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ELEVENTH QUARTERLY TECHNICAL PROGRESS REPORT

DOE CONTRACT NO. DE-AC22-86PC90013

Optimum Catalytic Process for Alcohol Fuels from Syngas

Pittsburgh Energy Technology Center

October 31, 1989

Solvents and Coatings Materials Division

Union Carbide Corporation
South Charleston Technical Center
South Charleston, West Virginia 25303

MASTER

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Patent Cleared by Chicago
OPC on November 27, 1989

Patent Hold

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I. CONTRACT OBJECTIVES

The objectives of this contract are to discover and evaluate the catalytic properties of novel homogeneous, heterogeneous, or combination catalytic systems for the production of alcohol fuel extenders from syngas, to evaluate analytically and on the bench scale novel reactor concepts for use in converting syngas to liquid fuel products, and to develop on the bench scale the best combination of chemistry, reactor, and total process configuration to achieve the minimum product cost for conversion of syngas to liquid fuel products.

II. SCHEDULE

This program was planned as a 33-month research and development effort, extending through September, 1989.

The contract work is composed of three tasks. Task 1, the preparation of a Project Work Plan, has been completed. Task 2 comprises the chemical investigation of novel and existing catalysts for the production of fuel alcohols from syngas, either directly or through a step-wise process. Task 3 consists of engineering activities which will support the chemical investigations and develop economic evaluations and process conceptualization. Tasks 2 and 3 will proceed for the entire duration of the program.

In current work under Task 2, the effort has been mainly on heterogeneous catalysts. Novel systems which may exhibit superior behavior are being investigated.

Task 3 work has involved engineering support for the chemical investigations. Economic evaluations of a base case process for conversion of syngas to fuel alcohols were also pursued. Task 3 work has also involved experiments with selected catalytic systems. Further work in Task 3 will include the evaluation of slurry-catalyzed processes for the production of fuel alcohols or their derivatives.

A ten-month no-cost extension of this contract has been applied for and granted.

III. ORGANIZATION

The development of an optimum process for alcohol fuels from syngas is the goal of a research and development program conducted by a group within the Solvents and Coatings Materials Division of Union Carbide Corporation. During the initial portion of the contract, this group was part of the Engineering, Manufacturing and Technology Services Division.

The work is performed at Union Carbide Corporation's South Charleston Technical Center, South Charleston, West Virginia 25303.

Principal investigaror is Dr. B. Duane Dombek.

Program manager is Dr. Donald C. Best.

IV. SUMMARY OF PROGRESS

A. Task 2: Catalyst Research

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. Our experimentation this quarter has resulted in catalysts with activity as great as 13 lb/ft^3/hr and 46 wt% alcohol selectivity, resulting from changes in catalyst formulation and metal impregnation procedures. Specifically, a particular metal additive was incorporated back into the spinel oxide to promote alcohol formation, and low concentrations of an additional additive were added to maintain high catalyst surface areas. Future work will concentrate on exploring catalyst preparation procedures and bracketing the alkali concentration, spinel composition, and metal loading.

B. Task 3: Engineering Studies

The construction of the continuous slurry reactor system is complete. The slurry reactor was designed to be used for continuous gas-solid-liquid reaction studies. The reactor is a two-liter autoclave with external heaters and internal cooling coils, agitator and baffles. Two liquid streams can be fed to the reactor from two-liter feed tanks. Gas streams of carbon monoxide, hydrogen and nitrogen can also be fed to the reactor. The system was designed to operate at pressures up to 1500 psig. The complete reaction system is located inside a Lexan hood except for the gas cylinders and the liquid pumps. The system is monitored and controlled by a Texas Microsystems industrial (IBM AT compatible) computer running the FIX control software with a μMAC-5000 programmable logic controller.

The system is currently undergoing pre-startup testing and calibration. Startup under reaction conditions is expected to commence in November, 1989. Initial work will involve rigorous testing of the best catalyst developed under Task 2 and reconciling the results with those observed in the fixed bed reaction tubes.

V. CHANGES

There were no contract changes during this quarter.

VI. FUTURE WORK

Work during the next quarter will continue on Tasks 2 and 3, as described in the schedule of Section II.

Task 2 work on heterogeneous catalysts for alcohol production will continue. This work will include the exploration of novel types of heterogeneous catalysts for the conversion of syngas to oxygenates.

Work on Task 3 will involve economic and engineering evaluations as required to support the chemical investigations. It will also involve the study of slurry-catalyzed systems for the production of fuel alcohols.

APPENDIXES

By J. G. Hippler and G. R. Sheffer

Appendix A. USE OF CODE SYSTEM

A code system is being used in this report and throughout the contract period to identify proprietary data or information which may be the subject of future patents. The code system consists of three classifications, each member of which is assigned a number.

Category A encompasses additives, such as ligands, metal complexes, or salts, which apparently function as catalyst promoters.

Category C consists of catalysts or co-catalysts.

Category S includes solvents for catalytic reactions.

Use of the code system has been approved by the Chief Office of Patent Counsel, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

The following coded information is included in this report:

A128 - A153: Metal catalyst additives

Appendix B. PROCEDURES FOR CATALYST TESTING

Catalyst tests carried out under this contract are assigned reference ID numbers which identify the appropriate researcher and the notebook reference of the experiment.

Procedure B(i)

All catalyst evaluations are performed on a microreactor system designed to operate three 6-milliliter u-shaped fixed-bed reaction tubes simultaneously at pressures of 15-1500 psig, at temperatures between 25 and 400°C, and space velocities between 600 and 6000 hr^{-1} (STP). This reactor system was described in detail in our Eighth Quarterly Report. The system is capable of automated on-line gas-phase product analysis with post-sampling knock-out pots to collect product for future analysis. Pressure, feed gas composition and velocity, and off-gas sampling may be operated independently for each reaction tube. However, because the tubes utilize a common sandbath, they must be operated at the same reaction temperature. The microreactor system is equipped with an Emergency Shutdown System (ESD) for unattended, overnight operation.

The standard start-up procedure consists of charging the catalyst, generally in powder form, to the outlet leg of a u-shaped 1/4 in. O.D. 304 stainless steel tube. The catalyst is always diluted with an equal volume of 0.5mm glass beads to minimize the pressure drop across the bed. The inlet leg of the u-tube is filled with activated carbon to trap and decompose any metal carbonyl in the feed gas. Glass wool plugs are used to hold all solids in place. The inertness of all non-catalytic materials has been confirmed. The catalysts are activated using H_2/N_2 gas mixtures at atmospheric pressure in a modified gas chromatograph. The tubes are then placed into the microreactor system. The system is subsequently pressurized with feed gas. The absence of gas leaks is verified with soap solution. After reaction pressure is established, the feed gas flow rate is set and measured. The sandbath temperature is then increased to the desired setpoint. Finally, the off-gas analysis system is activated to provide sampling of the reactor effluent for each reactor tube every four hours.

Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

Procedure C(f)

All product analyses are completed in the gas phase using heated lines to transfer reactor effluent samples. A single Varian 3700 gas chromatograph equipped with two detectors is used for off-gas analysis. Inorganics (H_2, N_2, CO, and CO_2) are separated on a 1/8 in. x 10 ft. 80/100 mesh Carbosieve S-2 column purchased from Supelco and are measured by a thermal conductivity detector. All organic products are resolved on a 1/8 in. x 12 ft. 80/100 mesh Tenax column obtained from Alltech and are measured using a flame ionization detector. The Tenax column has been calibrated on an absolute weight basis using quantified mixtures of C_1-C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Argon is used as the carrier gas for both columns. The following parameters are used for the GC oven and the two columns and detectors:

Temperature ramp: 50°C to 225°C at 8°C/min with a
10 minute hold at the upper temperature

Column	Flow Rate	Injector Temperature
Tenax	20 sccm	220°C
Carbosieve (sample)	20 sccm	170°C
Carbosieve (reference)	20 sccm	170°C

Detector	Temperature	Sensitivity	Attenuation	Other
TCD	200°C	5.0 mV	4X	Filament Temp. = 350°C
FID	250°C	10-10	8X	H_2 flow = 30 sccm Air flow = 300 sccm

Appendix D. TECHNICAL AND EXPERIMENTAL DATA

TABLE OF CONTENTS

I. TASK 2: Catalyst Research

A. Direct Syngas Conversion by Heterogeneous Catalysts

1. Introduction

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. In our last quarterly report, we reported that second-level experiments had predicted that a catalyst consisting of metals A129 and A133 on an alkali-promoted A139/A143 spinel oxide should be capable of an alcohol yield of 12 lb/ft^3/hr at greater than 90% alcohol selectivity. Our experimentation this quarter has resulted in catalysts with activity as great as 13 lb/ft^3/hr and 46 wt% alcohol selectivity but only after changes in catalyst formulation and metal impregnation procedures. Further statistical experimental designed sets to complete optimization of catalyst formulation, preparation, and pretreatment are planned. Our goal remains to develop a catalyst with activity of greater than 20 lb alcohols/ft^3 catalyst/hr and alcohol selectivity of greater than 95 wt%, with C_2-C_6 alcohols comprising at least 30 wt% of the alcohol product.

2. Catalyst Preparation and Characterization

Catalyst Preparation: Except as noted, catalysts this quarter were prepared by coprecipitation and calcination of alkalinized spinel components followed by aqueous impregnation of the transition metals. Coprecipitation was performed by mixing an aqueous solution of metal nitrates with an aqueous solution of potassium carbonate. The flowrate of each solution into the mixing beaker was adjusted to maintain a constant pH of 7. Precipitates were dried in a vacuum oven overnight, impregnated with alkali at a constant level of 9 mole %, and then calcined in air at 350°C for 4 hours. Transition metals were added by incipient wetness impregnation using aqueous solutions of the metal formates or nitrates. The amount of metal impregnated was determined with respect to a desired surface layer coverage of the metal by calculating the moles of metal needed based on the metallic radius of the element and the surface area of the calcined catalyst precursor. A new metal impregnation procedure has also been utilized, which will be described in more detail in the future.

Catalyst Characterization: Surface areas of all calcined catalysts were measured using nitrogen adsorption isotherms. Catalyst densities were determined by measuring the volume in a graduated tube of a specified weight of catalyst.

3. Catalyst Testing

All catalysts were evaluated using Procedure B(i) of Appendix B, and products were analyzed using Procedure C(f) of Appendix C. Before syngas reaction, catalysts were activated by passing a 5% hydrogen in nitrogen gas mix over the catalyst at 275°C for 4 hours using a temperature ramp of 2°C/min. The system was then pressurized with syngas containing an equimolar concentration of carbon monoxide and hydrogen to 1000 psig. The temperature was adjusted to 275°C and the syngas flowrate set at 65 cc/g catalyst/min. The reaction product in most cases consisted exclusively of normal, linear paraffins and alcohols.

4. Catalytic Results

The results of our second experimental design indicated that the best direction for further study was to look at A129/A133 bimetallics supported on an alkali-promoted A139/A143 spinel oxide. The beneficial attributes of impregnating A147 and A136 were to be further explored. In addition, the ranking of alkali promoters for this catalyst system was to be established. A third, five-variable, four-level Hyper-Greco-Latin Square was designed as the next step towards optimization of catalyst formulation (see Table 1).

Table 1. Hyper-Greco-Latin Square Design to Examine Catalyst Formulation

MIX	% A139 IN A139/A143 MIX	ALKALI PROMOTER	A136 LEVEL	A147 LEVEL	% A133 IN A133/A129
Level 1	0	A149	0 ML*	0 ML	0
Level 2	33	A150	1/6 ML	1/6 ML	15
Level 3	50	A151	1/3 ML	1/3 ML	30
Level 4	66	A152	1/2 ML	1/2 ML	45

*ML = monolayer

A total of sixteen catalysts were prepared for this third experimental designed set with compositions listed in Table 2. The total metal (A129 + A133) loading was maintained at 1/2 monolayer. Alkali was added to all catalysts by aqueous impregnation of coprecipitated catalyst precursors before calcination at a constant level of 9 mole %.

Table 2. Transition Metal On Spinel Oxide Catalyst Preparations

Preparation Notebook #	% A139 in A139/A143	Alkali Promoter	A136 Level (ML)	A147 Level (ML)	% A133 in A129/A133
5-GRS-70	0	A149	0	0	0
5-GRS-71	0	A150	1/6	1/3	45
5-GRS-72	0	A151	1/3	1/2	15
5-GRS-73	0	A152	1/2	1/6	30
5-GRS-74	33	A149	1/6	1/6	15
5-GRS-75	33	A150	0	1/2	30
5-GRS-76	33	A151	1/2	1/3	0
5-GRS-77	33	A152	1/3	0	45
5-GRS-78	50	A149	1/3	1/3	30
5-GRS-79	50	A150	1/2	0	15
5-GRS-80	50	A151	0	1/2	45
5-GRS-81	50	A152	1/6	1/6	0
5-GRS-82	66	A149	1/2	1/2	45
5-GRS-83	66	A150	1/3	1/6	0
5-GRS-84	66	A151	1/6	0	30
5-GRS-85	66	A152	0	1/3	15

The behavior of the individual catalysts is summarized in Table 3, while the analysis of the Latin Square is presented in Tables 4 and 5. A simple series of pluses and minuses has been used to indicate the magnitude of influence of each of the variables on the grand average of all responses. The grand average as well as the approximate magnitude of a single plus/minus sign is indicated for each category. Note that three was the maximum number of pluses or minuses given. The maximum result predicted for each category is also provided in the tables. A number of categories have been evaluated, including physical properties (surface area, surface area to catalyst volume ratio) and catalytic performance (alcohol selectivities and yields).

