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I Summary

During the month of August, work on the methanation project focused mainly on the initiation of the catalyst – liquid scan, as well as implementation of several system improvements; such as the high pressure rotameter and the differential pressure meter.

Using the Penndrake Code 4417 white mineral oil in connection with Girdler G65 – RS, Catalyst and Chemicals XC150-02, and Harshaw Ni -0104- 101 catalysts, we investigated the effect of temperature, liquid flow rate and gas flow rate on the reaction system. The experimental results indicate that

- all three catalysts have the desired selectivity and activity for the rapid reaction of CO and H_2 to produce methane.
- At temperatures slightly above 300°C, total pressure of 800 psig and VHSV's ranging from 500 to 1000 hrs^{-1} conversions in the 80-90% range have been attained.
- A reaction rate constant, assuming ideal plug flow and a rate of reaction first order in CO have been calculated. The rate constant increases with temperature and liquid flow rate.

However, the effect of gas flow rate is not so clear. The rate constant increases with increased gas flow rate with the CCI catalyst, but decreases with the other two catalysts. Carbon dioxide is produced to a small extent, about 1-3% of the water-free effluent, by all of the catalysts. The Girdler catalyst seems to require temperatures 40 to 50°C higher to reach the same conversion level attained with the CCI and Harshaw catalyst. The lower nickel content of the former may explain this difference since the rate constant calculated for all the catalysts are quite similar when expressed in terms of metal content of the catalyst.

II Introduction

During the month of August we initiated the catalyst - liquid scan as proposed at the July Project Review meeting. The liquid phase for this set of runs was Penndrake Code 4417 white mineral oil; the catalysts were Girdler G65 -RS, Catalyst and Chemical XC150-02, and Harshaw Ni -0104 - 101. All three catalysts were ground to 30-50 mesh and treated with hydrogen for at least 24 hours at 350-400°C. In addition, several improvements, as proposed in Progress Report #3, have been implemented. A discussion of these improvements as well as a more detailed examination of the experimental result follows:

II. System Improvements

1. Sample loop size in the Carle chromatograph was reduced to 200μl in order to eliminate errors due to column over loading. This problem arises because of the high methane concentrations in the product stream.

2. An atmospheric, low temperature (0°C) liquid-gas separator was added to the system to remove product water vapor and small amounts of liquid phase carryover. This is doubly important because water adversely effects the quantitative separation of components by the molecular sieve column.

3. A high pressure rotameter was added so as to insure accurate control of the gas flow in the reactor.

4. Addition of the differential pressure cell allows us to follow the progress of fluidization, since it will be possible to determine incipient fluidization and therefore more accurately determine bed expansions. Preliminary results indicate that fluidization occurs when the pressure drop is 85% of

the theoretical value for a liquid-only fluidized bed. This is in line with the results reported in Progress Report #2.

5. We have made changes in the piping system, so that pump suction draws from several inches above the bottom of the high pressure liquid - vapor separator. This is to prevent the pumping of any condensed water phase directly into the catalyst bed. The condensed water can result when the gas - liquid separation unit is cooled down after a days run. The catalyst manufacturers have noted that water can temporarily deactivate the catalyst due to adsorption on the catalyst active sites.

6. After several discussions with the catalyst manufacturers we have ascertained that the addition of nitrogen to the system will present no problem with respect to the formation of ammonia. In fact, nitrogen is the recommended gas whenever turning down a commercial methanation unit. An extra benefit is using a nitrogen purge rather than a hydrogen purge in the reduced time for the effluent gas to reach equilibrium concentrations.

III. Discussion of Results

After the initial work with the Girdler G65-RS Catalyst, an experimental program was initiated. In essence what was attempted was to carry out a temperature, flow-rate scan during the course of a week. A day for start up and another day for shut down was necessary thus leaving three days to carry out the experiments. During these three days the following experiments were carried out.

Day 1 - Temperature scan at low gas flow rate and low liquid flow rate

Day 2 - Temperature scan at low gas flow rate and high liquid flow rate

Day 3 - Repeat for first datum point of Day 1 followed by a temperature scan at high gas and low liquid flow.

The full data sheets are given in Appendix 1. The important data have been extracted and are presented in Tables 1 through 3 and Figures 1 through 3 for the three liquid - catalyst systems.

In order to examine the data in a systematic fashion, we have assumed ideal plug-flow in the reactor and a reaction rate first order in CO concentration, as a preliminary model. The integrated rate equation results in the following expression for the rate constant.

$$K = \text{VHSV} \quad \log\left(\frac{C_o}{C}\right)$$

where VHSV and K are given in units of $\frac{ft^3 \text{ gas @ STP}}{ft^3 \text{ fluidized bed-hr}}$ and C over C_o can be in any consistent concentration units. At constant pressure, mole fractions are the most convenient units to use in the concentration ratio expression. The feed concentration is known, and the reactor exit concentration may be evaluated by the following procedure.

Let the component formula represent its concentration in the effluent, in mole percent, as measured by the chromatograph. Since we trap out product water before entering the chromatograph, the actual component concentration in the reactor is lower than that measured by the chromatograph. We can account for this difference by calculating the theoretical water produced during the following reactions to the measured products:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$2CO + 5H_2 \longrightarrow C_2H_6 + 2H_2O$$

$$3CO + 7H_2 \longrightarrow C_3H_8 + 3H_2O$$

$$CO + H_2O \longrightarrow H_2 + CO_2$$

The resulting expression for the actual reactor exit concentration is then

$$X_{\substack{\text{reactor}\\ \text{exit}}} = \left[\frac{[CO + H_2 + CH_4 + C_2H_6 + C_3H_8 + CO_2]}{[CO + H_2 + CH_4 + C_2H_6 + C_3H_8 + CO_2] + [CH_4 + 2C_2H_6 + 3C_3H_8 - CO_2]}\right] X_{\text{chromatograph}}$$

By this procedure, it is possible to calculate the concentration of each component in the reactor and thus estimate rate constants. It should be noted that the rate constants are based on a volumetric gas flow at STP, and not at reaction pressure and temperature. This simplification is valid for the results presented in this report in which the total pressure was constant and the liquid phase has a negligible vapor pressure. Under varying pressure and temperatures and when liquids with a substantial vapor pressure are used this assumption is probably not valid.

As shown in Appendix I; conversions based both on CO consumed and methane produced are given. The difference between these two is a measure of the system's selectivity. In calculating the above mentioned conversions it is assumed that all the carbon seen in the effluent is balanced by the carbon fed in the gas feed. Thus carbon deposition and liquid degradation is assumed to be negligible. A check on this assumption is made via a hydrogen balance which is reported as the molar ratio of hydrogen in the gas feed to the hydrogen in the product gas. In most experiments the carbon and hydrogen balances are very close.

Another means to check the accuracy of the material balance as well as a mean to instantly ascertain more or less what conversion level is being attained is to compare inlet and outlet gas flow since the shrinkage in volumes is directly related to the conversion. All of these checks and balances are being used to monitor the reaction and to detect any unusual behavior of the system.

System I: Penndrake Code 4417 + Girdler G65-RS

The result for runs 50-26-1, 50-27-2 were briefly presented in Progress Report #3. In addition we completed several runs with a second charge of the catalyst - runs 50-28 and 50-29. The results are presented in Table 1 and Figure 1. Since these data had been taken before the program had been formalized, the reactions conditions are somewhat haphazardly distributed. It is apparent, however, that increase liquid and gas flow significantly increased the rate constant. This might result from a combination of increased mass transfer rates as well as a reduction in back mixing. It is also readly apparent from the data that temperature has a noticeable effect on the rate constant.

Table 1

Experimental Data

Girdler G65-RS (27% Ni)

(193 grams of catalyst)

Run	T	L*	V	VHSV	Rate		Rate Constants		
					lb-moles/hr-ft^3				
#	°C	gal/min-ft^2	L/hr.	hrs^{-1}	CO	CH_4	K_1	K_2	K_3
50-26-1	320	14.75	200	842	367	346	310	6.09	22.6
50-27-1	320	29.50	250	878	453	371	478	11.2	41.7
50-27-2	320	29.50	400	1338	494	412	313	7.75	28.7
50-28-1**	330	29.91	168	941	518	496	606	15.7	58.1
50-28-2**	340	30.24	398	2158	869	794	604	16.0	60.0
50-29-1**	300	21.26	70	420	236	227	313	7.59	28.1

$K_1 = ft^3$ gas/ft^3 of fluidized bed -hr

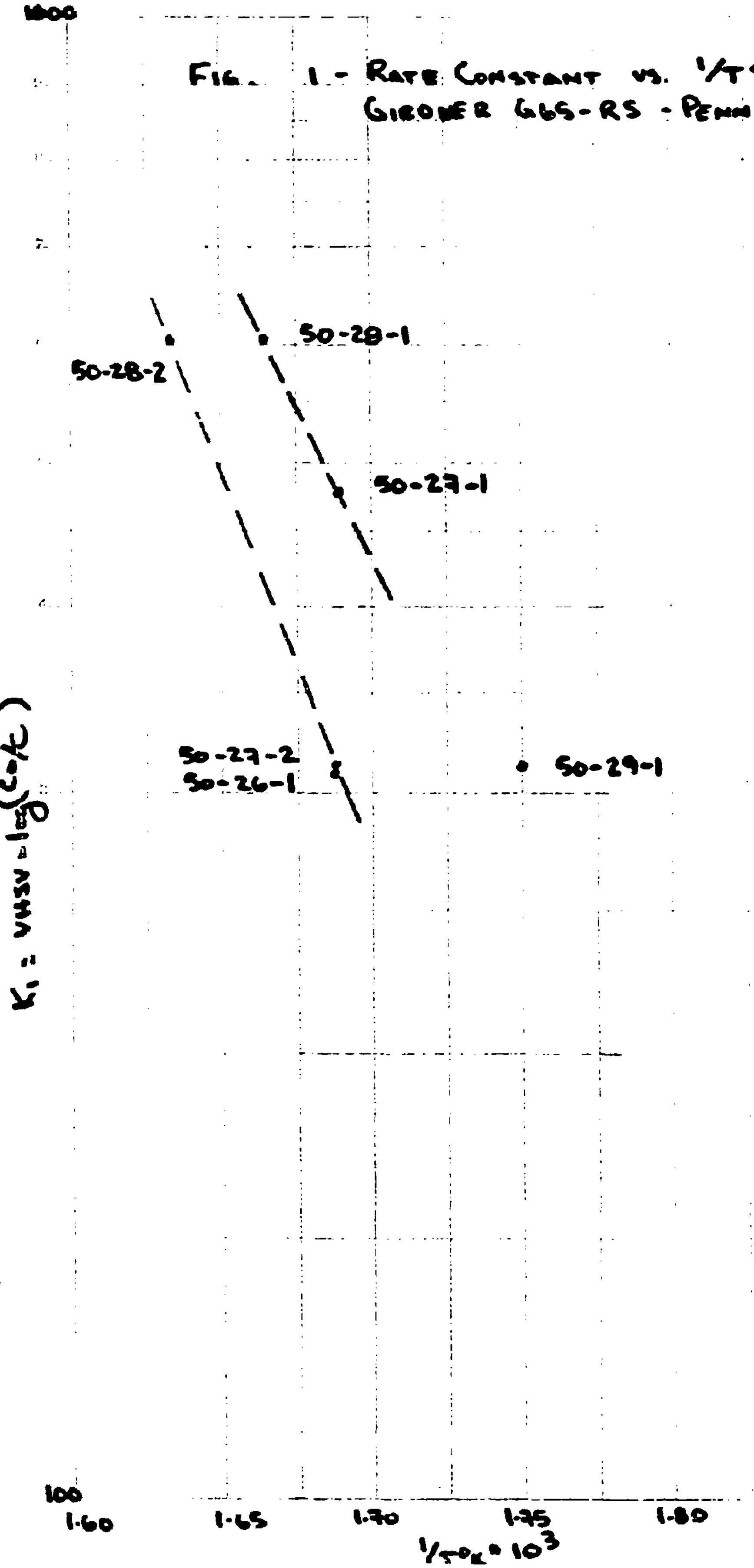
$K_2 = ft^3$ gas/lb of catalyst -hr

$K_3 = ft^3$ gas/lb of metal -hr

* - This is the liquid flow rate in gallons/min - cross sectional area

** - A new batch of catalyst was used with a total weight of 110 grams

FIG. 1 - RATE CONSTANT VS. 1/T°K
GIRDLER G65-RS - PENNDRAKE CODE 4417



System 2: Penndrake Code 4417 + CCI XC150-02

The results (Table 2 and Figure 2) for this catalysts follow the same trends observed previously with respect to temperature and flow rate. Temperature dependence is detailed in the series of Runs 50-30-1, 50-30-2, and the series 50-31-1 and 50-31-2. The curve in the 50-30 series is apparently due to the substantial CO_2 produced in Run 50-30-3, over 6%, which is almost 4 times the amount produced at the next lower temperature. The effect of liquid flow rate probably overstated by the comparison of the 50-30 runs (low liquid flow rate) with the 50-31 runs (high liquid flow rate), because close observation will show that Run 50-32-1 duplicates the conditions of Run 50-30-1, yet the K value is substantially higher. This seems to be an indication that the catalyst has become more active during the course of the tests. It is possible that the catalyst lost some of its activity by oxidation during the brief period in which the reduced catalyst was weighed prior to loading. The oxidized surface may very well have been reactivated during the initial runs causing the observed increase in activity at a later point.

Table 2

CCI XC -15- -02 (58% Ni)

(160 grams of catalyst)

Run	T	L*	V	VHSV	Rate		Rate Constants		
					lb-moles/hr-ft^3				
#	°C	gal/min-ft^2	L/hr.	hrs^{-1}	CO	CH_4	K_1	K_2	K_3
50-30-1	276	8.90	195	943	439	427	359	7.46	12.9
50-30-2	301	9.06	195	948	487	467	459	9.49	16.4
50-30-3	320	9.24	195	952	544	487	665	13.7	23.6
50-31-1	276	20.61	200	793	458	436	611	15.5	26.7
50-31-2	299	21.07	205	806	503	486	1097	27.4	47.2
50-32-1	277	8.96	205	992	508	483	500	10.4	17.9
50-32-2	278	8.93	413	1895	771	701	542	11.9	20.5

$K_1 = ft^3$ gas/ft^3 of fluidized bed -hr

$K_2 = ft^3$ gas/lb of catalyst -hr

$K_3 = ft^3$ gas/ lb of metal -hr

* - liquid flow in gal/min-cross sectional area

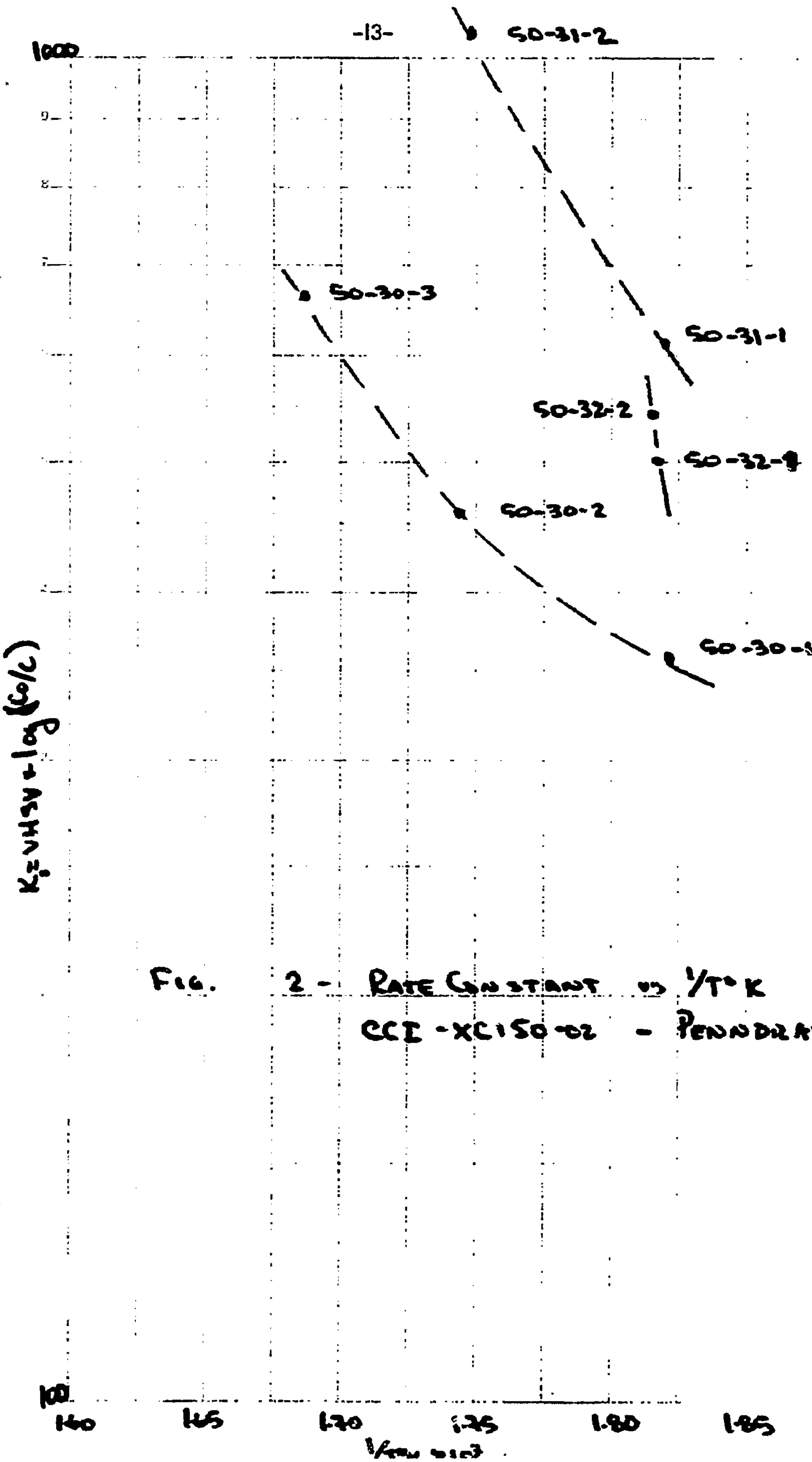


FIG. 2 - RATE CONSTANT vs 1/T° K
CCI-XC150-02 - PENNDRAKE CODE 4417

System 3: Penndrake Code 4417 - Harshaw Ni -0104- 101

The results (Table 3 and Figure 3) for the Harshaw catalyst are similar in value and trend to the CCI catalyst. Temperature dependence is detailed by the series of Runs 50-33-1, 50-33-2, and 50-33-3. The second series of Runs, 50-34, at the high liquid flow rate, unfortunately show no temperature dependence. We tend to attribute this to some deactivation process occuring during the days run. This hypothesis is supported by the significant drop in K value as exemplified by a comparision of Run 50-35-2 with the early Run 50-33-2. The cause of the deactivation is not yet known, though water adsorption on the catalyst might be a possible reason for the loss in activity. Additional data are necessary prior to fully ascertaining if catalyst activity is decreasing in our system.

