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(DE83007978)

ENERGY CONSERVATION

CONVERSION OF CELLULOSIC WASTES TO LIQUID FUELS

By
James L. Kuester

August 1982

Work Performed Under Contract No. AC02-76CS40202

Arizona State University
Tempe, Arizona

U. S. DEPARTMENT OF ENERGY

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CONVERSION OF CELLULOSIC WASTES TO LIQUID FUELS

Submitted
by

James L. Kuester
Principal Investigator

Interim Report to the
Waste Products Utilization Branch
Industrial Programs Division
Office of Conservation and Renewable Energy
U. S. Department of Energy
Contract No. DE-AC02-76CS40202

August 1982

College of Engineering and Applied Sciences
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SUMMARY

Progress for the period June 1, 1981 through May 31, 1982 and future plans for a project to convert various cellulosic materials to quality liquid hydrocarbon transportation fuels is described. The major accomplishment was achieving projected liquid hydrocarbon yields of 30-40 gals/ton of cellulosic feedstock (dry, ash free) for synthesis gas compositions corresponding to that obtainable for "average" feedstocks and using relatively inexpensive cobalt/alumina type impregnated catalysts. Further improvement is expected. The utility of using dolomite to adjust the H_2/CO pyrolysis gas ratio was demonstrated. An iron liquefaction catalyst study was completed that confirmed the detriment of olefins in the feedgas for these type of catalysts (as opposed to cobalt based catalysts). Two completely new fluidized bed reactor systems were designed and installed to accommodate the liquefaction catalyst development work.

An extensive simulator study on gasification transfer loop systems resulted in recommendations for system improvements. Modifications of the 6" fluidized bed liquefaction reactor were also started based on simulator work.

A staged indirect liquefaction system, microreactor system and slurry phase Fischer-Tropsch system were all completed during the reporting period with initial testing in progress at the end of the reporting period. The objective of the staged system is to achieve a lower breakeven commercial scale. The microreactor system is used to explore the feasibility of producing alternative, higher value products other than liquid fuels. The slurry phase system is being assessed as an alternative to the fluidized bed. A completely new control room was constructed to accommodate the increased experimental activity.

A study relating feedstock characterization data to conversion system performance was continued. Material and energy balances were upgraded for the integrated system and some consideration was given to gasification system regenerator fueling, environmental assessment and control of the integrated system.

Continuing laboratory research for the project will emphasize catalyst improvement studies, assess alternative feedstocks, process simplification, alternative product development and environmental assessment as well as a continuation of factor studies of interest.

INTRODUCTION

This report describes the current status and future plans for a project aimed at producing diesel type transportation fuels from various cellulosic materials via indirect liquefaction, i.e., gasification of a solid feedstock to a synthesis gas followed by liquefaction of the gas to a marketable product. A secondary objective is to assess the feasibility of producing alternative, higher value products with the same basic conversion scheme. The project has been under development since 1975 with major funding provided by ERDA/DOE. Sponsors of related work include U. S. Navy, USDA, Arizona Solar Energy Commission, Arizona State University and private industry. Progress in the laboratory scale system for previous ERDA/DOE contract periods (through May 1981) have been reported in three previous Interim Reports (1-3), project Progress Reports (4) and various publications and presentations (5-16). The status of the project at the start of the current reporting period can be summarized as follows:

(1) Liquid hydrocarbon products similar to diesel fuel, kerosene and jet fuels can be produced with the system. These products should be directly marketable as transportation fuels without the necessity of fuel blending or engine modifications.

(2) A wide variety of feedstocks can be processed in the system with comparable performance.

(3) Product yields of greater than 40 gallons diesel fuel/ton of dry ash free feedstock are possible with the system for feedstocks yielding a synthesis gas with olefin compositions of ~ 30 mole %. This olefin composition has been achieved for very few feedstocks to date. An explanation for high olefin production as a function of feedstock characteristics has not been determined.

(4) A decrease in olefin content of the synthesis gas results in a decrease in product yields for cobalt based liquefaction catalysts.

(5) The major operational weakness of the system is possible failure of the gasification system solids transfer loops.

(6) Considerable process simplification (and thus smaller profitable scale) could be achieved with successful implementation of a staged reaction system with both gasification and liquefaction stages operating at the same pressure. Development of a low pressure liquefaction catalyst is a requirement for this task.

(7) Alternative products (other than diesel type fuels) should be possible with the same basic conversion system. Alternative operating conditions and catalyst types should be the major modifications required.

(8) A slurry phase liquefaction reactor offers several possible advantages to a fluidized bed (residence time flexibility, enhanced heat transfer, etc.).

These areas were all addressed during the current reporting period. The current status and continuing research will be discussed in this report.

CURRENT STATUS

The Work Statement for the contract period from June 1, 1981 through May 31, 1982 is contained in the Appendix. The stated tasks were as follows: (1) staged reaction system, (2) alternative feedstocks, (3) alternative products, (4) gasification system regenerator analysis, and (5) factor studies. All tasks were addressed and are imbedded in the following sections. A considerable effort was expended during the contract period with regard to design, fabrication and assembly of new and modified experimental systems. Thus a description of these systems will be presented first followed by a discussion of progress for the various tasks.

Experimental Systems

A listing of major equipment grouping related to the Work Statement is contained in Table 1. Some of this equipment was fabricated during the present reporting period (microreactor system, slurry phase Fischer-Tropsch, several simulator units, liquefaction catalyst testing unit (parallel bank and recycle), some feedstock analysis apparatus, adsorption unit) while others were modified (large scale integrated unit, analytical support). A general description of each system follows:

1. Large Scale Integrated System. This indirect liquefaction system (under development since 1975) consists of a gasification system followed by a catalyst liquefaction system. Feedstock capacity is about 10 lbs/hr. Continuous processing is employed. While the unit is of laboratory scale, the processing steps and procedures are commercially realistic. A flow schematic of the conversion system is depicted in Figure 1 with photographs in Figures 3-4. The gasification system is comprised of two fluidized beds with connecting circulating solid transfer loops. One fluidized bed is used as a feedstock pyrolyzer while the second bed (regenerator) operates in a combustion mode to heat the circulating solids media. Both inert solids (sand) and catalytic materials are under investigation. The fluidized bed approach allows for efficient heat transfer, continuous solids recirculation and elimination of a combustion zone in the pyrolyzer (and thus avoid gas cleanup steps). Cellulosic (biomass) feedstocks are continuously fed to the pyrolyzer and flashed to a synthesis gas consisting of paraffins, olefins, carbon monoxide, hydrogen and carbon dioxide. The gas pass through a cyclone-scrubber system to a compressor. From the compressor, the gas can be distributed to the pyrolyzer and/or liquefaction reactor. Additional gas candidates for fluidizing the pyrolyzer are steam an off gas from the downstream reactor. The regenerator is fluidized by air and recycle gas from the pyrolyz and/or downstream reactors. The off gas from the regenerator is passed through a cyclone-scrubber system before being vented.

   The liquefaction systems consists of a catalytic fluidized bed reactor to produce paraffinic fuel (diesel, jet). A fluidized bed is used to control the reactor temperature with the presence of the significant exothermic heat of reaction that is evolved. Also the fluidization allows for continuous regeneration of

Table 1. Experimental Systems

System	Description
Large Scale Integrated Unit:	10" pyrolyzer-regenerator circulating solid heating system with 6" liquefaction reactor. SIHI compressor. Gas recycle from liquefaction to gasification.
Small Scale Integrated Unit:	3" pyrolyzer staged with 6" liquefaction reactor. Electrically heated. Intermediate scrubber stage. Nash compressor for recycle.
Microreactor System:	microscale fixed and fluidized bed reactors with fluidized bath heater.
Slurry Phase Fischer-Trospch Reaction System:	5" x 35" reactor with off gas and circulating catalyst slurry system.
Liquefaction Catalyst Testing Unit:	2" fluidized bed reactors with common synthesis gas feed system. Six units in parallel. Additional reactor with recycle capability with compressor.
Process Control Equipment:	electronic controllers, recorders, data reduction equipment, etc. to monitor and control the various conversion systems.
Simulator Equipment:	plastic model units -- cross riser transfer loop, injector transfer loop, internal recycle transfer loop, etc.
Feedstock Preparation:	cutting, hammer and ball mills, pulverizer, chipper, screeners.
Feedstock Analysis:	heating values, extraction analyses, ash content, etc.
Catalyst Preparation:	hot plate mixers, calcining furnaces, drying equipment, etc.
Analytical Support:	gas chromatographs, (5), gel permeation chromatograph.
Catalyst Characterization:	surface area, porosity, surface and bulk composition, etc.

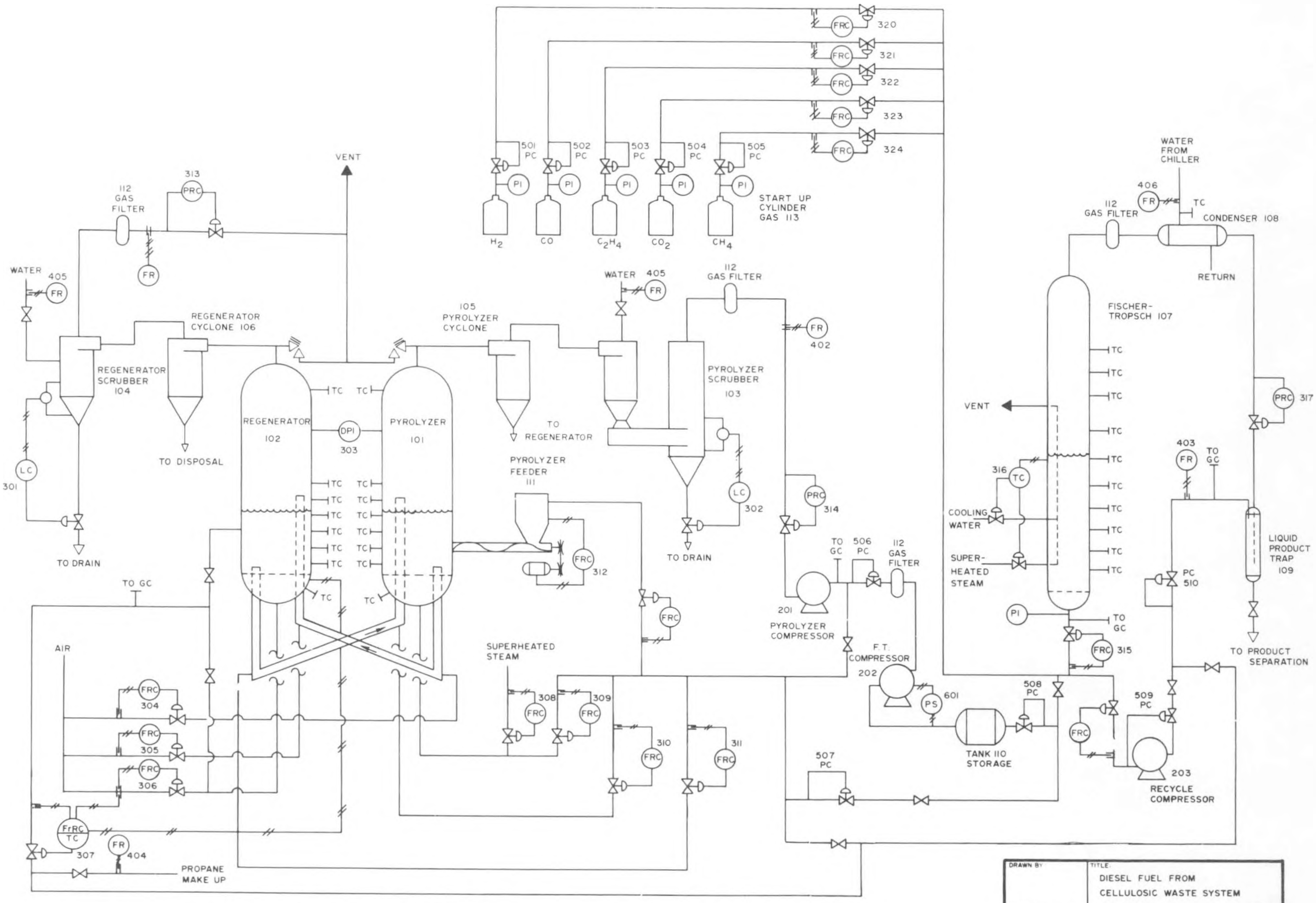

Figure 1. Large Scale Integrated Unit - Schematic

DRAWN BY

TITLE:
DIESEL FUEL FROM
CELLULOSIC WASTE SYSTEM

COLLEGE OF ENGINEERING AND APPLIED SCIENCES
ARIZONA STATE UNIVERSITY TEMPE, AZ 85281

DWG NO

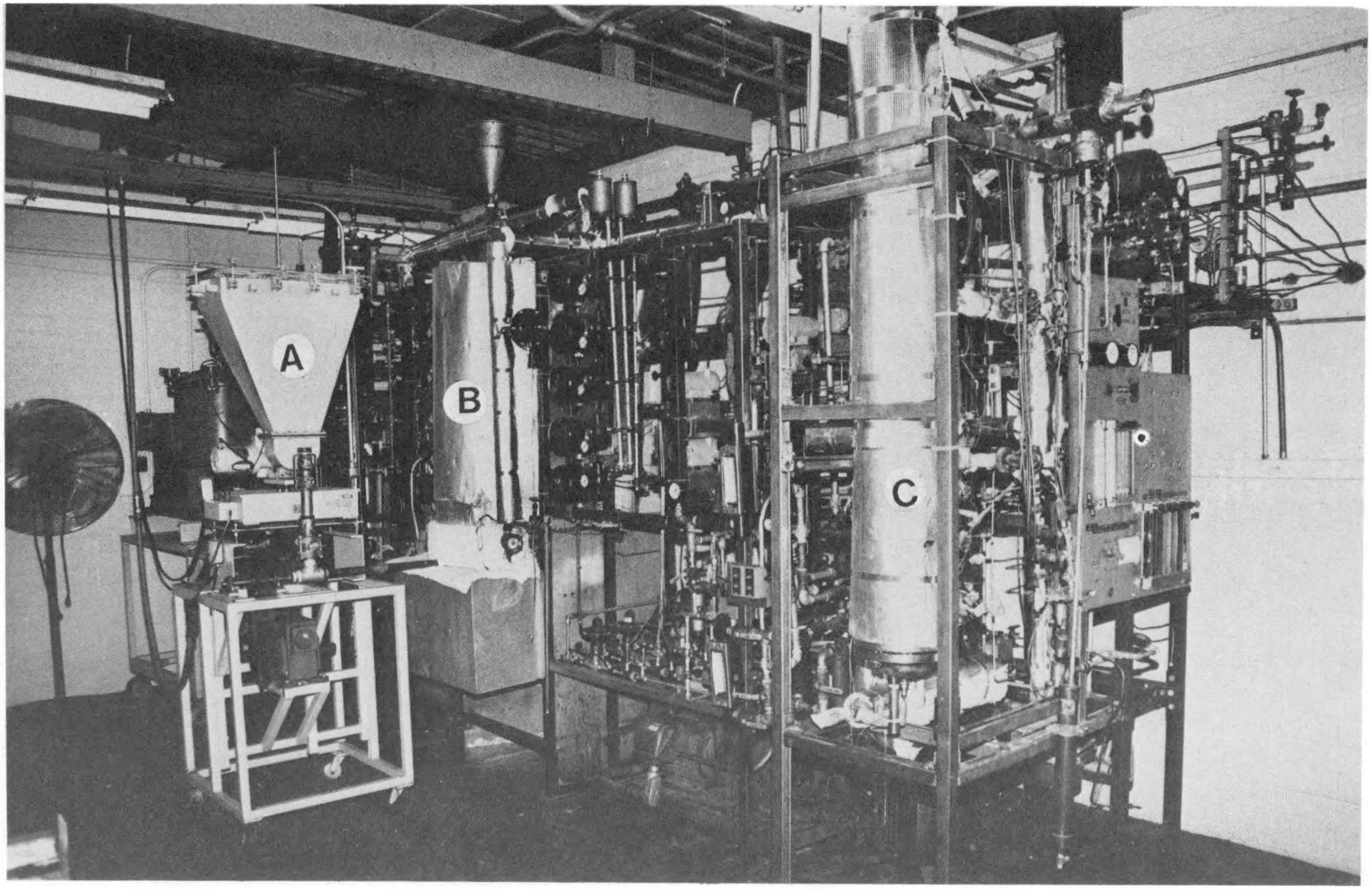

Figure 2. Large Scale Integrated Unit

(A=feeder, B=pyrolyzer, C=liquefaction reactor)

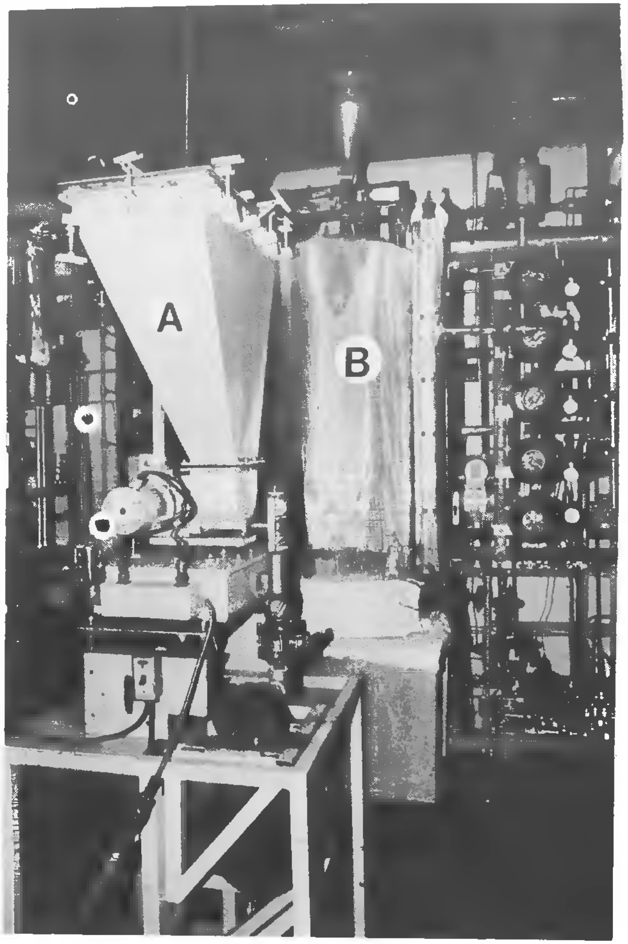

Figure 3.
Gasification System

(A=feeder, B=pyrolyzer)

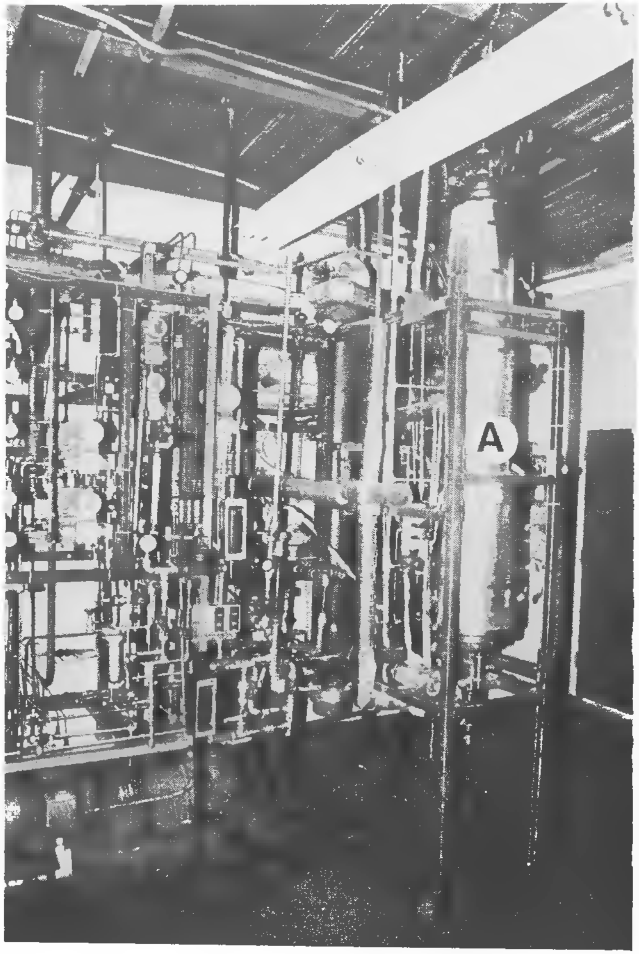

Figure 4.
Liquefaction System

(A=liquefaction reactor)

the catalyst if necessary. In the catalytic fluidized bed, the reactive components in the synthesis gas (olefins, carbon monoxide, hydrogen) are converted to a primary paraffinic hydrocarbon phase and a secondary alcohol-water phase. The off gas from this reactor accumulates an appreciable amount of normal paraffins plus carbon dioxide and can be recycled to the liquefaction reactor inlet, pyrolyzer and/or regenerator. A modified liquefaction reactor (see Factor Studies section) was under construction at the end of the present report period. A photograph is shown in Figure 5.

2. Small Scale Integrated System. This indirect liquefaction system consists of a staged gasifier-scrubber-liquefaction system. A schematic appears in Figure 6 and a photograph in Figure 7. Auxilliary equipment includes a continuous feeder, recycle compressor, condensors and traps. The system is electrically heated. Capacity is about 5 lbs/hr of feedstock.

3. Microreactor System. Test unit for initial catalyst screening. Small (~ 10 grams catalyst loading) reactors immersed in external fluidized bed heating bath. Both fixed and fluidized bed microreactors are available. Auxilliaries consist of a feed gas system, condensor and trap. A schematic is shown in Figure 8 with a photograph in Figure 10.

4. Slurry Phase Fischer-Tropsch Reaction System. A gas sparged, liquid media system alternative to a fluidized bed. The system includes a feed gas system, slurry circulation via a pump and product collection. A schematic appears in Figure 9 with a photograph in Figure 11. The scale is compatible with the integrated systems.

5. Liquefaction Catalyst Fluidized Bed Test Reactors. This systems consists of a bank of six parallel 2" fluidized beds with common feed gas system and condensor. One reactor is equipped with a quartz window for visual interpretation. See Figures 12 and 14. An additional 2" fluidized bed reactor is equipped with a recycle compressor (see Figures 13 and 15).

6. Process Control Equipment. Controllers, set stations, recorders, on line composition monitors, data reduction equipment, alarms, shut down circuits, etc. are housed in a control room (Figure 16). Process interface equipment (primary elements, transmitters, transducers, final control elements) are field mounted on the processing units in the adjacent laboratories.

7. Simulator Equipment. An array of transparent simulators have been constructed to aid the design of real (hot) reactor systems. Examples of simulators constructed and tested during the present reporting period appear in Figures 17-29. All of the simulators depicted are aimed at improvements in the gasification system.

8. Feedstock Preparation. A variety of size reduction mills (chipper, hammer, cutting, pulverizer, ball) are available. In addition, screen separators in a variety of configurations and sizes are utilized. See

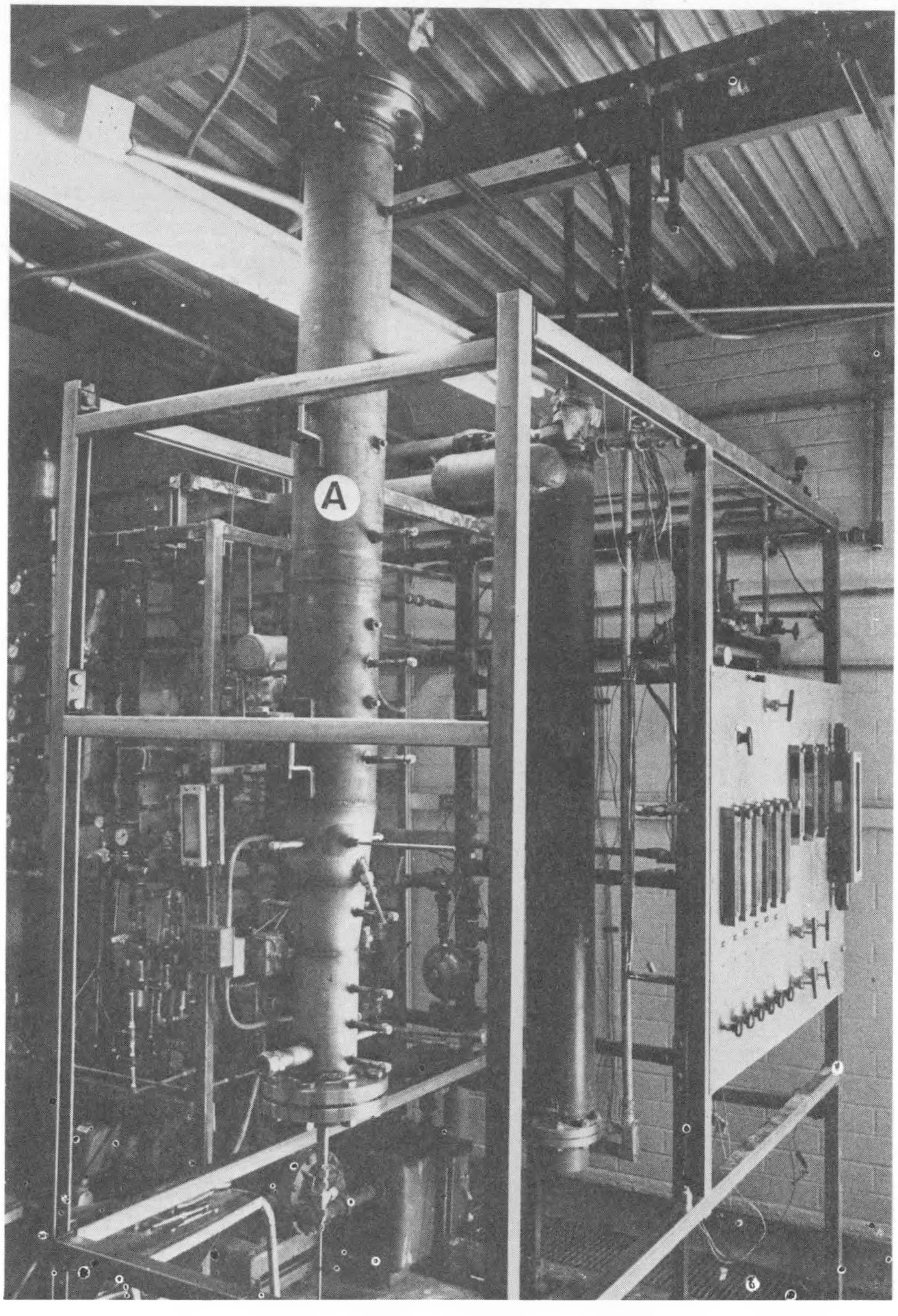

Figure 5. Modified 6" Liquefaction Reactor System (under construction)

(A=liquefaction reactor)

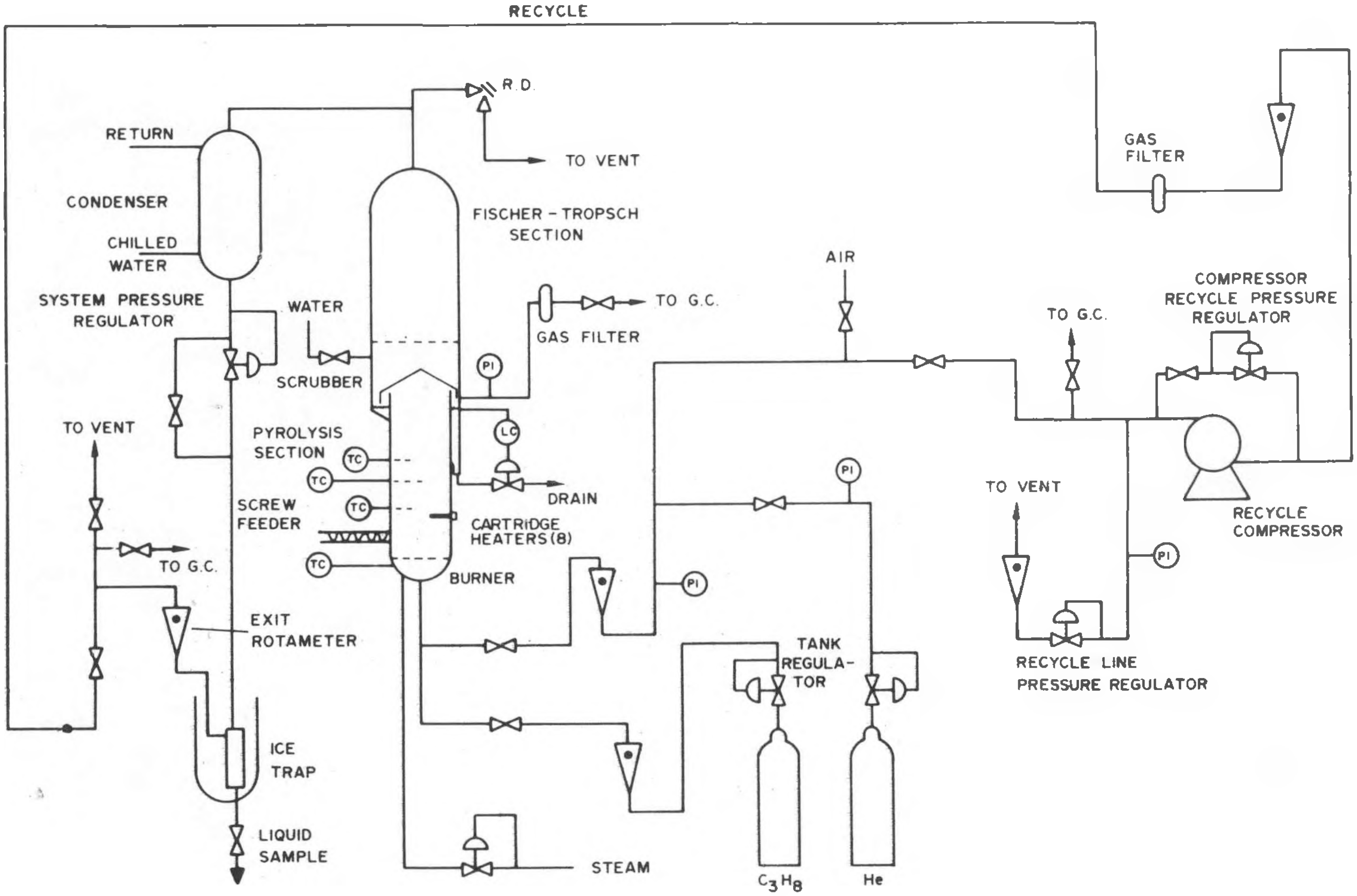

Figure 6. Small Scale Integrated Unit - Schematic

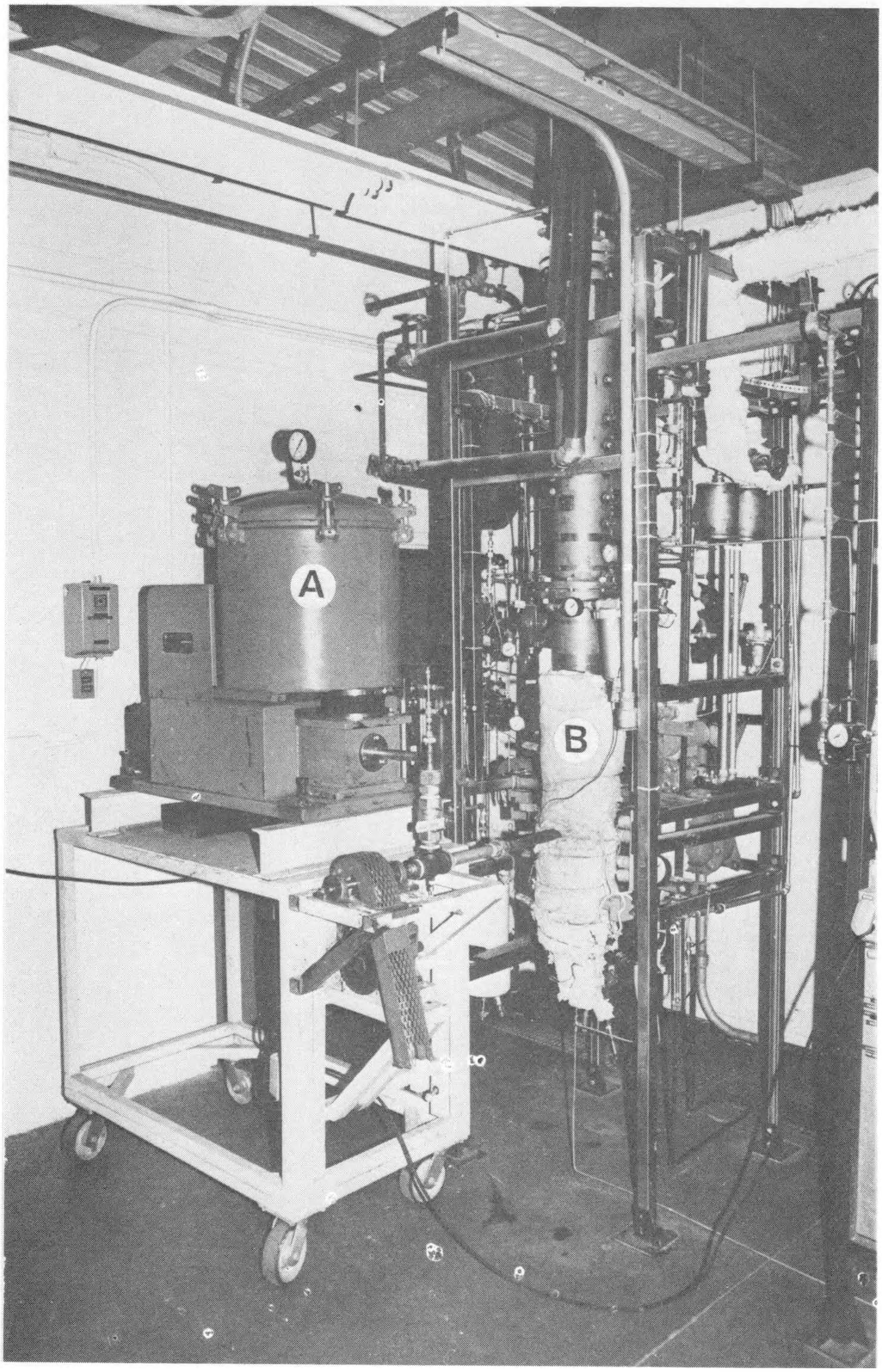

Figure 7. Small Scale Integrated Unit

(A=feeder, B=staged reactors)

