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THE ECONOMICAL PRODUCTION OF ALCOHOL FUELS FROM COAL-DERIVED SYNTHESIS GAS

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Executive Summary

At WVU, Mo_2S_3 was produced from gas-phase reactions at 1100°C. The gas-phase reactor was modified to increase product yields and to decrease particle size. Four Chevrel phases were synthesized, $M'MO_6S_8$ (M'=Sn, Sm, Pb, Co) for catalytic evaluation. In addition, four supported alkali-modified MoS_2 materials were prepared from a single-source precursor, $K_2Mo_3S_{13}$.

Screening runs have been carried out on some of these materials and others prepared earlier. Results are promising, especially on supported molybdenum-based nitrudes as a group and K-Mo/C in particular.

At UCC&P, test runs on the reactor system have commenced. Higher alcohols up to butanol were observed and identified at high temperatures. In spite of the acquisition of a new data handler and a new gas purifier, problems exist in the analysis of products from the reactor. Impregnation of catalyst on a zinc-chromium support will start shortly.

Gas-phase reactions for material synthesis have been summarized in a Topical Report sent to PETC entitled, "Surface Area and Crystallographic Modifications of Molybdenum Sulfide, Molybdenum Carbonitrides and Iron Carbonitrides Synthesized by Controlled Vapor-Phase Thermolysis". A related paper and presentation were given at the November 1994 Material Research Society meeting in Boston. A Master's thesis entitled, "Modelling and Simulation of Catalytic Reactors Used in the Production of Higher Alcohols from Synthesis Gas," was completed.

Significant progress has been made on the Monte Carlo uncertainty analysis. Frequency distributions have been determined for all of the equipment blocks for the Texaco gasifier cases. For these cases, there is a 10% chance that the actual installed capital cost could exceed the estimated installed capital cost by $40 million dollars. This work will continue with inclusion of variable costs and prediction of the uncertainties in the return on investment.

Modifications to the simulated annealing optimization program have been underway in order to increase the level of certainty that the final result is near the global optimum.

Alternative design cases have been examined in efforts to enhance the economics of the production of higher alcohols. One such process may be the generation of electric power using combustion turbines fueled by synthesis gas. This process would be an example of an energy park. The primary product would be electricity instead of higher alcohols. The investigation of a case of this nature is suggested given the considerable interest electric utilities have expressed with regard to the flexibility provided by modular facilities of this nature.

The fuel testing apparatus is up and running. There were initial problems with a pressure relief valve, making the initial data not valid. However, this problem has been fixed, and data collection is proceeding.

TASK 1. REACTION STUDIES

1.1 Introduction

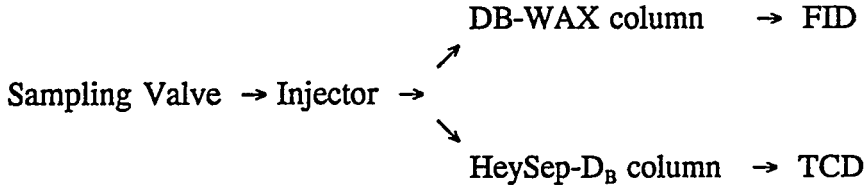
The objective of Task 1 is to prepare and evaluate catalysts and to develop efficient reactor systems for the selective conversion of hydrogen-lean synthesis gas to alcohol fuel extenders and octane enhancers.

Task 1 is subdivided into three separate subtasks: laboratory and equipment setup; catalysis research; and reaction engineering and modeling. Research at West Virginia University (WVU) is focused on molybdenum-based catalysts for higher alcohol synthesis (HAS). Parallel research carried out at Union Carbide Chemicals and Plastics (UCC&P) is focused on transition-metal-oxide catalysts.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory Setup

At WVU, the GC analytical systems on both reactors have been reconfigured as shown below:



With the new configuration, we can start the analysis at 40°C and separate H_2, N_2, CO, CO_2, methane, ethane, and methanol on the HeySep-D_B column. Nitrogen is the new internal standard, replacing argon which required cryogenic oven cooling to obtain separation. At the same GC conditions, the DB-WAX column clearly separates light hydrocarbons from methanol and higher alcohols. Aldehydes and ketones will also elute with the alcohols. The DB-WAX column has a few minor drawbacks: it does not separate light hydrocarbons by carbon number, nor can it separate light ethers from hydrocarbons. Nevertheless, this new GC configuration provides good analysis of alcohol products, with minimal confusion on the identity of a GC peak. This is a major analytical improvement for HAS catalysis.

We have discovered a new operating problem with unstable gas flow on one of the reactor units. We believe that the problem relates to flow range on the Brooks flow controllers, and this has been confirmed by the manufacturer . The controller ranges were too large (0-1000 sccm for H_2, for example) to give accurate control for the small flows used in catalyst screening (25 sccm). Two new controllers and parts for scaling down the flow

ranges of all flow controllers have been purchased.

At UCC&P, the first HAS run in the microreactor was completed early in the quarter. We used one gram of 11-DAN-45 catalyst. The goals of the run were to produce butanol from an HAS catalyst and to calculate a carbon balance on the reactor. We did produce butanol as intended, and the yield increased with temperature as expected. However, butanol results were somewhat variable. Consequently, we were unable to achieve the second goal of a carbon balance on the reactor.

The temperature of the effluent pipe between the reactor oven and the reactor backpressure regulator was probably too low to keep butanol in the vapor phase. After the run, we found that liquid had indeed been condensing in the backpressure regulator. We had lined the effluent tube with heat tape while the reaction was still in progress, but apparently the added heat was insufficient to vaporize the liquid before the reactor plugged due to coking.

After shut-down, we could see that the plugging which prevented sufficient feed flow was due to coking and/or catalyst physical degradation. Fines had also coated tubing walls both upstream and downstream from the reactor. All tubing inside the oven had to be rebuilt, and two valves had to be replaced. The backpressure regulator also needed to be cleaned and rebuilt.

A carbon balance is critical to producing reliable results in higher alcohol synthesis experiments. We need to repeat experiments with previously-tested catalysts until we can accurately and reliably quantify results. We did not accomplish that goal in this quarter. However, we have made progress with both the reaction and the analytical systems, and we anticipate accomplishing our goal in January.

We purchased and installed a Hewlett-Packard ChemStationR for gas chromatograph data handling (UCC-funded). Installation and operator training took more than a week, but the new ChemStationR has tremendously improved our capabilities to store, manipulate, and interpret our GC data. We also purchased and installed a Supelco High-Capacity Gas Purifier for our GC carrier gas feed line (UCC-funded). The purifier is intended to remove moisture and oxygen from the carrier gas.

We have had a nagging problem with an irregular contamination peak which co-elutes with hydrogen. Unfortunately, the integrators cannot discern the difference, and we have had to make calculations off-line to measure hydrogen concentrations with reasonable accuracy. With the new ChemStationR, we had hoped to be able to use the added integration options to make more accurate measurements of the hydrogen peak, but the contaminant peak has prevented this. However, we have been able to reduce its size such that it is barely discernible from the baseline. Further, by manipulating the carrier gas head pressure, we have been able to separate the hydrogen peak from the contaminant peak. Unfortunately, other peaks have begun to co-elute and we have had to change our temperature program to

separate those peaks.

1.2.2 Molybdenum-Based Catalyst Research

It was reported in TPR 10 that MoS_2 can be synthesized using a gas-phase technique. During this reporting period, Mo_2S_3 was produced at WVU using a procedure similar to that used for the MoS_2 vapor-phase synthesis. Two reactions were completed at 1100°C, with H_2S flow rates of 4 ml/min for Reaction 1 and 2 ml/min for Reaction 2. In Reaction 1, a mixture of MoS_2 and Mo_2S_3 was produced. The Mo_2S_3 fraction was roughly 10% of the MoS_2 phase. In Reaction 2, elemental molybdenum was also produced, in addition to a higher ratio of Mo_2S_3:MoS_2 relative to Reaction 1. During the reactions, the H_2S and He flow rates were monitored to insure invariant rates over the course of the reaction. Temperatures of the furnace and tube (containing $Mo(CO)_6$) were also constant throughout the run. The only variation that can account for the range of molybdenum products obtained from Reactions 1 and 2 is the variation in the flux of $Mo(CO)_6$ vapor during the reaction. As $Mo(CO)_6$ is vaporized, the amount of $Mo(CO)_6$ decreases, resulting in a lower amount of gaseous $Mo(CO)_6$ available for the reaction with H_2S. In the beginning of the reaction, the $Mo(CO)_6$ amount is greatest. In the early part of the reaction, a relatively high Mo:S ratio is produced, resulting in reduced molybdenum products, Mo_2S_3 (in Reaction 1) or Mo and Mo_2S_3 (in Reaction 2). Near the end of the reaction, a lower amount of gaseous $Mo(CO)_6$ is available, which results in the higher S:Mo ratios necessary to form MoS_2. If Mo_2S_3 proves to be of catalytic interest, additional research will be conducted on preparing pure phase Mo_2S_3 using the vapor-phase reaction technique.

