SAND75-0651
Unlimited Release

Chemical Studies on SYNTHOIL Process

Quarterly Report for the Period Sept. 1 to Nov. 30, 1975

Arthur W. Mullendore, Morton L. Lieberman

Prepared by Sandia Laboratories, Albuquerque New Mexico 87115 and Livermore, California 94550 for the United States Energy Research and Development Administration under Contract AT (29-1) 789

Printed December 1975

Sandia Laboratories

SF 2900 Q(7-73)

When printing a copy of any digitized SAND Report, you are required to update the markings to current standards.

Issued by Sandia Laboratories, operated for the United States Energy Research and Development Administration by Sandia Corporation.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22151
Price: Printed Copy $5.50; Microfiche $2.25

SAND-75-0651
Unlimited Release

CHEMICAL STUDIES ON SYNTHOIL PROCESS

Quarterly Report for the Period
September 1 to November 30, 1975

A. W. Mullendore
and
M. L. Lieberman
Editors

Chemistry and Materials Characterization Department
and
Geo Energy Technology Department
Sandia Laboratories
Albuquerque, New Mexico 87115

December 1975

ABSTRACT

This is the first quarterly report of a two year program of a study in support of the Pittsburgh Energy Research Center's SYNTHOIL process for coal liquefaction. The overall program consists of three tasks: Task 1, "Catalyst Improvement" in which the mechanisms of catalyst deactivation and methods of reactivation will be explored; Task 2, "Ash Effects" in which the effect of the mineral content of coals on liquefaction will be assessed in autoclave experiments; and Task 3, "Kinetic Studies" in which a bench scale reactor will be set up to study the effects of process parameters on the kinetics of hydrodesulfurization and liquefaction. Progress in each task area is reported.

A variety of analytical techniques were evaluated for Task 1 with respect to their ability to analyze structural and compositional aspects of catalysts in the new, used, and regenerated conditions. Surface areas, pore volumes and pore size distributions were measured and correlated with the microstructural features revealed by electron microscopy. Approximately 50% of the pore volume in fresh catalyst exists as pores of less than 4.0 nm diameter and a similar result was obtained for a regenerated (air oxidized at 550°C) sample. Elemental compositions

were measured by seven instrumental analysis techniques. The bulk composition (Co, Mo, Al + Si and O) was in reasonable agreement with the manufacturer's data except that Ca (not specified) was detected at the 1% level. Concentration gradients were found for Co and Mo in the first two microns of the new catalyst surface. In the used and regenerated catalysts Ti and Fe contaminants displayed strong concentration gradients in the first 100 microns below the surface of the pellet. Chemical state information from x-ray photoelectron spectroscopy has tentatively identified the bonding state of Mo (oxide, sulfide or carbide) in the three catalyst conditions.

The design of the autoclave facility for Task 2 has been completed. The system will utilize a fail-safe concept which will permit operation within a manned laboratory area. All components have been ordered and construction of the autoclave enclosure is being completed in the Sandia shops. High sulfur Eastern bituminous coal samples from Illinois, Indiana, Kentucky, Ohio, Pennsylvania and West Virginia have been received. Proximate and ultimate analyses, by standard ASTM procedures, have been completed. Ash analyses, by semiquantitative emission spectroscopy, have been completed on several of these samples. The Indiana coal had an extremely high (1300 ppm) zinc content, probably the result of a high sphalerite (ZnS) concentration.

The design of the modularized reactor system for Task 3 is nearly complete. Some of the significant design features are high-pressure strain gauge transducers for pressure measurements, load cell gravimetric measurements of liquid transfer rates, intermediate position product withdrawal facilities for both preheater and reactor, and digitization of analog instrumentation outputs for a data acquisition system. Purchase orders have been initiated for all items with anticipated long delivery times and module assembly is scheduled. An outline of the experimental plan for the kinetics studies is presented and includes residence time measurements, preheater kinetics studies and reactor kinetics studies.

ACKNOWLEDGMENTS

Numerous individuals contributed to both the writing and technical content of this report. The task leaders and the technical contributors are identified at the beginning of Sections II.A, B, and C. Authorship is indicated by names in parethesis following section titles.

TABLE OF CONTENTS

	Page
I. INTRODUCTION (M. L. Lieberman)	5
II. RESULTS	
A. Task 1 - Catalyst Improvement (P.H. Holloway)	
1. Approach	11
2. Results and status	12
3. Discussion and summary	22
B. Task 2 - Ash Effects (B. Granoff)	
1. Approach	36
2. Results and status	37
3. Summary	40
C. Task 3 - Kinetic Studies	
1. Introduction	43
2. Approach (E. J. Nowak)	43
3. Results and status (R. M. Curlee)	48
III. SUMMARY (A. W. Mullendore)	55

I. INTRODUCTION (M. L. Lieberman)

Large quantities of natural gas and low-sulfur fuel oil are currently being burned in the United States in order to generate electric power. If coal could be burned in an environmentally acceptable manner, the higher grade fuels could be diverted to other uses. As a result, the Pittsburgh Energy Research Center (formerly part of the U.S. Bureau of Mines) initiated a program several years ago which has as its objective the conversion of coal into a clean, utility liquid fuel [1]. In this coal liquefaction process, called SYNTHOIL, coal is liquefied and hydrodesulfurized in a turbulent-flow, packed-bed, catalytic reactor.

In the SYNTHOIL process, hydrogen and a slurry of coal are passed through a preheater and then the reactor, which is packed with pellets of Co-Mo/SiO_2-Al_2O_3 catalyst. Typical reactor temperature and pressure conditions are 450°C and 2000-4000 psi, respectively. Sulfur and nitrogen are removed as gaseous hydrogen sulfide and ammonia, respectively. Previous work has shown that sulfur removal increases with increasing hydrogen consumption [1]. For economy, however, minimal hydrogen consumption, consistent with an environmentally acceptable fuel, is sought. The lifetime of the catalyst has not yet been determined as a function of processing conditions. Indeed, recent work [2] suggests that some mineral matter in the coal may itself be catalytic and consequently contribute to the reaction kinetics.

The SYNTHOIL development schedule [3] is shown in Table I. 1. Experimentation with the 100 lb/day process development unit has been completed and work with the $\frac{1}{2}$ ton/day unit is in progress. Further scale-up to 10 and 700 ton/day units is being planned while data are being generated by the $\frac{1}{2}$ ton/day unit.

Because the Pittsburgh Energy Research Center has the major responsibility for the process development described above, the Energy Research and Development Administration granted contracts to other organizations for support activities which would otherwise have to be delayed. Accordingly, Sandia Laboratories was awarded a $1,636,400, two-year contract entitled "Chemical Studies on SYNTHOIL Process". The program was initiated on September 1, 1975, although formal notification of funding did not occur until September 25, 1975. The program is comprised of three major tasks, identified as catalyst improvement (Task 1), ash effects (Task 2), and kinetic studies (Task 3). Objectives of the three tasks are to determine: Task 1 - the causes of catalyst deactivation and techniques to improve catalyst life in the SYNTHOIL process; Task 2 - the role of mineral matter in coal liquefaction and hydrodesulfurization; Task 3 - the kinetics of coal liquefaction and hydrodesulfurization. Under the first task, a wide variety of surface and bulk analytical instruments will be applied to the characterization of new, used, and regenerated catalysts. In Task 2, batch autoclave studies are to be performed in order to qualitatively and quantitatively assess the contribution of mineral matter on the liquefaction of various coals. For the third task, a bench-scale continous flow reactor, similar to that employed in the SYNTHOIL process, will be established and employed to generate kinetics data and to evaluate the influence of process parameters such as system pressure, reactor temperature, hydrogen flow rate, slurry residence time, and hydrogen sulfide concentration.

A breakdown of each of the tasks into various phases of the work is given in Table I.2.

REFERENCES

1. Akhtar, Sayeed, Nestor J. Mazzocco, Murray Weintraub, and Paul M. Yavorsky. SYNTHOIL Process for Converting Coal to Nonpolluting Fuel Oil. Energy Comm. 1, (1975) pp. 21-36.
2. Friedman, Sam, Paul M. Yavorsky, and Sayeed Akhtar. The Synthoil Process. Presented at the Clean Fuels From Coal, II Symposium, Chicago, Illinois. June 23-27, 1975.
3. Akhtar, Sayeed, James J. Lacey, Murray Weintraub, Alan A. Reznik, and Paul M. Yavorsky. The SYNTHOIL Process -- Material Balance and Thermal Efficiency. Presented at the 67th Annual A.I.Ch.E. Meeting, Washington, D.C. December, 1-5, 1974.

TABLE I.1. SYNTHOIL Development Schedule [3]

PROCESS DEVELOPMENT UNIT SIZE	REACTOR ID	COMMENTS
100 LB/DAY	5/16"	OPERATED FEB. 1971 - DEC. 1972
1/2 TON/DAY	1"	CONSTRUCTED NOV. 1972 - MAR. 1973 OPERATE APR. 1973 - JUNE 1976
10 TON/DAY	4" (AND 6")	CONSTRUCTED MAY 1975 - JUNE 1976 OPERATE JULY 1976 - JULY 1978
7000 TON/DAY	36"	PRELIM. DESIGN APRIL 1975 - JULY 1976
		DES. FOR CONST. AUG. 1976 - AUG. 1977 CONST. SEPT. 1977

TABLE I.2. Chemical Studies on SYNTHOIL Process Schedule

Task	Phase	Description	Initiation	Completion
1	1	Preliminary catalyst analyses	9/1/75	12/1/75
	2	Detailed analyses of catalyst removed from three reactor runs as a function of level in the reactor.	12/1/75	5/1/76
	3	Detailed analyses of catalyst recently removed from reactor. Formulate preliminary hypotheses regarding catalyst activation and deactivation.	5/1/76	9/1/76
	4	Test activation/deactivation hypotheses via controlled reactor studies.	9/1/76	9/1/77
2	1A	Installation of equipment.	9/1/75	12/1/75
	1B	Development of evaluation procedures and preliminary screening tests conducted.	12/1/75	3/1/76
	2	Autoclave studies on nominally five coals.	3/1/76	10/1/76
	3	Evaluation of naturally occurring catalytic agents.	10/1/76	9/1/77
3	1	Design, construction, and testing of bench-scale reactor.	9/1/75	6/1/76
	2	Generation of kinetic data.	6/1/76	9/1/77

II. RESULTS

A. Task 1 - Catalyst Improvement (P. H. Holloway)

Task Leader - P. H. Holloway

Technical Contributors - G. C. Nelson, D. H. Huskisson, D. H. Heinze, J. E. Houston, J. A. Borders, L. A. West, P. F. Hlava, J. F. Wolcott, J. R. Woodworth, C. H. Hills, G. T. Gay, N. L. Richardson, J. K. Johnstone, D. O. Clarkson G. T. Noles, T. M. Massis

1. Approach. The purpose of Task 1 is to determine the most probable deactivation mechanism(s) for the Harshaw 0402T cobalt and molybdenum oxide catalyst used in the SYNTHOIL process as developed at the Pittsburgh Energy Research Center. To accomplish this goal, various analytical techniques will be used to characterize the following properties of used as well as new and regenerated catalyst:

a) Structure:
Topography and particle size

b) Composition:
Elemental analysis (average and versus depth)
Lateral composition variations
Chemical state (average and versus depth)

c) Electronic structure

d) Catalytic activity

The experimental program is divided into four phases. The first phase consists of a preliminary analysis of new, and the used and regenerated catalyst from run number FB44* to detail catalyst structure and composition and to assess the applicability of individual analytic techniques. The data for this phase are detailed in the results section below.

*Pittsburgh Energy Research Center SYNTHOIL reactor run number.

The second phase consists of examining catalyst from the inlet, middle, and outlet regions from three different reactor runs. The properties of used catalyst will be compared to that of new catalyst and catalyst reactivated by various techniques. In phase three additional samples of catalyst from current reactor runs will be analyzed. The data from phases two and three will result in postulates for the dominant deactivation mechanism(s) and postulates for the most promising reactivation procedures.

