Executive Summary

This project was divided into two parts. One part evaluated possible catalysts for producing higher-alcohols (C_2 to C_{5+}) as fuel additives. The other part provided guidance by looking both at the economics of mixed-alcohol production from coal-derived syngas and the effect of higher alcohol addition on gasoline octane and engine performance.

The catalysts studied for higher-alcohol synthesis were molybdenum sulfides promoted with potassium. The best catalysts produced alcohols at a rate of 200 g/ kg of catalyst/ h. Higher-alcohol selectivity was over 40%. The hydrocarbon by-product was less than 20%. These catalysts met established success criteria. The economics for mixed alcohols produced from coal were poor compared to mixed alcohols produced from natural gas. Syngas from natural gas was always less expensive than syngas from coal. Engine tests showed that mixed alcohols added to gasoline significantly improved fuel quality. Mixed-alcohols as produced by our catalysts enhanced gasoline octane and decreased engine emissions. Mixed-alcohol addition gave better results than adding individual alcohols as had been done in the 1980's when some refiners added methanol or ethanol to gasoline.

This summary has three parts, describing in turn: research on catalysts, estimation of process economics, and engine testing to determine product quality.

Catalyst Testing Results

Catalyst testing focused on alkali-promoted, molybdenum sulfide catalysts. Unsupported molybdenum sulfides were prepared by the vapor-phase reaction of molybdenum carbonyl and hydrogen sulfide. Carbon supported catalysts were prepared by conventional impregnation techniques that deposit molybdenum salts on a carbon support. These salts were reduced to molybdenum sulfides with hydrogen - hydrogen sulfide mixtures. Both supported and unsupported catalysts were promoted by alkali (potassium, rubidium or cesium) salts. Alkali addition significantly enhanced catalyst selectivity for alcohol production.

Catalyst performance was evaluated in two, computer-controlled, catalyst testing units. The testing units were constructed for this project. Each unit was designed to control gas feeds for both pretreatment and reaction over specified time periods. The reactor pressure could be set anywhere in the range of 0 to 1200 psig and the computer set up to test the catalyst in a prescribed sequence of steps. In a typical screening test, the reaction pressure was set at 750 psig and catalyst testing began at 200 ^{o}C; the temperature was increased in 20 ^{o} steps to 400 ^{o}C, then decreased back to 200 ^{o}C repeating the prior data points. The conversion of synthesis-gas feed was measured after each temperature change. Reaction products were analyzed with an on-line gas chromatograph. Liquid products were collected and analyzed by mass spectrometry with an off-line GC-MS.

High-surface-area molybdenum sulfides were prepared by gas phase reaction of molybdenum carbonyl and hydrogen sulfide. This material synthesis was carried out in the temperature range of 300-to-1100 $^{\circ}$C. Optimum preparation temperatures occurred at 500-700 $^{\circ}$C. A special vapor inlet system was built to introduce molybdenum carbonyl vapors into the hot zone of a materials-synthesis reactor away from the side walls. This design improved both product quality and product yields compared to introducing gas mixtures directly into a heated tube. The molybdenum sulfide powders produced were composed of nanoscale particles that were agglomerated to form powders large enough to be collected on paper filters. Individual particles in the agglomerated clusters were in the range of 20-to-50 nanometers ($1x10^{-9}$m). The surface areas of these materials averaged 80 m^2/g.

Unsupported molybdenum sulfides were tested as alcohol synthesis catalysts. The materials, as synthesized, produced mainly hydrocarbons. Adding alkali-metal salts to molybdenum sulfide suppressed the hydrocarbon-synthesis activity and promoted alcohol-synthesis. The effects of the catalyst-preparation temperature were studied, as well as the effect of the type and concentration of the alkali promoter. In all cases, the alcohols formed are primarily straight-chained, terminal-OH compounds. The variations of catalyst-preparation procedure have only small effects on the conversion and the selectivity to higher alcohols. Promoter concentration affects selectivity to both methanol and higher-alcohols. Good catalyst performance could be obtained with potassium, rubidium or cesium promoters, however optimum performance was obtained at different concentrations for each alkali metal. Increasing reaction temperature increased reaction rate but decreased selectivity to alcohols. Selectivity to alcohols was greater than 90% below 300 $^{\circ}$C. On heating above 300 $^{\circ}$C, both higher-alcohol and hydrocarbon selectivity increased. Alcohol-production rate and higher-alcohol selectivity went through separate maxima near 350 $^{\circ}$C. At reaction temperatures of 400 $^{\circ}$C, hydrocarbon selectivity predominated and increased to about 90%. At optimum conditions for higher alcohol synthesis, a very good catalyst would have an alcohol production rate of 200 g alcohol/ kg of catalyst/ h with 50% higher-alcohol selectivity, 30% methanol selectivity, and 20% hydrocarbon selectivity.