To improve the efficiency of the vapor-phase reactor and to produce materials with higher surface areas, a water-cooled injection tube was designed and built. Details can be found in MS40. With this addition, vapor-phase reactions can be performed up to at least 1000°C.

A Topical Report[1] detailing all the molybdenum and iron vapor-phase reactions was completed and submitted to PETC. A paper entitled, "Gas Phase Synthesis of Molybdenum and Iron Carbides, Nitrides and Sulfides" was completed and submitted to Material Research Society (MRS) Proceedings at the November MRS meeting in Boston (11/28/94-12/1/94). Also, during the MRS meeting, an oral presentation of the same title was given on November 29, 1994.

The Chevrel phases $M'Mo_6S_8$ (M' = Pb, Sm, Co and Sn) have been prepared in six-gram quantities. In each preparation, finely divided metal and sulfur were combined in appropriate stoichiometric ratios, pressed into pellets at 25,000 psi, using a 1-cm die, and sealed under vacuum in 15-mm fused silica tubes. All four materials were then heated to 1150°C using a heat ramp designed for volatile lead, tin and sulfur. The compounds were heated for 48 hours at 1150°C, air quenched and opened in air. The Pb, Sm and Sn precursors formed pure Chevrel phases as characterized by XRD, while the cobalt contained

a small amount of MoS_2 and an unidentified phase. Chevrel phases with varying ternary metals will be prepared if the current Chevrel phase materials show sufficient selectivity to higher alcohols.

In a series of experiments with supported K_xMoS_2, the support material and catalyst loading level were varied. Four samples were prepared by saturating three different supports with appropriate amounts of a $K_2Mo_3S_{13}$/dimethylformamide (DMF) solution. Details can be found in MS40. The material has been subjected to catalytic evaluation. The results are noted below and described in more detail in MS40. $Cs_2Mo_3S_{13}$ has also been prepared and will be used as a precursor to supported MoS_2 after the results with the potassium analogs are evaluated.

$K_2Mo_3S_{13}$ was prepared as a single-source precursor to alkali-modified MoS_2 by modifying the procedure for making $(NH_4)_2Mo_3S_{13}$.[2] If the proper deposition procedure is used, the single-source precursor should allow a high level of alkali dispersion throughout the catalyst.

During this quarter, the following catalysts were screened:

(a) MoN (I123A) and Mo_2C (I122A);
(b) $Fe_{2.8}MoC$ (49A), $Fe_{1.9}MoC$ (50A) and $Fe_{1.9}MoN$ (50C);
(c) K(H)-Co_6W_6C and K(L)-Co_6W_6C;
(d) $Cs_{0.3}MoN$ and $Cs_{0.5}MoN$;
(e) $Ni_{1.6}Mo_6S_8$ and $SmMo_6S_8$ Chevrel-phase sulfides;
(f) MoS_2 and K_2CO_3- and KNO_3-doped MoS_2;
(g) $K_{0.05}Mo_2S_3$, $K_{0.1}Mo_2S_3$, $K_{0.15}M_2oS_3$ and $K_{0.125}MoS_2$;
(h) supported $K_2Mo_3S_{13}$/C catalysts, various loadings;
(i) supported $K_2Mo_3S_{13}/TiO_2$ catalyst;
(j) supported Mo/C (ELK01) and K-Mo/C (ELK02).

Reaction temperatures were generally ramped up from 200°C to 400°C and then down to 200°C at a rate of 10°C/h. The pressure was 750 psig. The product was analyzed every 2h. The space velocities used ranged from 600 to 9000 l/h/kg-catalyst depending on the catalyst activity. The H_2-to-CO ratios ranged from 5/3 to 1/1.

The runs with Groups (a) and (b) catalysts were carried out under the previous GC configuration; therefore, positive identification of higher alcohols was not possible. However, the selectivity and conversion with these catalysts were sufficiently low that no re-run was deemed necessary under the new configuration. Catalysts in Group (c), (d) and (e) had been run previously (under the old system) but were re-run after the new GC configuration was made.

Among the above catalysts, the supported K-Mo/C (ELK02) show the highest oxygenates production rate and the highest CO_2-free selectivity to oxygenates (134 g/h/kg-catalyst and 80

wt%, respectively). The next higher values correspond to $K_{0.125}MoS_2$ (64 g/h/kg and 69 wt%), $Cs_{0.5}MoN$ (28 g/h/kg and 47 wt%) and K(H)-Co_6W_6C (26 g/h/kg and 31 wt%). Detailed results on production rates and selectivities to higher alcohols for these four catalysts are shown in Figures 1 to 4. The Chevrel-phase catalysts in general have shown low activity to oxygenates (less than 1 g/h/kg-catalyst).

1.2.3 Transition-Metal-Oxide Catalyst Research

At UCC&P, we decided to use a common zinc-chromium catalyst support rather than the proprietary support initially considered. Use of the zinc-chromium support enhances our ability to release information on our work and makes it easier to compare our results with other work found in the literature. The zinc-chromium catalyst support was manufactured in November and sent for surface analysis to verify that it had an appropriate composition. Confirmation of the surface properties was received in December. Impregnation of catalysts can begin in January.

1.2.4 Reaction Engineering

A Master's thesis entitled, "Modelling and Simulation of Catalytic Reactors Used in the Production of Higher Alcohols from Synthesis Gas," was completed by Ajit Subramanian who gratefully acknowledged the support of his research from PETC/USDOE. Manuscripts based on this work are currently being prepared for submission to refereed journals for publication.

1.3 Conclusions and Recommendations

The product analysis system at WVU has been reworked, and has led to significant improvements in the ease and accuracy of analysis. The delivery system for the reactants is being modified.

The plug-flow microreactor system at WVU has been used to screen a number of materials as potential HAS catalysts. These may be divided into four main groups:

(1) supported molybdenum-based nitrides (produced from decomposing a soluble molybdenum azide precursor, MoN_3Npy);
(2) bulk molybdenum-based carbides and carbonitrides prepared by vapor-phase reactions between metal carbonyls and ammonia;
(3) supported molybdenum-based sulfides prepared from K_2(or Cs)Mo_3S_{13};
(4) bulk molybdenum-based sulfides prepared from vapor-phase reactions between metal carbonyls and hydrogen sulfide.

Of these, the most promising catalysts (based on their activity and selectivity) appear to be those in Group (1). Of all of the materials used thus far, the single most promising one is the supported K-Mo/C.

The utility of the vapor-phase catalyst synthesis reactor has been extended to the synthesis of Mo_2S_3. A modification has been made to the gas-phase reactor to increase the yield, by reducing the amount of metal plating on the inner surface of the heated quartz reaction tube. More Chevrel-phase materials have been prepared for catalytic evaluation. With the catalytic data from these Chevrel phases, we will be able to determine the extent of our commitment to investigating the these materials as HAS catalysts. Two single-source precursors have been produced for preparing supported alkali-modified MoS_2: $M'_2Mo_3S_{13}$ (M'=K, Cs). Four supported catalysts have been prepared with SiO_2, TiO_2 and C supports. The materials were made to determine the effect of support and catalyst loading levels on conversion and selectivity.

At UCC&P, a zinc-chromium support has been prepared and characterized. Work is continuing on improving the reactor system.

1.4 Future Plans

At WVU, we expect to solve the mass flow control problem for one of our reaction system. We also plan to test more sulfide and nitride catalysts, especially supported systems.

