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

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Abstract

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.

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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 °C; the temperature was increased in 20 ° steps to 400 °C, then decreased back to 200 °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 °C. Optimum preparation temperatures occurred at 500-700 °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 (1×10^{-9} m). The surface areas of these materials averaged 80 m²/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 °C. On heating above 300 °C, both higher-alcohol and hydrocarbon selectivity increased. Alcohol-production rate and higher-alcohol selectivity went through separate maxima near 350 °C. At reaction temperatures of 400 °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 CO₂ 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 C₁ to C₅ 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 (C₁, C₂ and C₃) to gasoline improved knock resistance. Further improvement was achieved by increasing the oxygen content of the fuel blend. Adding individual higher alcohols (C₄ and C₅) 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 C₁-to-C₅ 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 C₁-to-C₅ 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, CO₂ 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.

Chapter 1

Introduction

This project was initiated in October 1991 as a joint project between West Virginia University and Union Carbide Technical Center. The project has two main tasks. Task 1 focuses on catalyst evaluation and reaction engineering. Task 2 includes process synthesis studies and engine performance tests on alcohols and mixtures of alcohols with petroleum-based fuels.

During the initial phase of the project, the Task 1 group installed and successfully operated two automated reactor systems and three types of reactors for catalyst testing. Over 100 catalysts were tested and evaluated for higher alcohol synthesis. The Task 1 group issued a topical report on higher alcohol synthesis from catalysts obtained by vapor phase thermolysis. Transition metal-based catalysts were prepared and evaluated. Reactor simulation models were developed as part of Task 1. The Task 1 coordinators were Ed Kugler and Dady Dadyburjor. Other Task 1 investigators were Jeff Peterson, Mike Close, Ray Yang, and Walter Hart of Union Carbide.

The Task 2 group developed a computational framework to evaluate the economics of syngas to alcohols processes. A topical report was prepared on the economics of seven base cases for alcohol fuels production. Lurgi, Shell, and Texaco gasification technologies were included, as well as a natural gas case for baseline comparisons. Task 2 included a test program using a single-cylinder variable compression engine to evaluate emissions from mixed alcohol/gasoline blended fuels. The Task 2 coordinator was Joe Shaeiwitz. Other investigators were Richard Turton, Tom Torries, Mridul Gautam, Reda Bata, Wallace Whiting and Manuk Colakyan of Union Carbide.

Carl Irwin, Alan Martin, and Duane Dombeck of Union Carbide were responsible for overall project management and coordination.

This Final Report consists of 20 chapters. Chapters two through six are based on peer reviewed publications resulting from Task 1 research. Chapters 7 through thirteen plus Appendices A through H are from the Topical Report on comparative process economics prepared by the Task 2 group. Chapters 15 through 17 are published in Proceedings of the Pittsburgh Coal Conference. Chapter 18 is a refereed conference paper. Chapters 19 and 20 are currently submitted for publication. Results, discussion, and conclusions are included with the particular chapter to which they apply. Similarly, reference and bibliography sections are retained with the applicable chapters.

In addition to extensive research results reported in refereed publications and conference presentations, the project supported approximately six Masters Degree students, one Ph.D. student and four post-doctoral students. These students are now all employed in academic or high-level technical positions in industry.

Chapter 2

Synthesis and Characterization of Nanoscale Molybdenum Sulfide Catalysts by Controlled Gas Phase Decomposition of Mo(CO)_6 and H_2S

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Abstract

Molybdenum sulfide catalysts with surface areas ranging from 16 to 120 m²/g were prepared by the thermal decomposition of Mo(CO)_6 and H_2S vapors in a specially designed tubular reactor system. The gas phase decomposition (GPD) reactions performed at 500 to 1100 °C produced only MoS_2 when excess H_2S was used. The optimum temperature range for the high yield production of MoS_2 was from 500 to 700 °C. By controlling the decomposition temperature, the Mo(CO)_6 partial pressure, or the inert gas flow rate, the surface area, oxidation state, chemical composition, and the grain size of the molybdenum sulfide product(s) were modified. At reactor temperatures between 300 and 400 °C, lower valent molybdenum sulfide materials, which were sulfur deficient relative to MoS_2 , were obtained with formal molybdenum oxidation states intermediate to those found for Chevrel phase compounds, $\text{M}'\text{Mo}_6\text{S}_8$ ($\text{M}'=\text{Fe, Ni, Co}$) and MoS_2 . By lowering the H_2S flow rate used for the GPD reaction at 1000 °C, mixtures containing variable amounts of MoS_2 and Mo_2S_3 were produced. Thus, through the modification of critical reactor parameters used for these GPD reactions, fundamental material properties were controlled.

