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

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Executive Summary

In Task 1, during this reporting period, the plug-flow reactor used for sulfided systems was converted to a Berty-type reactor. Subsequent to the conversion, we stopped screening sulfide catalysts. Prior to the conversion, six sulfide catalysts were prepared and evaluated: MoS_2, $K_{0.7}MoS_2$, $Rb_{0.7}MoS_2$, $Cs_{0.7}MoS_2$, $Fe_{1-x}S/SiO_2$ and $K_{0.8}Fe_{1-x}S/SiO_2$. These catalysts were all produced by vapor-phase reactions, followed by alkali addition using incipient wetness techniques. The alkali/molybdenum catalysts all satisfied the project requirements for product selectivity and activity. The iron sulfides were poor catalysts, with conversion rates less than 1 % and product distributions strongly favoring hydrocarbons. Materials produced subsequent to the conversion were all transition-metal nitrides or carbides. The nitrides/carbides were produced by three methods: vapor-phase synthesis, temperature programmed decomposition (TPD) of MoO_3 in flowing ammonia, or thermal decomposition of a silica-supported molybdenum azide. These molybdenum nitride/carbide catalysts are generally highly active catalysts at high temperatures, but most produce an Anderson-Schultz-Flory (ASF) distribution of alcohols, in addition to many higher-molecular-weight products.

We tested a commercial Zn/Cr catalyst support, both bare and impregnated with potassium and cesium at various loadings. None of these catalysts looks promising for the production of higher alcohols. We also manufactured two new Zn/Cr supports which are available for testing now.

Two presentations have been made during this reporting period. One presentation was given at the Tri-State Catalyst Club Spring Symposium on Heterogenous and Homogeneous Catalysis in Charleston, WV from April 12-13, 1995. The other was presented during the 14th North American Meeting of the Catalysis Society, held June 11-16, 1995, at Snowbird, Utah.

In Task 2, in order to complete revisions of the topical report on case studies originally submitted last summer, additions and revisions have been made to the design cases. Case 7 (power plant with alcohols as by-product), originally presented in the March 1995 Quarterly Report has been added. The alcohol synthesis loop has been modified for all of the cases. Now, all hydrocarbons produced in the synthesis reactor are recycled since there is no economical method to separate them from the light gases. Finally, the power production section of each case has been updated to reflect the efficiency of modern gas turbines. The energy balance for each case has been modified accordingly.

The simulated annealing optimization algorithm has also been improved. The parameters used in the program have been varied to determine their effect on the final solution. By studying these effects, we are identifying the major parameters and what values of those parameters are best. In this manner, the algorithm will become more efficient and accurate when it is used on the higher alcohol/gasoline blending problem.

Due to the excessively high degree of condensation during exhaust sampling, the design and construction of the emissions sampling system was completely overhauled. It was discovered that the warm-up mode on the system bypassed a mass flow controller which created a very low dilution ratio. Therefore, it was decided to dismantle and rebuild the entire sampling rig. Reconstruction of the sampling system is now done, and the mass flow controllers are working properly.

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 Corporation (UCC) is focused on transition-metal-oxide catalysts.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory Setup

A significant event during this reporting period was the (re-)conversion of one of the plug-flow reactor systems to a Berty-type reacting system. The Berty-type reactor had previously been set up, then replaced by the plug-flow system in order to increase the number of catalysts that could be subjected to a screening test. The plug-flow reactor system that had been exposed to sulfides was converted over to the Berty system. This allows us to continue testing selected non-sulfide catalysts in the other plug-flow reactor system.

Because of the large thermal lag resulting from the large mass of the Berty reactor, new temperature programs had to be developed and tested. Two test runs were made using standard methanol catalysts (supplied previously by Union Carbide and BASF). During the test runs, problems surfaced with the operating system, due to the non-use of the Berty system. These problems were identified and fixed.

