I. ABSTRACT

Chem Systems, Inc. has completed a two-year R&D program formulated to develop catalysts and a reaction system for the conversion of coal-derived synthesis gases to alcohol-based, synthetic transportation fuels. The program was initiated on September 14, 1979 and involved a four-task approach which included a catalyst formulation and screening phase, a process variables evaluation phase utilizing laboratory-scale and bench-scale reactors, and a technical and economic analysis phase. The work was funded as part of the DOE Indirect Liquefaction program for advancing the technology of coal gasification followed by conversion of the coal-derived synthesis gas to environmentally-acceptable liquid fuels.

The major accomplishments and conclusions achieved during the course of the program are summarized below:

- ALKANOL fuels, containing mixtures of methanol and C_2-C_6 saturated alcohols, represent a means of incorporating methanol into the gasoline pool while simultaneously circumventing most of the technical problems associated with the use of neat methanol-gasoline blends.

- Preferred catalysts and reaction conditions have been identified for the conversion of simulated coal-derived synthesis gases to ALKANOLS at high selectivity. An activity maintenance test made with one of these catalysts in a Berty gradientless, vapor-phase reactor indicated that the activity of the freshly reduced catalyst improved with on-stream time over the nominal 300-hour test while the selectivity to ALKANOLS maintained essentially constant.

- An analysis of the value of ALKANOLS as a gasoline pool blending stock indicates that there are certain scenarios in which specific ALKANOL fuel compositions have refining values equivalent to or better than some of the current octane improvement methods used by petroleum refiners.

II. EXECUTIVE SUMMARY

A. Summary of Accomplishments

Chem Systems has completed a 2-year R&D program aimed at developing a catalyst and reaction system for producing alcohol-based synthetic transportation fuels from coal-derived synthesis gases. The experimental program was carried out in laboratory-scale and bench-scale equipment. The following is a summary of the major accomplishments achieved during the course of the project:

- Eighty-three catalysts covering various combinations of the elements used in low pressure methanol and Fischer-Tropsch catalysts were prepared and tested in vapor-phase screening reactors. Some of these formulations resulted in high selectivities to higher alcohols (C_2 to C_6) but at low activity.

- Several proprietary catalyst formulations provided by a catalyst manufacturer were found to have high activity for producing mixtures of C_1-C_6 alcohols and C_4-C_9 hydrocarbons.

- A nominal 300-hour activity maintenance test made with one of these catalysts in a Berty backmixed, vapor-phase reactor indicated that the activity of freshly reduced catalyst improved with on-stream time such that per pass carbon monoxide conversions, on the order of 20-24 percent (carbon dioxide-free basis), were still increasing at the end of the 300-hour test. Selectivity to ALKANOLS remained essentially constant over the 300-hour test at a value of about 90 percent by weight (H_2O-free basis). The remaining product slate consisted of light hydrocarbon gases, namely, methane, ethane and propane.

- Similar catalyst performances were observed for processing synthesis gases utilizing a slurry autoclave reaction system in which the proprietary catalyst was finely divided and suspended in a paraffinic hydrocarbon oil. Over a 550-hour test period, catalyst activity as measured by per pass carbon monoxide conversion, remained essentially constant. The selectivity to the C_2-C_6 alcohols component (including some aldehyde precursors of the alcohols) of the ALKANOLS increased to a value of about 60 weight percent over the test period. Methanol selectivity was about 15 percent and C_4-C_9 hydrocarbon selectivity was 25 percent.

- A conceptual design of a 1280 short ton/day ALKANOLS facility from coal-derived synthesis gases utilizing a liquid-entrained reaction system has been prepared. This capacity is equivalent to the synfuel energy production rates of an 1800 short ton/day methanol plant or a 97 million gallon/year synthetic gasoline (MTG) plant.

- A comparative economic analysis of the costs of three synfuels - ALKANOLS, methanol and Mobil MTG gasoline - produced by indirect coal liquefaction has been performed.

- An analysis was made of the technical and economic factors affecting the utilization of ALKANOLS as gasoline pool blending stocks.

B. Conclusions

With present-day technology, coal can be gasified and converted to methanol for use as motor transportation fuel. However, its widespread use as a neat fuel will require major modifications to the conventional internal combustion engine and development of a new domestic motor fuel distribution system. A nearer-term approach for utilizing our coal resources through synthesis gas and methanol is to use the methanol as a blending component in existing gasoline fuels. The amount of methanol that can be added is limited in part by its solubility and vapor pressure

characteristics. This amount can be increased to relatively high levels by the addition of higher alcohol components. The method is currently practiced with t-butanol, derived from isobutane or isobutylene, used as the higher alcohol component. The ALKANOLS approach described herein provides a near-term, totally coal-synthesis gas based route to a similar motor fuel additive.

Production cost estimates (1981 Gulf Coast basis) indicate that ALKANOLS might be produced at relative costs to methanol and Mobil MTG of 1.15 and 0.86, respectively, when calculated on a constant product energy value basis. However, it should be realized that in all three cases about 84 percent of the respective product costs can be attributable to the cost of the coal-derived synthesis gases.

An analysis of the value of ALKANOLS as a gasoline pool blending stock indicates that there are certain scenarios in which specific ALKANOL fuel compositions have refining values equivalent to or better than some of the current octane improvement methods used by petroleum refiners. One example is the situation in which a refiner is adding toluene (valued at $1.27/gal) to unleaded gasoline (88 Road Octane Number). The computed refining value of an ALKANOL fuel containing 20% methanol and 80% C_2-C_6 alcohols and having a measured blending value octane number (RdBVON) of about 125, when blended at the 10 weight percent level in unleaded gasoline, is about $1.61/gal. Thus, these octane improvement economics calculations (1981 basis) suggest that there is a driving force between the estimated ALKANOLS refining value ($1.61/gal) and the estimated ALKANOLS production costs ($1.15/gal) for utilizing them as gasoline blending stocks.

The ALKANOLS synthesis reactions can be carried out in conventional fixed-bed reactor systems or in the liquid fluidized and slurry catalyst reactor systems, which are currently under development for methanol synthesis.

ALKANOLS synthesis catalysts require a carefully-controlled, two-step activation procedure in order to ensure the desired high selectivity and productivity to the C_2-C_6 alcohol component of the crude ALKANOL mixture.

Some C_2-C_6 aldehydes are coproduced with the alcohol component of the ALKANOLS. The ratio of the aldehydes/alcohols is a function of the activity of the particular catalyst element that provides the hydrogenation function. Although aldehydes are generally not desirable components of gasoline, they are readily upgraded to alcohols by conventional hydrogenation technology.