For the Group (1) materials, as classified above, a systematic study evaluating the effect of support material and catalyst loading levels will be accomplished. The Group (2) materials have not been modified with alkali; therefore the influence of alkali type and catalyst loading levels will be determined for selected molybdenum carbides and carbonitrides. For Group (3) supported sulfides, the effect of Cs doping will be evaluated by using the precursor, $Cs_2Mo_3S_{13}$. Other supports will be evaluated as necessary. The influence of adding other metals, such as Nb, Y, Zn and Li to supported MoS_2 will also be evaluated. Further work on the bulk sulfides of Group (4) will extend to adding variable amounts of alkali to high-surface-area MoS_2 and Mo_2S_3. Also, the effect of adding iron and/or cobalt by decomposing a mixture of the respective carbonyls in the gas phase reactor will be examined. Gas-phase reactions will also focus on preparing high-surface-area Chevrel phases, $M'Mo_6S_8$ (M' = Fe, Co, Ni).

At UCC&P, impregnation of transition-metal oxide catalyst on the zinc-chromium support is expected in January.

References

1. Close, M.; Petersen, J.; Topical Report, *Surface Area and Crystallographic Modifications of Molybdenum Sulfide, Molybdenum Carbonitrides and Iron Carbonitrides Synthesized by Controlled Vapor Phase Thermolysis*, Task One of the Economic Production of Alcohol Fuels from Coal-Derived Synthesis Gas, Contract No. DE-AC22-91PC91034, August, 1994.

2. Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch.* **1979**, 34b, 434-436.

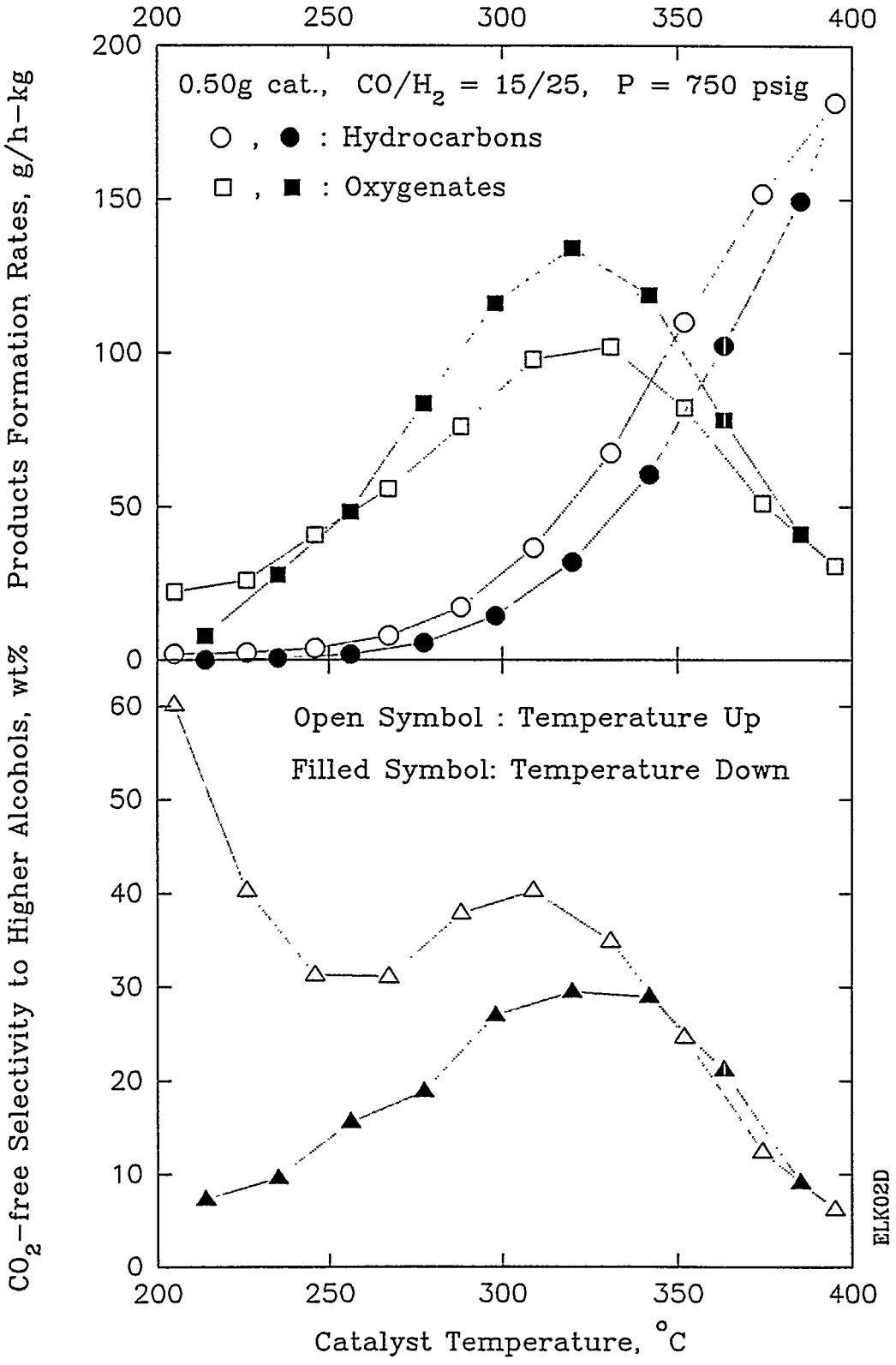


Figure 1. Performance of K-Mo/C catalyst.

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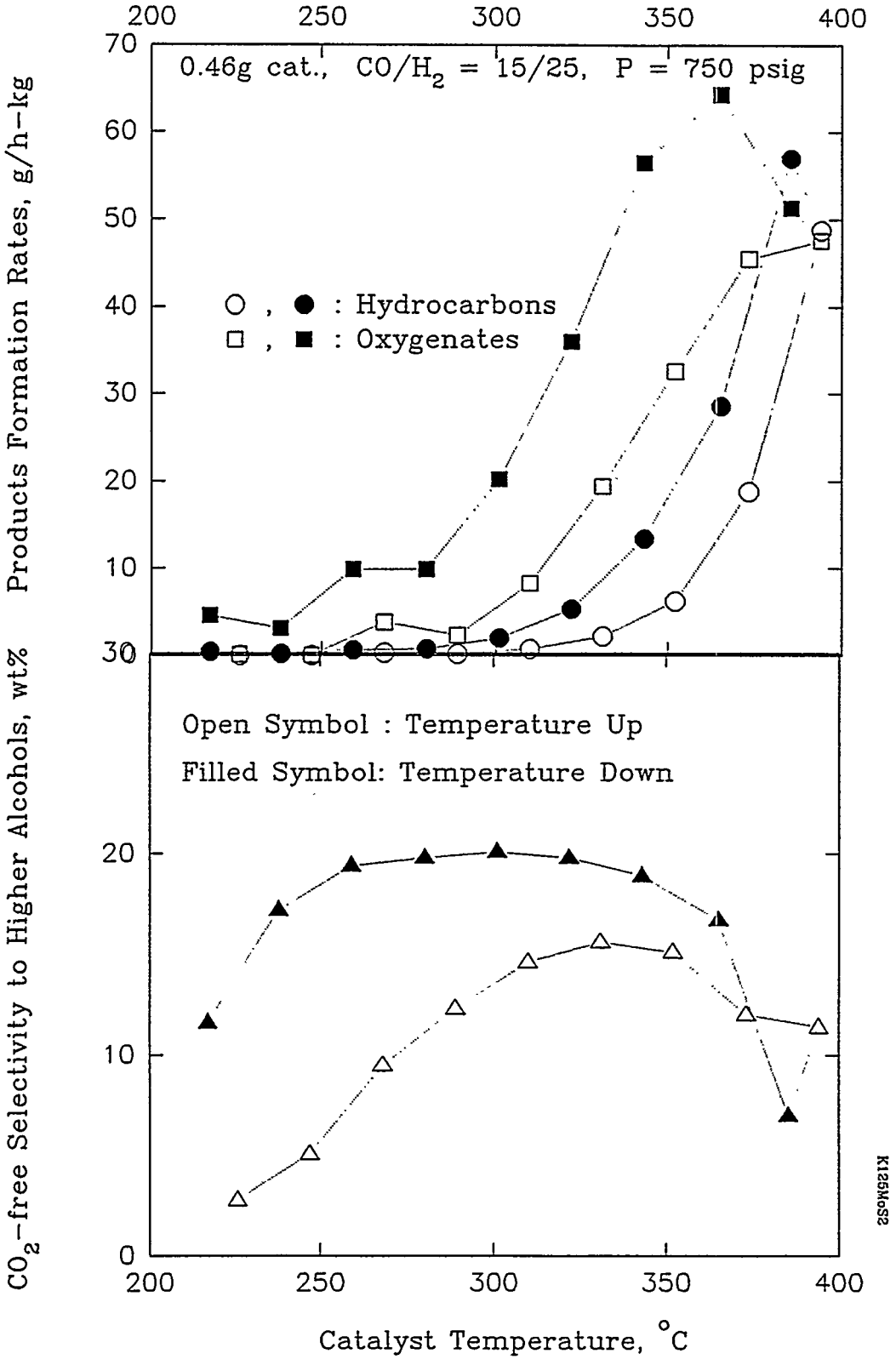

Figure 2. Performance of $K_{0.125}MoS_2$ catalyst.