In order to supplement current research in transition-metal carbides and nitrides, a temperature-programmed-decomposition (TPD) system is being developed at WVU. All the components for TPD have been purchased and assembled. In a preliminary reaction, γ-Mo_2N (1MRC163A) was prepared by decomposing fully oxidized MoO_3 (5.0 grams) in an ammonia stream (150 mL/min) from ambient temperature to 700 °C, using a heating ramp of 36 °C/hr. The product obtained from this thermolysis was identified as γ-Mo_2N from an X-ray powder diffraction study (see Figure 11, MS45). The BET surface area for 163A was 15.5 m^2/g.

1.2.2 Molybdenum-Based Catalyst Research

Materials prepared during this period are collected in Table I. Three of these, 2MRC157A, 2MRC157B and 2MRC157C were prepared by adding acetates of K, Rb, and Cs (0.7 mole of alkali/mole Mo) to high-surface-area MoS_2 prepared by vapor-phase thermolysis of $Mo(CO)_6$ and H_2S. The MoS_2 and alkali salts were weighed together in a dry box and subsequently exposed to air. Methanol was then added to the mixture to solubilize the alkali. The resulting viscous slurry was ground in a mortar and pestle and dried in air at 62°C for 12h. The dried powders were pressed into pellets and broken into smaller fragments before being screened for catalytic performance. This series of materials allows comparison of the cation size (or more importantly, the cation basicity) and the amount of cation. The results of the screening tests are discussed later.

$Fe_{1-x}S$-based materials were prepared by decomposing 6.0mL $Fe(CO)_5$ in a flowing stream of H_2S (11 mL/min) and argon (920 mL/min) at 500 °C. Pyrrhotite ($Fe_{1-x}S$, 2MRC149A) was formed under these conditions, as verified by XRD. Direct air exposure caused combustion of the material. In order to passivate the material, air was allowed to diffuse into the product chamber over a 24h period. This method of passivation yielded material that was air stable. Two catalysts were prepared based on 2MRC149A. 2MRC154A was prepared by mixing $Fe_{1-x}S$ (300.0 mg) with SiO_2 (300.0 mg) as a binder. 2MRC154B was prepared by grinding together a mixture of 2MRC149A (0.2401 g), $KC_2H_3O_2$ (0.2090 g), and silica (0.2401 g). Both catalysts were prepared as pellets and screened for catalytic performance.

Using a furnace temperature of 700 °C, crystallographically pure cubic Mo_2C (2MRC155A) was formed by the thermal decomposition of $Mo(CO)_6$ (3.0106) in flowing argon. The powder X-ray diffraction pattern shows only the cubic phase. (From previous studies, reactions with ammonia at similar temperatures produce the tetragonal Mo_2N and δ-MoN. Also, using flowing ammonia and temperatures ranging from 950-1050 °C, hexagonal Mo_2C can be formed.) The 2MRC155A (0.3000 g) was mixed with silica support material (0.3000 g) using a mortar and pestle. The SiO_2 was added to promote better binding when pelletized. The combined powders were pressed into pellets, cracked into smaller pieces and submitted for catalytic testing. A second molybdenum based catalyst was prepared from δ-MoN (see TPR14) and TiO_2 (2MRC154C). The TiO_2 was used to evaluate the influence of the support material on the MoN catalyst.

MoN(C) and $Mo_2N(C)$ were also produced from vapor-phase reactions. 2MRC161A (δ-MoN(C)) was prepared by decomposing thermally $Mo(CO)_6$ (3.0 grams) and ammonia (100 mL/min) vapors at 800 °C. XRD of 2MRC161A indicates a composition of 80-90% MoN and 10-20% Mo_2N, while the surface area is 12.3 m^2/g. Figure 12 in MS45 indicates that, while a small amount of the cubic-phase Mo_2N is present, the vast majority of the material in 2MRC161A is hexagonal MoN. 2MRC163A (γ-$Mo_2N(C)$) was produced by decomposing thermally $Mo(CO)_6$ (3.0 grams) and ammonia (100 mL/min) vapors at 600 °C. Based on the XRD pattern, 85-95% of the material was composed of γ-$Mo_2N(C)$ and the

remainder was MoN. 2MRC163A was prepared to compare with γ-Mo_2N prepared by TPD of MoO_3 (1MRC163A).