C. Recommendations

Chem Systems recommends that two development approaches be considered. One would be directed towards the longer-term objective of developing a liquid-entrained reaction system similar to that currently being developed for methanol under a separate subcontract to DOE. The other route would have a shorter-term objective of developing a fixed-bed, vapor-phase reaction system that might be incorporated into existing commercial-scale, methanol plants.

Table II-1 summarizes the proposed development programs for each of the two options. The liquid-entrained route would parallel the current development efforts in the liquid-phase methanol (LPMeOH) project. In essence, this approach would represent a contract modification to allow the investigation of additional catalysts that produce methanol-containing, alcohol-based transportation fuels. The programs are divided into four phases:

Phase I: Continuation of Bench-Scale Development
Phase II: Process Development Unit Studies
Phase III: Pilot Plant Development
Phase IV: Commercialization

At the end of Phases I, II and III, decision points are reached regarding whether or not to proceed on the work plan for the subsequent phase.

TABLE II-1

OUTLINE OF TASKS FOR OPTIONAL DEVELOPMENT PROGRAMS

Liquid-Entrained Reactor System Development	Fixed-Bed Reactor System Development (Fast-Track Route)
Phase I: Continuation of Bench-Scale Development	
1. Process variables (syn gas comp., T, P, SV) study in existing 1L stirred autoclave system using proprietary commercial catalysts.	1. Test catalysts previously identified in existing small-scale fixed bed reactor system.
2. Selected tests with several other catalysts to determine relationship between catalyst composition and product composition.	2. Develop phase equilibrium data.
3. Develop phase equilibrium data needed to design a product separation and recovery scheme.	3. Survey commercial methanol plants and make preliminary determination of modifications and cost needed to convert to higher alcohols production.
4. Update techno-economic evaluation of process concept.	
Phase II: Process Development Unit Studies	
1. Modify CSI LPMeOH PDU as necessary to include product recovery and separation system.	1. Assemble existing multi-tube salt-cooled reactor system at CSI's facility. Capacity approximately 25 gal/day.
2. Operate CSI LPMeOH PDU to develop scaleup information and information on catalyst life.	2. Operate system to develop scaleup information and information on catalyst life.
3. Update techno-economic evaluation of process concept.	3. Update techno-economic evaluation of producing ALKANOLS at commercial methanol plant.
4. Prepare data book and design package for modification of LaPorte LPMeOH PDU.	4. Prepare data book and design package for modifying commercial methanol plant.
	5. Identify candidate commercial methanol plant.

TABLE II-1 (Continued)

OUTLINE OF TASKS FOR OPTIONAL DEVELOPMENT PROGRAMS

Liquid-Entrained Reactor System Development	Fixed-Bed Reactor System Development (Fast-Track Route)
Phase III: Pilot Plant Development	
1. Modify and operate LaPorte PDU to produce higher alcohols.	
2. Update techno-economic evaluation of process.	
Phase IV: Commercialization	
1. Design and construct a world-scale commercial plant.	1. Modify and operate commercial methanol plant.

III. BACKGROUND AND PROGRAM DESCRIPTION

In 1978, Chem Systems began to explore the possibility of producing a higher alcohols-containing product from coal-derived synthesis gas as an extension of a new technology being developed for methanol synthesis. This work was motivated by an awareness of the potential for methanol to augment both the volume and octane requirements of the U.S. gasoline pool. However, the near-term, large-scale use of straight-run methanol as a transportation fuel was not expected to happen because methanol cannot readily be used in existing gasoline engines without extensive modifications. Further, its use would require the setting up of a new fuel distribution system. The alternative was to develop methanol-gasoline blends that were compatible with existing engines and fuel distribution systems. This has been the direction taken by industry. Because of the physical properties of methanol-gasoline blends, however, it was found necessary to add other components to the fuel mixtures in order to make a satisfactory motor transportation fuel.

Higher alcohols are particularly useful for this purpose. It thus seemed reasonable that if the nation viewed coal as one of the major alternative sources of liquid transportation fuels, then a coal-derived synthetic fuel containing methanol and higher alcohols, which could be used directly as a gasoline blending stock in the near term, and further down the line as a straight-run fuel, would be a justifiable objective. The same kind of reasoning has motivated the development of the Mobil MTG process.

The results of our preliminary work were brought to the attention of the Department of Energy's group responsible for the Indirect Coal Liquefaction program. This eventually led to Chem Systems' entering into a contract with The Department of Energy to develop catalysts and identify a preferred reactor system for the production of alcohol-based synthetic transportation fuels from simulated coal-derived synthesis gases. The contract was let on September 14, 1979.

The experimental program had the following objectives:

- Identify catalyst formulations having high selectivity and activity for producing alcohol mixtures rich in C_1 to C_6 saturated alcohols and useful as synthetic transportation fuels (either as straight-run fuels or as gasoline pool blending stocks);
- Study the performance of these catalysts in laboratory-scale and bench-scale fixed-bed and slurry-phase reactor systems;
- Prepare a conceptual process design of a commercial-scale facility;
- Perform a techno-economic assessment of the process to produce alcohol fuels from coal-derived synthesis gases;
- Select and test catalysts covering a range of compositions and preparation methods;
- Develop catalyst selectivity and activity criteria; and
- Correlate catalyst activity as a function of operating variables leading to a better understanding of the ALKANOLS synthesis reactions.

A work plan was developed to include four major tasks as delineated below:

Task Identification	Description
1	Catalyst Formulation & Screening Studies
2	Process Variables Studies
3	Engineering & Economic Studies
4	Catalyst Performance Studies

1. Catalyst Formulation & Screening Studies

The initial efforts in the Catalyst Formulation & Screening Studies centered on the evaluation of catalyst systems consisting of mixtures of copper/zinc/cobalt promoted with a transition metal (such as chromium, iron, vanadium, or manganese) and an alkali metal (such as potassium or sodium). Catalyst preparation included several alternative techniques such as evaporation of metal salts, coprecipitation, impregnation,

mechanical blending or a combination of such techniques. Finished catalyst was in the form of pellets, granules or powders. Catalyst calcination and activation (i.e., reduction) methods were also evaluated. Small batches of catalysts prepared in laboratory-scale equipment were evaluated either in a diluted-bed, plug-flow, vapor-phase reaction system or in a gradientless, backmixed, vapor-phase reaction system ("Berty" reactor). Also tested were three catalysts supplied by United Catalysts, Inc. (UCI) of Louisville, Kentucky under a confidential agreement. The work statement called for a minimum of 22 catalysts to be formulated and tested. In actuality, 107 catalyst formulations were prepared and 83 of these were tested.

