The Economic Production of Alcohol Fuels from Coal-Derived Synthesis Gas

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I. OBJECTIVES

The objectives of this project are:

1. to discover, study and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. Specifically, alternative methods of preparing catalysts are to be investigated, and novel catalysts, including sulfur-tolerant ones, are to be pursued. (Task 1)

2. to explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products. (Task 1)

3. to simulate by computer the most energy efficient and economically efficient process for converting coal to energy, with primary focus on converting syngas to fuel alcohols. (Task 2)

4. to develop on the bench scale the best holistic combination of chemistry, catalyst, reactor and total process configuration integrated with the overall coal conversion process to achieve economic optimization for the conversion of syngas to liquid products within the framework of achieving the maximum cost effective transformation of coal to energy equivalents. (Tasks 1 and 2)

5. to evaluate the combustion, emission and performance characteristics of fuel alcohols and blends of alcohols with petroleum-based fuels. (Task 2)

2.2 Catalyst Testing Units

Two computer controlled reactors were used for catalyst testing. One unit is used exclusively for testing sulfide catalysts whereas the other unit is used to test carbides and nitrides. Each unit has 4 gas feed lines independently controlled with mass flow controllers and one liquid feed line controlled by an HPLC pump. The units are designed to operate from atmospheric pressure to 1500 psig and with reactor temperatures up to 500°C. Operating conditions are set directly from the computer and data are logged at operator-determined intervals. Each unit uses a Hewlett Packard 5890 gas chromatograph for on-line product analysis. The product is sampled immediately below the reactor with a gas sampling valve at reactor operating pressure and at a minimum temperature of 250°C. Each unit is controlled by the commercial software package InTouch^{tm} by Wonderware and the gas chromatograph is controlled by Hewlett Packard Chemstation^{tm} software. All programs operate from the same computer in a multitasking MS Windows^{tm} environment. A figure for this unit was provided in our 1994 report (1).

Catalysts are tested in small, plug-flow reactors typically loaded with 0.5 g of catalyst and 3 g of crushed quartz. The screening procedure for sulfide catalysts is to pretreat the catalyst at 400°C with a 10% H_2S in H_2 mixture. After 1 hr presulfiding, the catalyst is purged with H_2 and the temperature lowered to 200°C. The system is then pressurized to 750 psig and the gas flows adjusted to 25 sccm H_2 and 25 sccm CO. The reaction temperature is ramped from 200 to 400 to 200°C at a rate of 10 °C/hr. Reaction product is sampled at 2 hr intervals.

The product is analyzed with a Hewlett-Packard 5890 gas chromatograph with a flame-ionization detector for hydrocarbon and alcohol analysis and a thermal conductivity detector for inorganic gas analysis. Flow from the sampling valve below the plug-flow reactor passes through the gc injector and is split between two columns: a 30' x 1/8" HayeSep D_B packed column and a 20m x 0.10mm J&W DB-WAX capillary column, temperature programmed from 40 to 230°C. The HayeSep D_B column provides quantitative analysis for N_2 (internal standard), CO, CO_2, H_2O. H_2 is separated but cannot be measured satisfactorily. The DB-WAX column separates all of the C_1-C_5 alcohols and groups all of the C_1-C_6 hydrocarbons as a single peak. This DB-WAX column provides excellent product analysis for catalysts that produce only alcohols and light hydrocarbons as we observe with MoS_2. However, aldehydes, ketones, ethers and heavy hydrocarbons also elute with the alcohols. Complicated product mixtures cannot be identified by gas chromatography alone.

The gc analysis with two columns in parallel is a significant advance beyond our prior analysis with a single Porapak Q packed column. Last year we could separate the inorganic gases, methanol and C_1-C_3 hydrocarbons by temperature programming from -60 to 250°C. However, we could not distinguish C_{4+} hydrocarbons from C_{2+} alcohols. With the current method, C_1-C_8 hydrocarbons are cleanly separated from all of the alcohol peaks.

II. ACCOMPLISHMENTS

1. Introduction

This is a joint project between West Virginia University and Union Carbide Chemicals & Plastics. The project has two parts. Task 1 focuses on catalyst evaluation and reaction engineering; Task 2 is studying process synthesis and fuel evaluation. This paper emphasizes the work at WVU on objectives 1 and 3: discovery, study and evaluation of molybdenum based catalysts for producing fuel alcohols from syngas, and computer simulation of the most economically efficient process for producing fuel alcohols.

In the period since the September 1994 review meeting, Task 1 has evaluated over 100 catalysts for alcohol fuels production while Task 2 has developed seven new economic cases where fuel alcohols are either the primary product or the byproduct of a power generation facility.

2. Experimental

2.1 Catalyst Preparation

Three methods of catalyst preparation have been used in this program. These are described below.

Vapor Phase Reaction Volatile metal carbonyls are decomposed in an H_2S or ammonia atmosphere to produce high-surface-area sulfides and nitrides. The reactor tube temperature is operated in the range of 300 to 1100°C. This method works well for producing both molybdenum and molybdenum-iron catalysts. Catalysts are in the form of fine powders.

Pore Volume Impregnation Incipient-wetness impregnation with salts or organometallic compounds was used to prepare supported catalysts. The catalyst precursor is then decomposed in a controlled atmosphere to produce the desired sulfide, nitride or carbide phase. Catalysts are in the form of the support material, either as a powder or a preformed pellets.