Introduction

Conventional solid state syntheses are typically performed by mechanical mixing of the precursors, pressing the resultant reaction mixture into pellets, and then heating the pellets under inert or reactive gas conditions. This synthetic approach generally produces materials with low surface areas (often less than 1 m²/g) and may afford a mixture of phases due to incomplete solid state diffusion. The utility of producing materials with higher surface areas and purity, while using lower reaction temperatures, has motivated researchers to investigate alternative molecular mixing methods including chemical vapor deposition,¹ sol-gel processing,² spray pyrolysis,³ and co-precipitation.⁴ These strategies rely on combining the requisite precursors on an atomic or molecular level *prior* to heat

processing, thus lowering solid state diffusional barriers and the energy requirements necessary for product formation. In addition, processing variables inherent to these techniques may provide synthetic control over fundamental material properties, such as the surface area, the chemical composition, and the crystallographic phase.

Precise control of product surface area, chemical composition, and crystallographic phase has significant application in the area of heterogeneous catalysis. Solid phase catalysts can be prepared in a variety of ways. For example, MoS₂ is an effective heterogeneous hydrogenation⁵ and hydrodesulfurization⁶ catalyst and has been used as a Fischer-Tropsch synthesis catalyst for the production of hydrocarbons, or alcohols when it is modified with alkali.⁷ MoS₂ has been prepared by the thermolysis of MoS₃^{7f, 8} and (NH₄)₂MoS₄,^{7e, 9} by the solid-state metathesis reaction of MoCl₅ and Na₂S,¹⁰ and by various molecular mixing approaches, such as laser pyrolysis,¹¹ liquid phase decomposition,¹² and CVD¹³ using Mo(CO)₆ and different sulfiding agents. Recently, Tenne and co-workers¹⁴ have employed the gas phase reaction of MoO_{3-x} and H₂S in a reducing H₂ atmosphere to produce a pure inorganic fullerene phase of MoS₂. Samples of MoS₂ prepared by these routes exhibit widely variable surface areas.

In conjunction with our efforts to develop efficient heterogeneous catalysts for the productions of higher alcohols, we decided to investigate the controlled gas phase decomposition (GPD) of Mo(CO)₆ and H₂S as a viable route for the generation of high surface area MoS₂. Mo(CO)₆ is well-suited for this purpose because the Mo(0) oxidation state eliminates the need to conduct the reaction in a reducing environment. Its inherent volatility further provides the flexibility of being able to alter the Mo(CO)₆ partial pressure in the reactive gas stream by simply varying the temperature used to sublime it.

In this paper, we describe the use of a continuous flow pyrolysis reactor for the production of MoS₂ by controlled gas phase decomposition of Mo(CO)₆ and H₂S. By varying the furnace temperature, the type of gas injection system, the carrier gas flow, and the Mo(CO)₆/H₂S composition in the reaction stream, we have been able to optimize yields and more importantly influence the surface area, crystallographic phase, and chemical composition of the GPD products. Although care must be taken in correlating catalyst surface area with catalytic activity, oxygen titration studies coupled with BET measurements of the MoS₂ produced by our reactor show that the mass density of active sites is proportional to surface areas of these materials.¹⁵ Specific details regarding the reactor design and the characterization of the molybdenum sulfide products by XRD, XPS, and SEM methods are also presented.

Experimental

Chemicals. Mo(CO)₆ was obtained from Strem Chemical Co. and purified by sublimation prior to use. H₂S (Matheson Gas Products) was used as received. He and Ar were purified by passage over supported copper and molecular sieves to remove oxygen and water, respectively.

Gas Phase Reactor. The reactor system illustrated in Figure 1 can be divided into three separate sections: sample introduction, sample pyrolysis, and material isolation. The sample

Figure 1. Gas phase reactor system used to form molybdenum sulfides. Mo(CO)_6 and H_2S vapor is mixed and then pyrolyzed in the furnace at temperatures from 300 to 1100 °C to produce finely divided molybdenum sulfides. The nanoscale particles resulting from these decompositions are isolated in tubes constructed from coarse porosity filter paper.

pyrolysis and material isolation segments were the same for each experiment described in this investigation, while two different configurations were used for the sample introduction (see Figure 2). Mo(CO)_6 vapor was produced by heating the section of the reactor containing 2-3 grams of

Figure 2. Two injector configurations used in the gas phase reactor. Reactor configuration A was used in initial experiments and produced relatively low yields due to metal decomposition on the quartz tube inner surface at the water jacket/furnace interface. Reactor configuration B was developed subsequently to increase the yield by reduction of material loss on the inner tube surface and to allow variation in the heating zone length by changing the relative position of the water-cooled injector within the furnace.

