MASTER

SOLAR-THERMAL ENERGY CONVERSION AND STORAGE: CYCLOHEXANE DEHYDROGENATION

Progress Report
for Period 30 September, 1977⁷-30 June, 1978

A.B. Ritter, G.B. DeLancey, J. Schneider and H. Silla
Stevens Institute of Technology
Hoboken, NJ 07030

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ABSTRACT

The objective of this project is to provide research support for the benzene/cyclohexane heat pipe development program at Sandia. We have measured the kinetics of the cyclohexane decomposition (energy collection) reaction over a commercially available naptha reforming catalyst (RD-150, Englehard Industries) in the temperature range 400-800°F and pressures of 1 to 40 atmospheres. Significant amounts of side products such as toluene and butane were identified at temperatures above 550°F at atmospheric pressure and significant mass transfer limitations on conversions were observed at the higher space velocities and higher temperatures. No significant decreases in catalyst activity were measured at temperatures below 800°F. However, at 800°F there was a significant decrease in catalyst activity which does not appear to be a poisoning problem but a thermal limitation on catalyst effectiveness.

A test facility has been fabricated to study the behavior of the benzene/cyclohexane (or any other gas phase catalytic reaction) system and its catalysts under long term cycling at temperatures up to 1000°F, and pressures up to 1000 psig at a wide variety of space velocities.

We have developed a mathematical model which simulates the dynamic behavior of the collector (endothermic) reactor and allows the evaluation of such things as startup, shutdown, switching and process control algorithms.

INTRODUCTION

The objective of this project is to provide research support for the benzene/cyclohexane heat pipe development program at Sandia. To this end we have undertaken a theoretical and experimental program to measure the kinetics of the cyclohexane decomposition (energy collection) reaction over a commercially available naphtha reforming catalyst (RD-150, Englehard Industries) in the temperature range 400-800°F and pressures of 1-40 atmospheres in a fully instrumented gradientless (stirred) reactor. The initial batch studies were aimed at providing conversion information for the design of a continuous catalyst cycling test loop. However, the production of significant quantities of side products at the higher temperatures led to a part of the program being devoted to the identification of the side products produced and the effects of the side products on the long term behavior of the cyclohexane/benzene cycle. In particular, the effects of temperature, pressure, and side product formation on the activity of the catalyst were to be investigated.

In addition to the batch-kinetic studies, a major effort this year went into the design and fabrication of a continuous catalyst cycling test loop for the cyclohexane/benzene system. The test loop was designed to enable us to study the long term behavior of both side product formation and catalyst activity at temperatures up to 1000°F and pressures up to 1000 psig.

Finally a mathematical model has been developed which will predict the transient behavior of a gas-phase catalytic reactor dedicated to the collection of thermal energy.

A discussion of the progress made to date in each of these areas is given below.

A. Kinetic Studies: Cyclohexane Dehydrogenation Reaction

We have measured the kinetics of the cyclohexane dehydrogenation reaction in the temperature range 400-800°F at several space velocities over a commercially available naphtha reforming catalyst (RD-150, Englehard Industries) in an internally recirculated (gradientless) stirred tank reactor (Autoclave Engineers). A schematic diagram of the basic experimental system is shown in Figure 1.

Cyclohexane feed is introduced into the reactor by means of a Harvard constant infusion syringe pump. This is a positive displacement pump that provides very precise control of flowrate over the range 0.025-38.2 ml/min depending on the size of the syringe used and the speed selected. A double syringe model is used along with a 3-way ball valve arrangement to insure virtually continuous precise flow of the cyclohexane feed to the reactor. The calibration of the pump has been checked at all speeds using a graduated cylinder and stopwatch. The reactor has a one gallon working capacity. The catalyst is supported in a cylindrically shaped bed approximately 5.8 cm in diameter by 13.0 cm long located on the axis of the fan. The catalyst bed is an integral part of the fan system which is designed to circulate the gas phase through the catalyst bed to insure intimate contact between the gas and catalyst. A rheostat allows the fan speed to be adjusted over the range 1000-2100 rpm. The speed is measured by means of a strobe tachometer. Two thermocouples located 2.0 cm from the top and 2.0 cm from the bottom of the catalyst bed allow us to monitor the temperature change across the bed. The location of these thermocouples can be adjusted to monitor the temperature at any two points along the catalyst bed. Temperature control is provided by means of three 650 watt resistance heaters located around the reactor. The three heaters provide 3 independently regulated zones of heat at the top, middle and bottom of the reactor. All 3 heaters are used for startup, while only the bottom heater is generally required for temperature control during operation. The reactor is well insulated and