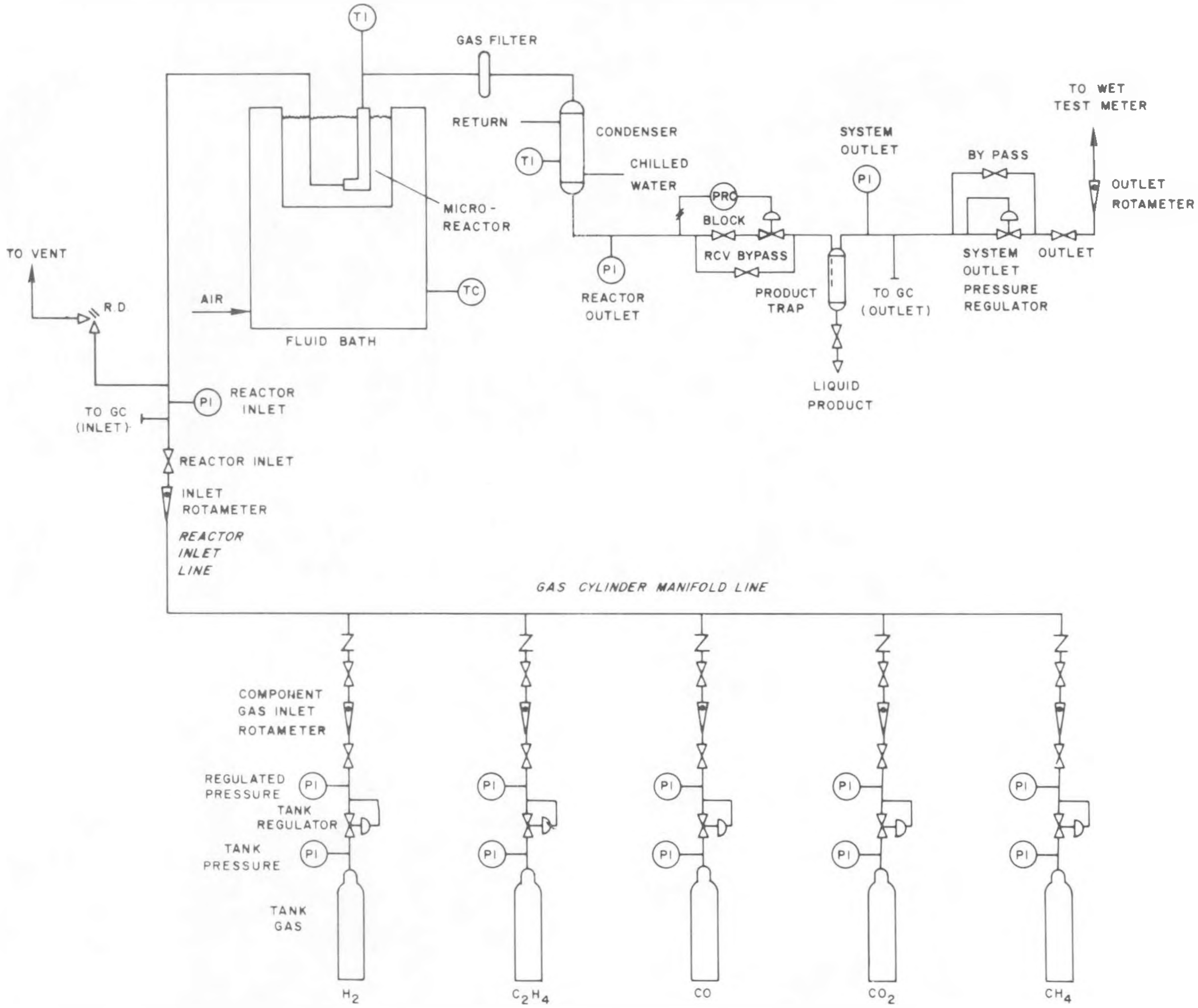

Figure 8. Microreactor System - Schematic

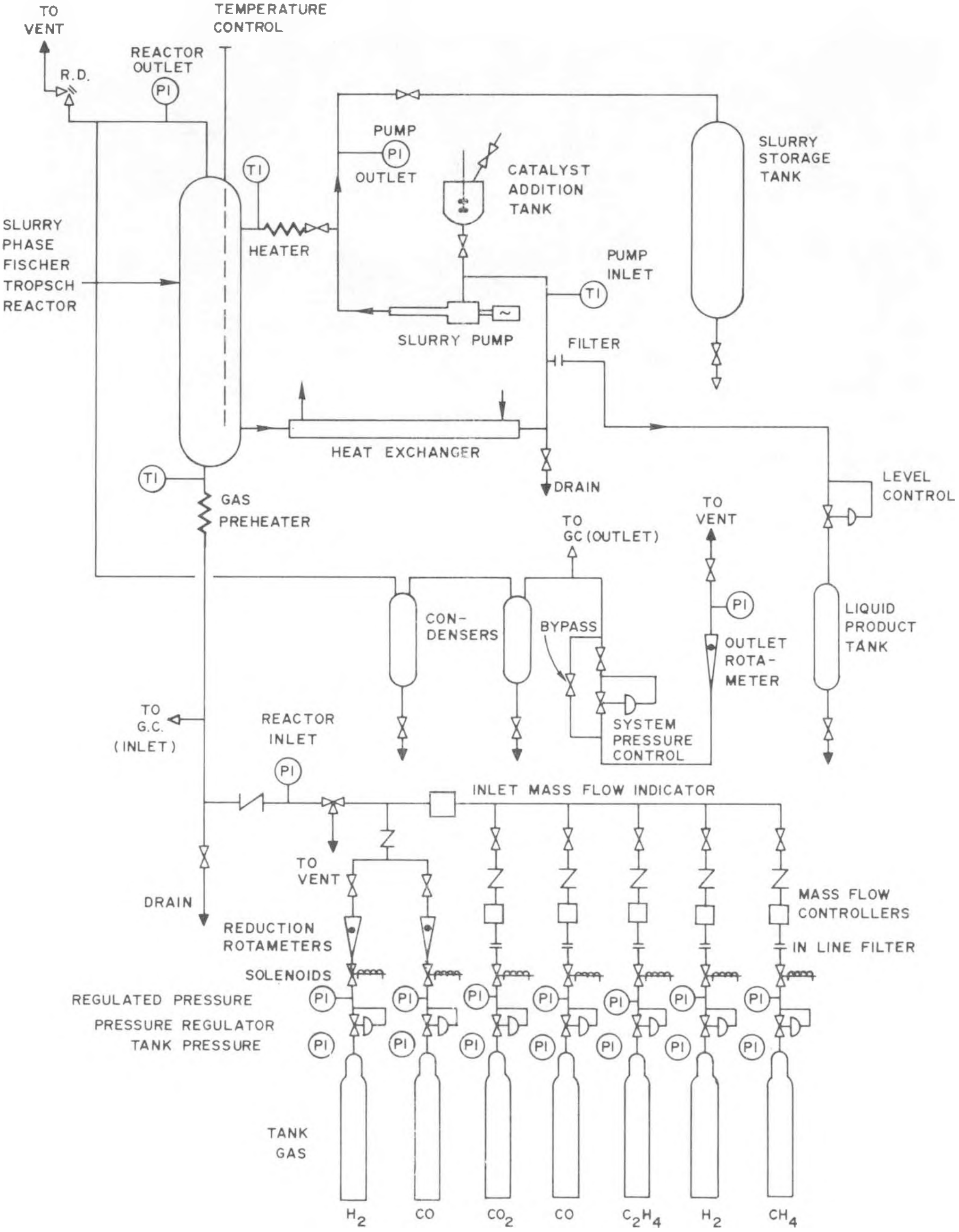

Figure 9. Slurry Phase Fischer-Tropsch Reaction System - Schematic

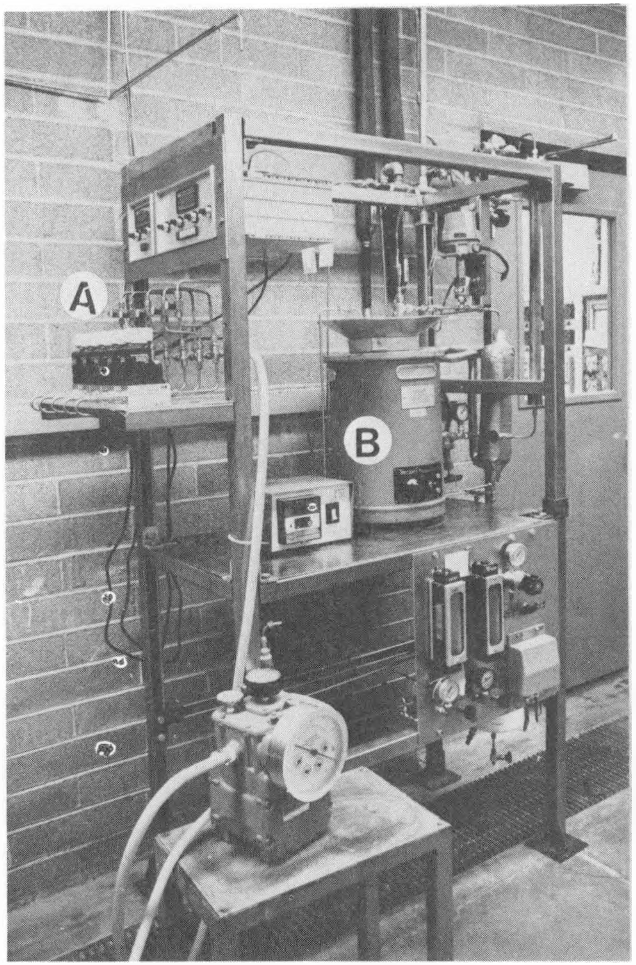

Figure 10.
Microreactor System

(A=mass flowmeters, B= reactor heater)

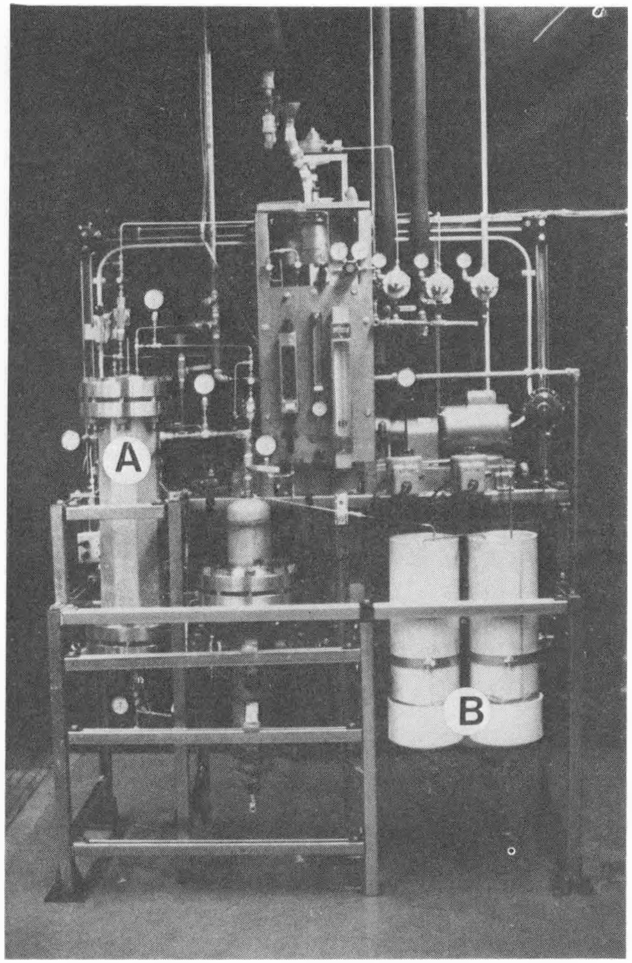

Figure 11.
Slurry Phase Fischer-Tropsch Reaction System

(A=reactor, B=product traps)

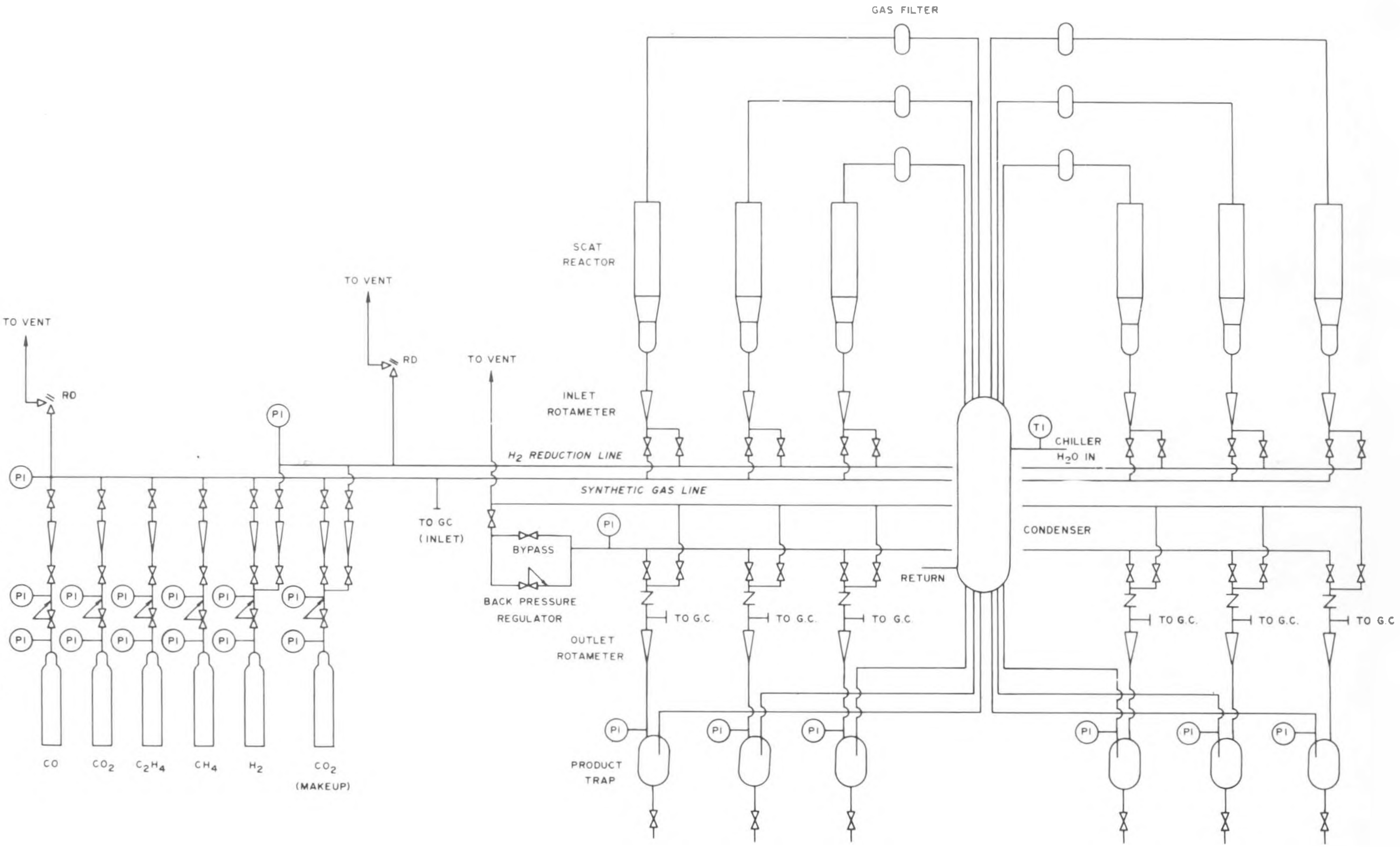

Figure 12. Liquefaction Catalyst Fluidized Bed Test Reactors (parallel bank) - Schematic

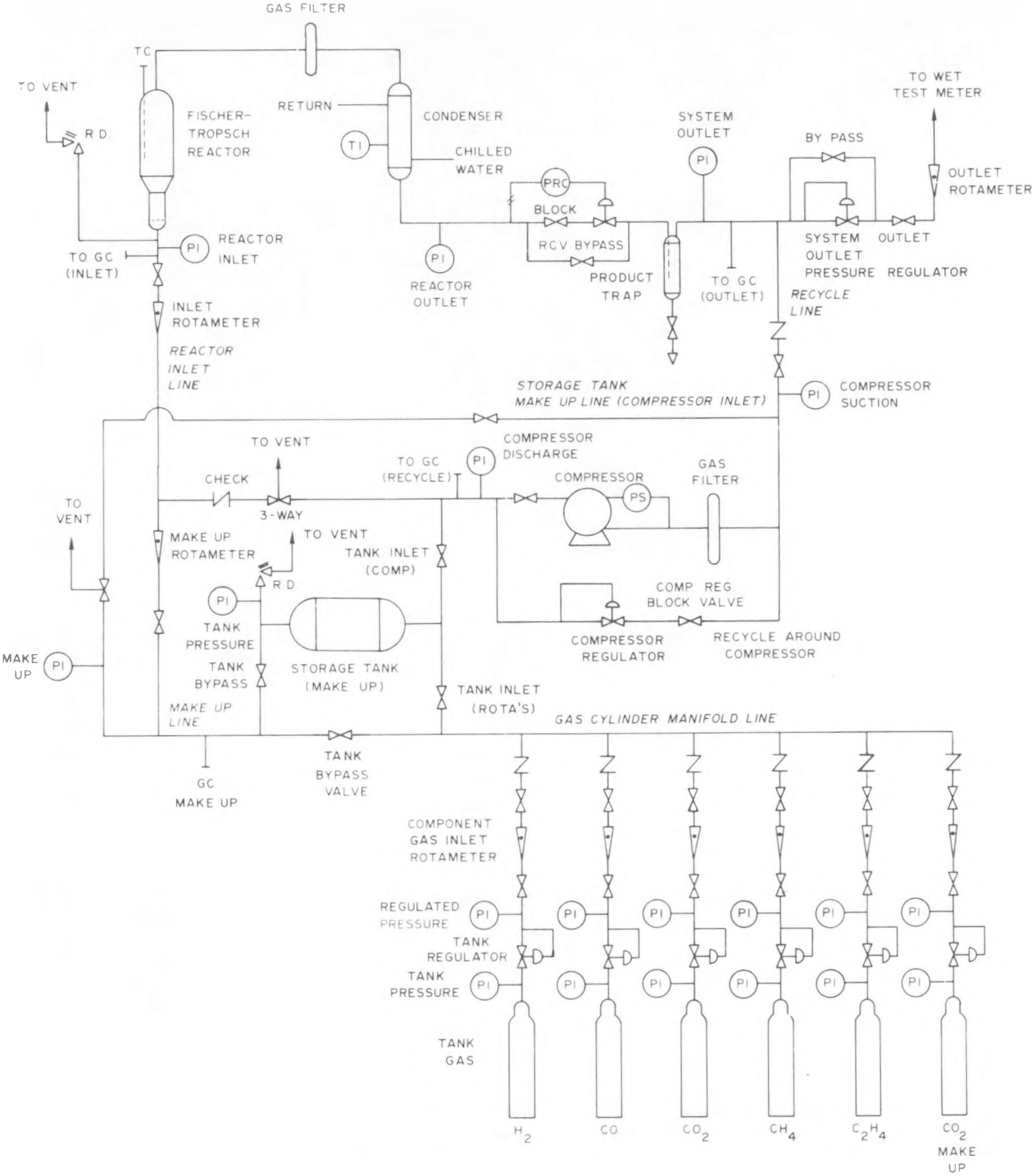

Figure 13. Liquefaction Catalyst Fluidized Bed Test Reactor (with recycle) - Schematic

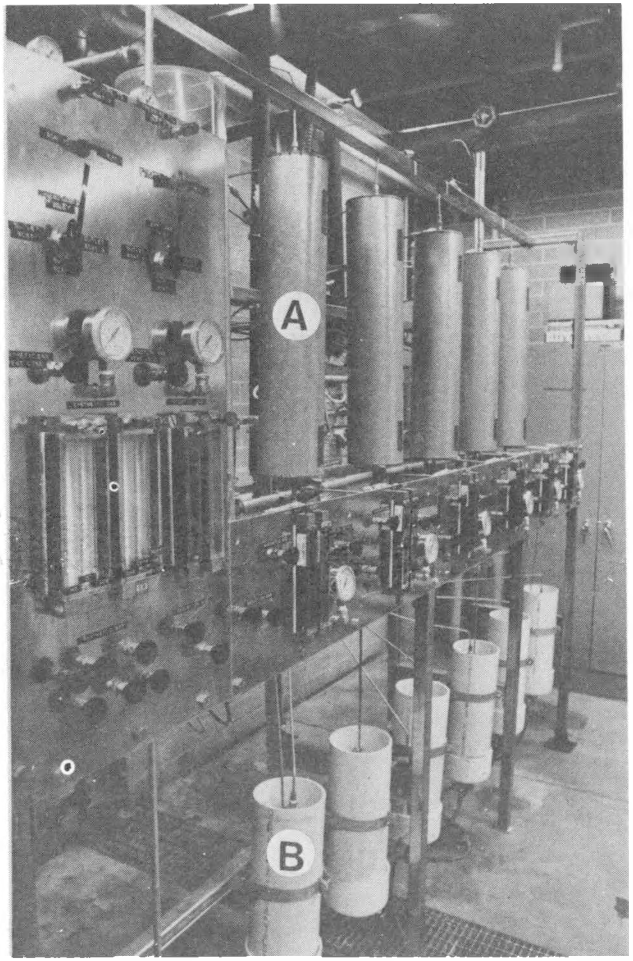

Figure 14.
Liquefaction Catalyst Fluidized
Bed Test Reactors
(parallel bank)

(A=reactors, B=product traps)

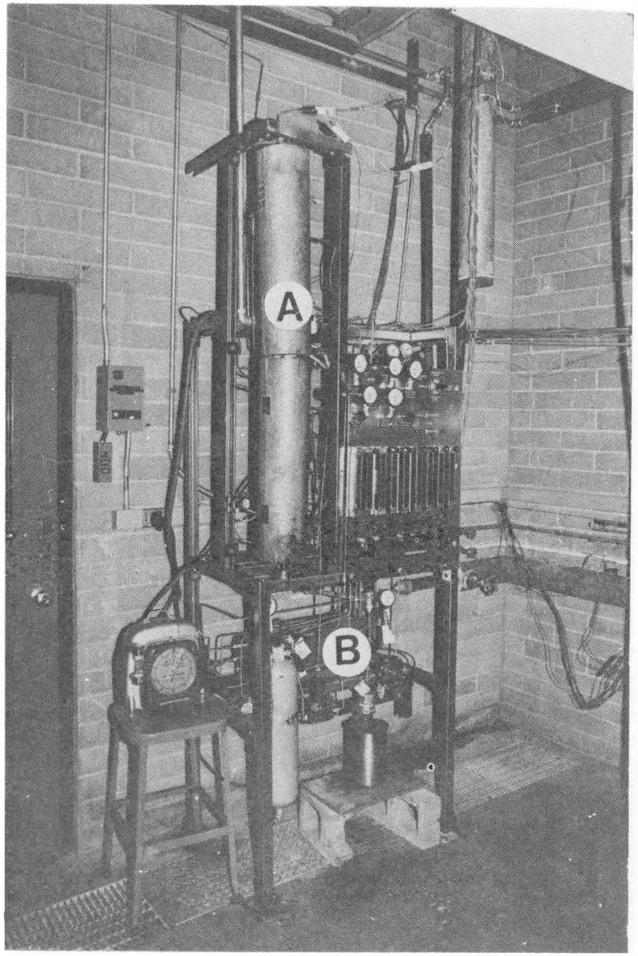

Figure 15.
Liquefaction Catalyst Fluidized
Bed Test Reactor
(with recycle)

(A=reactor, B=recycle compressor)

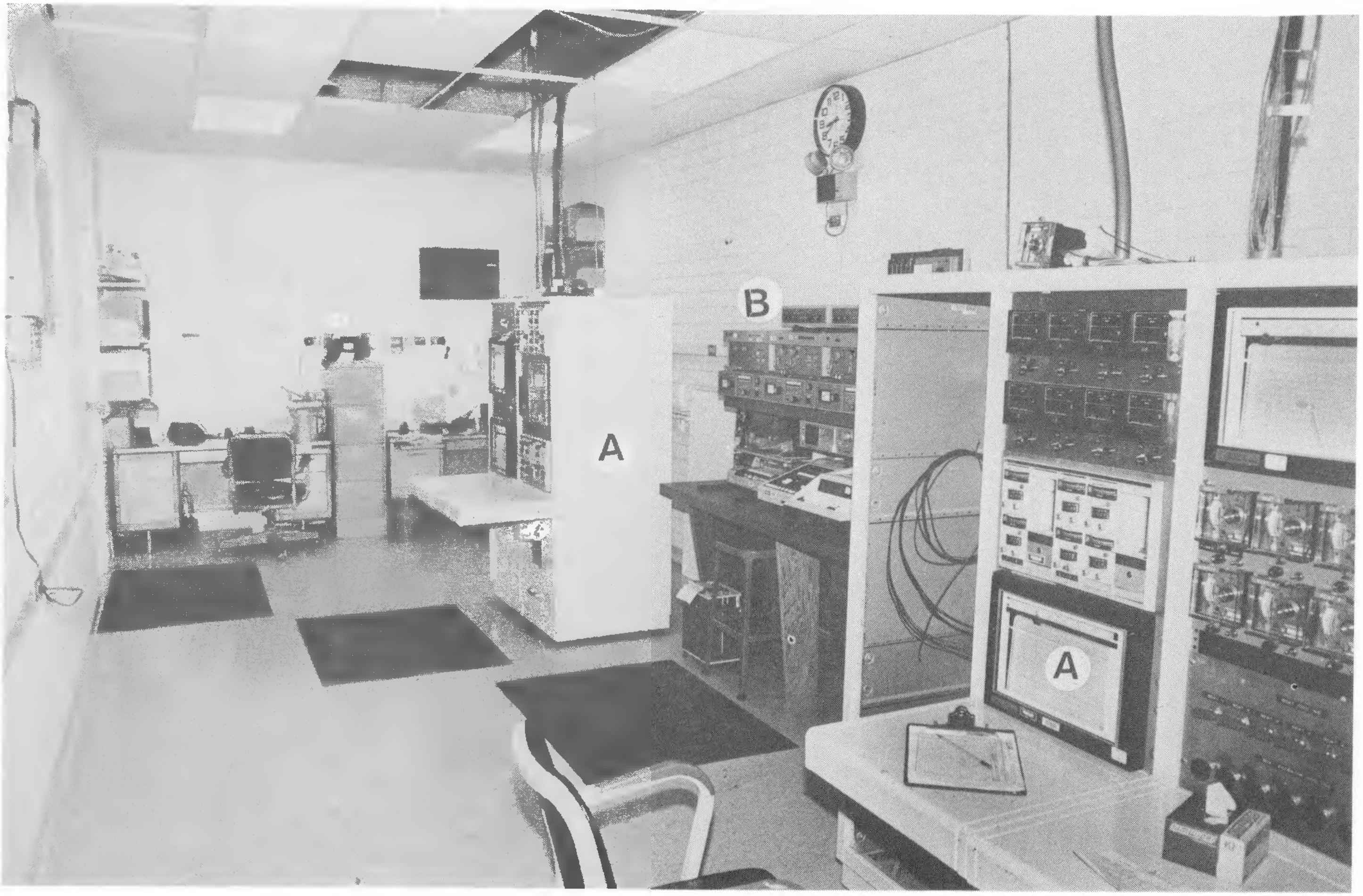

Figure 16. <u>Control Room</u>

(A=controllers, recorders; B=gas chromatographs)