Finally, a silica-supported nitride was prepared by thermal decomposition of a metal azide compound, $MoN_3N(C_6H_5N)$. The metal azide was dissolved in dichloromethane and added to the silica support using incipient wetness techniques. The azide had a low solubility, therefore multiple additions of the solution and interstage drying were required to obtain a 5% molybdenum loading. The supported azide was decomposed thermally at 500°C in flowing ammonia to produce the supported molybdenum nitride. A methanolic solution of potassium acetate was then added to the supported nitride to yield the final composition of $K_{0.71}MoN_x$ (1MRC160A).

A total of 32 catalysts were screened during this reporting period. These include 18 sulfides and 14 non-sulfides. For the sulfides, we have reported in detail on the formation rate of oxygenates and hydrocarbons, and CO_2-free selectivity to MeOH-free oxygenates in the monthly reports. For most of the non-sulfide catalysts, product identification continues to be a problem for us, due to formation of many heavier products. Calculations of yields and selectivities for non-sulfides are not possible at the present time. Only CO conversions (determined from an internal standard) and GC areas have been reported for the non-sulfide catalysts.

Among the 18 sulfide catalysts screened this quarter, 5 satisfy the criteria for the selection of catalysts for further development in the Berty-type reactor. The criteria, noted in MS33, include: an activity of 100g product/kg catalyst/h; 50% selectivity to alcohols, and 20% selectivity to higher alcohols. The 5 catalysts are listed in Table II, along with the formation rate of total products at the temperature corresponding to the maximum production rate of oxygenates, as well as the selectivities (to total oxygenates and to higher oxygenates) obtained at the same temperature.

The effect of alkali on the vapor-phase synthesized MoS_2 was studied using K, Rb and Cs, prepared as described above. The best performance of each catalyst is listed in Table II. It can be seen that K and Rb give better results than Cs for this type of MoS_2. Detailed comparisons can be found in MS45.

The effect on catalyst performance of H_2S in the feed stream was evaluated using alkali-doped C-supported MoS_2 catalysts Mo-K/C (ELK02) and Mo-Co-K/C (ELK03). At a concentration of 13.5 ppm in the feed, H_2S has little effect on catalyst activity. Detailed results can be found in MS45.

The effect of iron in the catalyst has also been investigated. Five of the 18 sulfide catalysts contain iron (Fe). The catalysts composition varied from $Fe_{1-x}S$ (see above) to K-doped $Fe_{1-x}S$ and to K-doped Fe- and Mo-sulfides. They were either unsupported or supported on carbon, or on SiO_2. In general, these catalysts show low activity towards alcohols. The exception is a K-Fe-Mo/C catalyst (FK11), for which the results satisfy the criteria for further investigation and are shown in Table II.

Two groups of non-sulfide catalysts were tested: gas-phase synthesized molybdenum nitride (8 catalysts), and carbon-supported and reduced molybdenum and nickel catalyst (6 catalysts). Both of these catalyst types form a significant amount of unidentified heavier products. Production rates, therefore, cannot be determined. While it is possible that some of these catalysts satisfy the minimum criteria for additional development, they are not listed in Table II.

1.2.3 Transition-Metal-Oxide Catalyst Research

At UCC, we tested an Engelhard Zn/Cr support (designated 2WMH61B) at 1000 psig pressure with 1:1 H2:CO syngas at 12000 GHSV from 260 - 440 °C. The first isobutanol was detected at 400 °C, but was being produced at a rate of only 5 g/kg/hr. At 440 °C, the isobutanol rate was up to 9 g/kg/hr.

