OUTLET, %													
Stream	S/G	Hot Spot	Bottom	Hot Spot	CO	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>16</sub>	C <sub>7</sub> H <sub>14</sub>		
150-1-01																						
15	.531	696	597	11.5	5.07	5.13	26.73	63.07	--	--	--	--	<.01	4.70	3.46	91.84	--	--	--	--	--	--
23	.538	751	589	11.5	5.17	5.43	28.71	60.69	--	--	--	--	.0125	4.76	3.15	92.09	--	--	--	--	--	--
73	.536	702	591	11.5	4.27	4.77	24.38	67.37	.186	.473	<.01	4.31	2.99	88.06	<.01	.066	<.01	.0021				
95	.538	730	592	11.5	4.92	4.23	24.57	69.67	.235	.061	.276	5.48	<.01	4.04	2.81	94.86	<.01	.072	<.01	.0041		
111	.537	834	620	11.5	4.73	6.68	24.90	64.17	.326	.051	.338	.475	.005	7.21	2.81	90.62	<.01	<.01	<.01	<.01		
161	.530	826	674	11.5	4.05	6.77	24.55	69.75	.333	.059	.481	.556	<.01	6.32	3.66	85.49	<.01	.0101	<.01	<.01		
150-1-03																						
6	.507	728	593	0.0	5.07	5.13	26.73	63.07	--	--	--	--	.0025	4.50	2.45	93.05	--	--	--	--	--	--
23	.484	760	600	6.9	5.17	5.43	28.71	60.69	--	--	--	--	.008	4.56	2.67	92.77	--	--	--	--	--	--
51	.505	762	600	6.9	5.06	5.19	25.28	69.01	.447	.088	.491	.162	<.01	5.17	2.21	104.6	<.01	.0695	<.01	<.01		
56	.485	695	721	20.7	4.91	4.16	21.95	71.80	.443	.093	.608	.669	<.01	5.01	2.36	88.35	<.01	.014	<.01	.0015		
95	.483	683	722	20.7	4.92	4.23	24.57	69.67	.235	.061	.276	.548	<.01	4.20	2.79	95.48	<.01	.021	<.01	.0037		
111	.505	787	644	20.7	4.73	6.68	24.90	64.17	.326	.051	.338	.475	.005	7.24	2.05	91.03	<.01	<.01	<.01	<.01		
121	.506	798	680	6.9	4.91	10.99	26.31	64.35	.353	.045	.321	.547	.0373	11.7	2.71	86.32	<.01	.0018	<.01	<.01		
161	.497	789	688	20.7	4.05	6.77	24.55	69.75	.333	.059	.481	.556	<.01	6.29	3.20	99.42	<.01	.0039	<.01	<.01		

## Discharged Catalyst Properties

	% C	% S	% Reduction
150-1-01	3.08 (New 2.58)	.048 (New .06)	62.0
150-1-03	6.14 (New 5.84)	.066 (New .09)	76.3

TABLE 18

EFFECT OF BENZENE ON CATALYST ACTIVITY

Hours Onstream	Catalyst	% Catalyst Bed Above Hot Spot	Gas Composition						C <sub>6</sub> H <sub>12</sub>		
			% Inlet			% Outlet					
			CO	CO <sub>2</sub>	H <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	H <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	
32	C150-1-03	0.0	5.91	5.90	23.11	-	.0025	5.45	2.13	-	-
58		16.7	5.57	5.76	23.36	.161	.0025	6.99	2.61	-	-
123		33.3	3.81	6.34	23.73	.410	.0025	6.32	3.58	.053	-
251		33.3	4.31	4.63	26.24	1.86	.01	5.31	7.38	1.281	.04589
304		100.0	4.47	7.26	25.79	3.64	.01	6.83	18.93	5.74	.29693
335	50.0	3.55	4.98	21.75	-	.01	5.69	12.50	-	-	
32	C150-4-03	0.0	5.91	5.90	23.11	-	.0025	5.49	1.96	-	-
51		16.7	5.98	5.59	24.53	.102	.0025	5.82	2.71	.095	.00037
84		33.3	3.81	5.65	23.02	1.09	.0025	5.82	3.05	.297	-
89		41.7	3.81	5.65	23.02	.361	.005	6.56	3.22	.720	.00015
145		50.0	3.44	5.06	24.5	.404	.005	5.77	4.57	.139	-
251		66.7	4.31	4.63	26.24	1.19	.01	5.18	9.06	1.018	.00279
304		83.3	4.47	7.26	25.79	5.53	.02	6.02	11.13	7.211	.1443
335	66.7	3.55	4.98	21.75	-	.01	5.18	9.35	-	-	