A series of carbon-supported catalysts was prepared by incipient wetness impregnation. The catalysts were promoted with alkali-metal salts. In most cases, potassium was used but similar performance was obtained with rubidium or cesium. Results were very similar to those obtained with unsupported molybdenum sulfides. However, supported catalysts are much easier to prepare and can be manufactured on a commercial scale. Cobalt was added to supported molybdenum sulfide as a second promoter along with potassium. Cobalt addition had a small, positive effect in shifting selectivity away from hydrocarbons and more toward higher alcohols. Parametric studies showed that increasing reactant flow rate led to increased alcohol selectivity and decreased hydrocarbon selectivity. It also increased methanol selectivity and decreased higher-alcohol selectivity. This type of performance is expected for sequential reactions. This suggests that some hydrocarbons may be formed by secondary reactions that consume alcohol products. It also suggests that higher-alcohol formation may involve methanol as an intermediate.

The kinetics of higher-alcohol formation were investigated with a carbon-supported molybdenum sulfide catalyst promoted with cobalt and potassium. The reaction was carried out in a gradientless, Berty-type recycle reactor using a statistically-designed set of experiments. A two-level fractional-factorial set consisting of sixteen experiments was performed. Five independent variables were selected for this study: temperature, partial pressure of carbon monoxide, partial pressure of hydrogen, partial pressure of inerts, and methanol concentration in the feed. The major oxygenated products were found to be linear alcohols up to n-butanol, but trace amounts of ethers and higher alcohols were detected in the products. Yields of hydrocarbons were non-negligible. The alcohol product distribution followed the Anderson-Schultz-Flory model. From the results of the factorial experiments, a preliminary power-law model was developed and the statistically significant variables in the rate expression for the production of each alcohol were found. Based on the results of the power law models, rate expressions of the Langmuir-Hinshelwood type were fitted. The observed kinetics were consistent with the rate-limiting step for the production of each higher alcohol being a surface reaction of the alcohol of next-lower carbon number. All other steps do not appear to affect rate correlations. This kinetic model was tested by adding methanol to syngas feed at 750 psig pressure. Increased methanol concentrations increased rates of higher-alcohol formation as predicted by the kinetic model.

The role of potassium in altering the selectivity of molybdenum catalysts is unclear. To understand more about the role of potassium, the reducibility of a series of carbon-supported molybdenum catalysts with and without potassium promoter was investigated using temperature-programmed reduction (TPR). The molybdenum loading and the potassium-promoter level were found to influence the reducibility of these catalysts. The TPR spectra generally consisted of four peaks. Three were associated with the reduction of molybdenum species while the fourth was associated with reduction of oxygen impurities in the carbon support. The addition of potassium to carbon-supported molybdenum catalyst shifted the distribution of molybdenum species, increasing the concentration of molybdenum that was reduced at lower temperatures. The potassium was not reduced, but its presence affected the reducibility of molybdenum.

Process Economics

The first step 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 among 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, on the basis of manufacturing cost, is one of the hybrids, a Shell gasifier with natural gas.

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, resource and marketing constraints limit the maximum scale at which a plant could be constructed.

Production of higher-alcohol fuel additives from natural gas is more economical, for the next 20 years, than production from coal at any scale at current or predicted (by DOE) natural-gas prices. Production of higher-alcohol fuel additives from coal and natural gas hybrids is more economical than production from natural gas at West Virginia natural gas prices ($3.00/MM BTU). The break-even natural-gas price for production of higher alcohols by natural gas versus the Shell gasifier/natural-gas hybrid is $2.45/MM BTU. 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 will increase, making natural gas the clearly superior option.