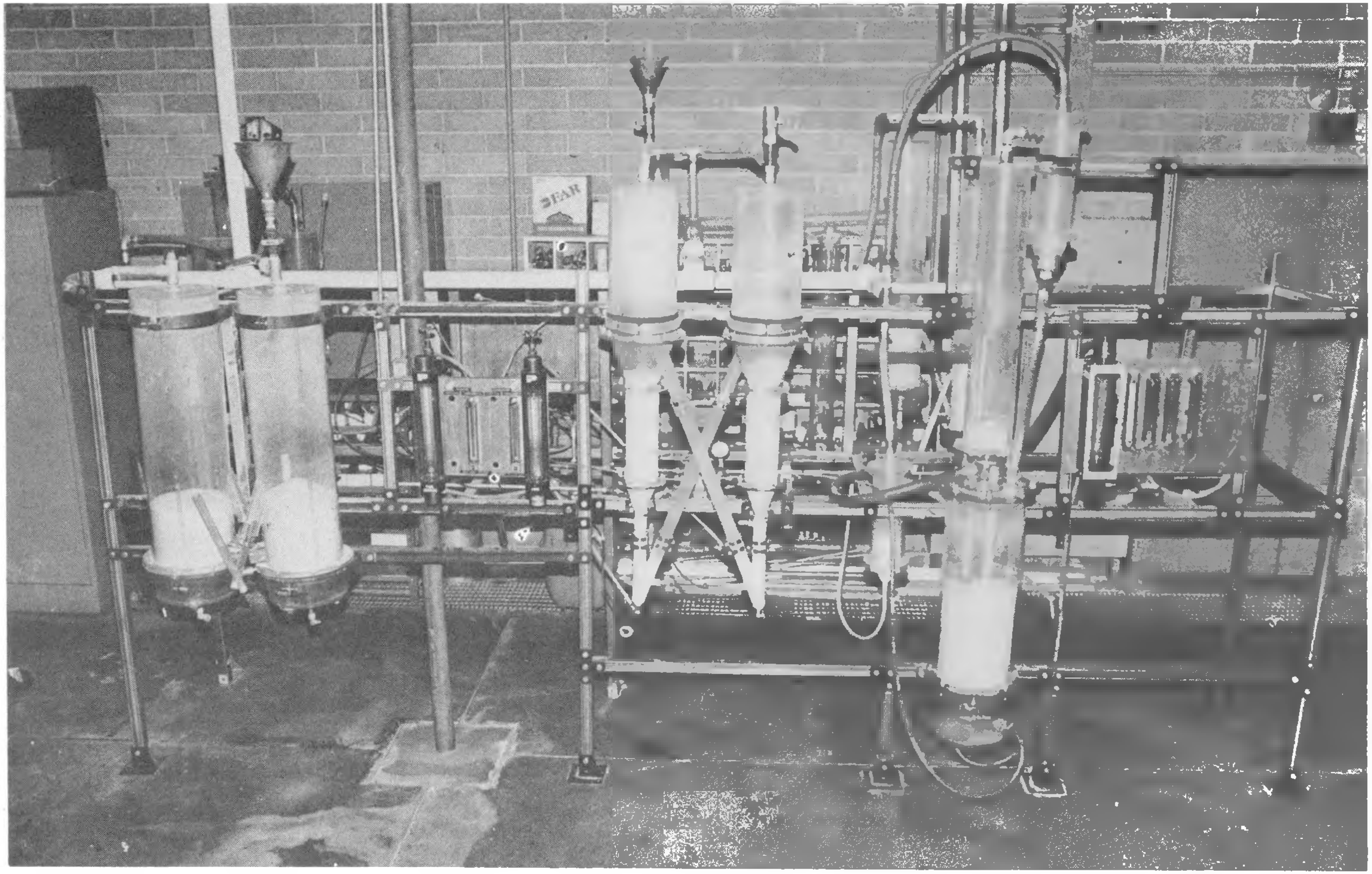

Figure 17. Simulator Equipment

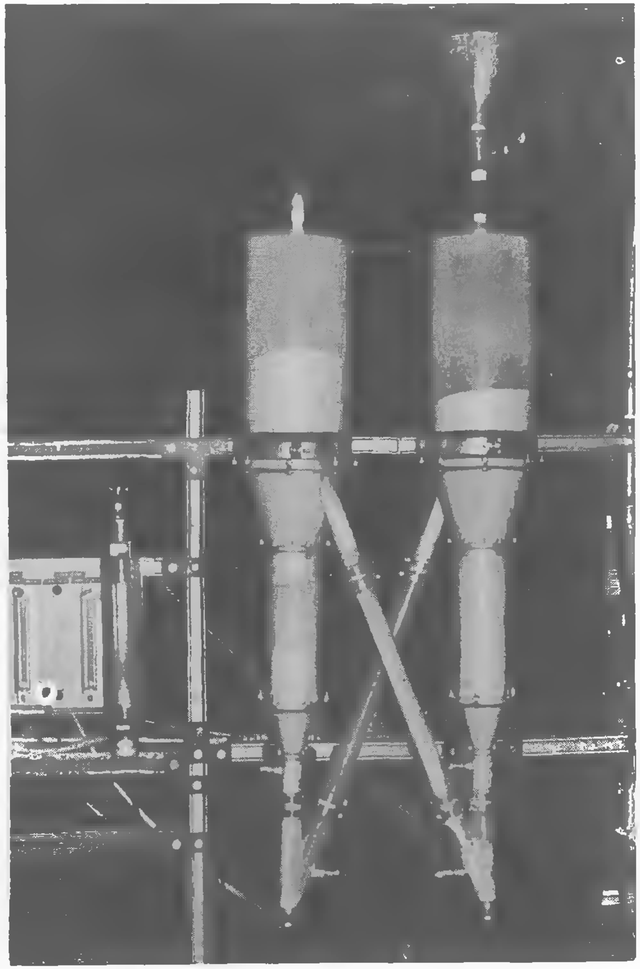

Figure 18.
Integral Riser System

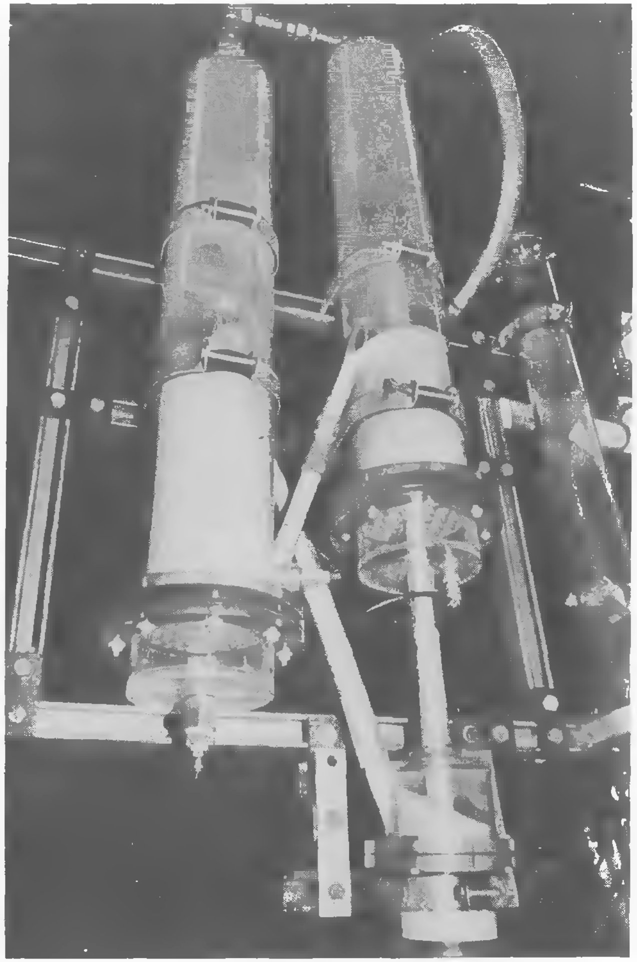

Figure 19.
Injector Loop System

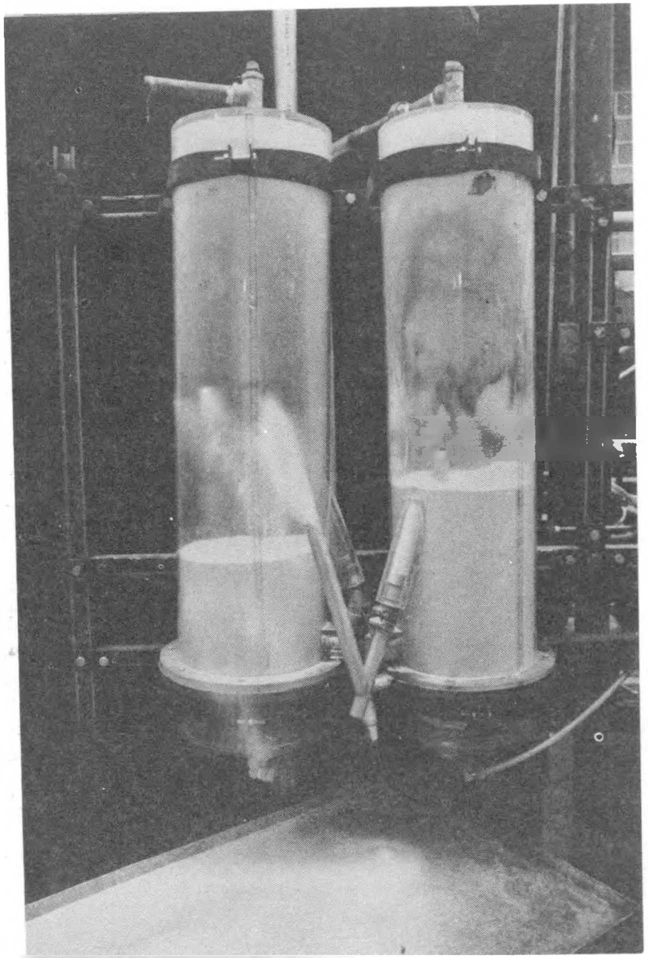

Figure 20.
V-Loop System

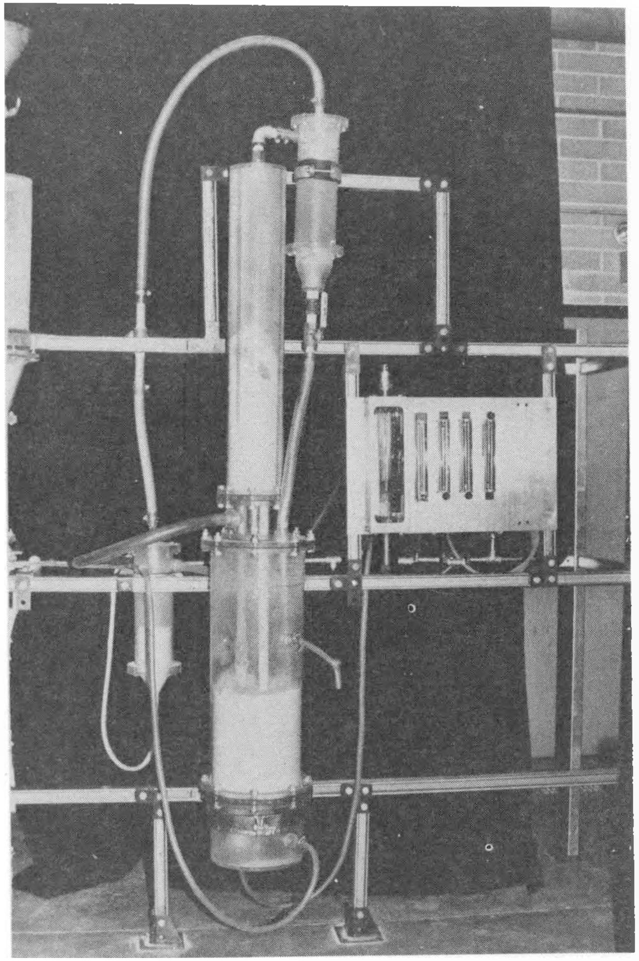

Figure 21.
Internal Circulation System

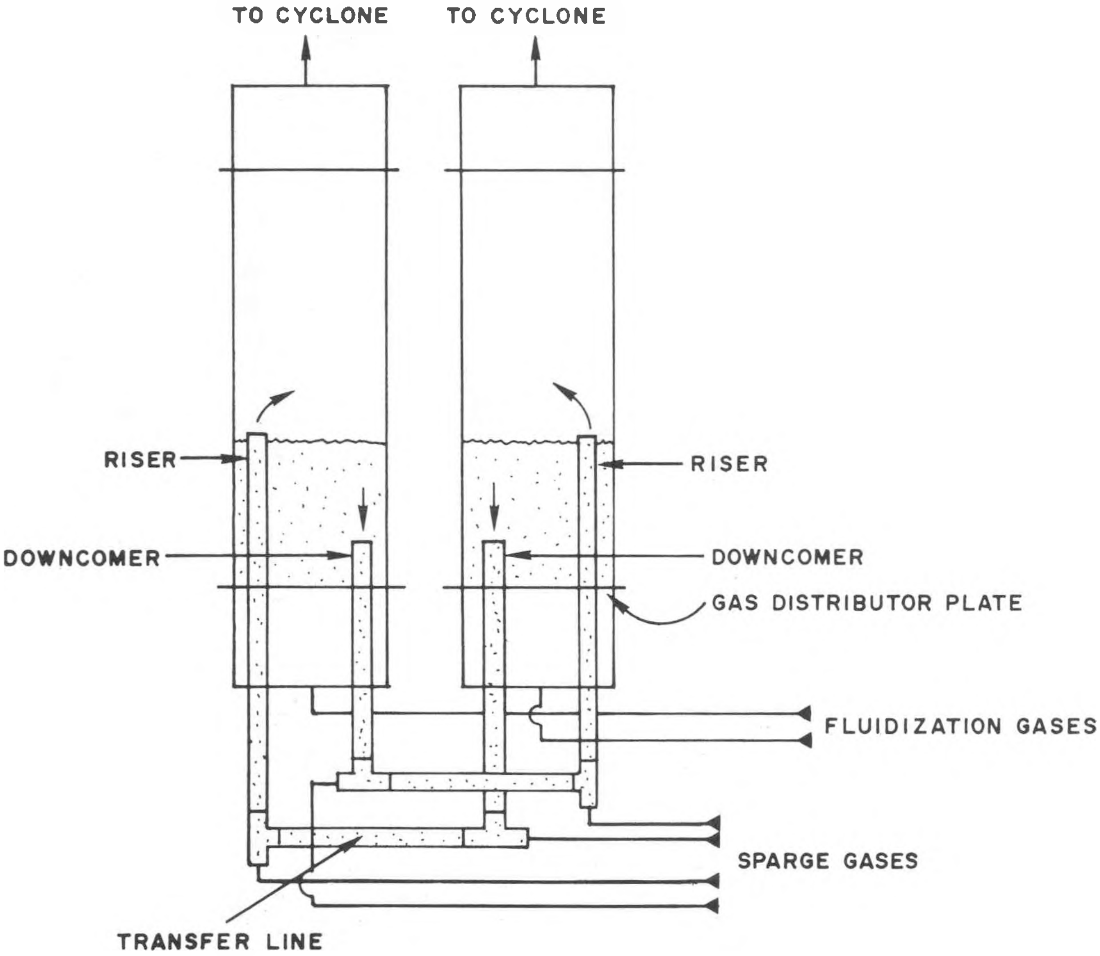

Figure 22. Present Solids Transfer System - Schematic

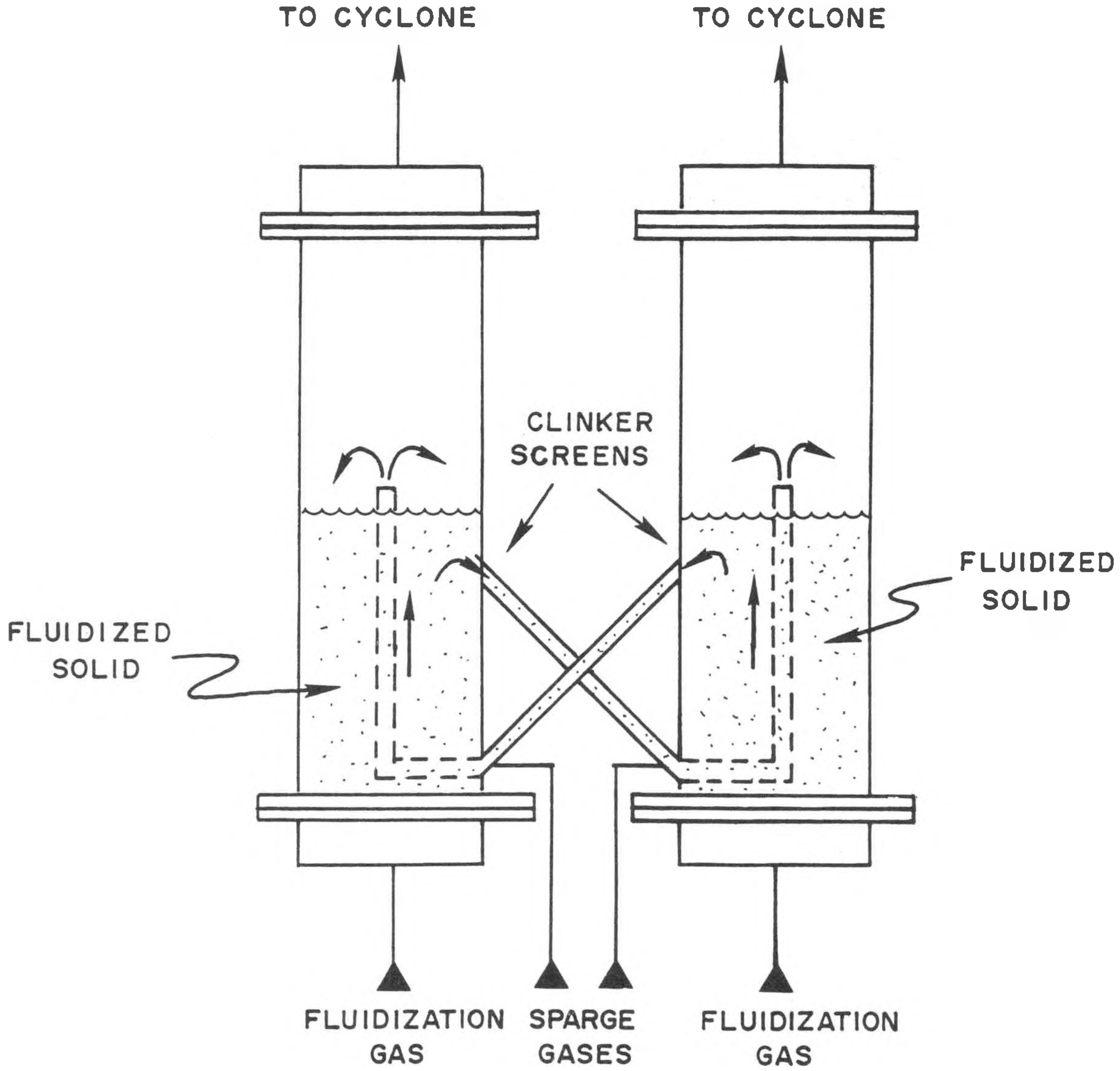

Figure 23. Cross Riser Transfer Loop System - Schematic

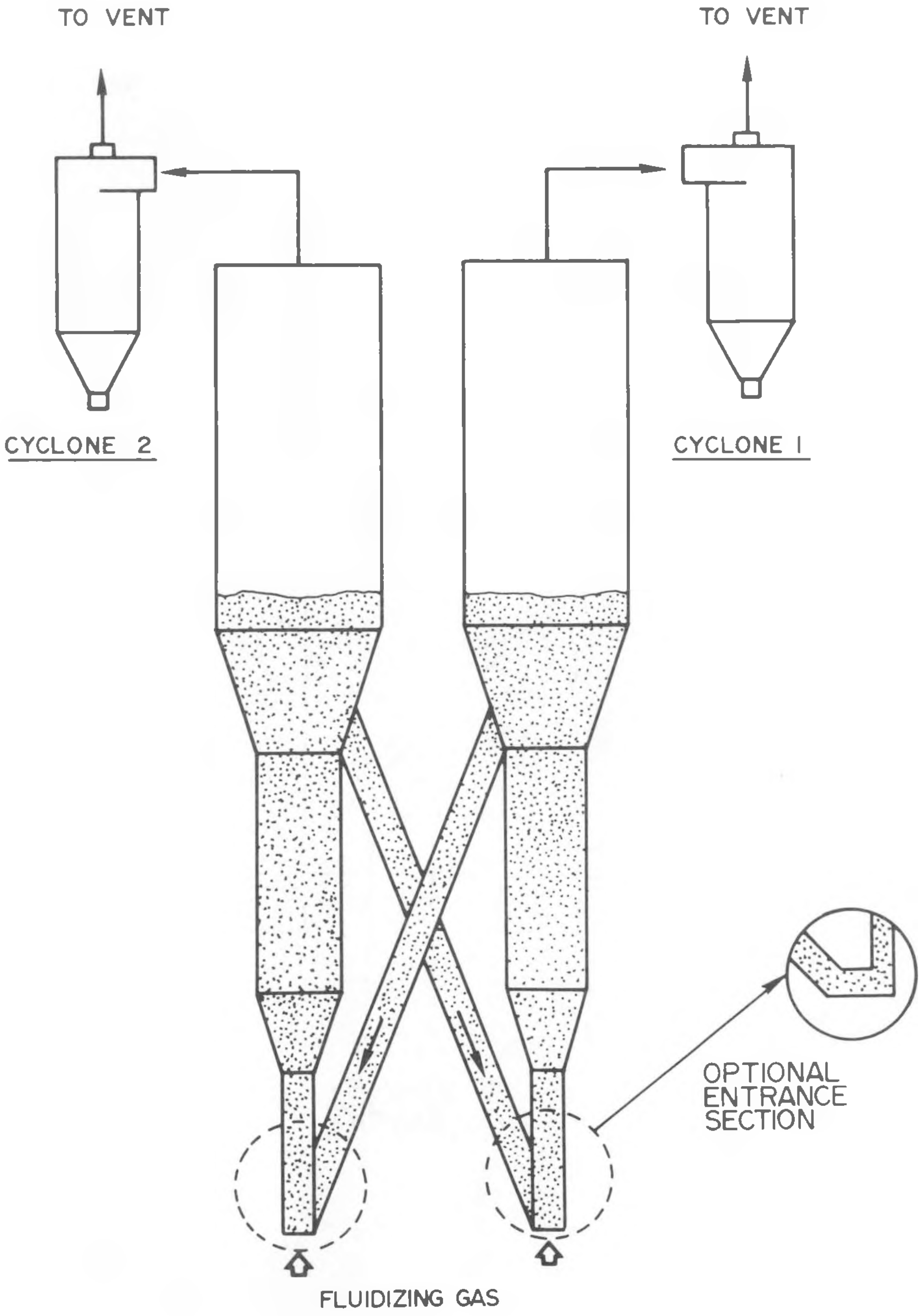

Figure 24. Integral Riser System - Schematic

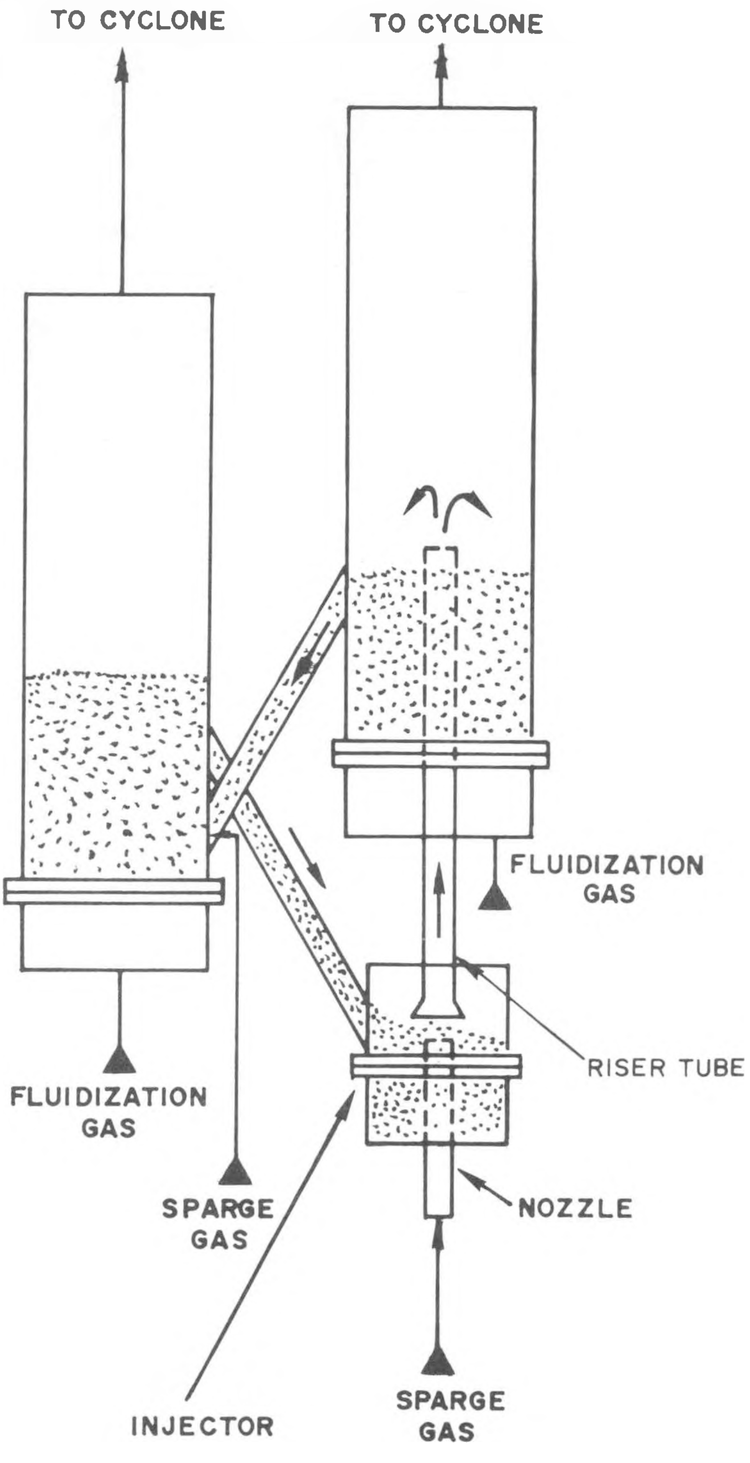

Figure 25. Injector Loop System - Schematic

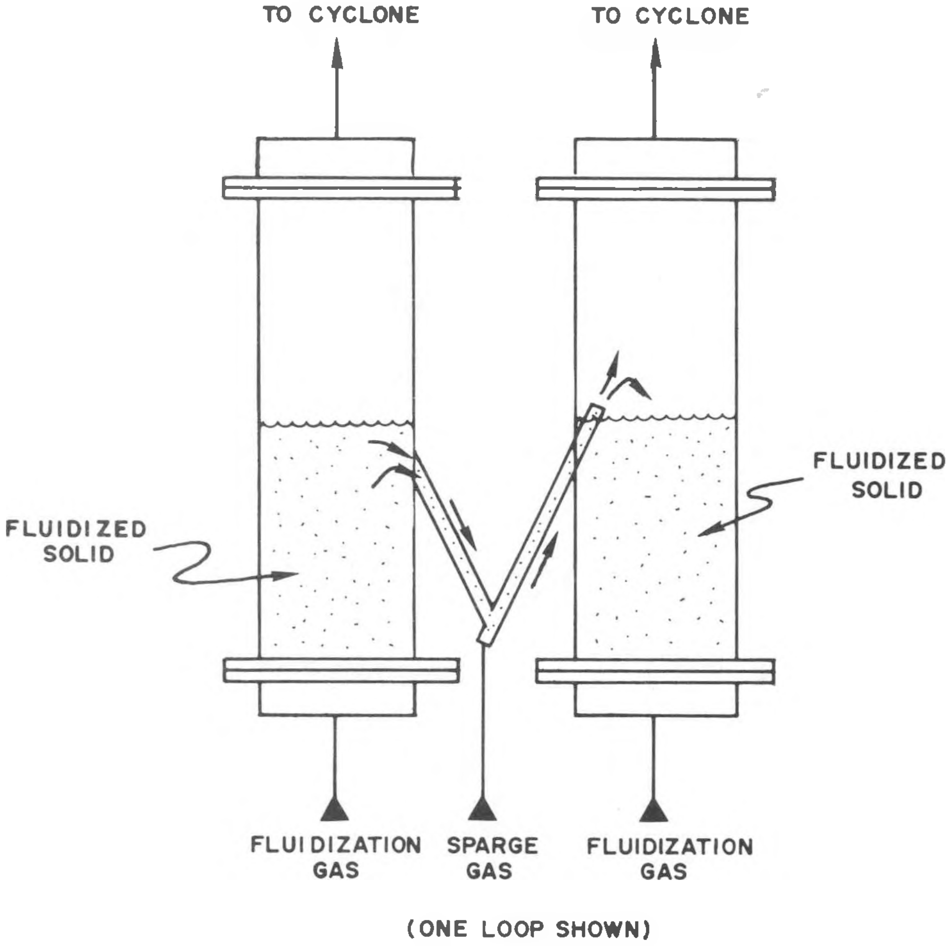

Figure 26. V-Loop System - Schematic

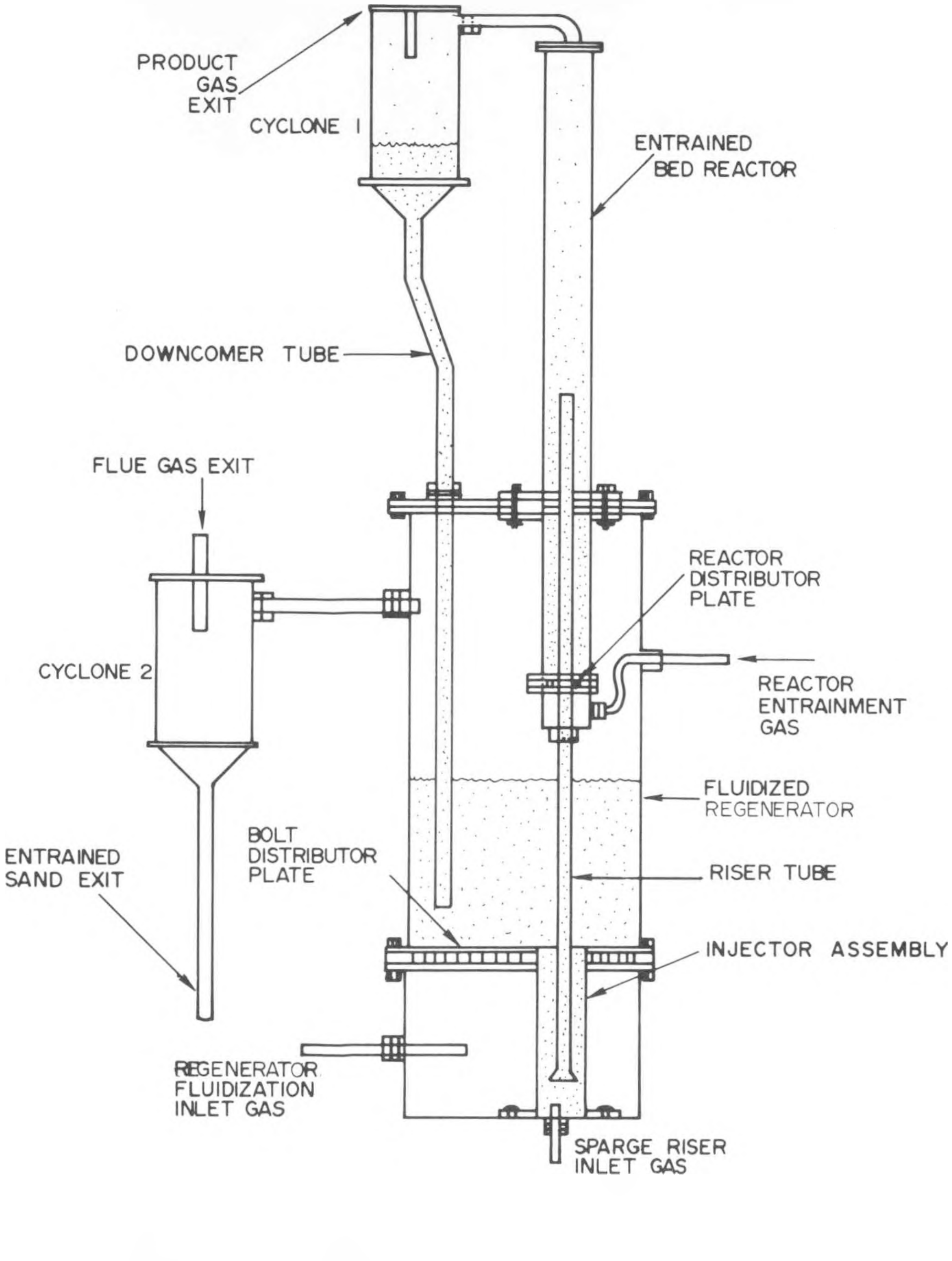

Figure 27. Entrained Circulation Loop System - Schematic

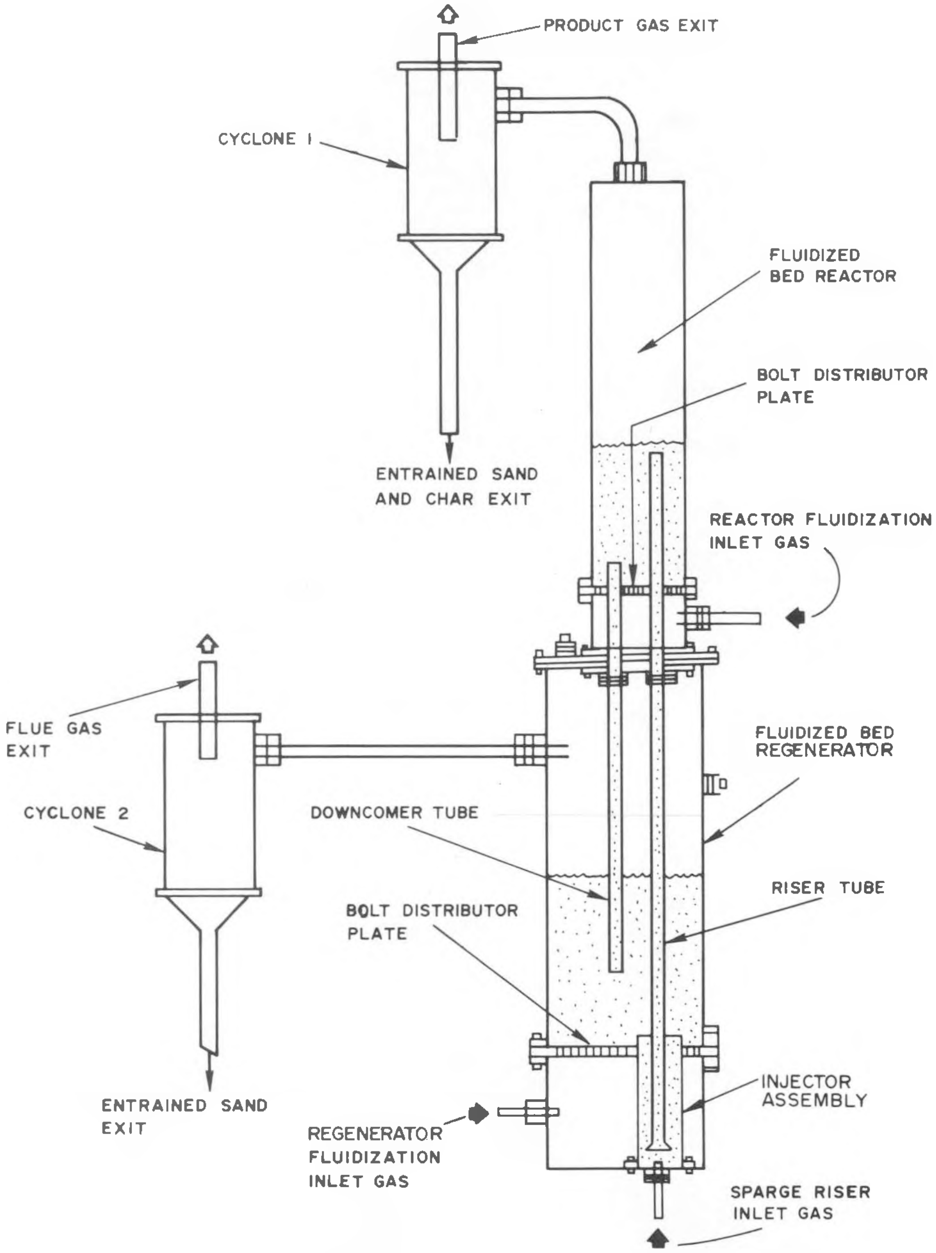

Figure 28. Internal Circulation Loop System - Schematic

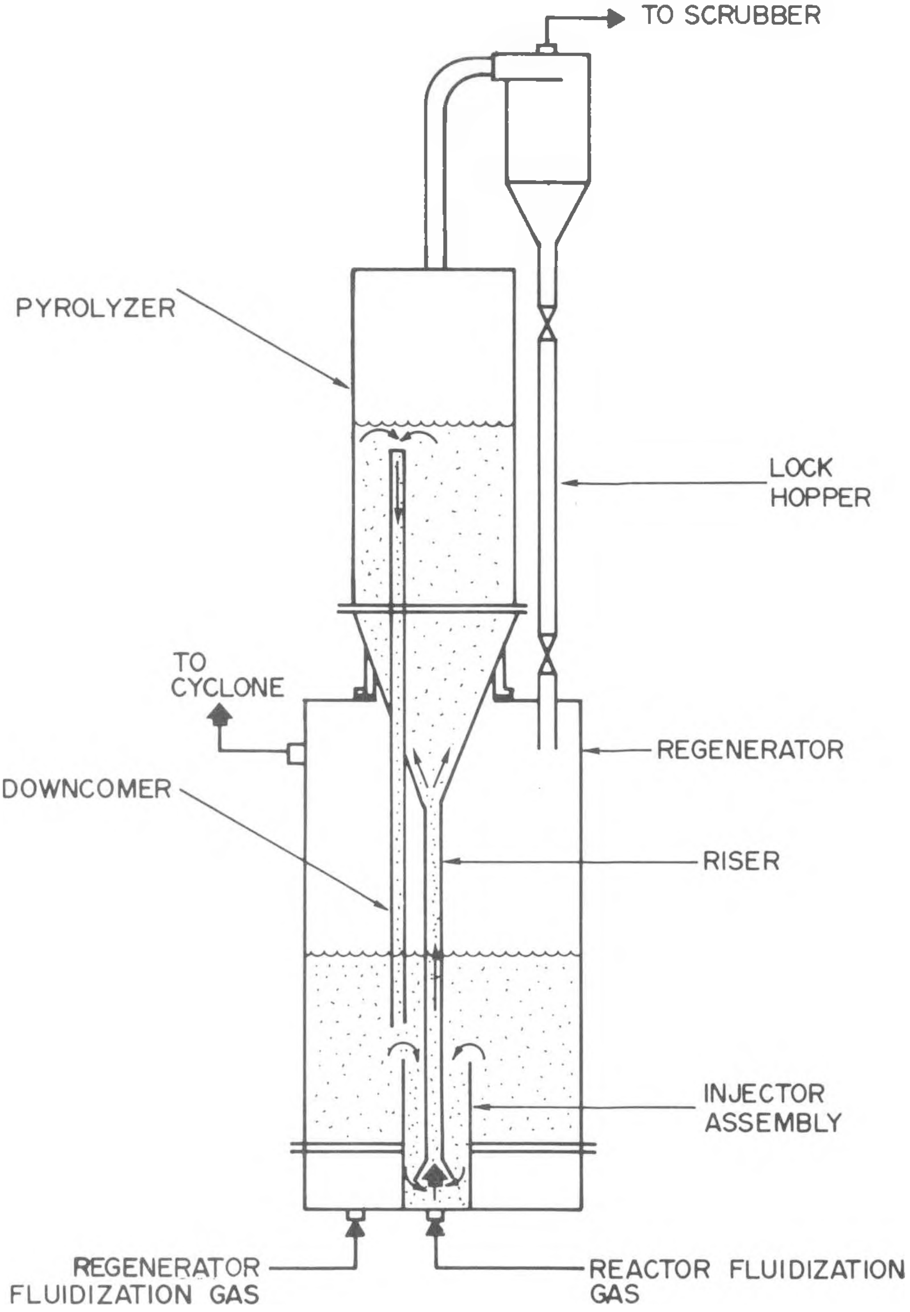

Figure 29. Modified Internal Circulation Loop System - Schematic

Figures 30, 31.

9. Feedstock Analysis. Extraction apparatus, bomb calorimeter, crude fiber analysis, protein analysis, etc. See Figures 32-34.

10. Catalyst Preparation. Mixing equipment, size reduction, calcining furnaces, etc. See Figures 35-38.

11. Analytical Support. Gas chromatographs (3) are located in the Control Room for on-line analyses of gas streams. Gas-liquid chromatographs (2) with temperature programming are used for liquid sample analyses. A liquid chromatograph (gel permeation) is used for high molecular weight compound analyses. See Figures 39, 40.

12. Catalyst Characterization. An adsorption apparatus (Figure 41, 46) is in the process of being fabricated on-site. X-Ray diffraction, X-Ray florescense, Auger electron spectrometer and electron microprobe are available for use on-campus (Figure 42-45).

Figure 30. <u>Feedstock Storage Area</u>

(A=stored feedstocks, B=mills)

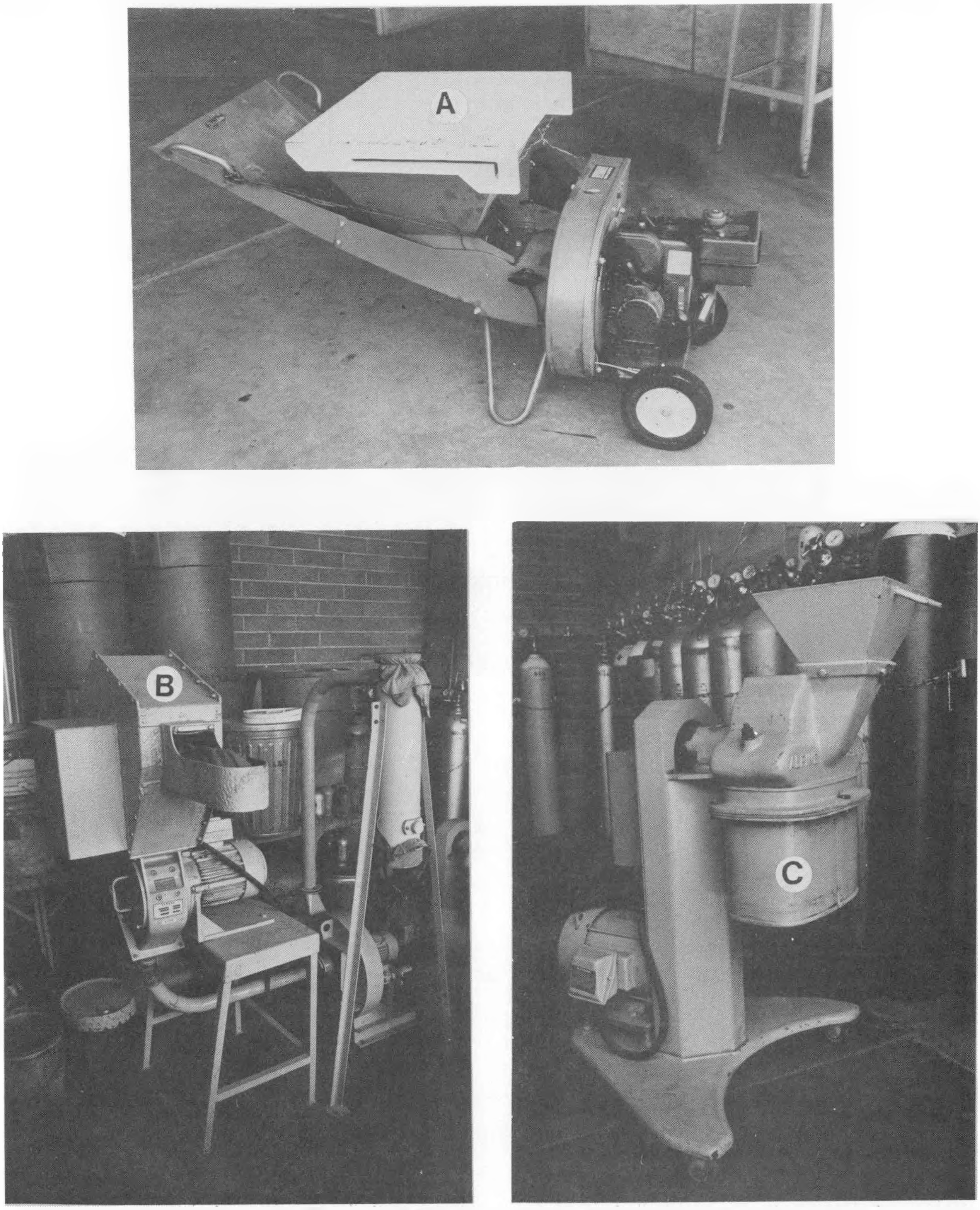

Figure 31. Size Reduction Equipment

(A=chipper, B=cutting mill, C =hammer mill)

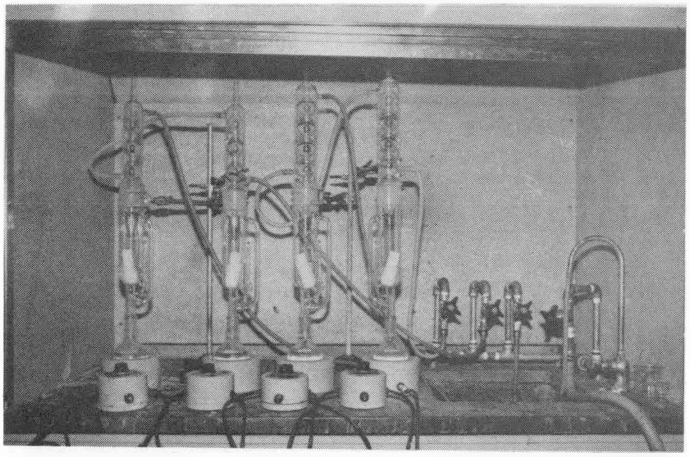

Figure 32. Soxhlet Extraction Apparatus

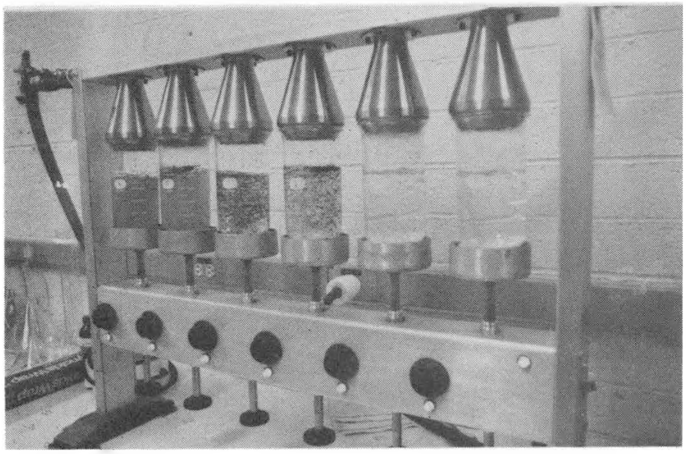

Figure 33. Crude Fiber Apparatus

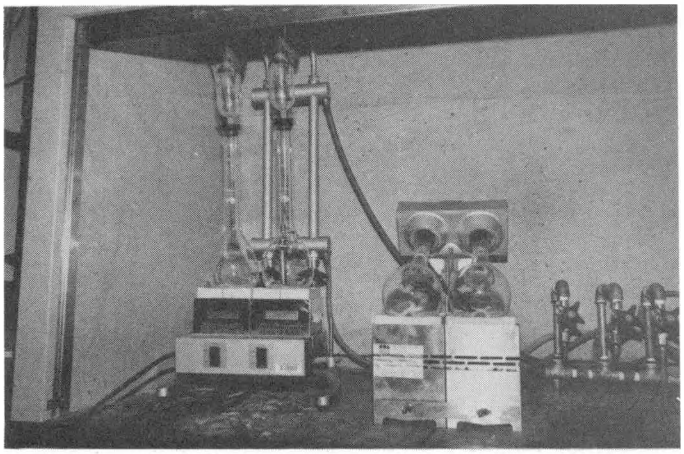

Figure 34. Protein Analysis Apparatus

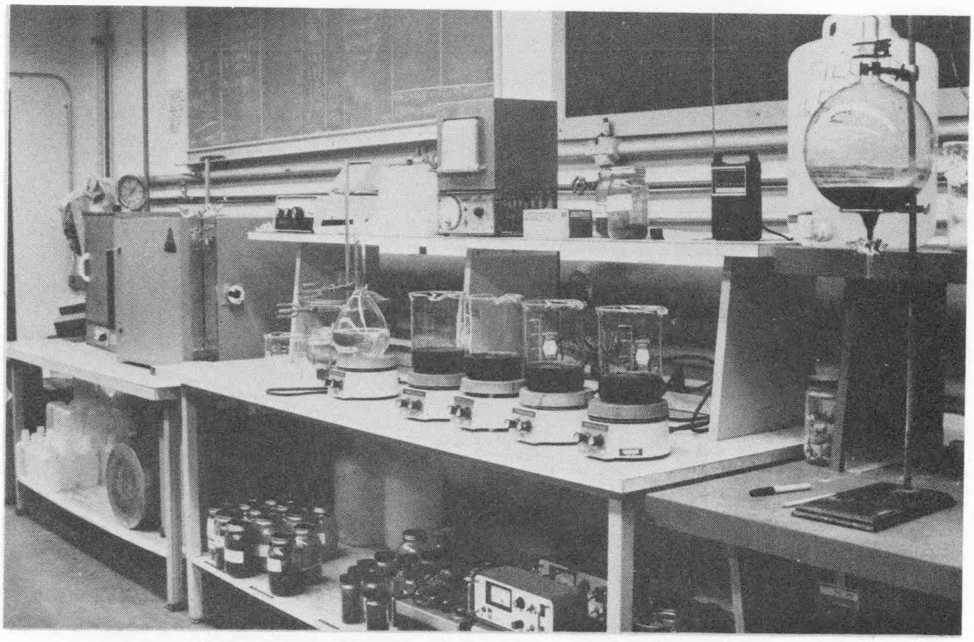

Figure 35. Catalyst Preparation

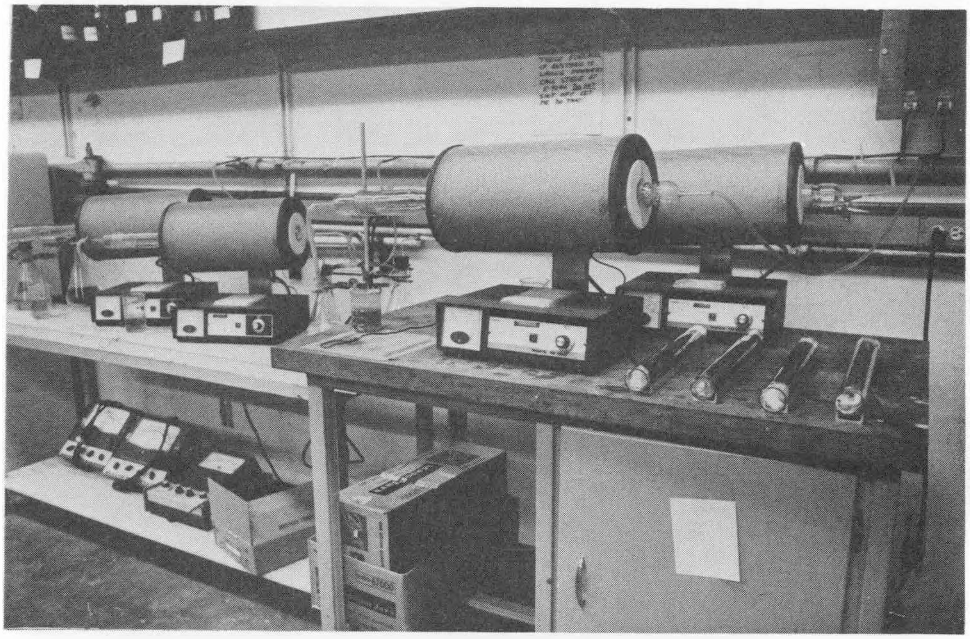

Figure 36. Calcining Furnaces (2")