Solid State Synthesis Solid-state synthesis by combining the appropriate elements and heating at high temperature in a controlled atmosphere was used to prepare molybdenum sulfide chevrel phase catalysts. The following chevrel phase materials have been prepared by this technique: $HoMo_6S_8$, $SmMo_6S_8$, $AgMo_6S_8$, $InMo_6S_8$, $Cu_{3.2}Mo_6S_8$, $Fe_{1.5}Mo_6S_8$, $Ni_{1.6}Mo_6S_8$, $Co_{1.6}Mo_6S_8$ and $K_XMo_2S_3$. Catalysts were produced as powders.

2.3 Titration of MoS_2 Reaction Sites

Oxygen chemisorption on molybdenum sulfide catalysts has been measured by a Micromeritics 2700 pulse chemisorption unit. In our measurement procedure, a catalyst sample is first reduced and sulfided in a flowing 10% H_2S in H_2 mixture at 400°C for 1 hour, then purged for 1/2 hour in helium at the same temperature. After sulfiding, the sample is cooled in flowing helium to -78°C where O_2 gas is added in small doses and the adsorption is measured with a thermal conductivity detector.

3. Results

3.1 Synthesis of Vapor Phase Reactor Catalysts

The primary method of catalyst preparation was vapor phase reaction of molybdenum carbonyl, $Mo(CO)_6$, in ammonia to produce nitrides or in hydrogen sulfide to produce sulfides. Figure 1 shows a diagram of the apparatus used. The heated zone of the reactor is 18 inches long. A detailed drawing of the injector is shown in Figure 2. Injector #1 is the original design. However, extensive carbonyl decomposition occurred at the inlet of the furnace and on the reactor walls so that product yields were often in the range of 40-50%. Injector #2 shows the current design. The outside wall of the reactor tube is swept with a laminar flow of inert gas to keep the reacting carbonyl away from the tube wall. The injector is also water cooled into the heated zone. This reduces the reaction zone from 18 to 10 inches, but keeps carbonyls below their decomposition temperatures until they are abruptly heated. The improved injector design increased product yields to 80-100%.

The effect of decomposition reactor conditions on MoS_2 products is shown in Table 1. The temperature of the furnace was increased from 300 to 900°C in preparing a series of catalysts. Samples prepared at 300°C showed a low yield of recovered product, its surface area was low, and the x-ray diffraction powder pattern described a poorly crystalline structure. On raising the decomposition temperature to 500°C, the product yield increased to from 27 to 83%, the surface area increased from 21 to 76 m^2/g, and the x-ray diffraction pattern started to show the characteristic lines of MoS_2. On raising reaction temperature from 500 to 900°C, the product yield increased to 98%, the surface area remained nearly constant at 66-78 m^2/g and the x-ray diffraction lines became larger and more defined, showing an increase in MoS_2 crystallinity. The percentage sulfur in the product increased with increasing decomposition temperature. The stochiometric amount of sulfur in MoS_2 is 40.06%. Samples from 300 and 400°C decompositions were sulfur deficient, suggesting that oxygen or carbon from the $Mo(CO)_6$ was present in the low temperature product. Samples produced at 500°C were nearly stochiometric. Samples produced above 500°C showed excess sulfur. This excess sulfur probably comes from the decomposition of H_2S into hydrogen and elemental sulfur.

In its current design, the vapor phase reactor is able to produce a consistent, high-surface-area MoS_2 product with 83-98% yield. This MoS_2 has been used as the basic starting