the temperature variation is usually less than $\pm 0.5^{\circ}\text{F}$ during a run. The pressure in the reactor is controlled manually by means of a needle valve and pressure gauge on the outlet line. The data in these studies were taken at a constant reactor pressure of 2.0 psig. The outlet from the reactor is split into two streams. The major part is passed through a total condenser. The cooling water for the condenser is provided by a refrigeration unit operating near 0°C (although capable of going to -10°C with the use of a heat transfer fluid such as Dowtherm). The condensed product (benzene and cyclohexane) is collected in glass containers and disposed of in a safe manner. Noncondensibles (mostly hydrogen saturated with benzene and cyclohexane vapors at 0°C) are vented through the laboratory hood system. A small portion of the outlet stream is piped directly to a Hewlett-Packard 5830A computer controlled gas chromatograph equipped with a heated, automatic, programmable gas sampling valve. The detector is a hydrogen flame ionization unit and excellent separation of benzene and cyclohexane is achieved by a $1/8" \times 6 \text{ ft.}$ column packed with carbowax. The chromatograph is calibrated both for concentration of cyclohexane and benzene and total sample size by injecting known amounts of carefully prepared mixtures of benzene and cyclohexane. A correction for sample size is required since at high conversions, large volumes of hydrogen are present in the product stream along with the cyclohexane and benzene. The hydrogen essentially acts as a diluent when the sample passes through the hydrogen flame ionization detector. The computer on the chromatograph automatically computes the total areas under all the curves (related to sample size) as well as the fraction of the areas under each curve. It should be emphasized that the experimental apparatus are flexible enough so that the kinetics of many gas phase catalytic reactions can be readily studied with only minor modifications to the system.

Experimental Procedure and Data

At the end of each days operation the flow system is thoroughly flushed with nitrogen and left overnight under a slight nitrogen positive pressure for safety. To start operation, the system is first brought up to the desired operating temperature, the nitrogen is shut off and cyclohexane feed is introduced at a liquid flowrate of about 2.75 ml/min to flush the reactor. After approximately 5 residence times of flushing (~25 min.) the cyclohexane flowrate is adjusted to the desired experimental value. Conditions of temperature, pressure and flowrate in the reactor are maintained constant until the concentration of benzene leaving the reactor (as indicated on the gas chromatograph) reaches a constant value. The rule of thumb is to wait at least 5 residence times after any system changes have been made to insure that a steady-state condition has been reached.

The feed to the reactor is reagent grade cyclohexane. As each new bottle of cyclohexane is opened, its purity is checked by running several samples through the chromatograph. Occasionally trace quantities of toluene and other impurities are detected in the cyclohexane. The naptha reforming catalyst is in the form of pellets approximately 1/16" D x 1/16" L. The catalyst is weighed and loosely packed into the cylindrically shaped bed support. Layers of glass beads of several different sizes are randomly interspersed with the catalyst pellets to fill the unused portion of the bed with inert material and provide a matrix to insure adequate flow in and around each catalyst pellet and through the bed. Before each new set of runs the catalyst is activated by a nitrogen flush (to eliminate any oxygen present) followed by a hydrogen purge at 900°F for 2 hours. The catalyst activity is checked at the beginning and end of each set of runs by duplicating a high conversion (>90%) data point at 600°F and comparing the conversion with the conversion obtained when the catalyst was fresh. We have used the same batch of catalyst over the past year and a half,

including over a dozen reactivations and many start ups and shut downs (temperature cycling). As far as we can tell the catalyst activity has remained constant at temperatures below 800°F (See discussion below).