The fourth phase involves evaluating different deactivation hypotheses via controlled experiments and to test different regeneration procedures. Other hydrodesurfurization catalysts may be investigated at this time. At the culmination of the experimental program the most probable mechanism(s) for deactivation of the SYNTHOIL catalyst will be defined. In addition, the most effective reactivation procedure will be reported.

2. Results and Status

a) General. The "CoMo - 0402T "catalyst is described by Harshaw as containing 3% CoO and 15% MoO_3 (by weight) on a silica promoted alumina support. The amount of silica is not specified nor are proprietary details on catalyst manufacture and processing techniques. The catalyst is in the form of cylindrical pellets 3.18 mm (1/8 in) in diameter and 3.18 mm (1/8 in.) long. Other manufacturers data on the fresh catalyst give a surface area of 180 m^2/g, an apparent bulk density of 1 g/cm^3 and a void volume of 0.4 cm^3/g. The surface area per unit weight of a sphere of material increases as the sphere diameter decreases, and a surface area of 150 m^2/g is equivalent to a sphere of Al_2O_3 10 nm in diameter. As we shall see, this figure agrees quite well with our initial particle size measurements for these catalysts. It is also interesting to consider that for

such a large specific surface area, the molybdenum oxide would constitute only about one layer of atoms on these Al_2O_3 spheres if it were uniformly distributed on the surface.

The catalyst has been examined in the new, used (FB44) and regenerated condition. The Pittsburgh Energy Research Center run FB44 used a West Virginia, Ireland Mine coal at a reactor temperature of 450°C and a pressure 4,000 psi. Several different regeneration techniques were attempted including solvent extraction, low temperature ashing, and heating in air. The technique of heating in air (with the oven pre-heated) was the most successful and one condition (550°C for 2.5 h) has been selected for extensive analysis as detailed below.

b. Structure. Transmission electron microscopy has been used to study the particle size and crystalline state of the catalyst. Transmission samples were prepared by crushing the catalyst pellet and incorporating the crushed material in an epoxy resin mount. Slices ~ 100nm thick were then microtomed from the resin stock for examination. Using dark field imaging, the Al_2O_3 crystallite size was measured to range between ~ 4 to 15 nm independent of whether the catalyst condition was new, used, or regenerated. This crystallite size is consistent with broadening of the electron diffraction pattern, and with the fact that x-ray diffraction detected no crystalline Al_2O_3 phase. It is also consistent with the surface area reported in Table II.A.1.

Apparently small 10nm crystallites of Al_2O_3 combine to form elongated particles. This is indicated in Figure II.A.1a, b, and c which show the transmission electron photomicrographs of new, used, and regenerated catalyst.

A rough acicular structure with lengths of ~ 100 nm is observed for the new and regenerated catalyst. The contrast which reveals this structure presumably results from porosity in the catalyst, and the reduction of contrast in the used catalyst probably indicates the presence of retained organic matter in the catalyst pores.

The grain size of ~ 100nm is consistent with scanning electron microscopy date. Typical secondary electron images of the outer and fracture surfaces of new and used catalysts are shown in Figure II.A.2. The smallest detectable particles are ~ 100nm in all photographs, but these small particles combine to form larger particles of ~ 1μm. In photographs at lower magnification (Figure II.A.3) grains with diameters of ~ 50 μm can be seen. This grain size can be seen in catalysts from all conditions, but details on the 100 nm particles are difficult to resolve in used catalysts, apparently because organic matter is retained in the pores which reduces the number of edges visible. In addition, some abrasion removal of particles from the outer surface of used catalysts may have occurred.

Similar particles can be seen on a polished cross-section of new, used, and regenerated catalyst pellets as shown in Figure II.A.3. In polished areas, very little detail is observed. Again however, detail is poor in used catalysts because of retained organic matter.

Retained organic affects the surface area and pore size distribution measurements as well as the electron microscopy data. The surface area of used catalyst is only 11 m^2/g compared to 136 m^2/g and 133 m^2/g for new and generated catalysts, respectively, as measured by the Brunauer-Emmett-Teller technique. Thus, the air regeneration restores the surface area of the catalyst. Other

regeneration techniques such as low temperature ashing and solvent extraction did not significantly restore the surface area.

Both the Brunauer-Emmett-Teller techniques and mercury porosimetry are being used to study the pore size distribution. Mercury porosimetry data in Figure II.A.4 indicate that 55% (by volume) of the pores in new catalyst have an effective diameter of $\lesssim$ 10nm. Preliminary data by the Brunauer-Emmett-Teller technique indicates that most of the pores have effective diameters of $\lesssim$ 3.5nm. In either case, these data are quite consistent with the catalyst support being composed of Al_2O_3 crystallites of $\sim$ 10nm diameter.

The change in slope of the pore size distribution at 100 to 200nm (Figure II.A.4) indicates that $\sim$ 5% of the pores have an effective diameter of this size. This is consistent with the observation of Al_2O_3 particle from 100nm to 1 μm in diameter. In addition, a significant number of pores have an effective diameter $\gtrsim$10 μm consistent with the 50 μm diameter grains. Thus, the topography and pore size data are in quite good agreement for new catalyst.

Good agreement is also observed for regenerated catalyst. An Al_2O_3 crystallite size of $\sim$ 10nm is consistent with the observed broadening of the diffracted beams in the electron microscope. The patterns indicate the Al_2O_3 is predominately η-Al_2O_3 with possibly some γ-Al_2O_3. Diffraction patterns from other unidentified randomly distributed phases have been observed from new, used, and regenerated catalysts. Diffraction patterns from the crust of regenerated samples were obtained and they most closely matched that of an aluminum silicate, $Al_2Si_2O_6(OH)_2$. Crystalline diffraction patterns have not been obtained using x-rays, presumably because the crystallite sizes are too small to give sharp diffraction lines.

c. Composition. Compilations of elements found on new, used, and regenerated catalysts are shown in Tables II.A.2 and 3. Data from Rutherford back-scattering, Auger electron spectroscopy, ion scattering spectroscopy, x-ray fluorescence analysis on the scanning electron microscope, and semiquantitative emission spectroscopy are shown in Table II.A.2. These data are self consistent in that Mo, Co, and Al are seen by all techniques in all samples. Because of interference between the Al and Si signals, Rutherford back-scattering cannot detect the Si but all other techniques detect Si in all samples. Calcium is generally observed on the outer surface of new, used, and regenerated catalyst, but the Ca signal is weak or not observed on surfaces exposed by fracturing the pellet in half with a razor blade.

The Rutherford back-scattering data are quantitative and therefore have been compared to the data reported by Harshaw. The weight percentages have been converted to atomic percentages assuming only MoO_3, CoO, and Al_2O_3 are present. SiO_2 was known to be present but the quantity was unknown; Ca was unknown prior to analysis. Comparing the values measured by back scattering on the fractured surfaces of new and regenerated samples, the concentration of Mo and Al + Si is about as expected while the Co is somewhat higher than expected.

The back-scattering data for Mo, Co, Al, Si, and Ca are consistent with the qualitative data from Auger electron spectroscopy, ion scattering spectroscopy, and x-ray fluorescence analysis on the scanning electron microscope, and with the semiquantitative data from emission spectroscopy (the pellets were crushed for emission spectrographic analysis). They are also generally consistent with the quantitative x-ray fluorescence data from the electron

microprobe shown in Table II.A.3. These data are averages of data taken at discrete points on a cross-section polished parallel to the flat ends of the cylindrical pellets. The initial spot analyzed was approximately 2 μm from the outer surface and the analyzed spot was then moved toward the center of the pellet in steps of 10 or 20 μm for a total traverse of between 90 μm and 240 μm. The data are analyzed by an iterative digital computer technique in terms of compounds, with the weight percent of a detected compound being reported. The data in Table II.A.3 show that the sum of the concentration of Al_2O_3 (~ 71%) and SiO_2 (~9%) agree quite well with the expected value (~82%) for the new and regenerated catalysts. The concentration of MoO_3 is about as expected (15%) but the concentration of CoO is somewhat lower than expected (observe ~ 2%; expect 3%). This is contrary to the Rutherford back-scattering data in Table II.A.2 which showed Co higher than expected (fractured surface of new and regenerated catalyst). The difference cannot be explained at this time.

The quantitative analysis for the used catalyst yielded data different from that for the new and regenerated condition. This is a result of large concentrations of carbon detected by the Rutherford backscattering analysis and of concentrations of sulfur detected by the electron microprobe analysis. Both C and S were easily detected by the surface sensitive techniques and, in addition, significant concentrations of Fe and Ti were detected in the used catalyst. Quantitative electron microprobe data indicated concentrations of Fe and Ti oxides of ~ 0.5% in the outer surface layer. Significant concentrations of Fe and Ti and lowered concentrations of C and S were detected in the regenerated condition. In addition, lower concentrations ($\gtrsim$ 0.1%) of several other elements were found by the electron microprobe and emission spectroscopy among which were Na, K, Mg, and B.

To summarize the average elemental composition data, the new and regenerated catalysts contained approximately 71% Al_2O_3, 15% MoO_3, 2-4% CoO, 9% SiO_2, and 1% CaO (by weight). The concentration of C, Fe, Ti, and S increased significantly in the used as compared to the new catalyst, but regeneration reduced the C and S concentrations. We turn next to a discussion of depth dependence of elemental composition.

The data in Table II.A.2 show that Rutherford back-scattering detected more Mo and Co on the outer catalyst surface as compared to the fracture surface. By observing decreasing signal yields versus depth, the Mo and Co were shown to be enriched over the first 2 μm of a new catalyst pellet. This surface enrichment of Co and Mo was not substantiated by the electron microprobe data, perhaps because either the first microprobe analysis point was ~ 2 μm from the surface, or because of scatter in the data. Scatter in the microprobe data will be reduced in the future by scanning the beam approximately parallel to the pellet surface.

The surface analytic techniques indicated a preferential enrichment of the outer catalyst surface in Ca, but the electron microprobe data do not support this conclusion. Again, scatter in the data may explain this discrepancy and in addition, some evidence for a non-homogeneous lateral distribution of Ca exists (see below).

Data from all of the analytic techniques indicate that the Fe and Ti in the used and regenerated catalyst is preferentially located near the outer catalyst surface. This is indicated in the Rutherford back-scattering, Auger electron spectroscopy, ion scattering spectroscopy, and scanning electron microprobe, and the data are shown in Figure II.A.5. This figure shows the

weight percent concentration of Ti as TiO_2 and Fe as FeO versus distance from the outer surface for used and regenerated catalyst. Both Ti and Fe decrease an approximately exponential manner with distance into the catalyst. The regenerated sample has more Ti on the surface presumably due to the segregation of Ti from the bulk. Very crude estimates of the values of the 1/e distance are 30 μm for Ti and 50 μm for Fe.

These data are consistent with the emission spectroscopy analysis (see Table II.A.4) of the crust material formed on the catalyst pellet as a result of the 550°C, 2.5 hrs air heat treatment. In addition to finding Co, Mo, and Al in the crust, large amounts of Ti, Fe, Si, Ca, K, and Mg were also observed along with several other elements in lower concentrations.

To summarize the elemental composition versus depth data, there is evidence that the Co and Mo are enriched over the outer 2 μm of a catalyst pellet. There is also evidence that Ca is preferentially located in the outer surface layer of the pellet, but it is definitely established that the concentration of Fe and Ti is a maximum near the outer surface and near zero at 100 μm into the catalyst pellet. Elemental analysis versus depth by discretely moving the Auger electron analysis spot is in progress. In order to accomplish analysis versus depth with techniques probing a larger size area (both Rutherford back-scattering and secondary ion mass spectroscopy require $\sim 1\ mm^2$ area for analysis), a technique for reproducibly removing as little as 2.5 μm from the flat ends of the cylindrical pellets has been developed. In addition, a sample holder for polishing catalyst surfaces without any type of permanent mounting (e.g. epoxy, etc.) has been designed. Preliminary data on sputtering to determine depth profiles of composition indicate that the

variations occur over such large distance that ion sputtering is ineffective as a profiling tool. Lateral composition variations have been studied using x-ray fluorescence analysis on both the scanning electron microscope and on the electron microprobe. In general, the Co and Mo are associated indistiguishably with the Al indicating they are distributed uniformly throughout the Al_2O_3 grains. In voids between grains where Co and Mo are of reduced intensity (Figure II.A 6 the Al signal is also reduced. There are, however, isolated regions where either Co or Mo or both Co and Mo are concentrated and an example of a Mo rich region is shown in Figure II.A.6. In addition, isolated regions are found where Si and Ca are concentrated. Both Co/Mo and Si/Ca rich regions are observed on new, used, and regenerated catalysts.