Table 3. Transition Metal on Spinel Oxides Designed Set 3: Catalyst Performance Data
Conditions: 275°C, 1000 psig, SV = 65 cc/g cat/min, $H_2/CO = 1.0$

Catalyst	Surface area (m^2/g)	Alcohol Selec. (wt%)		Alcohol Yield	
		total	(C_2+)*	(lb/ft^3/hr)	(g/g cat/hr)
5-GRS-70	114	13	78	0.3	0.005
5-GRS-71	86	53	60	0.5	0.009
5-GRS-72	78	43	70	0.9	0.015
5-GRS-73	62	57	50	0.9	0.016
5-GRS-74	165	21	88	1.6	0.035
5-GRS-75	125	34	86	2.7	0.060
5-GRS-76	96	31	69	1.1	0.024
5-GRS-77	100	55	49	0.2	0.005
5-GRS-78	111	25	85	0.9	0.025
5-GRS-79	69	25	69	0.6	0.014
5-GRS-80	73	24	76	1.2	0.027
5-GRS-81	75	22	73	1.0	0.022
5-GRS-82	119	11	77	2.3	0.037
5-GRS-83	75	20	90	3.5	0.051
5-GRS-84	65	13	80	0.5	0.008
5-GRS-85	70	43	57	0.6	0.009

*the weight fraction of higher (C_2+) alcohols in the overall alcohol product.

Table 4. Transition Metal on Spinel Oxides Designed Set 3: 5x4 Hyper-Greco-Latin Square Catalyst Chemical Reactivity Responses Relative to the Grand Average

Variable	Level	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)	Alcohol rate (lb/ft^3/hr)	Total rate (lb/ft^3/hr)
% A139 in spinel	0	++	--	--	---
% A139 in spinel	33	+	0	+	0
% A139 in spinel	50	-	+	-	-
% A139 in spinel	66	--	+	++	+++
Alkali Promoter	A149	---	++	0	++
Alkali Promoter	A150	0	+	+++	+
Alkali Promoter	A151	0	0	-	-
Alkali Promoter	A152	+++	---	--	--
A136	0	0	0	0	-
A136	1/6	0	+	-	0
A136	1/3	+	0	+	0
A136	1/2	0	-	0	+
A147	0	-	-	---	--
A147	1/6	0	+	+++	++
A147	1/3	+	-	-	--
A147	1/2	0	+	++	++
% A129 metal	0	--	+	+	+
% A129 metal	15	0	0	-	-
% A129 metal	30	0	+	0	0
% A129 metal	45	+	--	0	+
Grand Average		31 (+/– = 12%)	72 (+/– = 4%)	1.1 (+/– = 18%)	5.1 (+/– = 25%)
Maximum Predicted		73	97	3.4	19.8

Table 5. Transition Metal on Spinel Oxides Designed Set 3: 5x4 Hyper-Greco-Latin Square Catalyst Physical Property Responses Relative to the Grand Average

Variable	Level	Surface area (m^2/g)	Area/Volume (m^2/ml)
% A139 in spinel	0	-	0
% A139 in spinel	33	+++	++
% A139 in spinel	50	-	---
% A139 in spinel	67	-	+
Alkali Promoter	A149	+++	+++
Alkali Promoter	A150	0	0
Alkali Promoter	A151	--	-
Alkali Promoter	A152	--	--
A136	0	N/A	N/A
A136	1/6	N/A	N/A
A136	1/3	N/A	N/A
A136	1/2	N/A	N/A
A147	0	N/A	N/A
A147	1/6	N/A	N/A
A147	1/3	N/A	N/A
A147	1/2	N/A	N/A
% A129 metal mix	0	N/A	N/A
% A129 metal mix	15	N/A	N/A
% A129 metal mix	30	N/A	N/A
% A129 metal mix	45	N/A	N/A
Grand Average		93 (+/– = 5%)	76 (+/– = 7%)
Maximum Predicted		172	128

When the results are scrutinized, the following observations become apparent with respect to each of the variables examined:

1. % A139 in A139/A143 spinel: As the % of A139 in the spinel was increased, the yields and the selectivity to heavier products increased, but the overall selectivity to higher alcohols decreased. The optimum percentage of A139 in the spinel is bounded between $0 < \% < 67$.
2. Alkali Promoter: A149 results in a decrease in alcohol selectivity, but an increase in the higher alcohol fraction, while the effect of A152 is exactly the opposite. Overall, A150 appears to be the optimum alkali to use since it has the most pronounced positive effect on yield without sacrificing the alcohol selectivity. Mixtures of A150 and A152 appear to have some promise.
3. A136 Promoter: Compared to the case using no A136 at all, the addition of A136 had little effect. It will therefore not be examined further.
4. A147 Promoter: Compared to the case using no A147 , the addition of A147 results in an increase in both alcohol and total yield with a small increase in alcohol selectivity. The decrease in yield for level = 1/3 relative to level = 1/2 does permit setting a boundary on the upper limit and will require further study.
5. % A129 in A129/A133 mix: Relative to the case with no A129 in the catalyst, the addition of A129 results in an increase in alcohol selectivity and a small decrease in alcohol yield. The definition of boundaries on the optimum A129 percentage in the A129 and A133 metal mix is not evident from the data.

The maximum alcohol yield predicted using the best combination of variables studied is 3.4 lb/ft^3/hr, much lower than the 12 lb/ft^3/hr that appeared possible based on the data of design set 2. The data indicate a severe skewing of the alcohol distribution toward the higher alcohols (C_2^+ average = 72 wt%). If a methanol component could be added back into the catalyst such that the present C_2^+ yield would not be lost, a catalyst with an overall yield of 8.2 lb/ft^3/hr (30 wt% C_2^+) would be realized.

In order to explore whether the methanol synthesis function could be formulated into the catalyst again, a 4x3 Hyper-Greco-Latin incorporating elements that promoted the synthesis of methanol in previous design sets was constructed (see Table 6). Specifically, A144 was reincorporated into the spinel along with A139 and A143 (for surface area enhancement); A131 and A153 were studied as co-metals with A129; and the promotion effect of A146 relative to A147 was examined. In addition, the optimization of the alkali promoter was continued by exploring A150/A149 and A150/A152 mixtures. All the spinels contained 67% A139. The total alkali content was 9 mol% relative to the other cations forming the spinel. The co-metal loading, introduced by impregnation, was maintained at 1/5 monolayer with 1/4 monolayer of A129 and 1/3 monolayer of A146 or A147. The composition of the sixteen catalysts prepared for testing are given in Table 7.

Table 6. Hyper-Greco-Latin Square Incorporating Elements That Promote Methanol Synthesis

	A144/A143 RATIO IN SPINEL	A129 CO-METAL	PROMOTER	ALKALI
Level 1	3	A131	A147	A149/A150
Level 2	1	A153	A146	A150
Level 3	1/3	A133	A146/A147	A150/A152

Table 7. Hyper-Greco-Latin Square Statistical Designed Set 4: Transition Metal On Spinel Oxide Catalyst Preparations

Preparation Notebook #	A144/A143 Ratio in Spinel	A129 Co-metal	Promoter	Alkali
5-GRS-104-1	3	A131	A147	A149/A150
5-GRS-104-2	3	A153	A146	A152/A150
5-GRS-104-3	3	A133	A146/A147	A150
5-GRS-104-4	1	A131	A146	A150
5-GRS-114-5	1	A153	A146/A147	A149/A150
5-GRS-114-6	1	A133	A147	A152/A150
5-GRS-114-7	1/3	A131	A146/A147	A152/A150
5-GRS-114-8	1/3	A153	A147	A150
5-GRS-114-9	1/3	A133	A146	A149/A150

The results for the individual catalysts are shown in Table 8, while the analysis of the Latin Square is summarized, using pluses and minuses as outlined previously, in Tables 9 and 10. The H_2/CO ratio of the synthesis gas feed was increased in these experiments relative to the previous design sets as a practicality (gases in stock). It is intended to study the influence of reaction parameters later in the catalyst optimization process.