At each temperature and feedrate (space velocity), the reactor is run at several different agitator speeds to determine the effects of external mass transfer on the conversions. Figure 2 shows the results for several flowrates at 600°F. One can see that at low space velocities, where conversions close to equilibrium are obtained the external mass transfer can keep pace with the (relatively low) reaction rate. However, as the space velocities are increased and the reaction gets farther from equilibrium, the external mass transfer can't keep pace with the (relatively rapid) reaction rate and so the mass transfer effects limit the observed conversion. Under these conditions the conversion becomes a function of the agitator speed and the "true" conversion must be obtained from the data by extrapolation to infinite agitator speed (elimination of external mass transfer effects). Figure 3 is a plot of the conversion of cyclohexane obtained over a range of space velocities, with temperature in the range 500-800°F as a parameter. Comparing the 800°F data in Figure 3 with the 750°F data we see that the conversions at 800°F are the same or lower than those at 750°F and comparable space velocities. This may be attributed either to a decrease in catalyst activity due to poisoning or the fact that we have reached an upper temperature limitation on the RD-150 catalyst. We tend to favor the latter explanation since we reran the 600°F curve using the same batch of catalyst and did not observe any significant change in activity at 600°F.

We do know, however, that commercial reforming units operate at about 900°F and ~500 psig. Therefore, we suspect that pressure effects will be very important at the higher temperatures. Figure 4 shows the reaction rate times the space velocity - vs. - conversion at each temperature. The data in Figure 4 clearly point out the effects of mass transfer limitation. The dashed line is

data taken at 600°F at low agitator speeds. The data at each temperature approach the calculated equilibrium values at low space velocities.

High Temperature, High Pressure Modifications

We have made the following modifications to the basic system to enable us to run at temperatures up to 1000°F and pressures up to 1000 psig. Referring to Figure 1.

1. We have replaced the three 650 watt resistance heaters on the reactor with a 2-zone, 1000 watts/zone furnace. This will provide surface temperatures of up to 1300°F and should easily allow operation at temperatures up to 1000°F inside the catalyst bed.

2. We have replaced the glass condenser with a stainless steel heat exchanger and knockout drum to allow operation at the higher pressures.

3. We have added a specially designed high pressure, high temperature valve between ball valve, G, and the gas chromatograph to drop the high reactor pressure to atmospheric in order to protect the automatic gas sampling valve on the chromatograph.

4. We have added a high pressure gauge (0-2000 psig) in series with pressure gauges P2.

5. The Harvard Infusion pump, which gives extremely accurate low flowrates but employs glass syringes, has been replaced by a high pressure (up to 5000 psig) liquid chromatograph metering pump. However, the minimum flowrate of this pump is still 3 to 5 times higher than the lowest flowrate we have been using. This means we cannot duplicate the lowest 2 or 3 space velocities at the higher pressures, although we should be able to at least double the amount of catalyst in the bed and come close. High pressure, low flow metering pumps are extremely expensive and we have yet to find a high pressure pump able to duplicate the range of accurate, low flowrates possible with the Harvard Infusion system.

6. All the plastic purge lines and vent lines have been replaced with

Fig. 1 : THE EXPERIMENTAL FLOW SYSTEM FOR STUDYING THE KINETICS OF GAS-PHASE CATALYTIC REACTIONS

Fig. 2: THE EFFECTS OF EXTERNAL MASS TRANSFER ON CONVERSION AT 600°F

FIGURE 3: CYCLOHEXANE DECOMPOSITION KINETIC DATA

$r_g \times 10^3$ - MOLES OF BENZENE PRODUCED / (MINUTE-GRAM CATALYST)

FIGURE 4

NOTE 1: ALL DATA WAS EXTRAPOLATED TO ZERO MASS TRANSFER EFFECT EXCEPT FOR THE SET, INDICATED BY A DASHED LINE

stainless steel tubing.