2. Process Variables Studies

The three proprietary UCI catalysts were selected for a more in-depth evaluation in the process variables studies of Task 2. These studies included testing with three reaction systems: 1) vapor-phase, fixed-bed reactor using a Berty backmixed autoclave; (2) vapor-phase, fixed-bed reactor using a diluted-bed (inert alumina), plug-flow reactor; and (3) a three-phase reaction system in which the catalyst is finely divided and dispersed in an inert hydrocarbon liquid*. For the latter purpose, a 2-liter, stirred autoclave system was installed.

3. Catalyst Performance Studies

Based on the results of the process variables studies performed in the Berty vapor-phase reactor, UCI catalyst L-1122 was selected as the candidate catalyst to be evaluated in the slurry autoclave reaction system. More than 900 hours on-stream time were accumulated in the slurry reactor system with this catalyst.

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*Chem Systems has been developing technology for the conversion of synthesis gases to either SNG or methanol utilizing a novel, three-phase reaction system in which an inert hydrocarbon oil is used to suspend the catalyst particles while simultaneously serving as a heat sink for the exothermic heat of the synthesis reactions.

4. Engineering & Economic Studies

In support of the experimental efforts of Tasks 1, 2, & 4, an engineering assessment of the ALKANOLS synthesis reactions was performed. The assessment included three areas of investigation:

- Generation of a conceptual commercial plant design for producing ALKANOL fuels from coal-derived synthesis gases;
- Evaluation of the comparative economics of producing ALKANOLS, methanol and Mobil MTG synthetic gasoline from coal-derived synthesis gases; and
- Evaluation of the use of ALKANOL fuels as blending stocks for conventional petroleum-derived gasoline.

IV. EXPERIMENTAL APPARATUS AND PROCEDURES

Three experimental reaction systems were used during the catalyst screening studies and the process variables studies. The three reaction systems included a plug-flow, diluted-bed vapor-phase reactor, a "Berty" gradientless, vapor-phase reactor and a stirred, slurry-phase autoclave reactor.

A. Plug-Flow Vapor-Phase Reaction System

A schematic of the plug-flow reactor system is shown in Figure IV-1. This system was used throughout the duration of the catalyst screening studies (Task 1), supplementing the screening test data generated in the Berty reactor. A comparison of the plug-flow and backmixed data provided some insight into the mechanism of the ALKANOLS synthesis reactions[46].

The reactor (Figure IV-2) was fabricated from a 4-inch length of 1-inch Schedule 40 stainless steel pipe (Type 316L) with one inch Swagelok connectors welded to both ends. The reactor volume is approximately 75 ml. The reactor was heated and maintained at reaction temperature in a sand bath (Techne Model SBL-2D) which was controlled by a solid state temperature controller (ECS Model 6821). The temperature gradient between the top and bottom of the sand bath was less than $10^{o}C$ during steady-state operations. The synthesis feed gas was preheated prior to entering the reactor in a coiled 1/4-inch O.D. heat exchanger tube immersed in the sand bath. The preheated gas then passed upflow through the catalyst bed and exited through a heat-traced 1/4-inch O.D. tube to the back pressure regulator. A travelling thermocouple in the reactor allowed temperature measurements to be taken along the bed length, with the exception of the bottom 0.6 inches.

The catalyst charge to the reactor consisted of approximately 75 ml of a random mixture of catalyst pellets and an inert support (alumina beads, Rhodia SCS-9, 2-4 mm O.D.). The function of the inert support was to