Table 8. Transition Metal on Spinel Oxides Designed Set 4: Catalyst Performance Data
Conditions: 275°C, 1000 psig, SV = 100 cc/g cat/min, $H_2/CO = 2.0$

Catalyst	Surface area (m^2/g)	Alcohol Selec. (wt%) total	Alcohol Selec. (wt%) (C_2+)*	Alcohol Yield ($lb/ft^3/hr$)	Alcohol Yield (g/g cat/hr)
5-GRS-106	87	77	26	4.4	0.050
5-GRS-107	79	4	82	1.7	0.020
5-GRS-108	82	36	55	5.6	0.063
5-GRS-109	64	39	15	1.1	0.015
5-GRS-110	71	30	55	1.1	0.013
5-GRS-111	69	27	57	1.1	0.012
5-GRS-112	89	1	55	0.4	0.004
5-GRS-113	94	45	72	0.1	0.002
5-GRS-114	110	65	85	1.5	0.018

*the weight fraction of higher (C_2^+) alcohols in the overall alcohol product.

Table 9. Transition Metal on Spinel Oxides Designed Set 4: 4x3 Hyper-Greco-Latin Square Catalyst Physical Property Responses Relative to the Grand Average

Variable	Level	Surface area (m^2/g)	Area/Volume (m^2/ml)
A144/A143 ratio in spinel	3	0	+
A144/A143 ratio in spinel	1	---	--
A144/A143 ratio in spinel	1/3	+++	+
A129 co-metal	A131	N/A	N/A
A129 co-metal	A153	N/A	N/A
A129 co-metal	A133	N/A	N/A
Promoter	A147	N/A	N/A
Promoter	A146	N/A	N/A
Promoter	A146/A147	N/A	N/A
Alkali	A149/A150	+	++
Alkali	A150	0	--
Alkali	A150/A152	-	0
Grand Average		83 (+/–= 5%)	110 (+/– = 4%)
Maximum Predicted		110	138

Table 10. Transition Metal on Spinel Oxides Designed Set 4: 4x3 Hyper-Greco-Latin Square Catalyst Chemical Reactivity Responses Relative to the Grand Average

Variable	Level	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)	Alcohol rate (lb/ft^3/hr)	Methanol rate (lb/ft^3/hr)
A144/A143 ratio	3	++	0	+++	+++
A144/A143 ratio	1	0	--	-	-
A144/A143 ratio	1/3	--	++	--	--
A129 co-metal	A131	++	---	0	+
A129 co-metal	A153	0	++	-	-
A129 co-metal	A133	-	++	+	0
Promoter	A147	+++	-	0	+
Promoter	A146	--	+	-	-
Promoter	A146/A147	-	0	+	0
Alkali	A149/A150	+	0	0	+
Alkali	A150	++	-	0	0
Alkali	A150/A152	---	+	-	-
Grand Average		29 (+/– = 16%)	56 (+/– = 10%)	1.9 (+/– = 25%)	0.9 (+/– = 33%)
Maximum Predicted		81	99	6.3	3.2

Upon examining the results listed in Tables 9 and 10, the following observations become apparent with respect to each of the variables studied:

1. A144/A143 ratio in spinel: The addition of A144 to the spinel did increase both the alcohol selectivity and yield. At an A144/A143 ratio of 3, the catalyst surface area is stabilized by A143 as compared to catalysts utilizing only A144 (see 9th Quarterly report) where surface areas of 10-30 m^2/g were observed. The A144/A143 ratio is bounded by: $3 < A144/A143 < \infty$ and will be further optimized in future experiments.

2. A129 co-metal: As expected, A131 resulted in an increase in the methanol selectivity and yield. The effects of A133 and A153 are similar in that both resulted in greater C_2+ selectivities, but A133 did not decrease the oxygenate yield. Relative to A133, A131 does appear superior since the C_2+ alcohol fraction remains satisfactory despite the negative effect of A131.

3. Promoter: A147 continues to be a good promoter resulting in superior alcohol selectivity relative to A146 or an A146/A147 mixture. The promotion of alcohol yield was not as great as in designed set 3 but A147 should continue to be studied.

4. Alkali: Mixtures of A150 with A149 or A152 did not result in superior catalytic performance as compared to the use of A150 alone. The optimal amount of A150 for promotion needs to be further explored.

Overall, the results of the fourth experimental designed set indicate that the methanol synthesis component of the catalyst that was missing in designed set 3 could be "added back" into the catalyst by the incorporation of A144 and A131. The C_2^+ alcohol fraction is still greater than necessary (30 wt%). The maximum alcohol yield predicted by design set 4 is 6.3 lb/ft^3/hr, only 30% of our goal of 20 lb/ft^3/hr, but still greater than that predicted by designed set 3 (3.4 lb/ft^3/hr). If the C_2^+ alcohol yield could be held constant (3.5 lb/ft^3/hr) and the methanol yield increased from 2.8 lb/ft^3/hr to 8.5 lb/ft^3/hr (to yield an alcohol product with $C_2^+ = 30$ wt%), the overall alcohol yield would be 12 lb/ft^3/hr.

In order to increase the alcohol yield further, it was decided to study an alternative catalyst metal impregnation procedure, chosen to increase the dispersion of the catalytic metal employed. Recall that metal dispersion was found in our initial experiments (see

9th Quarterly report) to correlate strongly with the alcohol yield. A fifth, three-variable, two-level Hyper-Greco-Latin Square was designed to explore the influence of the new preparation (see Table 11). An effort to set a lower bound on the A143/A144 ratio (upper bound on A144/A143 ratio) was also incorporated. A133 was chosen as the co-metal for A129 since we had worked extensively with it in previous designed sets. In addition, A132 was also examined as a co-metal because of its chemical similarity and its somewhat comparable performance in designed sets 1 and 2 to A133. The compositions of the actual catalysts prepared are shown in Table 12.

Table 11. Hyper-Greco-Latin Square to Examine Impregnation Procedure

	IMPREGNATION PROCEDURE	A129 CO-METAL	A143/A144 RATIO IN SPINEL
Level 1	new	A133	0
Level 2	nitrates	A132	1/3

Table 12. Hyper-Greco-Latin Square Statistical Designed Set 5: Transition Metal On Spinel Oxide Catalyst Preparations

Preparation Notebook #	Impregnation Procedure	A129 Co-metal	A143/A144 Ratio
5-GRS-106	new	A133	0
5-GRS-107	new	A132	1/3
5-GRS-108	nitrates	A133	1/3
5-GRS-109	nitrates	A132	0

The performance of the individual catalysts is summarized in Table 13, while the analysis of the Latin Square is summarized, using pluses and minuses as outlined previously, in Tables 14 and 15.