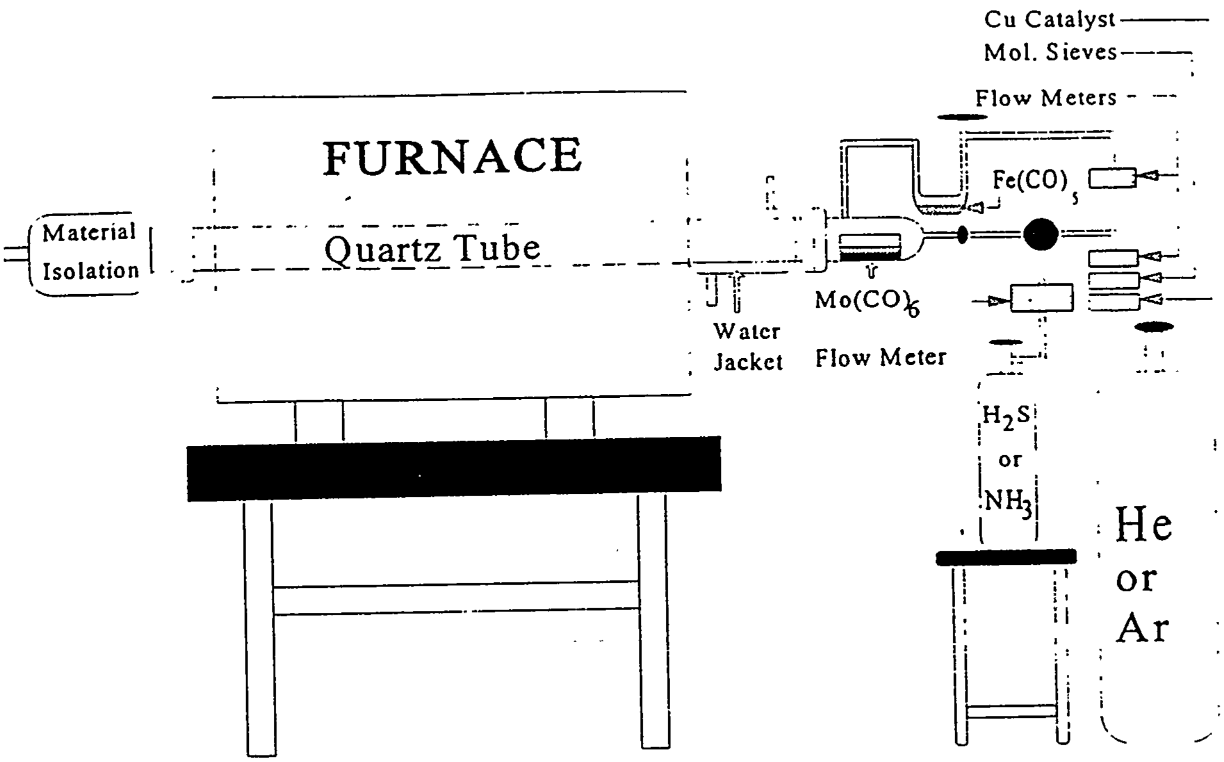

Figure 1: Vapor phase catalyst synthesis reactor for preparing molybdenum or molybdenum-iron sulfides and nitrides.

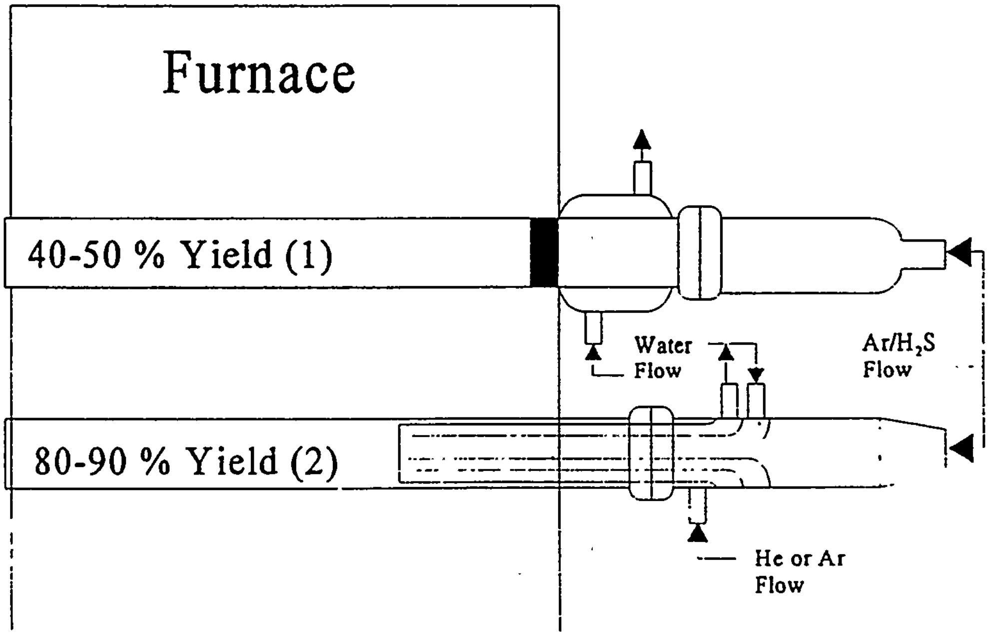

Figure 2: Detail of injector showing (1) original design and (2) improved design.

Table I Correlation of Furnace Temparature and Physical Properties for MoS_2 Catalysts Prepared by the Thermal Decomposition of $Mo(CO)_6$ and H_2S using injector #2.

Ref #	T_f^1	T_{Mo}^1	T_{wj}^1	Ar_i^1	Ar_o^1	H_2S rate (ml/min)	Yield %	XRD	Surface Area	Sulfur %
2MRC128A	300	98-99	85	220	700	11	26.7	Broad-26	21.4	22.6
2MRC129A	400	98-99	85	220	700	11	N/A	Broad-27	47.3	22.4
2MRC115A	500	98-99	85	220	700	11	82.7	Broad-18	76.53	37.85
2MRC116A	600	98-99	85	220	700	11	88.6	MoS_2	75.44	42.61
2MRC116C	700	98-99	85	220	700	11	95.0	MoS_2	77.96	45.95
2MRC118A	800	98-99	85	220	700	11	94.6	MoS_2	72.53	45.56
2MRC119A	900	98-99	85	220	700	11	98.2	MoS_2	66.15	46.03

T_f	Furnace Temperature, °C
T_{Mo}	Temperature of $Mo(CO)_6$, °C
Twj	Water Jacket Temperature, °C
Ar_i	Argon Flow, Inner Tube, sccm
Ar_o	Argon Flow, Outer Tube, sccm
XRD	X-ray Diffraction Characteristics
SA	BET Surface Area, m^2/g

material for alkali-promoted vapor phase reactor (VPR) catalysts. The form as a fine powder is well suited for a slurry reactor, but must be combined with a binder (silica) and compressed into pellets for testing in our plug-flow, catalyst screening units.

3.2 Titration of Reaction Sites on MoS_2

Carbon supported molybdenum sulfide catalysts have also been prepared in this study. The carbon support is a hard, 20-40 mesh solid that is well suited for reactor studies. Similar catalysts for alcohol synthesis have been reported previously by researchers at Dow Chemical Company (2).