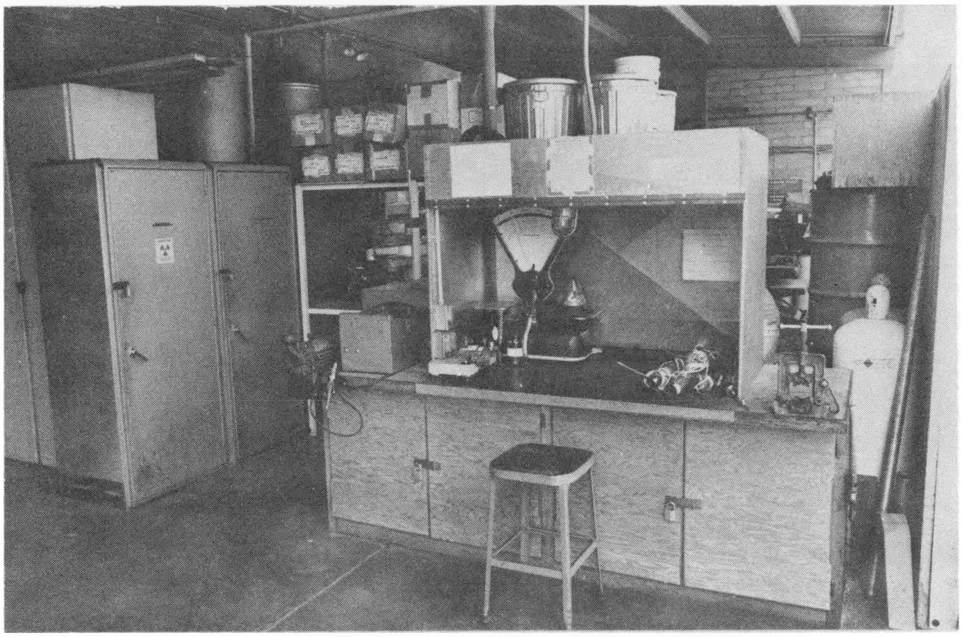

Figure 37. Catalyst Loading Area

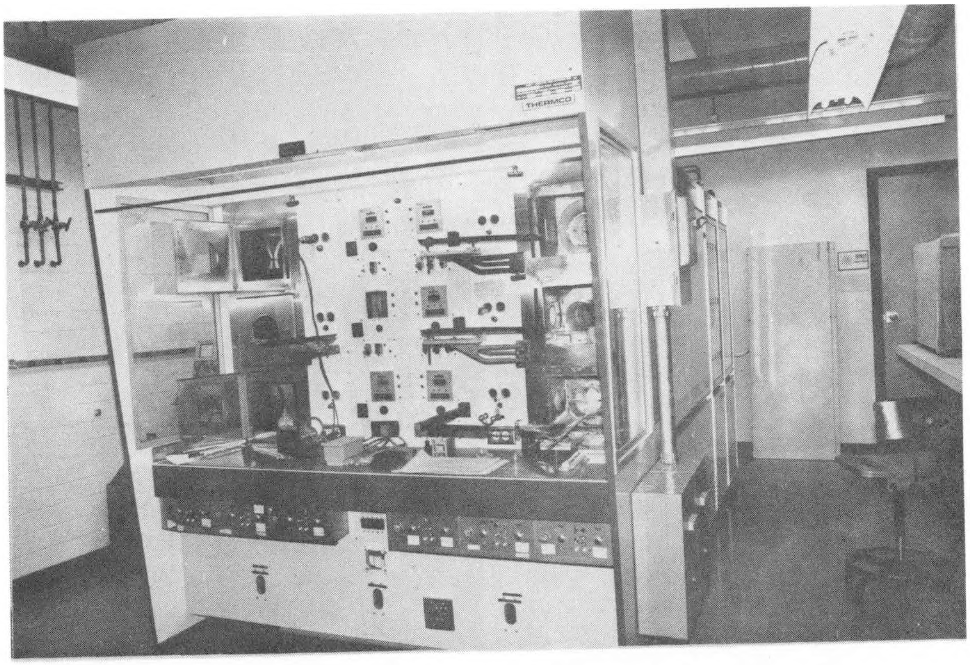

Figure 38. Calcining Furnaces (4")

Figure 39. Gas Chromatographs (on line)

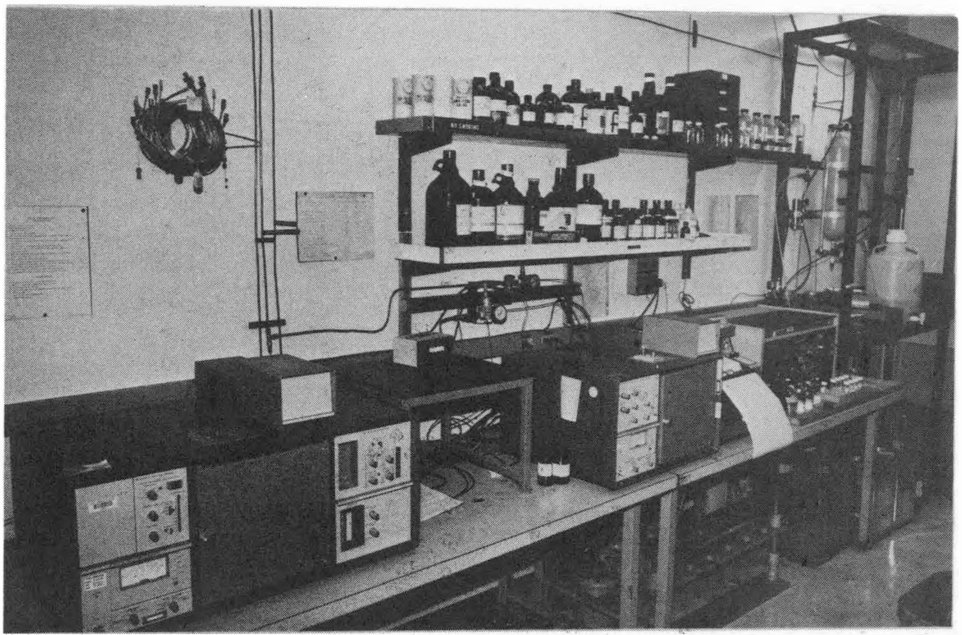

Figure 40. Gas-Liquid Chromatographs

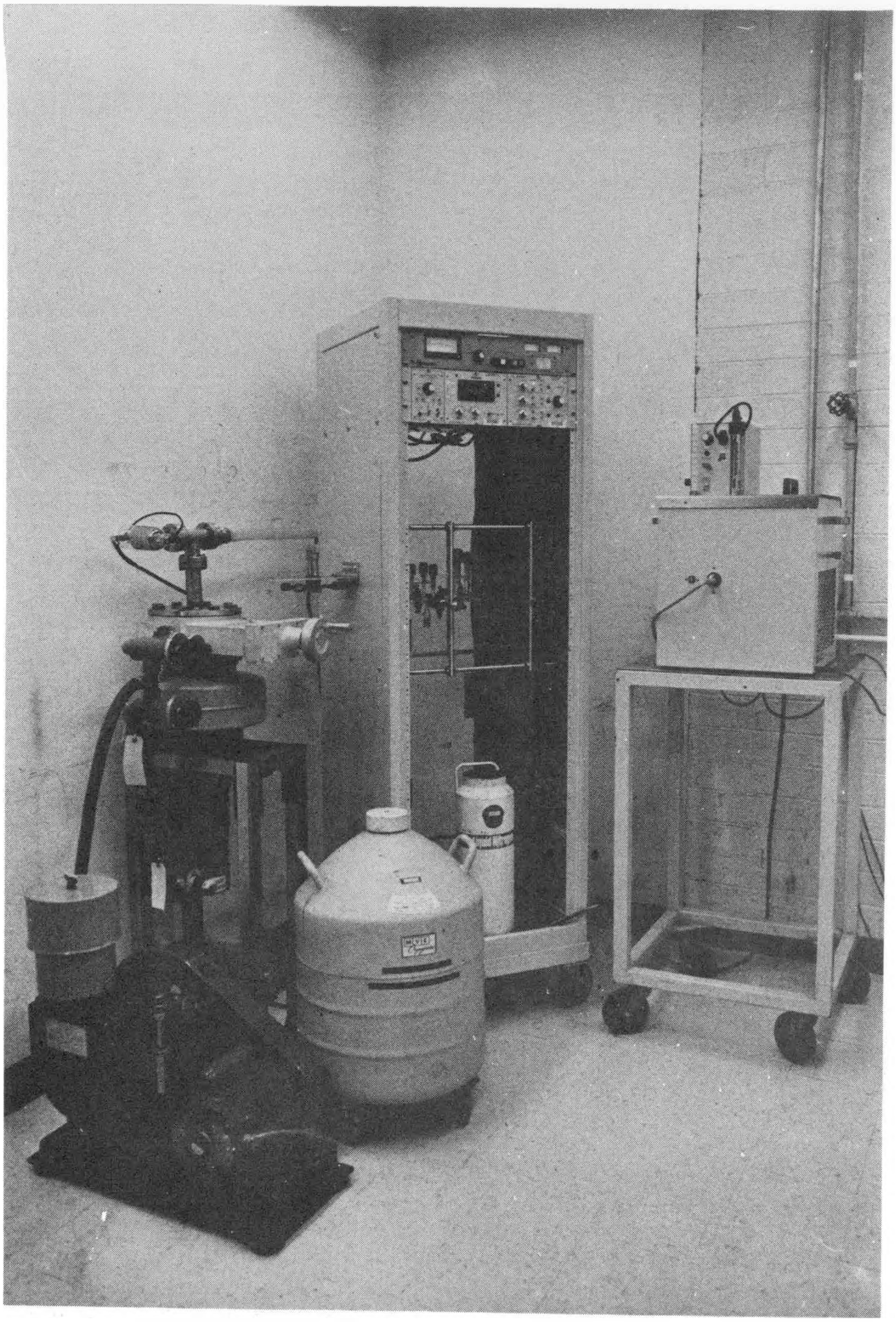

Figure 41. Adsorption Apparatus
(under construction)

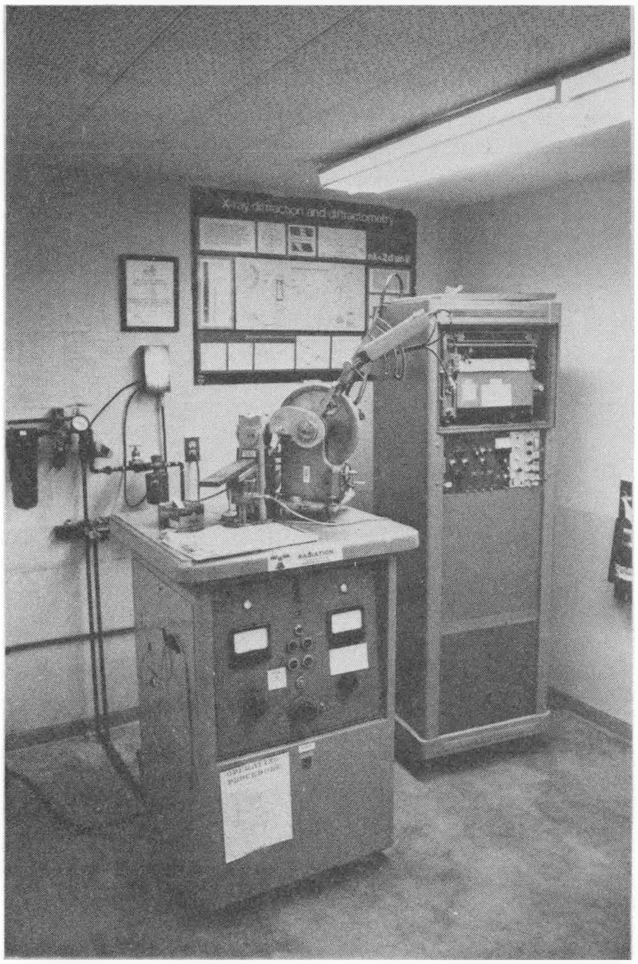

Figure 42. X-Ray Diffraction Unit

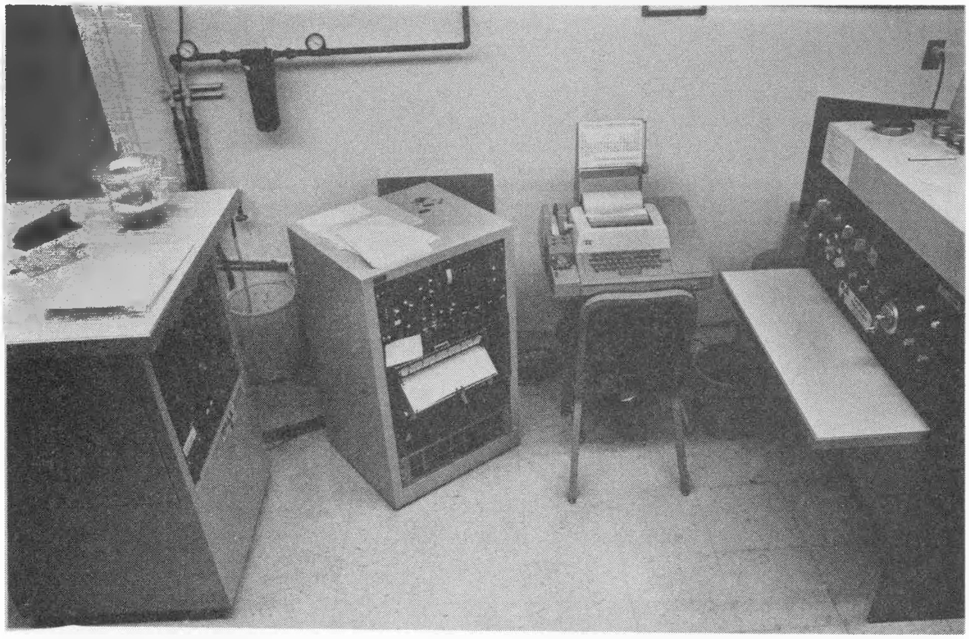

Figure 43. X-Ray Florescence Unit

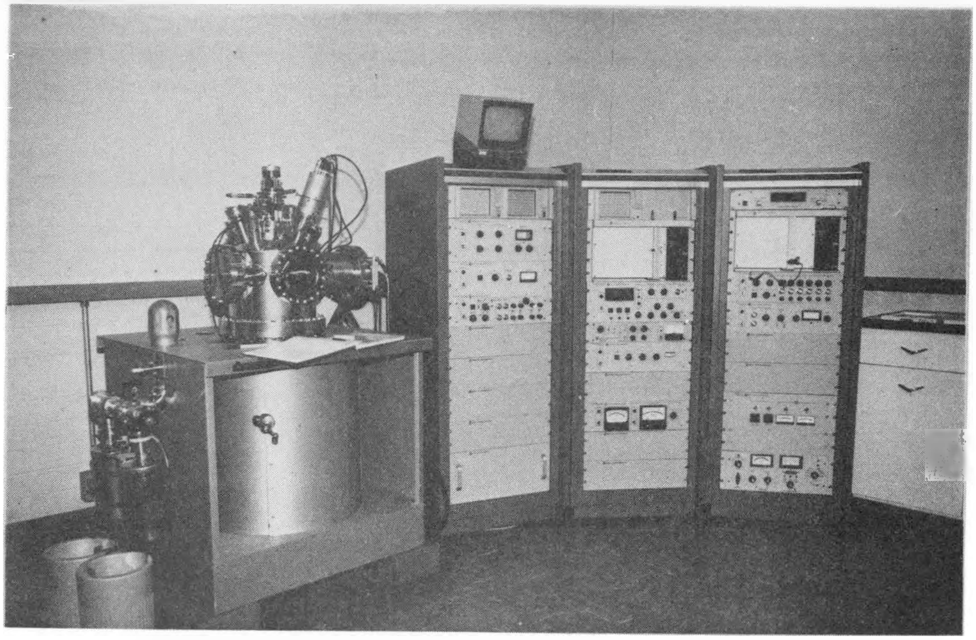

Figure 44. Auger Electron Spectroscopy Unit

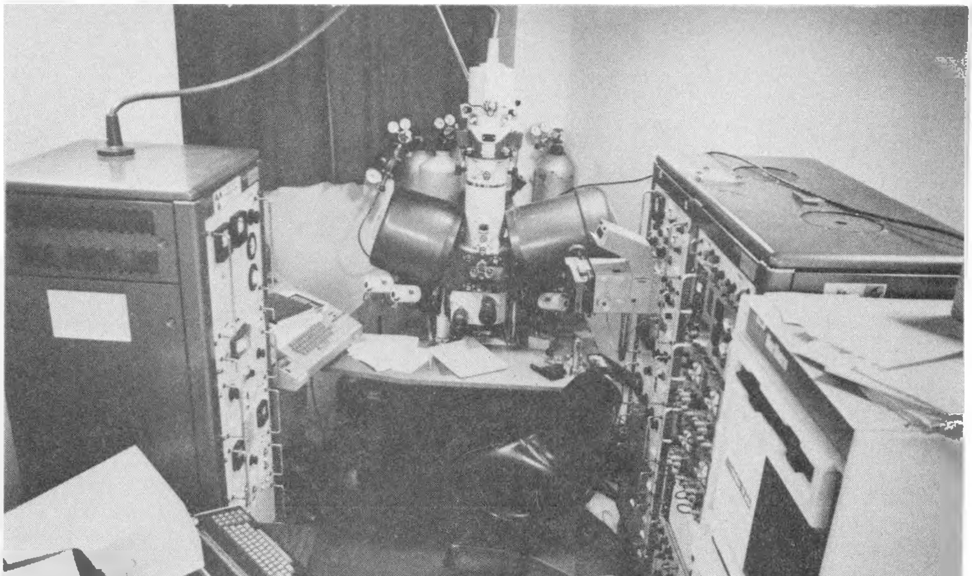

Figure 45. Electron Microprobe Unit

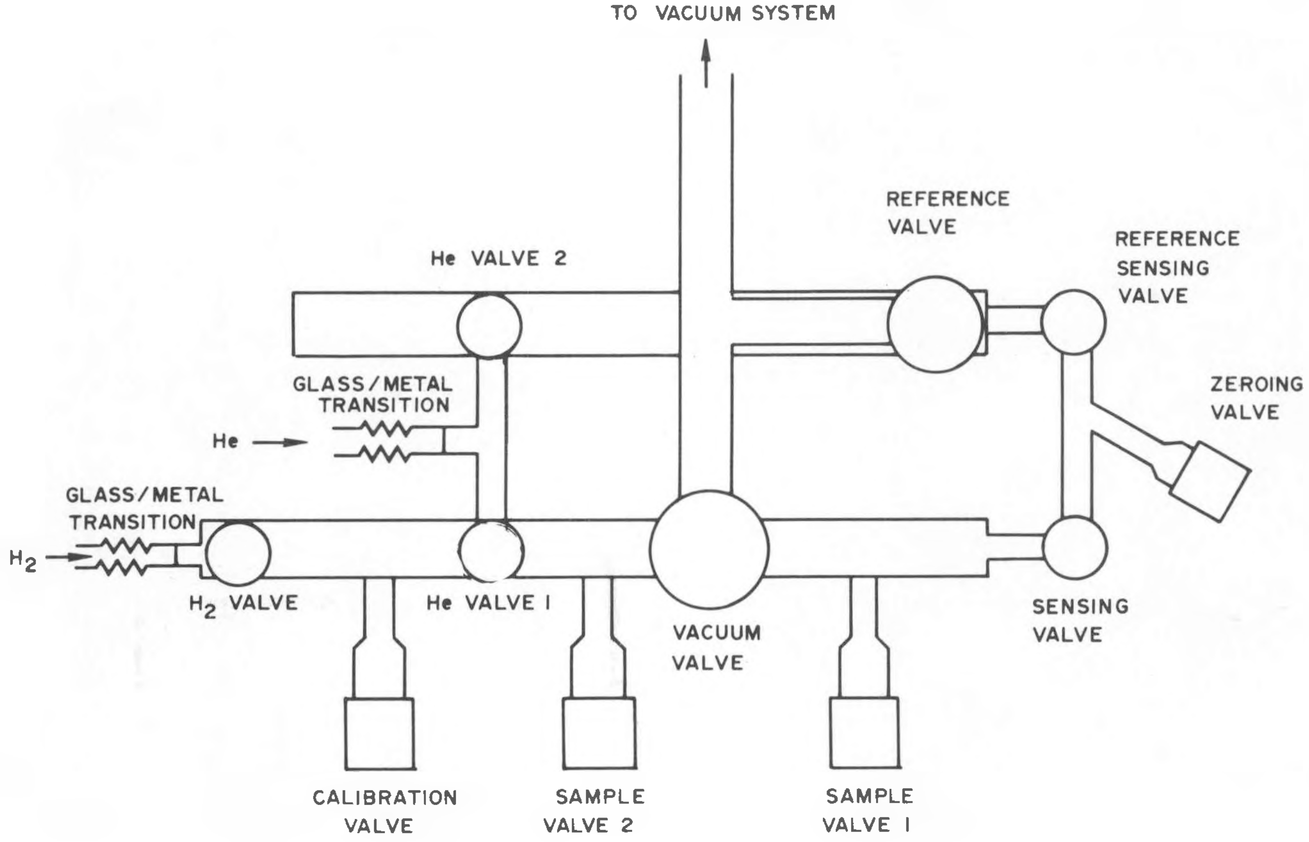

Figure 46. Chemisorption Unit - Schematic

Gasification System Factor Studies

Work in this task consisted of gasification catalyst development and gasification reaction system improvements.

1. Gasification Catalyst Development. Several runs were performed with the gasification system in the large scale integrated unit (see Figures 1-3) to study the effect of dolomite on pyrolysis reactor performance. Operating conditions and results are given in Table 2. Comparisons are listed for almond prunings, euphorbia lathyris, jojoba meal, raw guayule, fir bark, sassafras and honeysuckle. In each case, data with sand and dolomite is included. The fluidizing gas type varies (dependent on prime objective of the particular run for which the data was obtained). The feedstocks represent a random selection of materials with respect to past H_2/CO mole ratio performance. In every case, the presence of steam increases the H_2/CO ratio with the effect magnified enormously where dolomite is used as the fluidized solid. A summary is as follows:

Operating Mode	H_2/CO Mole Ratio
sand + recycle pyrolysis gas (RPG)	0.31, .32, .49, .51
sand + RPG + steam	0.89, .90, .97, 1.76
dolomite + RPG	0.84, 1.26
dolomite + RPG + steam	1.70, 1.70, 2.16, 2.99 3.12, 6.42, 8.82

The data is masked somewhat by the temperature variations in the data but the shift in H_2/CO level with dolomite usage is clear. The degree of the shift appears to be feedstock dependent in the following order: euphorbia > firbark > almond prunings > raw guayule > jojoba meal > sassafras, honeysuckle. A water gas shift effect ($CO + H_2O \rightarrow CO_2 + H_2$) appears in each case with the effect enhanced by the presence of dolomite. This result is considered to be quite significant if one is interested in a synthesis gas with high H_2/CO ratios (e.g., some methanol, Fischer-Tropsch, etc. processes). Note that dolomite is a readily available, inexpensive material.

The decision was made during the year to conduct further initial gasification catalyst screening runs in the small scale integrated unit (Figures 6,7). The rationale was that smaller amounts of catalyst were required and the complexity of a circulating solid heat transfer system could be eliminated. The intent was to do additional testing on promising catalysts in the circulating solid large scale integrated system. The remainder of the contract period was thus utilized to complete construction of the small scale integrated system and establish base point conditions with sand as the fluidized solid. An initial list of catalysts was determined (Table 3) and an initial experimental plan proposed (Figure 47). As indicated, the plan incorporates a study of the effect of operating temperature for various catalyst on the gas phase yields and composition at a fixed reactor pressure (P), residence time (θ), steam rate and feedstock type. The objective is to maximize gas phase yields and manipulate composition. Of particular interest is to minimize methane and carbon dioxide production, maximize olefin production and to manipulate the H_2/CO ratio over a

Table 2. Effects of Dolomite as a Pyrolysis Catalyst

	Feedstock: Almond Prunings				Feedstock: Euphorbia Lathyris		
Operating Conditions:	No Steam	Partial Steam	No Steam	Partial Steam	Partial Steam	No Steam	Partial Steam
Reactor Temperature, °F:	1340	1300	1390	1330	1145	1370	1370
Reactor Pressure, psig:	0.8	0.8	0.9	0.9	0.5	1.0	1.0
Residence Time, sec.:	5.2	3.8	4.9	3.2	4.5	5.0	3.0
Fluidizing Gas,[1] lbs/hr:	22RPG	44S+5RPG	29RPG	42S+5RPG	45S+5RPG	29RPG	45S+5RPG
Heat Transfer Media/Catalyst:	sand	sand	dolomite	dolomite	sand	dolomite	dolomite
Pyrolysis Gas Composition (mole%[2]):							
H_2	22.96	32.64	31.02	51.25	40.49	32.97	52.61
O_2	0.08	0.08	0.03	0.07	0.22	0.80	0.63
CO	44.87	33.52	36.82	16.43	23.05	26.27	5.96
CO_2	6.56	10.55	7.11	19.99	12.09	7.56	23.32
CH_4	14.89	7.38	16.65	9.25	7.99	14.69	4.03
C_2H_2	0.07	0.15	0.09	0.12	0.03	0.08	0.02
C_2H_4	6.11	6.28	5.15	0.60	4.40	3.84	1.32
C_2H_6	1.43	0.88	2.20	0.59	1.02	3.58	1.69
C_3+olefins	0.61	1.03	0.24	0.80	1.05	0.31	0.36
C_3H_8	0.03	0.04	0.04	0.04	0.07	0.04	0.02
C_4+olefins	0.18	0.36	0.08	0.25	0.43	0.10	0.13
C_4H_{10}	0.02	0.04	0.01	0.03	0.05	0.01	0.01
C_5H_{12}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_5+olefins	2.20	7.07	0.57	0.56	9.11	9.75	9.90
Total Unsaturated (mole%):	9.17	14.88	6.12	2.34	15.03	14.08	11.73
H_2/CO Ratio (mole%):	0.51	0.97	0.84	3.12	1.76	1.26	8.82
Gas Phase Yields (wt gas x 100/wt feedstock):	69	72	93	89	---	79	80

---

[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

[3] $C_5^=$, C_6^+ backflush peak assumed to be predominately C_5 olefins

Table 2. Effects of Dolomite as a Pyrolysis Catalyst (continued)

	Feedstock: Fir Bark		Feedstock: Sassafras		Feedstock: Jojoba Meal	
Operating Conditions:	No Steam	Partial Steam	No Steam	Partial Steam	No Steam	Partial Steam
Reactor Temperature, °F:	1400	1270	1190	1270	1320	1240
Reactor Pressure, psig:	0.9	1.1	0.9	0.9	0.9	1.3
Residence Time, sec.:	4.0	3.0	4.0	3.0	4.4	3.0
Fluidizing Gas,[1] lbs/hr:	23RPG	5.25RPG+45S	5.25RPG+45S	5.25RPG+45S	24RPG	5.25RPG+45S
Heat Transfer Media/Catalyst:	sand	dolomite	sand	dolomite	sand	dolomite
Pyrolysis Gas Composition (mole%[2]):						
H_2	16.58	46.54	31.87	32.28	11.96	39.12
O_2	0.10	0.48	0.07	0.50	0.41	4.35
CO	53.42	7.24	36.00	18.90	37.56	18.09
CO_2	2.99	13.21	8.91	14.36	10.32	7.58
CH_4	18.07	11.85	7.30	12.19	23.21	15.37
C_2H_2	0.05	0.05	0.08	0.13	0.00	0.04
C_2H_4	5.71	7.89	6.84	10.28	9.15	9.49
C_2H_6	1.60	4.46	1.62	3.90	3.44	2.22
C_3+olefins	0.37	1.87	2.29	2.22	2.01	0.82
C_3H_8	0.01	0.09	0.16	0.09	0.03	0.04
C_4+olefins	0.18	1.06	0.91	0.85	0.45	0.23
C_4H_{10}	0.02	0.09	0.09	0.08	0.01	0.02
C_5H_{12}	0.00	0.01	0.00	0.01	0.08	0.00
C_5+olefins	0.91	5.16	3.86	4.21	1.78	2.63
Total Unsaturated (mole%):	7.22	16.04	13.98	17.69	13.39	13.21
H_2/CO Ratio (mole%):	0.31	6.42	0.89	1.70	0.32	2.16
Gas Phase Yields (wt gas x 100/wt feedstock):	61	67.9	---	---	51	---

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[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

Table 2. Effects of Dolomite as a Pyrolysis Catalyst (continued)

	Feedstock: Honeysuckle		Feedstock: Raw Guayule	
Operating Conditions:	No Steam	Partial Steam	No Steam	Partial Steam
Reactor Temperature, °F:	1225	1250	1310	1230
Reactor Pressure, psig:	0.7	1.0	0.9	1.2
Residence Time, sec.:	5.2	3.0	4.6	3.0
Fluidizing Gas,[1] lbs/hr:	5.25RPG+30S	5.25RPG+45S	22RPG	5.25RPG+45S
Heat Transfer Media/Catalyst:	sand	dolomite	sand	dolomite
Pyrolysis Gas Composition (mole%[2]):				
H_2	25.32	32.24	17.28	42.69
O_2	0.01	0.51	0.00	1.87
CO	28.25	18.94	34.98	14.26
CO_2	27.06	14.51	8.51	12.22
CH_4	13.64	12.20	26.17	14.26
C_2H_2	0.11	0.13	0.04	0.04
C_2H_4	1.87	10.16	5.57	7.39
C_2H_6	0.99	3.91	2.31	3.37
C_3+olefins	0.14	2.21	1.50	1.14
C_3H_8	0.12	0.09	0.05	0.04
C_4+olefins	0.04	0.86	0.56	0.46
C_4H_{10}	0.01	0.08	0.01	0.04
C_5H_{12}	0.00	0.00	0.04	0.00
C_5+olefins	2.45	4.16	2.97	2.12
Total Unsaturated (mole%):	4.61	17.52	10.64	11.14
H_2/CO Ratio (mole%):	0.90	1.70	0.49	2.99
Gas Phase Yields (wt gas x 100/wt feedstock):	---	---	---	---

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[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

Table 3. Description of Pyrolysis Catalysts

A. Catalysts

1. HT-400 (Harshaw)

   Content - Cobalt Molybdate Catalyst

CoO	3%
MoO_3	15%

2. C12-3 (United Catalyst)

   Content - Iron/Chromium Catalyst

Fe_2O_3	89%
Cr_2O_3	9%

3. Dolomite

4. Potassium Carbonate (Baker)

   (Dry mixed or impregnated with the feedstock)

5. Fluid Cracking Catalysts

   Example: US-260 (Engelhard)

Al_2O_3	53%
SiO_2	41%
TiO_2	2.4%

B. Support Catalyst

1. Silica Alumina
2. Zeolon 900H - Norton Synthetic Mordenite
3. Zeolon 900NA - Norton Synthetic Mordenite

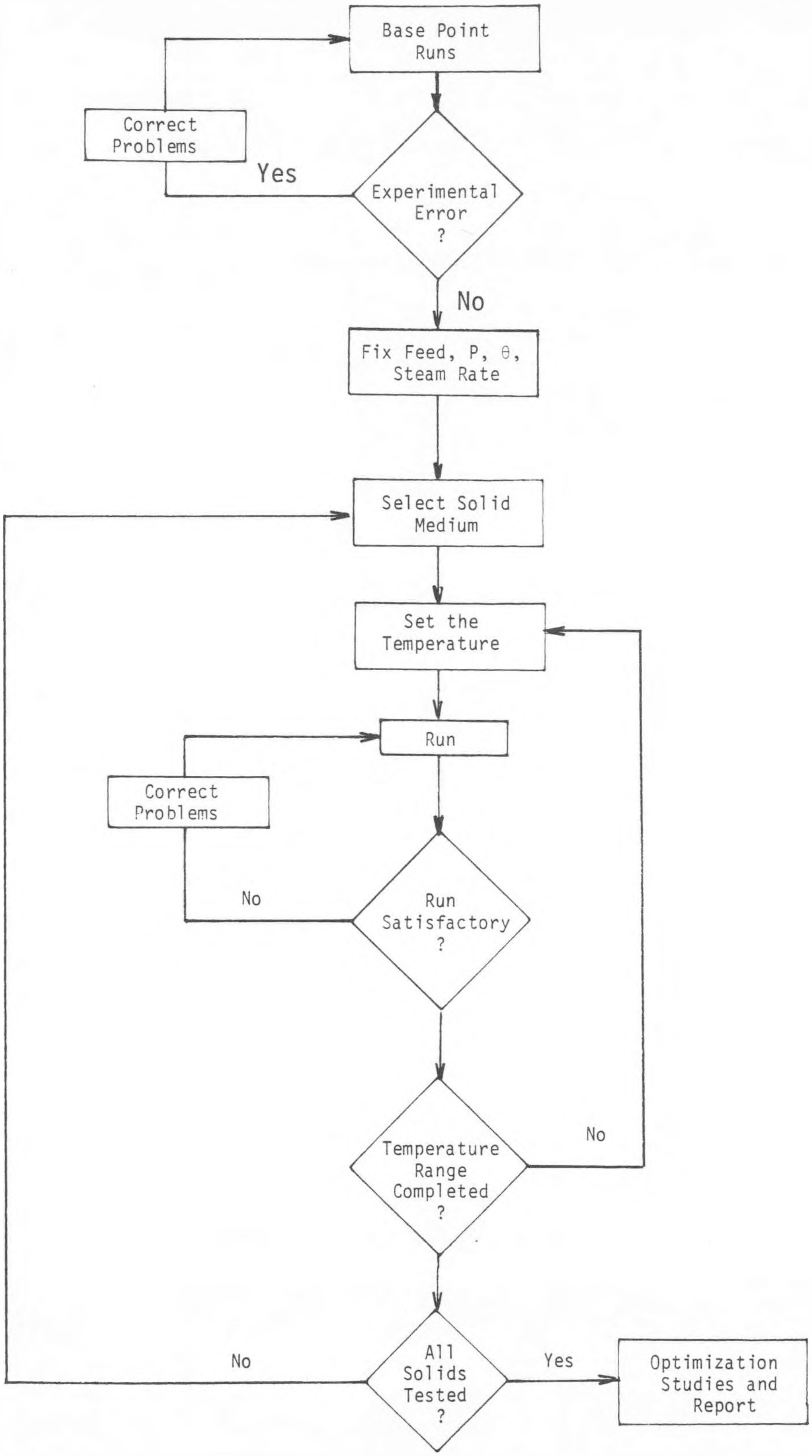


Figure 47. Experimental Plan - Pyrolysis Catalyst Study

broad range. The experimental plan was in progress at the end of the reporting period.