FIGURE IV-1

SCHEMATIC OF PLUG-FLOW DILUTED-BED, VAPOR-PHASE REACTION SYSTEM

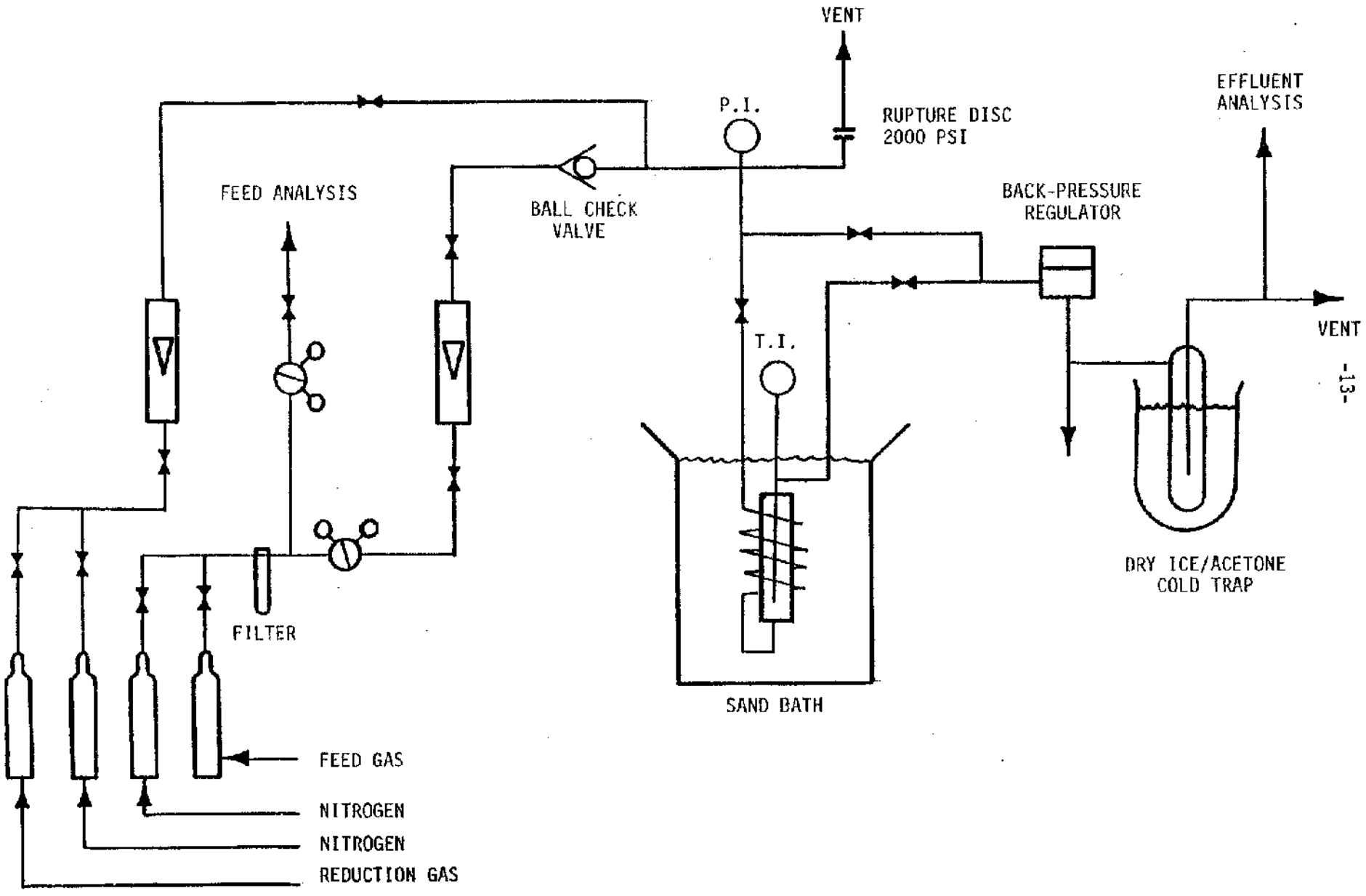
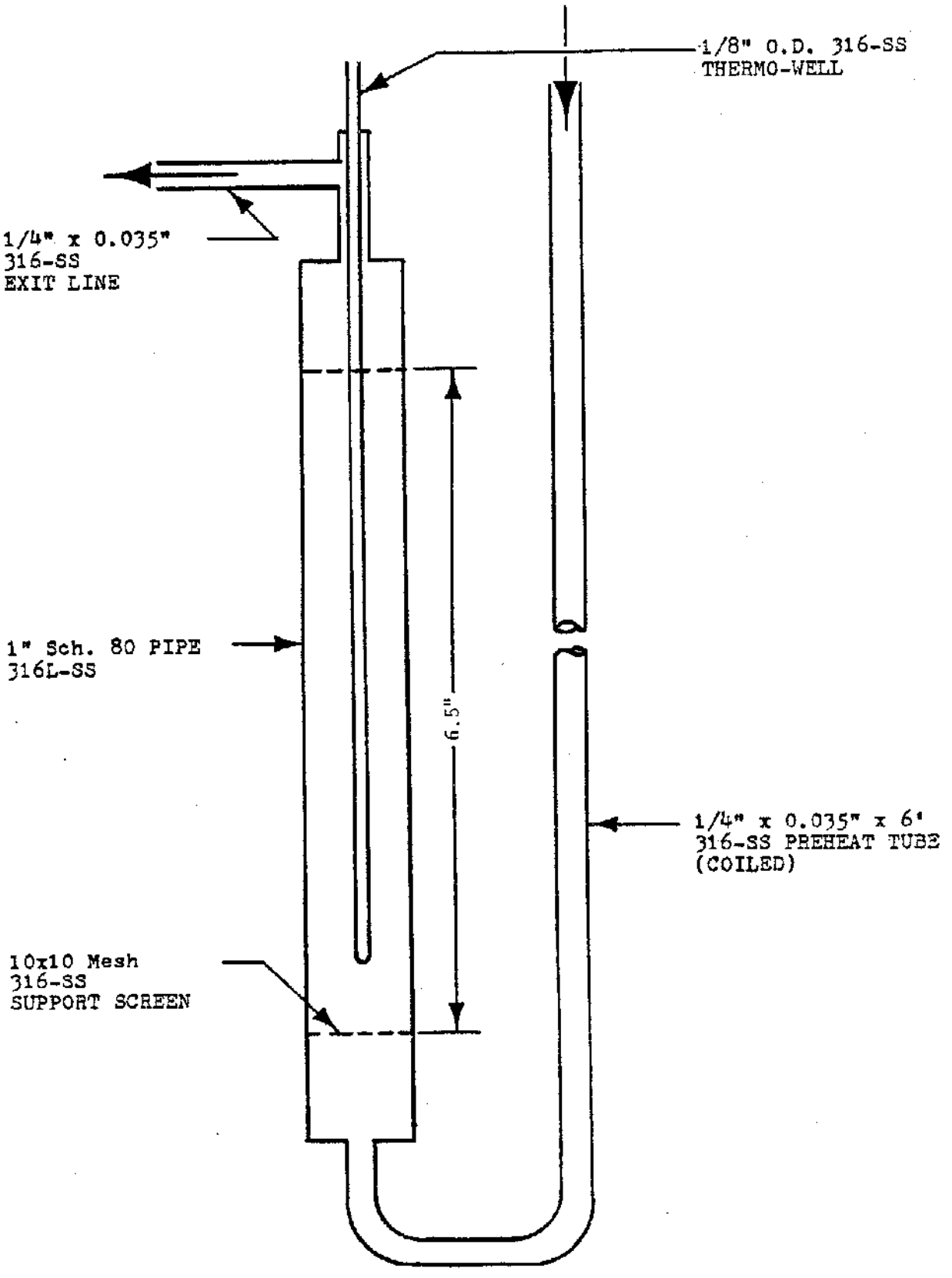


FIGURE IV-2

SCHEMATIC OF PLUG-FLOW DILUTED-BED, VAPOR-PHASE REACTOR



dilute the catalyst in order to limit any reaction exotherms to within about 10°C. The volume fraction of catalyst in the reactor was 25 percent during the early runs. This was increased to 33 percent in later testing.

The plug-flow unit was equipped with a high temperature alarm and pressure alarms to enable round-the-clock runs to be made without the continuous attention of a technician. Any alarm condition (e.g., reactor exotherm or pressure release) would immediately terminate feed gas flow and de-energize the sand bath heaters. The alarms would have to be manually reset in order to restart the system.

B. Berty Gradientless Reaction System

The Berty reactor provides a high internal recirculation of feed and product gases through the catalyst bed and minimizes the thermal and concentration gradients common in other types of fixed-bed reactors. Both the reaction rate and mass velocities that occur in commercial catalytic reactors can be simulated in the Berty reactor. The Berty reactor was received late in January, 1980 and was immediately installed in a parallel operation with the existing plug-flow reactor unit described above. A schematic of the Berty reactor and gas/liquid feed systems is shown in Figure IV-3.

The Berty reactor is equipped with a fixed catalyst basket (2 inch I.D. x 1.88 inch high) and an impeller mounted at the bottom. The catalyst is retained in the baskets by screens secured at both ends. The impeller is driven magnetically up to speeds of 2000 rpm. The reaction temperature is measured by two thermocouples positioned at the top and bottom of the catalyst basket. Further details of the reactor are given in Figure IV-4. A thin layer of Pyrex glass wool was placed on the bottom retaining screen with 25 cc of catalyst distributed evenly in the catalyst basket. Another thin layer of Pyrex glass wool was placed on top of the catalyst followed by the top retaining screen. Due to the high recirculation rate, the use of a diluted bed of catalyst and inerts was not necessary.