With supported molybdenum sulfide catalysts, it is important to know how much of the surface is active component and how much is support. Tauster and coworkers (3) have reported that active sites on molybdenum sulfides can be titrated by oxygen chemisorption. We have studied O_2 adsorption over a series of carbon supported molybdenum sulfides where the molybdenum concentration was varied from 0 to 30%. All of the samples were prepared by a pore-volume-impregnation technique using ammonium heptamolybdate solutions. These samples were then sulfided and tested using our standard oxygen chemisorption procedure. The results of these tests are shown in Figure 3.

The O_2 chemisorption was observed to increase linearly with increasing molybdenum concentration from 0 to 6%. The adsorption then goes through a broad plateau with little change in O_2 uptake with increasing molybdenum sulfide concentration. The maximum occurred at about 12%, suggesting that adding more molybdenum beyond that concentration does little to increase the number of active sites.

Alkali must be added to molybdenum sulfide catalysts to produce alcohols. Adding potassium to molybdenum in a 1:1 molar ratio causes O_2 adsorption to increase from about 50 to 250 umoles/g. This is not due to an increase in the number of reaction sites since potassium on carbon alone will adsorb about 200 umoles/g. This latter result shows that some potassium is reduced to its metallic form on the carbon support during pretreatment with H_2S/H_2, then reacts with O_2 to form a potassium oxide. Reduction of potassium to its metallic form is not expected for oxide supported materials.

The difficulty with potassium reacting with oxygen on carbon supported molybdenum sulfides has been used to our advantage. We have found that CO adsorption at -78°C can be used to measure the molybdenum sulfide sites on a potassium promoted catalyst. After CO adsorption, O_2 adsorption can then be used to measure the amount of reduced potassium. The amount of CO adsorption appears to correlate with catalyst activity.

3.3 Catalyst Screening Studies

In the experimental section, we stated that one catalyst testing unit is used exclusively for sulfide catalysts whereas the other testing unit is used exclusively for carbides and nitrides.

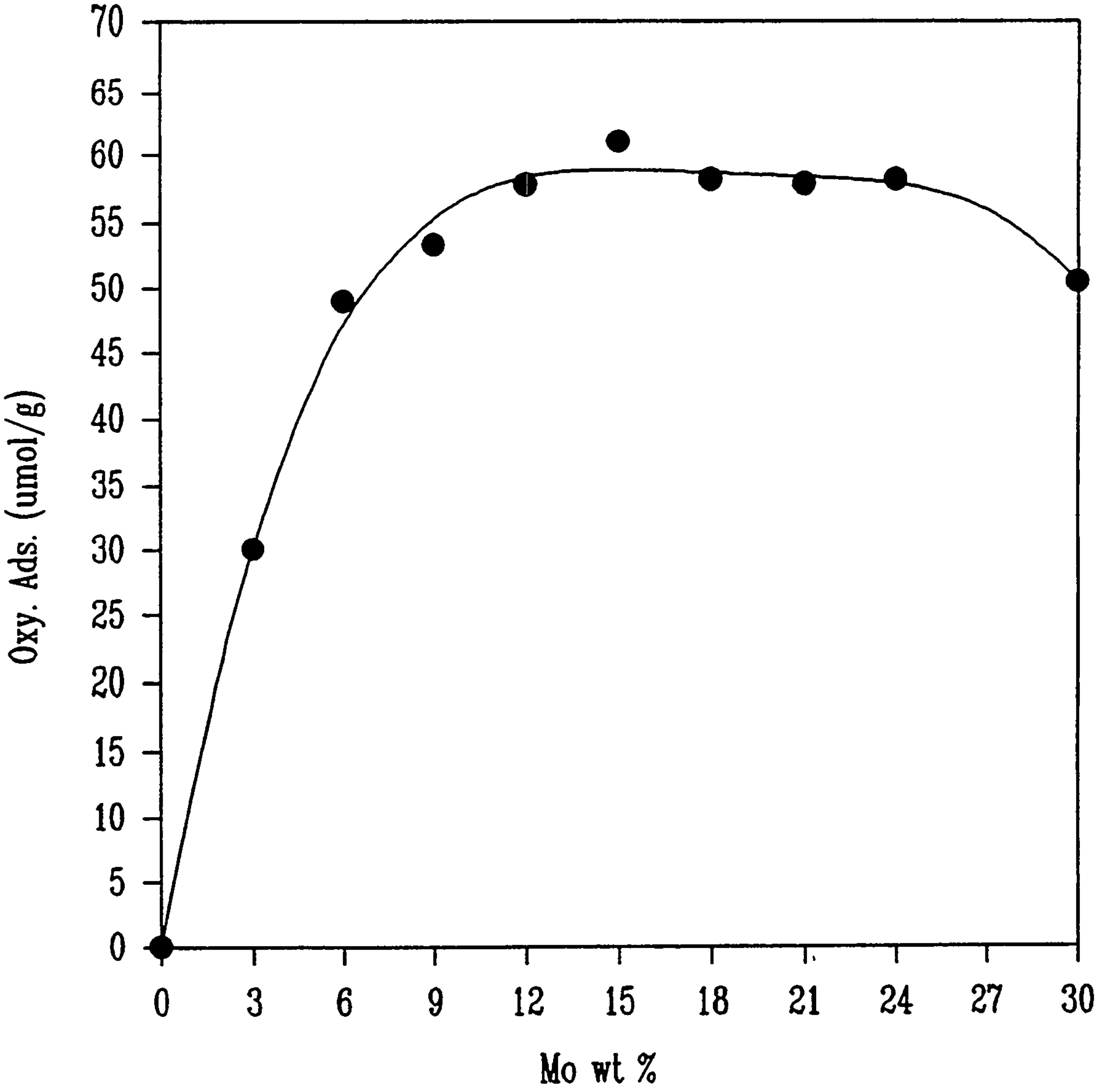

Figure 3: Change in O_2 chemisorption with molybdenum concentration for carbon supported MoS_2 catalysts.