The C in used catalyst seems to be localized in pores. This is indicated by less structure being observed in secondary electron examination. The Ti is localized to surface pores as shown by x-ray fluorescence mapping of used catalyst. In addition, Ti is in sufficiently large particles such that moving the 1 μm diameter probe beam to different spots causes large variations in the amount of Ti detected. For example, the Ti concentration at the outer surface of used catalyst in three different locations was found to be 2.6%, 0.63%, and 7.01% by the electron microprobe. Contrary to this, the Fe concentration did not vary widely from one spot to another indicating less lateral variation and possibly smaller particle size.

Preliminary scanning analysis by Auger electron spectroscopy has not detected large lateral composition variations suggesting the lateral composition variations are on a scale smaller than the resolution of the present instrument. Further work is in progress.

Chemical state data have been obtained with x-ray photoelectron spectroscopy (also known as electron spectroscopy for chemical analysis - ESCA) and with secondary ion mass spectroscopy. Photoelectron measurements indicated the cobalt was in an oxidized state for all conditions and literature data indicates this is probably a cobalt aluminate ($CoAl_2O_4$). The Ca, Si, and Al are also in oxidized states as indicated by photoelectron, secondary ion, and Auger electron measurements. Photoelectron measurements show the Mo is in an oxide (probably MoO_3) in the new catalyst but in both an oxide and sulfide (probably MoO_3 and MoS_2) in the used condition (see Figure II.A.7). In the regenerated condition (550°C, 2.5 h, air), Mo on the outer surface is oxidized (MoO_3), but Mo on the fracture surface is probably combined both in an oxide and in a carbide (see Figure II.A.7). Titanium appears to be bound as TiO_2 in all cases, while the bonding state of Ca may be changed by the regeneration process.

Secondary ion data are preliminary, but are consistent with Co remaining in the same oxide state and Mo changing states for used catalysts. However, the compound MoS_2 was not identified and further work is necessary.

d. Electronic structure. There has been no significant data to date on the electronic structure of the various constituents of the catalyst. Auger electron spectroscopy measures this only crudely and considerable development work would be required before the electronic structure could be extracted. The most promising technique to extract electronic structure is soft x-ray appearance potential spectroscopy and the present instrument is being modified to analyze the catalyst. These modifications should be completed within two months, and collection of data will follow immediately.

e. Catalytic activity. The relative activity of a catalyst is a measure of the extent of deactivation or regeneration. By measuring the catalytic activity, important information can be obtained concerning the deactivation mechanisms and the suitability of various regeneration schemes. To test the activity of the catalyst, a small reactor, which uses a gas chromatograph detection scheme, is being set up. The design of this reactor is similar to the one used at the Pittsburgh Energy Research Center for similar measurements. The new, used, and regenerated catalysts will be tested for the ability to a) crack, b) hydrogenate, and c) desulfurize hydrocarbons. The reactor should be operational within the next two weeks.

3. Discussion and summary. The objective of Phase 1 of this task, as outlined in the contract's Statement of Work, is to perform evaluations of appropriate analytical techniques useful in evaluating the physical structure and chemical composition of the catalyst. These evaluations have been completed. In addition, an attempt to relate electronic structure to activity is desirable and, further, a standardized measurement of activity is necessary for the evaluation of catalyst deactivation and reactivation. Therefore, we have incorporated these measurements into our future program.

With respect to the analytical techniques we have evaluated in the first quarter, we will continue to use both scanning and transmission electron microscopy to characterize the topography and particle size of the catalyst. Even though the scanning electron microscope used in this study has a resolution of 10nm, it is difficult to achieve this high resolution with a rough insulating substrate. Therefore, transmission electron microscopy is a very valuable asset.

The gas adsorption technique (Brunauer-Emmett-Teller) will continue to be

used to determine surface area of the catalysts and both the technique and mercury porosimetry will be used to determine the pore size distribution. Gas adsorption is best suited for pore sizes less than 20nm while mercury porosimetry is best suited for pores greater than 20nm; therefore they are very complementary techniques.

The crystalline state of the catalyst will be determined using electron diffraction rather than x-ray diffraction. Apparently, the crystallite size is generally too small to give discernible reflections by x-ray diffraction.

The elemental composition of the catalyst will be determined using Rutherford back-scattering, x-ray fluorescence analysis, Auger electron spectroscopy, ion scattering spectroscopy, and emission spectroscopy. Again, these are complementary techniques since both Rutherford back-scattering and x-ray fluorescence are quantitative, Auger electron and ion scattering spectroscopy are sensitive to both light and heavy elements near the surface, and emission spectroscopy is sensitive to elements in low concentrations. Some procedural modifications are appropriate such as improved standards, scanning during analysis to negate lateral composition variations, minimizing probing beam effects, etc. X-ray flourescence will also be used to investigate the lateral composition variations, primarily through the elemental mapping mode on either the electron microprobe or the scanning electron microscope. Initially mapping with 100 second data accumulation times indicate that longer accumulation times may generally be required.

The chemical state of the catalyst will be examined using X-ray photoelectron spectroscopy. Photoelectron chemical state data uniquely reflected that the regenerated catalyst investigated was not returned to the original

chemical state by regeneration. The 550° C heat treatment appeared to cause formation of a molybdenum carbide rather than an oxide. X-ray photoelectron data will be supplemented with secondary ion mass spectroscopy data as a check of its validity.

Depth analysis will be accomplished either by a stepped point analysis or by a mechanical surface removal. Sputtering appears to be of limited use because of the large distances over which compositions variations occur. The stepped point analysis will be accomplished using X-ray fluorescence or Auger electron tehcniques. These techniques and all others will be used with mechanical surface removal.

TABLE II. A. 1.

Apparent Bulk Density and Void Volume of
New, Used, and Regenerated Harshaw 0402T Catalyst

	Apparent Bulk Density (Packed) (g/cm^3)	Void Volume (cm^3/g)	Surface Area (m^2/g)
Nominal	1.0	0.4	180
New	1.13	0.30	136
Used	1.27	0.20	11
Regenerated	--	0.31	133

TABLE II. A. 2

Compilation of Elmental Analyses on New, Used and Regenerated Harshaw 0402T Catalysts

Element	Nominate Composition (%)[1]	New-Outer[6]			New-Fracture[7]				Used-Outer			Used-Fracture				Regenerated-Outer			Regenerated-Fracture		
		RBS[2] (%)	AES[3]/ ISS	XFA[4]	RBS (%)	AES/ ISS	XFA	ES[5] (ppm)	RBS (%)	AES/ ISS	XFA	RBS (%)	AES/ ISS	XFA	ES (ppm)	RBS (%)	AES/ ISS	XFA	RBS (%)	AES/ ISS	ES (ppm)
Mo	2.3	8.3	s	s	2.2	s	i	M	D	i	s	1.3	i	i	M	4.2	s	i	2.0	s	M
Co	0.9	2.0	w	i	1.2	w	i	M	D	w	w	0.9	w	w	M	2.0	w	w	1.6	w	M
Al	>35.9	>20.9	s	s	>33.5	w	s	M	D	s	i	>19.1	s	i	M	>21.1	s	s	>32.4	s	M
Si			i	vw		i	w	M	D	i	i		w	w	M		s	s	-	w	M
O	60.9	65.2	s	-	63.1	s	-	-	D	s	-	33.8	s	-	-	72.6	s	-	62.2	s	-
Ca		3.6	s	w	-	-	i	520	D	i	w	-	w	w	520	-	i	i	0.9	w	630
C		D	w	-	D	-	-	-	D	s	-	42.4	s	-	-	D	w	-	D	w	-
S		-	-	-	-	-	-	-	D	s	-	-	s	-	-	-	w	-	-	w	-
P		-	i	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ti		-	-	-	-	-	-	250	D	i	i	-	w	-	1000	-	i	i	-	vw	1600
Fe		-	-	-	-	-	-	1000	-	s	s	-	s	-	1000	-	i	i	-	vw	1000
B		-	-	-	-	-	-	25	-	-	-	-	-	-	330	-	-	-	-	-	1000
Na		-	-	-	-	-	-	500	-	-	-	-	-	-	500	-	-	-	-	-	1000
K		-	-	-	-	-	-	20	-	-	w	-	-	-	100	-	-	w	-	-	60

[1]Atomic percentage from C. L. Thomas, Catalytic Processes and Proven Catalysts (Academic Press, NY, 1970)

[2]RBS=Rutherford Back-Scattering; D=detected; atomic percent.

[3]AES=Auger Electron Spectroscopy, ISS=Ion Scattering Spectroscopy, s-strong signal, i=intermediate signal, w=weak signal, vw=very week signal

[4]XFA=X-ray Fluorescence Analysis on the electron microscope.

[5]ES=Emission Spectroscopy; M=major element; ppm=parts per million by weight (semiquantitative).

[6]Outer=outer surface of the as received catalyst pellet.

[7]Fracture-surface of catalyst pellet exposed by fracturing with a razor blade for RBS, AES/ISS, XFA, or exposed by crushing for ES.

TABLE II. A. 3.

Emission Spectroscopy Analysis of Crust Resulting from Regeneration (550°C, 2.5 h, air)

Element	Concentration (ppm)
Mo	25,600.
Co	6300.
Al	M[1]
Si	80,000.
Ca	10,000.
Ti	M[1]
Fe	80,000.
B	1600.
Na	1000.
K	10,000.
Ga	1600.
Ba	400.
Cr	630.
Sr	1300.
Cu	1000.
Mg	10,000.

[1] M = major element

TABLE II. A. 4.

Electron Microprobe X-Ray Fluorescence Analysis of Catalysts (weight percent)

Compound	Nominal[1] Composition	New[3]	Used[4]	Regenerated[5]
Al_2O_3	82[2]	71.9	65.6	70.5
MoO_3	15	14.4	13.4	15.6
CoO	3	1.8	1.9	2.2
SiO_2	( )[2]	10.5	5.5	6.8
CaO	--	0.4	0.4	0.6
SO_3	--	0.8	12.4	2.1
TiO_2	--	0.0	0.4	1.8
FeO	--	0.0	0.3	0.2
K_2O	--	0.1	0.1	0.1
Na_2O	--	0.2	0.2	0.5
ZnO	--	0.0	0.0	0.1
P_2O_5	--	0.1	0.2	0.2
MgO	--	0.1	0.2	0.1
NiO	--	0.0	0.0	0.1
CuO	--	0.0	0.0	0.0

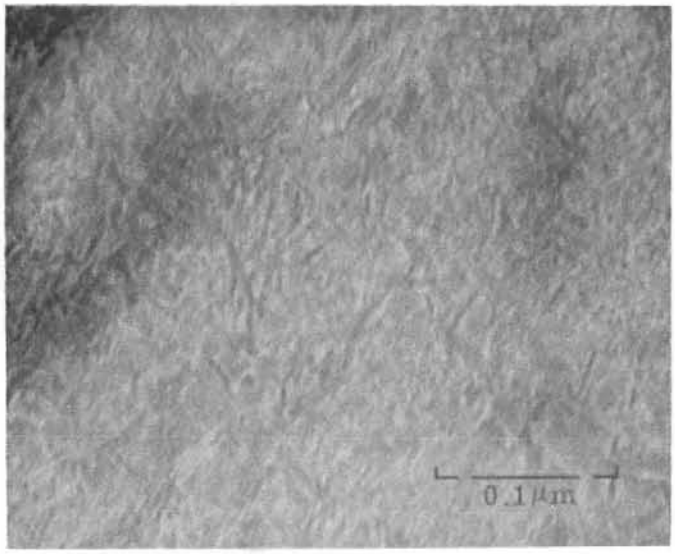
[1] Reported by C. L. Thomas, Catalytic Processes and Proven Catalysts (Academic Press, N.Y., 1970).

[2] Al_2O_3 percentage includes the unspecified weight percentage attributable to SiO_2.