Table 3
Harshaw Ni 0104 -101 (58%Ni)
(262 grams catalyst)

Run	T	L*	V	VHSV	Rate lb-moles/hr-ft^3		Rate Constants		
#	°C	gal/min-ft^2	L/hr.	hrs^{-1}	CO	CH_4	K_1	K_2	K_3
50-33-1	275	8.88	205	950	479	450	454	5.99	10.3
50-33-2	294	9.08	205	950	527	497	638	8.41	14.5
50-33-3	318	9.74	205	950	569	543	912	12.0	20.7
50-34-1	271	20.64	200	762	428	398	536	8.59	14.8
50-34-2	296	21.13	200	762	433	406	561	9.00	15.5
50-34-3	321	21.50	200	774	440	413	564	9.04	15.6
50-35-1	247	8.68	200	917	157	138	715	0.958	1.65
50-35-2	290	9.04	200	926	458	412	424	5.60	9.65
50-35-3	296	9.11	392	1817	661	581	440	5.80	10.0

K_1 = ft^3 gas/ft^3 fluidized bed -hr
K_2 = ft^3 gas/lb of catalyst -hr
K_3 = ft^3 gas/lb of metal -hr

* - liquid flow in gal/min-cross sectional area

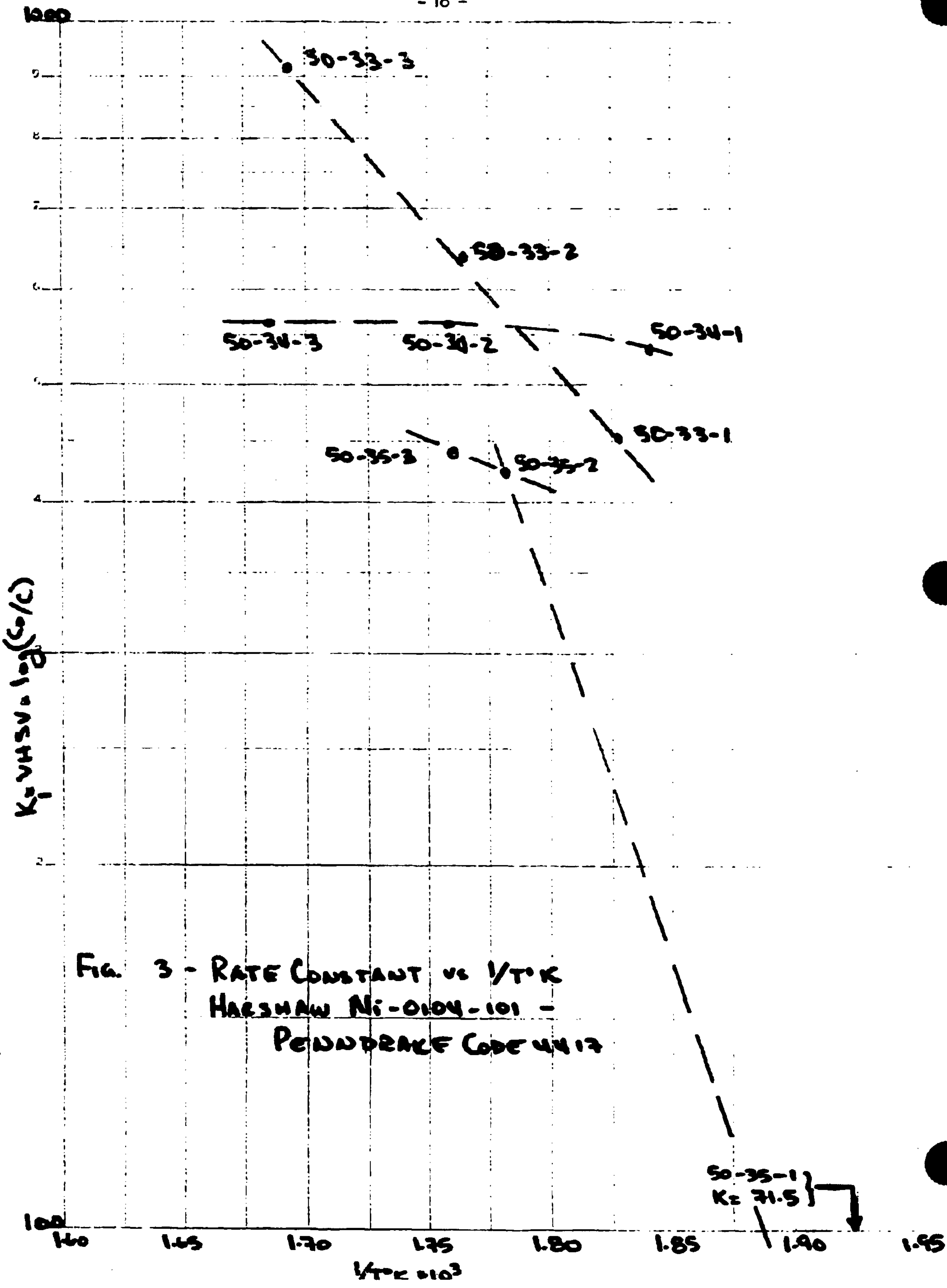


FIG. 3 - RATE CONSTANT vs 1/T°K
HARSHAW Ni-0104-101 -
PENNDRAKE CODE 4417

The data presented in the first three figures show a considerable scatter namely because of the varying liquid and gas flow rates. The effect of these two flow variables on the pseudo reaction rate constant is not unexpected in fluidized systems, particularly those in which gas and liquid are present along with the catalyst.

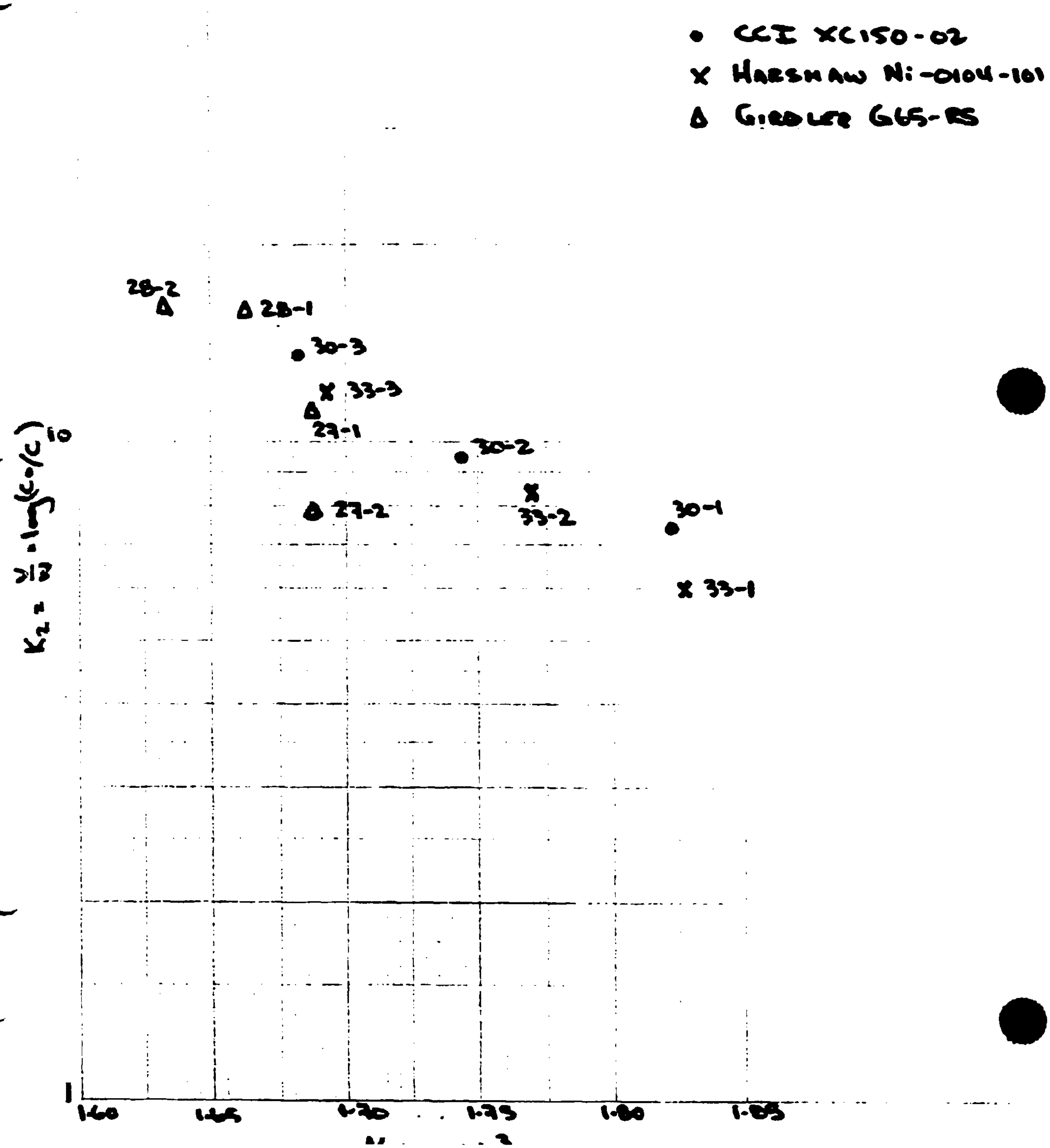
As indicated in Figure 4 and 5 a close correlation can be obtained if only those data points at similar liquid flow rates are considered. For the CCI and Harshaw catalysts the points chosen were for liquid flow rates of about 9 gallons/min-ft^2 and for the Girdler catalyst the liquid rate was close to 30 gallons/min-ft^2.

The first thing to notice is that the rate constant are pretty similar for all systems studied. This, to a certain extent, is not unexpected since all the catalysts are commercially used and clearly Girdler, CCI and Harshaw are selling catalysts of similar properities. The possibility that the similarity of rate constant is due to the fact that the system is mass transfer limited, or affected by mass transfer considerations cannot be disregarded. There are two experimental facts that seem to indicate a mass transfer affected system. Firstly, the relatively low energy of activation of the system and secondly, the noticeable effect of liquid flow rate.

At this point it is too early to clearly ascertain the effect of the flow variables. The second liquid scan will provide us with substantially more data ideally suited for evaluating the effect of mass transfer on the reaction. We will continue to evaluate in the future various rate expressions based both on reaction kinetics and mass transfer mechanisms, since the present model is too simplistic to explain all the experimental facts.

100 $K_2 \left[\frac{ft^3 \quad hr}{\# CATALYST-HR} \right]$ vs $1/T$ °K

FIGURE 4



K [[illegible]] vs 1/T°K

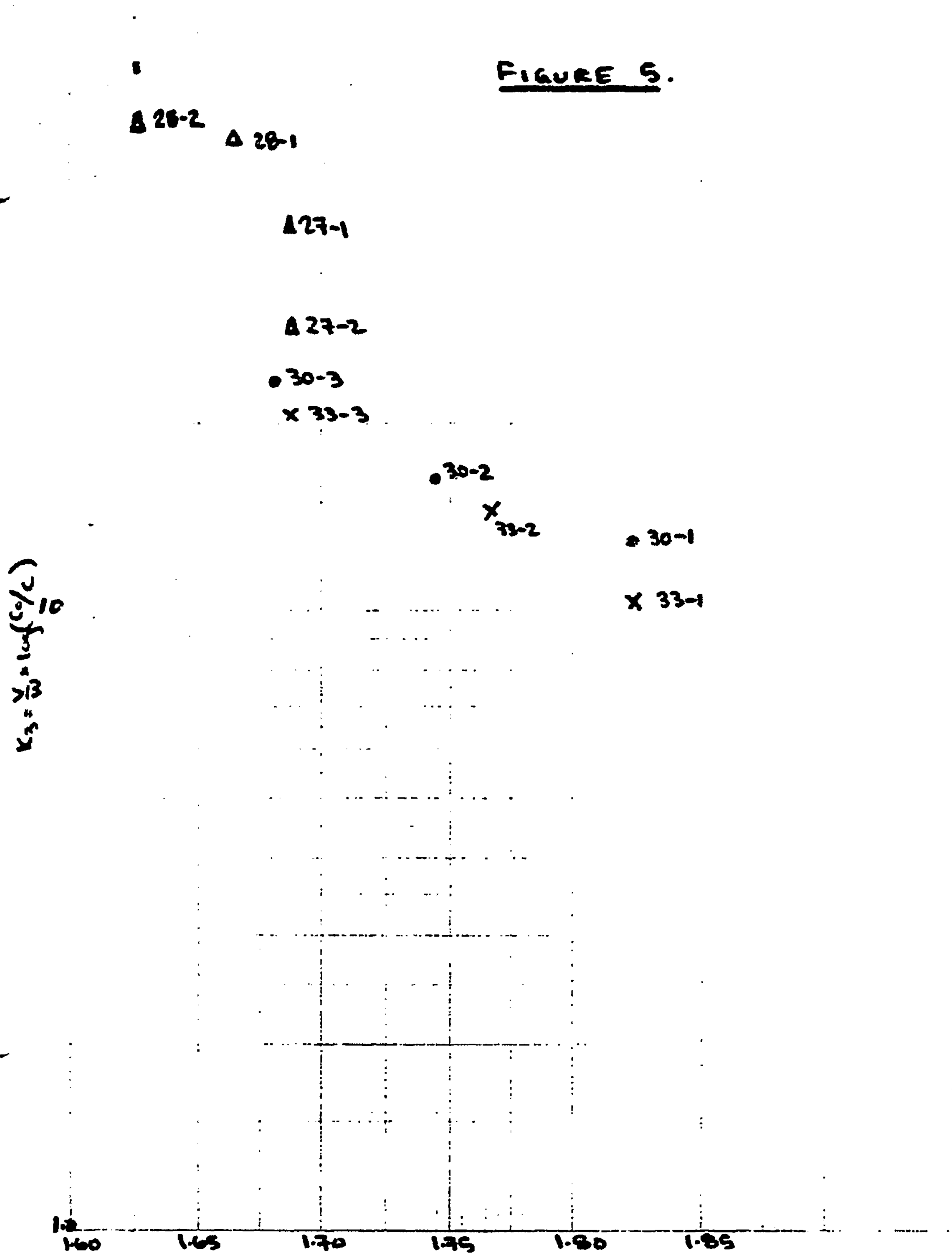


FIGURE 5.

IV. Future Program

In the coming six weeks we plan to finalize the catalyst liquid scan and thus arrive at the second milestone of our process development.

The high pressure – variable flow pump arrived at the end of August but it has not been put to use because of a small defect in the housing which causes it to buckle under pressure. The pump should be ready to use by September 15. At this point the following system will be evaluated.

System	Liquid	Catalyst	Variables to Investigate	Termination Date of Evaluation
1	Pseudocumene	Girdler	Temperature, Gas and Liquid Flow	9/22
2	Pseudocumene	CCI	"	9/30
3	Dowtherm	Harshaw	"	10/6
4	Dowtherm	Girdler	"	10/13
5	Best Combination of Liquid and Catalyst		"	10/27

At the completion of this experimental program, a realistic choice of catalyst and liquid can be made to initiate the third and last portion of the experimental program envisioned for Phase 1 of this project.

The results up to date are very encouraging since a number of catalysts have performed quite satisfactorily using a paraffinic oil as the recirculating liquid. On looking at the proposed time table to this project, it is clear that we must start our efforts on the design and procurement of the equipment needed for the process development unit. During the month of September it is planned to contact the vendors and contractors to get a better estimate of the lag time required to deliver equipment in the coming six months. Our preliminary process design figures will be updated based on the present experimental results which fortunately closely parallels the results predicted at the time that the research proposal was prepared.

In conjunction with these efforts, the data generation and analysis will be simplified by making use of an area integrator and a mini-computer; the goal being to automatically calculate feed and effluent compositions, conversion, selectivity and rates of reaction directly from the chromatograms.

Finally, in order to maximize the use of the present experimental unit, a staggered work schedule is being considered and probably will go into effect at the end of the month.

Run Number	50-. 1
Date	7/25
Operator	
Catalyst	Girdler G65-RS
Liquid	Penndrake Code 4417

Reactor Diameter; .ches	0.81 with a 1/8" thermow
Reactor Length; inches	480
Settled Bed Height; inches	240
Catalyst Weight; grams	193.5
Catalyst Size	30-50 mesh
Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	14.75			
Inlet Gas Flow; liters*/hr	200 (Approximate)			
Outlet Gas Flow; liters*/hr	115 (Approximate)			
Feed Gas Composition; Vol. %				
H_2	75			
CO	25			
Other	--			
Pressure; psig	800			
Estimated Catalyst Bed Height; inches	28.80			

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	306			
3	0	320			
6	3				
12	9	320			
18	15				
24	21	320			
30	27				
36	33	320			
42	39				
48	45	320			

Pressure Drop; psi				
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	842			
Outlet Gas Concentration; Vol. %				
H_2	51.0			
CO	12.25			
CH_4	25.0			
CO_2	1.0			
N_2	---			
Other H_2O	balance			
Other $C_2H_6 + C_3H_8$	0.3			
% Conversion Based On: CO	68.4			
CH_4	64.5			
moles H_2 in/moles H_2 accounted for in products	0.924			
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	.346			
Lb-moles CO/hr-ft^3 of Fluidized Bed	0.367			

*25°C, 1 atm

Run Number	50-27-1	Reactor Diameter; inches	0.81 with a 1/3" thermowell
Date	7/26	Reactor Length; inches	48.0
Operator		Settled Bed Height; inches	24.0
Catalyst	Girdler G65-RS	Catalyst Weight; grams	193 5
Liquid	Penndrake Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	29.50	29.50		
Inlet Gas Flow; liters*/hr	250 (Approximate)	400 (Approximate)		
Outlet Gas Flow; liters*/hr	105 (Approximate)	230 (Approximate)		
Feed Gas Composition; Vol. %				
H_2	75.	75.		
CO	25.	25.		
Other	--	--		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	34.56	36.29		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	306	306		
3	0	320	320		
6	3				
12	9	320	320		
18	15				
24	21	320	320		
30	27				
36	33	320	320		
42	39				
48	45	320	320		

Pressure Drop; psi	---	---		
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	878	1338		
Outlet Gas Concentration; Vol. %				
H_2	46.5	54.0		
CO	8.1	15.7		
CH_4	28.0	18.0		
CO_2	4.0	2.2		
N_2	---	---		
Other H_2O	balance	balance		
Other $C_2H_6 + C_3H_8$	0.9	0.6		
Conversion Based On: CO	80.8	57.9		
CH_4	66.3	48.3		
moles H_2 in/moles H_2 accounted for in products	0.959	1.027		
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	.371	0.412		
Lb-moles CO/hr-ft^3 of Fluidized Bed	.453	.494		

*25°C, 1 atm

Run Number	50-28 2	Reactor Diameter; inches	0.8 with a 1/8" thermowell
Date	8/11	Reactor Length; inches	480
Operator		Settled Bed Height; inches	150
Catalyst	Girdler G65-RS	Catalyst Weight; grams	110
Liquid	Penndroke Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	29.91	30.24		
Inlet Gas Flow; liters*/hr	165-170 (Approximate)	395-400 (Approximate		
Outlet Gas Flow; liters*/hr	55-58	185		
Feed Gas Composition; Vol. %				
H_2	75.	75.		
CO	25.	25.		
Other	--	--		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	21.60	22.35		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	307	---		
3	0	332	340		
6	3				
12	9	331	340		
18	15				
24	21	327	340		
30	27				
36	33	324	336		
42	39				
48	45	322	322		

Pressure Drop; psi	---	---		
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	941	2158		
Outlet Gas Concentration; Vol. %	40.0	56.0		
H_2 (was also used as purge)				
CO	9.1	16.3		
CH_4	55.0	25.5		
CO_2	1.6	1.7		
N_2	---	---		
Other $C_2H_6 + C_3H_8$	0.4	0.3		
Other	---	---		
Conversion Based On: CO	86.3	63.1		
CH_4	82.6	57.7		
moles H_2 in/moles H_2 accounted for in product	0.971	1.002		
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.496	0.794		
*25°C, 1 atm — Lb-moles CO/hr-ft^3 of Fluidized Bed	0.518	.869		

Run Number	50-29-1	Reactor Diameter; inches	0.81 with a 1/8" thermowell
Date	8/14	Reactor Length; inches	480
Operator		Settled Bed Height; inches	15.0
Catalyst	G65-RS Girdler	Catalyst Weight; grams	110
Liquid	Penndrake Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	

Liquid Flow; $gal/min\text{-}ft^2$	21.26			
Inlet Gas Flow; liters*/hr	70 Nominal			
Outlet Gas Flow; liters*/hr	35			
Feed Gas Composition; Vol. %				
H_2	75.			
CO	25.			
Other	---			
Pressure; psig	800			
Estimated Catalyst Bed Height; inches	20.25			

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	---			
3	0	---			
6	3				
12	9	300			
18	15				
24	21	---			
30	27				
36	33	---			
42	39				
48	45	---			

Pressure Drop; psi	---			
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	420			
Outlet Gas Concentration; Vol. %				
H_2	44.0			
CO	6.5			
CH_4	46.5			
CO_2	1.0			
N_2	---			
Other $C_2H_6 + C_3H_8$	0.4			
Other	---			
% Conversion Based On: CO	88.1			
CH_4	84.7			
moles H_2 in/moles H_2 accounted for in product	0.894			
Overall Reactor Rate; Lb-moles $CH_4/hr\text{-}ft^3$ of Fluidized Bed	.227			
Lb-moles $CO/hr\text{-}ft^3$ of Fluidized Bed	.236			

*25°C, 1 atm

Run Number	50-30-1,2,3	Reactor Diameter; inches	0.81 with a 1/8" thermowell
Date	8/23	Reactor Length; inches	48.0
Operator		Settled Bed Height; inches	23.0
Catalyst	CCI XC150 -0-	Catalyst Weight; grams	159.4
Liquid	Penndrake Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	8.90	9.06	9.24	
Inlet Gas Flow; liters*/hr	19.5	195	195	
Outlet Gas Flow; liters*/hr	80-89	71-80	----	
Feed Gas Composition; Vol. %				
H_2	75	75	75	
CO	25	25	25	
Other	--	--	--	
Pressure; psig	820	835	800	
Estimated Catalyst Bed Height; inches	20.07	24.96	24.85	

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	212	234	254	
3	0	276	299	322	
6	3				
12	9	276	301	320	
18	15				
24	21	277	303	318	
30	27				
36	33	277	304	320	
42	39				
48	45	274	297	311	

Pressure Drop; psi	---	---	---	
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	943.	948	952	
Outlet Gas Concentration; Vol. %				
H_2	48.0	39.0	27.0	
CO	14.3	12.0	7.7	
CH_4	37.5	47.5	59.0	
CO_2	0.6	1.6	6.2	
N_2	3.0	1.5	1.2	
Other $C_2H_2+C_3H_8$	0.2	0.2	0.3	
Other -				
% Conversion Based On: CO	72.9	80.5	89.5	
% Conversion Based On: CH_4	71.0	77.2	80.2	
moles H_2 in/moles H_2 accounted for in product	0.984	1.008	1.083	
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	.427	0.467	0.487	
Lb-moles CO/hr-ft^3 of Fluidized Bed	.439	0.487	.544	

*25°C, 1 atm

Run Number	50-31-1,2
Date	8/24
Operator	
Catalyst	CCI XC150-02
Liquid	Penndrake Code 4417
Reactor Diameter; inches	0.81 with a 1/8" thermowell
Reactor Length; inches	48.0
Settled Bed Height; inches	23.0
Catalyst Weight; grams	159.4
Catalyst Size	30-50 mesh
Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	20.61	21.07		
Inlet Gas Flow; liters*/hr	200	200		
Outlet Gas Flow; liters*/hr	66	53-58		
Feed Gas Composition; Vol. %				
H_2	75	75		
CO	25	25		
Other	--	--		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	30.59	30.13		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
0	-	---		228					
3	0	277		300					
6	3								
12	9	276		299					
18	15								
24	21	275		289					
30	27								
36	33	273		296					
42	39								
48	45	270		293					