In this section, we will only describe the results with sulfide catalysts. Many of the molybdenum carbides and nitrides tested are very active for CO conversion, but made many products other than alcohols and straight-chain hydrocarbons. Most of these products could not be identified by gas chromatography alone. A gas chromatography-mass spectrometry system has been ordered to improve product identification. Progress with carbide and nitride catalysts will be described in a future report.

Molybdenum sulfide studies were begun with the mixed metal chevrel phase catalysts. A listing of materials screened is in Section 2.1, Solid State Synthesis. Catalytic results showed that the 9 chevrel molybdenum sulfides studied had such low catalytic activities, that it was difficult to distinguish the catalytic reaction products from the background activity of the stainless steel reactor. No further work is planned for chevrel phase catalysts.

Vapor phase synthesis MoS_2 was found to have high activity for alcohol catalysis. Figure 4 shows results from a screening study with a potassium promoted molybdenum sulfide, $K_{0.7}MoS_2$. The catalyst was screened from 200 to 400 to 200°C by changing the temperature at a rate of 10 °C/hr and sampling the product stream at 2 hour intervals. Reaction pressure was 750 psig with a standard-condition space velocity of 6000 l/ kg catalyst/ hr. The top section of Figure 4 shows the space-time yield for alcohol and hydrocarbon products. The open symbols are for increasing ttemperature, the filled symbols for decreasing temperature. The alcohol production rate reached a maximum near 200 g product/ kg catalyst/ hr. The selectivity to alcohols at this maximum rate was over 80%. The selectivity to higher alcohols on a CO_2 free, weight basis is over 40% on both increasing and decreasing temperatures. The criteria we use for judging a promising catalyst is 100 g/kg/hr alcohol production, with 50% selectivity to alcohols and 20% selectivity to higher alcohols. Vapor phase reaction MoS_2 materials promoted with potassium exceeded this criteria 2-fold.

The alcohol product distribution of this $K_{0.7}MoS_2$ catalyst is shown in Figure 5. Data for decreasing temperatures is plotted, showing mole % at the top and wt % at the bottom of the figure. Looking at the mole % distribution data, the selectivity to methanol is seen to continuously decrease with increasing temperature. This effect probably has two causes. Methanol reacts to form higher alcohols through secondary reactions, so that as the absolute concentration of methanol increases, more of it reacts to form ethanol, decreasing its selectivity. The second effect is probably thermodynamic in origin, since methanol formation is less favored at higher temperatures. Similar behavior in selectivity is observed for ethanol. A maximum in selectivity is observed near 375°C. This maximum is probably caused by secondary reactions, producing higher alcohols or hydrocarbons. Selectivity to n-propanol and n-butanol grow to significant values as the selectivity to ethanol reached its maximum.

The lower section of Figure 5 shows how the selectivities to methanol, higher alcohols and hydrocarbons change with temperature on a weight basis. At the maximum in higher