7. We have ordered a water cooled magnetically driven agitator from Autoclave Engineers which, when adapted to our reactor, will allow us to operate at temperatures up to 1000°F and pressures up to 1000 psig. Our present reactor was only designed to operate at temperatures up to 650°F and agitator speeds up to 1500 rpm. To eliminate external mass transfer effects we regularly operate the agitator at speeds up to 2100 rpm. We have recently been operating the reactor at temperatures up to 800°F. Even though we have added a cooling coil at the base of the agitator, the combination of higher temperature and sustained operation above rated speed considerably reduces the operating life of the graphite bearings. Recently we have had to replace these after every third or fourth day of operation. Although the bearings are relatively inexpensive (\$18.00 per set), the 2-3 down days required for replacing the bearings, reactivating the catalyst and running an activity check make replacement of the drive essential to any sustained effort at high temperature studies. Autoclave has promised delivery of the new agitator by mid-August.

B. Side Product Identification

At high conversions (low space velocities) and at temperatures above 540°F at 2 psig, several side products are produced along with the benzene and hydrogen over the RD-150 catalyst. A typical output from the gas chromatograph is shown in Figure 5 for a recent run at 600°F, 0.029 hr^{-1} space velocity and an agitator speed of 1800 rpm. The benzene has a retention time of 3.11 min on this chromatograph column and the cyclohexane has a retention time of 1.48 min. The cyclohexane conversion in this run corresponds to 91.5% and 4 apparent side products were produced at retention times of 0.82, 1.11, 1.28 and 4.80 minutes. The product corresponding to a retention time of 4.80 minutes has been identified as toluene.

FIGURE 5: GAS CHROMATOGRAPH RESULTS
 600°F, #10 feed rate, .029 hr⁻¹ space
 velocity, 1800 RPM agitator speed.

RT	AREA	AREA %
0.82	159600	0.059
1.11	1901000	0.707
1.28	4773000	1.776
1.46	16320000	6.073
3.11	245200000	91.243
4.80	378200	0.141

XF: 1.0000 E+ 0

It is interesting to compare Figure 5 with a mass spectrometer analysis of a gas sample done on 8/16/77. The reactor conditions were identical; 600°F, 0.029 hr⁻¹ space velocity and an agitator speed of 1800 rpm. A sample of the vapor phase leaving the reactor was collected in a 500 cc glass bulb, and submitted to an independent analytical service for mass spectrometry analysis. The results are reproduced as Appendix I. Several observations are evident. First, air had obviously contaminated the sample as shown by the presence of oxygen, Argon and CO₂. Second, the spectrometer showed the presence of at least 3 side products, butene, toluene and an unknown aliphatic hydrocarbon, possibly butane or methyl pentane. This information is consistent with the presence of 3 unidentified peaks on the chromatograph which appear before cyclohexane (RT = 1.48) and the toluene (RT = 4.80) which appears after benzene (RT = 3.17). The extra unknown peak at RT = 1.28 is an unidentified impurity which entered with our reagent grade cyclohexane and came through the reactor unchanged. We have not been able to detect the presence of methylcyclopentane as a side product under our reaction conditions even though it is known to be a thermally induced isomer of cyclohexane. The chromatograph has not produced any extraneous peaks and of course the mass spectrometer would not be able to discriminate between cyclohexane and methylcyclopentane.

Over the past year we have installed a second chromatographic column on channel B of the chromatograph which will separate the lower molecular weight species such as butane, methylpentane and butene. We have also installed a 3-way valve on the chromatograph so that the contents of the automatic gas sampling valve can be sent to either column A or B. Finally, we have run various combinations of butene, methylcyclopentane, methylpentane, and butene through the new column to determine the characteristic retention times of these substances. This will enable us to identify them in gas samples taken from actual runs. Since the residence time of a substance on a chromatograph column

depends on many factors, we are in the process of installing a gas injection system so that we can inject a known quantity of one of the suspected side products into the sample stream from the reactor prior to its entering the chromatograph. This will enable us to enhance the chromatographic peak of the suspected side product during a run and positively identify the substance.