FIGURE IV-3

SCHEMATIC OF LIQUID AND GASEOUS FEED SYSTEMS FOR BERTY REACTOR

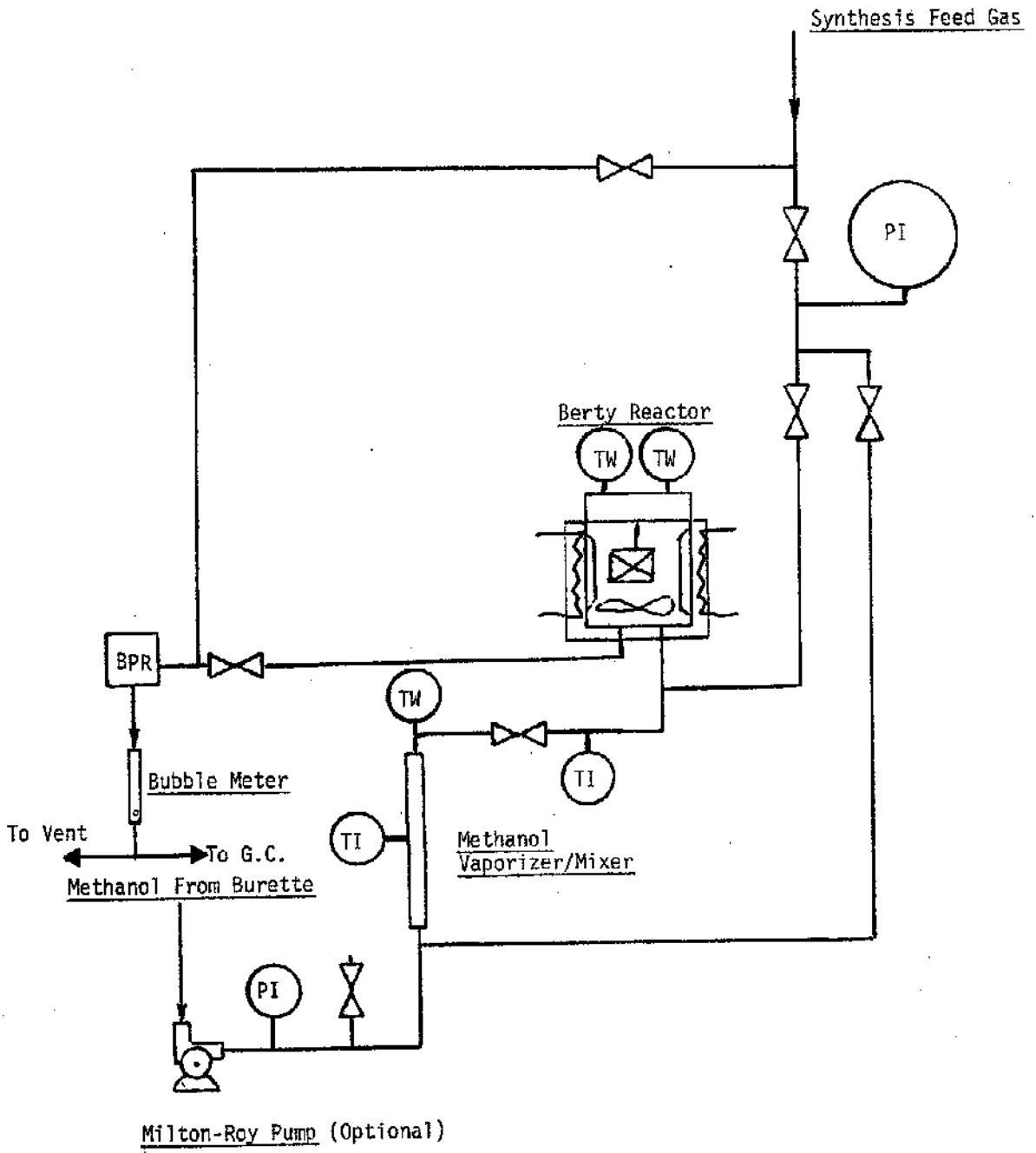
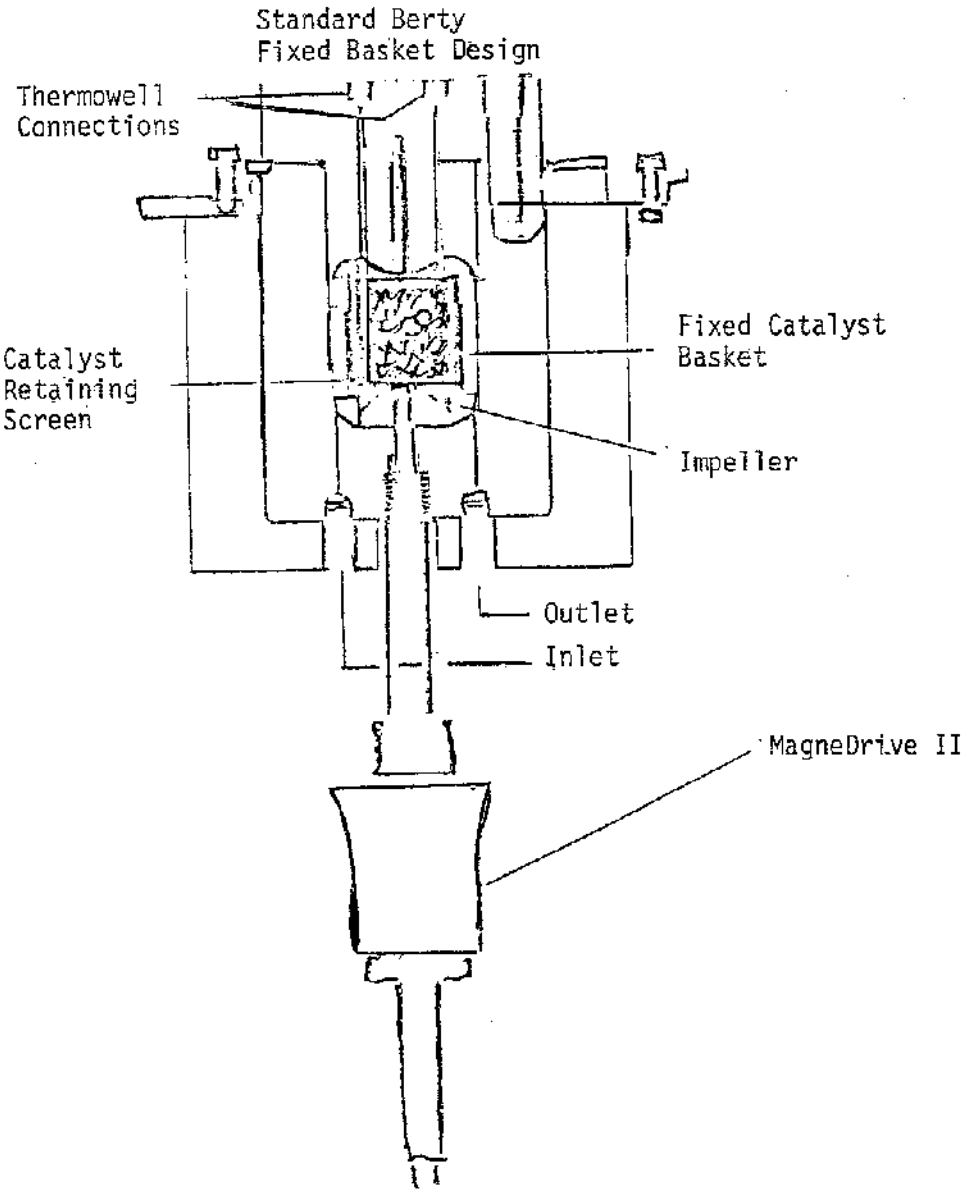