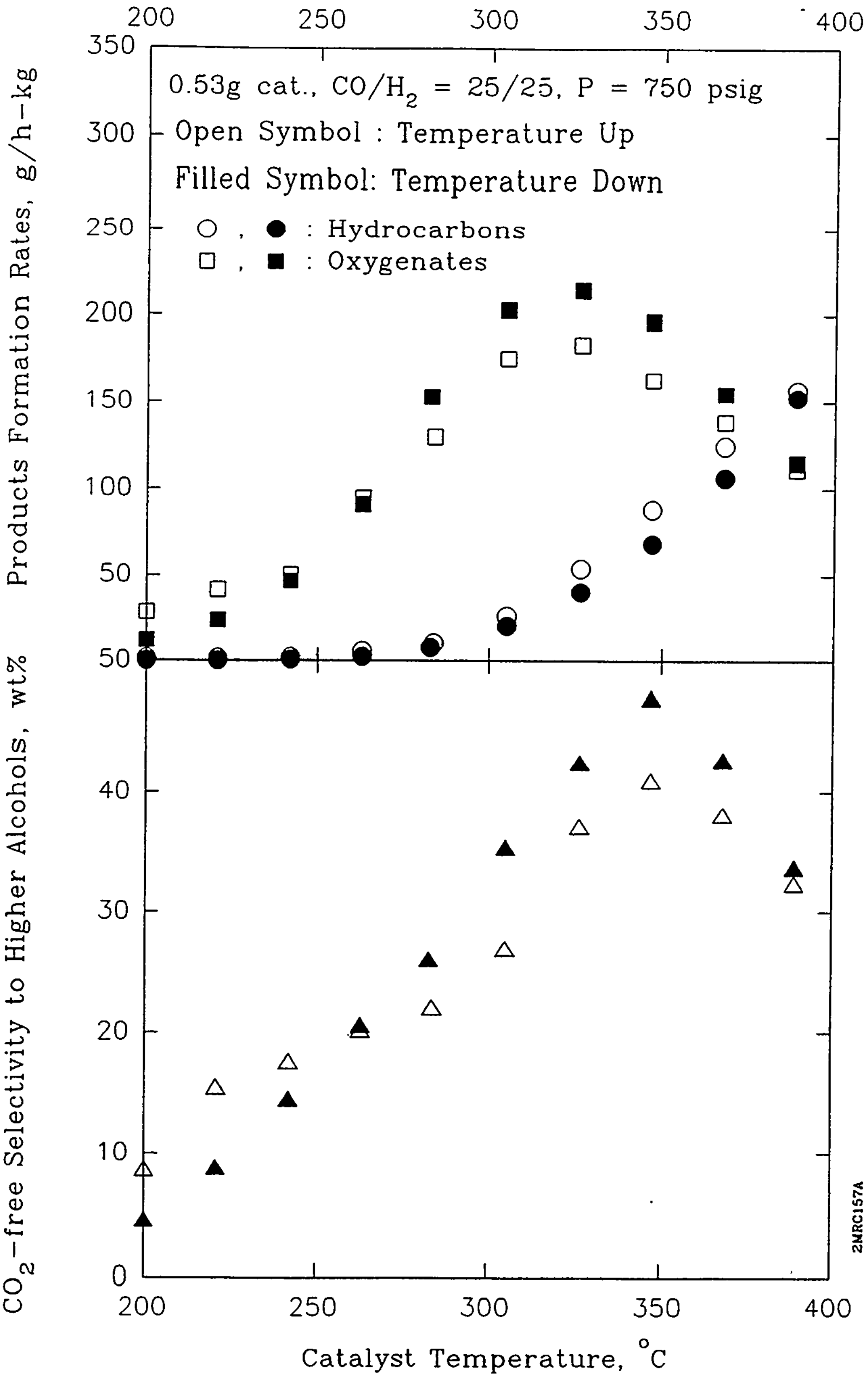

Figure 4: Product formation rates and alcohol selectivity for $K_{0.7}$ MoS_2 VPR catalyst tested at 750 psig and 6,000 l/kg/hr space velocity.