Pressure Drop; psi	---	---		
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	793	806		
Outlet Gas Concentration; Vol. %				
H_2	25.5	16.0		
CO	6.5	2.0		
CH_4	59.0	83.5		
CO_2	0.7	0.7		
N_2	11.8	0.8		
Other $C_2H_6 + C_3H_8$	1.0	1.0		
Other	--	---		
% Conversion Based On: CO	90.5	97.7		
CH_4	86.1	94.4		
moles H_2 in/moles H_2 accounted for in product	1.006	0.990		
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.436	0.486		
Lb-moles CO/hr-ft^3 of Fluidized Bed	.458	0.503		

*25°C, 1 atm

Run Number	50-32-1	Reactor Diameter; inches	.81 with a 1/8" thermowell
Date	8/25	Reactor Length; inches	480
Operator		Settled Bed Height; inches	23.0
Catalyst	CCI-XC150-02	Catalyst Weight; grams	159.4
Liquid	Penndrake Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	8.96	8.93		
Inlet Gas Flow; liters*/hr	205	413		
Outlet Gas Flow; liters*/hr	86-91	240-250		
Feed Gas Composition; Vol. %				
H_2	75	75		
CO	25	25		
Other	---	---		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	2507	26.45		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	208	184		
3	0	276	278		
6	3				
12	9	278	278		
18	15				
24	21	278	278		
30	27				
36	33	278	278		
42	39				
48	45	276	266		

Pressure Drop; psi	---	---		
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	992	1895		
Outlet Gas Concentration; Vol. %				
H_2	44.0	55.0		
CO	11.3	16.2		
CH_4	43.5	26.0		
CO_2	1.2	1.6		
N_2	2.2	0.3		
Other $C_2H_6 + C_3H_8$	0.6	0.6		
Other				
% Conversion Based On: CO	80.2	63.8		
CH_4	76.3	58.0		
moles H_2 in/moles H_2 accounted for in product	0.981	1.009		
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.483	.701		
Lb-moles CO/hr-ft^3 of Fluidized Bed	0.508	0.771		

*25°C, 1 atm

Run Number	50-33-. .3	Reactor Diameter; inches	0.81 with a 1/8" thermowell
Date	8/29	Reactor Length; inches	480
Operator		Settled Bed Height; inches	24.5
Catalyst	Harshaw Ni 0104-101	Catalyst Weight; grams	262.2
Liquid	~~Penndrake Code 4419~~	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	888	908	9.79	
Inlet Gas Flow; liters*/hr	205	205	205	
Outlet Gas Flow; liters*/hr	80-90	82-90	72-75	
Feed Gas Composition; Vol. %				
H_2	75.	75.	75.	
CO	25.	25.	25.	
Other	--	--	--	
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	26.2	26.2	26.2	
Temperature Profile: °C				

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	215	245	280	
3	0	276	300	326	
6	3				
12	9	276	296	323	
18	15				
24	21	271	286	306	
30	27				
36	33	269	280	300	
42	39				
48	45	264	272	290	

Pressure Drop; psi	0.72	0.72	0.72	
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	950	950	950	
Outlet Gas Concentration; Vol. %				
H_2	45.6	38.0	27.3	
CO	12.0	8.4	4.8	
CH_4	42.5	53.0	70.8	
CO_2	1.5	2.0	2.6	
N_2	1.5	0.5	0.3	
Other $C_2H_6 + C_3H_8$	0.5	0.5	0.4	
Other				
Conversion Based On: CO	79.0	87.0	93.9	
CH_4	74.3	82.0	89.5	
moles H_2 in/moles H_2 accounted for in product	0.989	0.982	0.987	
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.450	0.497	0.543	
Lb-moles CO/hr-ft^3 of Fluidized Bed	0.479	0.527	0.569	

*25°C, 1 atm

Run Number	50-34- 2,3	Reactor Diameter; .ches	0.81 with a 1/8" the[illegible]
Date	8/30	Reactor Length; inches	48.0
Operator	0	Settled Bed Height; inches	24.5
Catalyst	Harshaw Ni 0104-101	Catalyst Weight; grams	262.2
Liquid		Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	20.04	21.13	21.50	
Inlet Gas Flow; liters*/hr	200	200	200	
Outlet Gas Flow; liters*/hr	70-78	70-78	75-78	
Feed Gas Composition; Vol. %				
H_2	75	75	75	
CO	25.	25.	25.	
Other	--	--	--	
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	31.85	31.85	31.36	

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-	233	238	272	
3	0	275	300	326	
6	3				
12	9	271	298	324	
18	15				
24	21	270	295	318	
30	27				
36	33	266	293	315	
42	39				
48	45	261	290	311	

Pressure Drop; psi	0.69	0.61	0.65	
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	762	762	774	
Outlet Gas Concentration; Vol. %				
H_2	38.8	38.2	37.0	
CO	7.2	7.2	7.5	
CH_4	49.0	55.0	57.5	
CO_2	2.8	2.8	2.8	
N_2	4.0	0.4	0.2	
Other $C_2H_6 + C_3H_8$	0.4	0.4	0.4	
Other	---	---	---	
% Conversion Based On: CO	88.0	89.1	89.1	
CH_4	81.8	83.5	83.7	
moles H_2 in/moles H_2 accounted for in product	0.964	0.970	0.981	
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.398	0.406	0.413	
*25°C, 1 atm — Lb-moles CO/hr-ft^3 of Fluidized Bed	0.428	0.433	0.440	

Run Number	50-35 ,2,3	Reactor Diameter; inches	o.81 with a 1/8" thermowell
Date	8/31	Reactor Length; inches	48.0
Operator		Settled Bed Height; inches	245
Catalyst	Harshaw Ni-0104-101	Catalyst Weight; grams	262.2
Liquid	Penndrake Code 4417	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min·ft^2	8.68	9.04	9.11	
Inlet Gas Flow; liters*/hr	200	200	392.5	
Outlet Gas Flow; liters*/hr	155-170	95-97	220-240	
Feed Gas Composition; Vol. %				
H_2	75.	75	75	
CO	25	25	25	
Other	--	--	--	
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	26.46	26.22	26.22	

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)				
0	-		220	200	
3	0	250	300	302	
6	3				
12	9	248	290	298	
18	15				
24	21	242	280	290	
30	27				
36	33	234	275	280	
42	39				
48	45	228	267	272	

Pressure Drop; psi	0.68	0.72	0.61	
Catalyst VHSV; Vol. Gas @ STP*/hr-Vol. Fluidized Bed	917	926	1817	
Outlet Gas Concentration; Vol. %				
H_2	67.0	48.0	63.0	
CO	21.7	11.8	17.5	
CH_4	7.0	36.5	20.4	
CO_2	0.1	2.5	1.9	
N_2	0.8	---	---	
Other $C_2H_6 + C_3H_8$	0.4	0.7	0.3	
Other	---	---	---	
Conversion Based On: CO	26.9	77.5	57.0	
CH_4	23.6	69.7	50.1	
Moles H_2 in/moles H_2 accounted for in product	1.005	0.992	0.974	
Overall Reactor Rate; Lb-moles CH_4/hr-ft^3 of Fluidized Bed	0.138	0.412	.581	
Lb-moles CO/hr-ft^3 of Fluidized Bed	0.157	0.458	0.661	

*25°C, 1 atm

CSI-MPR--5

Chem Systems Inc.

LIQUID PHASE METHANATION

PROGRESS REPORT NO. 5

Prepared by Chem Systems Inc.
For the American Gas Association
September, 1972

TABLE OF CONTENTS

I SUMMARY

During the first half of September, work on the project dealt mainly with correcting several mechanical deficiencies in the new high pressure liquid circulation pump, as well as further development of the analytical and calculation procedures. For the latter half of the month, we continued with our liquid-catalyst scan as outlined in Progress Report No. 4.

Using pseudocumene (1,2,4-trimethyl benzene) in connection with Girdler G65-RS and Catalysts and Chemicals XC-150-1-02*, we investigated the effect of temperature, liquid flow rate, and gas flow rate on the reaction system.

The experimental results show that for the G65-RS catalyst, we have been unable to maintain catalyst activity for any length of time, a problem noted previously. In subsequent talks with the manufacturer, they have indicated that this material has relatively poor water resistance. They are sending us samples of other more water resistant catalysts for evaluation.

The results for the CCI catalyst, on the other hand, are very encouraging. For example, at a temperature of 300^{o}C, a pressure of 815 psia, with a VHSV of 2680(ft^3 gas at STP/ft^3 fluidized bed-hour), (this is equivalent to a VHSV of 2110 when not including the flow of pseudocumene vapor due to the liquid vapor pressure of 173 psig at 300^{o}C), one hundred percent of the feed CO had reacted, with molar selectivities to CH_4, CO_2, C_2H_6 and C_3H_8 of 92.26, 4.16, 2.66 and 0.92 percent respectively.

*This is the correct name for this catalyst; not XC-150-02 as noted in Progress Report No. 4.

Reaction rate constants, assuming ideal plug flow and a reaction first order in CO, have been calculated. The rate constant increased with increased temperature and liquid flow.

As the reaction rates in the pseudocumene system were substantially higher than those obtained when using mineral oil, we attempted to quantify these differences as a function of the liquid properties through mass transfer calculations. We have analyzed both mass transfer from the gas phase to the bulk liquid, and from the bulk liquid to the catalyst surface. Mass transfer rates, by either mechanism, are 2½ times greater in pseudocumene than they are in mineral oil; for the most part this accounts for the higher reaction rates obtained in pseudocumene.

In summary,

- The main cause of catalyst performance variations is suspected to be their resistance to water. Insufficient separator temperatures at high conversions have led to water condensation which is believed to be the main cause of catalyst deactivation noted in various instances.

- Aromatic polymethylbenzenes (eg. pseudocumene) seem to be satisfactory reaction solvents from both a reaction rate and stability viewpoint. Rates measured with pseudocumene seem to be as much as 10X greater than those realized with mineral oils and it is possible that this is due to a greater gas solubility and diffusion rate.

- Complete CO conversions have been realized at greater than anticipated flow rates and at relatively low temperatures (eg. $\leq$ 300°C).

- Future tests will be run at lower per pass conversion to (1) attain better rate data, (2) better compare aromatic vs. paraffinic liquids and (3) to better compare Harshaw vs. CCI catalyst. The best system will be utilized in a variable scan, the results of which will be used in a more sophisticated reaction model.

  Dowtherm will also be tested as a reaction solvent.

II DISCUSSION OF RESULTS

The full data sheets are given in Appendix I. The important data have been extracted, and are presented in Tables 1 and 2, and Figures 1 and 2. As a matter of convenience, we also present the values obtained with mineral oil for comparison.

The only basic change in reporting the data is that now the rate constants are reported based on the gas flow at the reactor temperature and pressure, rather than at standard conditions. These rates include the flow of organic vapor which is a result of the substantial liquid phase vapor pressure. The vapor pressure of the process liquid also affects the gas phase concentrations in such a way that CO feed concentrations vary from about 19.8 to 23.0 mole per cent, down from its tank value of about 25 per cent.

The reason for including the organic vapor in the gas flow rate is that it enables us to compare runs on an equivalent reactor vapor flow rate (or residence time) basis.

System 1: Girdler G65-RS + Pseudocumene (See Figure 1 and Table 1)

We again have had trouble maintaining activity levels with the G65-RS catalyst. While Run 50-36-1 falls right in line with the runs reported for the mineral oil scan, all subsequent runs with this catalyst charge show a severely reduced activity.

Because of this problem, we are not considering any further work with the G65-RS catalyst in this reactor. However, we have been sent samples of more water resistant (as indicated by the manufacturer) methanation catalysts (G60, G69, and G87-RS), and we will examine them, in comparison to G65-RS, in our small submerged bed reactor.

Mr. Richard Fritz, of Girdler, has indicated that aside from physical adsorption of water, catalyst deactivation may be a result of water induced oxidation of the active nickel component. He has not offered any precise mechanism for the deactivation.

In order to ameliorate the problem of water deactivation, we might run the reactor at a higher temperature, or at a reduced total pressure. Both of these would give us a greater margin of safety in operating the unit, with respect to the formation of a condensed water phase.

FIGURE I

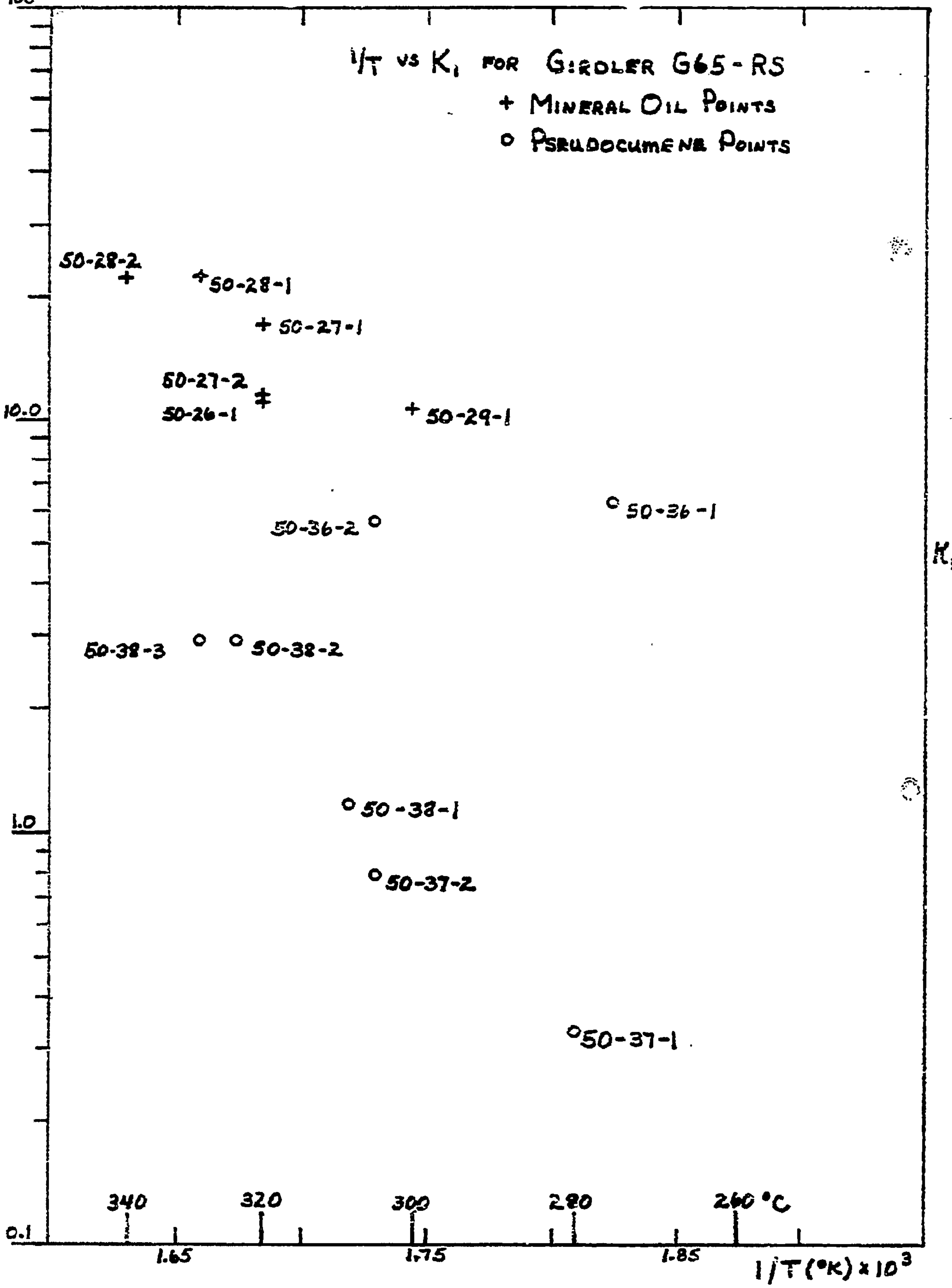

1/T vs K_1 for Girdler G65-RS
+ Mineral Oil Points
o Pseudocumene Points
100
10.0
1.0
0.1
50-28-2
50-28-1
50-27-1
50-27-2
50-26-1
50-29-1
50-36-1
50-36-2
50-38-3
50-38-2
50-38-1
50-37-2
50-37-1
K_1
340
320
300
280
260 °C
1.65
1.75
1.85
1/T (°K) x 10³

TABLE 1

Girdler G65-RS + Mineral Oil / Pseudocumene

Run	T °C	L; Gal/ min-Ft²	V; L/Hr Feed Gas	V/W[1] Ft³ Gas @ Reactor T & P/Lb Cat-Hr	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CO Reacted	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CH_4 Produced	Rate Constants K_1[1]	Rate Constants K_2[1]	Comments
Mineral Oil									
50-26-1	320	14.75	200	.596	7.23	6.81	11.13	.219	Initial Run
50-27-1	320	29.50	250	.743	10.60	8.68	17.16	.399	
50-27-2	320	29.50	400	1.19	12.25	10.22	11.24	.278	Catalyst Begins Deactivation (2)
50-28-1	330	29.91	168	.892	13.40	12.85	22.12	.573	Initial Run
50-28-2	340	30.24	398	2.15	23.03	21.04	22.41	.594	
50-29-1	300	21.26	70	.352	5.71	5.49	10.86	.263	Catalyst Subsequently Deactivated (3)
Pseudocumene									
50-36-1[4]	275	20.0	200	.604	4.01	1.57	6.10	.108	Initial Run
50-36-2[4]	309	21.7	200	.705	3.28	2.52	5.38	.0966	Catalyst Begins Deactivation
50-37-1[4]	280	79.9	200	.613	.379	.340	.330	.00864	Much Reduced Activity (Compare 50-36-1)
50-37-2[4]	305	84.7	200	.705	1.14	1.10	.795	.0300	Much Reduced Activity (Compare 50-36-1)
50-38-1[4]	308	21.9	200	.716	.660	.620	1.18	.0213	Much Reduced Activity (Compare 50-36-1)
50-38-2[4]	324	23.2	200	.802	1.79	1.69	2.97	.0537	Much Reduced Activity (Compare 50-36-1)
50-38-3[4]	330	23.7	400	1.68	1.14	1.14	2.93	.0536	Much Reduced Activity (Compare 50-36-1)

(1) Includes organic vapor present in gas phase due to vapor pressure of liquid.

(2) Reactor not purged at end of days run. Condensed water phase upon cooling renders catalyst totally non-active.

(3) Low temperature in separator during following days run probably caused condensed water phase. Activity not recoverable.

(4) 204.9 atms.

$$K_1^{(1)} = \frac{\text{Ft}^3 \text{ Gas @ Reactor T \& P}}{\text{Ft}^3 \text{ Fluid Bed-Hr.}}$$

$$K_2^{(2)} = \frac{\text{Ft}^3 \text{ Gas @ Reactor T \& P}}{\text{\# Catalyst-Hr.}}$$

System 2: CCI XC-150-1-02 + Pseudocumene (See Figure 2 and Table 2)

It is readily apparent that the rate constants and reaction rates for the pseudocumene runs are significantly higher than those obtained when using the mineral oil as the liquid phase. Reaction rates were up to four times greater, probably higher, since there was essentially no CO in the effluent even at the highest feed gas rates.

The difficulty in making quantitative judgments among the runs themselves is that the low CO concentration makes it difficult to accurately determine the $\log(C_0/C)$ ratio, and hence kinetic K values. This is especially so for the runs where effluent concentration is essentially zero, and might remain so even if the feed rate was made higher. Since we plan future runs with catalyst, we will do so at reduced catalyst loading so that we can obtain CO breakthrough, and therefore more accurately determine kinetic parameters.

Runs 50-39-1, 2 were obtained using a low liquid flow level with the first catalyst charge. The very low CO exit concentration for 50-39-1 makes the K value somewhat indeterminate. Because of a plugged line at the reactor inlet, we had to take the system down, clean it out and reload with a second charge of catalyst. Runs 50-43-1, 2, 3 were run at similar conditions to the 50-39 runs and fall right in line with the values obtained for 50-39-1, 2. We attribute the sudden decline in activity for Run 50-43-2 to an accumulation of water from the previous high conversion run, caused by too low a separator temperature to prevent a condensed water phase in the system.

By raising the temperature we were able to restore most of the activity (Run 50-43-3) within a short period of about 2 hours. Further work is planned to explore the effect of water on the catalyst-liquid system.

Runs 50-42-1, 2, 3 were run at a higher liquid flow which favors an increased mass transfer rate. The higher K values result chiefly from the higher gas flows as the effluent concentrations were again so low as to again make the $\log(C_o/C)$ term somewhat indeterminate.

Another substantial difference obtained with pseudocumene as compared to mineral oil is the higher CO_2 concentrations in the effluent. At this time it is not possible to draw conclusions because this may be a result, in part, of the lower H_2/CO ratio of this batch of feed tanks, and the higher conversion levels.