Capital and operating costs are estimated on the basis of conventional technology, equipment, processes, and environmental controls. Thus, 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 highly dependent on the natural-gas price. Capital costs are lower for natural gas cases than for coal-based cases. Therefore, raw material costs for the natural gas cases are a larger portion of the total annualized cost.

If the cost of natural gas exceeds $2.45/MM BTU, the coal/natural gas hybrid (Shell gasifier) is more economical than the natural-gas-only design. If the cost of natural gas exceeds $4.94/MM BTU, the all-coal design (Shell gasifier) is more economical than the hybrid. 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 coal, which is a cheaper raw material. 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.

The most energy-efficient design, by wide margin, uses only natural gas. If pollution credits based on CO_2 or other combustion products are obtainable in the future, this process will benefit relative to the coal cases. The major question is whether an increase in natural-gas prices would be completely offset by any potential gains realized by pollution credits.

Engine testing results

Alcohols with carbon numbers ranging from C_1 to C_5 were individually blended with unleaded test gasoline. All alcohol-gasoline blends had the same oxygen-mass content. The performance characteristics of the blends were quantified using a single-cylinder spark ignition engine. The knock-limiting spark timing was determined by analysis of the third derivative of the measured in-cylinder gas pressure versus crank angle. The engine operating conditions were optimized for each blend with two different values of matched oxygen-mass content (2.5 and 5.0%). Emission mass rates of carbon monoxide (CO), nitrogen oxides (NO_x), total unburned hydrocarbons (THC), alcohols and aldehydes were quantified. Adding individual lower alcohols (C_1, C_2 and C_3) to gasoline improved knock resistance. Further improvement was achieved by increasing the oxygen content of the fuel blend. Adding individual higher alcohols (C_4 and C_5) to gasoline showed degraded knock resistance when compared with neat gasoline. Generally, all alcohol-gasoline blends showed a reduction in carbon monoxide emissions. Higher alcohol-gasoline blends with oxygen-mass content of 5.0 % showed a pronounced increase in nitrogen oxides. This is attributed to the lower enthalpy of vaporization and higher flame temperature. All blends tested at optimized operating conditions showed reduced hydrocarbon emissions. Unburned alcohol emission rates were higher for blends with higher alcohol content, and aldehyde emissions were higher for all blends with formaldehyde being the major constituent.

Mixed C_1-to-C_5 alcohols, as might be produced in a catalytic process, were blended with gasoline. Comparisons of knock limits, indicated mean effective pressure, emissions and fuel characteristics between mixed-alcohol gasoline and neat gasoline were made to determine the advantages and disadvantages of blending alcohols with gasoline. The data show that mixed alcohol-gasoline blends have a greater resistance to knock than neat gasoline, as indicated by the knock resistance indicator (KRI) and the (RON + MON)/2 antiknock index. Ignition delay and combustion interval data show that mixed alcohol-gasoline blends tend to have faster flame speeds. Other fuel parameters including Reid vapor pressure (RVP) and distillation curve are affected by the addition of alcohols to gasoline. Methanol and ethanol cause the most dramatic increase in RVP and the largest depression of the distillation curve. Addition of C_1-to-C_5 alcohol mixtures tends to curb the effects of methanol and ethanol on RVP and distillation curves of the blends.

Comparisons of emissions and fuel characteristics were made between mixed alcohol-gasoline blends and neat gasoline. Emission tests were conducted at the optimum spark-timing-knock-limiting-compression-ratio combination for the particular blend being tested. The cycle emissions of CO, CO_2 and organic-matter hydrocarbon equivalent

(OMHCE) from the mixed alcohol-gasoline blends were very similar to those from neat gasoline. Cycle emissions of NO_x from the blends were higher than those from neat gasoline. However, for all emission species, the brake specific emissions were significantly lower for the mixed alcohol-gasoline blends than for neat gasoline. This was due to the fact that the blends had greater resistance to knock and allowed higher compression ratios, which increased engine power output. The contribution of alcohols and aldehydes to the overall OMHCE emissions was found to be minimal. Cycle fuel consumption of mixed alcohol-gasoline blends was slightly higher than neat gasoline due to lower stoichiometric air/fuel ratios required by the blends. However, the brake specific fuel consumption for the blends was significantly lower than that for neat gasoline.