Table 13. Transition Metal on Spinel Oxides Design Set 5: Catalyst Performance Data. Conditions: 275°C, 1000 psig, SV = 100 cc/g cat/min, $H_2/CO = 2.0$

Catalyst	Surface area (m^2/g)	Alcohol Selec. (wt%) total	Alcohol Selec. (wt%) (C_2+)*	Alcohol Yield ($lb/ft^3/hr$)	Alcohol Yield (g/g cat/hr)
5-GRS-114-1	55	12	60	2.1	0.024
5-GRS-114-2	120	46	51	13.0	0.160
5-GRS-114-3	120	9	57	0.7	0.008
5-GRS-114-4	55	33	56	4.0	0.039

*the weight fraction of higher (C_2^+) alcohols in the overall alcohol product.

Table 14. Transition Metal on Spinel Oxides Design Set 5: 3x2 Hyper-Greco-Latin Square Catalyst Physical Property Responses Relative to the Grand Average

Variable	Level	Surface area (m^2/g)	Area/Volume (m^2/ml)
Impregnation Procedure	new	N/A	N/A
Impregnation Procedure	nitrates	N/A	N/A
A129 co-metal	A132	N/A	N/A
A129 co-metal	A133	N/A	N/A
A143/A144 ratio	0	- - -	- - -
A143/A144 ratio	1/3	+ + +	+ + +
Grand Average		88 (+/– = 10%)	122 (+/– = 10%)
Maximum Predicted		120	160

Table 15. Transition Metal on Spinel Oxides Design Set 5: 3x2 Hyper-Greco-Latin Square Catalyst Chemical Reactivity Responses Relative to the Grand Average.

Variable	Level	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)	Alcohol rate (lb/ft^3/hr)	Methanol rate (lb/ft^3/hr)
Impregnation Proc.	new	+	0	++	++
Impregnation Proc.	nitrates	-	0	--	--
A129 co-metal	A132	+++	0	+++	+++
A129 co-metal	A133	---	0	---	---
A143/A144 ratio	0	0	0	+	+
A143/A144 ratio	1/3	0	0	-	-
Grand Average		25 (+/- = 20%)	56 (+/- = 10%)	5.0 (+/- = 20%)	2.2 (+/- = 33%)
Maximum Predicted		46	61	13.0	6.4

From analysis of the results presented in Tables 14 and 15, the following observations become apparent with respect to each of the variables examined:

1. Impregnation Procedure: The use of the new impregnation procedure has a very positive effect on alcohol yield as well as slightly improving the selectivity. Optimization of preparation procedures for these catalysts must continue to be studied including modifications of the new metal impregnation method.

2. A129 co-metal: A132 is clearly superior to A133 in both alcohol yield and selectivity. It is noteworthy that A132 did not appear to be as outstanding relative to A133 in designed sets 1 and 2.

3. A143/A144 ratio: The incorporation of A144 into the spinel stabilizes the surface area and results in an increase in alcohol yield with no negative effects on alcohol selectivity. The increase in yield is most likely a result of the higher metal loading on the higher surface area catalysts (constant metal monolayer coverage).

The results of the fifth experimental designed set demonstrate that catalysts much closer to our activity goals are indeed feasible. A132 now appears to be superior to A133 as an A129 co-metal. The new metal impregnation procedure results needs to be examined in more detail but initial results are encouraging. The C_2^+ alcohol fraction is still greater than necessary (30 wt%). If the C_2+ alcohol yield could be held constant (6.6 lb/ft^3/hr) and the methanol yield increased from 6.4 lb/ft^3/hr to 15.4 lb/ft^3/hr (to yield an alcohol product with C_2^+ = 30 wt%), the overall alcohol yield would be 22 lb/ft^3/hr, consistent with our activity goals.

A sixth statistical experimental designed set has been planned to bracket the optimal alkali loading, the A129/A132 metal ratio, the salt used to precipitate the spinel precursor, and the best oxide promoter. The design and results of these catalysts will be reported next quarter. It is anticipated that a set of experiments using a central composite design to determine the optimum catalyst formulation will follow the sixth design set.

B. Task 2 Summary

Work continues on optimization of higher alcohol catalysts consisting of transition metals supported on metal oxides with the spinel structure. Our experimentation this quarter has resulted in catalysts with activity as great as 13 lb/ft^3/hr and 46 wt% alcohol selectivity, resulting from changes in catalyst formulation and metal impregnation procedures. Specifically, A144 was incorporated back into the spinel oxide to promote alcohol formation with low concentrations of A143 to maintain high catalyst surface areas. A132 was found to be superior to A133 as an A129 co-metal. Future work will concentrate on exploring catalyst preparation procedures and bracketing the alkali concentration, spinel composition, and metal loading.

II. TASK 3: Engineering Research

A. Reaction Engineering Studies

1. Introduction

Reaction engineering programs for the past quarter have continued to support the Phase II Reaction Engineering Laboratory. This facility is being developed and constructed with Union Carbide capital funds as part of an overall effort to acquire state-of-the-art laboratory facilities in the catalytic reaction engineering arena. The Phase II facility is specifically designed for the experimental investigation of slurry-catalyzed reactions to produce fuel alcohols or derivatives in the continuous mode. For commercial purposes it is important that the slurry catalyst remain in the reactor to avoid the serious solids-handling problems and possible downstream product degradation that could occur if the catalyst were to leave the reactor in the product stream. The experimental system was designed for the investigation of continuous slurry catalyzed systems. Maximum designed operating pressure for the Laboratory was raised during the quarter to 1500 psig in anticipation of future requirements in this program.

2. Laboratory Facilities

The slurry reactor was designed to be used for continuous gas-solid-liquid reaction studies. Figure 1 shows the flow diagram of the slurry reaction system. Gilson metering pumps are used to feed two liquid streams to the reactor from two-liter feed tanks. Brooks flow meters are used to control the feed rate of carbon monoxide, hydrogen and nitrogen to the reactor. The gas and liquid streams are mixed at a 'T' and fed to the reactor. The reactor is a two-liter autoclave with external heaters and internal cooling coils, agitator and baffles. A switching system in place on top of the reactors allows reversal of the feed and discharge lines in order to backwash a filter on the product discharge line. The reactor effluent is cooled, depressurized, and fed to a two-liter liquid receiver with the gas routed to either a gas chromatograph for on-line analysis or a wet test meter of measurement of flow rate.

The system was designed to operate at pressures up to 1500 psig. Everything in the system has a pressure rating of at least 1500 psig except for the wet test meter and the pressure gauges on the liquid feed tanks and receiver. The complete reaction system is located inside the Lexan hood except for the gas cylinders and the Gilson pumps.

An Analog Devices µMAC-5000 Programmable Logic Controller and a Texas

Microsystems (IBM AT compatible) computer running the FIX software will monitor, control, and collect data for the slurry system. The system is designed for unattended operation and will operate around the clock.