FIGURE II

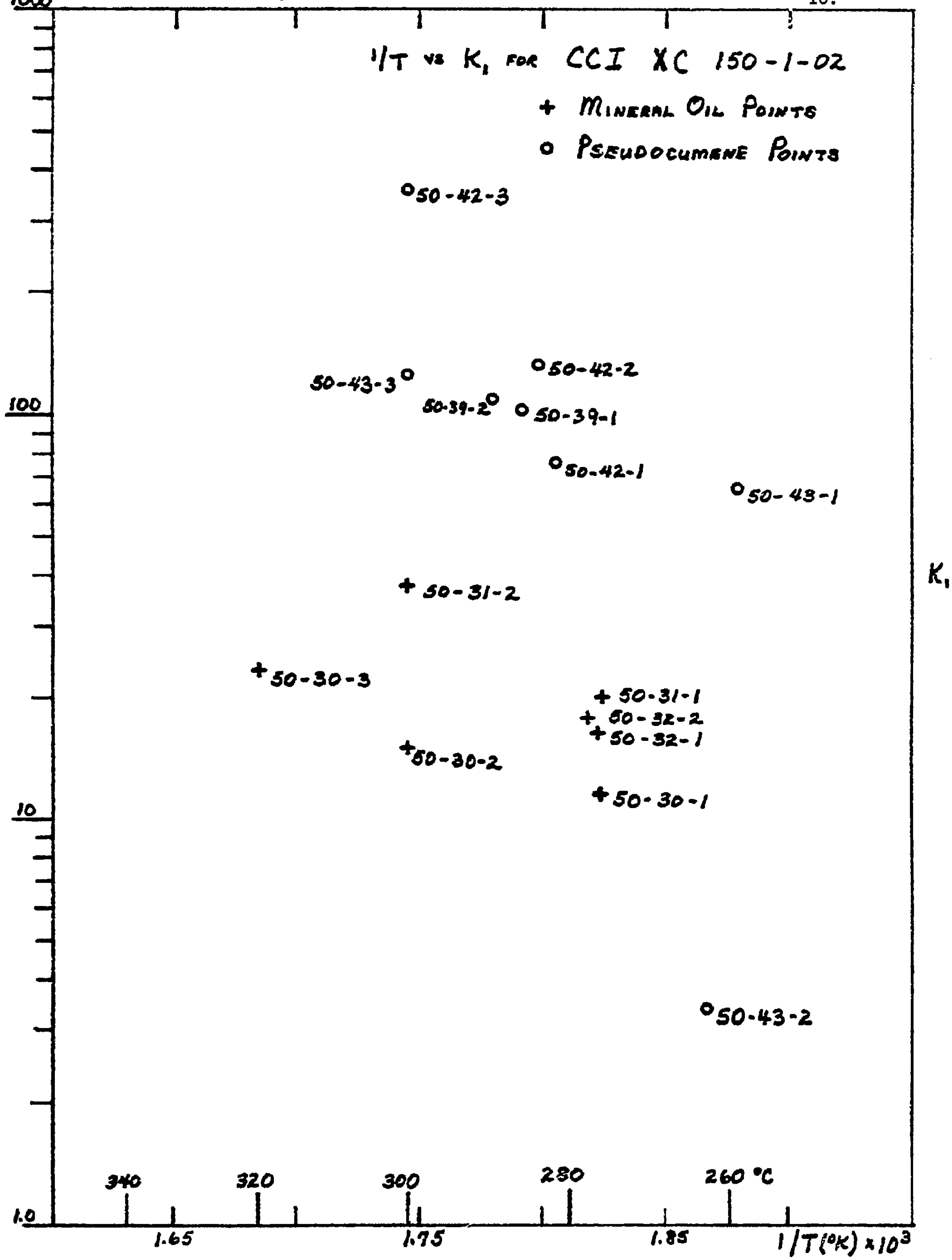

1/T vs K1 for CCI XC 150-1-02
+ Mineral Oil Points
o Pseudocumene Points
50-42-3
50-43-3
50-42-2
50-39-2
50-39-1
50-42-1
50-43-1
50-31-2
50-30-3
50-31-1
50-32-2
50-32-1
50-30-2
50-30-1
50-43-2
1000
100
10
1.0
340
320
300
280
260 °C
1.65
1.75
1.85
1/T(°K) x10³
K1

TABLE 2

CCI + Mineral Oil / Pseudocumene

Run	T °C	L; Gal/min-Ft^2	V; L/Hr Feed Gas	V/W[1] Ft^3 Gas @ Reactor T & P/Lb Cat-Hr	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CO Reacted	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CH_4 Produced	Rate Constants K_1[1]	Rate Constants K_2[1]	Comments
Mineral Oil									
50-30-1	276	8.90	195	0.649	9.13	8.88	11.9	0.247	Initial Run
50-30-2	301	9.06	195	0.679	10.1	9.67	15.9	0.329	
50-30-3	320	9.24	195	0.701	11.2	10.0	23.8	0.490	
50-31-1	276	20.61	200	0.666	11.6	11.1	20.2	0.513	
50-31-2	299	21.07	205	0.711	12.6	12.2	38.8	0.968	
50-32-1	277	8.96	205	0.684	10.6	10.0	16.6	0.345	Increases Activity - Compare 50-30-1
50-32-2	278	8.93	413	1.38	17.0	15.4	18.0	0.395	Still Active
Pseudocumene									
50-39-1[2]	285	19.6	200	0.793	11.9	11.2	>102	>2.38	Initial Run
50-39-2[2]	287	19.8	400	1.60	23.6	22.2	108	2.52	Reactor Inlet Plugged[4]
50-42-1[3]	281	48.6	400	1.56	23.6	22.0	75.8	2.60	Initial Run
50-42-2[3]	283	48.5	795	2.88	46.3	40.8	131	4.35	
50-42-3[3]	301	50.3	795	3.16	47.0	43.4	>350	>12.6	
50-43-1[3]	257	18.7	200	0.650	12.0	10.9	67.6	1.64	
50-43-2[3]	263	19.0	400	1.33	5.67	4.02	3.38	0.086	
50-43-3[3]	300	20.6	400	1.57	23.8	20.9	125	3.03	Still Active

(1) Includes organic vapor present due to vapor pressure of liquid.

(2) 162.4 grams catalyst

(3) 176.4 grams catalyst

(4) Plugged line required reactor to be emptied and refilled.

$$K_1^{(1)} = \frac{Ft^3 \text{ Gas @ Reactor T \& P}}{Ft^3 \text{ Fluidized Bed-Hour}}$$

$$K_2^{(1)} = \frac{Ft^3 \text{ Gas @ Reactor T \& P}}{\text{Lb Catalyst-Hour}}$$

In an attempt to explain the differences between runs made with mineral oil and pseudocumene, we have recalculated mass transfer rates at both the 50% and 95% conversion levels. Operating conditions were 300°C, 815 psia, and a liquid flow of 20 gal/min-ft^2. A summary of these calculations follow (see Progress Report No. 3, Section II for details).

	Mineral Oil	Pseudocumene
Diffusion Coefficient; cm^2/sec	$2.47\ (10)^{-4}$	$13.2\ (10)^{-4}$
Henry's Law Constant; atm/mole fraction	483	1095
Mass Transfer Coefficient; cm/sec		
1. Gas Bubble to Liquid	0.150	0.536
2. Liquid to Catalyst Surface	0.0387	0.122

Conversion Level	Mineral Oil 50%	Mineral Oil 95%	Pseudocumene 50%	Pseudocumene 95%
CO Partial Pressure; atm	9.23	1.32	7.30	1.04
Gas Concentration; moles/cm^3	$1.96(10)^{-4}$	$2.81(10)^{-5}$	$1.55(10)^{-4}$	$2.22(10)^{-5}$
Liquid Concentration; moles/cm^3	$3.9\ (10)^{-5}$	$4.6\ (10)^{-6}$	$4.9\ (10)^{-5}$	$7.0\ (10)^{-6}$
Mass Transfer Rate;* gram-moles/hr				
1. Gas Bubble to Liquid	25.5	3.81	61.5	8.82
2. Liquid to Catalyst Surface	86.9	10.2	344	49.0

*The conditions in our 0.81" diameter reactor are as follows:

(1) Volume of Fluidized Bed = 300 cm^3

(2) Gas Bubble Interfacial Surface Area $\simeq$ 1 cm^2/cm^3 Fluidized Bed

(3) Catalyst Interfacial Surface Area $\simeq$ 5.3 cm^2/cm^3 Fluidized Bed

Therefore, even at the highest gas flow rate, equivalent to about 8.2 gram-moles of CO per hour, we can see that the point value mass transfer rates by either mechanism are still larger than the amount of unreacted CO remaining. In theory, this means that the reaction rate is not mass transfer limited. Nevertheless, the fact that the mass transfer rate (from the gas bubble to the liquid phase) and the reaction rate are of the same order of magnitude, coupled with the knowledge that the calculations are not completely rigorous, leads us to believe that the higher mass transfer rates in pseudocumene, 2½ times the rates in mineral oil, are responsible for the substantially higher reaction rates in pseudocumene.

III PROCESS DEVELOPMENT UNIT

We are just beginning design of the process development unit (PDU) based on the latest reaction rate figures developed in the 0.81" liquid fluidized bed reactor. During October, after we have a more detailed idea of the type and size of equipment required for the PDU, we will contact vendors to ascertain lead times for the manufacture and delivery of the major items. Still to be resolved is whether or not we will purchase a packaged gas generator or we will build one of our own design.

IV FUTURE EXPERIMENTAL PROGRAM

We plan a series of experiments with the CCI-XC-150-1-02 catalyst in both mineral oil and pseudocumene at a reduced catalyst loading so that we can obtain the type of data suitable for a more rigorous kinetic analysis.

We hope to be able to operate within a range of conversions of about 50%-90%. The variable scan will be as follows:

Feed Composition: 25% CO, 75% H_2
Pressure:* 815 psia
Catalyst Loading: 40 grams

Set	Liquid Flow: gal/min-ft^2	Gas Flow: liters/hr	Temperature: ^oC
1	20.0	200	260
	20.0	200	285
	20.0	200	310
2	40.0	200	260
	40.0	200	285
	15.0	200	285
	30.0	200	285
3	40.0	400	260
	40.0	400	285
	40.0	400	310
	20.0	400	310
4	20.0	400	260
	20.0	400	285
	15.0	400	285
	30.0	400	285

*This might be lowered so as to reduce the chance for the formation of a condensed water phase.

APPENDIX I

[illegible]n Number	[illegible]-1	Reactor Diameter; i[illegible]hes	0.81 with 1/8" Thermowell
Date	9/19/72	Reactor Length; inches	48.0
[illegible]erator	RR	Settled Bed Height; inches	24.3
Catalyst	Girdler G65-RS	Catalyst Weight; grams	204.9
[illegible]quid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

L[illegible]quid Flow; gal/min-ft^2	20.0	21.7		
[illegible]let Gas Flow; liters*/hr	200	200		
Outlet Gas Flow; liters*/hr	135	121		
[illegible]ed Gas Composition; Vol. %				
H_2	74.3	74.3		
CO	25.3	25.3		
Other				
P[illegible]essure; psig	800	800		
Estimated Catalyst Bed Height; inches	27.5	27.9		

[illegible]mperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
0	-	249		272					
3	0	272	265	297	295				
6	3	272	274	303	303				
12	9	272	282	303	309				
18	15	276	286	306	314				
24	21	279	290	310	316				
30	27	286	292	314	316				
36	33	296	295	318	315				
42	39	296	250	321	207				
48	45	298		321					

P[illegible]essure Drop; psi	.51	.51		
C[illegible]talyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	.604	.705		
Outlet Gas Concentration; Vol. %				
H_2	70.8	70.4		
CO	18.5	19.7		
CH_4	4.8	7.3		
CO_2	0.4	0.8		
N_2	0.4	0.45		
Other - C_2H_6	1.1	0.45		
Other - C_3H_8	1.6	0.15		
% Conversion Based On: CO	39.7	32.5		
CH_4	15.6	25.0		
M[illegible]les H_2 In / Moles H_2 Accounted for in Products	.898	.908		
Overall Reactor [illegible]te x 10^3 — Lb-moles CO/hr-# Catalyst	4.01	3.28		
Lb-moles CH_4/hr-# Catalyst	1.57	2.52		

*25°C, 1 atm

Run Number	37-1,2
Date	9/20/72
Operator	R^2
Catalyst	Girdler G65-RS
Liquid	Pseudocumene
Reactor Diameter; inches	0.81 with 1/8" Thermowell
Reactor Length; inches	48
Settled Bed Height; inches	24.3
Catalyst Weight; grams	204.9
Catalyst Size	30-50 mesh
Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	79.9	84.7		
Inlet Gas Flow; liters*/hr	200	200		
Outlet Gas Flow; liters*/hr	168	146		
Feed Gas Composition; Vol. %				
H_2	74.0	74.0		
CO	25.0	25.0		
Other				
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	40.6	41.3		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
0	-	256		276					
3	0	274		297					
6	3	275	275	297	301				
12	9	278	275	304	301				
18	15	285	275	309	301				
24	21	285	275	311	301				
30	27	285	275	312	301				
36	33	287	275	315	301				
42	39	289	275	324	301				
48	45	289	213	321	239				

Pressure Drop; psi	.65	.65		
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	.613	.705		
Outlet Gas Concentration; Vol. %				
H_2	71.3	74.3		
CO	24.4	23.3		
CH_4	0.85	2.9		
CO_2	0.1	0.1		
N_2	1.0	1.0		
Other - C_2H_6	-	-		
Other - C_3H_8	-	-		
% Conversion Based On: CO	3.8	11.4		
CH_4	3.4	11.0		
Moles H_2 In / Moles H_2 Accounted for in Products	1.015	0.941		
Overall Reactor Rate x 10^3 - Lb-moles CO/hr-# Catalyst	0.379	1.14		
Lb-moles CH_4/hr-# Catalyst	0.340	1.10		

Run Number	[illegible] 3		Reactor Diameter; inches	0.6[illegible] with 1/8" thermowell	
Date	9/21/72		Reactor Length; inches	48	
Operator	R^2		Settled Bed Height; inches	24.3	
Catalyst	Girdler G65-RS		Catalyst Weight; grams	204.9	
Liquid	Pseudocumene		Catalyst Size	30-50 mesh	
			Empty Reactor Volume, cm^3	395.5	

Liquid Flow; gal/min-ft^2	21.9	23.2	23.7	
Inlet Gas Flow; liters*/hr	200	200	400	
Outlet Gas Flow; liters*/hr	136	134	276	
Feed Gas Composition; Vol. %				
H_2	74.5	74.5	74.5	
CO	24.7	24.7	24.7	
Other				
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	28.0	28.1	29.5	

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)							
0	-	274		294		290		
3	0	295	298	318	321	315	326	
6	3	295	298	319	322	316	326	
12	9	309	298	324	321	327	326	
18	15	312		334		340		
24	21	314	298	336	322	338	326	
30	27	314		338		339		
36	33	314	298	339	321	339	326	
42	39	314		339		339		
48	45	316	216	336	216	335	324	

Pressure Drop; psi	0.54	0.54	0.54	
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	.715	.802	1.68	
Outlet Gas Concentration; Vol. %				
H_2	72.0	70.0	74.6	
CO	23.7	22.4	23.5	
CH_4	1.6	4.7	1.4	
CO_2	0.2	0.3	-	
N_2	0.4	0.5	0.2	
Other - C_2H_6	-	-	-	
Other - C_3H_8	-	-	-	
% Conversion Based On: CO	6.7	18.2	5.6	
CH_4	6.3	17.2	5.6	
Moles H_2 In / Moles H_2 Accounted for in Products	0.998	0.986	0.952	
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	0.660	1.79	1.14	
Lb-moles CH_4/hr-# Catalyst	0.620	1.69	1.14	

*25°C, 1 atm

Run Number	51-3? ,2	Reactor Diameter; inches	0.81 with 1/8" Thermowell
Date	9/26/72	Reactor Length; inches	48
Operator	R^2	Settled Bed Height; inches	24.0
Catalyst	CCI XC-150-1-02	Catalyst Weight; grams	162.4
Liquid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	19.6	19.8		
Inlet Gas Flow; liters*/hr	200	400		
Outlet Gas Flow; liters*/hr	51	112		
Feed Gas Composition; Vol. %				
H_2	76.0	76.0		
CO	23.7	23.7		
Other				
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	28.8	28.8		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)	Reactor	Salt Bath	Reactor	Salt Bath				
0	-	278		277					
3	0	281	275	281	276				
6	3	285	277	284	276				
12	9	288		288					
18	15	288	279	292	276				
24	21	290		292					
30	27	292	276	292	276				
36	33	293		293					
42	39	292	276	294	278				
48	45	292	233	293	200				

Pressure Drop; psi	0.54	0.54		
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	0.793	1.60		
Outlet Gas Concentration; Vol. %				
H_2	6.7	17.7		
CO	0.05	1.09		
CH_4	86.1	76.7		
CO_2	4.13	3.03		
N_2	2.24	0.53		
Other - C_2H_6	0.48	0.45		
Other - C_3H_8	0.29	0.43		
% Conversion Based On: CO	99.9	98.7		
CH_4	93.5	92.9		
Moles H_2 In / Moles H_2 Accounted for in Products	1.111	1.057		
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	11.90	23.56		
Lb-moles CH_4/hr-# Catalyst	11.15	22.17		

*25°C, 1 atm

un Number	[illegible] ,2,3
Date	9/29/72
perator	R^2
Catalyst	CCI-XC-150-1-02
iquid	Pseudocumene

Reactor Diameter; hes	0.81 with 1/8" Thermowell
Reactor Length; inches	48
Settled Bed Height; inches	27.0
Catalyst Weight; grams	176.4
Catalyst Size	30-50 mesh
Empty Reactor Volume, cm^3	395.5

iquid Flow; $gal/min-ft^2$	48.6	48.5	50.3	
nlet Gas Flow; liters*/hr	400	795	795	
utlet Gas Flow; liters*/hr	111	225	199	
eed Gas Composition; Vol. %				
H_2	73.4	73.4	73.4	
CO	25.5	25.5	25.5	
Other				
ressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	42.1	44.2	43.9	

emperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)	Run 1 Reactor	Run 1 Salt Bath	Run 2 Reactor	Run 2 Salt Bath	Run 3 Reactor	Run 3 Salt Bath		
0	-	269		268		287			
3	0	277		276		295			
6	3	278	275	279	274	298	292		
12	9	282		282		301			
18	15	284	275	286	274	304	293		
24	21	286		289		307			
30	27	288	276	290		308	293		
36	33	288		293		309			
42	39	288	275	294		309	293		
48	45	288		294		308			

Pressure Drop; psi	0.54	0.54	0.54	
atalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	1.56	2.88	3.16	
Outlet Gas Concentration; Vol. %				
H_2	8.5	19.8	10.0	
CO	0.10	1.35	0.004	
CH_4	83.7	71.0	84.2	
CO_2	5.03	5.60	3.80	
N_2	1.67	0.45	0.46	
Other - C_2H_6	0.84	1.38	1.21	
Other - C_3H_8	0.12	0.41	0.28	
Conversion Based On: CO	99.9	98.4	100.0	
CH_4	93.2	86.7	92.3	
les H_2 In / Moles H_2 Accounted for in Products	0.996	0.996	0.985	
Overall Reactor ate $\times 10^3$ — Lb-moles CO/hr-# Catalyst	23.61	46.26	47.01	
Lb-moles CH_4/hr-# Catalyst	22.03	40.76	43.39	

*25°C, 1 atm

Number	50-43-1?,3	Reactor Diameter; in s	0.81 with 1/8" Thermowell
e	10/2/72	Reactor Length; inches	48
rator	R^2	Settled Bed Height; inches	27.0
talyst	CCI XC-150-1-02	Catalyst Weight; grams	176.4
uid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

uid Flow; gal/min-ft^2	18.7	19.0	20.6	
.et Gas Flow; liters*/hr	200	400	400	
let Gas Flow; liters*/hr	55	305	118	
d Gas Composition; Vol. %				
H_2	74.3	74.3	74.3	
CO	25.8	25.8	25.8	
Other				
ssure; psig	800	800	800	
stimated Catalyst Bed Height; inches	32.4	34.0	32.4	

perature Profile:

actor ght	Salt Bath Height (in.)								
0	-	245		247		256			
3	0	255	216	259	218	296			
6	3	256	250	263	252	301	298		
12	9	259	250	266	252	302			
18	15	260	250	265	252	303	299		
24	21	261	250	267	252	308			
30	27	263	249	269	251	312	298		
36	33	264	248	270	250	313			
42	39	264		270		313	299		
48	45	265		271		313			

essure Drop; psi	0.43	0.43	0.43	
lyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	0.650	1.33	1.57	
utlet Gas Concentration; Vol. %				
H_2	11.2	71.0	23.3	
CO	0.14	23.4	0.50	
CH_4	80.4	5.16	68.0	
CO_2	3.70	-	6.35	
N_2	2.61	0.16	0.40	
Other - C_2H_6	1.48	-	1.18	
Other - C_3H_8	0.45	0.07	0.26	
nversion Based On: CO	99.8	23.7	99.4	
CH_4	90.8	16.8	87.2	
s H_2 In / Moles H_2 Accounted for in Products	0.984	1.017	0.982	
erall Reactor e x 10^3 — Lb-moles CO/hr-# Catalyst	11.99	5.67	23.79	
.5°C, 1 atm — Lb-moles CH_4/hr-# Catalyst	10.86	4.02	20.86	

CHEM
SYSTEMS, INC.

Chem Systems Inc.