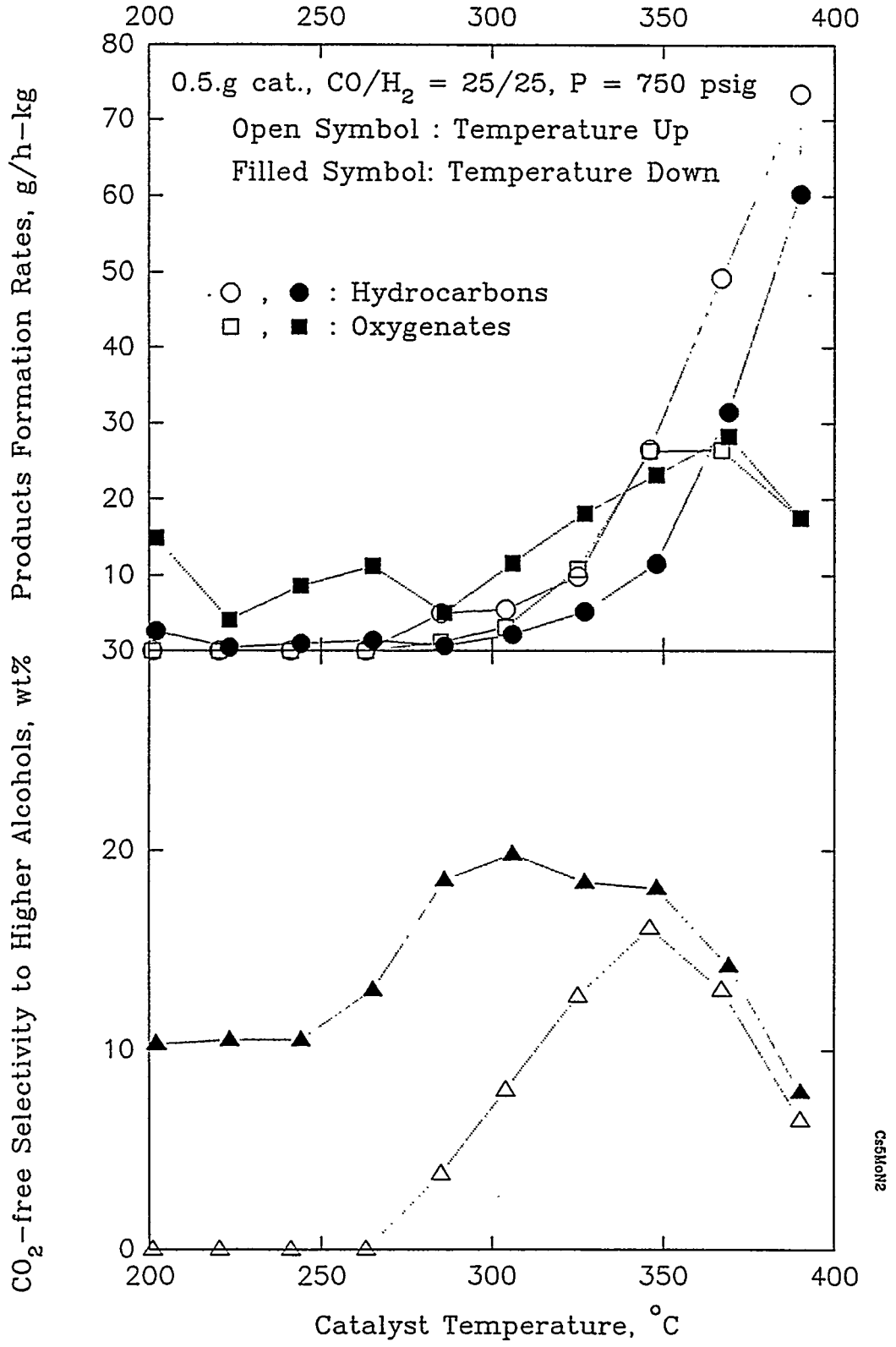

Figure 3. Performance of $Cs_{0.5}MoN$ catalyst.

dec94-3

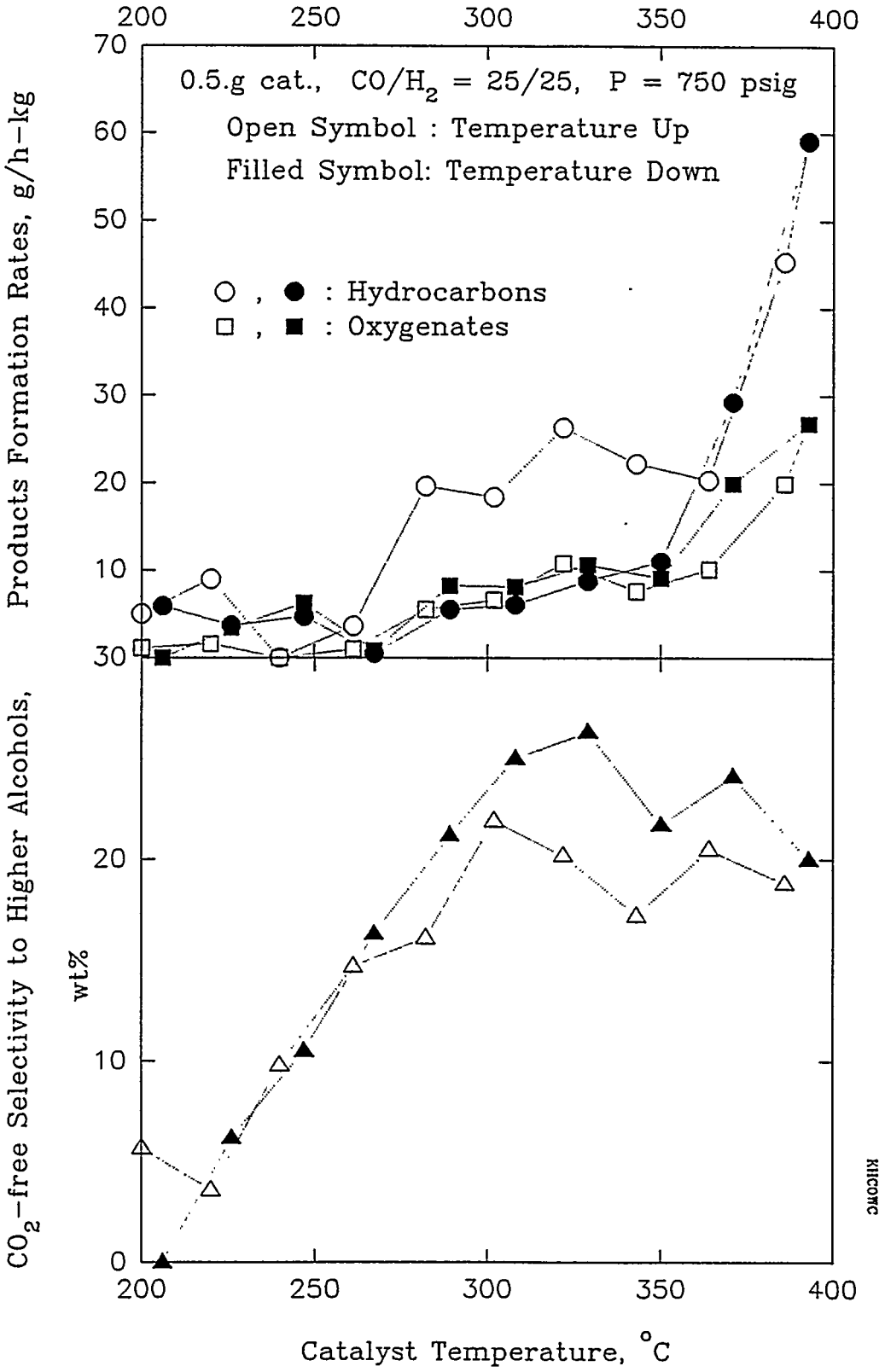

Figure 4. Performance of K(H)CoWC catalyst.