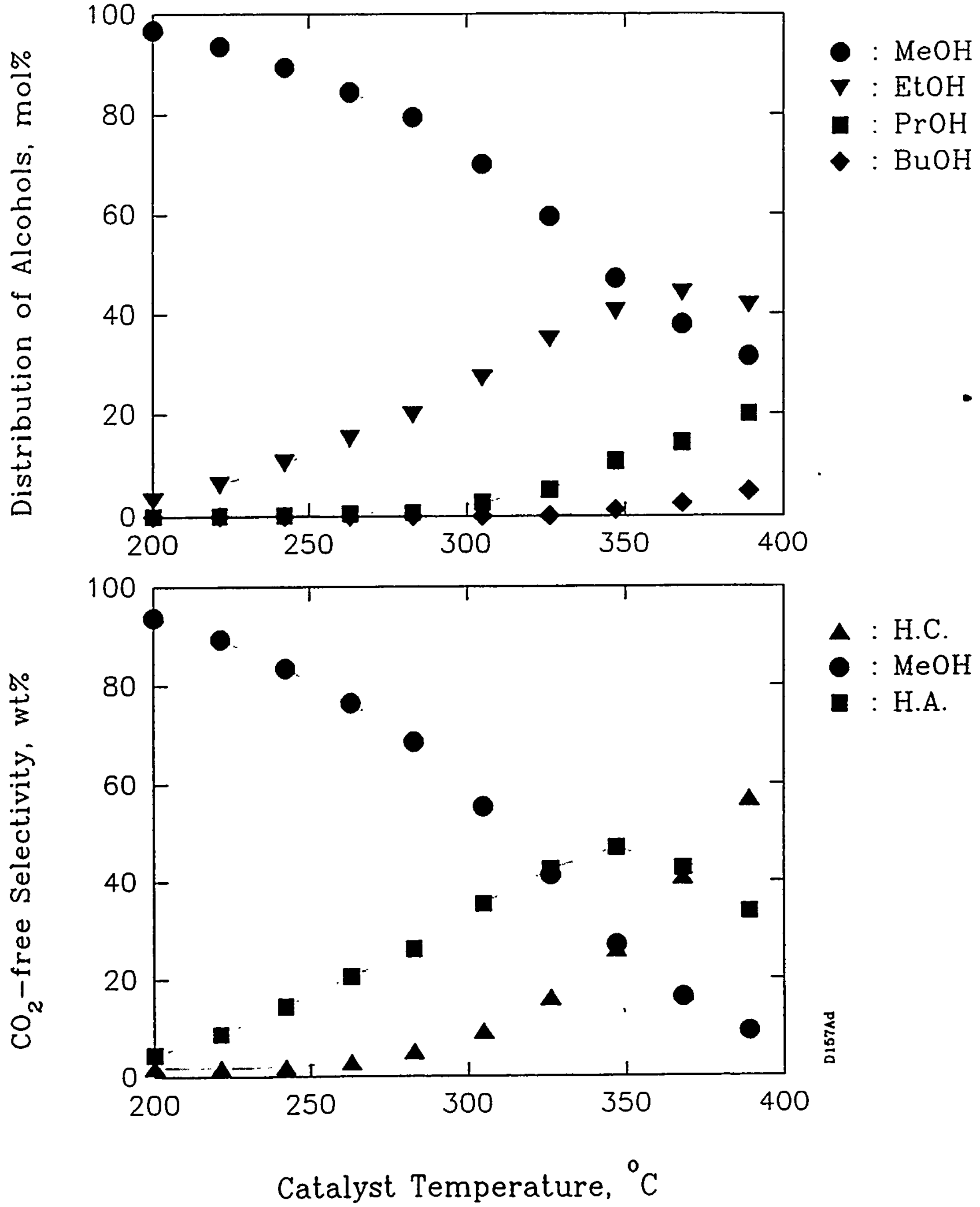

Figure 5: Alcohol selectivity of $K_{0.7}$ MoS_2 VPR catalyst at same conditions as Fig. 4.

alcohol selectivity, product concentrations are nearly 50% higher alcohols, 25% methanol and 25% hydrocarbons.

Similar performance is noted with vapor phase synthesis catalysts promoted with cesium or rubidium. A series of catalysts was prepared with similar concentrations of alkali on a molar basis: $K_{0.7}$ MoS_2, $Cs_{0.7}$ MoS_2 and $Rb_{0.7}$ Mos_2. The performance the potassium promoted sample was presented in Figures 4 and 5. The catalysts promoted with rubidium and cesium also had space-time yields of approximately 200 g/kg/hr and similar selectivities. The promoter level for potassium is believed to be near optimum. Optimum values are not known for the other two alkali promoters.

Data supporting hydrocarbon and alcohol formation by secondary reactions is presented in Figure 6. A molybdenum-cobalt-potassium on carbon catalyst with molar ratios of 1-0.3-1 was run isothermally at 350°C and 750 psig. During the initial 16 hr period, the space velocity was constant at 6,000 l/kg/hr. The rate of alcohol conversion was nearly constant at 160 g/kg/hr while the rate of hydrocarbon formation decreased initially, then leveled out below 40 g/kg/hr. The space velocity was then increased to 12,000 l/kg/hr. Increasing the flow rate increased the rate of alcohol formation but decreased the selectivity to hydrocarbons and higher alcohols. Increasing the space velocity decreases the residence time and decreases secondary reaction products. The same effect is observed when the space velocity is increased to 18,000 and 21,600 l/kg/hr, further supporting the hypothesis that higher alcohol formation involves secondary reactions of methanol product.

3.4 Process Synthesis Computer Modeling

The goal of Task 2 is to simulate, by computer, energy efficient and economically efficient processes for converting coal to energy (fuel alcohols and/or power). The first step for Task 2 was to develop computer simulations of alternative coal to syngas to linear higher alcohol processes, to evaluate and compare the economics and energy efficiency of these alternative processes, and to make a preliminary determination as to the most attractive process configuration. Seven cases were developed using different gasifier technologies, different methods for altering the H_2/CO ratio of the syngas to the desired 1.1/1, and with the higher alcohols as the primary product and as a by-product of a power generation facility. Texaco, Shell, and Lurgi gasifiers were used as to gasify coal, and steam reforming of natural gas, sour gas shift conversion, or pressure swing adsorption was used to alter the H_2/CO ratio of the syngas. In addition, a case using only natural gas was prepared in order to facilitate comparison between coal and natural gas as a source of syngas.

There are significant differences between the production costs for processes converting coal to syngas to higher alcohol fuel additives for cases involving Texaco, Lurgi, and Shell gasifiers, between cases involving natural gas reforming or sour gas shift conversion to alter the H_2/CO ratio, and for different plant capacities. The best case is one of the hybrids, a Shell gasifier with natural gas.