## DISCUSSION OF KINETIC SYSTEM

In various fields of commercial catalyst practice it has been customary for over thirty years (58) to use a very simple first order, or psuedo first order, equation in preliminary converter design where very great changes of conditions are not made. This equation, for constituent X may be written as

$$\begin{aligned}
 KW &= SVW \log_{10} \left( \frac{\text{Lb. mols/hr. of X in} - \text{Lb. mols/hr. of X}_{\text{eq.}}}{\text{Lb. mols/hr. of X out} - \text{Lb. mols/hr. of X}_{\text{eq.}}} \right) \\
 &= SVW \log_{10} A
 \end{aligned} \tag{1}$$

In equation 1, KW is a rate constant at a specific pressure and temperature, SVW is total wet gas space velocity, expressed as SCF of total gas per hour per cubic foot of bulk catalyst. X in refers to the lb. mols/hr. of constituent entering the section of catalyst for which the space velocity is measured, whereas X out indicated the lb. mols/hr. leaving the section. X<sub>eq.</sub> indicates the lb. mols/hr. which would pass through the section under equilibrium conditions. For reactions with large heats, it is necessary to divide a catalyst bed into a number of sections, so that each section is essentially isothermal.

Equation 1 almost necessarily has as its basis the concept that diffusion, either through pores or to the gross surface of the catalyst particle, controls the reaction rate.

Where the control is strictly by the gas film surrounding the catalyst, one would have to convert equation 1 to  $KW \sqrt{L} = SVW \log_{10} A$

where L is the catalyst bed depth in feet. This is required because the controlling film thickness is reduced as gas velocities are increased. In general equation (1) is satisfactory for commercial reactors. The differential equation from which (1) may be derived is:

$$- \frac{dX}{dV} = 6.07 \times 10^{-3} KW \left( \frac{\text{Lb. mols/hr. of X}}{\text{Lb. mols/hr. of Gas Flow}} - \frac{\text{Lb. mols/hr. of X}_{\text{eq.}}}{\text{Lb. mols/hr. of Gas Flow at equilibrium}} \right) \tag{3}$$

This may also be given as

$$- \frac{dX}{dV} = 6.07 \times 10^{-3} KW (N_x - N_x \text{ eq.}) \tag{4}$$

This refers to the total gas flow, through a plane of catalyst, where  $N_x$  is the mol fraction of X in the gas passing through the plane, and  $N_x \text{ eq.}$  is the mol fraction of X at equilibrium under conditions at this point in the catalyst bed.

Another equation which is helpful for computer use is:

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ & = \left(1 - 10 \frac{-K_w}{SVW}\right) \left(\text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}}\right) \end{aligned} \quad (5)$$

In cases where there is no volume change in the reaction, (1) and (5) may be readily derived from (3) or (4).

The solution of equation (3) is complicated when there is a volume change in the reaction which removes constituent X.

For these reactions equation (3) may be used, with  $dX$  replaced by  $\Delta X$ , and  $dV$  by  $\Delta V$ . This may be made as accurate a solution as one wants, if the increments are sufficiently small.