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TASK 2. PROCESS SYNTHESIS AND EVALUATION

2.1 Introduction

Much of the effort this quarter has focused on Monte Carlo uncertainty analysis. Frequency distributions have been determined for all of the equipment blocks. Mean costs vs. capacities and standard deviations of these costs were obtained from multilinear and nonlinear regression of reported data. Both functional valuation and U.S. Department of Energy (and other) projections are used. In the coming quarter, the simulation of return on investment will be started. Inputs will be the frequency distributions for the capital costs, raw materials costs, and product prices.

Modifications to the simulated annealing optimization program have been underway this quarter. The goal is to increase the level of certainty that the final result is near the global optimum.

Several alternative design cases have been examined in efforts to enhance the economics of the production of higher alcohols; however, all efforts in this area have had virtually little impact on the overall economics of the process. Given current economic conditions, the economics of the higher alcohols remains questionable in all cases in which they are the primary product. However, it may be economically feasible to produce higher alcohols as a by-product of another process. One such process may be the generation of electric power using combustion turbines fueled by synthesis gas. This process would fit into the realm of the proposed energy park suggested in the initial research proposal, although the primary product would become electricity instead of higher alcohols, as originally proposed. The investigation of a case of this nature may be justifiable given the considerable interest electric utilities have expressed with regard to the flexibility provided by modular facilities of this nature.

Fuel testing is continuing. Over the past three months, several items have been accomplished. These include ordering and installing instrumentation on the Waukesha engine, making necessary modifications to the computer program used in reading instrumentation on the Waukesha engine, finalizing the design of the emissions sampling system for the Waukesha engine, and ordering and assembling necessary parts for the emissions sampling.

2.2 Accomplishments, Results and Discussion

2.2.1 Monte Carlo Simulation

2.2.1.1 Capital Cost Uncertainties

Frequency distributions have been determined for all of the equipment blocks in Cases 1 and 4. Mean costs vs. capacities and standard deviations of these costs were obtained from multilinear and nonlinear regression of reported data. Consideration was given to the date of the cost data, especially with respect to significant design changes, such as in the gasifiers. As expected, certain units (e.g., cryoplant) have substantially lower uncertainties than do others (e.g., Shell Gasifier). Normal and log-normal distributions were used. All costs are on an installed basis and corrected for 1993.

In Figures 2.1 and 2.2 cumulative frequency distributions for the cases are shown. These figures depict the significant uncertainty in the capital cost for these Cases. For Case 1 (Texaco Gasifier with natural-gas steam reforming), the mean installed cost is $379 million, but there is a 10% chance that it could be greater than $417 million. Case 4 (Texaco Gasifier with sour-gas shift) shows a higher mean installed cost ($504 million) and substantially the same uncertainty (10% chance of cost higher than $572 million). As expected, in all coal Cases, the gasifier cost uncertainty has the greatest effect on the total cost uncertainty, measured by standardized regression coefficient, standardized rank regression coefficient, and partial rank correlation coefficient.

These cumulative frequency distributions for the installed capital costs of the Cases can now be used for two general purposes. First, the uncertainty in the capital requirements allows the quantification of risk. Second, the effects of more competitive gasifier costs can be shown via scenario analysis. These will be done in the coming quarter.

2.2.1.2 Variable Cost Uncertainties

The projected value of the alcohol product and the costs of the raw materials are uncertain inputs to the simulation model. Both functional valuation and U.S. Department of Energy (and other) projections are used.

The major products from the processes studied to date are the normal alcohols from methanol to pentanol. From the blending Reid vapor pressure, the blending octane number, and the oxygen concentration of these constituents, a functional valuation model has been developed. Inputs to this model are: MTBE price, gasoline (refinery gate) prices, and alternate blendstock values. Two linear models have been studied.

For the crude model, the alcohols are valued relative to their abilities to enhance octane, decrease RVP, and oxygenate the gasoline blend. If the value so calculated is greater than the current price for that alcohol, the lower price is used. According to this model, the value of the mixed blendstock is approximately $1 per gallon. In the coming quarter, uncertainties in the MTBE price and gasoline and alternate blendstocks will be included in a Monte Carlo simulation of this product value. The MTBE price will be estimated not on

historical data or projections alone. Rather, the "marginal producers cost" for MTBE will be estimated. This cost represents the variable costs for existing plant capacity and is a better estimate of prices in competitive environments. For example, Figure 2.3 shows historical data for MTBE prices. The local minima are first approximations to the marginal producers cost. Raw material costs will be estimated based on future projections of the Energy Information Administration. Statistical analyses of past projections vs. actual prices will be used to acquire the standard deviations of the projected costs.

For the linear-programming, blending model, only the values of the oxygenated fuels of various octane numbers need be input, along with the blendstock values. This model is being integrated with the simulated annealing program, and it guarantees conformance with existent EPA gasoline fuel waivers. Excess methanol is valued as fuel for enhanced electrical power production through an *energy park* scenario.

2.2.2 Optimization using Simulated Annealing

Modifications to the simulated annealing optimization program have been underway this quarter. The goal is to increase the level of certainty that the final result is near the global optimum.

Algorithm modifications include (1) the initial value of the system temperature, (2) the rate at which this temperature is decreased, and (3) the size of changes and the manner in which changes are made to the decision-variable vector during the optimization. Currently, the initial temperature is chosen to give a 90% probability that the maximum uphill move encountered in a test sequence will be accepted. In the modified procedure, the mean and standard deviation of the change in profit for a sequence of test moves are computed. Then the initial temperature is set so that a certain probability of accepting any move exists. The relationship between the starting temperature and the time required for the optimization and the degree of optimality will be tested on well-characterized problems. To enhance the cooling schedule, the number of accepted changes at a temperature level is prescribed and the mean and standard deviation of the change in cost is calculated. Then the temperature is adjusted to allow a lesser percentage of uphill moves to be accepted. Again, test problem experimentation will be used to determine the most efficient functional rate of decrease. Finally, the manner by which changes are made to the decision-variable vector is being studied. Currently, only one variable can be changed for comparison while the others are held constant. Further, the maximum change that can be made on that variable is independent of the temperature of the system. By changing more than one variable at a time, the program may be able to find better solutions that are more difficult to get to by allowing changes only on the specific variable axes. Varying the allowed size of change of the system variables, specifically by decreasing the range as temperature is decreased, makes intuitive sense. At high temperatures, the program needs more freedom to explore the solution space as it is not presumed to be near the optimum. At lower temperatures, where one expects to be near the optimum, the program should not be allowed to leap from near the optimum into

inferior sections of the solution space, because, at the reduced temperature it is less likely to be able to return to the region where it belongs. It remains to be seen whether or not the intuitive notion corresponds to the results of experimentation.

2.2.3 Economic Analysis

Electric utilities have expressed considerable interest in the phased implementation of IGCC units and any method that may improve their economics. Phased implementation may lend itself to the production of alcohols if the price of natural gas were to rise significantly justifying the retro-fitting of gas fired turbines with gasifiers on the front end. Since there is little flexibility with regard to capacity utilization, any additional syngas produced by the gasifiers could be diverted to the production of mixed alcohols. Methanol, which has to be separated from this product because of its undesirable properties for fuel additive usage, may be stored and burned to meet peak electric demands.

The economics of this process may be examined by simply modifying one of the current cases in order to produce electricity as the primary product. Figure 2.4 is an illustration of this new case. The design should be based on an acceptable average size power generation facility in the range of 400 to 600 MW with a peaking capacity of an additional 5 to 50 % of the base load. Peak power demand is regional and seasonal dependent; therefore, without a specific plant sight, it is difficult to narrow this range. Although some assumptions regarding the location of this facility will inevitably have to be made before the development of this case may proceed, some insight with regard to the minimum size of a peaking power loop may be provided by turbine availability. The logistical coal constraint established in the previous cases must also be recognized in the development of this new case.

Cost estimates for this case should be developed both with and without the production of the oxygenate so that the cost of producing the oxygenate by this type of process can be obtained. This should require only minor modifications to the design. The cost estimates for the process without the oxygenate may also be used for comparison purposes, since similar studies have been conducted examining the economic potential of producing and storing methanol for use in meeting peak power demands.

2.2.4 Fuel Testing

Over the past three months, we have accomplished several items which include ordering and installing instrumentation on the Waukesha engine, making necessary modifications to the computer program used in reading instrumentation on the Waukesha engine, finalizing the design of the emissions sampling system for the Waukesha engine, and ordering and assembling necessary parts for the emissions sampling.