Later, we tested 2WMH61B from 260 - 340 °C after impregnating (incipient wetness method) with 1, 3, and 5 wt% potassium. We ran at 12000 GHSV, 1000 psig and with 1:1 H2:CO as before. In all cases, higher-alcohol production is low. Isobutanol is formed in measurable quantities only for the case with the highest potassium loading (5%) at the highest temperature (340 °C). CO conversion increases with temperature, as expected. Higher temperatures also promote hydrocarbon selectivity at the expense of methanol selectivity. C_{2+} alcohol selectivity appears to increase significantly from 260 °C to 300 °C, but a further increase in temperature (to 340 °C) does not result in a corresponding increase in C_{2+} alcohol selectivity. Supports impregnated with potassium have higher C_{2+} alcohol selectivity than the bare supports at all temperatures. C_{2+} alcohol selectivity increases with potassium loading.

Also, we tested 2WMH61B from 260 - 340 °C after impregnating (incipient wetness method) with 3 and 5 wt% cesium. As with the potassium-impregnated catalysts, we ran at 12000 GHSV, 1000 psig and with 1:1 H2:CO. Again, higher-alcohol production is low. Isobutanol is formed consistently only for the case with the highest cesium loading (5%) at the highest temperature (340 °C). CO conversion increases with temperature as expected. Higher temperatures also promote hydrocarbon selectivity at the expense of methanol selectivity. Adding only 3% Cs does not improve C_{2+} alcohol selectivity. However, C_{2+} alcohol selectivity is improved with the addition of 5% Cs. At a loading of 5% Cs, C_{2+} alcohol selectivity appears to increase from 260 °C to 300 °C, but a further increase in temperature (to 340 °C) does not result in a corresponding increase in C_{2+} alcohol selectivity.

We manufactured two new Zn/Cr catalyst supports for use in later testing. The two supports differ mostly in the amount of ZnO used in their manufacture. The catalyst with less zinc (16DMM116) has a BET surface area of 94 m^2/g. XRD analysis indicates the catalyst support is composed mainly of a zinc chromium oxide spinel. Potassium exists as an impurity at around 700 ppm, but sodium concentration is less than 2 ppm. For the support with more zinc, 16DMM85, complete analytical results are not available.

Limited reactor testing indicated that bare 16DMM85 support performs as an inefficient

inefficient methanol catalyst at temperatures ranging from 400 - 440 °C at 1000 - 1500 psig pressure (12000 GHSV; 1:1 H2:CO). The isobutanol rate is less than 5 g/kg/hr, and there is a 40 - 70% range of selectivity to hydrocarbons.

1.3 Conclusions and Recommendations

Potassium and cesium affect the conversion and C_{2+} alcohol selectivity of Zn/Cr catalyst supports. The temperature also plays a role in the catalytic performance. Alkali-activated MoS_2 produced by vapor-phase decompositions effectively catalyzes the conversion of synthesis gas to alcohols. Typically, molybdenum- or iron-based carbides/nitrides catalyze the synthesis of a wide distribution of products. Vapor-phase methods have been used to prepare hexagonal MoN, cubic Mo_2N and cubic Mo_2C. A TPD system has been built to produce metal nitrides from selected precursors.

1.4 Future Plans

At WVU, the screening studies of the molybdenum sulfides have been completed. As a result, future catalyst preparations will be focused on the synthesis of transition metal nitrides and carbides. Detailed studies will commence on selected sulfide catalysts. At UCC, the newly prepared Zn/Cr catalyst supports will form the basis of catalysts to be tested.

Table I.

Summary of catalysts prepared during 4/1/95-6/30/95.
All iron or molybdenum sulfides or carbides were prepared by vapor phase reactions.