2. Gasification Reaction System Improvements. A major study was conducted during the year with regard to upgrading the gasification hot solids transfer loop configuration. The original intent in using a circulating solid system was based on eliminating gas separation equipment (as would be the case with single vessel pyrolysis with a combustion zone). However it was recognized (and confirmed) that the hot solids transfer loops would be a problem area with regard to continuous operational reliability. Thus if a failure in the loop transfer would occur, the chances of recovery during a run were remote.

The existing transfer system at the start of the contract period is depicted in Figure 22. The circulating solids transferred by gravity through the downcomer tube and then were sparged to and up the riser tube. Although this configuration operated successfully for many runs, the majority of unscheduled shutdowns were attributed to loop failures of some sort. Thus an extensive study of improved alternatives was implemented with the major objectives as follows:

(1) minimize possibility of depleting the fluidized solid from either bed,
(2) minimize possibility of gas backflow,
(3) minimize sparge gas usage,
(4) minimize heat loss,
(5) minimize erosion,
(6) maximize transfer rates, and
(7) maximize operational reliability.

The major alternative configurations studied can be grouped as follows: (1) cross riser transfer loop, (2) integral riser, (3) injector loop, (4) V-loop, (5) entrained circulation loop, and (6) internal circulation loop. All evaluations were performed with transparent (acrylic) simulators.

The cross riser configuration is illustrated in Figure 23 with directions of flow as indicated. Transfer rates were similar to the previous system (e.g., 150 lbs/hr sand with sparge flow of 5 lbs/hr). However level stability was much improved and the projected heat losses would be lessened due to the reduced exposed external loop area. Solids transfer was very stable and no significant gas backflow occurred. Sparge gas usage was still required however and excessive wear was anticipated, especially at the elbow of the riser tube. Modification of the existing gasification system to accommodate this revision would be relatively straightforward with the existing regenerator-pyrolyzer retained.

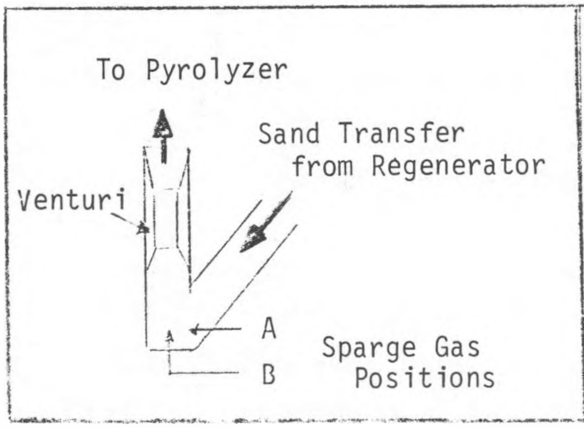
The integral riser simulator system is shown in Figures 18 and 24. The system was tested with two alternative downcomer entrance sections and with and without venturi inserts as illustrated in Table 4. As indicated, sand transfer rates varied from 300-700 lbs/hr. Gas backflow was common as well as the possibility of reverse flow of the circulating solids. The venturi inserts helped in this regard but were not a total cure. Sparge gas usage possibly could be eliminated and heat loss problems would be minimized. Fluidization was

Table 4. Integral Riser Simulator Performance

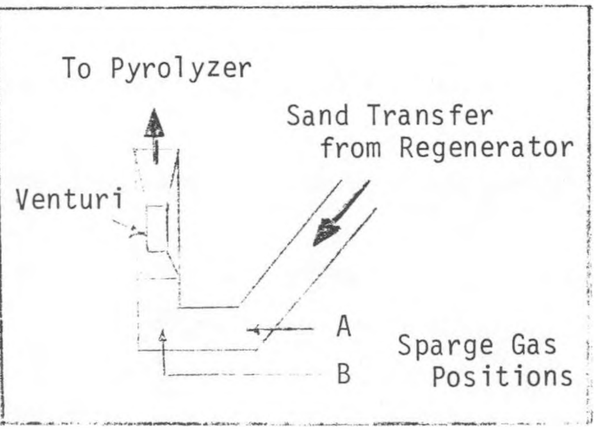
Sparge Configuration Description (ref. to lower drawing)	Sparge Flowrate lbs/hr		Sand Transfer Rate lbs/hr
	A	B	
Configuration #1*	1.6 60	55 1.6	531 695
Configuration #1 with venturi A - 1/8" nozzle B - 1/4" nozzle	5.3	33	313
Configuration #1 with venturi A - 1/4" nozzle B - 1/8" nozzle	41	6.7	797
Configuration #2	36 1.3	2.3 26	465 39
Configuration #2 with venturi A - 1/8" nozzle B - 1/4" nozzle	4.9	34	690
Configuration #2 A - 1/8" nozzle B - 1/4" nozzle	4.9	28	452

*Unless otherwise stated, data is without venturi

Configuration #1



Configuration #2



poor with considerable gas slugging occurring in the small diameter riser sections. This problem probably would be reduced on a larger scale. Fabrication would be relatively complex, requiring a major modification to the existing system. The system does not utilize gas distributor plates. Although this is an advantage with regard to fabrication and maintenance, the fluidization efficiency suffers, particularly at a small scale.

The injector loop transfer system is shown in Figures 19 and 25. The vessels are mounted at different heights with gravity flow to the lower vessel and sparge gas aided return via an injector box to the higher vessel. Sand transfer rates of about 230 lbs/hr were obtainable at sparge gas flow rates of 8 lbs/hr. Some gas backflow was observed in the higher tube (even with sparge gas usage at the lower vessel inlet). Heat losses are a consideration due to the external injector box. Fabrication modifications to the existing system would be moderate.

The V-loop system (Figures 20, 26) was a modification of the cross riser system that minimized fabrication problems and shortened the transfer loop lengths. Transfer rates of 350-400 lbs/hr for sparge gas flow rates of 4-5 lbs/hr were achieved. Flow was steady with minimal gas backflow. The optimum sparge gas location was determined to be about 1" below the downcomer tube intersection.

A schematic of the entrained circulation system is shown in Figure 27. The bottom section would serve as the regenerator and the top section as the pyrolyzer. Solids are blown up the riser tube and entrained to a cyclone where gases are removed and the solid returned to the fluidized bed regenerator section. The entrained bed mode allows for pyrolysis char to be returned to the regenerator. A designed experiment was performed on this system with solids transfer rates determined as a function of the three controlled gas flow rates. The results are shown in Table 5. A quadratic equation was fitted to this data (Table 6). The sparge riser inlet flow rate was deemed to be the most significant factor followed by the regenerator fluidization gas flow rate and entrainment inlet flow rate. Optimization of the regression model predicted a solids flow rate of 623 lbs/hr at flow rates of $\underline{X}$ = 16.1, 3.8, 2.5 lbs/min. Experimental verification at these settings resulted in a better value (703 lbs/hr solids transfer rate). For successful implementation of this system, a solids inventory would have to be maintained in the return cyclone to prevent gas blowback. Thus a level control system would have to be devised (generally true for all of the systems studied but more sensitive for systems with less surge capacity). Also erosion problems would be expected in the entrained sections. Fabrication modifications to the existing system would be major.

The internal circulation system is shown in Figures 21 and 28. Solids are blown up the riser tube and returned via the downcomer tube. A transfer rate of 115 lbs/hr of sand was achieved for sparge gas flows of 7 lbs/hr. As was the case for the entrained circulation system cyclone, a level control system would have to be devised for the reactor section to prevent solids depletion and gas blowback. Heat losses from this system should be minimal.

Table 5. Entrained Circulation Loop Simulator Data

Point	Regenerator Fluidization Inlet Flow (lbs/min) X_1	Sparge Riser Inlet Flow Rate (lbs/min) X_2	Entrainment Inlet Flow Rate (lbs/min) X_3	Rate of 60 Mesh Sand Transfer Through the Loop System Y lb/hr.
1	13.9	1.65	1.65	162.0
2	7.7	3.7	1.65	465.5
3	13.9	3.7	1.65	587.3
4	7.7	1.65	3.7	72.2
5	13.9	1.65	3.7	203.7
6	7.7	3.7	3.7	391.9
7	13.9	3.7	3.7	560.6
8	7.7	1.65	1.65	47.42
9	5.59	2.65	2.65	348.8
10	15.21	2.65	2.65	546.7
11	10.8	.928	2.65	1.19
12	10.8	4.37	2.65	509.4
13	10.8	2.65	.928	388.8
14	10.8	2.65	4.37	387.4
15	10.8*	2.65*	2.65*	471.3*
16	10.8*	2.65*	2.65*	461.1*

Note: * indicates base data point

Table 6. Entrained Circulation Simulator Regression Model

$$Y = A_o + A_1 X_1 + A_2 X_2 + A_3 X_3 + A_4 X_1^2 + A_5 X_2^2 + A_6 X_3^2 + A_7 X_1 X_2 + A_8 X_1 X_3 + A_9 X_2 X_3$$

where

$A_o = -1300.87158$
$A_1 = 53.8395386$
$A_2 = 641.421143$
$A_3 = 224.621216$
$A_4 = -2.07999611$
$A_5 = -82.4486237$
$A_6 = -38.1208801$
$A_7 = 1.77517986$
$A_8 = 2.53824806$
$A_9 = -19.4285736$

X_1, X_2, X_3 are lbs/min as defined in Table 5

Y is sand transfer rate (lb/hr)

The correlation coefficient (R^2) for the above equation was .974

The various circulation systems tested are compared in Table 7. Transfer efficiency is defined as the transfer rate of solids (lbs/hr) divided by the total sparge gas flow (lbs/hr) required to achieve stable performance. It is assumed that fluidization gas requirements will be approximately the same for all systems. Based on the results of the testing, it was decided to proceed with two paths: (1) short term implementation of an improved system with minimal risk and minor fabrication, and (2) further simulator testing and improvements to promising configurations that would require extensive changes from the existing system and thus assume a higher degree of risk. The two systems that required the least modification were the V-loops and cross riser configurations. The V-loops were selected based on a high transfer rate and less predicted heat losses. Fabrication modifications were in progress at the end of the reporting period. For the balance of the systems requiring significant modifications, it was decided to proceed with additional modifications and testing on the internal circulation system and reject the integral riser, injector loop and entrained circulation systems. For the integral riser system, the unstable operation problem was dominant although perhaps this would be lessened at a larger scale (i.e., poor fluidization and corresponding flow instability occurred at the small laboratory scale). The internal circulation system had the advantages of minimal sparge gas usage and heat loss. However transfer rates would have to be improved as well as implementation of a level control system in the top bed. A proposed configuration is illustrated in Figure 29. Here, the downcomer tube has been extended into the top bed to prevent solids depletion. Also this tube is held at only one location (thus minimizing thermal expansion problems). A conical section would replace the distributor plate used in the previous configuration and thus the separate sparge gas stream would be eliminated. This feature is analogous to that incorporated into the integral riser design and thus hopefully solids transfer rates will be improved without encountering the operational problems. Fluidization efficiency may be effected but should not contribute to any gas backflow problems such as occurred in the integral riser system. A lock hopper char recirculation leg is also shown in Figure 29. A solids level above the downcomer tube would still have to be maintained to avoid gas blowback (perhaps with temperature monitoring in a real system). The system is thus a hybrid of the attractive features of the various systems studied without the major disadvantages. The modifications were in the fabrication stage (simulator) at the end of the reporting period.

Liquefaction System Factor Studies

The major objectives in this area were as follows:

(1) demonstrate that liquid hydrocarbon fuel yields of 40+ gals per ton of cellulosic feedstock could be achieved for "typical" feedstocks,

(2) minimize catalyst costs, and

(3) minimize the liquefaction reactor operating pressure.

The major efforts to achieve these objectives can be grouped as follows: (1) catalyst test reactor system development, (2) cobalt catalyst development, (3) iron catalyst development, (4) slurry phase Fischer-Tropsch reaction system development, (5) catalyst characterization, and (6) large scale fluidized bed Fischer-Tropsch reactor improvements.

Table 7. Comparative Analysis - Solids Circulation System

	Existing Loops	Cross Riser	Integral Riser	Injector Loop	V-Loop	Entrained Circulation	Internal Circulation
Transfer Efficiency (max)	30	30	113	29	80	7	16
Bed Depletion (min)	-	+	+	+	+	-	-
Erosion Potential (min)	+	-	-	-	+	-	-
Heat Losses (min)	-	-	-	-	-	+	+
Operational Reliability (max)	-	+	-	+	+	+	+
Fabrication Complexity (min)	+	+	-	+	+	-	-

1. Catalyst Test Reactor System Development. Small scale catalyst testing equipment at the start of the reporting period consisted of a single reactor (either 1" schedule 40 x 2' fixed bed for iron catalyst testing or 2" schedule 40 x 2' for cobalt catalyst testing). This system is diagrammed in Figure 48. In the interests of increasing the level of effort, this system was replaced by a bank of six (2" schedule 40 x 2') parallel fluidized bed reactors. As shown in Figure 12 and 14, pressure and feed gas composition are common to all six reactors. However, different catalysts, temperatures and residence times could be varied independently for an experimental run. An additional system (2" schedule 40 x 2') was constructed to allow for recycle of off gas to the reactor inlet (Figures 13 and 15). The original constant diameter reactors were modified to incorporate a tapered entrance section. The purpose was to achieve a higher entrance velocity to combat a catalyst particle segregation problem, i.e., the larger particles tended to settle. One of the test reactors was also equipped with a quartz window to observe fluidization patterns. Details of the tapered reactors (with quartz window shown) appear in Figure 49.

2. Cobalt Catalyst Development. The two major Fischer-Tropsch type catalyst candidates for producing a liquid hydrocarbon fuel from synthesis gas are cobalt and iron. The choice is dictated largely by the synthesis gas composition. If the synthesis gas contains largely hydrogen and carbon monoxide, iron is probably the preferred choice. However if the synthesis gas also includes an appreciable quantity of olefins, cobalt should be more effective. For the configuration and operating conditions for the gasification system utilized to date for this project, significant quantities of olefins, hydrogen and carbon monoxide are to be expected thus favoring a cobalt based liquefaction catalyst. Thus the experimental effort on the project has concentrated on cobalt based liquefaction catalyst development. The areas investigated during this reporting period were composition, preparation method, washing, calcination, pretreatment, reduction and conversion variables. The factors varied for each study are as follows:

   preparation method: impregnation (excessive wetness, incipient wetness), precipitation, coprecipitation, base fixing
   composition: alumina, silica, natural and treated clays, zeolites, molecular sieves, other
   washing: bottle vs. filter paper, amount
   calcination: rapid vs. tube, temperatures, purge gas type and flow, time
   reduction: gas composition, temperature, pressure, time
   pretreatment: gas type
   conversion operating variables: gas composition, catalyst loading, gas recycle.

Previous catalyst preparation efforts were largely concentrated on blended catalysts (see Catalyst Characterization section). In this reporting period, the major effort was on impregnated and precipitated catalysts followed by calcination. The impregnated technique involves two methods - excessive wetness and incipient wetness. For the excessive wetness method, an excess amount of aqueous cobalt nitrate solution is mixed with the support and is absorbed into the pores of the support. The remaining solution is decanted and the

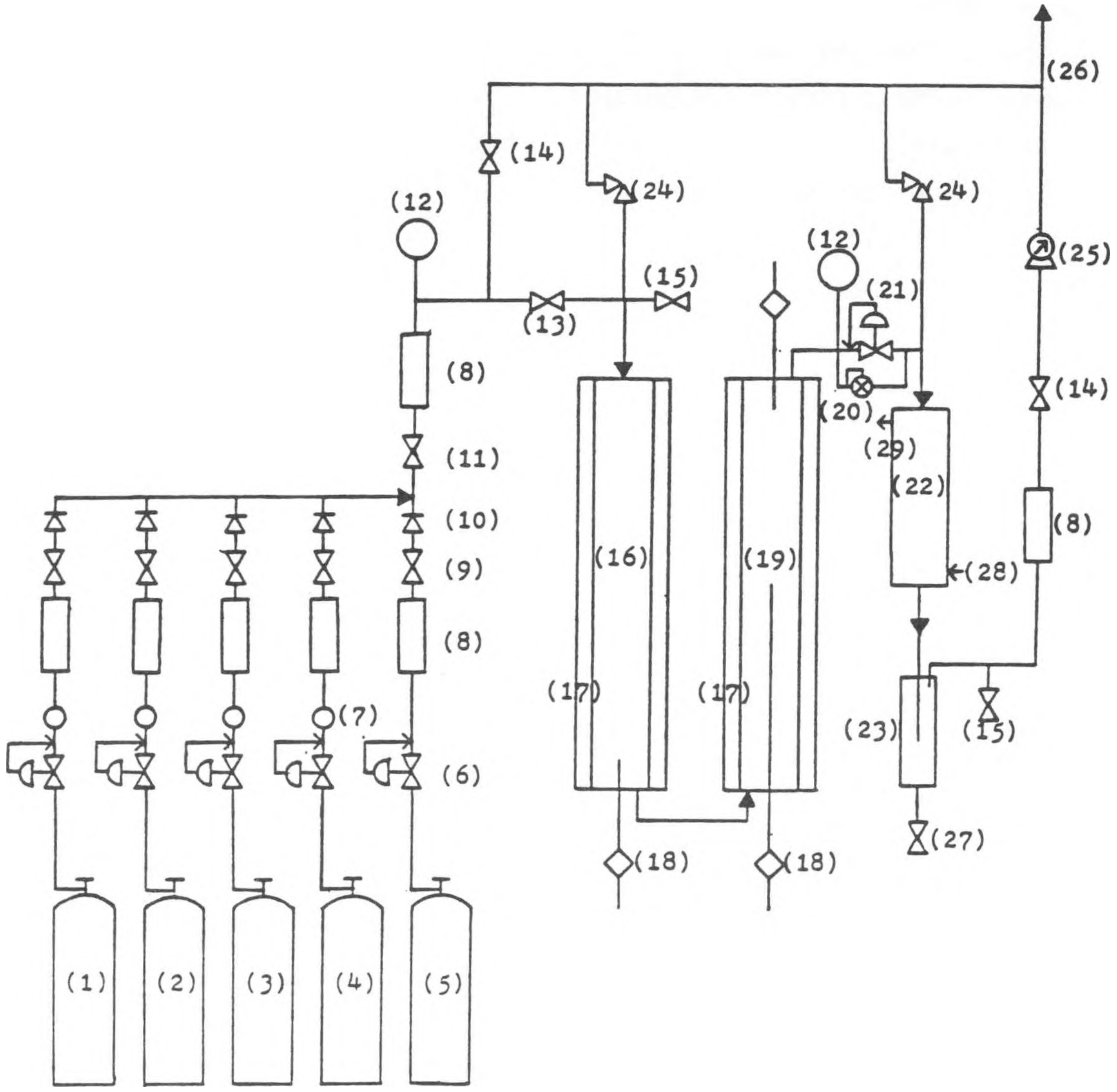


Figure 48. Fischer-Tropsch Catalyst Testing Unit - (single reactor)

Index of Figure 48

(1) Carbon Monoxide
(2) Hydrogen
(3) Methane
(4) Ethylene
(5) Carbon Dioxide
(6) Forward Pressure Regulators
(7) Safety Electrical Solenoid Valves
(8) Flow Meters
(9) Gas Inlet Ball Valves
(10) Check Valves
(11) Shut-Off Needle Valves
(12) Pressure Gauges
(13) Inlet Valve
(14) Release Valve
(15) Gas Sampling Valves
(16) Preheater
(17) Insulation
(18) Thermocouples
(19) Reactor
(20) Automatic Pressure Control System
(21) Back Pressure Regulator
(22) Condenser
(23) Liquid Collector
(24) Adjustable Relief Valves
(25) Wet Test Meter
(26) Vent
(27) Liquid Product Sampling Valve
(28) Cooling Water Inlet
(29) Cooling Water Outlet

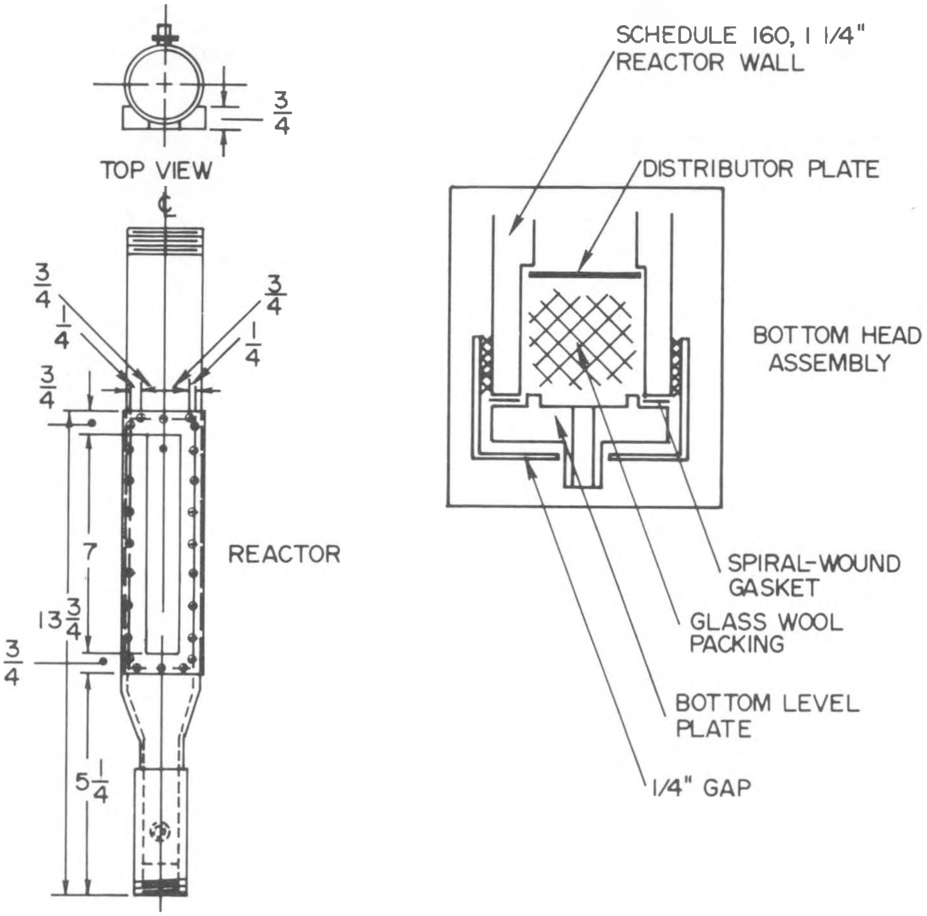


Figure 49. <u>2" Liquefaction Catalyst Test Reactor Details</u>

catalyst is filtered. An advantage to this method is that each support particle is exposed to the same concentration of cobalt nitrate. A disadvantage is that the exact amount of cobalt attached to the support is not exactly known due to filtration losses, etc. thus requiring a post analytical determination (see Catalyst Characterization section). For the incipient wetness method, cobalt nitrate is added in sufficient quantity to be absorbed completely in the pores of the support. Filtering is not required. The amount of impregnated species is more controllable than that for the excessive wetness method but the particle homogeneity is reduced with respect to cobalt nitrate absorption. Both the impregnation methods require a support with high pore volume and cannot be washed to remove impurities without removing the cobalt salt.

The precipitation method involves the mixing of a cobalt nitrate solution with the support. The support may be in the form of a salt solution ("coprecipitation"). A base (K_2CO_3, KOH, NaOH, etc.) is added to the solution to achieve a desired pH. The addition of the base precipitates the cobalt (either hydroxide or carbonate) with some of the cobalt coating the support. The primary advantage of the precipitation method is the option to wash the catalyst and remove impurities. The disadvantage is that the precipitated cobalt may not be attached to the support or that clusters may form if coprecipitation is utilized.

A hybrid method of preparation is referred to as base fixing. Here, the cobalt nitrate is impregnated on the support by the incipient wetness technique and then precipitated with a base to "fix" the cobalt on the surface of the support. The catalyst can be washed and formation of cobalt compared particles or clusters of cobalt and support particles are minimized. The procedure is complex however and reproducibility is a potential problem.

The catalysts prepared by the various methods were subjected to a calcination step to convert the cobalt compounds to cobalt oxides. Calcination was performed at elevated temperatures in either a purged externally heated tube or rapidly calcined on a hot surface. The calcined material was then reduced by a reduction gas (e.g., hydrogen) in the conversion reactors. This was followed by a gas "pretreatment" step if desired (to improve product selectivity). The conversion step followed with analysis of inlet and outlet streams.

Over 200 runs were completed with the cobalt based catalysts. Catalyst preparation and loading equipment are shown in Figures 35-38. The experimental conversion runs performed to study the effects of composition, preparation method, washing, calcination, pretreatment, and reduction were all performed in the parallel bank of 2" catalyst test reactors (see Figures 12, 14, 49). Reaction system operating conditions were approximately as follows:

Temperature, °F:	480-520	
Pressure, psig:	135-145	
Residence time, sec:	5-19	
Feed gas composition (mole %):	H_2	30
	CO	30
	C_2H_4	15
	CH_4	15
	CO_2	10

The conversion operating variable studies were performed in the 2" catalyst test reactor with gas recycle capabilities (see Figures 13, 15, 49). Fixed operating conditions for this system were approximately as follows:

Temperature, °F:	480-550	
Pressure, psig:	140 psig	
Feed gas composition (mole %):	H_2	30-34
	CO	26-28
	C_2H_4	13-27
	CH_4	11-15
	CO_2	6-12

The general strategy was to perform catalyst screening runs at fixed operating conditions on the parallel bank of fluidized bed reactors with operating variables "optimization" studies to be performed on current "best catalysts" in the recycle system. The net result was a "one-at-a-time" optimization sequence with respect to the large number of factors involved. A large number of interactions were apparent for the many factors. The "main effect" conclusions are somewhat premature as well as a meaningful assessment of experimental error. An assessment of results for each study follows. The response in each case was the liquid hydrocarbon product yield for the conversion runs.

(1) Composition. Various components studied are listed in Table 8. The amount of cobalt used was generally in the range of 12-15 wt% (as compared with 36% for the previous blended catalysts). The price of the cobalt salts was about \$3/lb. (as compared with up to \$100/lb for the cobalt oxides). Activated alumina was the most effective support (highest organic liquid yields) followed by Zeolon 900H, silica-alumina, molecular sieves and clays. Thorium oxide was an effective promoter for specified calcining conditions.

(2) Preparation Method. Incipient wetness was the most desirable method due to simplicity and the

Table 8. Catalyst Compositions (Cobalt Testing)

Alumina, Silica Supports

Co/Al_2O_3 Alcoa F200
ThO_2/Co/Al_2O_3
Co/ThO_2/Al_2O_3
Co/TiO_2/Al_2O_3
Co/Mn/Al_2O_3
Pt/Co/Al_2O_3
Co/Silica-Alumina Grace MS13/110
Co/Norton Silica-Alumina 3232
Co/Norton Silica-Alumina 6174
Co/Norton Silica-Alumina 6476
Co/Norton Silica-Alumina 3232
Co/La_2O_3/ThO_2/Al_2O_3
La_2O_3/Co/Al_2O_3
Co/MgO/Al_2O_3
Co/Norton Silica-Alumina 5202
Co/Norton Silica-Alumina 5104
Co/Grace Silica Gel Type ID

Natural and Treated Clays Supports

Co/Kaolite
Co/Dolimite
Co/MicroCel (Mansville)
Co/Red Clay
Co/Kieselguhr (J. T. Baker)
Co/ThO_2/Kieselguhr

Zeolite Supports

Co/Norton Zeolon 900 Na
Co/Norton Zeolon 900H
Co/Norton Zeolon 500
Co/Norton Zeolon 400
Co/ThO_2/Zeolon 900H
Co/Norton Zeolon 700

Molecular Sieve Supports

Co/Linde M. S. Type 3A
Co/Linde M. S. Type 4A
Co/Linde M. S. Type 5A
Co/Linde M. S. Type 13X
Co/Applied Sciences M. S. Type 13X

Other Compositions

Co/TiO_2
Co/ThO_2
Co/La_2O_3
Co/ThO_2/La_2O_3
Co/Activated Charcoal
Co/ThO_2/Activated Charcoal
Co/MnO_2/Al_2O_3
Co/MgO/Al_2O_3

apparent lack of need to wash impurities from the catalyst. A pH of 8 was the most effective for cobalt/alumina catalysts prepared by a precipitation method.

(3) Washing. A limited filter wash with distilled water for precipitated catalysts was the most effective. Thus no washing or an increased washing severity gave worse results indicating that an "optimum" level of impurities existed for precipitated catalysts.

(4) Calcination. Rapid calcination was effective for catalysts containing thorium oxide only. A temperature of 400°F was optimal and larger calcining times beyond four hours did not improve yields. Helium, argon and air were tested as the purge gas. The type of gas used (and flows) appeared to be catalyst composition dependent. Thus helium purge at high flows was the most effective for cobalt/thoria/alumina formulations whereas other combinations were more effective for other catalyst formulations.

(5) Reduction. Hydrogen reduction gas was used exclusively. No yield improvements resulted with incorporation of diluents (CO_2, N_2). No improvements in yields were observed at elevated pressures (greater than atmospheric) or for reduction times greater than about three (3) hours. High temperatures were desirable with an upper limit of 750°F dictated by equipment limitations, i.e., Teflon reactor thread sealant (flange modifications are in progress to allow for higher temperatures).

(6) Pretreatment. Carbon monoxide, ethylene and carbon dioxide each were tested on a reduced cobalt/alumina catalyst (2 hours at 500°F, 140 psig). Yield improvement was insignificant vs. unpretreated catalysts. Carbon dioxide pretreatment gave the best yields for the pretreatment study.

(7) Conversion. Four catalysts were tested on this unit: cobalt/alumina (12 wt% cobalt), cobalt/thoria/alumina (15 wt% Co), cobalt/thoria/alumina (30 wt% Co), and cobalt/Zeolon 900H (15 wt% cobalt). The higher cobalt loading (30 wt%) resulted in excessive carbon formation. The major factor explored in this system was effective residence time. This was implemented both by varying the catalyst loading (2' and 4' reactor length) and by varying the recycle rate of reactor off gas to the reactor inlet. Selected results are shown in Tables 9 and 10. The results indicate that an expected tradeoff exists between recycle compressor capacity and reactor size. Thus at equivalent recycle rates, an increased catalyst loading (larger reactor) increases the single pass conversion of reactants therefore reducing the "quality" of synthesis gas available for recycle. Calculated yields of up to 36 gals/ton of cellulosic waste (dry, ash free) were achieved for "typical" biomass feedstocks, i.e., those yielding 10-20 mole % olefins. Although higher yields were achieved (> 40 gals/ton) for olefin

Table 9. Recycle Study - 2' Reactor (Cobalt Testing)

Catalyst: Co/Al_2O_3, ~ 12 wt%

Reactor Length: 2 ft

Operating Conditions:

Pressure: 140 psig

Temperature: 480-530°F

Residence Time: 4-5 sec. (single pass)

Catalyst Loading: 300 grams

Gas Compositions (mole %):

Run:	1			2			3		
	M[1]	I	R	M	I	R	M	I	R
H_2	34	27	14	32	24	14	30	26	15
CO_2	6	8	12	9	10	12	6	6	9
C_2H_4	17	10	2	17	10	2	27	21	8
C_2H_6	--	6	11	--	6	12	--	6	14
CH_4	13	18	27	12	20	26	11	14	21
CO	30	31	34	30	30	34	26	27	33
H_2/CO	1.13	0.87	0.41	1.06	0.80	0.41	1.15	0.96	0.45
Recycle Ratio:	1.43			1.25			1.25		
Yield[2]:	36 gal/ton			31 gal/ton			41 gal/ton		

[1] M-make up, I-total inlet, R-recycle

[2] gals liquid product/ton biomass (ash free) assuming gas conversion 85%, ash content 5%

Table 10. Recycle Study - 4' Reactor (Cobalt Testing)

Catalyst: Co/Al_2O_3, ~ 14 wt%

Reactor Length: 4 ft

Operating Conditions:

Pressure: 140 psig

Temperature: 480-530°F

Residence Time: 18-19 sec. (single pass)

Catalyst Loading: 1200 grams

Gas Compositions (mole%)

Run:	1			2		
	M[1]	I	R	M	I	R
H_2	36	26	9	36	28	8
CO_2	6	10	17	6	9	18
C_2H_4	12	9	1	13	10	1
C_2H_6	--	5	10	--	4	12
CH_4	10	18	26	15	19	35
CO	36	33	37	30	30	26
H_2/CO	1.0	0.8	0.2	1.2	0.9	0.2
Recycle Ratio:		1.1			1.1	
Yield[2]:		31 gal/ton			34 gal/ton	

[1] M-make up, I-total inlet, R-recycle

[2] gals liquid product/ton biomass (ash free) assuming gas conversion 85%, ash 5%

compositions of > 20 mole % in the makeup gas, these compositions are not currently possible except for selected feedstocks (see Alternative Feedstocks section).

A run was performed with a mixed olefin feedgas (10 mole % C_2H_4, 5 mole % C_3H_6) to simulate the variations in olefin composition typical of pyrolysis gas streams. No significant change in product yields was observed (as compared with that obtained for 15 mole % C_2H_4 feed gas).

3. Iron Catalyst Development. A study on iron based catalysts was started during the previous reporting period and completed during the present reporting period. The general plan is depicted in Figure 50. The catalyst screening phase (top portion of Figure 50) has been previously reported (3). A blended catalyst consisting of G64-D (United Catalyst) and Zeolon 900H (Norton) gave the best liquid organic yields at a H_2/CO mole ratio of ~ 0.8 (as compared with ~ 1.2 for cobalt catalysts). All runs were performed in an adiabatic, fixed bed operating mode with the equipment depicted in Figure 48. General conclusions for the balance of the study as depicted in Figure 50 are as follows:
   (1) catalyst activity declined rapidly after about 10 hours for G64-D + Zeolon 900H and C73-1 (United Catalyst) + MgO (the second best catalyst) due to carbon formation (coking). Profiles are shown in Figures 51 and 52. This perhaps would be lessened with isothermal operation in a fluidized bed.
   (2) optimum conditions (maximum organic yields) for G64-D + Zeolon 900H was approximately 270°C, 140 psig and 16 seconds residence time over the range of conditions explored. Results are shown in Tables 11-13 and Figures 53-55.
   (3) mixed feed gas (H_2, CO, C_2H_4, CH_4, CO_2) results in a substantial decrease in product yields with all components except hydrogen and carbon monoxide being relatively inactive.
   (4) repelletized catalyst runs (catalyst pellets ground, mixed and repelletized) gave essentially the same results as the original pellet blend.
   (5) material balance calculations predict a yield of 10-15 gals of liquid hydrocarbon product per ton of cellulosic feedstock (dry ash free) with H_2-CO synthesis gas. Yields dropped to < 5 gals/ton for typical mixed feed gas.

The Sasol facilities in South Africa report yields of 40-50 gals/ton of coal with synthesis gas isolation of hydrogen and carbon monoxide, entrained bed liquefaction reactors and off gas recycle (17). Thus product yield improvements are to be expected with iron based catalysts utilizing cellulosic type feedstocks. However operation of the gasification system to maximize for olefin production does not appear to be a virtue, i.e., one should operate to achieve an optimum H_2/CO ratio with minimum formation of other components (see Gasification Catalyst Development section).

Further details on this study may be found elsewhere (18).