C. Catalyst Deactivation Studies

We have designed a test loop for measuring adsorption isotherms (H_2 , He, N_2). This is shown schematically in Figure 6. Measurements of hydrogen adsorption isotherms is a standard technique for determining the amount of active surface available in platinum catalysts. Changes in the measured active surface area reflects activity changes in the catalyst. Appendix II contains a proposed procedure for measurement of the number of moles of hydrogen adsorbed by the catalyst.

All of the components for the test loop have been purchased including a conditioning furnace ($500^\circ C$), a constant temperature oven ($250^\circ C$), a high vacuum pump, McCloud gauge, a gas manifold and several gas sampling tubes. We expect to have measured H_2 adsorption isotherms for samples of both fresh and used catalyst prior to the end of the contract.

We may also be able to arrange for scanning electron microscope pictures of the same catalyst surfaces. There have been some problems in getting our student the training necessary to operate the scanning electron microscope since it is heavily used by the metallurgy department at Stevens for both teaching and research. For these reasons it may be more efficient for us to subcontract our scanning E.M. work to the metallurgy department.

D. Catalyst Cycling Test Loop

Process Description

The catalyst cycling test loop which is shown schematically in Figure 7, consists of four major subsystems: the collector, the boiler, the hydrogen

PROPOSED VACUUM RACK APPARATUS

FIGURE 6

storage and the steam generating systems. While there are many opportunities for improving the thermal efficiency of the process (e.g., by using the hotter streams to preheat the inlet stream), for simplicity the reactor feed streams are all preheated electrically. All streams will be mixtures of two or more components. However, to keep the flow diagram uncluttered only the major component is shown on each stream line in Figure 7.

Starting with the collector subsystem; cyclohexane, containing a small amount of benzene, is fed to a electrically heated vaporizer by a diaphragm pump before being preheated to the reacting temperature by a second electrical heater. In the collector reactor, the thermal energy source, which may be solar, (or any other thermal source), is simulated by electrical heaters. The heaters are clamped to a tube packed with catalyst (the collector reactor). In the reactor, cyclohexane is converted to benzene and hydrogen with the absorption of ~52 Kcal of thermal energy per mole of cyclohexane converted. After exiting from the reactor, the reaction products are cooled to a safe temperature by a heat exchanger to protect both a pressure control valve, located after the cooler, and the condenser. After condensation the benzene and unreacted cyclohexane are separated from the hydrogen in the storage vessel. The hydrogen is then compressed and stored.

With the exception of the reactor, the boiler subsystem is identical to the collector subsystem. The boiler reactor consists of several tubes in parallel packed with catalyst pellets. In the boiler reactor hydrogen is reacted with benzene producing cyclohexane and releasing ~52 Kcal of thermal energy per mole of cyclohexane produced. The energy is removed by boiling water to produce steam which is condensed and recycled. The steam pressure will be controlled by a control valve located before the condenser.

Unreacted hydrogen from the boiler reactor is combined with the hydrogen from the collector reactor. Before compression the small amounts of cyclohexane and benzene are removed from the hydrogen in the refrigerated cooler to prevent condensation within the compressor. The condensed vapors, which contain mostly benzene, are mixed with the boiler reactor feed. The system was initially designed to be operated without a compressor by purchasing high pressure tanks of hydrogen for the boiler reactor and venting the hydrogen produced in the collector. Besides the nuisance of continually replacing the hydrogen, this procedure is technically questionable because the vented hydrogen is in effect a purge. Since the major purpose of the test loop is to study the behavior of the catalyst over many cycles and one of the unknown factors is the possible buildup of unwanted side products, leading to poisoning of the catalyst, a vented hydrogen stream could prevent the detection of these effects.

Project Status

Activation of the test loop will proceed in several stages. In the first stage the collector subsystem will be constructed and tested at atmospheric pressure. After this phase is completed the collector reactor will be brought up to 1000 psi and 1000°F, the design pressure and temperature. Following this the boiler and steam generating systems will be constructed and tested. Next the hydrogen storage subsystem will be designed, constructed and tested. Finally, all systems will be integrated and operated simultaneously.