LIQUID PHASE METHANATION

PROGRESS REPORT NO. 6

Prepared by Chem Systems Inc.
For The American Gas Association
October, 1972

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I SUMMARY

During the month of October we attempted to evaluate Dowtherm A as the inert reaction medium. However, both effluent gas analysis as well as a liquid phase chromatograph indicate that the biphenyl ether constituent of Dowtherm A is highly reactive in the presence of an active nickel hydrogenation catalyst at the high H_2 concentrations used. A conservative estimate shows that approximately 65% of the biphenyl ether had reacted within a period of several hours yielding degradation products tentatively identified as benzene, toluene, cyclohexane, lower aliphatics, at least one higher alkylbenzene, as well as a moderate amount of phenol. At this time the decision was made to cease further experiments with Dowtherm A.

Subsequently, we examined Harshaw Ni 0104-101 with pseudocumene to complete the catalyst scan with pseudocumene (results for Girdler G65-RS and CCI C-150-1-02 were reported in Progress Report No. 5). The Harshaw catalyst performed fairly successfully for two days before plugging of the lines (due to a previously accumulated residue caused by an overheat condition during the Dowtherm runs) caused us to take the system down. The performance in pseudocumene was superior to the performance in mineral oil but the level of activity is still somewhat less than with CCI C-150-1-02.

Because the gas feed requirements had been so high for the previous runs and because conversion levels were about 100%, we used a reduced catalyst loading for the next series of runs in which we re-examined CCI C-150-1-02 in pseudocumene. Using approximately ¼ of the previous catalyst loading and ½ of the previous gas feed rate, we were able to obtain reaction rates between two and three times as high as those previously obtained with this catalyst-liquid combination. Accordingly, calculated kinetic rate constants were also higher.

For the first time in the program we have had difficulty maintaining catalyst activity with the CCI catalyst. Further improvements in heat input distribution and temperature monitoring are being implemented so as to insure complete removal of the product water which is considered to be the culprit for the decrease in catalyst activity. In addition, analysis of the pseudocumene shows that sulfur concentration is less than 0.6 ppm, while arsenic concentration is less than 0.4 ppm. At these concentration levels, these poisons are probably not the cause of deactivation.

A preliminary design for the process development unit (PDU), consisting of a Syn-Gas generator capable of producing 6000 SCFH of a gas containing 20% CH_4, 20% CO and 60% H_2, and a Liquid Phase Methanation Reaction System, has been completed. We have contacted at least three vendors for each of the two main process sections and we will be receiving their cost estimates shortly. We are also investigating the extent of site preparation necessary to accommodate the PDU at the planned location.

The experimental work presented in this progress report completes the catalyst and liquid scan and initiates the experimental program designed to generate the process data necessary for the design of the PDU unit. We propose to generate data for four systems which comprise two liquids (pseudocumene and a paraffinic oil) and two catalysts (Harshaw's and CCI's methanation catalysts).

II DISCUSSION OF RESULTS

The full data sheets are given in Appendix I. The important data have been extracted and are presented in Tables 1 and 2. As a matter of convenience, we present some of the previous data for comparison.

Because of the simplistic nature of the kinetic model, the listed kinetic k values will serve only as a guide to the response of the system to various design parameters. Studies are currently underway to formulate a more realistic kinetic model.

System 1: Harshaw Ni-0104-101 + Dowtherm A

As soon as this system was put on-stream, it was readily apparent from effluent gas analysis that something unusual was occurring. Carbon dioxide effluent concentrations of greater than 30% were recorded as compared to the usual level of only 5%. In addition, the gross hydrogen imbalance indicated major side reactions were occurring.

A liquid phase chromatogram was performed (Appendix II) on both the organic and aqueous overhead phases. The organic phase was the less dense one. This is opposite to the relative densities of the starting material; Dowtherm A being denser than water. As indicated in Appendix II, a chromatogram of the virgin Dowtherm A shows two peaks; equivalent to biphenyl ether and biphenyl in a 2.1/1.0 area ratio. The organic phase effluent shows these peaks to be in a ratio of only 0.77/1.0 with the biphenyl area only slightly changed. Since it is impossible to effect a single stage separation between these components, this reflects the change in composition in the reactor liquid phase and indicates that about 60% of the original amount of biphenyl ether had reacted to products consisting heavily of benzene, with lesser amounts of toluene, cyclohexane, lower aliphatics, and one high boiling alkylbenzene. Analysis of the aqueous phase indicated a single large peak corresponding to phenol. A distinctive phenolic odor was readily apparent.

System 2: Harshaw Ni-0104-101 + Pseudocumene

The results for this catalyst-liquid scan are presented in Table 1 along with the results when mineral oil was used as the liquid phase. As with the CCI catalyst, it is readily apparent that the rate constants and reaction rates for the pseudocumene runs are significantly higher than those obtained when using mineral oil as the liquid phase. Reaction rates were up to four times higher than previously obtained.

During the first day of running, Runs 50-45-1,2, at a liquid flow rate of 20 gal/min-ft^2, a gas VHSV of about 1800 ft^3 feed gas/ft^3 bed-hour, and a temperature of about 272^oC, we reacted over 97% of the feed CO with selectivity to hydrocarbons of 87.5%; the rest being converted to CO_2. An increase in reaction temperature to 300^oC was more than sufficient to completely react all the feed CO with the selectivity to hydrocarbons increasing to just over 93%.

The catalyst started to deactivate during the second day of running (Run 50-46-1) but by raising the temperature we were able to partially restore the activity, as indicated by Run 50-46-2. Unfortunately, before we could proceed further, an accumulation of deposits (formed during an overheat condition while running with Dowtherm A) caused the pump to plug. The reactor system, including the high pressure separator, was then completely disassembled and cleaned before the next catalyst-liquid scan was performed.

Table 1

Harshaw + Mineral Oil / Pseudocumene

Run	T °C	L; Gal/ min-Ft^2	V; L/Hr Feed Gas	V/W(1) Ft^3 Gas @ Reactor T & P/Lb Cat-Hr	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CO Reacted	CH_4 Produced	Rate Constants K_1(1)	K_2(1)	Comments
Mineral Oil (2)									
50-33-1	275	8.88	205	0.416	6.32	5.93	15.1	0.199	Initial Run
50-33-2	294	9.08	205	0.430	6.95	6.55	21.9	0.289	
50-33-3	318	9.74	205	0.448	7.50	7.16	32.6	0.429	
50-34-1	271	20.64	200	0.403	6.87	6.39	17.7	0.283	
50-34-2	296	21.13	200	0.422	6.95	6.52	19.3	0.310	Decrease in Activity
50-34-3	321	21.50	200	0.440	6.95	6.53	20.3	0.325	
50-35-1	247	8.68	200	0.385	2.09	1.84	2.25	0.0302	Severely Reduced Activity
50-35-2	290	9.04	200	0.416	6.04	5.43	14.5	0.191	Substantial Recovery From Run 50-35-2
50-35-3	296	9.11	392	0.818	8.72	7.66	15.2	0.198	
Pseudocumene (3)									
0-45-1	272	18.6	400	0.95	16.93	13.90	86.8	1.21	Initial Run
0-45-2	301	20.3	400	1.11	17.47	15.77	336.8	4.73	
0-46-1	273	46.8	800	1.93	7.39	6.39	6.31	0.116	Started to Deactivate - Raised Temperature and Activity Partially Recovered
0-46-2	301	50.1	800	2.21	30.90	25.85	139.7	2.58	Reactor Inlet Plugged(4)

1) Includes organic vapor present due to vapor pressure of liquid.

2) 262.2 grams catalyst

3) 253.7 grams catalyst

4) Plugged line required reactor to be emptied and refilled.

$$K_1^{(1)} = \frac{\text{Ft}^3 \text{ Gas @ Reactor T \& P}}{\text{Ft}^3 \text{ Fluidized Bed-Hour}}$$

$$K_2^{(1)} = \frac{\text{Ft}^3 \text{ Gas @ Reactor T \& P}}{\text{Lb Catalyst-Hour}}$$

System 3: CCI C-150-1-02 + Pseudocumene

Because of the extremely high conversion levels obtained at the high catalyst loadings previously used with this catalyst-liquid pair, we re-examined this system at a low catalyst loading in order to ascertain the maximum rates of conversion obtainable. Overall reaction rates were from 2-4 times greater than previously obtained. The results for both the high and low catalyst loadings are presented in Table 2, while the summary run sheets are given in Appendix I.

The reaction rates for this catalyst are some four times greater than the rates obtained with Harshaw Ni-0104-101 under similar operating conditions. However, since the runs using the Harshaw catalyst were done with extremely high conversions, we are also going to re-examine this system at a reduced catalyst loading.

For the first time in this research program, we have had trouble maintaining catalyst activity with this CCI catalyst. Sometimes the catalyst immediately begins to deactivate (Runs 50-47-1 or 50-50-1) on the initial test, or it may deactivate at some later point in the variable scan (Run 50-52-1). This is an indication that deactivation is being caused by some mechanical malfunction of the unit and that it is not a problem inherent of the reaction system investigated. We are examining our heat input distribution and temperature monitoring systems so as to insure complete removal of our product water. There is some evidence that the (1) recorded reactor temperatures may be up to 20^{O}C lower in reality, and (2) the recorded salt bath temperature may be up to 20^{O}C higher in reality than indicated by the temperature indicator. The problem has been tentatively identified as a combination of (1) an irregular malfunction within the Minimite temperature indicator, and (2) a faulty thermocouple lead. It is possible, therefore, that temperatures we assumed to be safe were in fact close to the point where water vapor might form a condensed phase. Steps have been taken to correct the temperature monitoring system malfunctions and thus guarantee that the product water is continuously removed from our system with the CH_4 and unreacted CO and H_2.

Table 2

CCI + Pseudocumene

Run	T °C	L; Gal/min-Ft^2	V; L/Hr Feed Gas	V/W[1] Ft^3 Gas @ Reactor T & P/Lb Cat-Hr	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CO Reacted	Rate x 10^3 (Lb Moles/Lb Cat-Hour) CH_4 Produced	Rate Constants K_1[1]	Rate Constants K_2[1]	Comments
seudocumene									
0-39-1[2]	255	19.6	200	0.793	11.9	11.2	102	2.38	Initial Run
0-39-2[2]	287	19.8	400	1.60	23.6	22.2	108	2.52	Reactor Inlet Plugged
0-42-1[3]	281	48.6	400	1.56	23.6	22.0	75.8	2.60	Initial Run
0-42-2[3]	283	48.5	795	2.88	46.3	40.8	131	4.35	
0-42-3[3]	301	50.3	795	3.16	47.0	43.4	350	12.6	
0-43-1[3]	257	18.7	200	0.650	12.0	10.9	67.6	1.64	
0-43-2[3]	263	19.0	400	1.33	5.67	4.02	3.38	0.086	
0-43-3[3]	300	20.6	400	1.57	23.8	20.9	125	3.03	Still Active
0-47-1[4]	260	20.0	300	Initial Run - Catalyst showed a continuous non-recoverable decline					in activity.
0-48-1[4]	283	16.9	400	6.06	80.8	69.1	-	3.21	Initial Run
0-48-2[4]	302	19.8	400	6.68	88.2	78.5	-	5.12	
0-48-3[4]	327	21.7	400	8.09	94.4	86.0	-	9.57	
0-49-1[4]	284	47.8[5]	400	6.05	80.4	72.2	-	3.45	
0-49-2[4]	302	51.3	400	6.68	86.7	76.5	-	5.24	Pump lost prime, line plugged; emptied and refilled.
0-50-1[6]	275	50.0	600	Initial Run - Catalyst showed a continuous non-recoverable decline					in activity.
0-51-1[6]	300	49.1	400	8.67	116.0	102.0	-	7.11	Initial Run
0-51-2[6]	315	51.3	550	13.33	137.0	123.0	-	6.31	
0-52-1[6]	296	19.6	600	12.73	69.7	63.6	-	1.35	Catalyst losing activity irreversibly.

1) Includes organic vapor present due to vapor pressure of liquid.
2) 162.4 grams catalyst
3) 176.4 grams catalyst
4) 42.0 grams catalyst
5) Pump may have initially lost prime in one head which would give a flow of approximately 25 gal/min-ft^2.
6) 32.5 grams catalyst

$$K_1^{(1)} = \frac{Ft^3 \text{ Gas @ Reactor T \& P}}{Ft^3 \text{ Fluidized Bed-Hour}}$$

$$K_2^{(1)} = \frac{Ft^3 \text{ Gas @ Reactor T \& P}}{\text{Pound Catalyst-Hour}}$$

Reaction Modeling

As soon as an improved reaction model is formulated, we will attempt to examine our data in light of the proposed mechanism. At the present time we can say that there appears to be some mass transfer restraint in the reaction system as indicated by the strong effect of liquid phase properties and, to a lesser extent, by the effect of liquid phase velocity. It is also apparent that the strong temperature dependence indicates the kinetic rate of reaction can also be a dominant factor.

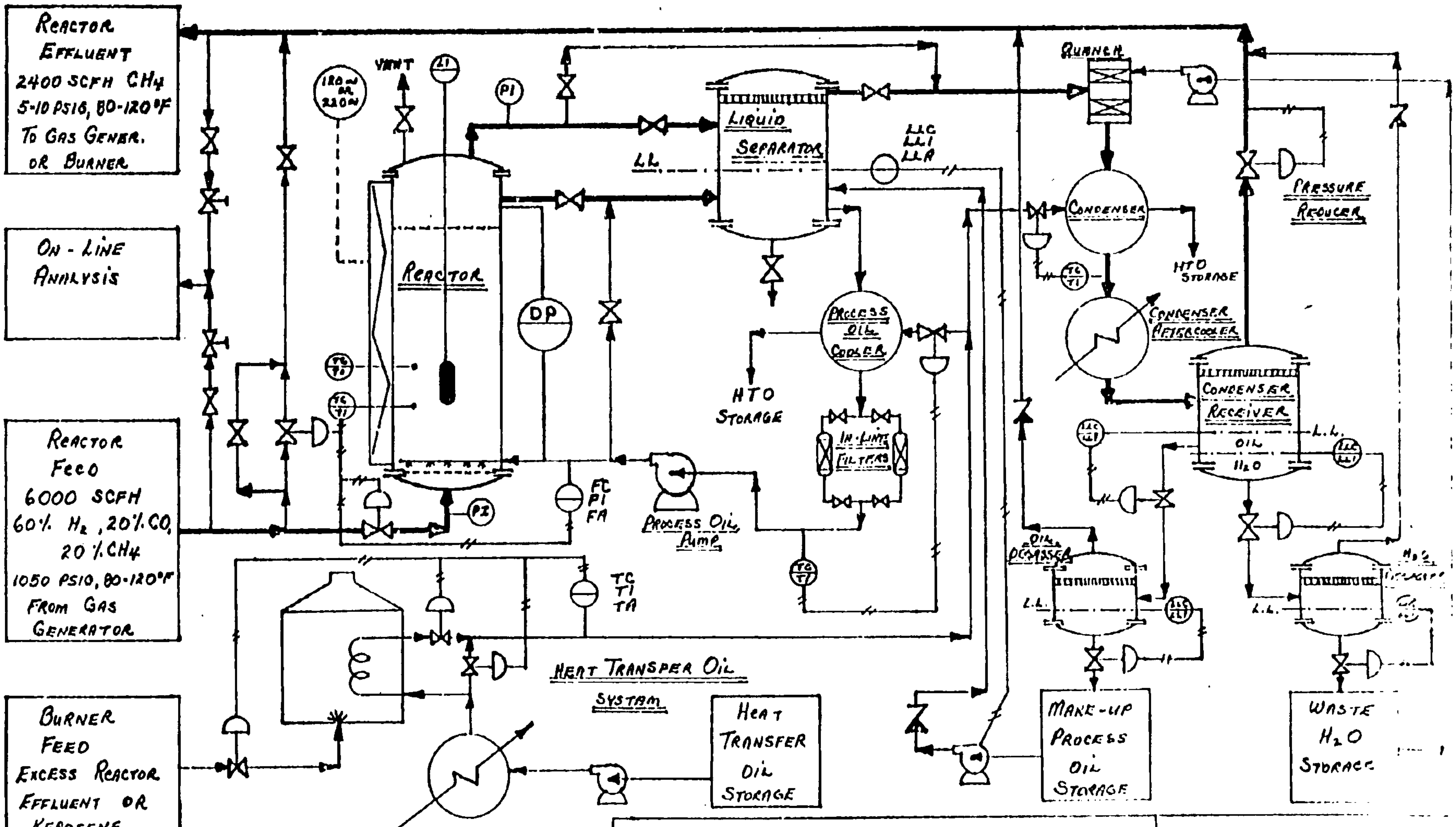
The model to be developed will have to be able to take into account both of these factors. A literature review of liquid-solid fluidization systems is underway in order to provide a starting point for mathematical modeling efforts.

III PROCESS DEVELOPMENT UNIT

We have finished the preliminary design for the liquid phase methanation reactor system; a schematic is shown in Figure 1 while more detailed descriptions of the individual units are given in Appendix III. It was our feeling that the synthesis gas generator should be designed as a complete package by a company with considerable expertise in that area. For this reason we have contacted at least three companies who will submit a design proposal and cost estimate for a gas generator to deliver 6000 SCFH of a 20% CO, 20% CH_4 and 60% H_2 stream to our reactor at a pressure of 1050 psig. The companies are (1) Gas Machinery/ Gas Atmospheres Inc. (Roy Bednarski), Strongsville, Ohio; (2) Howe-Baker Engineers Inc. (Larry Roesler), Tyler, Texas; and (3) Demarkus Corp. (O. Rudy Matzner), Buffalo, New York. We have contacted other companies but for a variety of reasons they were unable to submit a proposal. A schematic flow diagram of the synthesis gas generator is given in Figure 2.

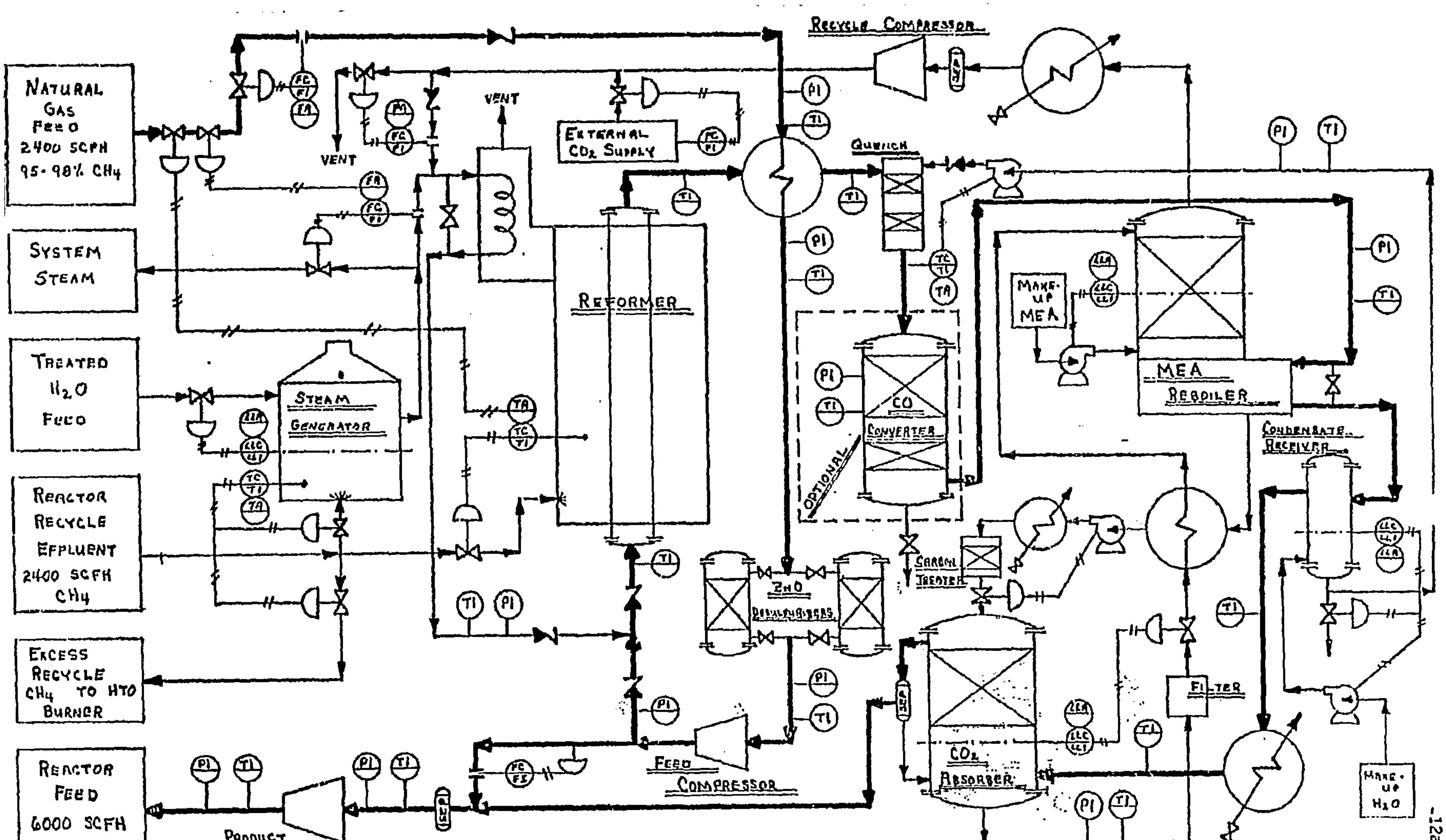
In addition, we have contacted three companies to submit a design proposal and cost estimate for the complete slurry methanation reactor system including all major process equipment, instrumentation and controls, and auxiliary equipment. These companies are (1) Artisan Industries Inc. (Dr. Francis Brown), Waltham, Massachusetts; (2) Chem-Pro Inc. (Philip Schweitzer), Fairfield, New Jersey; and (3) Demarkus Corp. (O. Rudy Matzner) Buffalo, New York. We are currently receiving the required information.