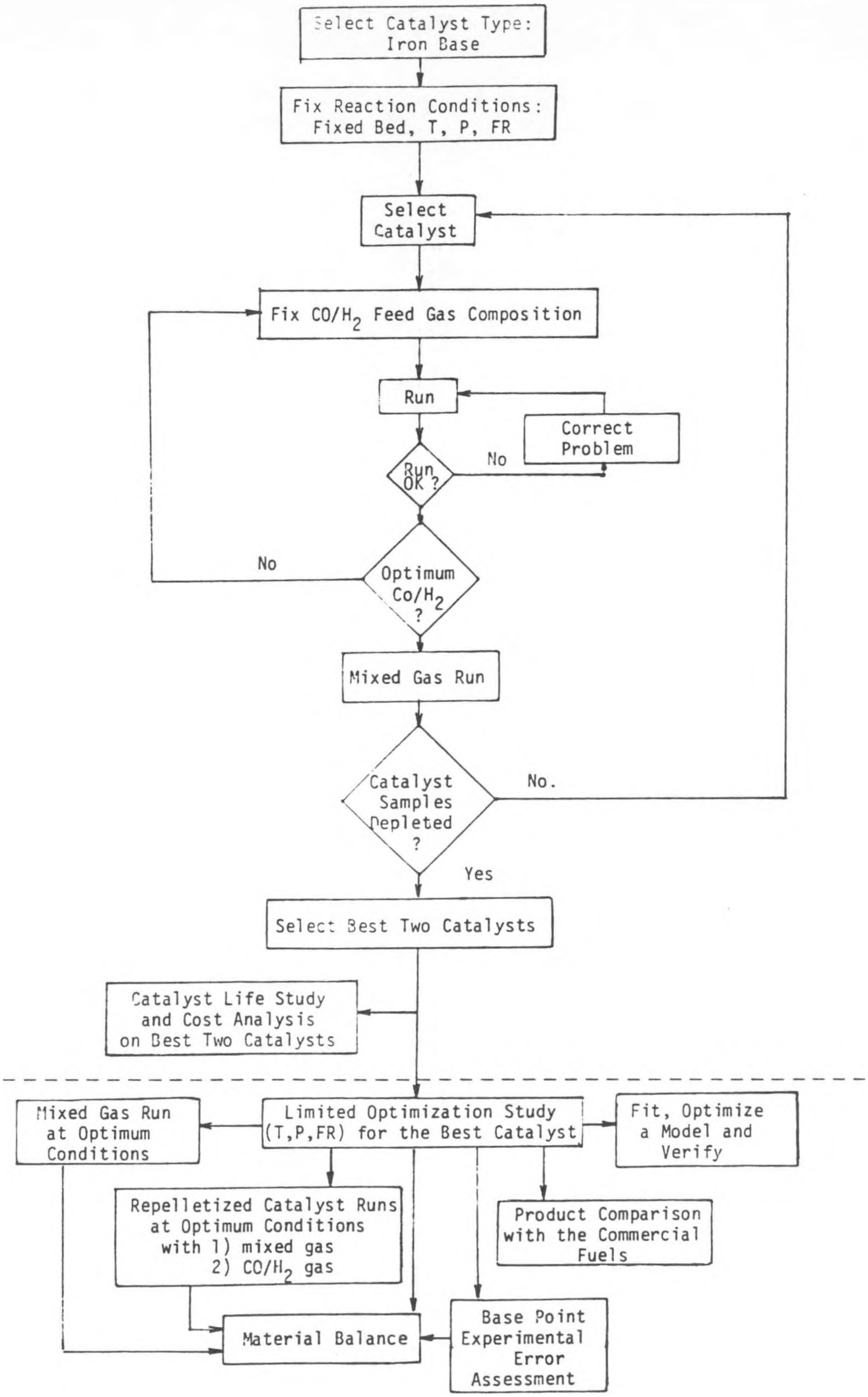


Figure 50. Schematic Diagram for Study of Iron Based Catalysts

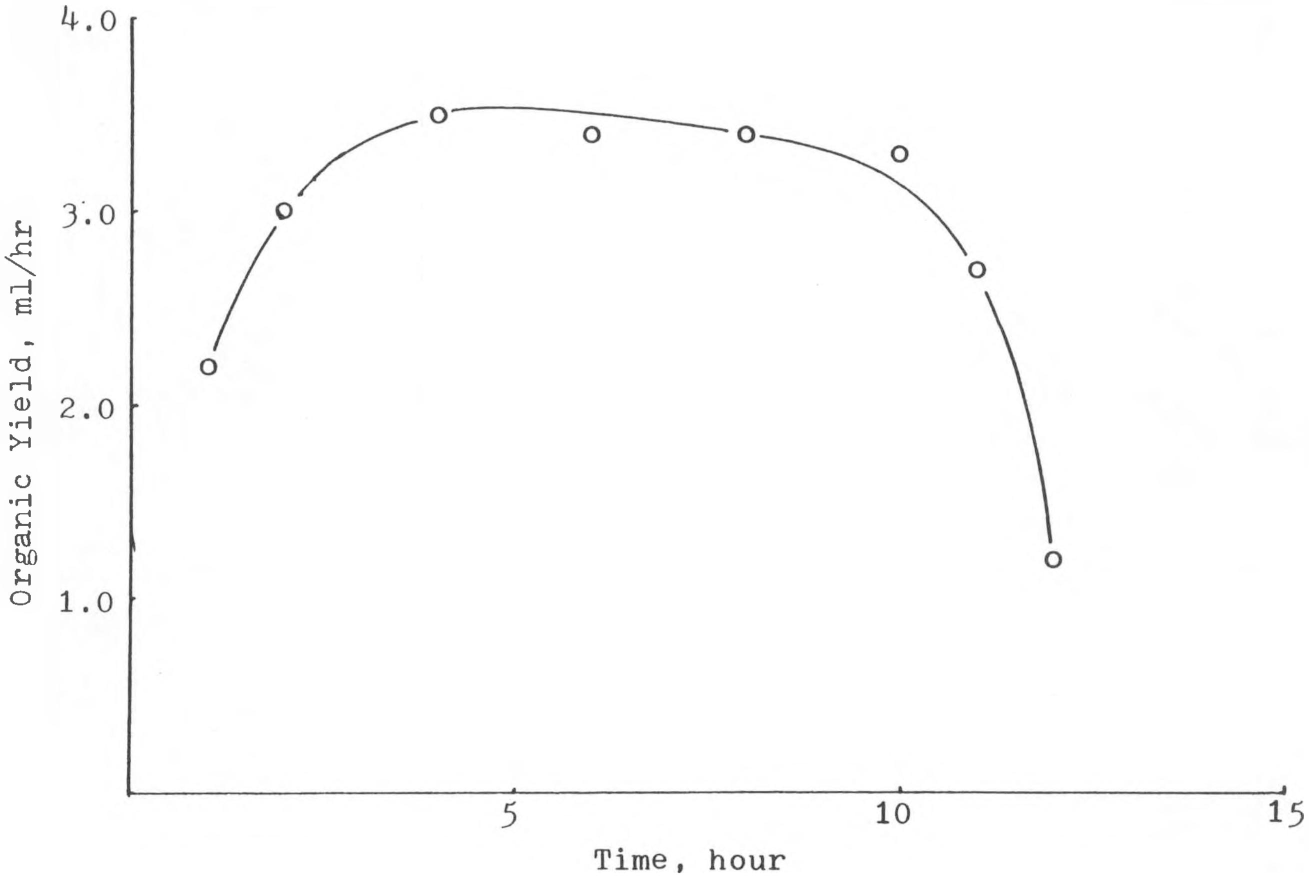


Figure 51. Catalyst Activity of G64-D/Zeolon 900H

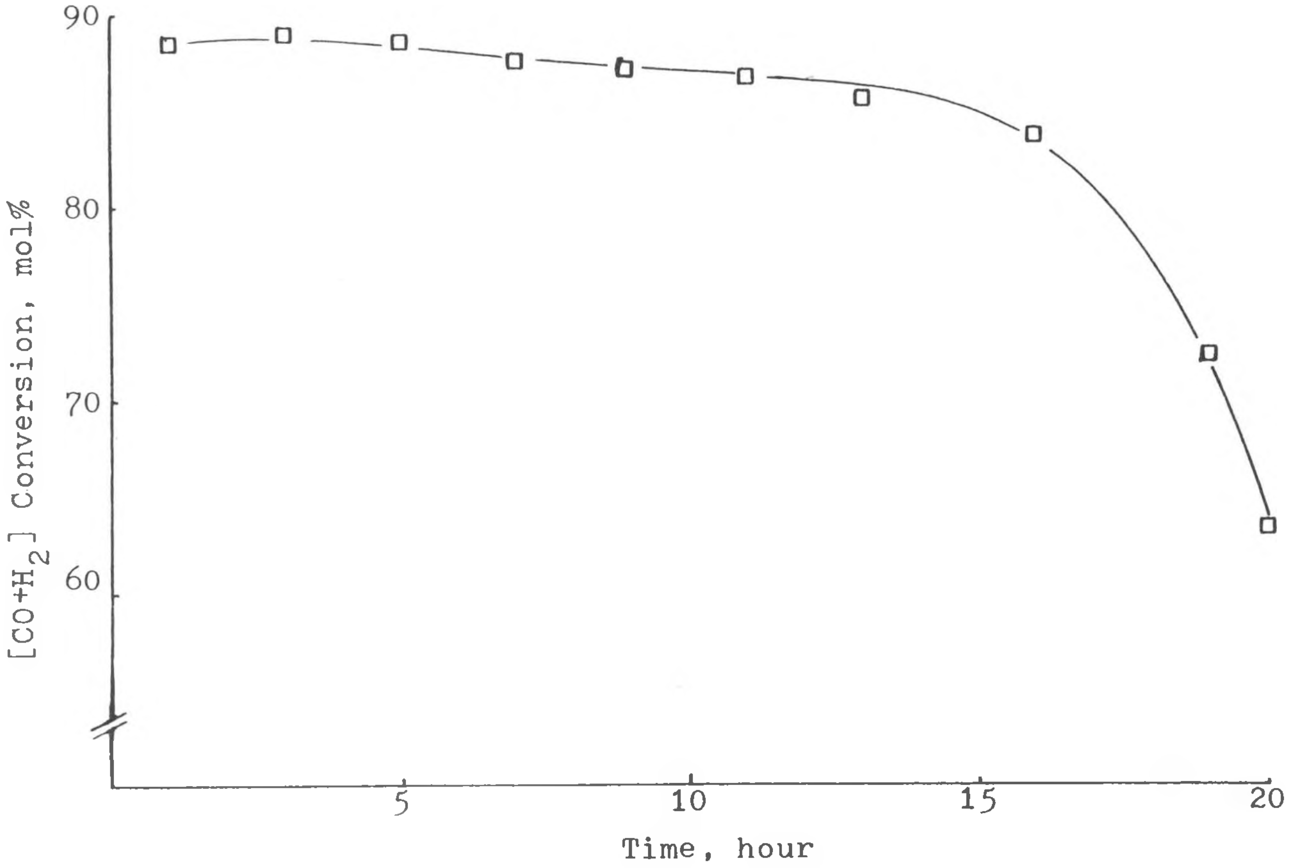


Figure 52. Catalyst Activity of C73-1/MgO

Table 11. Liquid Product Analysis - Temperature Study (Catalyst: G64-D/Zeolon 900H)

Temperature,°C	200	240	270	300	350
Organic Product:					
Yield, ml/hr	2.0	3.0	3.1	2.9	Trace
Yield, g/g Cat-g feed x 10^6	100	151	157	144	---
Composition, wt%					
Paraffins	41.45	37.29	41.37	47.47	
Isoparaffins	39.45	38.94	37.59	37.23	
Olefins	6.74	6.90	6.32	5.43	---
Aromatics	7.11	6.35	6.32	5.43	
Others	5.25	10.52	8.40	7.72	
Aqueous Product:					
Yield, ml/hr	2.3	2.6	2.5	2.4	Trace
Composition, wt%					
Water	99.27	99.10	98.45	99.18	
Alcohols	0.73	0.90	1.55	0.72	

Fixed Operating Conditions:

Pressure, psig: 140
Feed composition, mole%: H_2 46.1
CO 53.9
Feedrate, SCFH: 2.5
Residence time, sec: 19.4

Table 12. Liquid Product Analysis - Pressure Study (Catalyst: G64-D/Zeolon 900H)

Pressure, psig	50	90	110	125	140	155
Organic Product:						
Yield, ml/hr	1.7	2.2	2.7	2.9	3.1	3.0
Yield, g/g cat-g feed x 10^6	88	113	138	144	157	151
Composition, wt%						
Paraffins	55.54	49.50	46.78	50.79	45.97	50.02
Isoparaffins	33.76	38.30	32.98	34.50	33.78	31.51
Olefins	1.27	1.32	5.21	1.94	3.68	3.16
Aromatics	4.28	5.14	7.83	7.15	9.87	6.35
Others	5.15	5.48	7.20	5.62	6.70	8.96
Aqueous Product:						
Yield, ml/hr	1.0	1.2	2.5	2.5	2.7	2.5
Composition, wt%						
Water	98.35	98.11	97.33	98.30	98.34	97.65
Alcohols	1.65	1.89	2.67	1.70	1.66	2.35

Fixed Operating Conditions:

Temperature, °C:	250	
Feed composition, mole%:	H_2	46.1
	CO	53.9
Feedrate, SCFH:	2.5	
Residence time, sec :	19.4	

Table 13. Liquid Product Analysis - Residence Time Study (Catalyst: G64-D/Zeolon 900H)

Residence Time, sec.	32.4	24.3	19.4	16.2	13.9	9.7
Organic Product:						
Yield, ml/hr	0.7	2.1	3.1	3.8	4.4	4.0
Yield, g/g cat-g feed x 10^6	60	131	156	159	157	100
Composition, wt%						
Paraffins	44.52	42.58	44.36	46.89	33.64	43.36
Isoparaffins	31.62	34.70	31.58	29.10	33.26	34.98
Olefins	6.16	3.79	7.33	6.70	15.24	4.53
Aromatics	8.31	9.33	8.65	10.52	8.43	9.11
Others	9.39	9.60	8.08	6.79	9.43	8.02
Aqueous Product:						
Yield, ml/hr	0.9	1.8	2.3	2.9	3.0	4.0
Composition, wt%						
Water	97.92	98.44	98.67	99.64	98.75	98.13
Alcohols	2.08	1.56	1.33	0.36	1.25	1.87

Fixed Operating Conditions:

Temperature, °C: 270

Pressure, psig: 140

Feed composition, mole%: H_2 46.1
CO 53.9

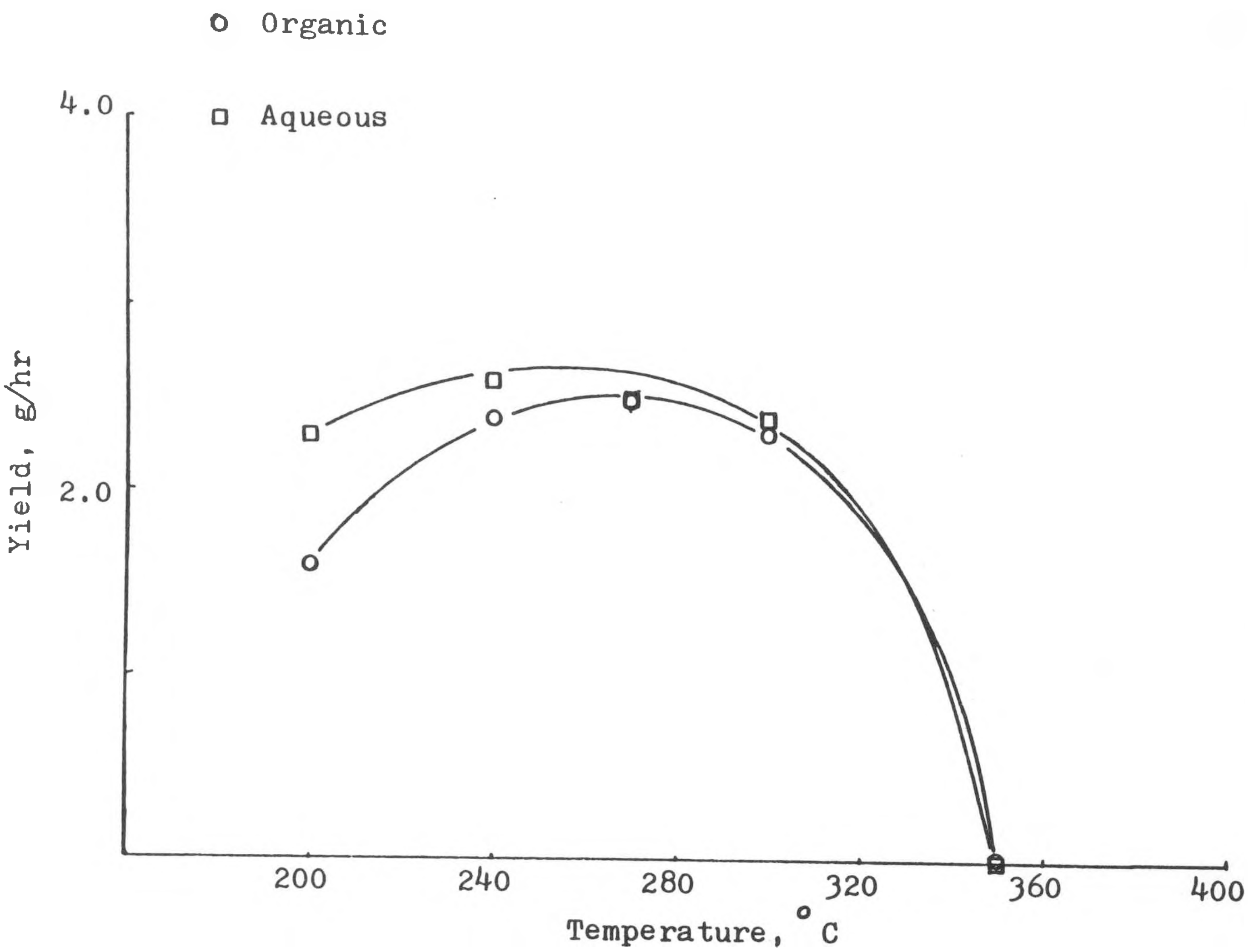


Figure 53. Effect of Temperature on Liquid Product Yield (Catalyst: G64-D/Zeolon 900H)

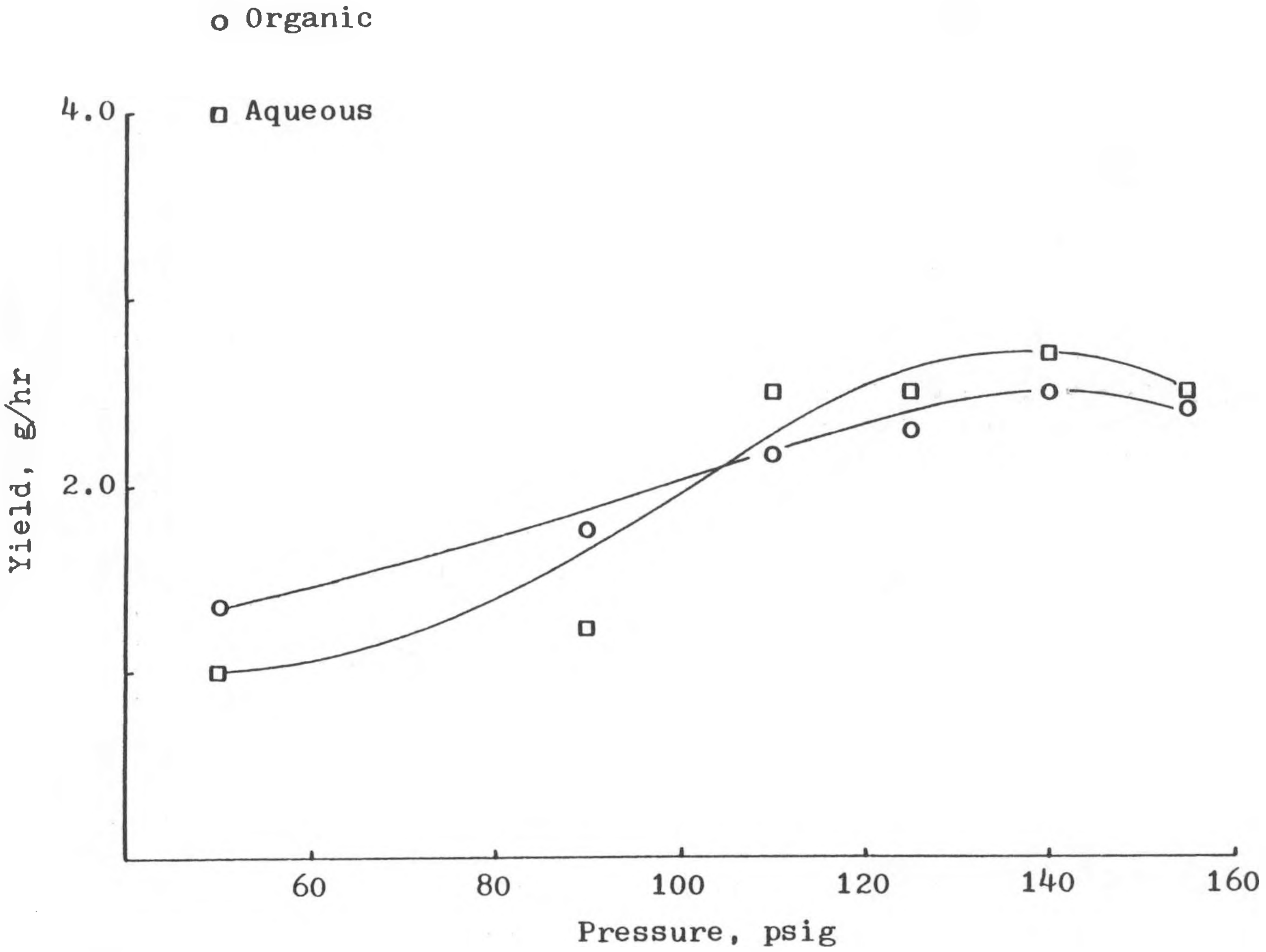


Figure 54. Effect of Pressure on Liquid Product Yield (Catalyst: G64-D/Zeolon 900H)

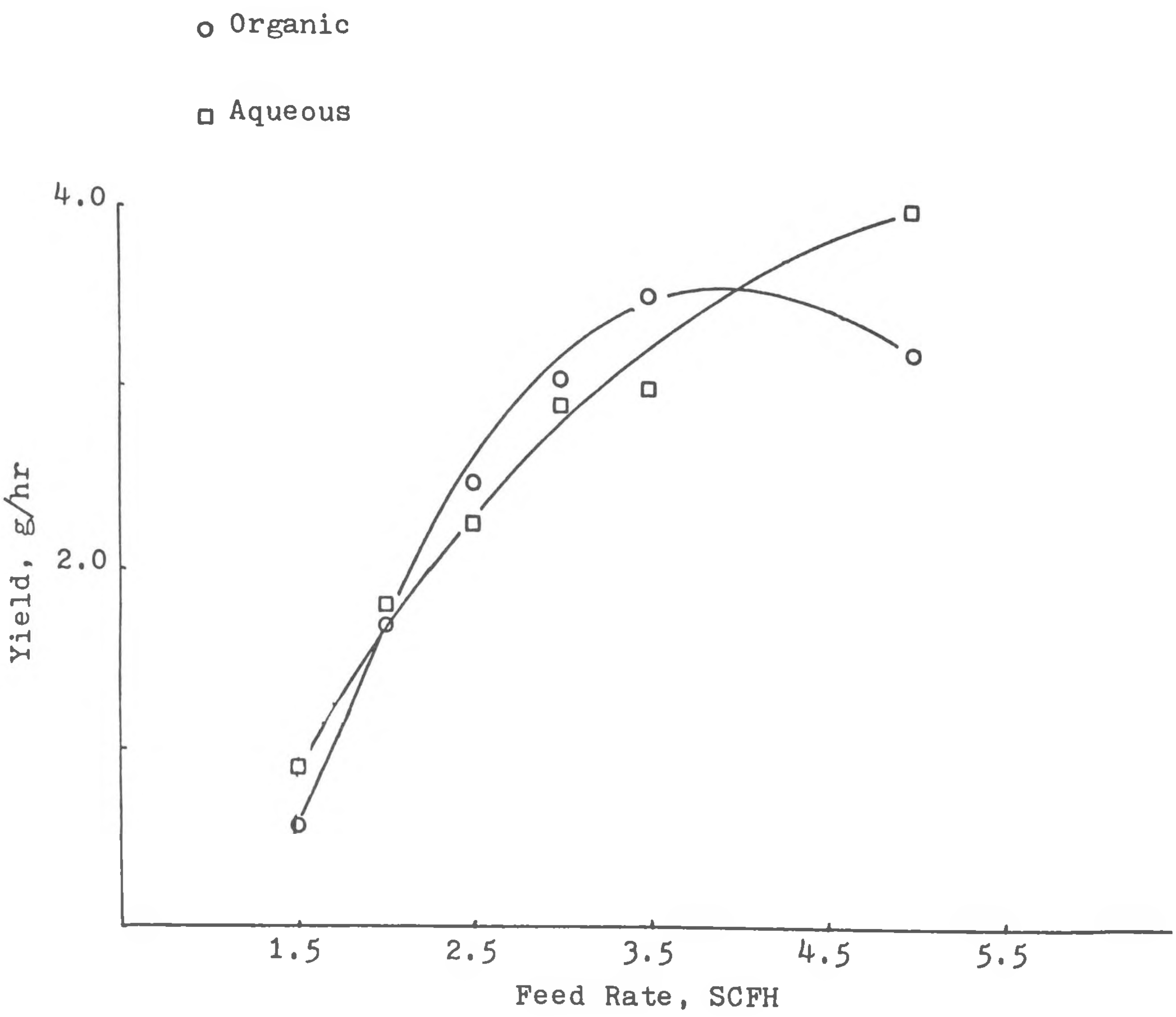


Figure 55. Effect of Residence Time on Liquid Product Yield (Catalyst: G64-D/Zeolon 900H

4. Slurry Phase Fischer-Tropsch System. A project was started to design, develop and assess a slurry phase catalytic liquefaction reactor as an alternative to the fluidizied bed liquefaction reactor. The work is sponsored by the Energy Systems for Agriculture program funded by the Department of Energy and administered by the Agricultural Research Service (ARS), Science and Education Administration of the U. S. Department of Agriculture (Grant No. 59-2043-1-6-062-0). The project was proposed and is currently being implemented as a "stand alone" system suitable for linking to various gasification systems under development. Attractive features of a slurry reactor are indicated in Table 14. A flow schematic of the system appears in Figure 9 and a photograph of the laboratory equipment is shown in Figure 11. This project relates to the project described in this report in that the slurry phase system may prove to be superior to the present fluidized bed liquefaction system. Of particular interest is increased options for higher product yields, flexibility with regard to alternate products and elimination of the control complexity of operating fluidized beds in series (gasification + liquefaction (see Process Control section)). The scale of the slurry phase system is compatible with the existing large scale integrated gasification system and consideration of a link will be reviewed as the project progresses.

   The near term experimental plan for the slurry phase system is depicted in Figure 56. The objective is to establish operational reliability, optimize for diesel fuel production and compare the performance of the system with that of the fluidized bed.

5. Catalyst Characterization. Liquefaction catalyst formulations prior to this reporting period were dominated by physical mixtures of cobalt oxides and alumina. The alumina was originally added as a fluidization promoter, i.e., new alumina was inactive as a catalyst. Although this was a successful catalyst for producing a quality product, large variations in product yields would occur with different vendors and different lots from the same vendor for cobalt oxide compounds. Thus a major effort was started towards establishing identification and control of catalyst characteristics. A longer term goal of this effort was to aid in the development of cheaper catalysts and achieve lower operating pressures. Initial characterization work included analysis for oxidation state, surface area, pore volume, pore radius, elemental composition, surface composition and bulk composition. The bulk of the analysis was performed by external laboratories on a low priority, complementary basis. A clear correlation of the characterization data with the liquefaction reactor performance was not achieved. However it was observed in this period that the alumina portion from a used cobalt-alumina catalyst blend(screened) gave essentially the same product yields as the original blends. Thus the active cobalt sites appeared to be bonded to the alumina and the bulk cobalt was not significantly active. This indicated that a significant cost savings and perhaps yield improvements could be achieved via examination of alternative preparation techniques supported by appropriate catalyst characterization determinations. The catalyst preparation effort has been previously discussed (see Cobalt Catalyst Development section). To minimize time and translation problems, it was decided to implement the catalyst characteristics capability on-site as much as possible. Since catalysis is in essence a surface phenomena, properties such as surface area, exposed metal surface area, void fraction, pore size distribution,

Table 14. Slurry Reactor Features

1. Good heat transfer
2. Catalyst continuous regeneration
3. Minimal dust collection problems
4. Minimal equipment erosion, catalyst attrition
5. Non-supported catalyst option
6. Operating conditions flexibility

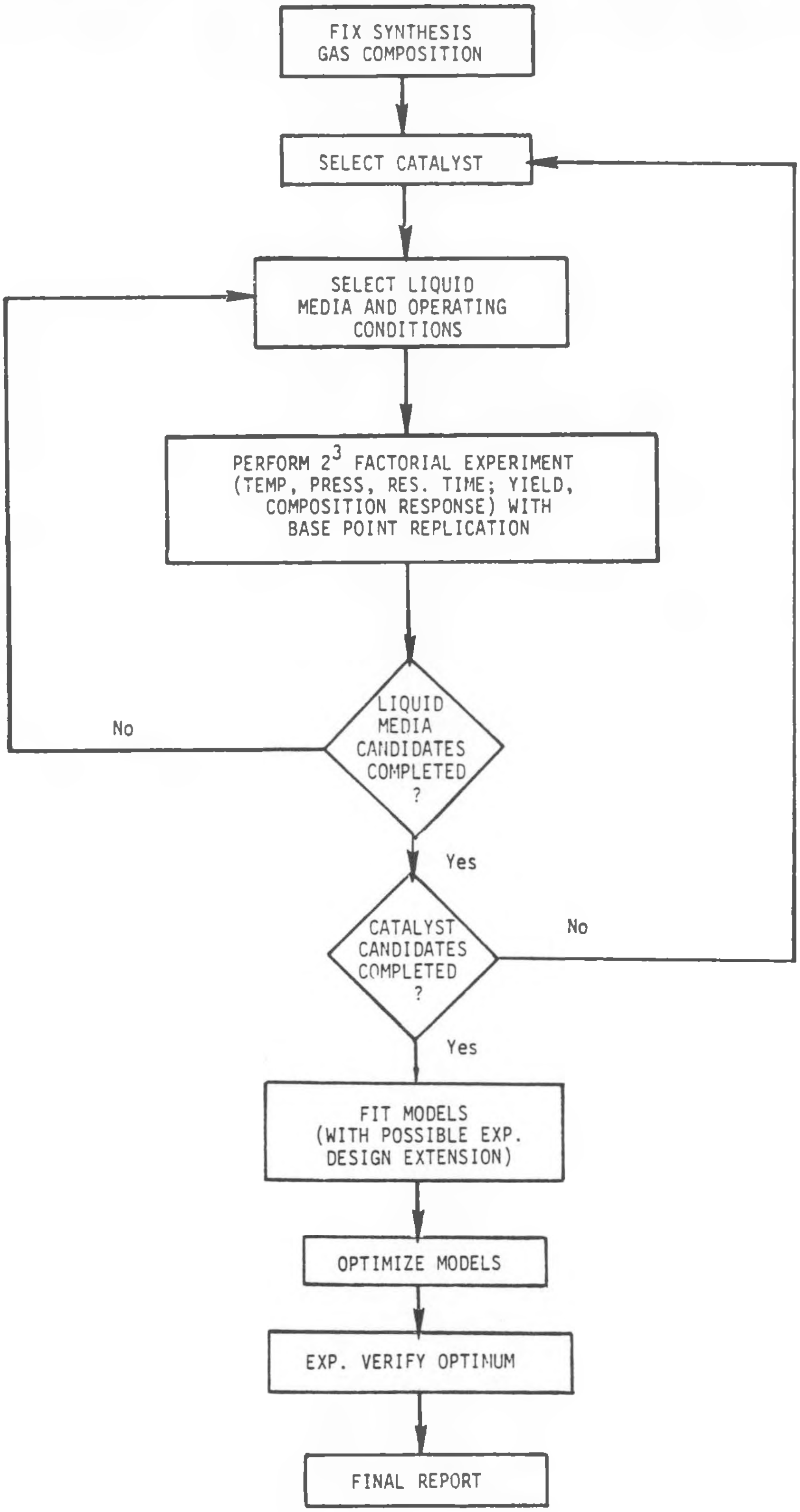


Figure 56. Slurry Phase Reaction System Experimental Plan

crystallite size and surface compositions are of major interest. The capability to determine these properties as well as bulk composition was addressed in the current reporting period.

Table 15 lists the various properties of interest, the corresponding analytical technique and the present status of development. Figures 41-46 show the various instruments. For supported metal catalysts, a very important property is the exposed metal surface area. This can be determined by selective chemisorption. The principle is to simply measure the amount of selective adsorbate gas attached to the active metal and to calculate the exposed metal surface via chemisorption stoichiometry. A schematic of this equipment is shown in Figure 46 and a photograph in Figure 41. A physisorption addition to this system is planned to determine total surface areas and pore volumes. A X-ray diffractometer and X-ray fluorescent spectrometer are currently used to determine the identification and bulk concentrations of the metals in the catalyst (Figures 42,43). The former provides qualitative type identification of chemical species existing in the catalyst sample while the latter provides quantitative results utilizing calibration standards. Figure 57 is a typical calibration curve of standards and Table 16 lists the necessary data to plot the calibration curve. The chemical analysis information has been used as a check on the accuracy of catalyst preparation methods (see Cobalt Catalyst Development section).

Auger electron spectroscopy and electron microprobe methods are the tools under study for the detection of minor species (e.g., promoters). The equipment is shown in Figures 44, 45.

6. Large Scale Fluidized Bed Fischer-Tropsch Reactor Improvements. The 6" fluidized bed reactor system was modified extensively during the reporting period. The major improvements were as follows:
   (1) modification of the reactor to incorporate a tapered entrance section to improve fluidization at the inlet,
   (2) modified heating and cooling coils, temperature monitors, preheater and controls to improve temperature control,
   (3) fabrication of a cyclone for small particle collection,
   (4) installation of a recycle loop via a Worthington compressor to allow for recycle of the off gas to the reactor inlet, and
   (5) installation of new liquid product traps to accommodate higher product yields.

   A sketch of the modified reactor, coils and cyclone is shown in Figure 58. A flow schematic appears in Figure 1 and a photograph of the modifications during construction appears in Figure 5.