Figure 2 shows the details of the liquid feed system. The feed tanks are two-liter Hoke cylinders suspended from weigh cells. Liquid drains from the feed tanks through 15-micron filters to Gilson (piston-type) metering pumps. A nitrogen blanket can be maintained above the liquid in the feed tanks.

Figure 3 shows the details of the gas feed system. Carbon monoxide, hydrogen, and nitrogen can be separately metered into the reactor. The flow of these gases is measured and controlled by Brooks flow meters. The desired flow rate is entered through the computer. Each Brooks meter has a flow-control regulator upstream and a back-pressure regulator down stream which are used to maintain a 50 psi pressure differential across the Brooks meter. The pressure differential is important to ensure the Brooks meters yields accurate readings.

Figure 4 shows a diagram of the slurry reactor. The liquid and gas feed streams are mixed together at a tee and fed to the reactor. The reactor is a two-liter autoclave which is heated by an external heaters and cooled with an internal cooling coil. The reactor is set to ESD (emergency shut-down) on high temperature, high pressure, or low agitator speed. The low agitator speed can be by-passed for start-up. The exit (and feed) line in the reactor have a filter on the end to keep the solid catalyst in the reactor. The feed and exit lines can be swapped with a four-valve switching system (which is controlled by the computer) in order to back-flush the filters. The pressure is maintained in the reactor with a Research motor valve which is controlled by the computer.

Two autoclaves have been purchased for use as the reactor. The primary reactor is a two-liter Zipperclave from Autoclave Engineers. This vessel can be quickly opened and closed for quick replacement of catalyst charges. However, due to the O-ring seal, this vessel can only be operated at temperatures up to 250°C–280°C. For higher temperature studies (up to 350°C–400°C), a standard bolted-closure autoclave will be used in place of the Zipperclave.

Figure 5 shows a diagram of the product collection system. The effluent from the reactor is collected in one of two two-liter Hoke cylinders (identical to the feed tanks). A three-way valve, which is controlled by the computer, directs the flow to the appropriate receiver. Both receivers can also be used simultaneously by opening the line that joins the base of the two receivers.

The vapors from the liquid receivers are routed to an IBM 5890 Series II gas chromatograph for online analysis for hydrogen, carbon monoxide and reaction products. Liquid samples will be periodically taken from the liquid receivers for GC analysis.

FIGURE 1

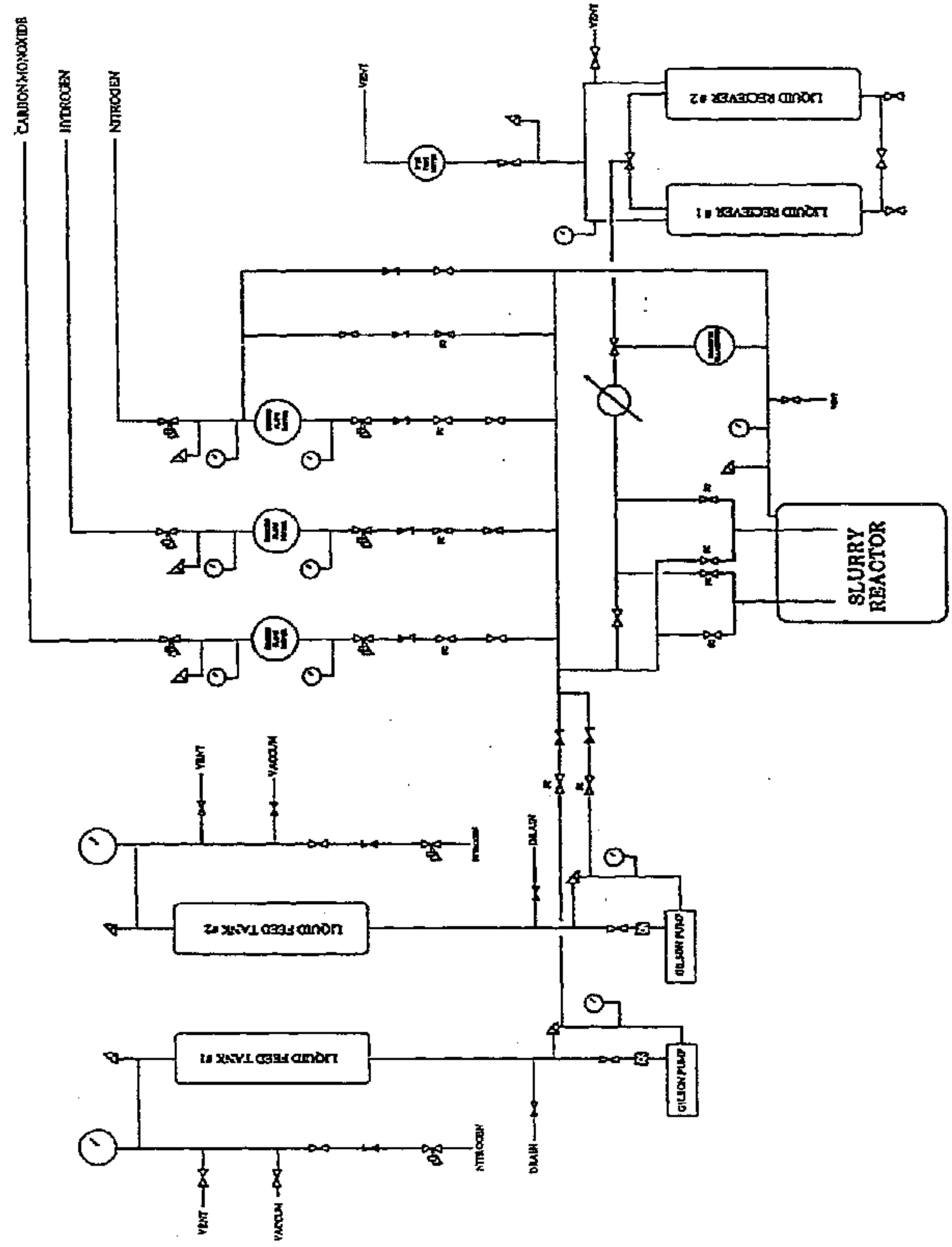

CARBON MONOXIDE
HYDROGEN
NITROGEN
VENT
LIQUID RECIEVER # 2
LIQUID RECIEVER # 1
SLURRY REACTOR
R
VENT
VACUUM
NITROGEN
DRAIN
LIQUID FEED TANK #2
LIQUID FEED TANK #1
GILSON PUMP
GILSON PUMP
VENT
VACUUM
NITROGEN
DRAIN