We have also contacted several contractors to obtain estimates for site preparation with respect to utility requirements (gas, electricity and water) and the installation of necessary safety equipment.



CHEM SYSTEMS, INC.
METHANATION PDU FLOWSHEET

Date: 11/?/??
Figure 1



CHEM SYSTEMS, INC. SYN GAS GENERATOR FLOWSHEET	Figure 2 DATE: 11/10/72

IV FUTURE EXPERIMENTAL PROGRAM

In addition to the ongoing program to obtain reliable kinetic data suitable for reaction modeling, two further refinements in operation procedure have been planned. Future runs will be performed at a pressure of 1000 psig and the catalyst will now be reduced in situ. This will give us some necessary experience in the reduction procedure as it will be performed in the process development unit.

We are currently using a mini-computer to handle the routine data analysis. The scope of each of the two programs is described in Appendix IV with a description of the actual calculations performed. Sample printouts of actual results are presented for each program.

On a short term basis, we plan to concentrate on learning how to operate the unit in such a manner that catalyst deactivation is avoided. In our opinion, this will require closer monitoring of temperatures in the gas-liquid separator as to prevent water condensation and recycle of large amounts of this product with the liquid phase. In addition, we will examine the effect of various shutdown procedures on the catalyst behavior. This is another plausible reason for the observed catalyst deactivation. Upon satisfactory operation of the unit with no catalyst deactivation for a run period greater than a week, we will initiate a process variable scan.

The purpose of this is essentially two-fold. First, to ascertain the effect of mass transfer in the system; another reason for the variable study is to generate the process engineering data necessary for the design of the process development unit. It should be kept in mind that a choice of catalyst and liquid must be made prior to starting the experimental work in the above mentioned PDU. Variables to be explained are gas and liquid flow, temperature, particle and reactor size, feed concentration, and operating pressure.

APPENDIX I

Run Data Sheets

R ı Number	50-52	Reactor Diameter; hes	0.81 with a 1/8" Thermowell
Date	10/31/72	Reactor Length; inches	48
O erator	RR	Settled Bed Height; inches	5
Catalyst	CCI C-150-1-02	Catalyst Weight; grams	32.5
L quid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

L quid Flow; gal/min-ft^2	19.64			
I..let Gas Flow; liters*/hr	600			
Outlet Gas Flow; liters*/hr	350			
F ed Gas Composition Volume Percent: H_2	74.6			
CO	25.4			
P ssure; psig	800			
Estimated Catalyst Bed Height; inches	6.0			

Te perature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
3	0	296	284						
6	3	300	290						
12	9	300	295						
24	21	300	295						
36	33								

Pressure Drop; psi				
Ca alyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	12.73			
Ou let Gas Concentration; Vol. %				
H_2	64.48			
CO	22.67			
CH_4	11.93			
CO_2	0.16			
N_2	0.29			
Other - C_2H_6	0.40			
Other - C_3H_8	0.06			
% Conversion Based On: CO	36.56			
% olar Selectivity to: CH_4	91.32			
CO_2	1.24			
C_2H_6	6.14			
C_3H_8	1.31			
Moles H_2 In / Moles H_2 Accounted for in Products	1.02			
Ove all Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	69.66			
*25 C, 1 atm — Lb-moles CH_4/hr-# Catalyst	63.62			

n Number	50-51 .2	Reactor Diameter; hes	0.81 with 1/8" Thermowell
ate	10/27/72	Reactor Length; inches	48
erator	RR & AW	Settled Bed Height; inches	5
atalyst	CCI C-150-1-02	Catalyst Weight; grams	32.5
quid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

quid Flow; gal/min-ft^2	49.05	51.31		
nlet Gas Flow; liters*/hr	400	550		
tlet Gas Flow; liters*/hr	110	190		
ed Gas Composition olume Percent: H_2	74.8	74.8		
CO	25.2	25.2		
essure; psig	800	800		
Estimated Catalyst Bed Height; inches	7.69	7.72		

mperature Profile:

Reactor ight	Salt Bath Height (in.)								
3	0	299	290	308					
6	3	301	294	317					
12	9	303	296	320					
24	21	304	304	320					
36	33		304	320					

essure Drop; psi				
atalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	8.67	13.33		
let Gas Concentration; Vol. %				
H_2	29.78	44.03		
CO	5.82	11.72		
CH_4	56.80	39.97		
CO_2	6.12	3.27		
N_2	0.66	0.35		
Other - C_2H_6	0.74	0.61		
Other - C_3H_8	0.07	0.06		
onversion Based On: CO	91.74	79.19		
Molar Selectivity to: CH_4	87.91	89.56		
CO_2	9.47	7.32		
C_2H_6	2.31	2.73		
C_3H_8	0.30	0.37		
les H_2 In / Moles H_2 Accounted for in Products	1.05	1.02		
rall Reactor ate x 10^3 — Lb-moles CO/hr-# Catalyst	115.7	137.3		
Lb-moles CH_4/hr-# Catalyst	101.7	123.0		

2 °C, 1 atm

Run Number	50-49 2	Reactor Diameter; inches	0.81 with 1/8" Thermowell
Date	10/24/72	Reactor Length; inches	48
Operator	RR	Settled Bed Height; inches	6
Catalyst	CCI C-150-1-02	Catalyst Weight; grams	42.0
Liquid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; $gal/min\text{-}ft^2$		47.81	51.32*		
Inlet Gas Flow; liters*/hr		400	400		
Outlet Gas Flow; liters*/hr		-	-		
Feed Gas Composition Volume Percent:	H_2	75.1	75.1		
	CO	24.9	24.9		
Pressure; psig		800	800		
Estimated Catalyst Bed Height; inches		8.44	9.34*		
Temperature Profile: Reactor Height (in.) / Salt Bath Height (in.)					
3	0	282 |	300* | 288		
6	3	284 | 268	| 290		
12	9	285 | 274	| 290		
24	21	286 | 274	| 290		
36	33	286 | 275			
Pressure Drop; psi		0.14	0.14		
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst		6.05	6.68		
Outlet Gas Concentration; Vol. %					
H_2		41.95	42.05		
CO		9.71	5.81		
CH_4		44.05	45.87		
CO_2		2.24	5.30		
N_2		0.77	0.58		
Other - C_2H_6		1.05	0.36		
Other - C_3H_8		0.22	0.03		
% Conversion Based On:	CO	83.47	89.94		
% Molar Selectivity to:	CH_4	89.80	88.27		
	CO_2	4.57	10.21		
	C_2H_6	4.30	1.37		
	C_3H_8	1.34	0.15		
Moles H_2 In / Moles H_2 Accounted for in Products		0.992	0.938		
Overall Reactor Rate x 10^3	Lb-moles CO/hr-# Catalyst	80.43	86.67		
*2 °C, 1 atm	Lb-moles CH_4/hr-# Catalyst	72.22	76.5		

Pump may have already lost prime in one of the two heads. Subsequently stopped at end of run when we attempted to change flow conditions.

Thermocouple broke before profile could be made

Run Number	50-4^ 1,2,3	Reactor Diameter; inches	0.81 with 1/8" Thermowell
Date	10/23/72	Reactor Length; inches	48
Operator	RR & AW	Settled Bed Height; inches	6
Catalyst	CCI C-150-1-02	Catalyst Weight; grams	42.0
Liquid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	18.9	19.8	21.7	
Inlet Gas Flow; liters*/hr	400	400	400	
Outlet Gas Flow; liters*/hr	120	113	101	
Feed Gas Composition Volume Percent: H_2	74.7	74.7	74.7	
CO	25.3	25.3	25.3	
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	7.21	7.20	7.26	

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
3	0	280	272	303	285	326	310		
6	3	283	272	306	294	328	313		
12	9	287	272	306	296	330	314		
24	21	288	273	309	297	330	314		
36	33	288		309	298	330	314		

Pressure Drop; psi	0.14	0.14	0.14	
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	6.06	6.68	8.09	
Outlet Gas Concentration; Vol. %				
H_2	41.0	35.1	25.6	
CO	10.37	6.4	2.67	
CH_4	41.88	51.87	65.01	
CO_2	5.27	5.64	5.82	
N_2	0.64	0.59	0.66	
Other - C_2H_6	0.69	0.37	0.24	
Other - C_3H_8	0.16	0.03	< 0.005	
% Conversion Based On: CO	82.53	90.11	96.39	
% Molar Selectivity to: CH_4	85.48	88.92	91.16	
CO_2	10.75	9.67	8.17	
C_2H_6	2.79	1.27	0.66	
C_3H_8	0.98	0.14	0.01	
Moles H_2 In / Moles H_2 Accounted for in Products	1.06	1.02	1.01	
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	80.80	88.23	94.37	
Lb-moles CH_4/hr-# Catalyst	69.06	78.45	86.04	

*2 °C, 1 atm

Run Number	50-46 2	Reactor Diameter; inches	0.81 with 1/8" Thermowell
Date	10/10/72	Reactor Length; inches	48
Operator	RR	Settled Bed Height; inches	23.5
Catalyst	Harshaw Ni 0104-101	Catalyst Weight; grams	253.7
Liquid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	46.8	50.1		
Inlet Gas Flow; liters*/hr	800	800		
Outlet Gas Flow; liters*/hr	585	210		
Feed Gas Composition Volume Percent: H_2	74.85	74.85		
CO	25.15	25.15		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	35.3	35.5		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)								
3	0	272	256	299					
6	3	272	258	300					
12	9	274	260	302	276				
24	21	275	260	303					
36	33	277	260	305					

Pressure Drop; psi	0.65	0.65		
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	1.93	2.21		
Outlet Gas Concentration; Vol. %				
H_2	69.88	33.28		
CO	23.40	2.83		
CH_4	6.02	55.13		
CO_2	0.03	6.52		
N_2	0.24	0.28		
Other - C_2H_6	0.38	1.62		
Other - C_3H_8	0.05	0.33		
% Conversion Based On: CO	22.93	95.88		
% Molar Selectivity to: CH_4	86.44	83.67		
CO_2	0.45	9.90		
C_2H_6	10.79	4.93		
C_3H_8	2.32	1.50		
Moles H_2 In / Moles H_2 Accounted for in Products	1.00	1.01		
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	7.39	30.90		
Lb-moles CH_4/hr-# Catalyst	6.39	25.85		

*2 ^oC, 1 atm

Run Number	50-45-1 ?	Reactor Diameter; inches	0.81 with 1/8" Thermowell
Date	10/9/72	Reactor Length; inches	48
Operator	RR	Settled Bed Height; inches	23.5
Catalyst	Harshaw Ni 0104-101	Catalyst Weight; grams	253.7
Liquid	Pseudocumene	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow: gal/min-ft^2	18.6	20.3		
Inlet Gas Flow; liters*/hr	400	400		
Outlet Gas Flow; liters*/hr	150	100		
Feed Gas Composition Volume Percent: H_2	72.7	72.7	The hydrogen analysis may be 1% or 2% too low.	
CO	27.3	27.3		
Pressure; psig	800	800		
Estimated Catalyst Bed Height; inches	26.8	27.0		

Temperature Profile:

Reactor Height (in.)	Salt Bath Height (in.)	Reactor	Salt Bath	Reactor	Salt Bath				
3	0	268		296					
6	3	269	265	299	282				
12	9	272	265	302	283				
24	21	277	264	306	283				
36	33	279	265	306	283				

Pressure Drop; psi	0.68	0.68		
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	0.95	1.11		
Outlet Gas Concentration; Vol. %				
H_2	28.3	4.80		
CO	2.26	<0.005		
CH_4	58.2	86.4		
CO_2	8.89	6.57		
N_2	0.67	0.97		
Other - C_2H_6	1.43	1.07		
Other - C_3H_8	0.32	0.20		
% Conversion Based On: CO	96.9	100		
% Molar Selectivity to: CH_4	82.08	90.26		
CO_2	12.54	6.86		
C_2H_6	4.03	2.24		
C_3H_8	1.34	0.64		
Moles H_2 In / Moles H_2 Accounted for in Products	0.960	0.966		
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	16.93	17.47		
Lb-moles CH_4/hr-# Catalyst	13.90	15.77		

*25°C, 1 atm

Ru Number	50-44-1 3,	Reactor Diameter; inches	0.81 with 1/8" Therm[illegible]
Date	10/4	Reactor Length; inches	48
Operator	RR	Settled Bed Height; inches	32.5
Catalyst	Harshaw Ni 0104-101	Catalyst Weight; grams	308
Liquid	Dowtherm A	Catalyst Size	30-50 mesh
		Empty Reactor Volume, cm^3	395.5

Liquid Flow; gal/min-ft^2	~15	~15	~15	
Inlet Gas Flow; liters*/hr	800	800	800	
Outlet Gas Flow; liters*/hr	125	125	125	
Feed Gas Composition Volume Percent: H_2	75.3	75.3	76.0	
CO	24.7	24.7	24.0	
Pressure; psig	800	800	800	
Estimated Catalyst Bed Height; inches	-	-	-	
Temperature Profile.				
Reactor Height (in.) / Salt Bath Height (in.)				
3 / 0	280	300	320	
6 / 3				
12 / 9				
24 / 21				
36 / 33				
Pressure Drop; psi	---	---	---	
Catalyst V/W; Ft^3 Gas @ Reactor T & P/Hr-Lb Catalyst	---	---	---	
Outlet Gas Concentration; Vol. %				
H_2	29.91	6.12	4.69	
CO	9.50	.93	.22	
CH_4	27.56	43.51	63.04	
CO_2	30.08	46.92	30.63	
N_2	1.51	.66	.45	
Other - C_2H_6	1.04	1.01	.57	
Other - C_3H_8	.40	.85	.41	
% Conversion Based On: CO	86.5	99.0	99.8	
% Molar Selectivity to: CH_4	45.2	45.8	65.6	
CO_2	49.4	49.4	31.9	
C_2H_6	3.43	2.13	1.18	
C_3H_8	1.98	2.67	1.29	
Moles H_2 In / Moles H_2 Accounted for in Products	2.38	2.91	1.80	
Overall Reactor Rate x 10^3 — Lb-moles CO/hr-# Catalyst	--	--	--	
25 C, 1 atm — Lb-moles CH_4/hr-# Catalyst	--	--	--	

APPENDIX II

Analysis of Dowtherm A and Pseudocumene

Chem Systems Inc.

INTEROFFICE MEMORANDUM

TO: David Blum

CC:

DATE: 23 October 1972

SUBJECT: Analysis of Dowtherm A and Pseudocumene Used as Liquid Phase in Methanation

FROM: Thomas Pletzke

All samples were analyzed on a 10' x 1/8" Durapak (n-octane/Poracil C) column programmed from 50-180°C at 13°/minute using a FID.

Dowtherm A

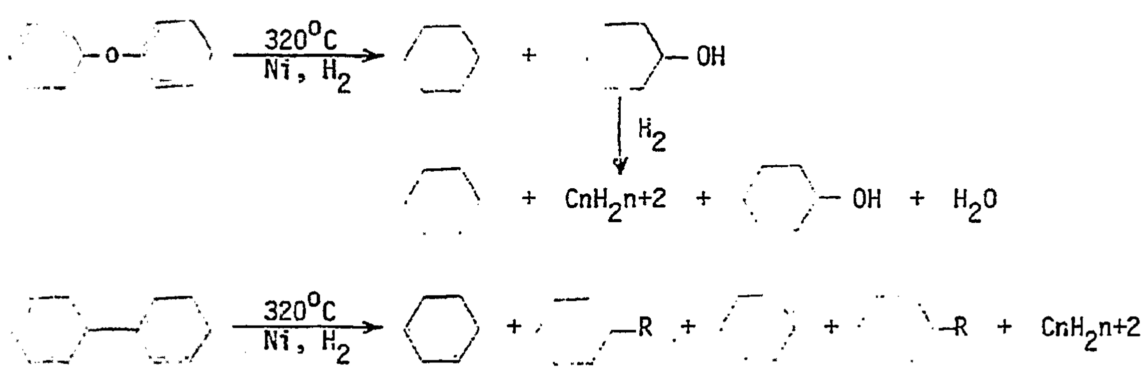
A sample composed of two immiscible layers which had been taken from the reactor overhead after being subjected to 320°C was analyzed and compared to unused Dowtherm A.

Unused Dowtherm A showed two distinct peaks (biphenyl and biphenyl ether) at an area ratio of 2.1 biphenyl ether to biphenyl. The organic (top layer) of the used Dowtherm A showed the same two peaks at a ratio of 0.77 biphenyl ether to biphenyl. In addition, there was a heavy concentration of a compound with a retention time corresponding to benzene plus lesser concentrations of what appear to be toluene, cyclohexane, lower aliphatics and one high boiling alkylbenzene. The water (bottom layer) showed only one peak which corresponded in retention time to phenol.

It can be concluded that the biphenyl ether undergoes a more severe breakdown at operating conditions as evidenced by the change in area ratios of used to unused Dowtherm A. A conservative estimate is 65% of biphenyl ether loss and a slight loss of biphenyl after use.

Analysis of Dowtherm A and Pseudocumene
Used as Liquid Phase in Methanation

A proposed breakdown route is:



A quantitative comparison of used and unused Dowtherm A with internal standards would have to be made in order to determine the extent of degradation accurately and the amount of polymer formation which is non-detectable by G. C.

Pseudocumene

Pseudocumene used in three different runs (Harshaw, CCI and Girdler catalysts) and taken from the reactor overhead were analyzed. The chromatograms indicate that a slight degree of hydrodealkylation occurred causing formation of alkylcyclohexane and predominantly components corresponding in retention time to toluene and xylenes. Overall, degradation appeared to be minimal and the presence of lower boiling materials was magnified due to the nature of the sample, i.e. more lower boiling materials would concentrate in the reactor overhead.

Analysis of Dowtherm A and Pseudocumene
Used as Liquid Phase in Methanation

More meaningful information could be obtained, if needed, by sampling the liquid phase in the reactor during operation and quantifying major components by use of internal standards.

APPENDIX III

Major Equipment Descriptions

Major Equipment Descriptions

Methanation Pilot Plant

A. Syn-Gas Generator

1. Desulfurizer

Two methods are available: (1) activated carbon which must be reactivated with steam on a one to two week basis (room temperature operation), and (2) ZnO which is renewed every six months (old bed is discarded). This unit operates at 700-800^{0}F.

2. Reformer Furnace

Circular design. Contains two to three 2"-3" packed and flanged catalyst tubes. Overall height, floor to top of fired section, must be 15' or less. Direct fired - burners must be capable of handling gas of heat content from 450 BTU/SCF to 1000 BTU/SCF. Total furnace input heat demand is approximately 1.3-1.6 mm BTU/hour.

3. Amine Reboiler

Does not need to be directly fired. Enough waste heat is available from furnace process effluent to regenerate MEA. Usual method is to quench furnace effluent (at 1500^{0}F) with recycled condensate to saturation temperature ($\sim$700^{0}F), then recovering entire condensate from reboiler effluent.

4. CO_2 Absorber

Maximum height is 17'.

5. Blender

Equipment needed to blend CO_2 absorber effluent with 1200 SCFH CH_4 at about 150 psig.

6. Compressors

Three compressors are needed: (1) precompressor to compress 2400 SCFH of CH_4 from 5 psig to 150-160 psig, (2) CO_2 recycle compressor to compress 500 SCFH of CO_2 (from MEA reboiler) from 130 psig to 160 psig, and (3) after compressor to compress 6000 SCFH of 60% H_2, 20% CO, and 20% CH_4 from 130-150 psig to 1050 psig.

7. Steam Generator

Packaged unit to deliver approximately 250-300 #/hour steam at 160 psig (365^{o}F). Heat input is approximately 0.7 mm BTU/hour.

8. Cooling Water Tower

Capable of handling 400-500 gpm of treated water. Roof mounted, designed for 20^{o}F ΔT. For use with both Syn-Gas Generator and PDU.

9. Water Treatment

Deionization and/or softening unit. Delivery to be normally 36 gph, up to a maximum of 150 gph. Maximum rate includes about 70 gph for the cooling tower which may not be needed.

10. Flow and Product Composition

Natural gas feed to furnace = 1200 SCFH of CH_4. CO_2 absorber effluent = 4800 SCFH of 75% H_2, 25% CO. Flow from generator to be 6000 SCFH of 60% H_2, 20% CO, and 20% CH_4 at 1050 psig. Turn-down ratio on generator to be 2/1 with greater turn-down via bypass. Total natural gas feed to Syn-Gas Generator = 2400 SCFH CH_4 (1200 SCFH for reaction and 1200 SCFH for blending). Product H_2/CO ratio variable from 3/1 upward, ratio less than 3/1 obtainable via external injection of CO_2 into recycle line.