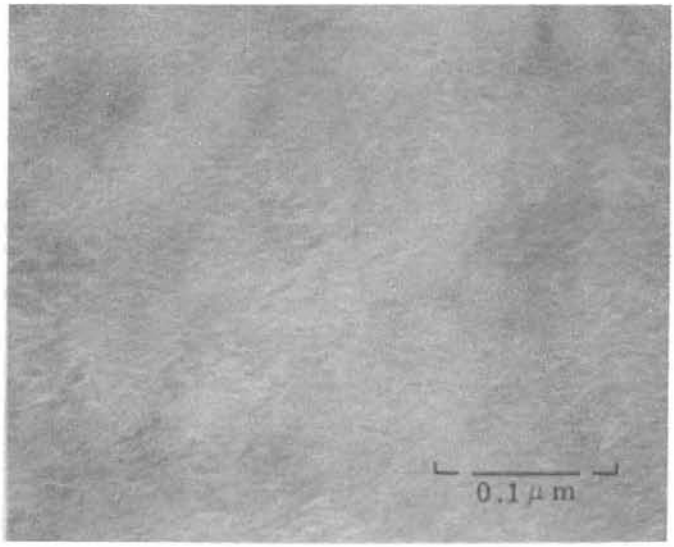
[3] Average of 22 sets of data.

[4] Average of 60 sets of data; C was not measured.

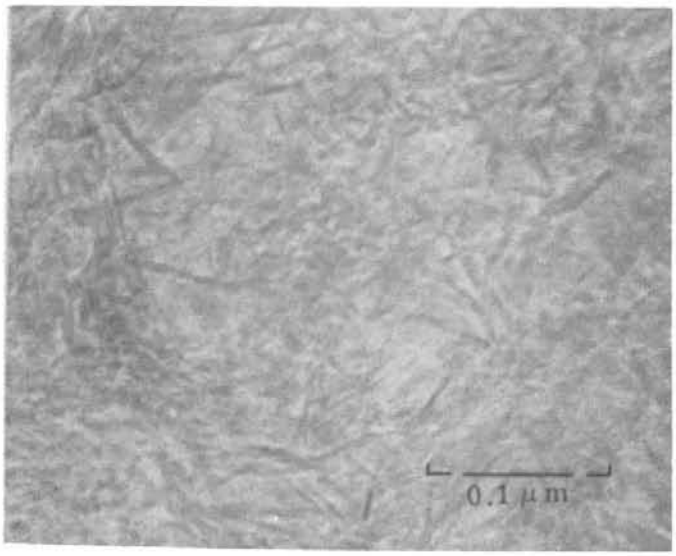
[5] Average of 25 sets of data.



a) New

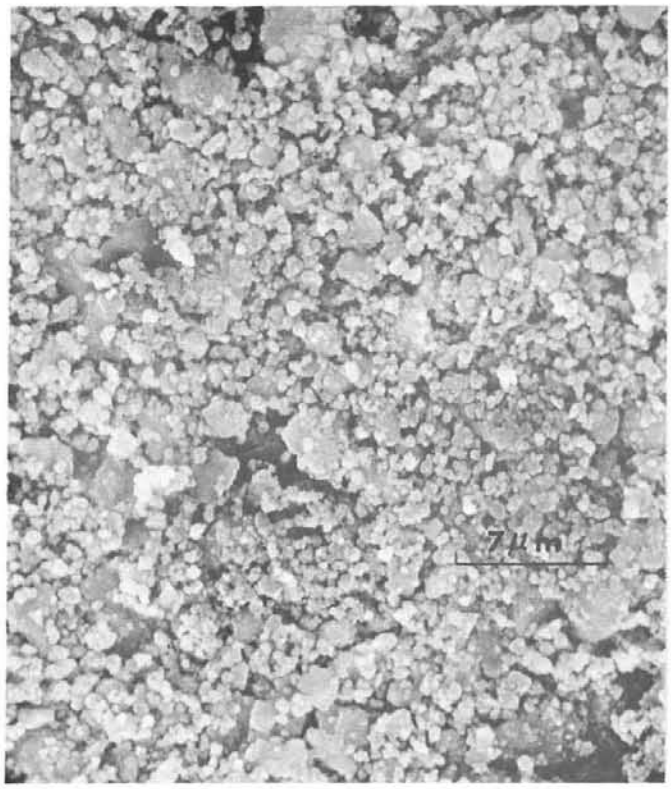


b) Used



c) Regenerated

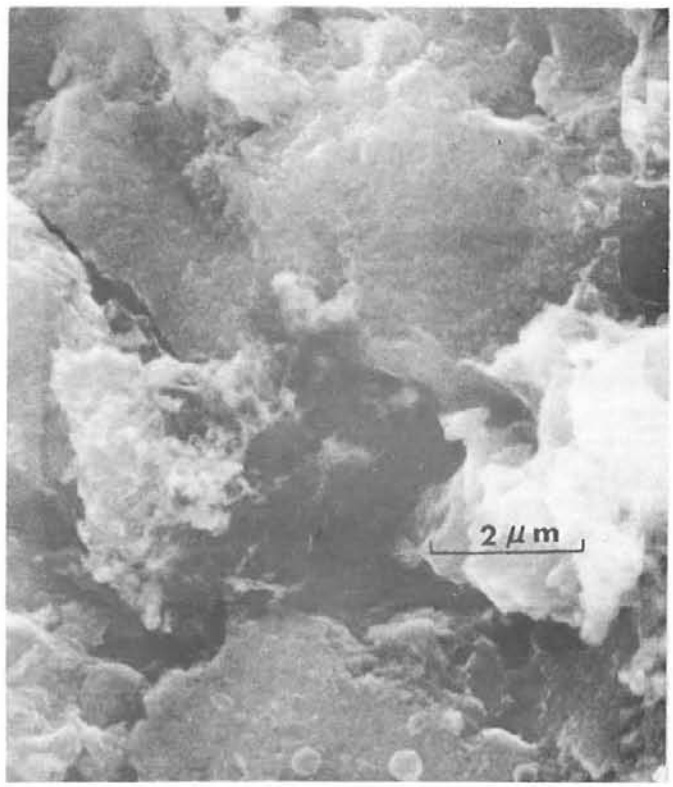
Figure II.A.1. Transmission electron photomicrographs of catalysts showing a coarse, irregular structure in the new and regenerated conditions, but a lack of structure in the used condition.



a) New Outer Surface

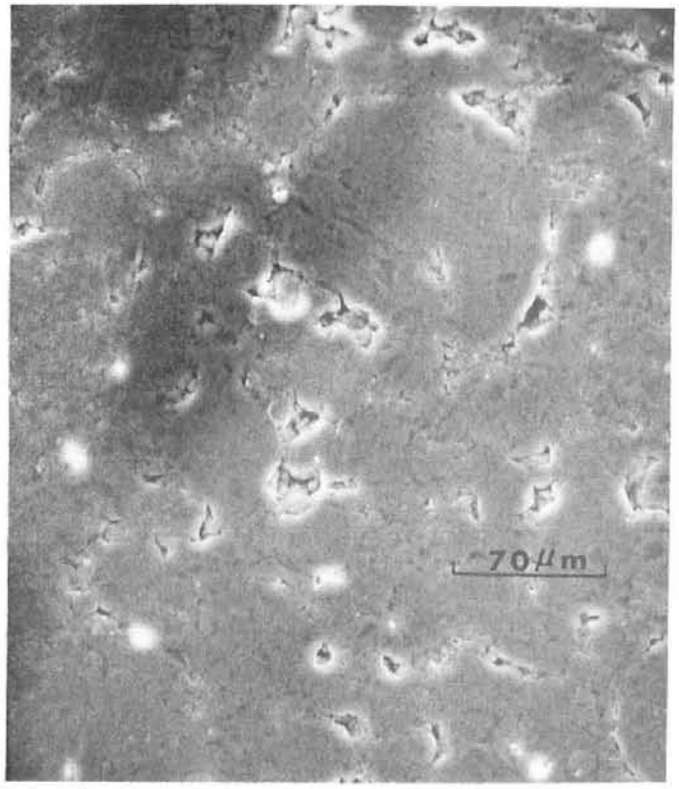
b) New Fracture Surface

c) Used Outer Surface

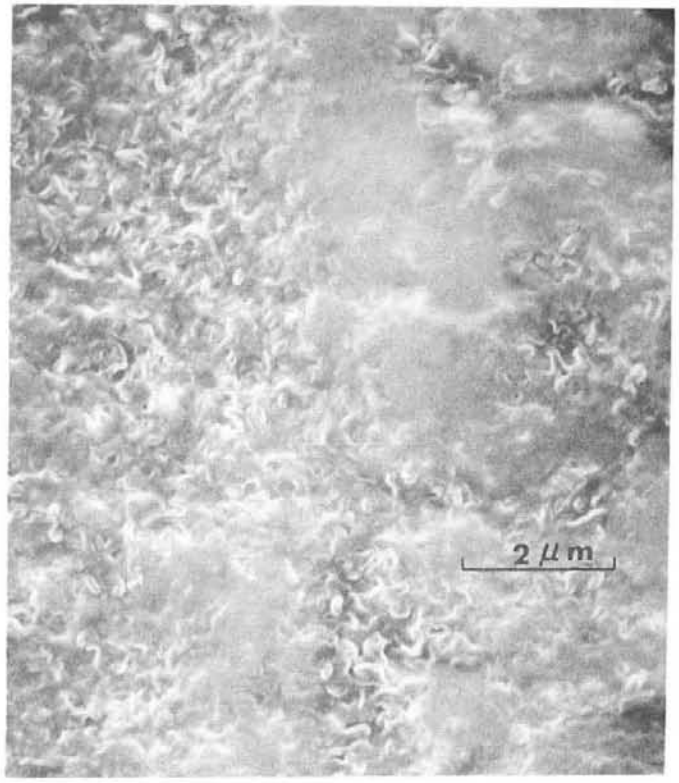


d) Used Fracture Surface

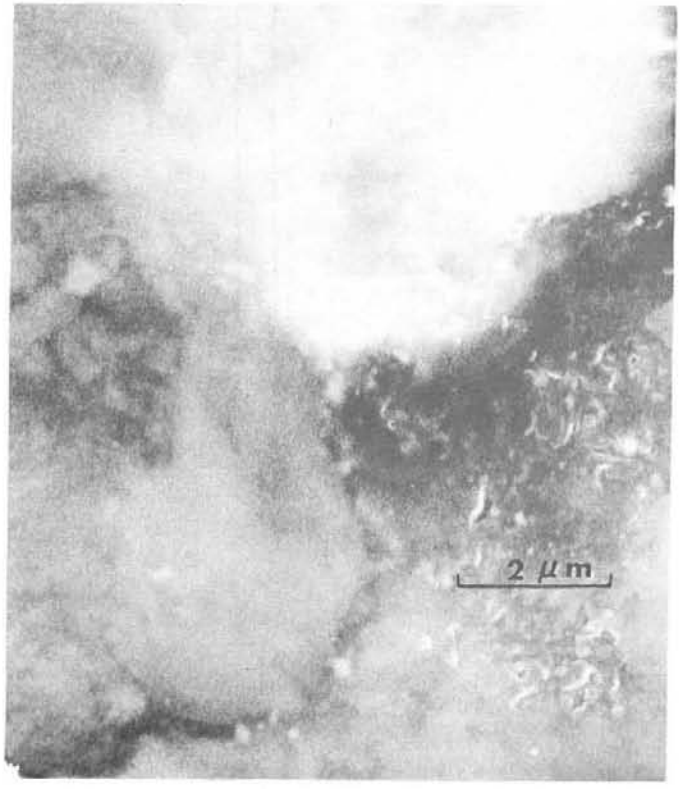
Figure II.A.2. Secondary electron photomicrographs of new or fractured surfaces of new and used (FB #44) Harshaw 0402T catalyst.