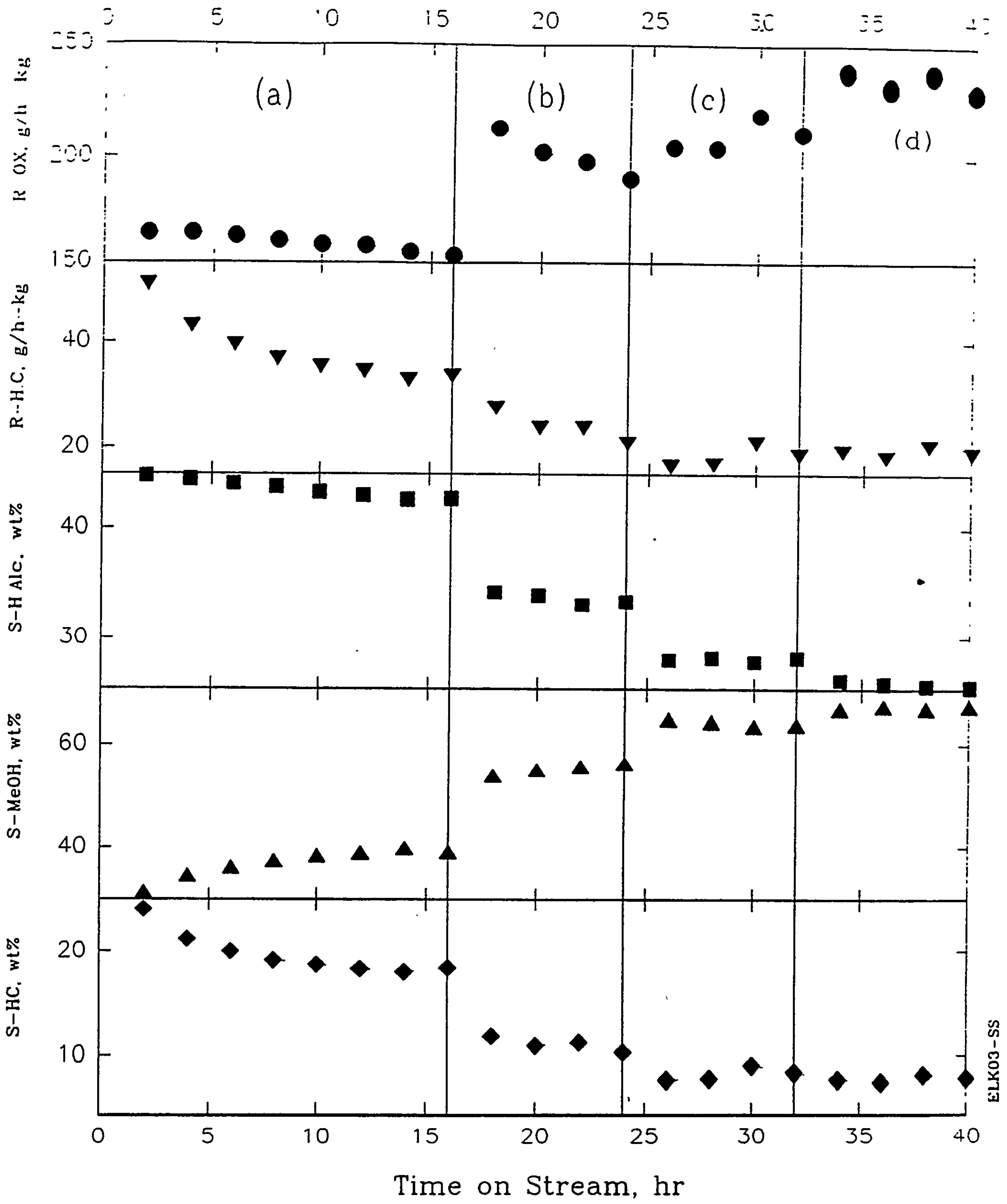

Figure 6: Performance of carbon supported Mo-Co-K catalyst at increasing space velocities: (a) 6,000; (b) 12,000; (c) 18,000; (d) 21,600 l/kg/hr. Catalyst tested at 350°C and 750 psig.

Production of 5.1 billion liters/yr (32 MM bbl/yr) of alcohol fuels from coal is considered the maximum feasible process scale. As expected, there are economies of scale favoring larger-scale over smaller-scale processes. However, there appear to be diminishing economies of scale above this plant size.

Production of higher alcohol fuel additives from natural gas is more economical than production from coal at any scale at current or predicted natural gas prices. Production of higher alcohol fuel additives from coal and natural gas hybrids may be as economical as production from natural gas at West Virginia natural gas prices ($3.00/MM BTU). However, if the natural gas and hybrid cases were compared at scales consistent with the same net power produced, the manufacturing cost for the natural gas case would be significantly lower than that for the hybrid cases. Furthermore, if a plant life of 10 years were used, which is more typical in the chemical process industry, then all of the manufacturing costs for the cases using coal gasification would increase, making natural gas the clearly superior option.

Since capital and operating costs are estimated on the basis of conventional technology, equipment, processes, and environmental controls, it is possible that future emission control requirements could significantly increase capital and operating costs of all coal-based processes described.

The manufacturing cost of the alcohol derived from natural gas is a strong function of the natural gas price. The capital costs are lower for these cases than they are for the coal-based cases. Thus, raw material costs for the natural gas cases are a larger portion of the total annualized cost.

The cost of producing syngas from coal or from coal and natural gas is currently greater than or equal to producing it from natural gas only. This is primarily a result of the high capital investment for the gasifier and accompanying cryogenic oxygen plant. This higher investment outweighs the benefit of using a cheaper raw material, coal. The only way for coal based processes to be more competitive than natural gas under all conditions is either for the relative price of coal and natural gas to change or for a major development to occur in coal gasification technology. Price variations would have greater impact on the natural gas reference cases, since raw material costs for these cases are a larger portion of the total annualized cost. Therefore, the competitiveness of the coal-based cases would be enhanced more by increases in the price of natural gas than by decreases in coal cost.

III PLANS

Molybdenum sulfide catalysts have been found to meet our criteria for more detailed study. Kinetic studies in a continuous, stirred-tank reactor are planned to measure rate constants and predict the best operating conditions for this type of catalyst. One catalyst testing unit will be used for this work.

Molybdenum carbides and nitrides have been found to be very active catalysts but make a complicated product mixture that has been very hard to identify. Most of these products are believed to be oxygenates. We have ordered a gc/ms to measure the mass spectra of the compounds that are separated in the gas chromatograph. This will be installed on-line with our carbide and nitride catalyst testing unit, so that small concentrations of product can be analyzed. The main feature of this instrument will be chemical ionization capability. This will produce molecular ions that should allow identification of product compound classes. Traditional electron impact ionization in a mass-spectrometer at 70 eV causes such extreme fragmentation that unknown molecules are very hard to identify. Catalyst screening of carbides and nitrides will continue with the goal of identifying promising catalysts for alcohol synthesis.

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