Staged Reaction System

This system was designed to achieve the goal of producing quality liquid hydrocarbon fuels at a smaller scale than that anticipated for the current separated indirect liquefaction systems. Thus, with success in this task, a number of additional potential applications would be viable commensurate with the typical distributed supply

Table 15. Catalyst Characterization Status

Property	Method	Status
Total surface area	Physisorption	In planning
Specific surface area	Chemisorption	In construction
Pore volume	Physisorption	In planning
Pore-size distribution	Physisorption	In planning
Crystallite size	X-ray line broadening	In study
Species identification	X-ray diffraction	In use
Bulk concentration	X-ray fluorescence	In use
Element analysis	Auger electron spectroscopy or electron microprobe	In study, conditional availability

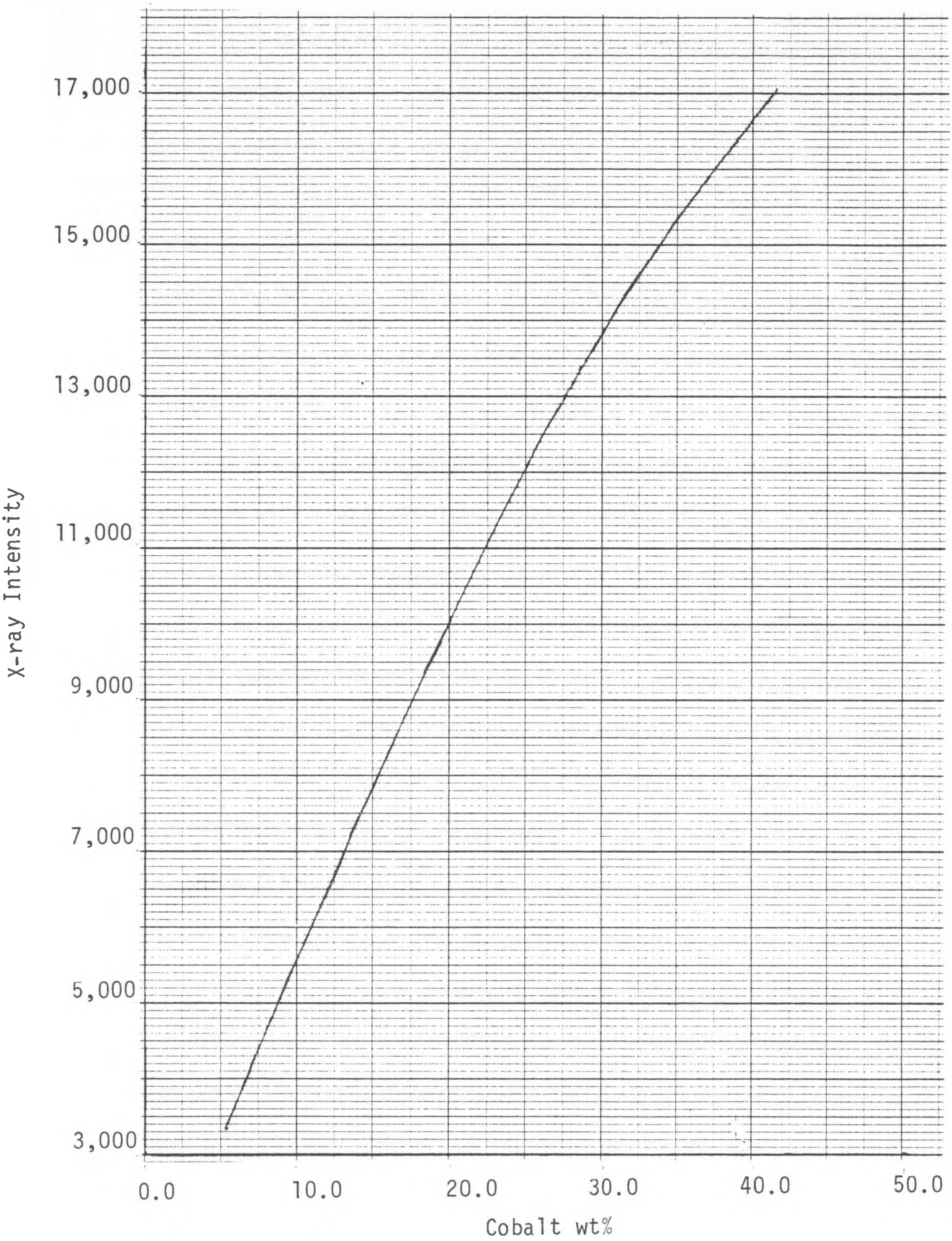


Figure 57. X-Ray Fluorescence Calibration for Cobalt Scanning

Table 16. Data for Plotting Cobalt XRF Calibration Curve

Standard Code	Co wt%	XRF Intensity		
		One-side	Other-side	Net
Std. 5	5.0	2765.73	3348.7	3057.22
Std. 10	10.0	6229.75	5666.11	5947.93
Std. 15	15.0	8028.88	8085.71	8057.30
Std. 20	20.0	10062.7	10111.4	10087.05
Std. 25	25.0	11960.3	12313.5	12136.9
Std. 30	30.0	13676.6	13686.1	13681.35
Std. 35	35.0	15596.9	14841.9	15219.4
Std. 40	40.0	16631.9	16859.9	16745.9

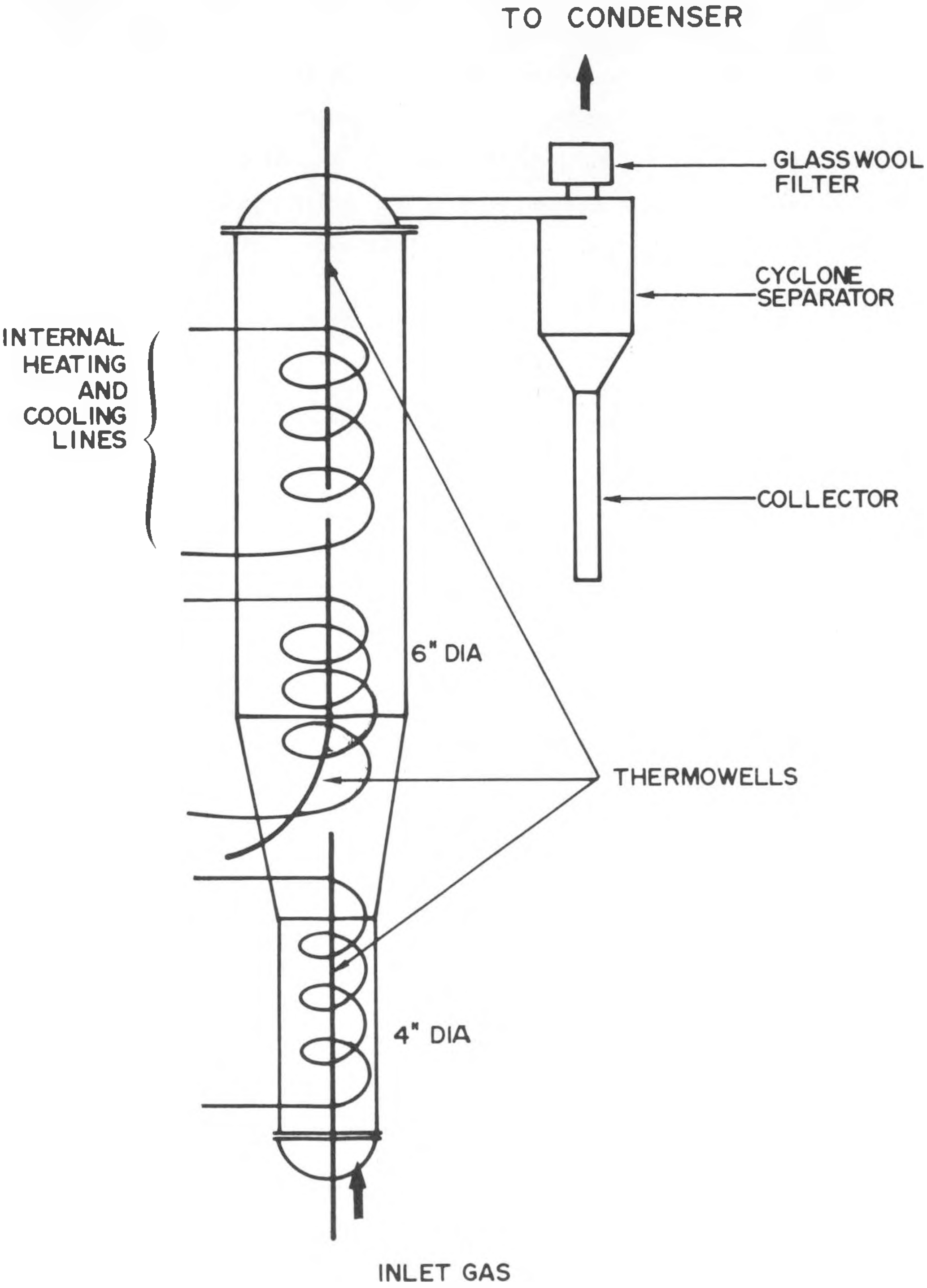


Figure 58. 6" Liquefaction Reactor Modifications

of cellulosic feedstocks. The ultimate goal would be a portable unit.

A schematic of the system is shown in Figure 6 and a photograph appears in Figure 7. Reactor details are shown in Figure 59. As shown, the first stage serves as the gasifier and the second stage as the liquefaction reactor. Separate reactors and an intermediate compressor have been eliminated. However both stages must operate at essentially the same pressure. To achieve this, a suitable liquefaction catalyst will have to be developed (see Liquefaction System Factor Studies section). During the current reporting period, installation of the system was completed and initial experimental work started utilizing the pyrolysis stage for gasification catalyst and alternative feedstock testing (see Gasification Catalyst Development section and Alternative Feedstocks section).

Alternative Feedstocks

Efforts were continued to identify characteristics of various cellulosic feedstocks that would correlate with gasification reaction system performance. The intent was to extrapolate this information to identify a broad range of attractive feedstock candidates for the conversion system. The project is partially sponsored via the Special Research Grants Program, Science and Education Administration, U. S. Department of Agriculture (Grant No. 59-2043-0-2-094-0). The project relates to the project described in this report in that the characterization data should help in identifying feed stocks of commercial importance.

The general approach for the project is diagrammed in Figure 60. A large data bank of gasification data exists. Feedstock characterization is escalated on an iterative basis dependent on regression analysis results.

A list of feedstocks, suppliers and current status of the study is indicated in Table 17. A listing of current data being analyzed appears in Table 18. The primary responses (dependent variables) of interest are total olefin composition and H_2/CO mole ratio. The factor candidates (independent variables) are the feedstock analysis data and reactor operating conditions. Some "blocking" of the data is necessary to eliminate extraneous factors from the analysis (e.g., sand vs. catalytic heat transfer media, etc.) An indication of various quadratic equation combinations and assessment are indicated in Table 19. Note that the combination of factors involving ash, heating value and polyphenol + oil + hydrocarbon gave the best fits for both olefin content and H_2/CO ratio (highest correlation coefficients). Equation coefficients for this combination of factors is given in Table 20.

Photographs of some of the feedstock analysis equipment are shown in Figures 32-34. The study will continue with an escalation in additional feedstock characterization data of interest. Further information on this project may be found elsewhere (19).

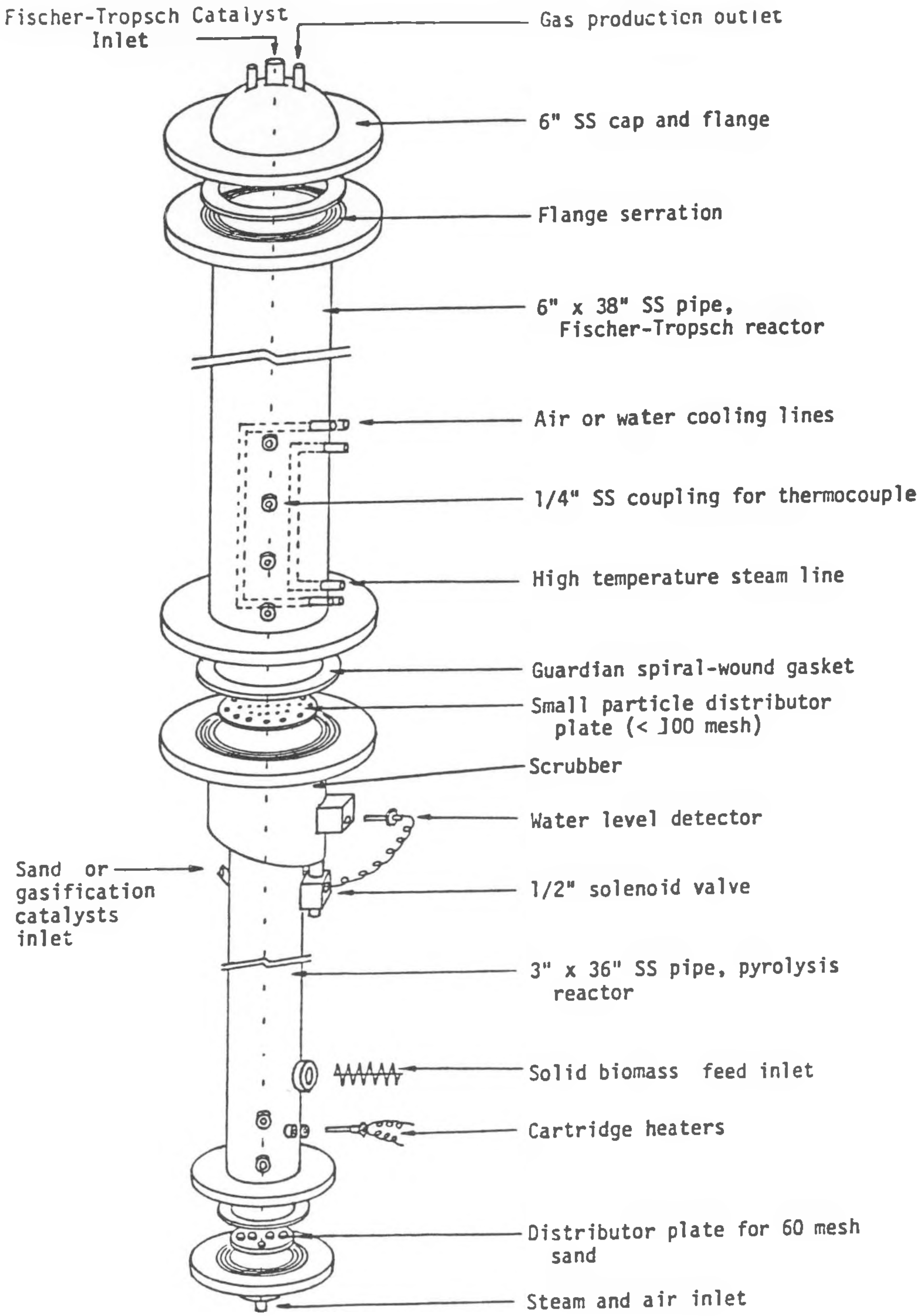


Figure 59. Staged Reactor Details

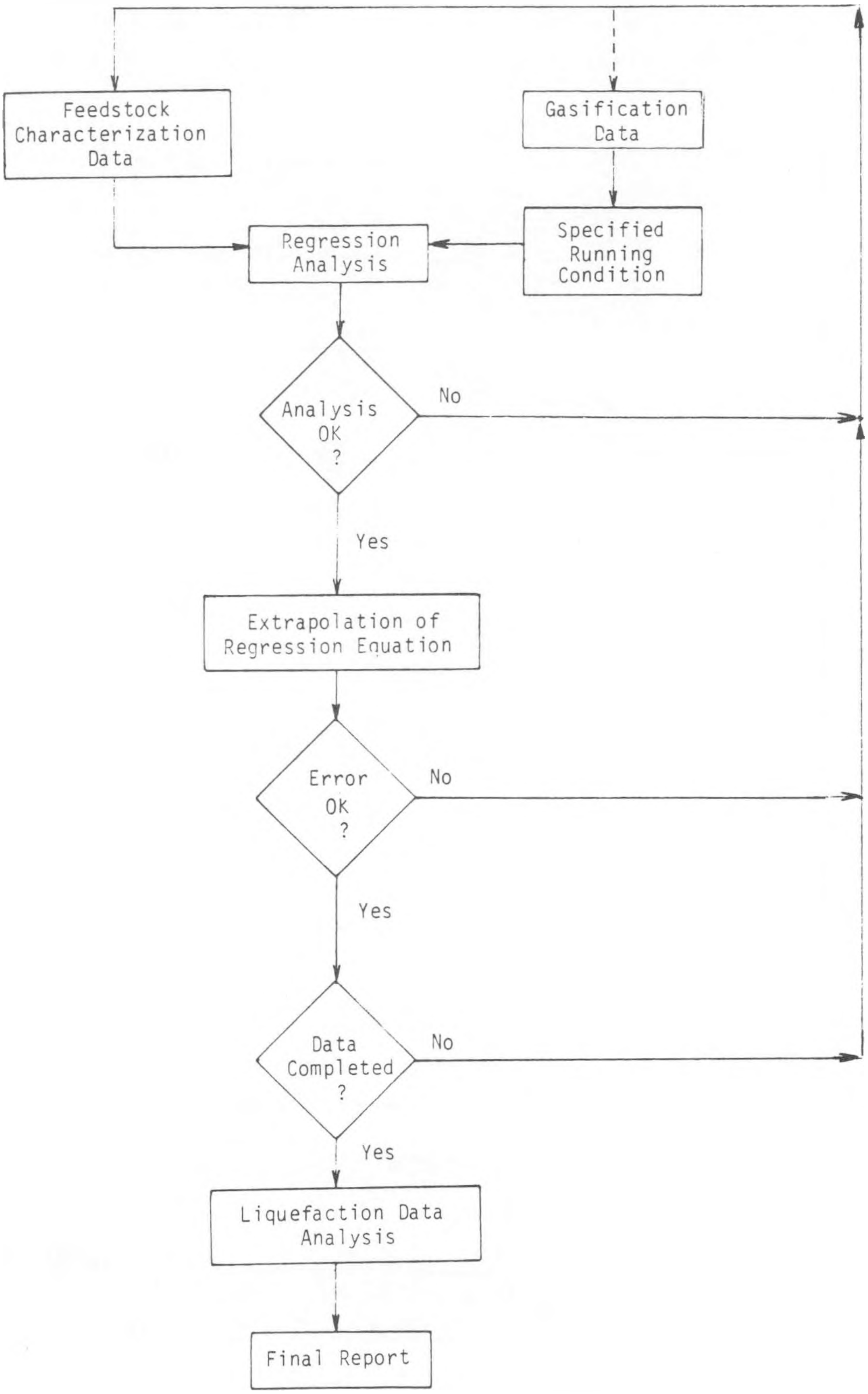


Figure 60. Alternative Feedstock Study Plan

Table 17. Feedstock Characterization Study Status Summary

Feedstock	Supplier	Characterization			Gasification
		H	A	E	
Industrial Wastes					
Sawdust	Phoenix Source	*	*	*	*
Paperchips	"	*	*	*	*
Fir bark	Weyerhaeuser Corporation	*	*	*	*
Hog Fuel	Weyerhaeuser Corporation	*	*	*	*
Cotton gin trash	Anderson Clayton		*		
Guayule bagasse	Cento de Investigation en Quimica Aplicada (CIQA)	*	*	*	*
Guayule cork	"	*	*	*	*
Candelilla bagasse	"	*	*	*	*
Guayule resins	"				
Jojoba meal	San Carlos Apache Reservation	*	*	*	*
Lignin	Westvaco		*		
Kelp residue	Kelco		*		
Almond hulls	Golden Byproducts	*	*	*	*
Almond shells	"	*	*	*	*
Almond prunings	"	*	*	*	*
Almond prunings (cured)	"	*	*	*	*
Sugarcane bagasse	Combustion Equipment Associates	*	*	*	*
Wheat straw	Billings, Montana source	*	*	*	*
Forest Residues					
Creosote bush	U.S. Forest Service	*	*	*	*
Sugar sumac	"		*	*	*
Arizona cypress	"	*	*	*	*
Pringle manzanita	"	*	*	*	*
Wright silktassel	"	*	*	*	*
Pointleaf manzanita	"	*	*	*	*
Shrub live oak	"	*	*	*	*
Hairy mountain mahogany	"	*	*	*	*
Utah juniper	"	*	*	*	*
Pinion pine	"	*	*	*	*
Greasewood	"		*	*	
Velvet mesquite	"	*	*	*	*
Urban Wastes					
Eco-Fuel II	Combustion Equipment Associates	*	*	*	*
Sewage sludge	Phoenix source		*		
Energy Crops					
Russian thistle	University of Arizona	*	*	*	*
Water hyacinth	"	*	*	*	*
Raw kelp	Kelco	*	*	*	*
Euphorbia lathyris	Diamond Shamrock Corporation	*	*	*	*
Silver maple	U.S. Dept. of Agriculture	*	*	*	*
Smooth sumac	"	*	*	*	*
Common milkweed	"		*	*	
Red tartarian honeysuckle	"	*	*	*	*
Common elder	"		*	*	
Giant ragweed	"	*	*	*	*
Field thistle	"		*	*	
Cherry eleagnus	"		*	*	
Pokeweed	"	*	*	*	*
Tall boneset	"	*	*	*	*
Rosin weed	"	*	*	*	*
Compass plant	"		*	*	
Tall goldenrod	"	*	*	*	*
Canada wildrye	"	*	*	*	
Sassafras	"	*	*	*	*
Coral berry	"	*	*	*	*
Wild bergamot	"	*	*	*	*
Smiling sumac	"	*	*	*	
Swamp milkweed	"		*	*	
Grass leaved goldenrod	"		*	*	
Sow thistle	"		*	*	
Tall bellflower	"		*	*	
Pale indian plantain	"		*	*	
Raw guayule	Centro de Investigation en Quimica Aplicada (CIQA)	*	*	*	*
Sweet sorghum	Spreckels Sugar		*		
Others					
Corn starch	Diamond Shamrock Corporation	*	*	*	*
Coal	Southern Utah Fuel Company		*		
Polyethylene	Phillips Petroleum	*	*	*	*
Polypropylene	"	*	*	*	*
Peat	Colony Farms	*	*	*	*
Portugese oak cork	Dependable Cork	*	*	*	*

Notes:
H = heating value analysis
A = ash analysis
E = extraction analysis

Table 18. Summary of Feedstock Analyses, Operating Conditions, and Gasification Results

No.	Feedstock	Feedstock Analysis[1]			Pyrolysis Reactor Performance								
		Heating Value (Btu/lb)	Ash (wt%)	Extraction Fractions[2] (wt%)	Operating Conditions[3]			Composition (mole%)[4] Summary					H_2/CO Ratio
					Fluidizing[5] Gas (lb/hr)	Temp. (°F)	Res. (sec)	H_2	CO	C_2H_4	Total Olefins	Paraffins	
	Industrial Wastes												
1	Sawdust	8579	7.0	0.53,3.17,0.71,0.58	23 RPG	1200	4.5	15.13	55.57	2.63	4.13	18.83	0.27
2	Paper chips	8664	0.6	0.10,0.38,0.26,0.08	25 RPG	1280	5.5	14.77	58.86	3.70	5.76	17.20	0.25
3	Fir bark	10076	5.1	1.23,17.2,4.98,0.18	22 RPG	1100	7.5	18.98	48.21	7.34	13.43	15.44	0.39
4	Fir bark				60S + 5 RPG	1250	3.2	29.24	44.41	7.30	11.61	11.24	0.65
5	Hog fuel	8991	6.2	2.06,6.14,1.35,0.22	30S + 5 RPG	1200	4.8	16.36	36.25	4.73	13.25	25.25	0.45
6	Guayule bagasse	7838	3.9	3.7,5.9,2.0,4.5	24 RPG	1450	4.2	25.33	37.00	7.75	13.60	19.46	0.68
7	Guayule bagasse				60S + 5 RPG	1170	2.5	29.93	33.15	2.71	13.70	14.85	0.90
8	Guayule cork	11376	2.1	6.2,6.6,6.0,2.3	19 RPG	1210	4.7	17.55	20.86	9.92	21.10	32.67	0.84
9	Guayule cork				19 RPG	1210	4.6	14.32	22.23	11.03	20.60	34.58	0.64
10	Guayule cork				22 RPG	1300	7.5	20.57	22.14	14.80	22.30	31.06	0.92
11	Guayule cork				95S + 5 RPG	1200	1.3	24.51	10.87	16.67	38.73	14.65	2.25
12	Candelilla bagasse	8570	10.7	4.54,7.88,2.48,0.56	45S + 5 RPG	1420	3.4	33.69	36.17	7.86	9.82	10.13	0.93
13	Jojoba meal	9809	2.5	25.3, 13.0,9.2,0.1	23 RPG	1320	4.4	11.96	37.56	9.15	13.39	26.69	0.32
14	Jojoba meal				45S + 5 RPG	1240	3.0	39.12	18.09	9.49	13.21	17.65	2.16
15	Almond hulls	7727	5.9	6.92,3.78,1.04,0.56	18 RPG	1250	6.9	29.08	35.44	4.01	6.27	16.29	0.79
16	Almond shells	8311	8.8	5.32,2.27,0.75,0.13	18 RPG	1280	4.6	26.03	38.06	3.09	4.76	19.01	0.68
17	Almond prunings	8235	2.8	2.17,7.26,0.59,0.27	23 RPG	1340	5.3	22.96	44.87	6.11	9.17	16.37	0.51
18	Almond prunings				45S + 5 RPG	1280	3.5	31.21	42.39	5.74	10.67	7.81	0.74
19	Almond prunings (cured)	8550	25.4	9.02,6.23,0.6,0.38	22 RPG	1520	3.7	39.15	33.75	4.41	5.49	15.60	1.16

Table 18. Summary of Feedstock Analyses, Operating Conditions, and Gasification Results (continued)

No.	Feedstock	Feedstock Analysis[1]			Pyrolysis Reactor Performance								
		Heating Value (Btu/lb)	Ash (wt%)	Extraction[2] Fractions (wt%)	Operating Conditions[3]			Composition (mole%)[4] Summary					H_2/CO Ratio
					Fluidizing[5] Gas (lb/hr)	Temp. (°F)	Res. (sec)	H_2	CO	C_2H_4	Total Olefins	Paraffins	
20	Sugarcane bagasse	9060	8.3	7.08,4.45,0.82,0.8	30S + 5 RPG	1400	4.8	28.60	36.74	7.29	10.38	15.31	0.78
21	Wheat straw	8726	8.2	,1.14,0.28,0.57	22 RPG	1600	4.7	30.19	48.27	2.57	2.57	14.7	0.63
	<u>Forest Residues</u>												
22	Creosote bush	8822	3.8	6.4,5.7,0.5,0.08	22 RPG	1380	4.5	25.99	39.43	6.48	10.24	16.61	0.65
23	Sugar sumac		5.3	3.7,16.3,2.8,nil	22 RPG	1200	4.1	28.89	31.88	5.75	10.42	18.25	0.90
24	Arizona cypress	7955	4.5	1.6,9.5,2.0,nil	22 RPG	1350	4.6	26.64	38.40	6.40	10.34	17.52	0.69
25	Pringle manzanita	8775	2.2	2.1,11.4,0.6,0.27	22 RPG	1400	4.6	24.99	40.68	6.29	11.11	16.42	0.61
26	Wright silktassel	9265	3.2	1.8,4.6,2.6,0.38	22 RPG	1320	4.7	25.64	38.69	7.30	11.89	18.32	0.66
27	Pointleaf manzanita	8444	1.7	2.0,10.4,0.9,0.33	22 RPG	1380	5.2	24.46	35.50	5.69	12.85	16.28	0.68
28	Shrub live oak	8524	3.1	4.6,7.4,1.0,0.09	22 RPG	1400	5.2	27.99	41.28	5.56	8.13	18.00	0.67
29	Hairy mountain mahogany	9076	4.2	6.0,4.75,2.16,0.21	22 RPG	1380	4.2	27.61	37.84	10.26	12.83	16.91	0.72
30	Utah juniper	8589	4.2	3.4,6.7,1.3,0.19	22 RPG	1300	4.5	28.83	39.54	6.56	7.33	17.86	0.73
31	Pinion pine	9060	3.3	2.6,5.0,3.0,0.26	22 RPG	1420	5.3	25.82	41.78	6.33	10.00	17.56	0.61
32	Velvet Mesquite	8507	4.4	6.5,4.8,0.96,0.08	21 RPG	1690	3.5	33.01	44.35	2.61	5.01	18.46	0.74
	<u>Urban Wastes</u>												
33	Eco-Fuel II (Cambridge)	9572	14.7	2.59,5.36,2.16,0.99	22 RPG	1250	4.2	20.85	48.51	5.16	8.20	19.35	0.42
34	Eco-Fuel II (Cambridge)				12S + 5 RPG	1180	4.8	23.62	45.24	7.90	13.47	13.83	0.52

Table 18. Summary of Feedstock Analyses, Operating Conditions, and Gasification Results (continued)

No.	Feedstock	Feedstock Analysis[1]			Pyrolysis Reactor Performance								
		Heating Value (Btu/lb)	Ash (wt%)	Extraction[2] Fractions (wt%)	Operating Conditions[3]			Composition (mole%)[4] Summary					H_2/CO Ratio
					Fluidizing[5] Gas (lb/hr)	Temp. (°F)	Res. (sec)	H_2	CO	C_2H_4	Total Olefins	Paraffins	
	Energy Crops												
35	Russian thistle	7936	15.4	9.2,3.1,0.8,0.2	20 RPG	1280	4.5	26.37	36.08	3.21	4.98	17.96	0.73
36	Water hyacinth	7740	35.9	7.8,6.1,1.0,0.4	19 RPG	1270	5.6	23.00	42.43	3.52	4.56	16.02	0.54
37	Raw kelp	6448	31.7	15.32,0.82,0.34,0.33	22 RPG	1500	3.7	42.44	27.36	1.43	1.43	8.88	1.55
38	Euphorbia lathyris	8725	3.1	3.0,2.9,1.4,0.2	31 RPG	1370	6.4	32.97	26.27	3.84	14.08	18.66	1.26
39	Euphorbia lathyris				45S + 5 RPG	1370	3.0	52.61	5.96	1.32	11.73	5.75	8.82
40	Silver maple	8838	4.7	16.3,19.8,2.4,0.39	30S + 5 RPG	1080	5.0	15.89	44.64	4.39	13.53	16.99	0.36
41	Smooth sumac	8817	7.7	7.1,20.2,5.9,0.21	30S + 5 RPG	1330	4.9	34.98	25.36	9.83	14.55	13.67	1.38
42	Red tartarian honeysuckle	8949	5.2	10.2,15.8,3.4,1.77	45S + 5 RPG	1400	3.4	44.08	28.41	8.47	9.86	8.33	1.55
43	Giant ragweed	8461	11.4	11.4,4.4,8.3,0.6	30S + 5 RPG	1420	4.1	37.14	28.49	7.79	9.95	13.29	1.30
44	Pokeweed	8396	11.5	15.5,5.9,3.4,0.17	30S + 5 RPG	1260	5.0	42.29	18.20	7.46	13.42	11.24	2.32
45	Tall boneset	8913	6.5	8.6,10.8,5.9,0.56	30S + 5 RPG	1140	4.7	20.32	35.15	8.22	15.29	19.44	0.58
46	Rosin weed	8264	9.4	6.2,7.0,2.8,0.79	30S + 5 RPG	940	5.2	9.91	52.32	1.07	4.98	21.32	0.19
47	Tall goldenrod	9304	7.5	9.8,5.7,2.8,0.92	35S + 5 RPG	1260	4.2	37.02	29.29	2.78	8.77	17.08	1.26
48	Sassafras	7431	3.1	8.9,14.4,5.7,0.23	45S + 5 RPG	1190	4.0	31.87	36.00	6.84	13.98	9.17	0.88
49	Coral berry	8676	4.8	5.9,11.1,2.3,0.81	30S + 5 RPG	1200	5.3	28.37	31.33	6.58	13.88	14.75	0.90
50	Wild bergamot	8674	7.2	7.22,6.9,2.4,1.24	30S + 5 RPG	1220	5.2	36.85	24.14	6.01	10.57	17.11	1.53
51	Raw guayule	10820	5.2	4.3,8.9,2.3,10.4	20 RPG	1310	4.6	17.28	34.98	5.54	10.61	28.58	0.49
52	Raw guayule				45S + 5 RPG	1230	3.0	42.69	14.26	7.39	11.14	17.81	2.99

Table 18. Summary of Feedstock Analyses, Operating Conditions, and Gasification Results (continued)

No.	Feedstock	Feedstock Analysis[1]			Pyrolysis Reactor Performance								
					Operating Conditions[3]			Composition (mole%)[4] Summary					
		Heating Value (Btu/lb)	Ash (wt%)	Extraction[2] Fractions (wt%)	Fluidizing[5] Gas (lb/hr)	Temp. (°F)	Res. (sec)	H_2	CO	C_2H_4	Total Olefins	Paraffins	H_2/CO Ratio
	Others												
53	Corn starch	7532	0.1	0.41,0.16,0.03,0.03	30S + 5 RPG	970	4.8	7.19	59.41	1.82	9.49	6.34	0.12
54	Polyethylene	19986	0.04	---,0.03,0.08,0.42	19 RPG	1240	4.5	14.19	0.96	19.29	33.28	50.36	14.78
55	Polypropylene	19563	0.03	---,0.14,nil,nil	19 RPG	1240	4.5	13.57	0.69	13.34	37.13	48.62	19.67
56	Peat	9805	7.6	8.53,2.0,1.65,0.60	9S + 5 RPG	1280	5.1	45.05	18.48	4.15	7.50	12.69	2.43
58	Portugese oak cork	12676	0.3	7.7,3.2,2.0,0.1	30S + 5 RPG	1160	4.9	14.18	33.07	11.74	26.80	22.18	0.43

[1] moisture free basis

[2] ash free basis; listed in following order: protein, polyphenol, oil, hydrocarbon fractions

[3] fluidizing media either dolomite (No. 14,38,39,52) or sand (rest); operating pressure 0.7-1.4 psig

[4] water, N_2 free basis; balance of analysis = CO_2

[5] S = steam, RPG = recycled pyrolysis gas

Table 19. Factor Combinations and Correlation Coefficients

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_1^2 + A_5X_2^2 + A_6X_3^2 + A_7X_1X_2 + A_8X_1X_3 + A_9X_2X_3$$

Independent Variables, X			Responses, Y	
X_1	X_2	X_3	Olefin Content	H_2/CO
A	HV	P	0.8607	0.9622
A	HV	O	0.9085	0.9533
A	HV	POH	0.9891	0.9843
A	HV	T	0.9529	0.9053
A	P	O	0.8782	0.9578
A	P	POH	0.8957	0.9780
A	P	T	0.8396	0.9392
A	O	POH	0.8574	0.9708
A	O	T	0.9208	0.9762
A	POH	T	0.8583	0.9692
HV	P	O	0.8629	0.9327
HV	P	POH	0.9528	0.9423
HV	P	T	0.9115	0.9071
HV	O	POH	0.9333	0.9434
HV	O	T	0.7892	0.9272
HV	POH	T	0.9256	0.9454
P	O	POH	0.9325	0.5816
P	O	T	0.9032	0.6736
P	POH	T	0.8738	0.5811
O	POH	T	0.9315	0.6984

Note: A = Ash; HV = Heating Value; P = Polyphenol; O = Oil; POH = Polyphenol + Oil + Hydrocarbon; T = Temperatures, °F.

The date from Table 18 used for analysis for the recycles pyrolysis gas fluidized runs were as follows: 3, 6, 8, 13, 17, 21, 22, 24, 25, 28, 30, 31, 32, 33, 37, 51.

Table 20. Quadratic Equation Coefficients (Factors: Ash, Heating Value and POH)

Responses	Olefin Content	H_2/CO Ratio
Coefficients		
A_0	1.600×10^{2}	-2.434
A_1	-4.861	5.490×10^{-1}
A_2	-4.387×10^{-2}	4.859×10^{-4}
A_3	9.167	-5.805×10^{-2}
A_4	1.141×10^{-1}	-5.692×10^{-3}
A_5	3.334×10^{-6}	-2.681×10^{-8}
A_6	1.110×10^{-1}	-4.667×10^{-3}
A_7	7.745×10^{-5}	-4.759×10^{-5}
A_8	1.791×10^{-1}	-1.555×10^{-3}
A_9	-1.358×10^{-3}	1.874×10^{-5}

Alternative Products

The basic indirect liquefaction system should be appropriate for producing a variety of products other than liquid hydrocarbon fuels. Thus any product that can be produced from a synthesis gas typical of that obtained from a cellulosic feedstock is a candidate. The incentive for producing alternative products would be location (market) dependent. A study was started in the current reporting period in this regard. Product candidates were constrained to liquids that were worth more than No. 2 diesel fuel and had a current U. S. production of at least 1000 tons/day. The general project steps are as follows:

(1) Literature survey to identify appropriate products based on value and composition. It is anticipated that the list will be limited to compounds containing hydrogen, carbon and oxygen only.

(2) Thermodynamics calculation to establish the feasibility of producing the selected products from realistic synthesis gas compositions.

(3) Kinetic assessment and catalyst - operating conditions selection to produce the desired products subject to selectivity and yield constraints.

(4) Experimental testing of selected systems, on a microreactor system.

(5) Scaleup to larger conversion systems available in the laboratory as appropriate.

An example list of chemicals satisfying the price, market and elements constraints is given in Table 21. Example high priced specialty chemicals with low markets are listed in Table 22. Thermodynamic calculations were performed to establish the feasibility of producing the products. A feed gas containing 15 mole% C_2H_4, 28 mole% CO and 28 mole % H_2 was assumed and reaction paths established. Standard Gibbs free energy values and corresponding reaction equilibrium constraints were calculated. Equilibrium conversions (moles product/mole reactants x 100) ranged from 0.05 to 0.14 at 25°C and 1 atm for the chemicals listed in Table 21. No calculations were performed at this point to maximize the equilibrium conversion as a function of temperature and pressure. It was decided to concentrate on production of aromatics for the initial catalyst screening work. This effort was in progress at the end of the reporting period.

The microreactor conversion system utilizied for this work is shown in Figure 8 and 10. Initial "base point" runs were performed with a cobalt/alumina catalyst and reactor conditions previously tested on a larger scale in other laboratory equipment (see Liquefaction System Factor Studies section). Product yields and compositions were essentially the same as that for the larger equipment thus indicating that the microreactor system should be an effective tool for predicting performance at the larger scales.

The study falls into the exploratory category with a broad range of catalyst candidates and operating conditions to be screened. Promising studies will be confirmed on the larger scales (2", 6" fluidized beds, slurry phase system) as appropriate.

Table 21. Product Candidates Satisfying Constraints (20-25)

Chemical and Fuels	U. S. Production (million lb/yr)		Price $/lb	
No. 2 Diesel	292000		.14	
Kerosene	9010		.17	
Gasoline	674000		.19	
n-Butyl Alcohol	767	767	.21	.36
Ethyl Alcohol	1409	1220	.19	.19
Isopropyl Alcohol	1901	1790	.17	.19
Acetic Acid	3270	2820	.16	.26
Butyraldehyde	951		.18	.35
Methyl Methacrylate	930		.41	.58
Vinyl Acetate	1980	1920	.22	.38
Ethylene Glycol	4730	4240	.22	.33
Ethylene Oxide	5670	4950	.27	.45
Propylene Oxide	2250	1770	.25	.41
Benzene	12290	10980	.21	
Toluene	11860	11270	.23	
Styrene	7480	6900	.38	
P-xylene	4650	3830	.31	
Phenol	2980	2460	.36	
Ethylbenzene	8450	7610	.30	
Acetone	2650	2120	.29	
Cyclohexane	2430	1970	.29	
Cumene	3920	3160	.28	
Acetic Anhydride	1510	1470	.41	
Adipic Acid	1800	1200	.57	
Butadiene	3580	2890	.42	

Table 22. Specialty Chemicals (low production) (20)

Chemical	U. S. Production (million lb/yr)	Price $/lb
Benzyl Alcohol	.0076	1.37
Benzophenone	.0017	3.3
Benzyl Acetate	.0023	1.67
Benzyl Benzoate	.0008	1.67
Benzyl Propionate	.018	1.75
Cinnamyl Acetate	.020	5.65
Isobutyl Phenylacetate	.029	2.42
2-Methoxy-4-Propenylphenol	.034	6.20
Methyl Phenylacetate	.034	3.23
Methyl Acetate	.018	8.00
3-Phenyl-1-Propane	.046	4.55
Phenethyl Isobutyrate	.009	4.75
2-Phenethyl Phenylacetate	.021	4.61
B-Carylphyllene	.215	1.88
Cedryl Acetate	.479	4.37
Allyl Heptanoate	.004	6.22
Citronellyl Formate	.028	6.13
4-Allyl-2-Methoxyphenol Acetate	.004	6.48
4-Allyl-2-Methoxyphenol	.441	4.3

Integrated System

No integrated runs were performed on the large scale integrated system (Figures 1, 2) during the current reporting period in favor of concentrating resources on liquefaction catalyst development. However a number of modifications were designed, fabricated and/or installed. In addition to those described previously (see Gasification Reaction System Improvements and Large Scale Fluidzied Bed Fischer-Tropsch Reactor Improvements sections), scrubber, cyclone separator, piping, insulation, etc. improvements were implemented. Also an entirely new control room was constructed (Figure 16) and all control gear and on-line chromatographs remounted and reconnected to the process units.