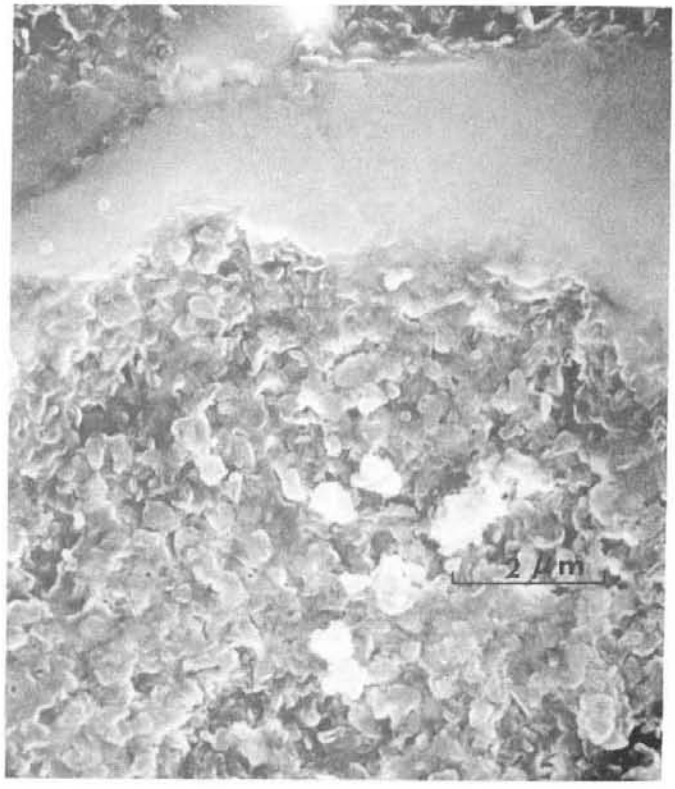
a) New



b) New



c) Used



d) Regenerated

Figure II.A.3. Secondary electron photomicrographs of polished cross sections of new, used (FB #44), and regenerated (550°C, 2.5 hrs, air) Harshaw 0402T catalyst.

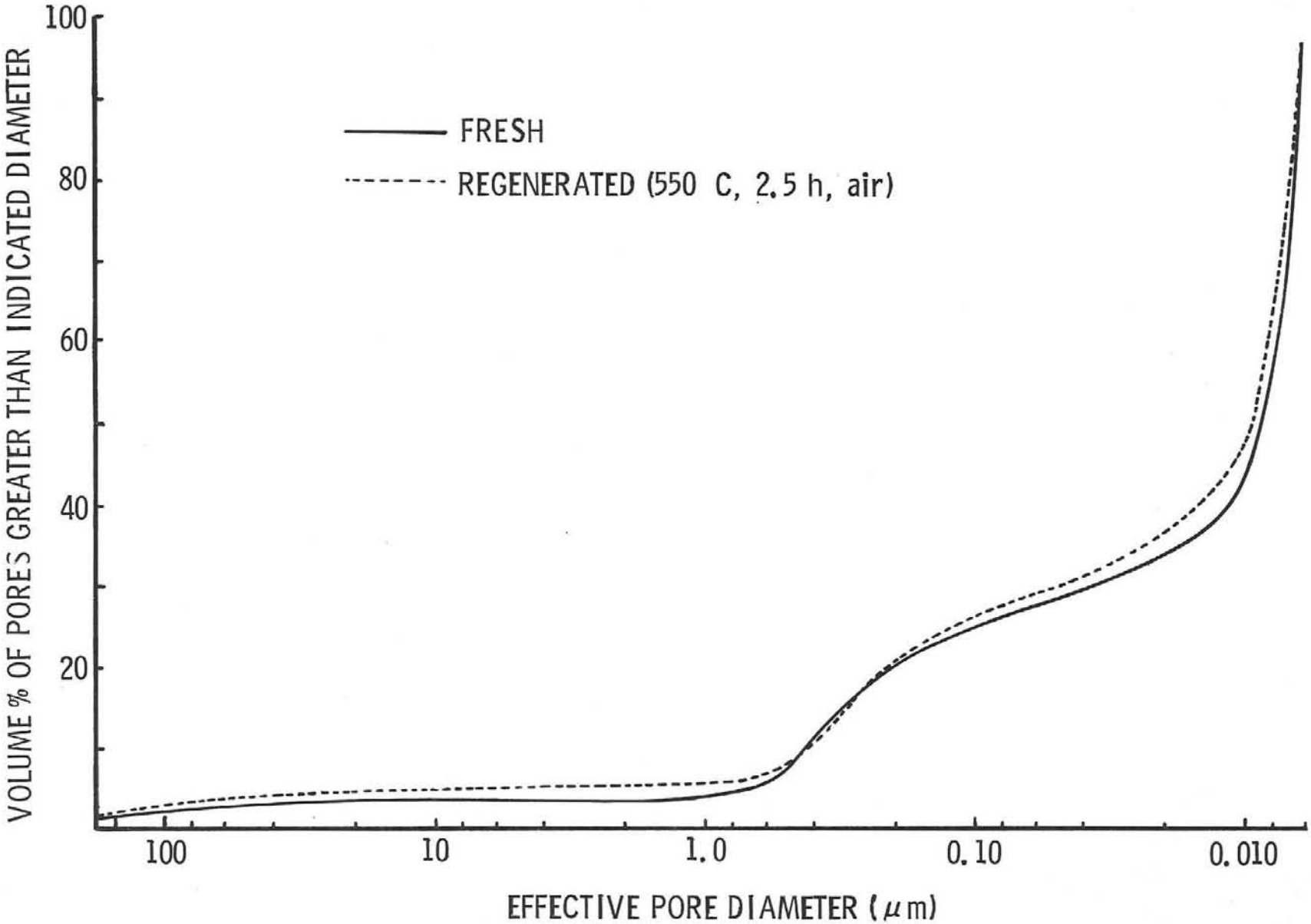


Figure II.A.4. Cumulative volume percent of pores with a diameter greater than the value indicated on the abscissa.

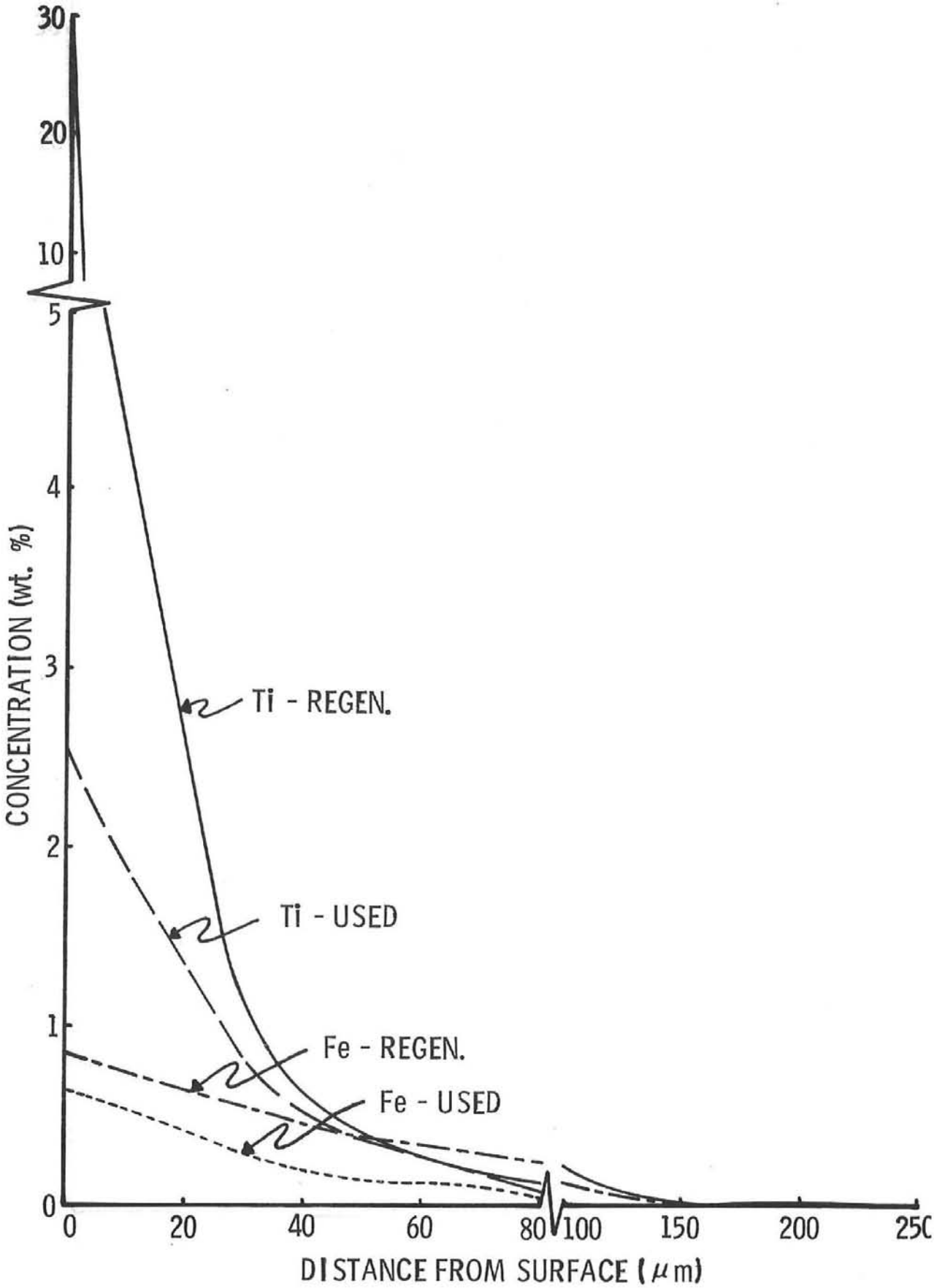


Figure II.A.5. Concentration of Fe or Ti in used or regenerated catalyst versus distance from outer catalyst surface as measured on the electron microprobe.

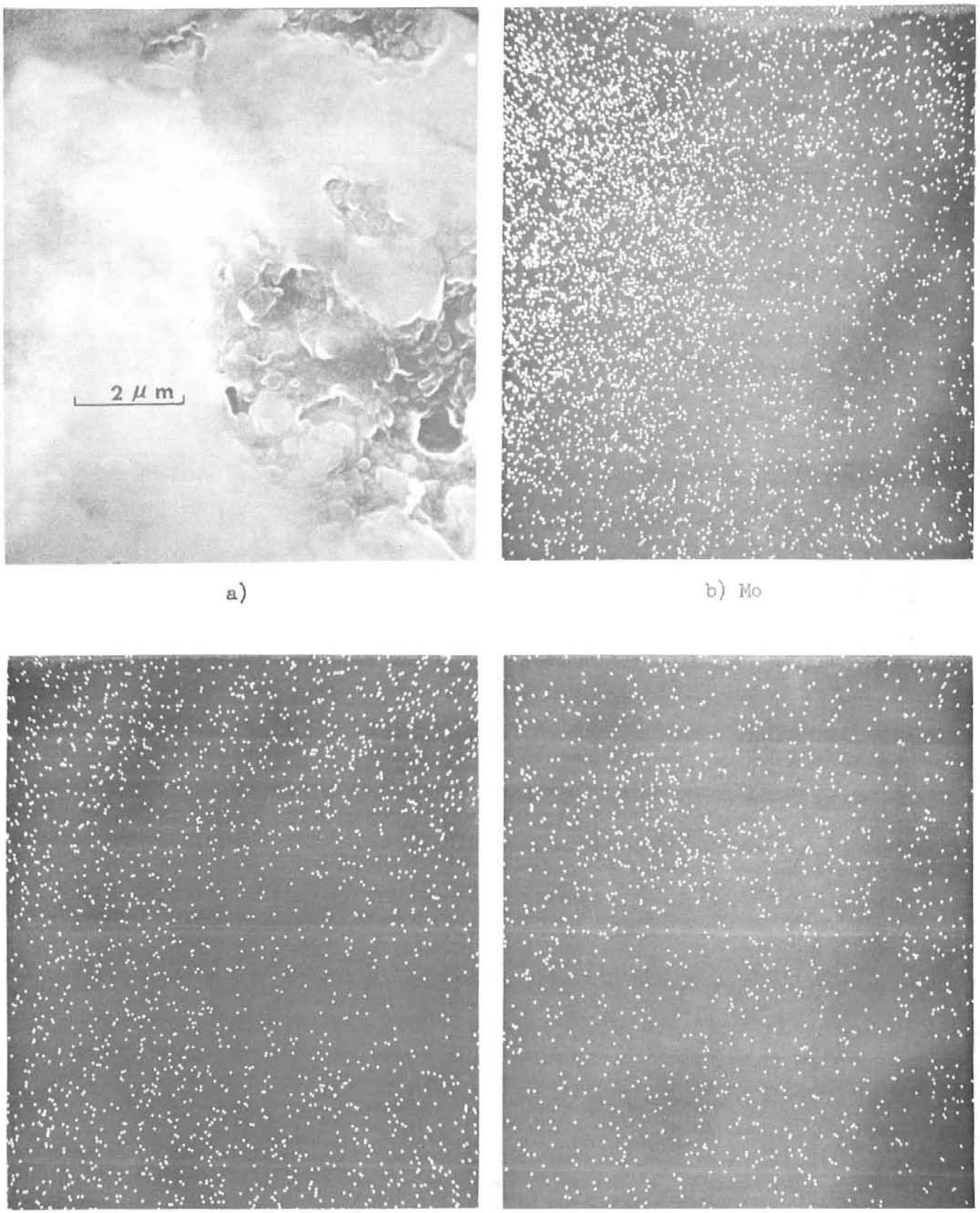


Figure II.A.6. Secondary electron photomicrograph (a) of new Harshaw 0402T catalyst with x-ray fluorescence mapping of Mo (b), Al (c), and Co (d) showing a Mo-rich region.