FIGURE IV-4

SCHEMATIC OF BERTY REACTOR



Temperature control was provided by the use of two solid-state temperature controllers (ECS Model 6403), each controlling one ECS Model 6103 power module. All effluent lines were electrically-traced with power being supplied by variacs. Type K thermocouples were used to monitor reactor skin temperatures and line tracings.

C. Slurry-Phase Autoclave Reaction System

A 2-liter, stirred three-phase autoclave reaction system was constructed for testing catalysts in the slurry mode. This unit was utilized in both the process variables studies of Task 2 and the catalyst performance studies of Task 4.

Synthesis feed gas entered the reactor through a dip tube slightly above the bottom of the reactor. A turbine impeller provided the agitation. The vessel was baffled to prevent vortexing. The agitator shaft was also designed as a draft tube to circulate gas from the vapor space back into the slurry. Typical agitator speeds were 600-1200 rpm. These speeds were based on data collected during cold-flow studies which indicated that gas holdup due to the circulation induced by the draft-tube was about an order of magnitude greater than the incremental gas holdup due to the actual synthesis feed gas flow.

The reactor effluent passed through a 3 foot by 1/2-inch O.D., vertical-packed demister column to remove entrained slurry oil from the effluent stream. The demister was heated to 200°C to avoid condensation of any heavier product components. The demister removed about 85 percent of the slurry oil from the effluent stream, returning it to the reactor through a separate line.

Directly after the demister, a slipstream of the reactor effluent gas was taken to the analytical system. The sample lines were heat traced to 310°C to prevent condensation of any high boilers and/or slurry oil. Pressure reduction of the sample stream was achieved by a bellows-sealed, metering valve. The bulk of the effluent proceeded to a cooler and a vapor/liquid separator where the product was condensed and collected. The

non-condensible gases exiting the system were constantly metered by use of a dry test meter. A schematic of the slurry-phase autoclave reaction system is shown in Figure IV-5. All heaters in the system were controlled by solid-state, temperature controllers (ECS Model 6401). The synthesis gas feed rate was monitored by a turbine flow meter. An extensive alarm/shutdown system was employed for use during round-the-clock, unattended operation.

A typical catalyst charge consisted of 100g of calcined catalyst slurried in 600-1000 ml of n-heptadecane or Witco-40, a paraffinic mineral oil. The catalyst was ground and sieved to -20 mesh prior to reduction. Catalyst reduction was carried out in a downflow vapor-phase reactor according to the procedures described in Section E. The reduced catalyst was transferred into the slurry medium in a nitrogen glove box. Care was taken during the entire transfer and loading procedure to avoid exposure to air and potential re-oxidation of the catalyst.

D. Analytical Procedures

Four different analytical procedures were generated and utilized during the test program. A chronological list of each method is described below:

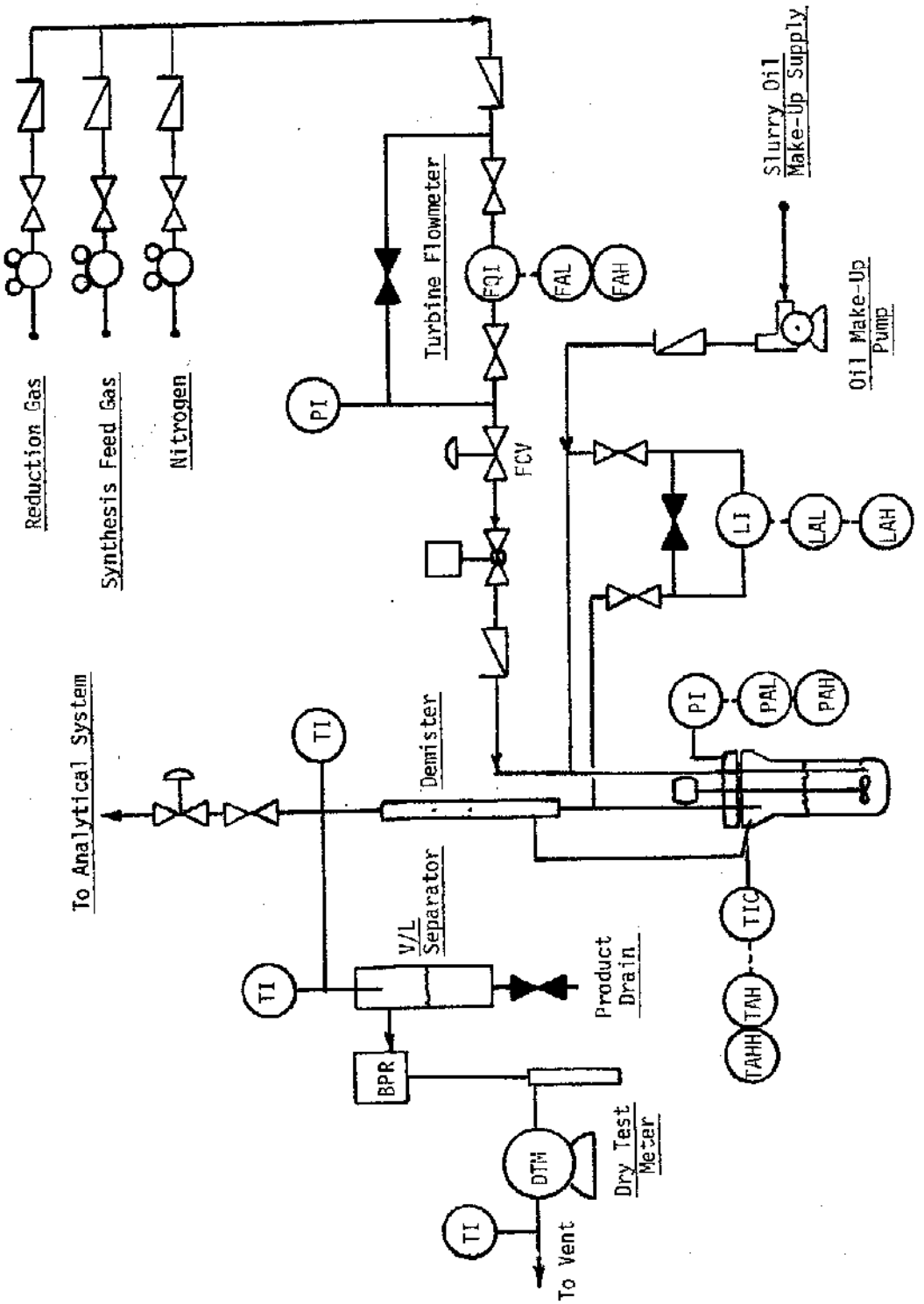
- On-line gas chromatographic (single unit) analysis of a non-condensible effluent sample with batch analysis of condensed products.