Reference	Catalyst Composition
2MRC157A	$K_{0.7}MoS_2$ (2MRC145A)/KAc. 41.9 % Mo.
2MRC157B	$Rb_{0.7}MoS_2$ (2MRC145A)/RbAc. 36.7 % Mo.
2MRC157C	$Cs_{0.7}MoS_2$ (2MRC145A)/CsAc. 32.6 % Mo.
2MRC154A	$Fe_{1-x}S/SiO_2$ (300 m^2/g). 30.53 % Fe.
2MRC154B	$Fe_{1-x}S$/KAc/SiO_2 (300 m^2/g). K/Mo= 0.7; 30.53 % Fe.
2MRC157D	Mo_2C (21.9 m^2/g)/SiO_2 (300 m^2/g). 47.05 % Mo.
2MRC162A	δ-MoN (12.3 m^2/g)/SiO_2 (144 m^2/g). 43.6 % Mo.
2MRC154C	δ-MoN (12.3 m^2/g)/TiO_2 (150 m^2/g). 43.6 % Mo.
2MRC163A	γ-Mo_2N (15.5 m^2/g). 93.1 % Mo.
1MRC160A	$K_{0.71}MoN_x$ (supported). 5.0 % Mo.

Table II.

Sulfide catalysts tested in this quarter that meet the criteria for additional work in the Berty-type reactor.

CATALYST	TOTAL PRODUCTION RATE AT MAXIMUM OXYGENATE RATE [g/kg/h]	SELECTIVITY TO TOTAL OXYGENATES AT MAXIMUM OXYGENATE RATE [wt%]	SELECTIVITY TO HIGHER OXYGENATES AT MAXIMUM OXYGENATE RATE [wt%]
EZ02H [K-$Mo/_C$]	163	58	27
FK11 [K-Fe-Mo/C]	108	52	24
2MRC157A [$KMoS_2$,VPR]	254	84	43
2MRC157B [$RbMoS_2$,VPR]	252	85	37
2MRC157C [$CsMoS_2$,VPR]	176	83	33

TASK 2. PROCESS SYNTHESIS AND FUEL EVALUATION.

2.1 Introduction

Much of the effort during the past quarter has been updating the topical report originally submitted last summer. Case 7 (power plant with alcohols as by-product), originally presented in the March 1995 Quarterly Report has been added to the topical report. Improvements to the designs in the other six cases have also been made.

Improvements have been made to the simulated annealing routine. Other optimization problems are being studied using the annealing algorithm. At the same time, the parameters used in the program are varied to determine what effect they have on the final solution. By studying these effects, we hope to determine what the major parameters are and what values of those parameters are best. In this manner, we will make the algorithm more efficient and accurate when it is used on the higher alcohol/gasoline blending problem.

The design and construction of the emissions sampling system was completely overhauled due to the excessively high degree of condensation during exhaust sampling. It was discovered that the warm-up mode on the system bypassed a mass flow controller which created a very low dilution ratio. Thus, the dew point of the diluted exhaust was above ambient conditions, and the mass flow controllers filled with oily water. Therefore, it was decided to dismantle and rebuild the entire sampling rig.

2.2 Accomplishments, Results, and Discussion

2.2.1 Design

Much of the effort during the past quarter has been updating the topical report originally submitted last summer. Case 7 (power plant with alcohols as by-product), originally presented in the March 1995 Quarterly Report has been added to the topical report. The synthesis loop has been modified for all of the cases. Now, all hydrocarbons produced in the synthesis reactor are recycled since there is no economical method to separate them from the light gases. Finally, the power production section of each case has been updated to reflect the efficiency of modern gas turbines. The energy balance for each case has been modified accordingly.

Work is continuing on the economic analysis of an alcohol and gasoline blending operation. This operation will be optimized using the simulated annealing algorithm that is currently being developed (see below). In addition to work on this algorithm, we are revising both the capital cost estimates for the facility and the amounts and compositions of the mixed alcohol stream produced by the synthesis reactor. Also, we are optimizing the recycle around the synthesis reactor in each of the seven cases.

We are optimizing the purge ratio in the synthesis loop based on power production

and manufacturing costs. The purge ratio affects the concentration of methane in the recycle loop, which in turn affects the amount of unused syngas that is purged to power production.