Some effort was expended on material and energy balance calculations, gasification system regenerator analysis, environmental assessment and process control

1. Material and Energy Balances. Balances based on a liquid hydrocarbon product yield of 40 gals per ton of cellulosic feedstock (dry, ash free) are given in Table 23 corresponding to the flow schematic illustrated in Figure 61. This yield would be considered realistic at the present time with higher values subject to progress in the gasification and liquefaction system factor studies. Thermal efficiencies (energy value of product/(energy value of feedstock + energy added to the system)) would be relatively low at this yield level (~ 30%).

2. Gasification System Regeneration Analysis. This laboratory scale gasification system regenerator is fueled with bottled propane and oxygen plus char that is transferred in the solids circulation loops. On a commercial basis, the fuel would be air + char (transfer loops + cyclones), scrubber tars, recycle gas (pyrolysis, liquefaction reactor) and/or direct cellulosic feedstock. A lock hopper type configuration was designed to return char collected in the pyrolysis reactor cyclone to the regenerator. This will be implemented in the new contract period. Also piping will be installed to allow for liquefaction system off gas to be returned to the regenerator, although this requires some priority logic with regard to distribution (see Process Control section). Air will replace oxygen as soon as convenient. Most equipment is available for feeding cellulosic feedstock to the regenerator if this proves to be desirable. No major effort has been placed on implementing a scrubber water recycle system. The approach has been to minimize tar production in the pyrolysis reactor (via operating conditions, use of catalysts, etc.).

3. Environmental Assessment. The non-product streams exiting the system (Figure 61) are regenerator and pyrolyzer scrubber effluent, regenerator off gas, ash from the regenerator cyclone and alcohol-water from the liquid product trap. For long term continuous operation, a periodic ash removal system probably would have to be added to the gasification system transfer loops. Ideally, any combustible materials in the water streams would be separated and burned in the regenerator with corresponding recycle of the water. The

Table 23. Material and Energy Balance

Stream Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Temperature, °F	70	1000	70	70	1180	800	700	70	95	100	100	80	80	80	[illegible]	70	500	70
Pressure, psia	19.7	95	64.7	64.7	15.1	15.0	15.0	14.7	14.7	14.7	64.7	264.7	162	162	162	55	154	154
Flow Rate, lb/hr	12.2	44	1.5	1.5	58.7	57.9	0.8	1080	1123.6	14.3	14.3	14.3	14.3	17.1	31.4	290	31.4	31.4
Heat Content, Btu/hr	115724	67294	19140	19140	269369	251855	9000			188913	188913	188913	188913	220411	103124		399305	397739
Component:																		
H_2	0.04		0.02	0.02	0.47	0.47				0.47	0.47	0.47	0.47	0.29	0.76		0.48	0.48
N_2																		
O_2																		
CO	0.55		0.38	0.38	4.44	4.44				4.44	4.44	4.44	4.44	4.31	8.76		7.28	7.28
CO_2	0.55		0.37	0.37	2.33	2.33				2.33	2.33	2.33	2.33	4.75	6.52		7.18	7.18
CH_4	0.36		0.24	0.24	1.59	1.59				1.59	1.59	1.59	1.59	2.76	1.[illegible]		4.66	4.66
C_2H_2																		
C_2H_4	0.05		0.04	0.04	1.48	1.48				1.48	1.48	1.48	1.48	0.42	1.90		0.72	0.72
C_2H_6	0.23		0.16	0.16	0.38	0.38				0.38	0.38	0.38	0.38	1.82	[illegible]		3.08	3.08
C_3H_6	0.04		0.03	0.03	0.42	0.42				0.42	0.42	0.42	0.42	0.33	0.75		0.55	0.55
C_3H_8	0.07		0.05	0.05	0.01	0.01				0.01	0.01	0.01	0.01	0.58	0.59		0.98	0.98
C_4H_8	0.01		0.00	0.00	0.18	0.18				0.18	0.18	0.18	0.18	0.05	0.23		0.09	0.09
C_4H_{10}	0.10		0.07	0.07	0.02	0.02				0.02	0.02	0.02	0.02	0.76	0.78		1.29	1.29
C_5 and above	0.20		0.14	0.14	2.38	2.38				2.38	2.38	2.38	2.38	1.53	3.91		2.59	2.59
C_2H_5OH																	0.01	0.01
1-Propanol																	0.06	0.06
2-Propanol																	0.00	0.00
H_2O		44			44	44		1080	1123.4	0.60	0.60	0.60	0.60		0.60	290	1.23	1.23
C_5-C_{19} N-Alkanes																	0.85	0.85
C_5-C_{19} Branched Alkanes																	0.24	0.24
C_5-C_{10} Alkenes																	0.04	0.04
Cycloparaffins																	0.01	0.01
Aromatics																	0.01	0.01
Biomass	10																	
Condensibles																		
Char					1.0		1.0											
Ash																		
Sand																		
Unknowns																	0.05	0.05

Table 23. Material and Energy Balance (continued)

Stream Number	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Temperature, °F	70	70	70	70	70	70	70	70	70	1200	800	900	70	95	100	1200	1540
Pressure, psia	14.7	64.7	64.7	64.7	19.7	64.7	64.7	64.7	64.7	15.1	15.0	15.0	14.7	14.7	14.7	15.1	15.1
Flow Rate, lb/hr	2.5	28.9	11.8	17.1	2.2	6.6	3	3	52.63	65.73	0.5	65.23	600	604.11	61.12	303.5	301.5
Heat Content, Btu/hr	25511	372228	151818	220411	28474	85068											19140
Component:																	
H_2		0.48	0.19	0.29	0.04	0.11											0.02
N_2							2.3	2.3	40.37	44.97		44.97			44.97	2.3	
O_2							0.7	0.7	12.26							0.7	
CO		7.28	2.97	4.31	0.55	1.66											0.38
CO_2		7.18	2.91	4.25	0.55	1.64				13.63		13.63			13.63		0.37
CH_4		4.66	1.90	2.76	0.36	1.07											0.24
C_2H_2																	
C_2H_4		0.72	0.30	0.42	0.05	0.16											0.04
C_2H_6		3.08	1.26	1.82	0.23	0.70											0.16
C_3H_6		0.55	0.22	0.33	0.04	0.13											0.03
C_3H_8		0.98	0.40	0.58	0.07	0.22											0.05
C_4H_8		0.09	0.04	0.05	0.01	0.02											0.00
C_4H_{10}		1.29	0.53	0.76	0.10	0.30											0.07
C_5 and above		2.59	1.06	1.53	0.20	0.59											0.14
C_2H_5OH	0.01																
1-Propanol	0.06																
2-Propanol	0.00																
H_2O	1.23									6.63		6.63	600	604.11	2.52		
C_5-C_{19} N-Alkanes	0.85																
C_5-C_{19} Branched Alkanes	0.24																
C_5-C_{10} Alkenes	0.04																
Cycloparaffins	0.01																
Aromatics	0.01																
Biomass																	
Condensibles																	
Char																	
Ash										0.5	0.5					0.5	
Sand																300	300
Unknowns	0.05																

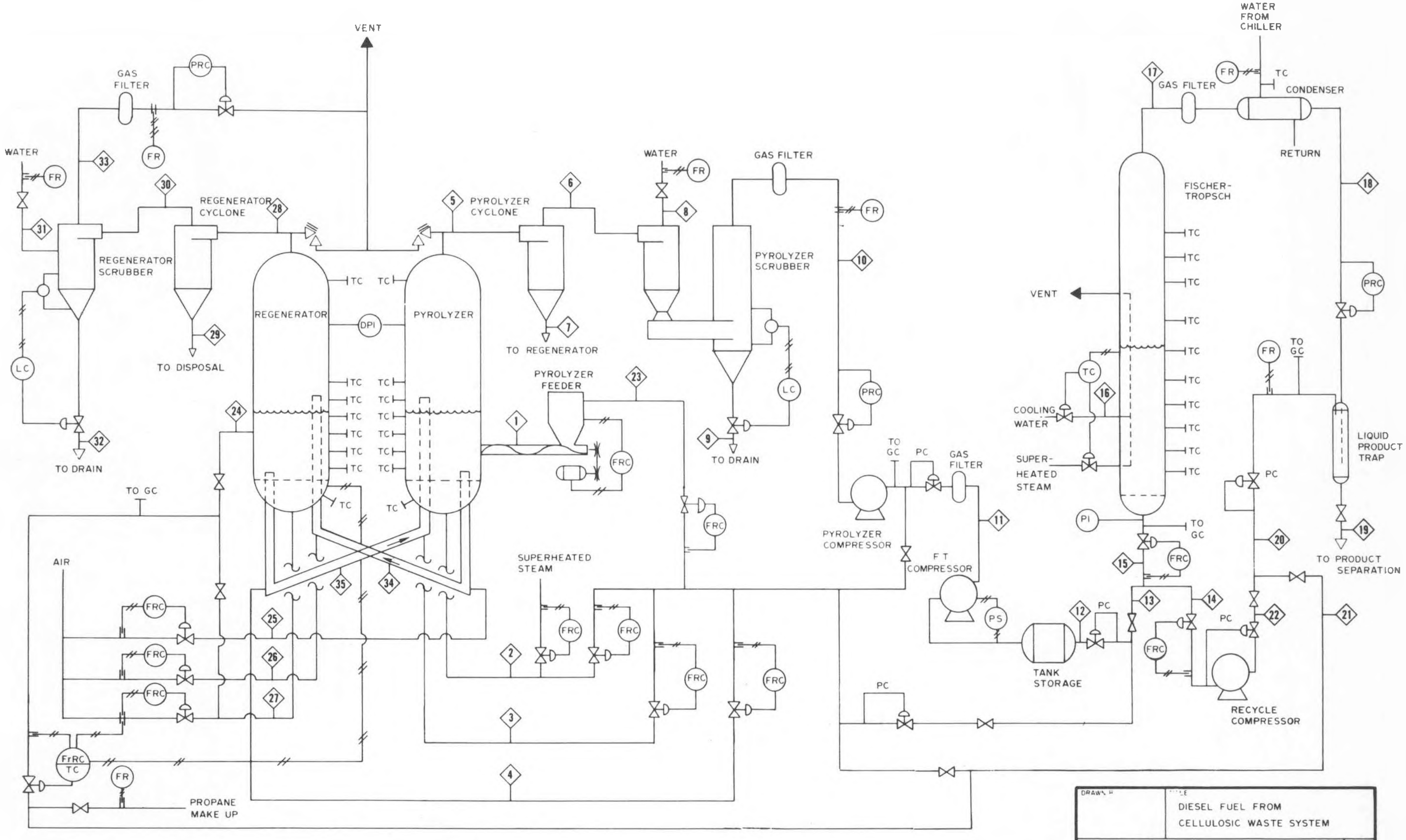


Figure 61. Material and Energy Balance Schematic

practicality of this would be dependent on the amount of combustible material available and the cost of the separation system. The major consideration would be levels of flammable and/or toxic material exiting the process to a sewage treatment plant. Air quality (regenerator off gas) should not be a problem with the nature of the fuels used in this system. Ash handling (as well as any size reduction steps) would involve achieving acceptable particulate levels.

No specific standards have been established for this type of processing. Projected standards appear in Table 24.

4. Process Control. The major process control complexities are (1) the operation of fluidized beds in series consistent with gas velocity constraints to achieve effective fluidization, and (2) optimal recycle distribution of the liquefaction reactor off gas stream.

The general process control problem is to produce the desired amount of diesel fuel type product for a selected feedstock. The major process control variables and responses for the conversion system are specified in Table 25, and a simplified schematic reference for the location of these decision variables in the process is given in Figure 62. Table 25 designates the relationship and interactions of the various process variables. For example, a change in the combustor temperature (C_T), perhaps resulting from an upset in the recycle off gas composition (LO_C), would affect the operating temperature of the pyrolysis reactor (P_T). This temperature alteration would provoke a shift in pyrolyzer gas composition (PG_C), consequently causing a change in the inlet gas composition (LI_C) to the liquefaction reactor. The product yield (P_F) of fuel (diesel, jet) and the off gas composition (LO_C) will vary due to a change in the inlet gas composition (LI_C). Note that a full cycle could occur, but probably the response time of the individual processes within the conversion system would allow for control corrections and stable operation.

Other control complexities are observable from the relationship as listed in Table 25. The liquefaction reactor off gas stream (high Btu gas) is employed in fueling the conversion system via combustion in the regenerator. The amount of off gas available for combustion is directly related to the feedstock flow rate. The feed flow rate (C_F) set point must be manipulated as required to hold the desired combustion temperature (C_T). The situation is further complicated by additional options for using the liquefaction reactor off gas. Thus this gas can either be recycled to the pyrolysis unit (i.e., cracking paraffins to olefins) and/or recycled to the liquefaction reactor inlet (i.e., further conversion of unused reactants). The control aspects of this off gas stream distribution would be a candidate for management under supervisory computer control since priority allocations are required. Start up, shutdown, and emergency default control schemes present additional control problems beyond the scope of this report.

Catalyst life is an important consideration in any catalytic process. The catalyst life is limited by catalyst coking which is partly a function of the inlet gas composition. Control constraints on an acceptable

Table 24. Projected Emissions Standards (26)

Emissions	Unit	Limit
Air:		
Sulfur	Pounds of SO_2 in combustion products per 10^6 Btu/HHV of biomass feed to pyrolyzer	0.20
	H_2S content of boiler fuel gas grains per dry standard cubic foot	0.10
Nitrogen	Pounds of equivalent NO_2 in combustion products per 10^6 Btu/HHV of biomass feed to pyrolyzer	0.30
Particulates	Pounds of total suspended particulates in combustion products per 10^6 Btu/HHV of biomass feed to gasifier	0.30
Water:		
BOD	mg/l in treated water	50
COD	mg/l in treated water	300
Oil and grease	mg/l in treated water	20
Phenolics	mg/l in treated water	1
Ammonia	mg/l in treated water	10
Acidity	pH range of treated water	6-9
Metals	mg/l in treated water	
	Silver	0.5
	Arsenic	0.5
	Barium	10.5
	Cadmium	0.1
	Chromium	0.5
	Lead	0.5
	Selenium	0.1
Chlorine	mg/l in treated water	250

Table 25. Control Variables and Responses

Response	Control Variables
Product flow rate (P_F)	Liquefaction reactor inlet composition (LI_c), temperature (L_T), pressure (L_P), inlet flow rate (LI_F), catalyst coking rate (CC_R).
Liquefaction reactor inlet composition (LI_c)	Pyrolysis gas composition (PG_c); liquefaction reactor off gas composition (LO_c), recycle flow rate (R_{3F}).
Liquefaction reactor inlet gas flow rate (LI_F)	Pyrolysis gas flow rate (PG_F), liquefaction reactor off gas recycle flow rate (R_{2F}).
Pyrolysis reactor gas composition (PG_c)	Pyrolysis reactor temperature (P_T), liquefaction reactor off gas recycle flow rate (R_{2F}) and composition (LO_c), steam flow rate (S_F).
Liquefaction reactor off gas composition (LO_c)	Liquefaction reactor inlet gas composition (LI_c), reactor temperature (L_T).
Pyrolysis reactor temperature (P_T)	Regenerator temperature (C_T), solids circulation rate (SCR).
Regenerator temperature (C_T)	Liquefaction reactor off gas recycle flow rate (R_{1F}) and composition (LO_c), air flow rate (A_F), solids circulation rate (SCR).
Solids circulation rate (SCR)	Sparge gas flows (SR)
Pyrolysis gas flow rate (PG_F)	Feedstock flow rate (F_F), liquefaction reactor off gas recycle flow rate (R_{2F}).

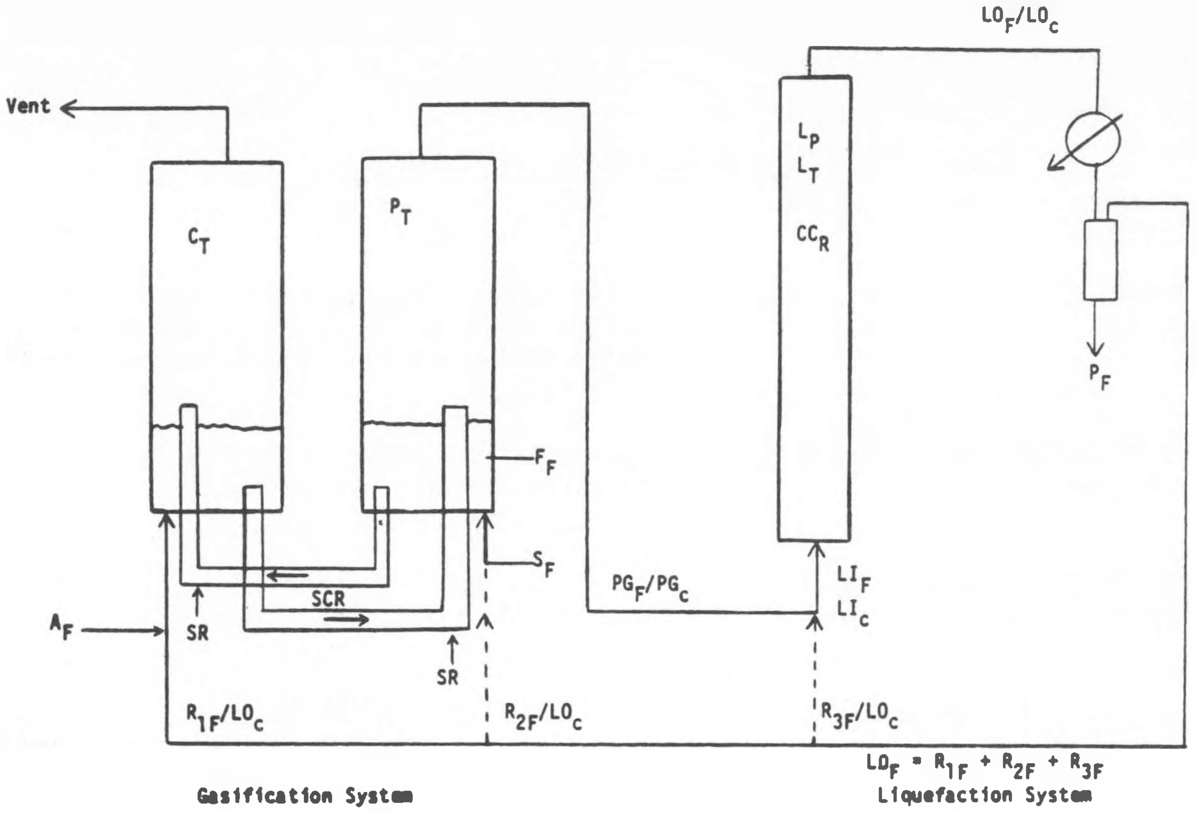


Figure 62. Control Variables and Responses

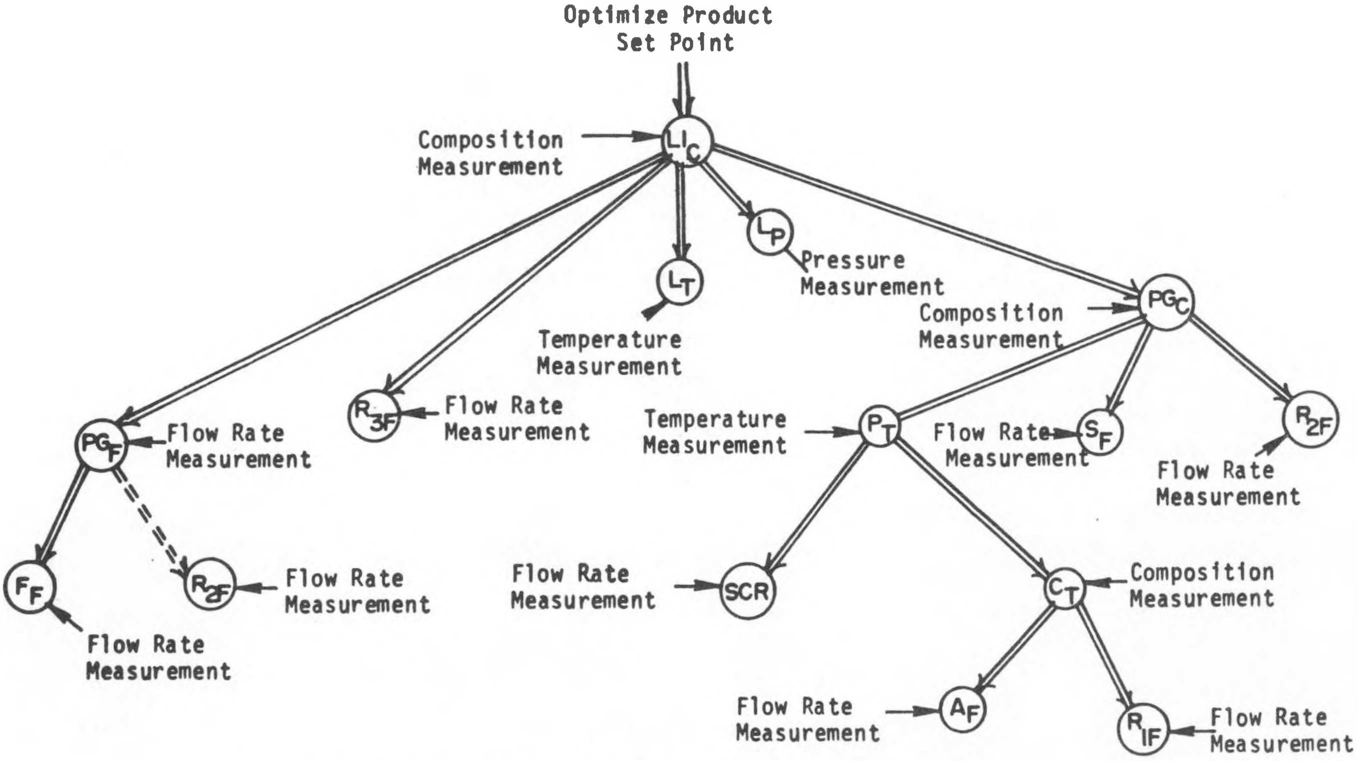


Figure 63. Example Control Algorithm Organization

inlet gas composition (LI_C) range are crucial to reduce the coking rate. As the catalyst activity depreciates, the process control scheme should respond accordingly and to the limit of shutdown for regeneration if necessary. Other operating constraints must be honored by the control scheme. Fluidization, reactor temperatures, and pressures must be controlled in a finite range to insure stable operation.

Present process control gear on the experimental unit consists of dedicated analog controllers, in which standard (4-20 mA) transmitters, and transducers are employed. The control scheme has been an evolving effort contingent upon process experience, and the usefulness of a distributed supervisory control scheme has now become apparent. The problem is how to organize the interrelated process control variables described in Table 25 into a workable algorithm. Figure 63 illustrates one plausible control loop organization. The overall control algorithm would be seeking a maximized product yield under the operating constraints of the system. The primary controlled element would be the liquefaction inlet gas composition, which is measured by a gas chromatograph (i.e., slow response times). For control purposes, product yields are now assumed to be solely a function of inlet gas composition. An optimum liquefaction reactor temperature and pressure is also assumed to exist for a given composition. The inlet liqeufaction gas composition can be manipulated by changing the pyrolysis gas flow rate, composition, and/or by selection of how the liquefaction reactor off gas recycle stream is split. Pyrolysis gas composition can be altered by the pyrolysis reactor temperature (P_T), the steam flow (S_F) and/or the recycle flow (R_{2F}). Pyrolysis temperature can be varied by either a change in the solids transfer circulation rate (SCR), or by manipulating the regenerator temperatures. Both are interrelated and require logic decision procedures.

Present control systems utilized on the process are diagrammed in Figure 1 and pictured in Figures 2-4, 16 and 39. The long term goal is to simplify the control hardware and logic commensurate with the relatively small projected scale of cellulosic waste conversion facilities. The laboratory is well equipped to monitor and characterize the process and establish the control sensitivity of the system.

Mathematical Modelling

A continuing effort is in progress on the project to predict the performance of the gasification and liquefaction systems via theoretical mathematical modelling. For both systems, the major complexities in implementing this task are as follows: (1) obtainment/development of reliable reaction rate equations, and (2) estimation of reliable transport coefficients for realistic fluidized bed mass and energy balances. The rate equations are being developed using a grouped species reaction network ("lumped kinetics") with kinetic constants evaluated on a microreactor scale. The transport constants are initially estimated from the literature and then upgraded via regression techniques utilizing fluidized bed experimental data. At the end of the current reporting period, the predictive model work was in an early stage of development and thus details and results will be delayed for a later report.

CONTINUING RESEARCH

The Work Statement for the laboratory research for the renewal period from June 1, 1982 to May 31, 1984 consists of the following tasks: (1) catalyst improvement, (2) alternative feedstocks, (3) process simplification, (4) product development, (5) environmental assessment, (6) factor studies, and (7) reports. A description follows:

(1) Catalyst Improvement

Catalyst activity/regeneration profiles shall be assessed for alternative cobalt formulations on a small scale. In addition, non-cobalt liquefaction catalysts shall be developed and tested from the screening stage using synthetic gas mixtures to integrated runs utilizing real synthesis gas. This is continuation of a program currently in progress. The objective is to achieve desired product quality and yields with an inexpensive catalyst. If the catalyst price for acceptable performance is high, the regeneration characteristics will have to be determined. Also, potential catalyst usage in the gasification step shall be evaluated. Anticipated benefits include tailoring of synthesis gas composition and maximization of gas phase yields with minimal tar/organic liquids formation.

(2) Alternative Feedstocks

Over forty feedstocks have been tested through gasification in the conversion system to date. For the most part, these have been "survey" runs, i.e., performed at a single fixed set of operating conditions deemed desirable at the time. With improvements in system performance, an update on some of these feedstocks shall be performed. It should be emphasized that the processing scheme is not necessarily restricted to cellulosic materials, i.e., waste polymers, rubber, peat, etc. are also feedstock candidates. Finally, promising feedstocks (particularly those of commercial importance) shall be evaluated in an integrated run mode to a liquid product. A complementary auxiliary program in this task area is the characterization of the compounds in the feedstocks via extraction studies for the purpose of relating and extrapolating feedstock characteristics to processing performance.

(3) Process Simplification

The current system configuration limits the applications to a minimum capacity of about 300 tons/day of feedstock at a delivered feedstock cost of $20-30/ton. The ultimate goal is to produce a high quality product, marketable in the local area at as small a scale as possible (preferably a portable unit). This does not exist at the present time. To achieve this goal, the process shall be simplified through catalyst improvements and optimization of process performance to reduce construction, operation and maintenance cost and improve yields.

(4) Product Development

The current potential products are a 500 Btu/SCF gas, paraffinic fuels (diesel, kerosene, jet), high octane gasoline and normal propanol. Other possibilities exist such as olefins, specialty chemicals, etc. The basic processing scheme appears sound for tailoring to different products. The process shall be varied to optimize yields of various commercially viable products. Sufficient data shall be generated to determine yields, economics and design. Thus if a high molecular weight alcohol were desired, the major modification would probably be the choice of a liquefaction catalyst.

(5) Environmental Assessment

Environmental assessment and control are a complementary part of any process development project. However, on a research scale, one is primarily concerned with achieving viable yields and product quality first. Potential emissions and control modifications required for an engineering test facility shall be assessed initially at the research scale.

(6) Factor Studies

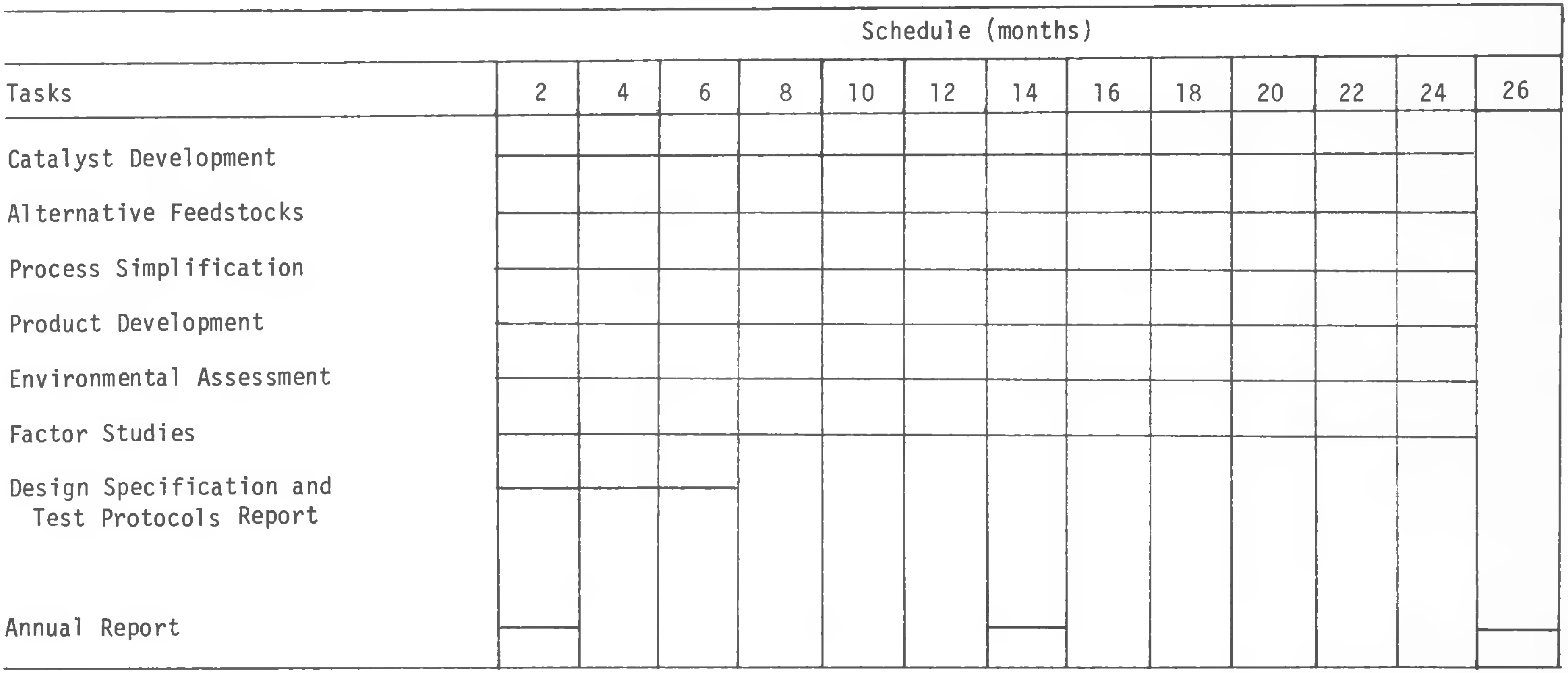
Factor studies area continuing phase of any chemical process development project. Thus any alternative feedstock, catalyst, product or process change will require adjustment of process conditions to optimize process performance. The normal factor candidates are reactor temperature, pressure, residence time, and reactant composition and geometry.

(7) Reports

1. Design Specifications and Test Protocols - flow sheets, equipment list, material/energy balances, experimental plan, operating/safety procedures and site specifications for a larger scale Engineering Test Facility.
2. Technical Progress Report (bimonthly).
3. Contract Management Summary Report (quarterly).
4. Interim/Final Technical Report (yearly).
5. System Input Data Form (yearly).

Figure 64 is the projected schedule for the new contract period.

Figure 64. Conversion of Cellulosic Waste to Liquid Hydrocarbon Fuel Task Schedule



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APPENDIX

WORK STATEMENT

Project:	Conversion of Industrial Wastes to Liquid Hydrocarbon Fuels and Chemical Feedstocks
Contract No.:	DE-AC02-76CS40202
Period:	June 1, 1981 to May 31, 1982
Contractor:	Arizona State University
Principal Investigator:	James L. Kuester

The following tasks are proposed for the renewal period: (1) staged reaction system development, (2) alternative feedstock development, (3) alternative products development, (4) gasification system regenerator analysis, and (5) factor studies.

Staged Reaction System. The objective is to develop a 2 stage reaction system within a single vessel where the first stage serves as the gasifier and the second stage is the liquefaction reactor. A prototype system is presently being developed with "seed" funds from the Arizona Solar Energy Commission. The virtues are considerable process simplification with elimination of separate reactors via a compressor. The major obstacle is development of suitable catalysts whereas both stages can be operated at the same pressure. Success with this task will result in a significant reduction in economically viable commercial plant capacity.

Alternative Feedstocks. A number of feedstocks have been investigated thru the gasification step. A few have been processed thru the gasification-liquefaction system. The list includes cellulosic materials, synthetic polymers, preprocessed municipal refuse and peat. Many requests are received from industry, government laboratories and other university projects. It is anticipated that this role will be continued with increased emphasis on utilizing the "total" waste materials from an industrial process (say leaves, bagasse, resins for a plant extraction process). Thus liquid feed capabilities will be added to the system for waste oils and resin type materials. Compound analysis of feedstocks is anticipated in this task area.

Alternative Products. The product emphasis to date has been centered on paraffinic liquid fuel (e.g., diesel) and high octane gasoline. Other products are possible with the same basic equipment, e.g., olefins, oxygenated hydrocarbons. Again, the major development effort will be on alternative catalysts to optimize for desired products.

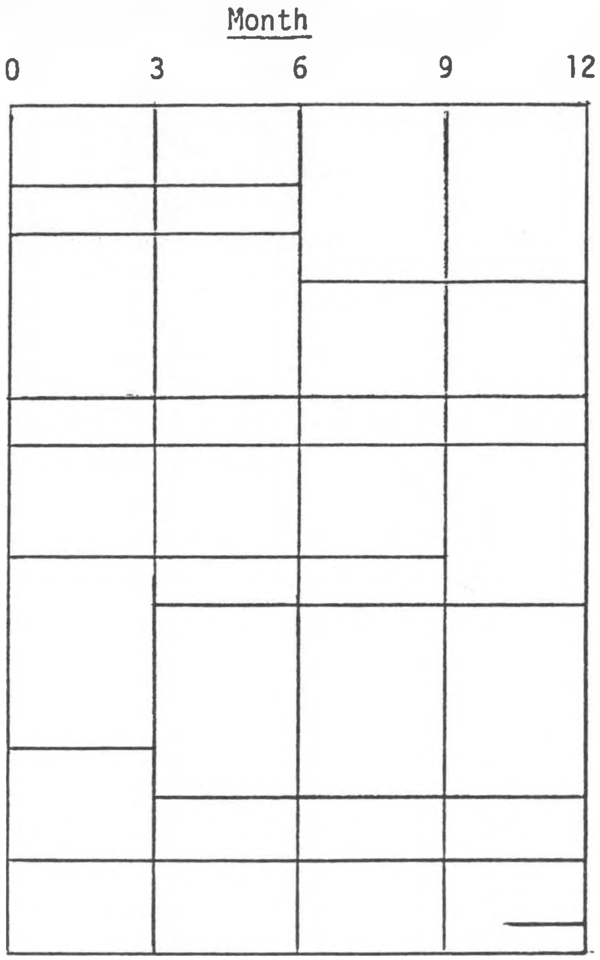
Gasification System Regenerator Analysis. All work to date has involved fueling the regenerator with propane. On a commercial scale, the fuel will be char, recycle gas and/or solid feedstock. This task will implement, characterize and assess a realistic commercial heating mode.

Factor Studies. Factor studies are a continuing phase of any chemical process development project. Thus any alternative feedstock and/or product will require adjustment of process conditions to optimize process performance. The normal factor candidates are reactor temperature, pressure, residence time, reactant composition and/or geometry and catalyst type and composition.

A budget and task schedule are attached.

TASK SCHEDULE

1. Staged Reaction System
   a. catalyst development
   b. fabrication
   c. testing
2. Alternative Feedstocks
   a. compound analysis
   b. processing
3. Alternative Products
   a. catalyst development
   b. process testing
4. Gasification Systems Regenerator Analysis
   a. fabrication
   b. testing
5. Factor Studies
6. Report



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