- On-line analysis of all components by use of two gas chromatographic systems. Non-condensible gases were sampled after passing through a cold-trap maintained at -80°C.

- On-line analysis of all components by use of two gas chromatographic systems with all sampling done prior to cold trap. A backflush column was used in one of the gas chromatographs in order to prevent high molecular weight components from entering the column.

FIGURE IV-5

SCHEMATIC OF SLURRY-PHASE AUTOCLAVE REACTION SYSTEM



- On-line analysis of all components by use of two gas chromatographic systems with all sampling done prior to cold trap or V/L separator on the slurry unit. Both gas chromatographs were equipped with backflush columns to prevent high molecular weight components from entering the columns.

1. Analytical Procedure For Runs 194-39 Through 194-91

The initial analytical method relied upon condensing the products out of the effluent gas stream followed by analysis of the collected liquids. Mass balances and carbon accountability tended to be poor with this method, since some condensible materials were not completely condensed. The amount of water in the sample was determined by Karl Fischer analysis. Organics analysis was performed on a Perkin-Elmer, 3920 gas chromatograph equipped with a 6 foot x 1/4-inch O.D. glass column packed with Porapak QS 80/100 mesh and a flame ionization detector. After being held at an initial temperature of 100°C for four minutes, the column temperature was increased to 220°C at 8°C/min. and held there for 32 minutes. The carrier gas flow was 30 cc/min. of helium. Integration was done with an Autolab Systems IVB Chromatography data analyzer.

Four standard solutions were prepared containing the expected products (C_1-C_8 alcohols, C_4-C_{10} paraffins and olefins) using 2-(2-ethoxyethoxy)-ethanol as an internal standard. This internal standard was also added to each sample to be injected. The following calculations were used to determine the response factors and weight percentages of the product components in the collected liquid samples:

$$RF_i = \frac{A_i \text{ (Standard Inj.)} \times \text{wt}_{\text{int. std.}} \text{ (Standard Sol.)}}{A_{\text{int. std.}} \text{ (Standard Inj.)} \times \text{wt}_i \text{ (Standard Sol.)}} \qquad (1)$$

$$\text{Wt\%}_i \text{ (Sample)} = \frac{A_i \text{ (Sample Inj.)}}{A_{\text{int. std.}} \text{ (Sample Inj.)}} \times \frac{100}{RF_i} \times \frac{\text{Weight of Sample}}{\text{Weight}_{\text{int. std.}} \text{ Added}} \qquad (2)$$

Where A_i = area count of component i

RF_i = response factor of component i

A sample gas chromatogram chart and integrator printout for this analysis is shown in Figure IV-6.

On-line gas chromatographic analysis was done using a Carle 311 H chromatograph, which analyzed a gas sample downstream of a dry ice/acetone cold trap. The Carle was equipped with a 16.5 foot x 1/8 inch SS Porapak QS 80/100 mesh column, a 10 foot x 1/8 inch SS molecular sieve column, and a thermal conductivity detector. A hydrogen transfer system enabled the quantitation of hydrogen. Oven temperature was maintained at 60°C with carrier flows maintained at 60 cc/min. helium (main carrier gas) and 60 cc/min. nitrogen (carrier gas to hydrogen transfer system). The Carle instrument analyzed for the following gases: hydrogen, nitrogen, argon, carbon monoxide, methane, and carbon dioxide.

A Columbia Scientific Industries Supergrator 3 was used as the chromatograph integrator for the Carle. Besides integrating the component peaks, the Supergrator also controlled the sample valve and the two internal series bypass valves for the columns.

Calibration of the Carle instrument was performed using a standard gas blended by use of volume measurements and having the following composition:

50.145%	Hydrogen
14.971%	Argon
24.918%	Carbon monoxide
9.966%	Carbon dioxide

The response factors were calculated as follows:

$$RF_i = \frac{A_i}{C_i} \qquad (3)$$

Where A_i = area count of component i from standard injection and
C_i = mole % i in standard gas.