11. Utilities Consumption

Utilities should try to be minimized, but estimated at:

Gas	2400 SCFH
Water	72 gph for steam generation + cooling tower make-up
Electricity	30 KW @ 120 v
	75 KW @ 440 v (3 phase)

12. Instrumentation

Generator to be completely equipped with all instrumentation necessary for flow and temperature control. All controls fail-safe for safety purposes. Effluent product to be continuously analyzed for all components via optical or gas chromatographic methods.

13. Materials of Construction

Dictated by temperature/pressure/concentration requirements.

14. Electrical Connections

Must be explosion-proof.

B. PDU Unit

1. Reactor

Flanged. 8" I.D. x 10' L flange to flange. Internals - scintered disc gas dispersion and catalyst support plate located at bottom flange. Liquid dispersion ring with downflow jets located below liquid inlets. 200-300 mesh screen 4"-6" below top flange. (See Notes 1 and 2). Operating pressure = 1050 psig and operating temperature = 480-680^{o}F.

2. Liquid Separator

Flanged, 12" I. D. x 5' L with liquid-gas demister and liquid level control/indicator/alarm. Operating pressure = 1050 psig and operating temperature = 580-680^{o}F.

3. Gas Quench and Condenser

Condenser is shell and tube. Total exchange area is about 40 ft^2. Dimensions are approximately 12" I.D. x 5' L. Cooling media is high temperature heat transfer oil. Quench uses waste water from water degassifier. Operating pressure = 1050 psig and operating temperature = 550-600^{o}F. Approximate heat duty on condenser = 70,000-100,000 BTU/hour.

4. After Cooler

Shell and tube, same size as condenser. Cooling media is H_2O from cooling tower. Operating pressure = 1050 psig and operating temperature = 100-300^{o}F. Approximate heat duty = 50,000-75,000 BTU/hour.

5. Condenser Receiver

Flanged, 12" I.D. x 5'L. With liquid-gas demister, oil liquid level control/indicator and oil/H_2O interface control/indicator. Operating pressure = 1050 psig and operating temperature = 100-150^{o}F.

6. Oil Degassifier

Flanged, 12" I.D. x 3'L with liquid-gas demister and liquid level control/indicator. Operating pressure = 10 psig and operating temperature = 80-150^{o}F.

7. H_2O Degassifier

Same as Item 6.

8. Process Oil Storage

May be 55 gallon drum depending on code requirements. Otherwise is flanged, 12" I.D. x 4' L with liquid lev indicator (sight glass). Operating pressure = 0-5 psig and operating temperature = 80-100^{o}F.

9. Process Oil Make-Up Pump

Flow = 20-40 gph, self-priming, ΔP = 1050 psig. Operating temperature = 80-100^{o}F.

10. Process Oil Cooler

Shell and tube type. Total exchange area = 50 ft^2. Dimensions are approximately 12" I.D. x 5' L. Cooling media is high temperature heat transfer oil. Exit temperature controlled by varying cooling oil flow. Operating pressure = 1050 psig and operating temperature = 480-680^{o}F. Approximate heat duty = 350,000-400,000 BTU/hour.

11. Process Oil Pump

Flow = 20-40 gpm, self-priming, ΔP = 10-20 psig. Operating pressure = 1050 psig and operating temperature = 480-580^{o}F; with flow rate indicator/ control/alarm.

12. Filters

High temperature and pressure. About 100 mesh. Operating pressure = 1050 psig and operating temperature = 480-580^{o}F.

13. Heat Transfer Oil System

Packaged system capable of delivering 25-30 gpm of oil at 300-400^{o}F with self-priming pump, H_2O or air cooler, 60-100 gallon storage tank and direct fired furnace capable of burning gas of heat content from 450 BTU/SCF to 1000 BTU/SCF or kerosene.

14. Materials of Construction

All units and piping to be made of 316 stainless steel and constructed to meet any necessary code requirements.

15. Electrical Connections

Must be explosion-proof.

Note 1: Sliding float or other instrumentation to determine catalyst bed height inside reactor.

Note 2: Externals - Removable, electrically heated jacket. Thermocouples vertically along wall at 12" intervals extending into reactor 2"-3". T/C at about 4'-5' level connected to temperature alarm. Differential pressure cell capable of compensation for cold and hot leg.

16. Material and Heat Balances

Basis: Material Balance At 100% Feed Conversion With Volatile Oil

Quantity		Rate	% H_2	% CO	% CH_4	% H_2O	% Oil	^oF Temperature	Psig Pressure
Reactor Feed		6,000SCFH	60	20	20	--	None	80 - 120	1,050
Liquid Separator Effluent	Gas	4,340SCFH	Nil	Nil	55.3	27.7	17.0	570 - 670	1,050
	Liquid	20-40 GPM	--	--	--	--	100	570 - 670	1,050
Oil Degasser Input		22 GPH	--	--	--	--	100	80 - 120	10
# 20 Degasser Input		8-9 GPH	--	--	--	100	--	80 - 120	10
Condenser Receiver Gas Effluent		2,400SCFH	Nil	Nil	100	Nil	Nil	80 - 120	10
Process Oil Pump Output		20-40 GPM	--	--	--	--	100	480 - 570	1,050
Process Oil Make-Up Pump Output		20-40 GPH	--	--	--	--	100	80	1,050
Quench Pump Output		4-5 GPH	--	--	--	100	--	80	1,050

Heat Balance (Reactor):

For Reactor Temperature -

Inlet = 250°C

Outlet = 300°C.

Feed Composition = 60% H_2, 20% CO, 20% CH_4

Conversion = 100%

$H_{H_2} = (6.97)(9.2)(572-77) = 31\ 741$

$H_{CO} = (7.07)(3.1)(572-77) = 10\ 849$

$H_{CH_4} = (10.29)(3.1)(572-77) = 15\ 790$

$\Sigma H_R = 58\ 380$

$H_{CH_4} = (10.29)(6.2)(572-77) = 31\ 580$

$H_{H_2O} = (8.215)(3.1)(572-77) = 12\ 606$

$\Sigma H_P = 44\ 186$

$\Delta H_f = (-102,632)(3.1) = 318,159$

Value for ΔH_f taken from Bureau of Mines Report, "Operation of a Sprayed Raney Nickel Tube Wall Reactor for Production of a High-BTU Gas."

$\Delta H = \sum H_P - \sum H_R + \Delta H_T = -332,353$ BTU/H

FOR PSEUDOCUMENE @ 300°C (VOLATILE OIL): $C_p = 0.75$ BTU/lb·°F

$\mu = 0.05$ cp

$P^* = 170$ PSIG

$S_p G = 0.56$

$K = 0.048$ BTU/hr·ft² (°F/ft)

FOR MINERAL OIL @ 300°C (NON-VOLATILE OIL): $C_p = 0.69$ BTU/lb°F

$\mu = 0.46$ cp

$P^* = 0.55$ PSIA

$S_p G = 0.68$

$K = 0.065$ BTU/hr·ft² (°F/ft)

FOR REACTOR WITH $\Delta T = 50°C = 90°F$

$Q = C_p \, \Delta T \, \dot{m}$

$\dot{m} = Q / C_p \Delta T$

$\dot{m}_{PSEUDOCUMENE} = 4933$ #/hr $= 1058$ GPH $= 18$ GPM

$$\dot{G}_{PSEUDOCUMENE} = \frac{18.0 \text{ Gal}}{\text{min} \times 0.35 \text{ ft}^2} = 50.5 \text{ GPM/ft}^2$$

$\bar{V}_{PSEUDOCUMENE} = 3.5$ cm/sec.

$\dot{m}_{mineral\ oil} = 5302$ #/hr $= 947$ GPH $= 16$ GPM

$\dot{G}_{mineral\ oil} = 45\ GPM/ft^2$

$\overline{V}_{mineral\ oil} = 3.1\ cm/sec.$

FOR PROCESS OIL COOLER USING DOWTHERM G AS COOLING OIL:

$\Delta T_{\text{process oil}} = (300 - 250\ °C) = 50°C = 90°F$

$\Delta T_{\text{cooling oil}} = (200 - 150\ °C) = 50°C = 90\ °F$

$\dot{m}_{\text{cooling oil}} = (333{,}000\ BTU/H)\left(\frac{lb \cdot °F}{0.51\ BTU}\right)\left(\frac{1}{90°F}\right) = 7255\ \#/hr$

$\dot{G}_{\text{cooling oil}} = (7255\ \#/hr)\left(\frac{gal}{8.33\ \#}\right)\left(\frac{1}{.89}\right) = 979\ GPH = 17\ GPM$

$Q = UA(\Delta T)_{Lm}$

$$(\Delta T)_{Lm} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2/\Delta T_1)} = \frac{(100 - 100)\ °C}{\ln(100/100)} = 0\ °C = \Delta T$$

assuming $U \approx 60$, then

$$A = (333{,}000\ BTU/H)\left(\frac{Hr \times ft^2\ °F}{60\ BTU}\right)\left(\frac{1}{180\ °F}\right) = 31\ ft^2$$

For 3/4" BWG 12 Heat Exchanger tubes $S/L = 0.17\ ft^2/ft$

FOR 5' tubes $S = 0.84\ ft^2/tube$, THEN:

$$N_{TUBES} = 31\ ft^2 / 0.84\ ft^2/tube = 37\ tubes.$$

$+50\% = 55$ tubes,

THEN PROCESS OIL COOLER SHOULD BE ABOUT 12" D.

Quench = 3.5 GPH H_2O to lower temperature to $\approx 250\,^\circ C = 480\,^\circ F$.

FOR THE CONDENSER:

$$\Delta T_{EFFLUENT\ STREAM} = (250 - 170)^\circ C = 80^\circ C = 144^\circ F$$

$$\Delta T_{COOLING\ OIL} = (200 - 150)^\circ C = 50\,^\circ C = 90\,^\circ F$$

$$\dot{m}_{COOLING\ OIL} = (90{,}000\ BTU/HR)\left(\frac{lb\ ^\circ F}{0.51\ BTU}\right)\left(\frac{1}{90^\circ F}\right) = 1961\ \#/hr$$

$$\dot{G}_{COOLING\ OIL} = (1961\ \#/hr)\left(\frac{gal}{8.33\ \#}\right)\left(\frac{1}{.89}\right) = 265\ GPH = 4.4\ GPM$$

$$Q = UA\,(\Delta T)_{LM}$$

$$(\Delta T)_{LM} = \frac{50-20}{\ln(50/20)} = 33\,^\circ C = 59\,^\circ F$$

again assuming $U \approx 60$, then

$$A = (90{,}000\ BTU/H)\left(\frac{H \cdot ft^2 \cdot {}^\circ F}{60\ BTU}\right)\left(\frac{1}{59\ ^\circ F}\right) = 26\ ft^2$$

For 3/4" BWG 12 Heat Exchanger tubes:

$$N_{TUBES} = 26 / 0.84\ ft^2/TUBE = 31$$

+50% = 46 TUBES.

FOR the CONDENSER AFTERCOOLER:

$$\Delta T_{EFFLUENT\ STREAM} = (170°C - 50°C) = 120°C = 216°F$$

$$\Delta T_{COOLING\ H_2O} = (42 - 30) = 12°C = 22°F$$

$$\dot{m}_{COOLING\ H_2O} = (70,000\ BTU/H)\left(\frac{lb \cdot °F}{1\,BTU}\right)\left(\frac{1}{22°F}\right) = 3182\ \#/hr$$

$$\dot{G}_{COOLING\ H_2O} = (3182\ \#/hr)\left(\frac{gal}{8.33\#}\right) = 382\ GPH = 6.4\ GPM$$

$$Q = UA(\Delta T)_{Lm}$$

$$(\Delta T)_{Lm} = \frac{128 - 20}{\ln(128/20)} = 58.2\ °C = 105\ °F$$

also assuming $U \approx 60$, then

$$A = (70,000\ BTU/H)\left(\frac{H \cdot ft^2 \cdot °F}{60\ BTU}\right)\left(\frac{1}{105\ °F}\right) = 11\ ft^2$$

FOR 3/4" BWG TUBES:

$$N_{TUBES} = 11 / 0.84\ ft^2/tube = 14\ tubes \quad (BWG-12)$$

$$+50\% = 21\ tubes.$$

REACTOR EFFLUENT FEED TO REFORMER FURNACE AND TO STEAM GENERATOR AND TO HEAT TRANSFER OIL FURNACE WILL VARY FROM 6000 SCFH OF 60% H_2, 20% CO, 20% CH_4 to

2400 SCFH OF 100% CH_4. So THAT TOTAL HEAT CONTENT / HOUR WILL VARY FROM 2.7 mm BTU FOR FEED GAS TO 2.4 mm BTU FOR 100% CH_4 GAS.

Reformer furnace will demand 1.3 - 1.6 mm BTU/hr and Steam generator at 300# STEAM/hr will demand 0.7 - 0.8 mm BTU/hr. Total demand 2 - 2.4 mm BTU/hr, leaving an excess of 0 - 0.7 mm BTU/hr.

APPENDIX IV

Programs and Printout

To: WD
From: TWS
DATE: 10/30/72

SUBJ.- METHANATION DATA REDUCTION PROGRAM

THIS PROGRAM PERFORMS THE FOLLOWING CALCULATIONS IN THE ORDER INDICATED.

1. INPUT - LIQUID FLOW IN L/HR = F_L
   - LIQUID DENSITY IN g/cc at PUMP TEMPERATURE = ρ_L^P
   - LIQUID DENSITY IN g/cc at REACTOR TEMPERATURE = ρ_L^R

   OUTPUT - LIQUID FLOW IN gal/min·FT² = F_L^*
   - LIQUID VELOCITY IN cm/sec = u

   EQUATIONS:

$$F_L^* = F_L(\ell/hr) \times \frac{1\,gal}{3.785\,\ell} \times \frac{1\,hr}{60\,min} \times \frac{(2.54\times 12)^2\,cm^2/ft^2}{3.24\,cm^2} \times \frac{\rho_L^P}{\rho_L^R}$$

$$F_L^* = F_L(1.263)\left(\rho_L^P/\rho_L^R\right) \quad \text{(PRINTED)}$$

IN WHICH 3.24 cm² = REACTOR CROSS SECTIONAL AREA.

$$u = F_L(\ell/hr) \times \rho_L^P/\rho_L^R \times \frac{1\,hr}{3600\,sec} \times \frac{1000\,cc}{\ell} \times \frac{1}{3.24\,cm^2}$$

$$u = F_L^*(0.0679) \quad \text{(STORED)}$$

2. INPUT - LIQUID VISCOSITY AT REACTOR TEMPERATURE IN POISE = μ_L
   AVERAGE CATALYST PARTICLE DIAMETER IN cm = d_p
   (ARITHMETIC AVERAGE OF CATALYST MESH SIZE) = d_p

TWO CHARACTERISTIC CATALYST CONSTANTS $= K_1$ & K_2

CHARACTERISTIC FLUIDIZATION REYNOLDS NUMBER $= Re_{pt}$

Height of the undisturbed catalyst bed in inches $= H_{SB}$

GAS FLOW BED EXPANSION FACTOR $= F_{EX} = 1.0 - 1.1$

OUTPUT - FLUIDIZATION REYNOLDS Number correlation $= C_d (Re_{pt})^2$

ADJUSTED (FOR GAS FLOW) ESTIMATED EXPANDED CATALYST BED height in inches $= H$

EQUATIONS:

$$\varphi_L^S = K_1 (\varphi_L^R) + K_2$$

$$C_d (Re_{pt})^2 = \frac{4(980)}{3} \frac{dp^3 \varphi_L^R (\varphi_L^S - \varphi_L^R)}{\mu_L^2}$$

$$= (1307) \left(\frac{dp^3 \varphi_L^R (\varphi_L^S - \varphi_L^R)}{\mu_L^2} \right) \quad \text{(PRINTED)}$$

A GRAPHICAL CORRELATION EXISTS BETWEEN $C_d (Re_{pt})^2$ & Re_{pt}, THE Reynolds number INPUT IS USED TO CALCULATE LIQUID TERMINAL VELOCITY, U_t, FROM:

$$U_t = \frac{(Re_{pt})(\mu_L)}{(\varphi_L^R)(dp)} \quad \text{(STORED)}$$

and,

$$\epsilon = 0.736 \left({}^{U}/_{U_t} \right)^{0.164} \quad \text{(STORED)}$$

and, $H^{\circ}/H_{SB} = \frac{(1-\epsilon_{SB})}{(1-\epsilon)} = \frac{0.51}{(1-\epsilon)}$ (STORED)

and, $H = (H^{\circ})(F_{ex})$ (PRINTED)

3. INPUT
- TOTAL GAS INPUT IN ℓ/HR = F_{g_0}
- MOLE % N_2 IN FEED = $C^{\circ}_{N_2}$
- MOLE % CO IN FEED = C°_{CO}
- MOLE % N_2 IN EFFLUENT = C_{N_2}
- MOLE % CO IN EFFLUENT = C_{CO}
- % CO CONVERSION = K
- % CH_4 YIELD = Y
- mole % CO_2 SELECTIVITY = S_{CO_2}
- CATALYST Weight (gms) = W'
- TOTAL Reactor PRESSURE IN PSIA = P_T
- LIQUID VAPOR PRESSURE at REACTOR TEMPERATURE IN PSIA = P^*
- REACTOR TEMPERATURE IN °K = T_R

OUTPUT
- OVERALL REACTOR Rate $\times 10^3$ in lb-moles CO/lb CATALYST-hr = R_{CO}
- OVERALL REACTOR RATE $\times 10^3$ IN lb-moles CH_4/lb CATALYST-hr = R_{CH_4}
- EFFLUENT WATER DILUTION FACTOR = F_{H_2O}
- LIQUID VAPOR PRESSURE DILUTION FACTOR = $P_T - P^*/P_T$
- VAPOR FLOW RATE AT REACTOR TEMP. & PRESSURE IN ft^3/hr = V
- CATALYST V/W in ft^3 gas at REACTOR T & P / lb CATALYST-hr = V/W
- CORRECTED mole % CO IN FEED = $C^{\circ\prime}_{CO}$
- CORRECTED mole % CO IN EFFLUENT = C'_{CO}
- $\log(C^{\circ\prime}_{CO}/C'_{CO})$

EQUATIONS:

W = CATALYST WEIGHT IN lbs = $W' / 454 \ \text{gms} / \text{gms/lb}$ (STORED)

$$R_{CO} = \frac{F_q\,(\ell/\text{hr})\,(K)\,(C^{\circ}_{CO})}{28.32\,(\ell/\text{ft}^3)\left(359 \times \frac{300}{273}\right)\left(\text{ft}^3/\text{lb-mole}\right)(10)\,W\,(\text{lb})}$$

$$R_{CO} = \cancel{\frac{(F_q)\,(K)\,(C^{\circ}_{CO})}{(W)\,(111730)}}$$ (PRINTED)

$$R_{CH_4} = \frac{(F_q)\,(Y)\,(C^{\circ}_{CO})}{(W)\,(111730)}$$ (PRINTED)

$$V = F_q\,(\ell/\text{hr}) \times \frac{T_R}{T_{amb}} \times \frac{P_{AMB}}{P_T} \times \frac{P_T}{(P_T - P^*)} \times \frac{1}{28.32\ \ell/\text{ft}^3}$$

$$V = (F_q)\,(T_R)\left(\frac{0.00174}{[P_T - P^*]}\right)$$ (PRINTED)

$$V/W = V/W$$ (PRINTED)

$$C^{\circ\prime}_{CO} = C^{\circ}_{CO}\left(\frac{P_T - P^*}{P_T}\right)$$ (PRINTED)

$$C'_{CO} = C_{CO}\left(\frac{P_T - P^*}{P_T}\right)(F_{H_2O})$$ (PRINTED)

TO CALCULATE F_{H_2O}, Let:

T = TOTAL MOLES IN EFFLUENT LESS ANY H_2O FORMED

100 = TOTAL MOLES IN Feed.

S_i = % SELECTIVITY TO i PRODUCT

F_i = MOLES OF i COMPONENT IN FEED

E_i = MOLES OF i COMPONENT IN EFFLUENT

THEN:

$$\frac{F_{CO}}{100} \times 100 = C^{o}_{CO} = F_{CO}$$

$$\frac{E_{CO}}{T} \times 100 = C_{CO}, \quad E_{CO} = \frac{T\,C_{CO}}{100}$$

$$K \equiv \left(\frac{F_{CO} - E_{CO}}{F_{CO}}\right)100 = \left(\frac{F_{CO} - T\,C_{CO}/100}{F_{CO}}\right)100$$

$$K = \frac{100\,C^{o}_{CO} - (T)(C_{CO})}{C^{o}_{CO}}$$

therefore:

$$T/100 = \frac{C^{o}_{CO}(1 - K/100)}{C_{CO}} \quad \text{(STORED)}$$

and if:

N_i = NUMBER OF CARBON ATOMS IN i COMPOUND

C_i = MOLE % OF i COMPOUND IN EFFLUENT

P_i = MOLES OF i PRODUCT IN EFFLUENT.