However, equation (5) may be used as is, but a more accurate solution is:

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ & = \left(1 - 10 \frac{-K_w}{SVW}\right) \left(\text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}} \times \frac{\text{Flow}}{\text{Flow}_{\text{eq.}}}\right) \end{aligned} \quad (6)$$

Equation (6) has been used in correlating the data of this paper; however, a more accurate approximation solution of (3) is

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ & = \left(1 - 10 \frac{-K_w \text{ Flow}^*}{SVW \text{ Flow}_{\text{eq.}}}\right) \left(\text{Lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}}\right) \end{aligned} \quad (7)$$

Where  $\text{Flow}^*$  is the volume of gas which would pass if 100% of constituent X were reacted.

Finally, a fairly complicated exact solution of (3) may be derived. It must be noted, however, that equation (3) itself cannot be strictly accurate, since only the diffusion of a single constituent has been considered.

The application of equation (3) to the methanation of CO by the reaction  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ , starting with a mixture of say 90% CO and 10%  $\text{H}_2$ , using CO as X, would lead to the erroneous conclusion that methanation is impossible under these conditions. The requirement is that equation (3), operating on one constituent, can only be accurate (even when diffusion is strictly controlling) if X is present at a low concentration. To solve the 90% CO - 10%  $\text{H}_2$  case previously mentioned, it would be necessary to consider the diffusion of constituents other than CO.

In view of the above, and the fact that all of the various approximate solutions of equation (3) give about the same answer when the reactant concentration is low, it did not seem worthwhile to work on obtaining better accuracy in the solution of (3).

Equation (7) is, however, of interest when one does comparisons of various kinetic equations. It may be rewritten as

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X out} \\ & = (1 - 10 \frac{-K_w}{SVW} x Q) \left( \text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X eq.} \right) \end{aligned} \quad (8)$$

Thus, (7) is a special case of (8) where

$$Q = \text{Flow}^*/\text{Flow eq.} \quad (9)$$

In computer operations with other kinetic systems equation (8) may be used, and all of the unique features of the kinetic system may be incorporated into the value of Q, which may, of course, be a very complex expression. This technique is only of interest in that it simplifies the work necessary to analyze data using any specific kinetics for a chemical reaction. The technique requires sectioning of the catalyst bed; in most cases with normal space velocities 50 to 100 sections, involving two or three minutes of time on a small computer, appear to be sufficient even when very complex equations are used.

$K_w$  in the foregoing equations is a function of pressure and temperature. Although the effect of pressure and temperature on strictly diffusion controlled processes is small, the effect of these variables on surface reactions is generally quite large. Thus, although diffusion may be the major contributor to the mathematical form of the kinetic equations, a residuum of influence from the basic process taking place at the end of the catalyst pores will also affect the rate constant. The usual balance achieved with respect to pressure is a rate increasing with the square root of the total pressure. Since essentially all of the experimental work in this project was at essentially the same pressure, this study gives no information on the pressure dependence of rate. It should be noted, however, that the form of several proposed kinetic equations (25, 57) would give this type of pressure - rate relationship. Data are available from commercial ammonia plant methanators, and laboratory studies relative to them, which show this type of pressure dependence.

For this reason a square root of pressure term has been introduced into the equation for  $K_w$ . Further experimental work would be desirable if pressures greatly different from 25 atm were to be used.

The effect of temperature on  $K_w$  has been introduced through an activation energy term. This follows the normal form for this type of reaction, with a very high activation energy below the "threshold" temperature, and a lower value, tending to diminish with increasing temperature, at higher temperatures. This reflects an increasing dependence of reaction rate on diffusion as the temperature is

raised. Activation energies for rate data derived from experiments (7, 28, 30, 32, 48, 50) on the hydrogenation of CO and CO<sub>2</sub> at low pressures and low temperatures using small catalyst particles of .01 to .03 in. diameter generally run from 15,000 to 30,000 cal/g mol. On the other hand, for work at higher pressures and temperatures, with commercial size catalyst (1/8 to 1/4 in. diameter), values of 0 to 10,000 cal/g mol are obtained (32, 33, 25, 50, 57).