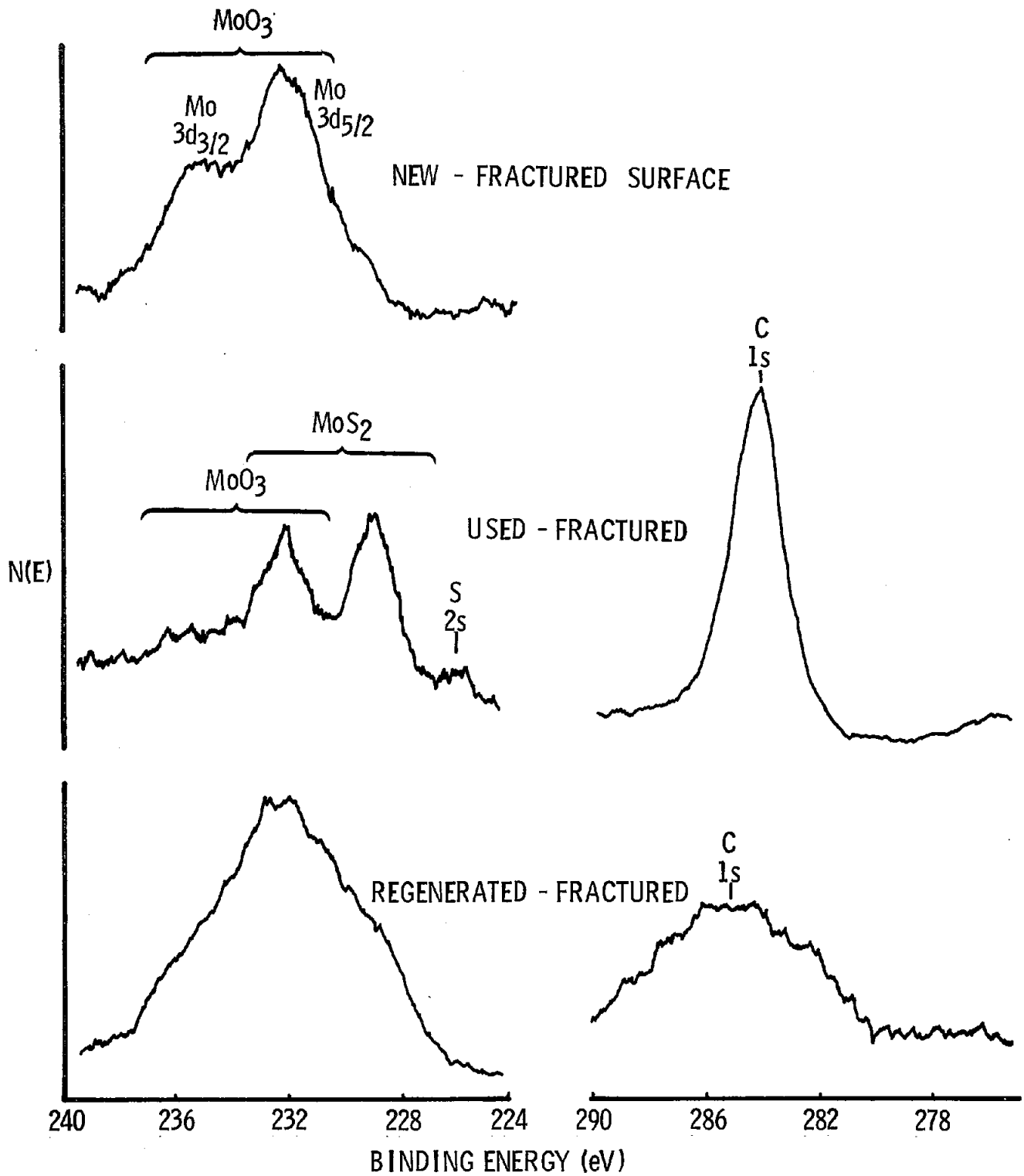


Figure II.A.7. Mo and C x-ray photoelectron spectra from the fractured surface of new, used, and regenerated catalyst. The Mo is bound as an oxide in the new catalyst, as an oxide and sulfide in the used catalyst, and probably as an oxide and carbide in the regenerated catalyst.

B. Task 2 - Ash Effects (B. Granoff)

Task Leader: B. Granoff

Technical Contributors: L. P. Baudoin, J. M. Freese, J. R. Woodworth, N. L. Richardson, E. J. Graeber, G. T. Gay, G. T. Noles

1. Approach. The objective of Task 2 is to determine the catalytic effects of naturally occurring mineral matter on the conversion of high-sulfur coals to low-sulfur liquid products. The work will primarily involve Eastern bituminous coals, but some Western coals (both bituminous and sub-bituminous) will be included for comparison. The technical approach will uitlize data obtained from liquefaction runs carried out in a stirred autoclave.

A statistical screening procedure will be developed in the first phase of this work. A set of "standard" run conditions will be established by determining those parameters (coal/solvent ratio, pressure, heating rate, temperature and residence time) required for an 80 to 85 percent conversion of a West Virginia coal to a liquid product. A number of coals (15 to 20) will then be liquefied using the standard screening conditions. The conversion, sulfur content, viscosity and offgas composition will be determined for each run. The coals will be order-ranked on the basis of overall reactivity and product quality.

The second phase of this task will concentrate on four or five coals (identified in the first phase) in order to establish correlations between mineral matter content, conversion and product quality. Demineralized samples will be prepared by acid extraction and pure minerals will be added to these in order to assess specific catalytic effects. Comparisons with commercial hydro-desulfurization catalysts will be made.

The third phase will utilize the results of the second phase in order to optimize the conditions required for catalysis of coal liquefaction by the naturally occurring mineral constituents. Catalyst decay, reactivation and recycling will be evaluated. Hydrogen consumption and ease of solids separation (filtration, centrifugation, etc.) will also be investigated.

2. Results and status.

a. Autoclave facility. The liquefaction runs will be carried out in an Autoclave Engineers one-liter, magnetically stirred autoclave. This unit, including all necessary fittings, has been ordered and will be shipped to Sandia in January. The autoclave will be located in a barricaded enclosure which has been designed for safe operation within a manned laboratory area. The enclosure is currently being fabricated in the Sandia shops, and will be available by the middle of December.

A unique feature of the autoclave facility is the fail-safe design. This has been accomplished by utilizing switches and latching relays which will permit the autoclave to be charged with hydrogen only after the entire system has first been evacuated and purged with an inert gas. Most of the mechanical and electrical components of the fail-safe system have already been received. Final construction of the facility will take place as soon as the autoclave arrives. It is anticipated that the first coal screening runs will be carried out in February.

b. Coal samples and solvents. The first coal samples, provided by H. R. Appell of the Pittsburgh Energy Research Center, have arrived. These include bituminous coals from West Virginia (Ireland Mine), Indiana (Spencer Company, Chrisney Mine) and Pennsylvania (Bruceton and Clearfield). Analyses

(ASTM) of these coals have been completed and will be given below.

Several companies have been contacted in an effort to obtain additional samples of Eastern coals for the screening study. All of the companies have responded favorably, and will supply us with samples from Illinois, Kentucky, Ohio and West Virginia. In addition, some Western coals from New Mexico, Wyoming and Utah have been made available to us. All of these coals will be crushed, pulverized and submitted for analysis as soon as they arrive.

Samples of creosote oil (heavy end) have been supplied by the Reilly Tar and Chemical Company. These will be used as the solvent for the initial runs and for establishing the screening procedures. A five gallon drum of SYNTHOIL (run FB-46), made from Ireland Mine, West Virginia coal, has been received. This sample has relatively high ash content (1.6 w/o) and will have to be filtered prior to use. Present plans are to use this material as the solvent for most of the screening runs. The viscosity and composition of this SYNTHOIL will be checked frequently in order to assess any aging effects.

c. Analytical procedures. The proximate and ultimate analyses of the coal samples that were supplied by the Pittsburgh Energy and Research Center are given in Table II.B.1. It is interesting to note the high ash content of the Clearfield coal and the very low ash content of the Bruceton sample. The oxygen content of the Indiana coal is high, but the value for the Clearfield coal is quite low.

The results of a semiquantitative emission spectroscopic analysis of the coal is given in Table II. B.2. The Indiana coal is very high in zinc, but is lower in silicon, aluminum and titanium than any of the other samples. The iron content is highest for the west Virginia coal and lowest for the Bruceton coal.

Note the extremely low boron content of the Clearfield coal. These observations may have potentially important consequences vis-a-vis catalytic effects.

Product analysis will require the determination of viscosity and sulfur content. Viscosity measurements will be carried out with a Saybolt Viscosimeter which has already arrived. The sulfur content will be obtained with a Leco Sulfuranalyzer which is available within the analytical chemistry group at Sandia. Work is currently under way to utilize these instruments for the characterization of the SYNTHOIL sample that has been received.

d. Ancillary activities. Correct identification of the mineral matter in coal requires a technique for separating the minerals without chemically altering them. We have decided to utilize the low temperature ashing procedures which have been described by workers at the Illinois State Geological Survey and at Pennsylvania State University. A low temperature asher has been installed at Sandia Laboratories, and has been successfully used to ash samples of a West Virginia (Ireland Mine) coal. These and other coal samples will be analyzed by means of x-ray diffraction techniques. The minerals will be identified by comparing the data with results from known mineral (pyrite, quartz, calcite, clays, etc.) samples. Calibration curves will be prepared so that quantitative determinations of the mineral matter in the coals can be made.

A micropulsed catalytic reactor is under construction (see Task 1). The unit is similar to the one used at the Pittsburgh Energy Research Center for catalyst activity studies. The purpose here will be to determine the catalytic activity of low temperature ash, reaction insolubles and individual mineral

components. Tests will include reactivity towards desulfurization, hydrogenation and cracking of hydrocarbons. Comparisons with commercial catalysts will be made.

3. Summary. Primary emphasis during the Quarter has been on the design of an autoclave facility and on the placing of purchase orders for all of the required components. As soon as this had been accomplished, emphasis was shifted to the activities required for carrying out the screening runs. These included procurement of coals and solvents, the establishment of product workup procedures and the development of techniques for the analysis and characterization of coals, liquid products and mineral matter. These activities are all in progress. While awaiting delivery of the autoclave components, we have been concentrating on those analytical and ancillary techniques that will be required for the successful performance of Task 2.