Mo(CO)_6 with either a heating tape (reactor configuration A) or a band heater (reactor configuration B). He, Ar and H_2S gas flow rates were measured by Matheson rotameters, which were locally calibrated. The reaction tube consisted of 25 mm fused silica tubing (3 foot length) with No. 25 O-ring quartz joints (G.M. Associates). The products were collected in filter tubes constructed from Fisher P8 coarse porosity filter paper. An optically clear glass disk was incorporated into the collection device to allow visual monitoring of the GPD reactions. Mo(CO)_6 vapor was introduced into the reactor

using either an outer (reactor configuration A) or an inner (reactor configuration B) water jacket injection system, both made of Pyrex. Configuration A was used initially whereas configuration B was developed later to increase material yields and to reduce annealing time. Configuration B consists of three concentrically aligned Pyrex tubes which provide water cooling of the gas flow tube up to 8 inches inside the furnace. An additional gas port was added in the design of configuration B to minimize the material loss on the fused silica tube surface by establishing a laminar flow of inert gas around the water-cooled injector. Both of the water jackets were maintained at the same temperature with a temperature-controlled circulating water bath. A 24" Lindberg split furnace controlled by a Eurotherm 818 programmable controller was used to heat the reaction tube.

Mo(CO)₆ Gas Phase Reactions. Three series of reactions were performed using reactor configuration A and reactor configuration B. Reactor configuration A was used in the first set of reactions to prepare four molybdenum sulfide samples by decomposing Mo(CO)₆ and H₂S vapors at 500 (A1), 800 (A2), 900 (A3), and 1100 °C (A4). In a second series of GPD reactions of Mo(CO)₆/H₂S, eleven molybdenum sulfide samples were prepared using reactor configuration B at temperatures ranging from 300 to 900 °C. A third study using configuration A was performed for the purpose of preparing lower valent molybdenum sulfides, samples C1 and C2, by lowering the H₂S flow rate. Experimental parameters for the GPD reactions are summarized in Table 1.

Table 1. Experimental Conditions and Yields for the Gas Phase Decompositions of Mo(CO)_6 and H_2S .

Run	Mo(CO)_6 mass (g)	T_f^a	T_{Mo}^a	T_{wj}^a	Ar_i^a	Ar_o^a	H_2S rate (mL/min)	Yield %
A1	2.0	500	69	-	635	-	26	49.1
A2	2.0	800	69	-	549	-	26	64.3
A3	2.0	900	69	-	529	-	26	40.1
A4	2.0	1100	69	-	654	-	26	41.3
B1	3.0	300	98-99	85	220	700	11	26.7
B2	3.0	400	98-99	85	220	700	11	45.0
B3	3.0	500	98-99	85	220	700	11	82.7
B4	3.0	600	98-99	85	220	700	11	88.6
B5	3.0	700	98-99	85	220	700	11	95.0
B6	3.0	800	98-99	85	220	700	11	94.6
B7	3.0	900	98-99	85	220	700	11	98.2
B8	3.0	500	93	80	220	635	11	82.8
B9	3.0	500	104	80	220	635	11	82.8
B10	3.0	500	93	70	0.00	415	15	<20
B11	3.0	500	98-99	85	250	700	11	75.5
C1	2.0	1000	80	N/A	300	N/A	5	0.844 g ^b
C2	2.0	1000	80	N/A	300	N/A	2.5	0.779 g ^b

^a T_f = furnace temperature; T_{Mo} = Mo(CO)_6 temperature; T_{wj} = temperature of the water jacket injection tube; Ar_i = argon flow rate (mL/min) through the inner tube containing the Mo(CO)_6 ; Ar_o = argon flow rate (mL/min) through the reaction tube outer section.

^b Mixture of phases produced, therefore the amount given is the total product weight.

In a typical GPD reaction, Mo(CO)_6 powder (2.0 or 3.0 grams) was weighed into a cylindrical Pyrex boat and placed into the sample introduction section. The reactor system was assembled and purged with He (or Ar) and H_2S for 20-30 minutes. The H_2S flow was terminated and the furnace was heated to an operating temperature ranging from 300 to 1100 °C at a rate of 1000 °C/hr. When the temperature reached 100 °C below the set point, the H_2S and inert gas flows were adjusted to the appropriate processing values. The water in the water jacket and the reservoir containing Mo(CO)_6 were heated to predetermined settings and the GPD reaction was allowed to proceed until all of the Mo(CO)_6 was depleted. The reaction time was approximately 1 hour per gram of Mo(CO)_6 consumed. Although the bulk molybdenum sulfide products do not appear to react in air, XPS data show that samples exposed to air contain more surface oxygen than

those stored under inert gas. The samples produced by reactor configuration A were stored under an inert nitrogen atmosphere, whereas the samples produced by reactor configuration B were exposed briefly to air prior to storage. The yields for these GPD reactions ranged from <20 to 98 %, depending on the reaction conditions. Temperature cycling studies, which involve the heating of the MoS₂ samples between 200 °C and 400 °C for 80 hours, show that their catalytic properties (activity/selectivity) remain unchanged and thereby indicate that these materials are stable to thermal treatment for an extended period of time over this temperature range.