Y_i = MOLE % Yield to i PRODUCT.

then:

$$S_i \equiv \left(\frac{N_i\,(P_i)}{F_{co} - E_{co}}\right)100$$

and,

$$(S_i)(K) = \frac{N_i\,(P_i)}{(F_{co} - E_{co})} \times \frac{(F_{co} - E_{co})}{F_{co}} \times (100)^2 = Y_i$$

$$Y_i = \frac{N_i\,(P_i)}{F_{co}} \times (100)^2,$$

$$(Y_i)(C^o_{co}) = N_i\,P_i\,(100)^2$$

$$P_{H_2O} \equiv P_{CH_4} + 2P_{c_2} + 3P_{c_3} - P_{co_2}$$

$$P_{H_2O} = \left(\sum N_i P_i\right) - 2P_{co_2}$$

$$P_{H_2O} = \left(\sum \frac{(S_i)(K)(C^o_{co})}{100^2}\right) - \frac{2\,(S_{co_2})(K)(C^o_{co})}{100^2}$$

$$P_{H_2O} = \left[\frac{(K)(C^o_{co})}{(100)^2}\right]\left[\left(\sum(S_i)\right) - 2(S_{co_2})\right]$$

$$= \left[\frac{(K)\,(C^o_{co})}{(100)^2}\right]\left[100 - 2(S_{co_2})\right], \text{ or}$$

$$P_{H_2O} = \left[\frac{K \cdot C^o_{co}}{100}\right]\left[1 - 0.02\,(S_{co_2})\right] \quad \text{(STORED)}$$

$$F_{H_2O} = \frac{T - E_{N_2} + F_{N_2}}{T - E_{N_2} + F_{N_2} + P_{H_2O}}$$

and:

$$C_{N_2} = \frac{E_{N_2}}{T} \times 100$$

$$E_{N_2} = \frac{(C_{N_2})(T)}{100}$$

$$C^{o}_{N_2} = \frac{F_{N_2}}{100} \times 100 = F_{N_2}$$

therefore:

$$F_{H_2O} = \frac{T - (C_{N_2} \times T/100) + F_{N_2}}{T - (C_{N_2} \times T/100) + F_{N_2} + P_{H_2O}} \quad \text{(STORED)}$$

ON THE FOLLOWING PAGE IS A SAMPLE PRINT-OUT OF THE PROGRAM WITH THE VARIOUS ENTRIES AND RESULTS LABELED.

RESULTS			ENTRIES
	30.0000		Liq. Flow (l/hr.)
	0.7250		ρ_{Liq} @ Pump
	0.5000		ρ_{Liq} @ Reactor
Liq. Flow (gal/min-ft²)	49.0540	A	
	400.0000		Gas Flow (l/hr)
	0.0004		μ_{Liq} @ Reactor (POISE)
	0.0450		dp (cm)
	0.8290		K_1
	1.2400		K_2
$C_d (Re_{pt})^2$	331234.6345	A	
	315.0000		Re_{pt}
	5.0000		Height of Settled Bed (in)
	1.0000		Expansion Factor
Expanded Bed Height (in)	7.5871	A	
	0.0000		N_2 } mole % in Feed
	25.2100		CO } mole % in Feed
	0.6600		N_2 } mole % in Eff.
	5.3200		CO } mole % in Eff.
	91.7400		% CO Conversion
	80.6400		% CH_4 Conversion
	9.4700		% CO_2 Selectivity
	32.5000		Cata. Wt. (gms)
moles / R = ~~Hr·gm~~ { $R_{CO} \times 10^3$	115.6629	A	
moles / R = ~~Hr·gm~~ { $R_{CH_4} \times 10^3$	101.6684	A	
	814.7000		P_T } PSIA
	172.0000		P^* } PSIA
	573.0000		T_R (°K)
Gas Flow (ft³/hr) @ React T & P	0.6205	A	
V/W	8.6681	A	
CO^0 (m/o)	19.8876	A	
CO (m/o)	3.0058	A	
$\log_e (CO^0/CO)$	0.3206	A	

METHANATION DATA REDUCTION PROGRAM.

To: DB

From: TWS

Date: 10/31/72

SUBJ: METHANATION GAS CONVERSION PROGRAM

THIS PROGRAM PERFORMS THE FOLLOWING CALCULATIONS THE ORDER INDICATED.

1. INPUT - H_2 STD. ADJUSTMENT FACTOR = $165{,}000 / A_{H_2}(STD) = F^S_{H_2}$

- CO STANDARD AREA = A^S_{CO}

- MOLE % CO IN STANDARD = C^S_{CO}

- CO FEE AREA = A^F_{CO}

OUTPUT - MOLE % H_2 IN FEED = $C^o_{H_2}$

- MOLE % CO IN Feed = C^o_{CO}

EQUATIONS:

$$C^o_{CO} = A^F_{CO}\left(C^S_{CO} / A^S_{CO}\right)$$

$$C^o_{H_2} = 100 - C^o_{CO}$$

THESE FEED CALCULATIONS OCCUPY THE FIRST TWO BRANCH POINTS OF THE PROGRAM, and THE PROGRAM NORMALLY LOOPS BACK TO THE BEGINNING OF BP 2, SO THAT FEED DATA IS RETAINED FROM ONE SET OF EFFLUENT ANALYSES TO ANOTHER. A RETURN TO THE BEGINNING OF THE PROGRAM MUST BE PERFORMED MANUALLY, BY DEPRESSING T( ) - 0 - RESUME.

2. INPUT - UNCORRECTED mole % H_2 in EFFLUENT = C'_{H_2} (FROM STANDARD CHART OF AREA VS % H_2)

- C_2 EFFLUENT AREA = A_{C_2}

- CO_2 " " = A_{CO_2}

- C_3 EFFLUENT AREA = A_{C_3}
- N_2 " " = A_{N_2}
- CH_4 " " = A_{CH_4}
- CO " " = A_{CO}

OUTPUT
- EFFLUENT mole % H_2 = C_{H_2}
- " " " CO = C_{CO}
- " " " CH_4 = C_{CH_4}
- " " " CO_2 = C_{CO_2}
- " " " N_2 = C_{N_2}
- " " " C_2 = C_{C_2}
- " " " C_3 = C_{C_3}
- % CO CONVERSION = K
- mole % CH_4 Yield = Y
- mole % SELECTIVITY TO CH_4 = S_{CH_4}
- " " " " CO_2 = S_{CO_2}
- " " " " C_2 = S_{C_2}
- " " " " C_3 = S_{C_3}
- moles H_2 in Feed = H_{in}
- MOLES H_2 ACCOUNTED FOR BY EFFLUENT ANALYSIS = H_{OUT}
- H_{in} / H_{OUT}

EQUATIONS:

N_i = NUMBER OF CARBON ATOMS IN i COMPONENT

F_i = PUBLISHED THERMAL CONDUCTIVITY FACTOR FOR i COMPONENT.

$$C_{H_2} = C'_{H_2}\left(F^{S}_{H_2}\right)$$ (PRINTED)

$$C_i = \frac{A_i}{F_i} \times \frac{(100 - C_{H_2})}{\sum A_i/F_i}$$ (PRINTED)

$$K = \left[\frac{(\sum N_i C_i) - C_{CO}}{\sum N_i C_i}\right] \times 100$$ (PRINTED)

$$Y = \left(\frac{C_{CH_4}}{\sum N_i C_i}\right) \times 100$$ (PRINTED)

$$S_i = \left(\frac{C_i}{\left(\sum N_i C_i\right) - C_{CO}}\right) \times 100$$ (PRINTED)

$$H_{in} = C^{o}_{H_2}/C^{o}_{CO}$$ (STORED)

$$H_{OUT} = \left[C_{H_2} + 3C_{CH_4} + 5C_{C_2} + 7C_{C_3} - C_{CO_2}\right] / \sum N_i C_i$$ (STORED)

$$H_{in}/H_{OUT} = H_{in}/H_{OUT}$$ (PRINTED)

ON THE FOLLOWING PAGE IS A SAMPLE PRINT-OUT OF PROGRAM WITH THE VARIOUS ENTRIES AND RESULTS LABELED

RESULTS			ENTRIES
	1.0000	ENTER ONCE FOR SERIES OF CALCS.	H_2 FACTOR $\left(= \frac{168{,}000}{\text{STD } H_2 \text{ AREA}}\right)$
	47520.0000		STD CO AREA
	19.4600		CALCULATED MOLE % CO (STD)
	61772.0000		FEED CO AREA
MOLE % H_2 (FEED)	74.7036	A	
MOLE % CO (FEED)	25.2963	A	
	....	.	
BP 2	....	.	
	41.0000		MOLE % H_2 IN EFF.
	1973.0000		C_2H_6 (EFF. AREAS)
	14239.0000		CO_2 (EFF. AREAS)
	530.0000		C_3H_8 (EFF. AREAS)
	1504.0000		N_2 (EFF. AREAS)
	84135.0000		CH_4 (EFF. AREAS)
	24525.0000		CO (EFF. AREAS)
	....	.	
EFF. MOLE % H_2	41.0000	A	
EFF. MOLE % CO	10.3706	A	
EFF. MOLE % CH_4	41.8807	A	
EFF. MOLE % CO_2	5.2684	A	
EFF. MOLE % N_2	0.6359	A	
EFF. MOLE % C_2H_6	0.6843	A	
EFF. MOLE % C_3H_8	0.1597	A	
	....	.	
% CO CONV.	82.5314	A	
	....	.	
% CH_4 CONV.	70.5445	A	
	....	.	
MOLE % SELECTIVITY CH_4	35.4759	A	
MOLE % SELECTIVITY CO_2	10.7526	A	
MOLE % SELECTIVITY C_2H_6	2.7936	A	
MOLE % SELECTIVITY C_3H_8	0.9778	A	
	....	.	
H_2 IN / H_2 OUT	1.0566	A	

METHANATION GAS CONVERSION PROGRAM

GOOD ONLY WHEN FEED CONTAINS ONE CARBON COMPOUND

Chem Systems Inc.
Research Center: 275 Hudson Street, Hackensack, N.J. (07601) *Telephone 201-342-2866*

December 21, 1972

Dr. Ab Flowers
American Gas Association
1515 Wilson Boulevard
Arlington, Virginia 22209

Dear Dr. Flowers:

Enclosed is a copy of the monthly progress report covering the work done during the month of November and the first week in December. Copies are being sent to OCR, the AGA advisors and C. F. Braun.

As indicated in the report our work this month has been limited to one catalyst-liquid system, that is Harshaw and pseudocumene. Since we experienced a substantial number of experimental mishaps the amount of experimental data collected are relatively small. During that time the catalyst was kept in the reactor for close to three weeks; and while it is true that the activity decreased by a factor of three, even at the low activity level, it corresponds to a substantial productivity level. We feel, moreover, that the loss in activity is largely due to the aforementioned experimental problems which resulted in numerous shut downs. As discussed in our review meeting of December 6, 1972 we are concentrating on ascertaining the reasons for the catalyst activity changes with time. We have now run the same catalyst for four days, shutting down the unit at night, without observing a loss in activity and attaining conversions close to 100 percent at a VHSV of 4000 hrs^{-1} at 300°C. Next week we plan to carry out a continuous run of a minimum length of 48 hours. If successful in maintaining activity we will then start our process variable scan.

In the last week we have visited the companies bidding for construction of the synthesis gas generator and the methanation unit to be used in the process development phase.

A final decision will be made early next week and the successful bidders will initiate the work on the basis of a letter of intent.

Very truly yours,

CHEM SYSTEMS INC.

Ramon L. Espino
Director of Research of Development

RLE/hu

enclosure

Chem Systems Inc.

LIQUID PHASE METHANATION

Progress Report No. 7

November 1972

Prepared By Chem Systems

For

The American Gas Association

LIQUID PHASE METHANATION

A. Experimental Work

During the month of November we attempted to evaluate the system: Ni-0104-101 + Pseudocumene, at a low catalyst loading, so that we could operate at conversion levels less than 100%. The first series of runs (50-53-1, 2, 3) were fairly successful. At a VHSV of greater that 8,500 SCFH/Ft^3 fluidized bed we obtained conversions of over 92%.

However, during subsequent operation, a sharp decline in catalyst activity was noted. In an attempt to ascertain the cause of this deactivation a study of the effect of start-up and shut-down procedure was initiated. Early results indicate a strong relationship between activity loss and the start-up/shut-down, intermittent operation.

In addition, a peculiar cyclic conversion pattern was noted during at least two of the runs, 50-57-1 and 50-60-1. After reviewing the data along with the reactor operation procedure we have concluded that the cyclic operation is induced, for the most part, by the wide separator temperature fluctuations (over 80^{o}C) which result from the intermittent pumping of recycle pseudocumene back into the separator. We have subsequently modified our equipment and operation procedure to alleviate these problems. First, we have added block valves to the reactor inlet and outlet so that after purging the catalyst bed at the end of the run we can isolate the reactor and maintain temperature and pressure over night. In addition, we have added a reactor bypass line so that during start-up we can circulate the liquid while it is being heated to reactor temperature before sending it to the reactor. In this way we hope to be able to maintain a relatively constant environment over the catalyst bed, in an attempt to simulate round-the-clock operation.

The data collected during the month are summarized in Table II-1. The drop in activity is clearly shown in terms of the decrease in rate of consumption of CO and generation of methane in terms of moles per hour per pound of catalyst. It should be noted that even when the reaction rate decreased by a factor of three, the productivity of the system is very substantial. This is shown in the table below:

	Predicted preference for an economic liquid phase methanator plant.	Performance of Harshaw - pseudocumene system at low activity level.
VHSV	1000	8550
#moles CH_4/hr-#catalyst	8.5	20.0-18.0

It should also be noted that the activity loss decreased in a step-wise manner rather than following a slow decline with time. This behavior lead us to believe that the loss in system activity is due to maloperation of the reactor rather than to an irreversible catalyst poisoning effect.

B. Design of Process Development Unit

During the month we began to receive bids from the various contractors which had been asked to present preliminary bids on the construction of both the synthesis gas generator and the liquid phase methanation unit. These bids and their timing are summarized in Table II-2.

C. Future Work

i. Experimental

Our efforts will be mainly concentrated on investigating the reasons for the decrease in catalyst activity with reaction time. This will include a non-interrupted run lasting a minimum of 48 hours. Upon completion of this work we will initiate a program designed to achieve the goals enumerated below.

- Generate Data for Operation of PDU and for Preliminary Process Evaluation
- Evaluate Mass Transfer Effects
- Choose Best Reaction Liquid
- Study Catalyst Life and Determine Most Suitable Catalyst

Variables and Systems to be Investigated

Temperature	Particle Diameter
Pressure	Catalyst Loading
Liquid	Reactor Configuration
Catalyst	Feed Composition
Liquid Flow	Time - Catalyst Activity Effects
Gas Flow	

ii. Design of PDU

Early in December a visit will be paid to Gas Machinery Atmospheres, Demarkus and Artisan. We have already narrowed down our choice to these three. Largely on the basis of our discussions with them, we will let out work for both the syn-gas generator and the liquid phase methonator not later than December 20.

Both Chem Systems and C. F. Braun will review the engineering provided by the chosen contractors.

iii. Other Items

On December 6 we had our second review meeting with the advisors from the AGA and Mr. Dykstra of OCR. Based on the encouraging results up to date we were given permission to proceed with the construction of the process development unit (PDU). Moreover, in order to meet the July 1974 deadline for start-up of the 10MM SCF/day pilot plant; we will prepare a bid book to be given to the contractors enumerated below on January 16, 1973. A contractor will be chosen early in February 1973 and hopefully construction of this plant will begin in June 1973.

Chemico
Lummus
Brown and Root
A. G. McKee
Daniel Construction
Pritchard
Stearns-Rogers
Olsen Engineering

Harshaw Ni-0104-101 + Pseudocumene - 53.5 gms. Catalyst

V L/Hr.	VHSV SCFH Feed Gas Ft^3 Fluidized Bed	V/W(1) Ft^3/# Cat-Hr.	Rate x 10^3 #Moles/#Cat-Hr CO Reacted	Rate x 10^3 #Moles/#Cat-Hr CH_4 Produced	Cumulative contact hours with liquid.	Comments
400	8550	.576	64.4	57.1	3	Initial run
400	8600	.616	70.4	63.1	5	Raised temperature
400	6915	.626	71.0	63.4	7	Raised liquid flow. Shut down with N_2 overnight.
400	7700	.546	22.7	17.7	29	Catalyst showed a continuous decline in activity at start-up. Finally leveled off after 7 hours.
400	8550	.622	46.1	38.4	133	Activity somewhat below than previous run. Shut down with N_2 for 168 hours in order to repair pump.
400	8215	.604	39.9	35.8	205	Activity slightly lower than previous run.
400	8215	.475	45.4	40.3	208	Pressure 1000 psig. Slight increase in activity. Shut down with N_2 for 60 hours.

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Harshaw Ni-0104-101 + Pseudocumene - 53.5 gms. Catalyst

Run	$T^{o}C$	L Gal/ Min-Ft^2	V L/Hr.	VHSV SCFH Feed Gas / Ft^3 Fluidized Bed	V/W(1) Ft^3/# Cat-Hr.	Rate x 10^3 #Moles/#Cat-Hr CO Reacted	Rate x 10^3 #Moles/#Cat-Hr CH_4 Produced	Cumulative contact hours with liquid.	Comment
50-53-1	285	18.5	400	8550	.576	64.4	57.1	3	Initial run
50-53-2	298	18.6	400	8600	.616	70.4	63.1	5	Raised temperatur
50-53-3	302	46.5	400	6915	.626	71.0	63.4	7	Raised liquid flo overnight.
50-54-1	275	29.4	400	7700	.546	22.7	17.7	29	Catalyst showed a activity at start off after 7 hours
50-55-1	303	18.8	400	8550	.622	46.1	38.4	133	Activity somewhat Shut down with N_2 repair pump.
50-56-1	300	23.2	400	8215	.604	39.9	35.8	205	Activity slightly
50-56-2 (2)	300	23.2	400	8215	.475	45.4	40.3	208	Pressure 1000 psi activity. Shut d

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TABLE II-1

Harshaw Ni-0104-101 + Pseudocumene - 53.5 gms. Catalyst

V -/Hr.	VHSV SCFH Feed Gas / Ft^3 Fluidized Bed	V/W(1) $Ft^3/\#$ Cat-Hr.	Rate x 10^3 #Moles/#Cat-Hr CO Reacted	Rate x 10^3 #Moles/#Cat-Hr CH_4 Produced	Cumulative contact hours with liquid.	Comments [redacted]
400	8550	.620	25.2	23.4	270	Cyclic variation in apparent activity at a level much lower than previous run. This might be due to wide temperature variation in separator. Shut down with H_2 for 60 hours.
400	8550	.620	28.9	26.5	271	
400	8550	.620	19.8	18.3	272	
400	8550	.620	23.5	21.8	273	
400	8550	.620	19.14	18.17	337	Pump seals failed soon after start up. Shut down with N_2 for 16 hours.
400	8550	.620	- -	- -	350	Pump coupling failed during early part of run. Shut down with H_2 for 150 hours to make pump repairs.
400	8550	.620	20.9	18.6	503	Cyclic variation in apparent activity. Shut down with N_2. Back pressure regulator failed at night and system depressurized.
400	8550	.620	16.3	15.3	505	
400	8550	.620	24.7	22.7	507	
400	8550	.620	29.0	20.5	525	Sharp change in product distribution. Reactor emptied after this run. Catalyst showed a change in color from its reduced state black to a metallic grey.

esent due to vapor pressure of liquid and it is measured at reaction conditions.

Harshaw Ni-0104-101 + Pseudocumene - 53.5 gms. Catalyst

Run	$T^{o}C$	L Gal/ $Min\text{-}Ft^2$	V L/Hr.	VHSV SCFH Feed Gas / Ft^3 Fluidized Bed	$V/W^{(1)}$ $Ft^3/\#$ Cat-Hr.	Rate x 10^3 #Moles/#Cat-Hr CO Reacted	Rate x 10^3 #Moles/#Cat-Hr CH_4 Produced	Cumulative contact hours with liquid.	Comme
50-57-1									
A	300	19.3	400	8550	.620	25.2	23.4	270	Cyclic variatio
B	300	19.3	400	8550	.620	28.9	26.5	271	level much lowe
C	300	19.3	400	8550	.620	19.8	18.3	272	might be due to
D	300	19.3	400	8550	.620	23.5	21.8	273	separator. Shu
50-58-1	~ 300	19.3	400	8550	.620	19.14	18.17	337	Pump seals fail Shut down with
50-59-1	~ 300	19.3	400	8550	.620	- -	- -	350	Pump coupling f run. Shut down make pump repai
50-60-1									
A	300	19.3	400	8550	.620	20.9	18.6	503	Cyclic variatio
B	300	19.3	400	8550	.620	16.3	15.3	505	down with N_2.
C	300	19.3	400	8550	.620	24.7	22.7	507	failed at night
50-61-1	300	19.3	400	8550	.620	29.0	20.5	525	Sharp change in Reactor emptied showed a change state black to

(1) Includes organic vapor present due to vapor pressure of liquid and it is measured at reaction conditions.

(2) Pressure is 1000 psig.

TABLE II - 2

Syn-Gas Generator

Company	Cost	Construction Time
Demarkus	$135,000	5-6 Months
Gas Machinery	173,000	8-10 Months
Howe Baker	343,000	9-11 Months

Methanation Unit

Company	Cost		Construction Time
	SS	(CS)	
Artisan Industries	$ 91,000	(78,500)	7-8 Months
Chem-Pro	251,600	(227,950)	5-6 Months
Demarkus	75,000	(69,700)	5-6 Months
Howe Baker	183,500	(Not Given)	7-8 Months

Site Preparation

Company	Cost	Construction Time
Meschel Construction Company	$18,000	Compatible with Plant Installation
Vanas Construction Company	17,000	Compatible with Plant Installation

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National Technical Information Service
Springfield, VA 22161 (703) 605-6000