TABLE II. B.1

Analysis of Coal Samples Supplied by the Pittsburgh Energy Research Center

Proximate (%)	West Virginia[a]	Indiana[b]	Bruceton Pa	Clearfield Pa
Moisture	2.19	1.43	1.58	0.54
Ash	9.82	13.34	3.68	15.82
Fixed Carbon	47.70	43.87	60.46	60.17
Volatile Matter	40.29	41.36	34.28	23.46
Ultimate[c] (%)				
C	73.01	63.85	81.25	72.35
H	5.23	4.62	5.34	4.28
N	1.16	1.23	1.58	1.28
S	4.48	6.34	1.20	3.99
O	6.08	10.43	6.89	2.19
Ash	10.04	13.53	3.74	15.91
Heating Value[c]				
(BTU/lb)	13,257	11,549	14,499	12,916

[a]Ireland Mine

[b]Spencer County

[c]Dry Basis

TABLE II.B.2

Semiquantitative Emission Spectroscopy of Coal Ash

	Coal Sample (Results in ppm)			
Element	West Virginia (Ireland Mine)	Indiana (Spencer Co.)	Bruceton, Pa.	Clearfield, Pa.
Aluminum	81000	40000	100000	100000
Barium	810	810	810	520
Boron	1300	1300	1600	80
Calcium	10000	16000	10000	6300
Chromium	400	250	400	250
Copper	1300	520	1300	2100
Gallium	250	400	200	130
Iron	210000	160000	130000	160000
Lithium	60	25	60	400
Magnesium	6300	5200	5200	5200
Manganese	630	810	400	400
Nickel	1600	1300	1600	1000
Potassium	4000	6300	1300	2500
Rubidium	60	30	30	50
Silicon	160000	63000	130000	100000
Sodium	1300	320	1300	520
Strontium	1600	200	1300	2000
Titanium	8100	3200	5200	8100
Vanadium	520	250	400	520
Zinc	ND<10*	1300	ND<10*	ND<10*
Zirconium	520	400	520	520

*Not detected.

C. Task 3-Kinetic Studies

Task Leader: R. W. Lynch

Contributors: E. J. Nowak, R. M. Curlee, L. P. Baudoin

1. Introduction. Rate equations for coal conversion to liquid product, for coal conversion to gaseous products, and for coal desulfurization are to be developed in Task 3 and presented in a form suitable for SYNTHOIL process scaleup. Data for that purpose are to be obtained using a bench-scale reactor which is described below. The variables to be studied for kinetic interpretation are operating pressure (2000 to 4000 psi), reaction temperature (400° to 475° C), reaction time (residence time of liquid in both preheater and reactor to be measured), hydrogen flow rate (Reynolds number for hydrogen in a packed bed of uniform particles to be in the range of 200 to 1000), and hydrogen sulfide concentration. Hydrogen sulfide is a reaction product, and its concentration is to be varied over a yet to be determined range of concentrations by additions to the feed in order to deduce the kinetic form of its inhibiting effect.

2. Approach. (E. J. Nowak)

a. General. This section describes the planned experimental approach for the development of SYNTHOIL rate equations suitable for process scaleup. It includes characterization of the flow properties in the bench scale unit to be used and determination of the chemical kinetics in the preheater as well as the reactor described below. Because the supply of liquefied coal for use as feed solvent is limited, the approach was designed to minimize the number of experimental runs to be made. Following demonstration of the operability of the reactor system in early summer 1976, the program will begin with liquid

residence time measurements to be made with SYNTHOIL simulant (chosen to simulate density and viscosity at preheater and reactor operating conditions). Then, kinetics shakedown runs using both preheater and the reactor are to be made to establish the reproducibility of the kinetic data that can be obtained. Next, the preheater kinetics are to be measured under conditions optimized from the results of the residence time and reproducibility studies. Finally, kinetics measurements on the combined preheater and reactor systems are to be made. Mass transport rate effects are to be isolated first, followed by elucidation of the chemical kinetics. A more detailed description of each of these parts of the program follows.

b. Residence time measurements. Measurements are to be made with a SYNTHOIL simulant having the appropriate density and viscosity at preheater and reactor conditions. Residence time distributions will be estimated from the time history of liquid flow emerging from the preheater alone and then from the preheater-reactor combination for three feed rates within a Reynolds number range of 200 to 1000 for hydrogen. The oil-hydrogen ratio is to be typical of the process. The hydrogen pressure is to be 2000 psi and two preheater outlet and reactor temperatures will be selected in the range 400 to 450°C. Good time resolution of preheater and reactor effluent rates is expected through the use of a small product receiver and frequent total product sampling. It is desirable to obtain kinetics data in a regime for which the average residence time is proportional to the feed rate. If necessary, the temperature and pressure will be varied to establish the range of reaction conditions for that regime.

c. Reproducibility of data runs. After the residence time characteristics of the apparatus are determined, it will then be necessary to establish the

attainable reproducibility of kinetics data. That is to be accomplished for one type of coal during at least three shakedown runs taking product from the reactor outlet only and measuring liquid and gaseous product compositions over a period of several hours. These data are to establish a baseline of performance for comparison with other reaction conditions. Planned operating conditions are 400°C, 2000 psi, and Reynolds number N_{Re} = 1000 in order to minimize conversion and hence detect process variations with the greatest sensitivity. (These conditions may be modified after interpretation of the residence time measurements). If unacceptable reproducibility is obtained, then the reproducibility of the preheater operation will be determined separately in order to isolate the cause. Kinetic measurements will not begin until satisfactory reproducibility is attained. It will be attempted to obtain most of the kinetics data under conditions of highest reproducibility. For example, if reproducibility is relatively poor at low feed rates, then the variables of pressure, temperature, and residence time will all be studied at a high feed rate.

d. Preheater kinetics. Kinetics measurements are to begin with the preheater. Since coal dissolution in the preheater is known to be rapid at process conditions, measurements are to begin at the highest temperature and pressure and at the lowest feed rates compatible with good reproducibility as defined in the preceding part of the program. This set of conditions will be used in order to determine whether there exists a range over which the extent of coal dissolution is nearly complete and relatively insensitive to preheater conditions. This is done to find an optimum regime for subsequent reactor studies. Next, a kinetics study of the preheater will be done in the regime of greatest preheater

sensitivity to the process variables. First, the relative kinetic importance of fluid-phase mass transport will be assessed by measuring product composition changes as a function of feed rate at constant contact time (preheater length changed with changing feed rate to yield constant contact time). An appreciable dependence of the extent of reaction on feed rate would indicate that fluid-phase mass transport is a significant factor in the overall kinetics. In that case, a fit with correlations for mass transport in packed beds would be attempted in order to later separate mass transport and chemical kinetics contributions. Second, the kinetic effects of contact time, temperature, and pressure on liquefaction and gas production in the preheater would be measured in a region where effects of fluid-phase mass transport are as low as possible.

The preheater study is expected to require a minimum of 12 runs for each type of coal. That number might be decreased somewhat by withdrawing liquid-phase in the preheater at two or more well-separated locations, thus obtaining data for more than one contact time during a single run. Perturbations caused by withdrawals could be eliminated by first withdrawing product at the full length of the preheater and then at points progressively closer to the preheater inlet. It is also possible to economize on the required number of runs by postponing most of the studies of the effect of temperature until the sequence and interactions of rate processes are understood well enough that one can be highly selective in the choice of conditions for the temperature studies.

e. Reactor kinetics. After the preheater is understood sufficiently, rate measurements will be made for the combined preheater and catalytic reactor system. As in the preheater studies, the magnitude of the kinetic effects of fluid-phase mass transport will be assessed first by measuring the product

composition as a function of feed rate at constant contact time. Next, the magnitude and nature of any particle-phase mass transport effects are to be estimated by measuring the effect of catalyst particle size on product composition while operating in a regime of minimum influence by fluid-phase mass transport. Crude models for kinetics determined by particle-phase mass transport are well known in the kinetics literature. If the rates of fluid-phase mass transport cannot be made large compared with the other rate processes, then it will be very difficult to estimate the extent to which particle-phase mass transport affects the overall conversion rates, and it may not be possible to develop a rate expression based on a simple mechanistic model, e.g., a Langmuir-Hougen and Watson type of rate expression. However, in that event, a best fit model for transport effects based on flow rate and particle sizes will be developed in order that the overall rate equations predict process responses are reliably as possible. Then, the variables of total pressure, contact time, hydrogen sulfide concentration, and temperature will be studied in the regime of minimum influence by mass transport rates. This reactor study is expected to require a minimum of 15 runs for each type of coal. Some decrease in this number might result from multiple point product withdrawals and selective temperature studies, as described above for the preheater. Considerable reduction in the number of experiments can be attained by deferring most of the temperature studies until the isothermal kinetics of the process is understood. Then, the critical regimes may be properly chosen for temperature studies. Similarly, the rate studies of a second coal type may be focused on the critical kinetic parameters identified in the studies of the first type of coal. In that way, the minimum anticipated number of runs may be

fewer than the 27 estimated for the first coal type.

3. Result and status. (R. M. Curlee)

a. Reactor system. A schematic diagram of the proposed reactor system is shown in Figure II.C.1. This drawing should be considered preliminary as it does not reflect recent changes in the sample collection apparatus and other changes that have not been formalized to drafting release status. It is presented here merely as an aid in discussing design and operational parameters to be addressed below.

As indicated, the system will be modularized in design, fabrication, and function into three basic units. Module "A" is the low-pressure slurry circulation system. The high-pressure slurry metering system is labeled Module "B" and the preheater, reactor and sample collection system is designated as Module "C". The modular concept affords flexibility permitting independent module construction and evaluation at an alternate laboratory site pending completion of the modifications to the permanent reactor site. Module fabrication and evaluation should begin during February 1976.

b. Low-pressure slurry circulation system -- Module "A". Because the function of this unit is to blend and suspend the coal particles in the carrier oil, the feed tank and pump are the critical elements.

The feed tank is a continuously heated and stirred ASME rated pressure vessel. It will be counter-balanced and fitted with a load cell to measure slurry feed rate to the high-pressure metering pump by weight loss at the slurry tank. Maximum capacity of this system using a single batch process will be about 25 liters. The slurry will be maintained under a slight positive pressure of N_2, heated (up to 100°C), and circulated at a flow velocity of 6 ft/sec to the

high-pressure metering pump.

A Moyno type pump has been recommended for slurry circulation and will be installed in the final construction. It is doubtful that this type pump will be available for initial installation because of lengthy fabrication schedules to produce the tool steel parts required for operation with an abrasive slurry. Alternate pump types will be employed until this equipment can be received. Slurry pressures will be measured with strain-gage transducers attached to isolator/transmitters of Sandia design. Most components of this system will be constructed of stainless steel.

c. High pressure slurry metering system -- Module "B". The blow-down pot, venting, and relief system is based upon the design employed in the catalyst lifetime unit used at the Pittsburgh Energy Research Center. The high-pressure metering pump will be a Bran and Lubbe N-J52 unit. Accurate and reliable operation of this pump may well be the most critical function in the entire system. The manufacturer is reluctant to guarantee accurate performance below metered rates of 1 lb/hr. Limited availability of vehicle oil requires that feed rates be at most this value and preferably lower. Special speed controls have been specified in the purchase request but performance cannot be guaranteed and remains to be demonstrated. An acceptable substitute has not been found. Maximum allowable operating pressure of the N-J52 pump is approximately 14000 psi.

Pressures will be measured in this module, as throughout the high-pressure system, by strain-gage transducers with a modified diaphragm unit.

d. Preheater, reactor and collection system -- Module "C". The preheater and reactor will be constructed of 3/8 in O.D. x 0.203 in I.D. tubing wound in

a helical configuration for upward flow operation. All tubing, valves and other apparatus will be rated for considerably greater than 5000 psi service. Sandia safety regulations require that manned pressure system have calculated burst pressures exceeding maximum allowable working pressures by a factor of four. The system must be demonstrated by test to withstand pressures exceeding the maximum allowable working pressure by a factor of 1.5.

Present design calls for a maximum of five 20 ft lengths of tubing to be used in the preheater section. Total length will be determined by operating parameters, preheater performance, and heat transfer considerations. Temperature will be monitored at points in the flow stream, at the tubing outer wall, and in the heating device. The tubing will be packed with Al_2O_3 or quartz beads. Not shown in the schematic is the capability to bypass the reactor section to perform experiments to study residence time and reactions in the preheater. In practice, the reactor may be bypassed and effluent collected in the existing receiver system, or an alternate receiver system may be incorporated for preheater studies.