We have recently received an updated version of ASPENPlus (Release 9.0) simulation software, which includes updates on capital cost estimation. We will be using this software to generate capital costs for various units in the blending facility at different process stream conditions and compositions. We can regress these data to equations which will then be used in the optimization algorithm.

Using data from Quarderer [1], we are making estimates of the level and composition of alcohol production in the synthesis reactor. We will continue to use these estimates until such time as data are available from Task 1.

2.2.2 Optimization by Simulated Annealing

While the data above are being compiled and analyzed, the simulated annealing routine is being improved. Other optimization problems are being studied using the annealing algorithm. At the same time, the parameters used in the program execution are varied to determine what effect they have on the final solution. By studying these effects, we hope to determine what the major parameters are and what values of those parameters are best. In this manner, we will make the algorithm more efficient and accurate when it is used on the blending problem.

Presently, we are studying the effects of the parameters that control the cooling schedule of the algorithm. As explained in previous reports, simulated annealing is not a greedy algorithm, that is, it will move in directions that are locally not optimal. This feature allows the algorithm to avoid being trapped in local optima, increasing the probability that the global optimum will be found. The current temperature of the system controls the probability that a non-optimal move will be accepted, and the cooling schedule controls the temperature. We believe that both the initial temperature and the rate of change of the temperature are both important parameters that affect the algorithm's accuracy and efficiency. Other parameters that control the number, size, and direction of moves will also be studied to improve the algorithm.

2.2.3 Fuel Testing

2.2.3.1 Emissions Testing

Due to the excessively high degree of condensation during exhaust sampling, the design and construction of the emissions sampling system was completely overhauled. It was discovered that the warm-up mode on the system bypassed a mass flow controller which created a very low dilution ratio. Thus, the dew point of the diluted exhaust was above ambient conditions, and the mass flow controllers filled with oily water. Furthermore, some of the tubing connections were

found to be installed improperly, which caused leaks. Therefore, it was decided to dismantle and rebuild the entire sampling rig. While reconstruction took place, the mass flow controllers were sent back to Sierra Instruments for cleaning and recalibration. Reconstruction of the sampling system is now done, and the mass flow controllers are working properly. A diagram of the rebuilt system is shown in Figure 2.1. With this new system, reliable and repeatable data should be obtained.

2.2.3.2 Cylinder Pressure Data Analysis

In addition to emissions data, cylinder pressure data will also be collected from the engine. Cylinder pressure data from the engine will allow the computation of several internal combustion engine performance parameters. Heat release analysis, mass fraction burned analysis, and indicated mean effective pressure analysis will all be derived from cylinder pressure data. Although several assumptions are made in deriving the equations, the calculations will still lead to acceptable results.

Heat release analysis gives insight as to how much energy the fuel is providing to the engine. Mass fraction burned analysis shows how fast a particular fuel burns in an engine. Indicated mean effective pressure analysis points out the amount of work done by the gas on the piston, which can lead to an indication of frictional losses. With this information comparisons could be made about the performance of the engine under different loading conditions, spark timings, air to fuel ratios, compression ratios, different fuel blends, etc. For our tests, parameters such as engine speed, air to fuel ratio, spark timing, and compression ratio will be held constant, and the fuel will be varied to arrive at a comparison of the performance of different fuels.

2.3 Conclusions

An improved, more accurate topical report will be completed very soon. The improved design cases will reflect more modern technology and more exact details of the higher alcohol synthesis loop.

The simulated annealing algorithm will be ready to be applied to optimization of the alcohol synthesis loop when kinetic data are made available. The algorithm will be able to determine rapidly and efficiently optimum conditions for the reactor, separation, and blending operations.

The sampling part of the fuel testing apparatus has been rebuilt. Results are anticipated in the near future.

2.4 References

1. Quarderer, George J., "Mixed Alcohols from Synthesis Gas," paper presented at the 78th Spring National AIChE Meeting, New Orleans, Louisiana, April 6-10, 1986.