FIGURE 2

LIQUID FEED SYSTEM

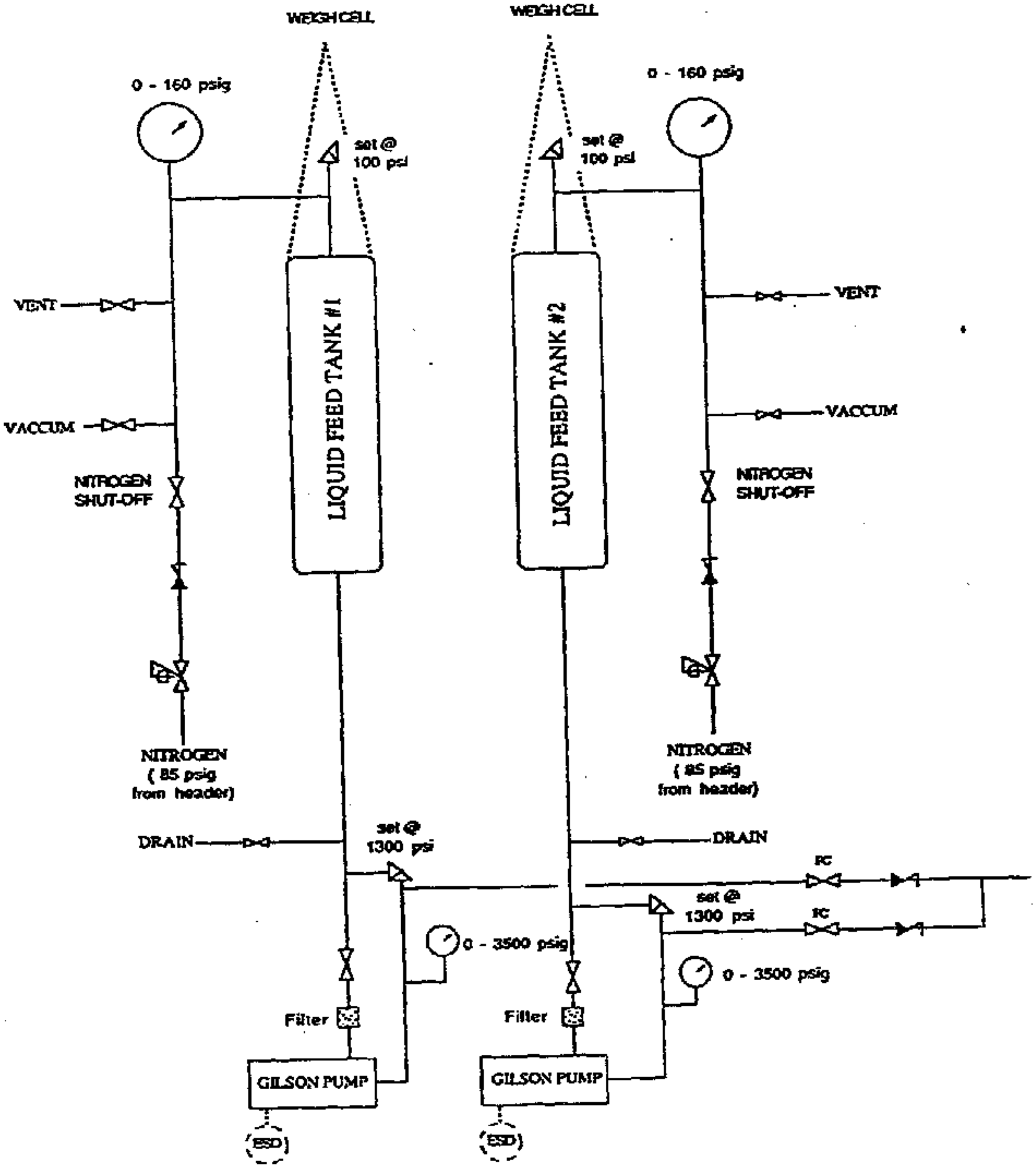


FIGURE 3

GAS FEED SYSTEM

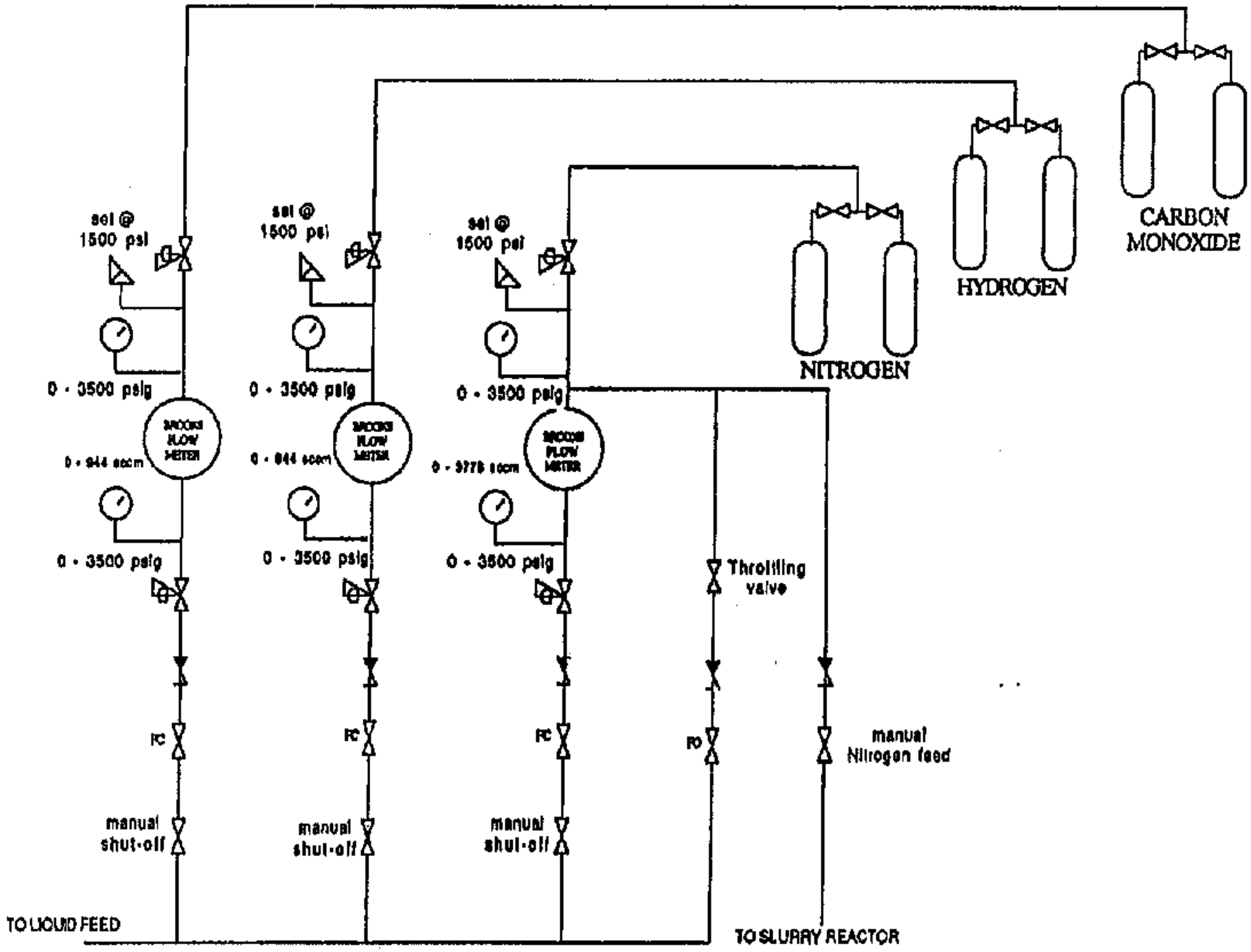


FIGURE 4

SLURRY REACTOR

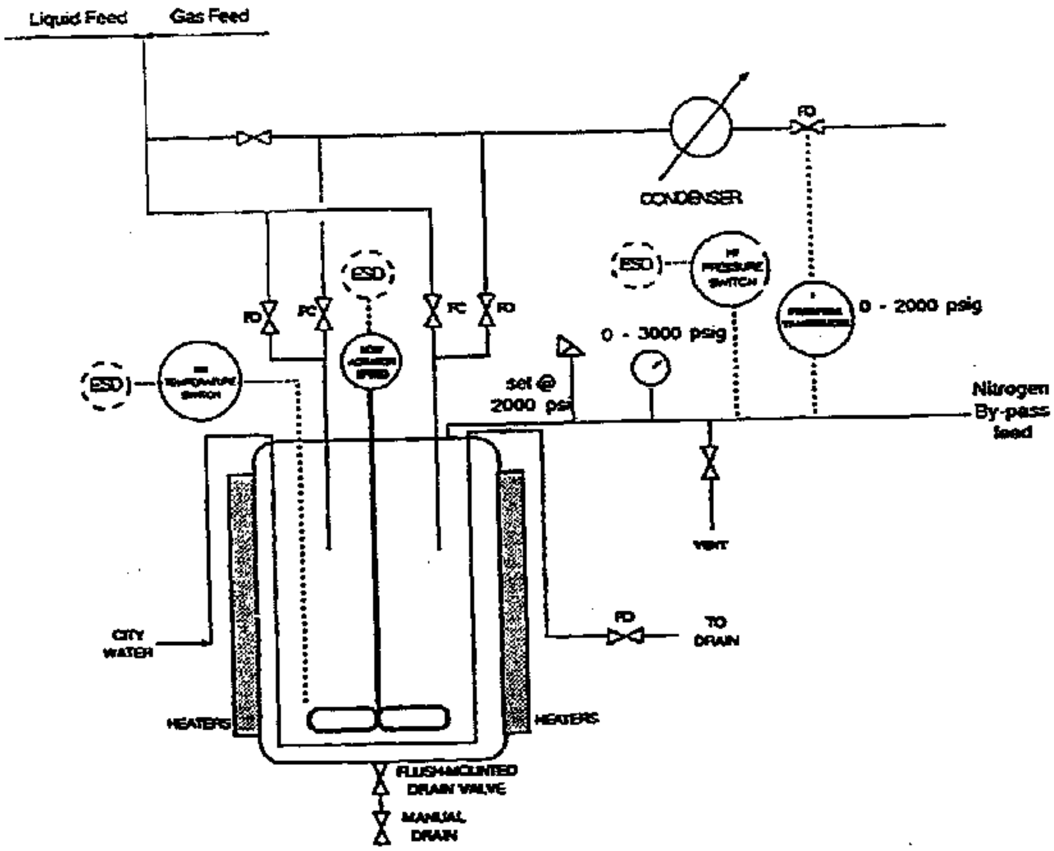
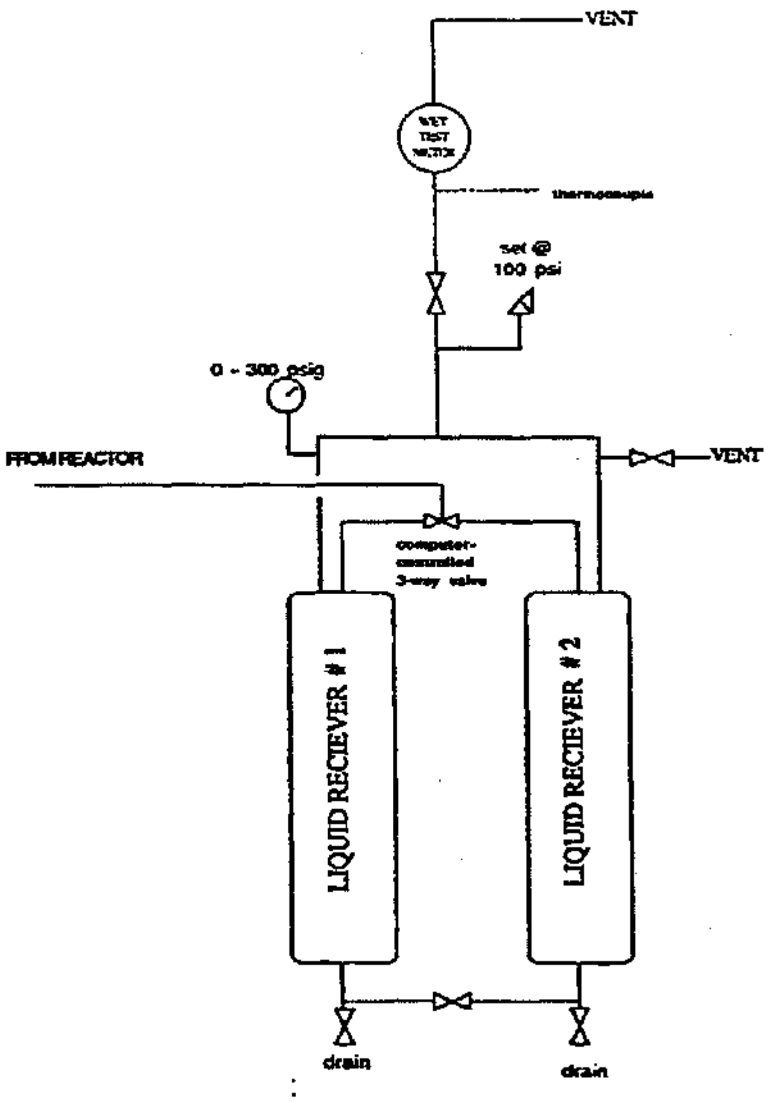


FIGURE 5

PRODUCT COLLECTION SYSTEM



B. Task 3 Summary

The construction of the continuous slurry reactor system is complete. The slurry reactor was designed to be used for continuous gas-solid-liquid reaction studies. The reactor is a two-liter autoclave with external heaters and internal cooling coils, agitator and baffles. Two liquid streams can be fed to the reactor from two-liter feed tanks. Gas streams of carbon monoxide, hydrogen and nitrogen can also be fed to the reactor. The system was designed to operate at pressures up to 1500 psig. The complete reaction system is located inside a Lexan hood except for the gas cylinders and the liquid pumps. The system is monitored and controlled by a Texas Microsystems industrial (IBM AT compatible) computer running the FIX control software with a μMAC-5000 programmable logic controller.

The system is currently undergoing pre-startup testing and calibration. Startup under reaction conditions is expected to commence in November, 1989. Initial work will involve rigorous testing of the best catalyst developed under Task 2 and reconciling the results with those observed in the fixed bed reaction tubes.