The reactor will be of similar construction to the preheater although shorter in length. Residence time experiments will be performed by varying reactor lengths. Fractured catalyst particles will be used to pack the reactor. As much as 60 ft of coiled tubing can be contained in the reactor heating furnace.

Hydrogen will be supplied from a tube trailer and compressed to test pressure using an Aminco A2C-400 or a similar diaphragm compressor of the comparable capacity. This unit will deliver 250 SCFH at 5200 psi utilizing a suction pressure of 450 psi. The oncethrough use of hydrogen requires

this rather large capacity and the compressor has been sized to produce flow yielding turbulent conditions in the packed reactor (modified N_{RE} ~ 200 to 1000) as requested in the original statement of work. Hydrogen flow rate will be measured by means of a mass flow meter as shown in Figure II.C.1.

One method for the addition of H_2S to the hydrogen gas stream is shown in Figure II.C.1. However, it is anticipated that this circuit will be added to the system later in the program and other methods will be considered. The H_2S injection system will be sized to produce a maximum H_2S concentration of 5 vol% based upon anticipated H_2 feed rates.

Product oil will be collected in standard, stainless steel, Autoclave Engineers pressure vessels. Approximate volumes of these units are 2 liters and 4 liters. Manual sampling values are shown in Figure II.C.1. However, an automatic pressure reduction scheme is under consideration, the critical design criteria being the operability and reliability of the automatic pressure activated valves. The objective is to minimize system pressure drop by taking small incremental samples into the low-pressure receivers. This concept would also afford better analytical resolution as smaller samples could be taken in a convenient manner.

The remainder of the high-pressure system consists of apparatus to cool, condense and depressurize the gas stream. Gas analysis will be made on-stream with a gas chromatograph. Preferably gas composition and exhaust flow rate will be determined before scrubbing to remove H_2S and NH_3. However, corrosion induced malfunctions of volmetric flowmeters are anticipated above H_2S concentrations of 1-2%. Therefore, the system as shown may be modified for experiments where concentrations of H_2S of this magnitude or more are expected.

e. Instrumentation. Thermocouples (most of which are not shown in Figure II.C.1.) will be utilized to make temperature measurements. As stated previously, pressures will be monitored by strain-gage transducers modified to function at high temperatures and in the presence of the coal/oil slurry. Analog output from these devices, load cells, and flowmeters will be digitized and recorded on an Kaye 8000 data acquisition system capable of fold paper or magnetic tape data recording. Essential temperature and pressure data will be displayed visually to the system operators on panel meters.

f. Phase I status. Although all design details for the reactor have not been completed, it is felt that the first phase of Task 3 is progressing satisfactorily. Purchase orders have been initiated for items with anticipated long delivery times. These items are:

Slurry feed tank
Slurry feed tank stirrer mechanism
Low-pressure slurry feed pumps
Blowdown pot
Condenser
Low-pressure receivers
High-pressure slurry metering pump
High-pressure hydrogen compressor

It appears that a system evaluation should be possible by early summer 1976 following completion of module assembly and test which should begin in February 1976.

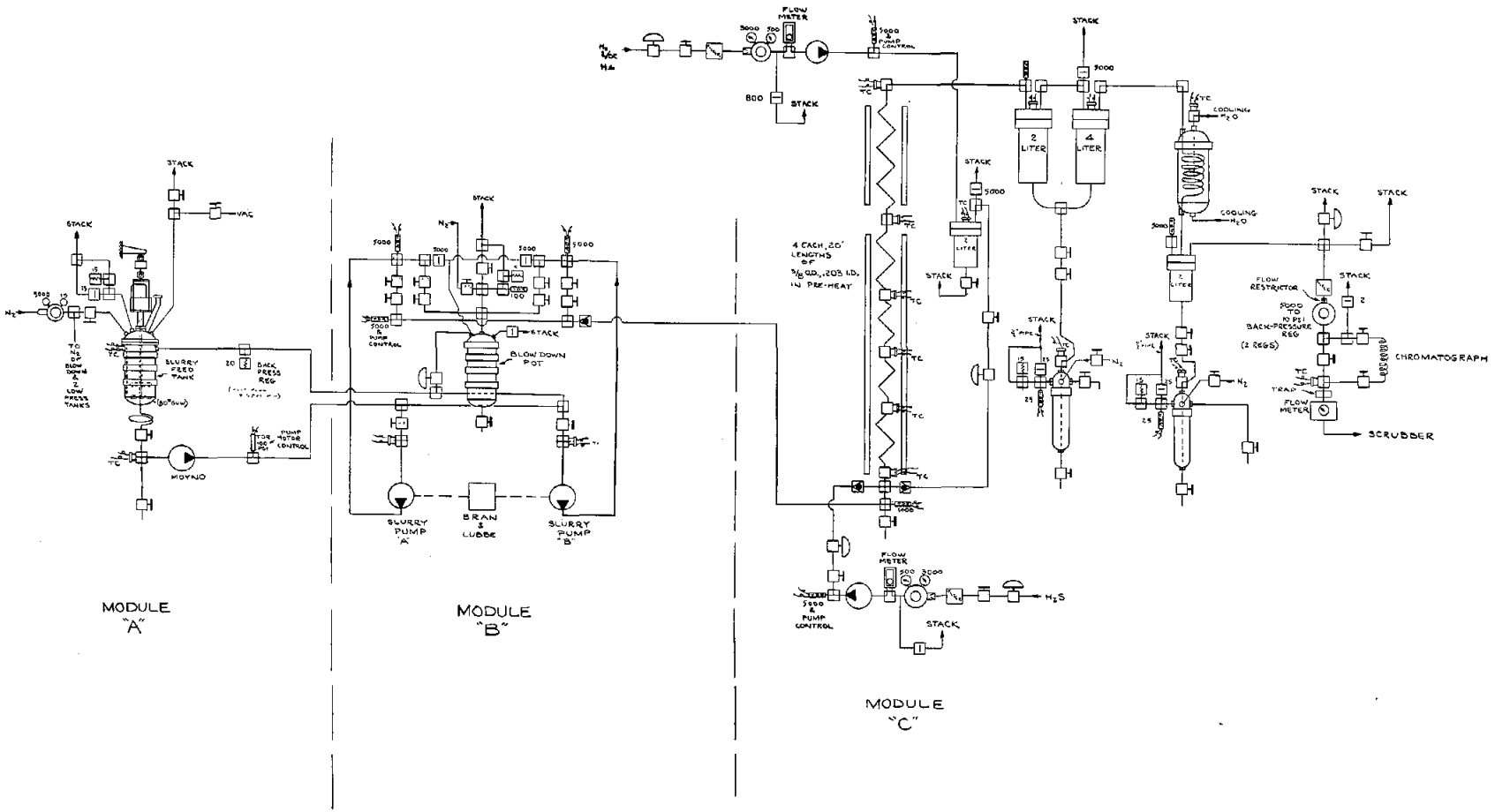


Figure II.C.1. Schematic diagram of reactor

III. SUMMARY (A. W. Mullendore)

A. Task 1. All appropriate analytical techniques which will be utilized in assessing the structure and compositional aspects of catalyst deactivation and reactivation have been evaluated in this quarter. In general the various techniques were found to be complementary; mercury porosimetry and Brunauer-Emmett-Teller techniques are both necessary to span the pore size range of interest, both scanning and transmission electron microscopy are required to reveal the existing range of topographic features and each of the elemental analyses (Rutherford backscattering, Auger electron spectroscopy, ion scattering spectroscopy, x-ray photoelectron spectroscopy, emission spectroscopy and electron microprobe) provides some particular advantages with respect to quantitative capability, sensitivity to particular elements, surface versus bulk sensivitivity, lateral resolution, chemical state information etc. Thus, each technique will have its place in future analyses. Additional capability for evaluation of electronic structure and catalytic activity are thought necessary and provisions are being made for inclusion of these analyses in future work.

B. Task 2. The design of the autoclave system for hydrogen reactivity studies of coals has been completed and purchase orders placed for the required components. Fabrication of the system is underway. A number of coal samples have been recieved and ASTM analyses and emission spectroscopy results obtained. Product workup procedures and capabilities for analytical and characterization techniques for the coals, liquid products and mineral matter are being established.

C. Task 3. An outline of studies to be performed in this task has been constructed which defines the sequence of experiments necessary to determine residence time factors, reproducibility of kinetics data, preheater kinetics and reactor kinetics in the bench scale reactor based on the SYNTHOIL concept. The design of the reactor is at an advanced stage and the procurement of all long delivery time components has been initiated. Facility preparation is underway, module assembly will commence in February, 1976 and complete system evaluation should be possible in early summer of 1976.

DISTRIBUTION:

D. K. Nowlin, Director
Special Programs Division
U. S. ERDA
Albuquerque, NM 87115

David H. Duke
Acting Assistant Director
Program Services
U. S. ERDA/Fossil Energy
711 14th St., N.W. Rm. 804
Washington, DC 20545

Jim Batchelor (1)
William Jones (1)
Dr. Martin Neuworth, Synthetic Fuels Development Division (1)
Dr. G. Alex Mills, Director, Div. of Fossil Energy Research (1)
Dr. Paul R. Wieber, Acting Branch Chief, Oil, Gas & Shale Tech. (1)
U.S. ERDA/Fossil Energy
20 Mass. Ave., N.W.
Washington, DC 30545

A. W. Decora (1)
L. A. Schrider (1)
Laramie Energy Research Center
U.S. ERDA
Laramie, WY 82070

A. A. Pitrolo (1)
C. Karr, Jr. (1)
Morgantown Energy Research Center
U.S. ERDA
Morgantown, WV 26505

I. Wender (1)
P. Yavorsky (1)
J. Sharkey (1)
H. Appel (1)
S. Friedman (1)
S. Akhtar (1)
F. R. Brown (1)
Pittsburgh Energy Research Center
U.S. ERDA
4800 Forbes Avenue
Pittsburgh, PA 15213

R. Balzhiser
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304

U. S. ERDA
Bethesda Technical Library
Washington, DC 20545

U. S. ERDA
ERDA Library
Washington, DC 20545

U. S. ERDA
Attn: R. A. Anderson
Office of Assistant General
Counsel for Patents
Washington, DC 20545

U. S. ERDA
Albuquerque Operations Office
P.O. Box 5400
Albuquerque, NM 87115

U. S. ERDA
Attn: Reports Librarian
New York Operations Office
376 Hudson Street
New York, NY 10014

Union Carbide Corporation
Attn: Library
P.O. Box X
Oak Ridge, TN 38730

E. F. Hammel, Assistant Director for Energy (1)
R. B. Duffield, A Division - Energy (1)
Attn: Reports Librarian (1)
Los Alamos Scientific Laboratory
P. O. Box 1663
Los Alamos, NM 87544

National Aeronautics and Space Admin.
Attn: L. B. Russel, Librarian
John F. Kennedy Space Center
Kennedy Space Center, FL 32899

A. Jonke (1)
J. Fischer (1)
Library Services Dept., Report Sect., Bldg. 203, Rm. CE-125 (1)
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

Brookhaven National Laboratory
Attn: Research Library
Information Division, Upton, L. I , NY 11973

Asst. Director for Research Applications
National Science Foundation
1800 G. Street
Washington, DC 20550

1000 G. A. Fowler
2000 E. D. Reed
Attn: J. C. King, 2500
1300 D. B. Shuster
5000 A. Narath
5100 J. K. Galt
5110 F. L. Vook
5150 J. E. Schirber
5200 E. H. Beckner
5400 A. W. Snyder
5700 J. H. Scott
5710 G. E. Brandvold
5730 H. M. Stoller (5)
5731 M. L. Lieberman (5)
5732 D. A. Northrop
5740 V. L. Dugan
5800 R. S. Claassen
5810 R. G. Kepler
5820 R. L. Schwoebel (5)
5825 A. W. Mullendore (5)
5830 M. J. Davis
5840 D. M. Schuster
8000 T. B. Cook, Jr.
8310 R. H. Meinken
3141 C. A. Pepmueller (5)
3151 W. L. Garner (3)
for ERDA/TIC (25)
Attn: R. P. Campbell, 3171-1
8266 E. A. Aas (2)