2.2.4.1 Fuels for Testing

With the above items completed, the next step was to decide which fuels to test using the testing setup. The fuels to be tested include:

1. Baseline fuel (Indolene)

2. Alcohol/Indolene blend of 2% Methanol, 6.4% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.125% Water, 90% Indolene

3. Alcohol/Indolene blend of 1.5% Methanol, 6.9% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.13% Water, 90% Indolene

4. Alcohol/Indolene blend of 1.3% Methanol, 7.1% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.13% Water, 90% Indolene

5. Alcohol/Indolene blend of 1.0% Methanol, 7.4% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.13% Water, 90% Indolene

6. Alcohol/Indolene blend of 0.5% Methanol, 7.9% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.13% Water, 90% Indolene

7. Alcohol/Indolene blend of 0.0% Methanol, 8.4% Ethanol, 1.2% Propanol, 0.2% Butanol, 0.1% Pentanol, 0.13% Water, 90% Indolene

All of the above alcohol/indolene blends consist of 10% alcohols and 90% indolene, and all of the blends contain no more than 3.7% oxygen by weight.

2.2.4.2 Engine Operating Conditions

The engine was operated at the following settings: Compression ratio 8.7:1, spark timing 25° BTDC, speed 900 RPM. These settings were kept constant throughout each test and the entire series of tests. The A/F ratio was varied between two settings: stoichiometric, and then slightly lean.

2.2.4.3 Test Procedure

The following test procedure was followed:

1. Warm up the engine using indolene, when steady state conditions are reached, a bag sample will be drawn for 7 minutes (bag #1)

2. Switch the fuel to the alcohol/indolene blend to be tested. The engine is allowed to stabilize on the blend for 10 minutes, then a bag sample is drawn for 7 minutes (bag #2).

3. Run the engine for 10 minutes without sampling.

4. Draw another bag sample for 7 minutes (bag #3).

5. Run the engine for 10 minutes without sampling.

6. Draw another bag sample for 7 minutes (bag #4).

7. Switch the fuel back to indolene, change the A/F ratio to a slightly lean mixture, and allow the engine to stabilize for 10 minutes. Then draw a bag sample for 7 minutes (bag #5).

8. Switch the fuel to the alcohol/indolene blend to be tested. The engine is allowed to stabilize on the blend for 10 minutes, then a bag sample is drawn for 7 minutes (bag #6).

9. Run the engine for 10 minutes without sampling.

10. Draw another bag sample for 7 minutes (bag #7).

11. Run the engine for 10 minutes without sampling.

12. Draw another bag sample for 7 minutes (bag #8).

The purpose of this testing procedure was to ensure the consistency of the results. The results from bags 2,3,4 were expected to be the same, and, likewise, the results from bags 6,7,8 were expected to be the same.

2.2.4.4 Explanation of Exhaust Sampling Apparatus

Figure 2.5 is a flow diagram of the exhaust sampling apparatus. In the diagram, the abbreviations are as follows: MFC = mass flow controller, P = pump, BX and DX are filters, $3V_x$ = three way valves. The flow rates through the mass flow controllers were as follows:

MFC1: 8.16 SLPM
MFC2: 7.2 SLPM
MFC3: 2.9 SLPM
MFC4: 0.48 SLPM

These flow rates yield a dilution air to exhaust gas ratio of 3.37:1.

2.2.4.5 Results of Testing

The test procedure mentioned earlier was used on one of the alcohol/indolene blends. Unfortunately, the results were inconsistent. The concentrations of hydrocarbons, oxides of nitrogen, carbon monoxide, and carbon dioxide varied from bag to bag with the engine running at the same conditions with the same fuel. Possible problems that could have caused the results to be inconsistent were:

- Engine operation
- Fuel flow rate
- Leaks in sample bags
- Drift in the mass flow controllers
- Leakage in the sampling system

Each of the above were individually checked. The bags were checked for leaks using a vacuum gage; the mass flow controllers were checked for accuracy and consistency using a bubble flow meter; the engine operating conditions were monitored closely, and the sampling system lines were checked for leaks. It turned out that the pressure relief valve was choking the flow of fresh dilution air into the system through MFC1 (see Figure 2.5). So the pressure relief valve was removed from the system entirely and then we ran straight indolene using the testing procedure mentioned before to check for consistency in the exhaust gas emissions. The results were far more acceptable.

2.3 Conclusions and Recommendations

It is recommended that a new case be prepared, as a power plant with peaking capacity. Higher alcohols would be a by-product. Although higher alcohols may not be the primary product in this new case, this case should not be dismissed because it provides potential to provide sufficient quantities of higher alcohols. However, more facilities may be required due to lower capacities at each facility. This should not present a problem since electric utilities have proposed the installation of numerous IGCC units to meet future power demands. Facilities like the one proposed in this new case would provide electric utilities with flexibility, lower emissions, and a potential low cost method of storing power, while simultaneously providing oxygenates to aid in emission reductions in the transportation sector.

2.4 Future Plans

2.4.1 Monte Carlo Uncertainty Analysis

In the coming quarter, the simulation of return on investment will be started. Inputs will be the frequency distributions for the capital costs, raw materials costs, and product prices. Scenario analyses will then be performed.

2.4.2 Optimization using Simulated Annealing

The plan for the immediate future involves running experiments on known problems. From the results of these experiments, general trends between parameters of the simulated annealing routine and the degree of optimality of the final solution and the time required to obtain that solution will be inferred. Those parameters of primary interest are the initial system temperature, the rate of temperature change, and the manner and size of changes to the decision-variable vector.

2.4.3 Economic Analysis

The new case, in which higher alcohols are made as a by-product of power generation, will be analyzed in order to determine whether it is economically attractive.

2.4.4 Fuels Testing

Tests that were run earlier, which were unsuccessful, will be re-run on the alcohol/indolene blends using the same procedure.