In the early phases of study, temperature surveys were run on various catalyst with the object of finding the "threshold" temperature for CO methanation. The following rather typical results were calculated for 1/4 in. C150-1-02 catalyst.

<u>Average Temperature, °F</u>	<u>Kw</u>	<u>Activation Energy, cal/g mol, calc. from previous temperature value</u>
320	170	-
362	710	24,000
389	6020	61,000
416	11850	21,000
529	24300	6,100

In general, considering that these tests are on catalyst which has not been aged, a Kw value below several thousand is indicative of a catalyst not practical for commercial use, so from a utilitarian standpoint these data show a "threshold" temperature slightly below 400°F. Because of the small amount of reaction at the lower temperatures, and the effect of small temperature errors on the activation energy calculation, the three values at low temperatures are not very consistent; however, the average of 35,000 cal/g mol is not in bad agreement with the results of other investigators. The value of 6100 cal/g mol is typical for the diffusion control region.

An examination of laboratory data on C150-1-01 and C150-1-02 catalysts for CO hydrogenation tends to show essentially no change in Kw value between 500, 600 and 700°F. This would suggest an activation energy of zero. Although these data show a small, essentially zero, temperature dependence from 500-700°F (33) the difficulties in unraveling the relationship between the rates of CO and CO<sub>2</sub> methanation, and the water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ) prevent one from getting a good value for the activation energy for any one reaction. Considering these tests, as well as various literature studies (32, 33, 25, 50, 57) an activation energy of 5,000 cal/g mol was used below 700°F, and 2,000 cal/g mol above 700°F. One must bear in mind that below the "threshold temperature" any predicted performance would be virtually meaningless. It may be noted that a kinetic equation which in practice is very close to the simple Kw expression (25, 57) uses a 6900 cal/g mol over the entire temperature range (525 - 900°F).

Finally, one needs to know the effect of catalyst particle size on Kw. For a pore diffusion controlled reaction activity should be inversely proportional to catalyst particle diameter; that is, directly proportional to external catalyst surface area.

Several studies (48, 50, 51) show that above 400°F, pore diffusion will control catalyst activity if the particle diameter is above .02 to .03 in. This is far below any practical commercial catalyst particle diameter.

In this investigation (Table 8) values of Kw for CO hydrogenation were found to be dependent on the 0.9 power of the reciprocal of the particle diameter. In view of this, and the literature results, a linear (first power) dependence on reciprocal of particle diameter was used in the Kw expression. Measurement accuracy is certainly insufficient to distinguish between a 0.9 and 1.0 power dependence.

If KWS is a standard value of Kw at a base temperature in °Rankine (TB), a base absolute pressure, PB, and a base catalyst particle diameter, DB, then, at other values of temperature (°R=T), and pressure, P, and catalyst diameter D,

$$K_W = K_{WS} \sqrt{\frac{P}{P_B}} \times \frac{D_B}{D} \times F_W \times 10^{-.3934 \Delta H \left( \frac{1}{T} - \frac{1}{T_B} \right)} \quad (10)$$

FW in commercial reactors is near one; it is the ratio of number of catalyst tablets per cubic foot to the number per cubic foot one would have in a reactor of infinite diameter. P and PB, and D and DB must be in consistent units.

Where two activation energies are used, TB should be the temperature at which the change is introduced. Thus, in our system TB is 1159.67 (700°F), and 2000 is used for Delta H if T > 1159.67, and 5000 if T < 1159.67.

The value used for PB is one atmosphere, and since activity calculations are made by computing the square feet of catalyst area per cubic foot of catalyst, this amounts to using a standard DB of 45.144 inches in a reactor of infinite diameter.