The funds currently allocated to the project are not sufficient to complete the entire test loop. Since the operation of the collector reactor is more technically uncertain the initial effort has focused on this part of the test loop. The design of the collector subsystem has been completed, a major part of the equipment has been received and construction has begun. Although an effort was made to purchase standard equipment to save time and expense, the reactor with the furnace, the preheater and the storage vessel all required

special designs. Arrangements have been made for welding all the components. Because of the large consumption of power for the reactor, preheater and vaporizer the electrical power supplied to the laboratory will have to be increased. No automatic controls have been included in the design of this system but will be added as experimental information on the system behavior is obtained and funds become available.

Since the hydrogenation of benzene is a commercial process, more information was available for the design of this subsystem and a proven catalyst supplied by the Harshaw Chemical Co. is being used. The major parts of the boiler reactor subsystem have been designed, purchased and constructed. Although these components will be installed, the boiler reactor itself cannot become operational until additional funds become available. To complete this part of the test loop the preheater and vaporizer must be purchased along with piping, fittings and valves to connect the various components and instrumentation. The estimated cost to DOE for completing this part of the test loop is \$4500.

The hydrogen storage system was not included in the original design, but because of the technical considerations discussed earlier it was decided that a storage system would be necessary. For preliminary testing, however, the hydrogen supply will be from pressurized tanks. Fortunately, a used compressor was donated by the Central Operating Co. of West Virginia Power and Lighting, New Haven WV. Overhaul of the compressor and replacement of used and missing parts will cost \$2600. This is approximately 10% of the price of a new compressor alone. To complete the hydrogen storage system a storage vessel, instrumentation and controls, and the necessary piping, mounting pad and electrical outlets will be required. The estimated cost to DOE of adding the hydrogen storage subsystem to the test loop is \$6910.

FIGURE 7: CATALYST CYCLING TEST LOOP: BENZENE/CYCLOHEXANE SYSTEM

E. Mathematical Modeling Studies

A mathematical model has been developed describing the transient behavior of a gas-phase catalytic chemical reactor. The details of the model have been reported previously (5). The model has been revised to account for the heat transfer between the catalyst pellet and the gas phase, which was perceived to be a limitation on the original model. While the revised model has been programmed for solution on the digital computer, there has not been sufficient time or manpower to debug all parts of the program, while still collecting kinetic data, building the catalyst cycling test loop and modifying the batch reactor for the high pressure-high temperature studies. We have not actively pursued the modeling studies as we believed the experimental portion of our program should have a higher priority on our limited resources. We do, however, plan to return to these studies in the fall as the other parts of the program become less demanding of our time.

Contractual Compliance

With the exception of task B, subtasks B and C, which we will complete to the extent of our budget⁽¹⁾, and task C, subtasks C and D, which we cannot complete, again because of limited resources, we expect to be in substantial compliance with the rest of the contract by the expiration date of September 30, 1978.

Effort of Principal Investigator

Arthur B. Ritter, Ph.D., Associate Professor of Chemical Engineering, has been the principal investigator on this project. He has devoted 20% of his time to the project (only 10% charged to DOE) during the academic year (September 1977--May, 1978) and 60% of his time during the months of June, July and August, 1978.

(1) Appendix III is a copy of our correspondence with Mr. Matthew Rosso, Jr., of Brookhaven National Laboratory who is the technical monitor on this contract concerning our noncompliance with this phase of the contract and his reply.

He will return to the 20% level during September, 1978.

Harry Silla, Ph.D., Professor of Chemical Engineering, has devoted 10% of his time to the project during the academic year and 100% of his time during the months of June and July. He will be on vacation during August and return to the 10% level during September, 1978.

James Schneider, graduate student. Mr. Schneider has devoted 50% of his time during the academic year (at no charge to DOE) and 100% of his time during the months of June, July and August. He will return to the 50% level in September.