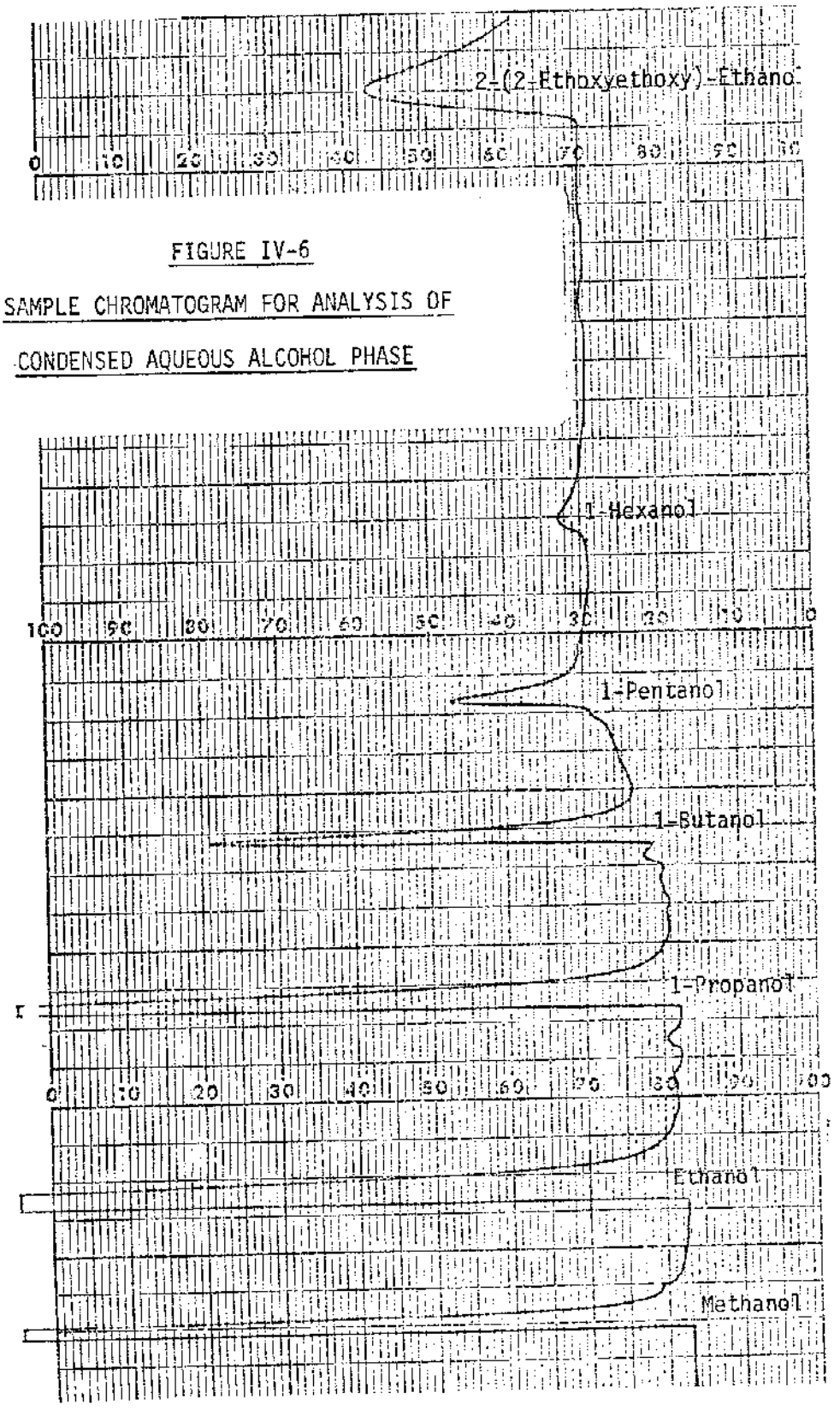


FIGURE IV-6

SAMPLE CHROMATOGRAM FOR ANALYSIS OF CONDENSED AQUEOUS ALCOHOL PHASE

The concentrations of a component in a sample injection is determined by:

$$C_i = \frac{A_i}{RF_i} \qquad (4)$$

Where A_i = area count of component i from sample injection

This entire analysis was very time consuming and not very accurate. This system was used for only the first seven runs (194-39 through 194-91) before being replaced by the following procedure.

2. Analytical Procedure For Runs 194-95 Through 201-74

To improve on the previous analysis, an on-line Hewlett-Packard 5720A gas chromatograph equipped with a flame ionization detector was added. This eliminated the need to separately analyze the collected condensate and resulted in improved carbon accountability. A sample stream was taken off the effluent line just after the back pressure regulator through an electrically-traced sample line to the chromatograph valve oven. The valve oven was equipped with a selection valve (to select plug-flow reactor or Berty reactor effluent) and a sampling valve having a one cc sample loop. All of the sample lines and the valve oven were maintained at 150°C to avoid product condensation.

The Hewlett-Packard gas chromatographic system was equipped with a 12 foot x 1/8 inch O.D. SS column packed with 80/100 mesh Porapak QS. Carrier gas flow was maintained at 30 cc/min of helium. The oven temperature was increased at 6°C/min. from 120°C to 220°C, where it remained for 30 minutes. The Hewlett-Packard was used to analyze for C_1-C_9 hydrocarbons and C_1-C_6 alcohols (aldehydes and esters, if any) in the effluent gas. An Autolab Minigrator (Spectra Physics) was used as an integrator for the chromatograph.

The Hewlett-Packard was calibrated by injecting small amounts (about 2 microliters) of dilute standard solutions, where the components of interest were dissolved in water or methanol. The product concentrations are related to the standard solution concentrations as follows:

$$\frac{W_i/V}{MW_i} \times 3.471 = \text{Mole \%/Microliter}_i \qquad (5)$$

Where W_i/V = grams of component i per liter of standard solution;
MW_i = molecular weight of component i;
V = volume of sample loop, ml and;
3.471 = system conversion factors.

These calculations assume that the sample loop experiences no back pressure, which was a valid assumption due to the low sample flow rates used. Using the above calculations, the equivalent mole percent/microliter injected could be calculated for all of the components in a standard solution at an oven temperature of 150°C. For example:

C_1-C_5 Alcohol Standard (201-4-2)

Component	MW	g/l	Mole %/Microliter
Methanol	32	3.5430	0.3843
Ethanol	46	3.4775	0.2624
1-Propanol	60	3.4543	0.1998
1-Butanol	74	3.4699	0.1638
1-Pentanol	88	3.4304	0.1353

The standards were prepared by mixing up a stock solution of the desired components, and diluting a portion or all of the stock solution volumetrically to the desired concentration. Standards and stock solutions were kept refrigerated when not in use and periodically replaced to avoid error due to potential loss of volatile components.

To calculate response factors and concentrations of components in sample injections, the following equation was used:

$$RF_i = \frac{A_i \text{ (Standard Inj.)}}{\text{mole \%/microliter}_i \times \text{microliter (injected)}} \qquad (6)$$

$$\text{mole } \%_i = \frac{A_i \text{ (Sample Inj.)}}{RF_i} \qquad (7)$$

Where A_i = area count of component i.

C_1-C_4 hydrocarbons were calibrated by injecting a standard gas directly through the sample loop. The composition of the volumetrically-blended standard was:

4.99%	Methane
0.175%	Ethylene
2.03%	Ethane
0.227%	Propylene
2.03%	Propane
0.395%	Isobutylene
0.530%	Butane
Balance	Hydrogen

The attenuation during the C_1-C_4 hydrocarbon calibrations was changed to 512 from 32. The corresponding calculations for the response factors were:

$$RF_i = \frac{A_i}{C_i \times 16} \qquad (8)$$

Where C_i = Mole % of component i in the standard gas.

3. Analytical Procedure For Runs 201-77 Through 213-82

In the previous procedure, the two gas chromatographs each sampled a different gas stream. The Hewlett-Packard analyzer sampled the entire reactor effluent gas; the Carle analyzer sampled only the non-condensible gases. Since this led to inaccuracies in the calculation of the results, the analytical system was modified to allow complete analysis of a single sample of the reactor effluent stream.

To prevent higher boiling components from entering the columns in the Carle gas chromatograph, a backflush column was added between the sample loop and the columns. Both the sample valve and the backflush valve were located in a second valve oven (at 150°C) and were operated by the integrator. A schematic of the new system is shown in Figure IV-7. The

FIGURE IV-7

GAS CHROMATOGRAPHIC SYSTEM FOR ANALYSIS OF BERTY REACTOR EFFLUENT STREAM