Where DV is vessel diameter (in the same units as D),

$$F_W = 1 - .4912 D/DV \quad (11)$$

A characteristic of most equations for surface controlled kinetics, as opposed to diffusion controlled kinetics, is a number of partial pressure terms, often to high powers. When large changes in partial pressures are made, differences between observed and calculated reaction can easily equal a factor of 1000 or more. Where diffusion type kinetics are used, one seldom finds differences of more than a factor or two or three. While this may not seem very accurate, the comparison between the two methods can be rather startling.

Table 19 compares activities of two catalysts, C150-1-01 and another commercial catalyst. First, from literature data, a catalyst activity is obtained using their kinetics, and another by using equation (5). Then, from typical data taken on the C150-1-01 catalyst, the same procedure is followed. Table 19 reports the activity ratios that are obtained.

It is evident that the equation for reference 1 has broken down completely for CO hydrogenation. The other equations for CO hydrogenation give correlations similar to those obtained by the simple kinetics. These equations are all, however, of relatively simple form. They use low activation energies, and in general, would show an activity dependence on the square root of the pressure, similar to that of the simple kinetics.

For the CO<sub>2</sub> kinetics, the literature kinetics gives more reasonable correlation than the simple, though the difference is not great. However, reference 4 involves methanation of over 50% CO<sub>2</sub> in H<sub>2</sub>, under conditions where equation (3) would break down, and 12 involves only the initial hydrogenation (less than the first one or two percent) of the CO<sub>2</sub> present. Furthermore, there is a possibility that the reverse shift would produce enough CO to poison the CO<sub>2</sub> methanation in these experiments, which would make it difficult to obtain agreement between various runs.

TABLE 19

## RATIO OF C150-1-01/OTHER COMMERCIAL CATALYST

Reference	Reactant	Literature Equation	Activity Ratio, Literature Equation	Activity Ratio, Equation 3, Approximation Equation 5
1	CO	$r = \frac{pCOpH_2^3}{(A+BpCO+DpCO_2^4 + EpCH_4)}$	9000	5.8
33	CO	$r = \frac{1.1pCOpH_2}{1 + 1.5pH_2}$	$1/2$ 1.2	2.3
2	CO	$r = \frac{KpCOpH_2}{1+K_2pH_2+K_3pCH_4}$	$1/2$ 2.3	2.6
4	CO <sub>2</sub>	$r = \frac{C_1pCO_2pH_2^2}{(pH_2^{1/2}+C_pCO_2+C_3)}$	2.2	3.9
12	CO <sub>2</sub>	$r = \frac{kpCO_2pH_2^4}{(1+K_1pH_2+K_2pCO_2)^5}$	6.2	13.1

A number of measurements made on the methanation of  $\text{CO}_2$  may be correlated using equations (5) and (10), with the same values of  $\Delta H$  as for the CO hydrogenation. Based on diffusion considerations, the value of KWS for  $\text{CO}_2$  hydrogenation was taken as 0.8 of that for CO.

Attempts were made to correlate data where both CO and  $\text{CO}_2$  were methanated, using simple diffusion for both, with the  $\text{CO}_2$  rate set at 80% of the CO rate. In order to get good agreement with experimental data it is necessary to introduce a variable water-gas shift reaction activity.

An examination of some laboratory runs with diluted C150-1-02 catalyst can illustrate this problem. In one run, with 579°F inlet, 598°F exit, 97297 outlet dry gas space velocity, the following results were obtained after minor corrections for analytical errors. 99.9885 percent of the CO present (out of an inlet 2.04 mol %) disappeared in reaction, while the  $\text{CO}_2$  present (from an initial 1.96%), increased by over 30%. Equilibrium carbon oxides for both methanation reactions was essentially zero, while the equilibrium CO based on the water-gas shift reaction at the exit composition, was about one-third of the actual CO exit of 0.03 mol %. From these data activities for the various reactions may be estimated, based on various assumptions. Table 20 shows the effect of two differing assumptions.