In addition, there have been approximately 5 undergraduate students supported by federal work-study funds who have each devoted 15 hours per week to the project during the academic year and two masters students who have devoted 4-8 hours per week to the project during the academic year at no cost to DOE. During June, July and August we have employed 2 full time undergraduates and one half-time graduate student (in addition to Mr. Schneider) on the contract while a third undergraduate has been working full time on the project during July and August at no cost to DOE. We expect that 3-5 work-study undergraduates and at least 2 masters candidates will each be working 10-15 hours on the project at no cost to DOE starting in September. The availability of these additional personnel has allowed us to do significantly more with the available funds than we could have done and are an invaluable addition to the program.

Publications

We have presented a talk at the DOE (STOR) Contractors review meeting held in November, 1977, at Hunt Valley, Maryland. The paper has been published in the proceedings (6).

A paper based on this work has been accepted for presentation at a symposium on the use of recycle reactors in chemical reaction engineering to be held at the Fall meeting of the American Institute of Chemical Engineering in November,

1978, at Miami Beach.

We have also agreed to present a progress report at the next DOE (STOR) contractors review meeting to be held in November, 1978.

In addition, several talks based on this work have been presented at local seminars and meetings. An invited talk was given at the Stevens Chapter of Sigma Xi in December, 1977, and one at the New Jersey Section AIChE monthly dinner meeting in March, 1978.

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TO: Mr. J. C. Schneider
Chemistry and Chem. Eng. Department
Stevens Institute of Technology
Castle Point Station
Hoboken, New Jersey 07030

G.A.S. REPORT No. 38976
Date Reported: 8/16/77
Date Requested: 8/12/77
P. O. No. 25710

MATERIAL SUBMITTED: 1 Glass Bulb 500 CC Sample #1

INFORMATION REQUESTED: Mass Spectrometry Analysis

NOTEBOOK REFERENCE: NB 464, page 31

RESULT OF INVESTIGATION

<u>Constituents</u>	<u>Concentration % Volume/Volume</u>
Nitrogen	1.8
Oxygen	0.10
Argon	0.0090
Carbon Dioxide	0.0080
Hydrogen	Balance
Butene	0.16
Cyclohexane	0.23
Benzene	0.26
Toluene	0.0005
Unknown*	0.10

* An aliphatic hydrocarbon, possibly butane or methyl pentane.
The organic concentrations are semi-quantitative.

cc: V. Murphy

ja 8/16/77

By

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CHEMISORPTION PROCEDURE

INITIAL CALIBRATION - the volume of the system is calibrated as described below:-

1) Weigh the dosing bulb before and after filling it with Hg of known density. The difference in the weights divided by the density yields the volume of the dosing bulb.

2) Fill the dosing bulb with He or H₂ to a known pressure P₁ (V₁ determined above). Open the stopcock to the manifold. The new pressure P₂ is read off the manometer. Assuming an ideal gas at constant temperature, $P_1 V_1 = P_2 V_2$, and thus, V₂ is determined.

3) The same procedure described in 2) is used to determine the volume of the sample tube.

PRETREATMENT - every sample to be tested must be pretreated as described below:-

- 1) Outgas the system (samples in sample tube) at 500°C for 3 hours.^(2,3)
- 2) Subject the system to 1 atm of H₂ at 500°C for 30 min.⁽²⁾ to ensure adequate reduction of the catalysts.
- 3) Outgas the system overnight (16 hrs) at 500°C.^(2,3,4)

DEAD SPACE DETERMINATION - dead space in the sample tube must be determined for every sample tested⁽¹⁾.

- 1) Evacuate the system.
- 2) Charge system, keeping the sample tube isolated, with 200 mm. He^(1,4).
- 3) Open stopcock and note pressure change. Once again assuming an ideal gas at constant temperature, $P_1 V_1 = P_2 V_2$, and thus, the effective volume of the sample tube is determined. The difference between this value and the sample tube volume determined in the "initial calibration" is the dead space volume for a given sample.

H₂ ADSORPTION - the H₂ adsorption is determined for every sample as described below:-

- 1) Evacuate the system.
- 2) Charge system with 100-200mm. H₂ at 250°C^(2,4).
- 3) Take pressure reading after 2 hrs⁽⁴⁾. For an ideal gas, constant pressure, and constant temperature, $V \Delta P = RT \Delta n$, and the number of moles of H₂ adsorbed, Δn , can be determined.