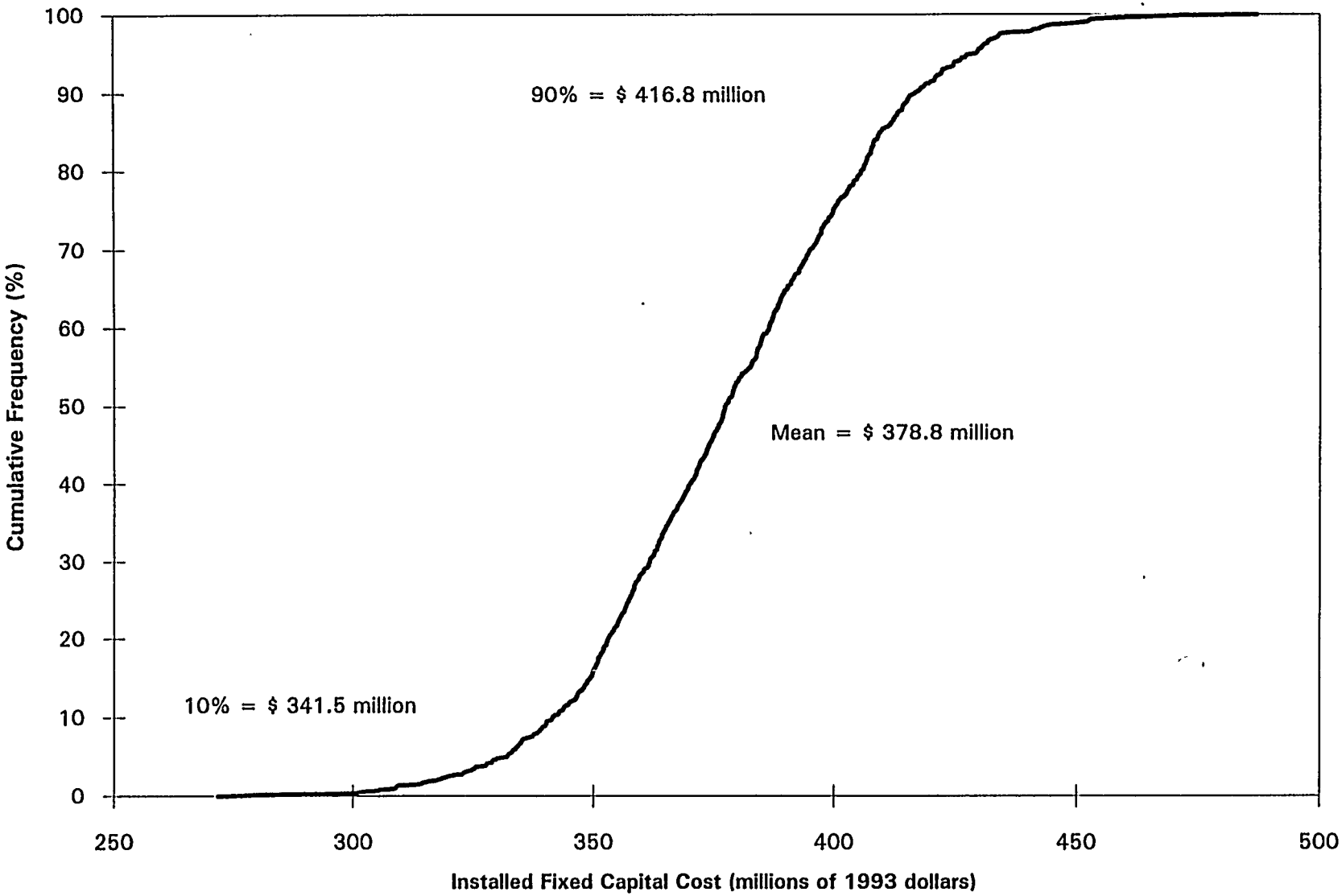

Figure 2.1. Capital Cost Uncertainty for Case 1

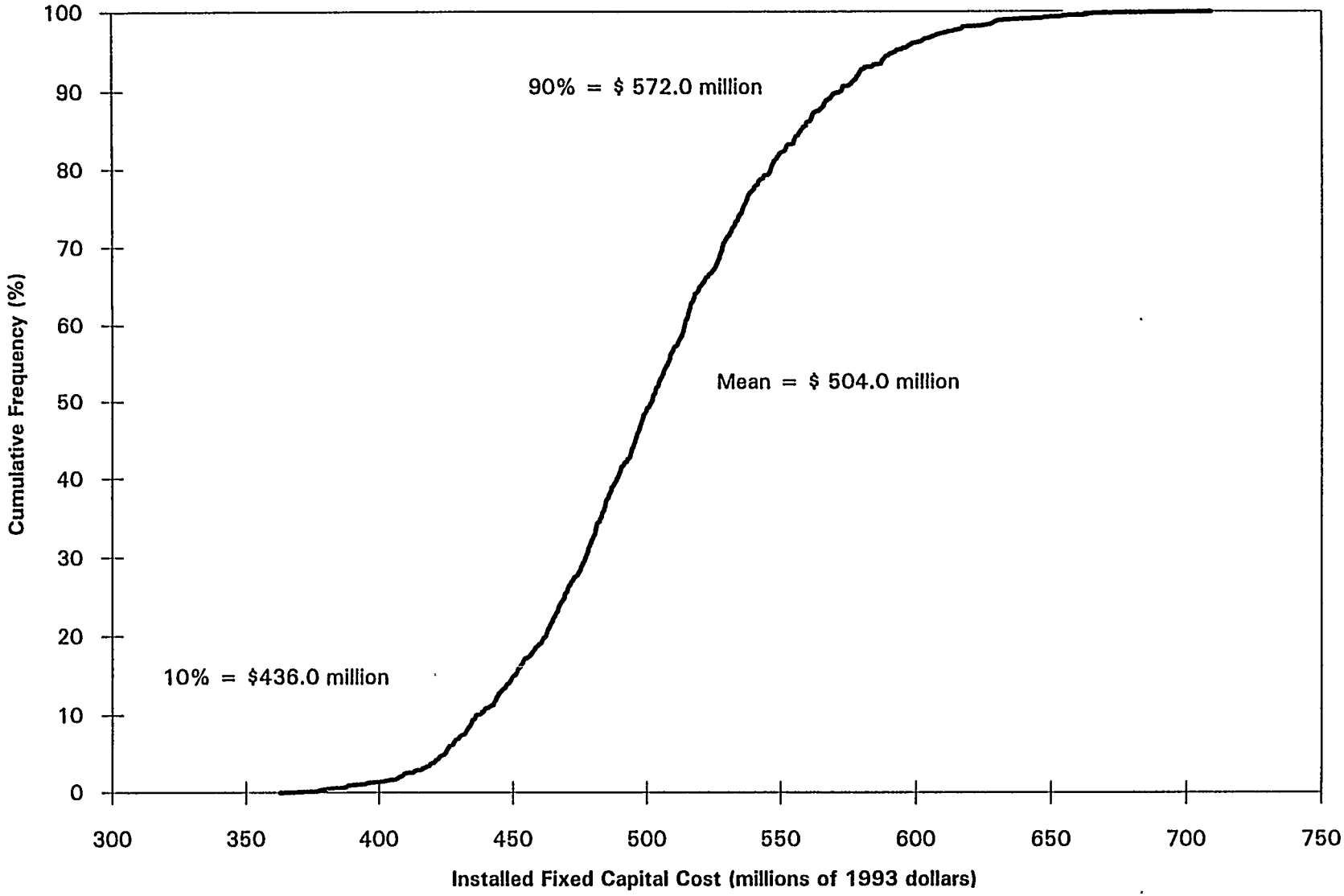

Figure 2.2. Capital Cost Uncertainty for Case 4

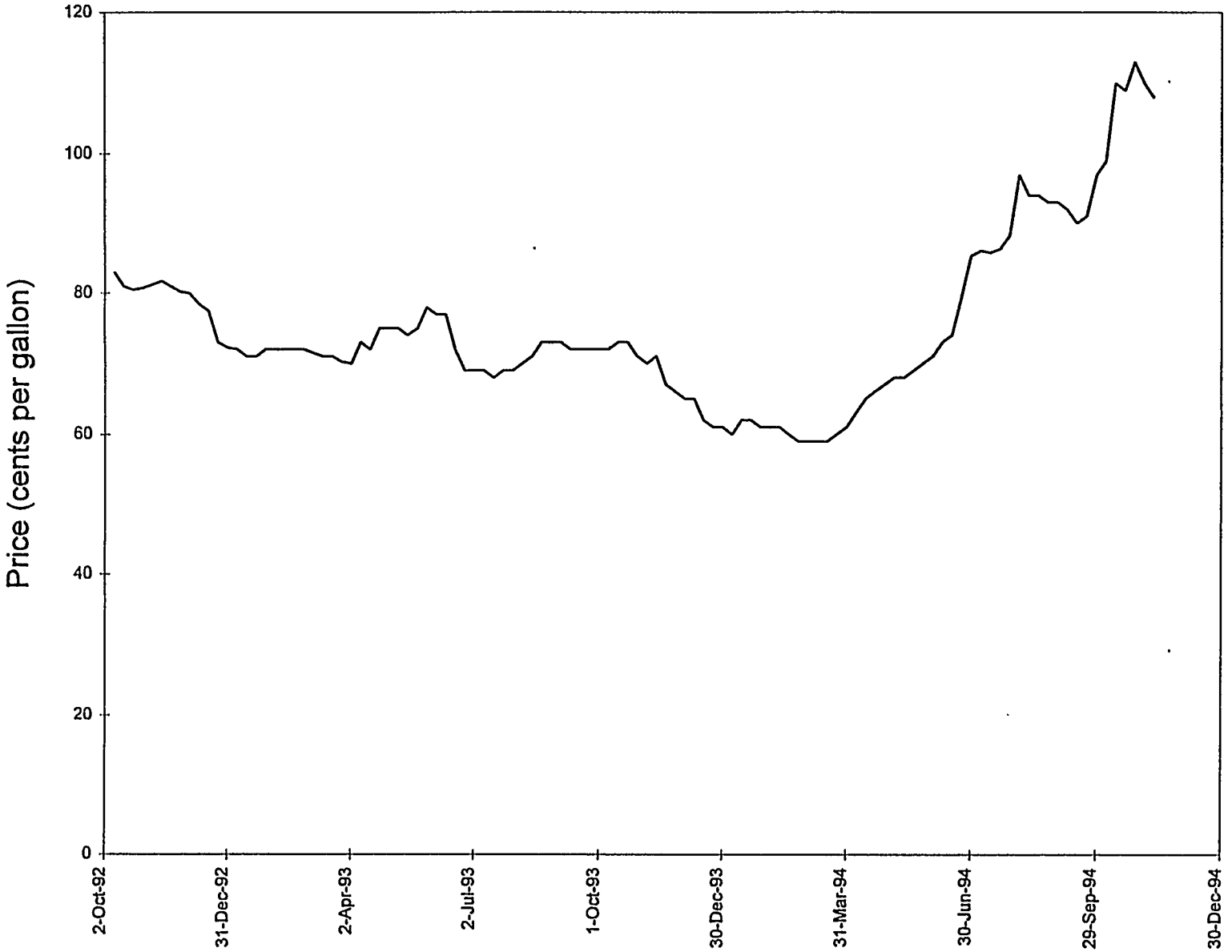