TABLE 20

Water-Gas Shift Kw	350000	50000
$\text{CO}_2$ Methanation Kw	56000	0
CO Methanation Kw	70000	150000

For the first assumption, the value of Kw for shift appears too high. It must be this high because of the necessity of making  $\text{CO}_2$  appear while both  $\text{CO}_2$  and CO are being consumed rapidly by methanation. The data may be tested to see if the indicated rate appears unreasonable from the standpoint of mass transfer to the gross catalyst surface.

Regardless of the rate of diffusion in catalyst pores, or the surface reaction rate, it is unlikely that reaction can proceed more rapidly than material can get to the gross pill surface unless the reaction is a homogeneous one, catalyzed by free radicals strewn from the catalyst into the gas stream.

The following equation has been derived for testing mass transfer limitation to the gross catalyst particle (56).

$$Kw = \frac{8100}{D} \sqrt{\frac{L \times SVW}{M \times D \times T}} \quad (12)$$

Here M is average molecular weight of the gas, T is temperature in °Rankine, D is catalyst particle diameter, inches, and L is bed depth in feet. For this calculation, involving a diluted bed, SVW and L must be computed as if all of the active catalyst were gathered into one place. In this experiment L is then .02 feet, SVW is 130000 (counting the steam present), D is .078 in., M is about 16, and T is 1048. This leads to a limiting Kw of about 150000.

Although 150000 is somewhat of an average value of expected maximum Kw, and uncertainties in the computations make the minimum Kw about 15000, below which no mass transfer to gross surface could be expected to be limiting, whereas the maximum possible Kw might be over 1000000, assumption 2 certainly gives the more reasonable explanation of the data.

Many references discuss the inhibition of CO<sub>2</sub> methanation by CO (15, 30, 37, 42, 48, 49, 51). At 320°F, and 300 psig, there is indication that as little as 65 ppm of CO would stop CO<sub>2</sub> methanation (51). Under atmospheric pressure, with .015 inch catalyst (48) CO poisoning of CO<sub>2</sub> methanation was shown with 200 ppm of CO, at up to 446°F.

It is to be expected that the poisoning of the CO<sub>2</sub> methanation by CO will be observed at lower CO concentrations when catalyst particle diameters are smaller. This is because the smaller particle will be poisoned throughout, whereas at some depth in the pores of larger sized catalyst the poisoning effect will drop off, and some significant methanation of CO<sub>2</sub> be permitted to take place. It is noteworthy that the only results in this investigation, such as those considered in Table II, where poisoning was likely at very low CO concentrations, were obtained with very small catalyst particles.

It is concluded that a fully satisfactory system for calculating simultaneous reactions of CO and CO<sub>2</sub> with H<sub>2</sub> and H<sub>2</sub>O will require a schedule of the effect of CO on CO<sub>2</sub> methanation as a function of temperature. This effect will probably be different with different particle sizes. From a commercial standpoint the possible size range may be too small to require much difference in the treatment, but in laboratory somewhat lower than the CO methanation rate. A simple kinetics system, such as that derived from equation (3), may be satisfactory for all the reactions. It is unlikely that reliable data will soon be collected for the shift reaction (since it is of a somewhat secondary nature and difficult to study by itself) to justify a more complicated treatment.

For CO methanation one of the simple literature kinetic systems (25, 57) should be as reliable or better than the one used in this study. With CO<sub>2</sub> methanation it is less certain that a simple system is indicated. It is probably of more urgency to elucidate the quantitative effect of the CO on the CO<sub>2</sub> methanation than to find a complex kinetic expression for the CO<sub>2</sub>-H<sub>2</sub> reaction itself.

It is expected that the actual rate of CO methanation will always be high, at least under industrial conditions, whereas the CO<sub>2</sub> methanation rate will vary from about the same as the CO rate down to zero, depending on the operating pressure, temperature, CO content of the gas, and catalyst particle size. Meanwhile a water-gas shift (or reverse shift) reaction will be going on at all times at a fairly high rate.

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