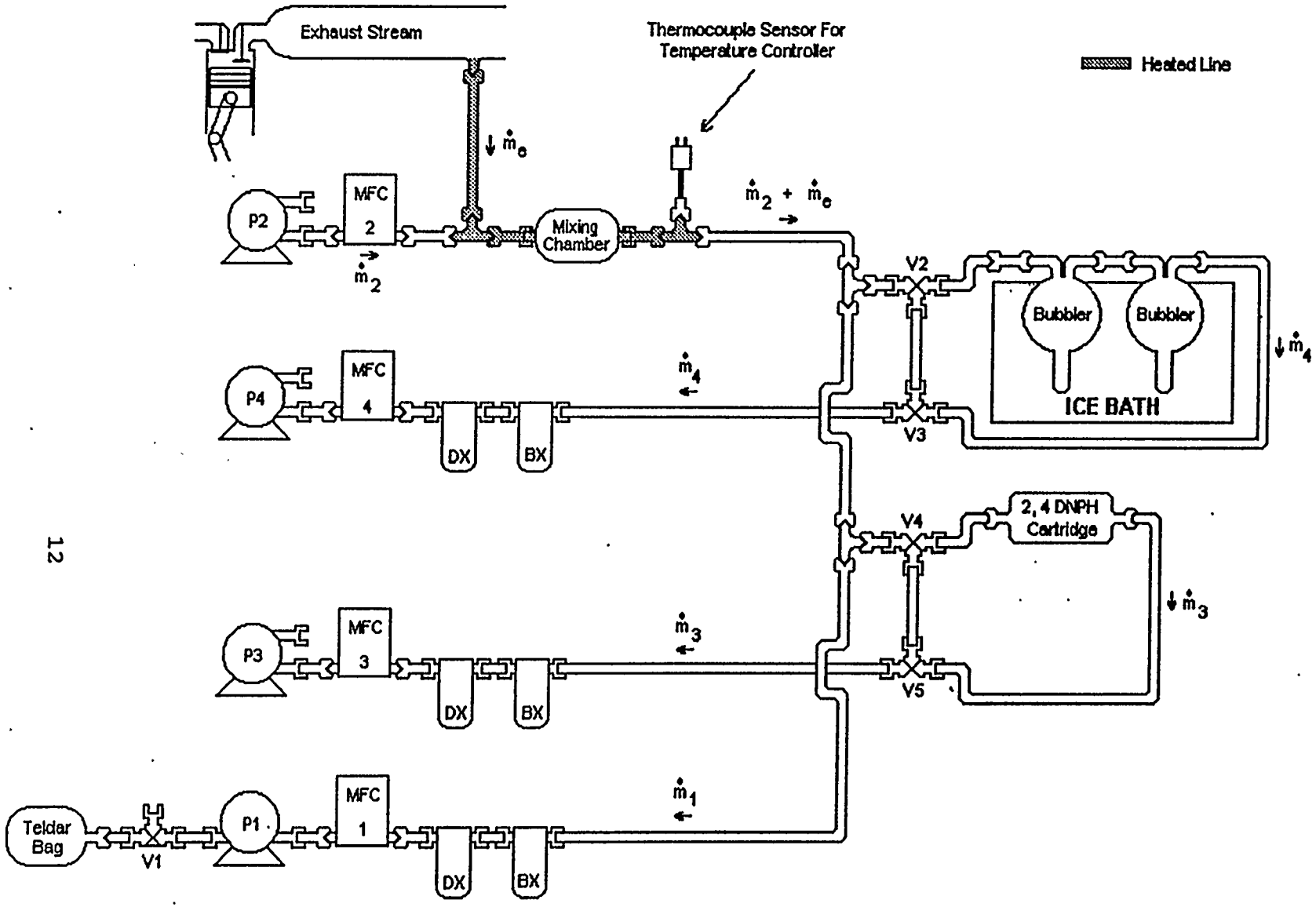

Figure 2.1 Bag Sampling System