Figure 2.3. MTBE Weekly Spot Price History

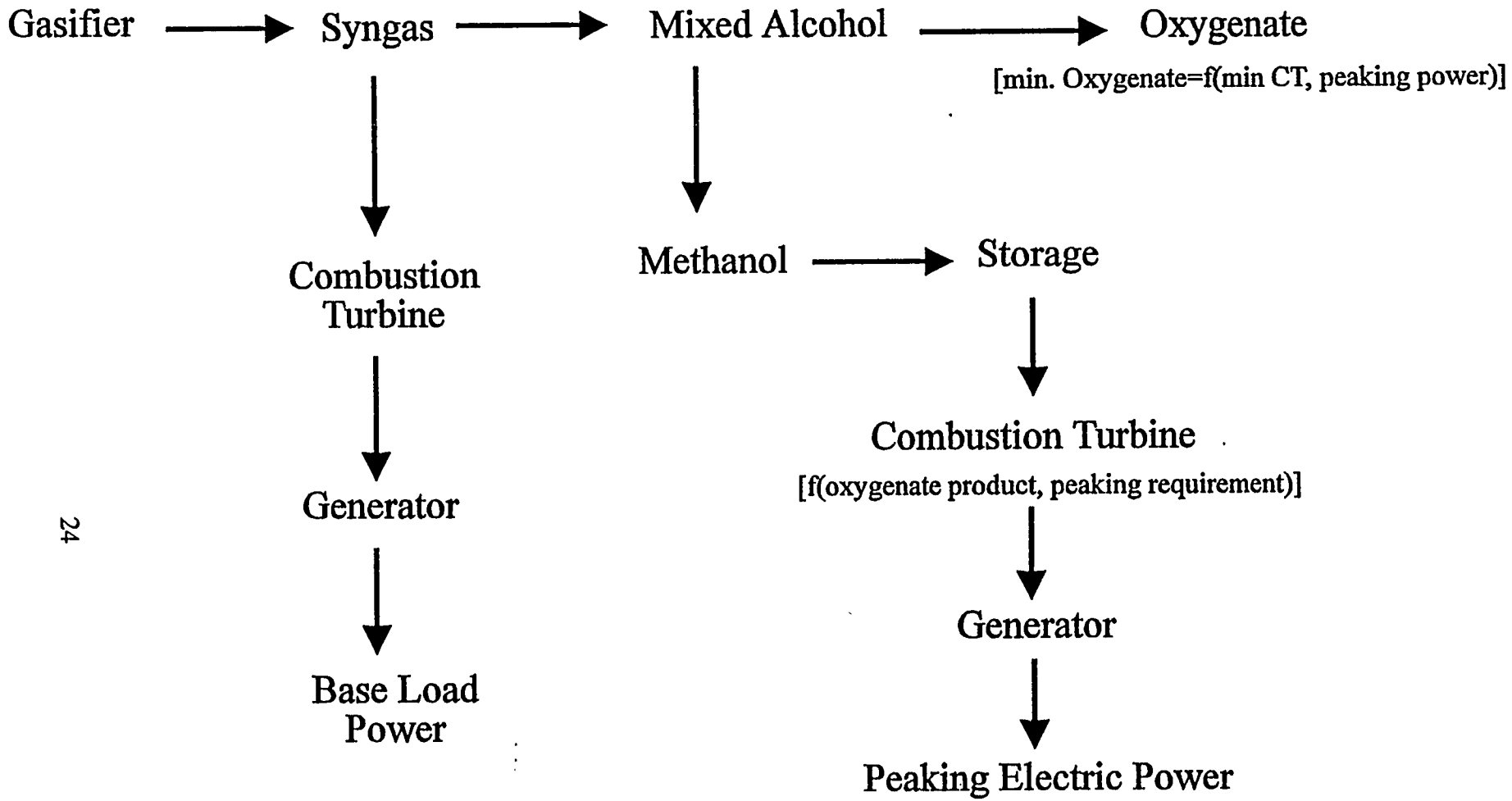

Figure 2.4: Preliminary Flow Diagram for New Design Case

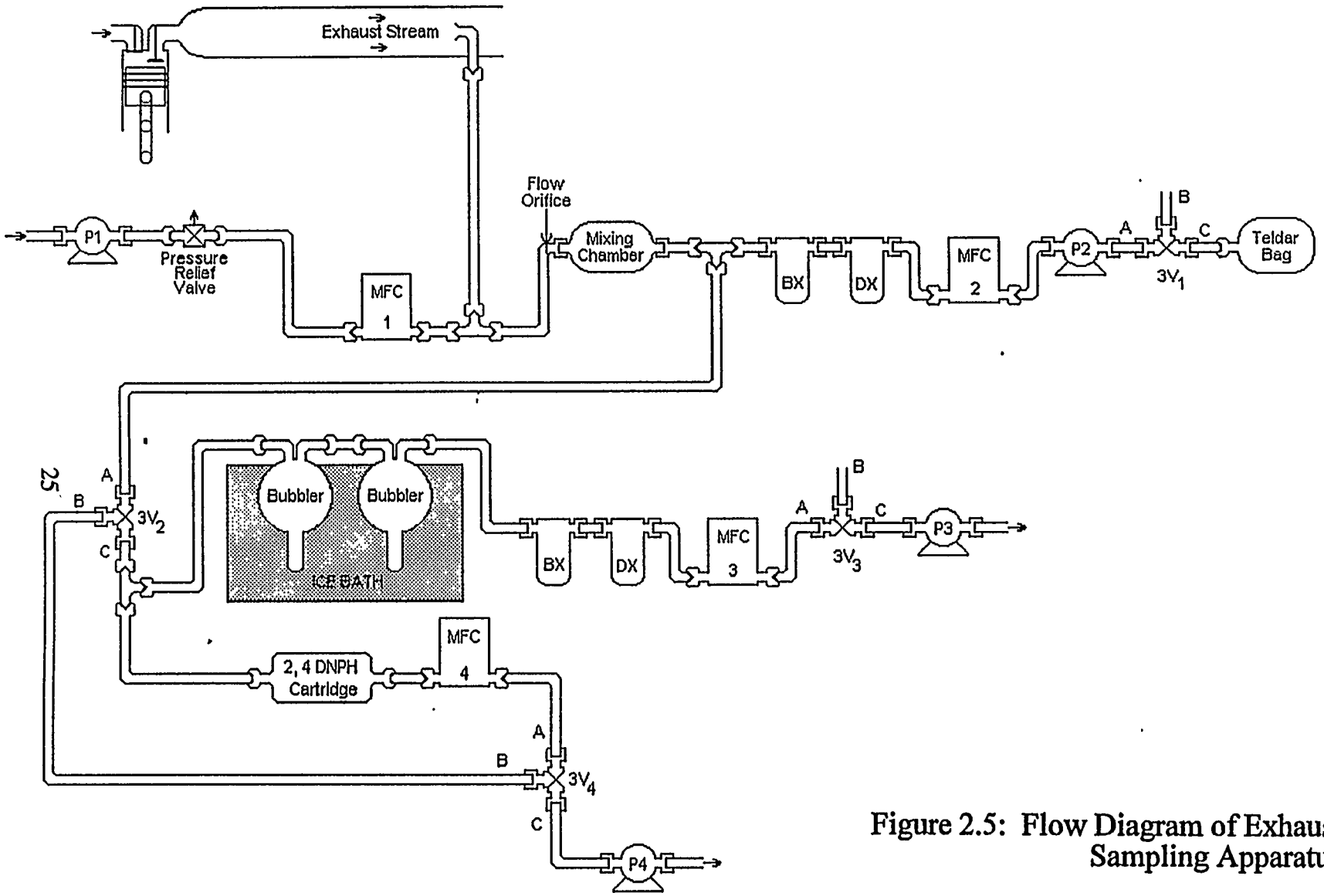

Figure 2.5: Flow Diagram of Exhaust Sampling Apparatus