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY 07030

Department of
Chemistry and Chemical Engineering

July 27, 1978

Mr. Matthew J. Rosso, Jr.
Department of Applied Science
Brookhaven National Laboratories
Upton, New York 11973

Dear Matt,

This is to inform you that we will not be able to complete task B on contract EC-77-C-02-4583 this year. Specifically subtasks b through d can not be completed within the present budget because actual equipment costs were higher than those budgeted. The major reason for this, in addition to general inflation, is that the original design called for operation of the test loop at 400 - 600°F and atmospheric pressure. We agreed to change the design specifications so that the test loop could operate at up to 1000°F and 1000 psig and try to accomplish this within the original budget. At the time we believed this was possible. Unfortunately these temperatures and pressures are outside the design ranges of most standard commercially available equipment such as heat exchangers, pumps, heaters and valves and we had to go to specially fabricated and/or high pressure commercially available units which are considerably more expensive than the standard, off-the-shelf items they replaced.

Even so we thought that we could, by simplifying the design and eliminating the automatic controls, still complete the task as specified. However, after reviewing the costs to date and estimating the current costs of the remaining items we find that in order to complete the task we would have to overrun the budget by \$5750.00 and at this point, ask that the contract be extended by about one month. The one month extension is based on the additional funds being allocated no later than August 15, 1978. A list of the specific items to be purchased with the additional funds are enclosed.

An alternative arrangement would be to have the completion of task B be part of the renewal contract.

I would like to apologize for the delay in informing you of this problem. My experience in administering contracts rather than grants is very limited and I believed that as in the case of a grant, the contract budget was fixed and I had to accomplish as much as I could within the stipulated budget. I had no idea I could request additional funds to complete the task or I would have brought this to your attention about a month earlier.

Mr. Matthew J. Rosso, Jr.

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July 27, 1978

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Please let me know which course you would like to pursue. In any case, we will have the purchase orders for all the items ready to go.

If there is anything else I can do please let me know.

Sincerely

Arthur B. Ritter
Associate Professor of
Chemical Engineering

ABR/jh

Enclosure

cc: Dean Ehrlich, Research
Dr. David Haaland, Sandia
Dr. DeLancey
Dr. Silla

Supplemental Budget Task BContract EC-77-C-02-4583Collector Reactor Subsystem

Pressure control valve	\$650.00
Pressure switch	100.00
Product sampling system	500.00
Plumbing (valves, fittings, etc.)	500.00

Boiler Reactor Subsystem

Variacs for electric heaters (3 each @ \$150.00)	450.00
Temperature measurements (3 each @\$100.00)	300.00
Reactor Pressure Control Valve	650.00
Feed Pressure Control Valve	650.00
Steam Pressure Control Valve	650.00
Water Preheater	300.00
Condensate Storage tank	250.00
Plumbing (valve, fittings, etc.)	650.00
Insulation	<u>100.00</u>

Total \$5750.00

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

Upton, New York 11973

Department of Energy and Environment

(516) 345-4506

August 4, 1978

Dr. Arthur Ritter
Chemistry & Chemical Engineering Dept.
Stevens Institute of Technology
Hoboken, New Jersey 07030

Dear Art:

This is in response to your letter dated July 27, 1978, informing us that Task B of contract #EC-77-C-02-4583, will not be completed unless additional funds and time are provided by the DOE. Please be advised that of the two options presented we have chosen to not commit additional funds at this time and request that you complete as much of the contracted work as possible with the existing support.

The need for these data, in the heat pipe application, is obvious and it is a natural extension of the General Electric work. We assume that Sandia, Albuquerque, will see the value of completing this work in any follow-on program in FY 79.

Thank you for calling our attention to this problem and we feel certain that you have explored every possible alternative to avoid not completing all the tasks for which we have contracted.

Sincerely,

Matthew J. Rosso, Jr.

MJR:bl

cc: M. Bonner
A. Mezzina
F. Salzano
G. Strickland