Material Characterization. X-ray powder diffraction measurements were performed on a Philips PW 1800 diffractometer using Cu K α radiation. The powders were loaded on zero background single crystal quartz disks¹⁶ by either packing the samples into a cavity in the disk or by dispersing the powders in pentane and depositing the dispersion on the surface of the disk. Mo and S binding energies and ratios were determined by X-ray photoelectron spectroscopy performed on a Physical Electronic Industries 5600 XP using monochromatic Mg radiation. The binding energies were referenced to C(1s) = 284.8 eV. The sulfur compositions were determined by combustion analysis using a Leco SC-432DR instrument. A Perkin Elmer 2400 CHN combustion analyzer was used to determine the carbon percentages. BET surface areas were determined with nitrogen using a Coulter Omnisorb 360 instrument operated in a static adsorption mode. Equilibrium nitrogen adsorption was measured over the pressure range of 0 to 120 Torr (1 Torr = 1.33 x 10² Pa). The scanning electron micrographs were obtained on a JOEL 6300L Field Emission SEM located in the WVU Department of Geology. Results Mo(CO)₆/H₂S Decompositions with Reactor Configuration A. In the initial series of GPD reactions, molybdenum sulfide samples were prepared by reacting Mo(CO)₆ and H₂S vapors at 500 (A1), 800 (A2), 900 (A3), and 1100 °C (A4) using reactor configuration A. The results summarized in Tables 1 and 2 indicate that the MoS₂ surface area decreased significantly from

Table 2. Analytical Data for the MoS₂ Samples Prepared by the GPD of Mo(CO)₆ and H₂S with Reactor Configuration A.

Run	T _f (°C) ^a	Binding Energies (eV)				S/Mo (XPS)	Yield (%)	XRD ^b FWH H	Surface Area (m ² /g)	Sulfur % (Carbon %)
		Mo 3d _{3/2}	Mo3d _{5/2}	S 2p _{1/2}	S 2p _{3/2}					
A1	500	232.4	229.2	163.2	162.1	2.34	49.9	2.4	82.0	38.85 (0.05)
A2	800	232.4	229.3	163.4	162.2	2.11	64.3	2.0	57.4	56.9 (<0.01)
A3	900						40.6	1.6	29.6	48.7 (<0.01)
A4	1100	232.4	229.2	163.3	162.1	1.94	41.3	1.3	16.7	49.4 (<0.01)

^a Furnace temperature.

^b Full width at half height measurement in 2 θ for the Bragg powder diffraction peak for the (0 0 2) reflection.

82.0 to 16.7 m²/g as the furnace temperature was increased from 500 to 1100 °C, respectively. The scanning electron micrographs of samples A1 and A4 shown in Figure 3 indicate that the

Figure 3(a)

Figure 3(b)

Figure 3. Scanning electron micrographs (40,000x) of the MoS₂ samples produced by the GPD reactions of Mo(CO)₆ and H₂S at (a) 500 °C and (b) 1100 °C using reactor configuration A.

MoS₂ particles in these samples are agglomerated and individually exhibit dimensions well-below 100 nm. Similar morphological features are evident in the corresponding SEMs of samples A2 and A3, which are not shown. As the reaction temperature increased, the products became more crystalline. The narrowing of the X-ray diffraction peaks (Figure 4) due to MoS₂ is consistent with a concomitant increase in crystallite grain size.

Figure 4. X-ray powder diffraction patterns for materials prepared by the thermal decomposition of Mo(CO)_6 and H_2S at 500 (A1), 800 (A2), and 1100 C (A4). A3 omitted for clarity.

The results of the XPS analyses performed on samples A1, A2, and A4 show that the S:Mo ratio near the surface is consistent with that found for MoS_2 . Bulk sulfur analyses of these compounds, however, gave nominal molecular formulas of $\text{MoS}_{1.9}$, $\text{MoS}_{3.95}$, $\text{MoS}_{2.84}$, and $\text{MoS}_{2.92}$ for products A1 - A4, respectively. The excess sulfur in samples A2 - A4 corresponds to elemental sulfur, which was observed in the X-ray diffraction patterns and verified by the S 2p peaks corresponding to elemental sulfur in the respective XPS spectra. For sample A1 the only phase observed in the X-ray diffraction powder pattern was MoS_2 , although a very small peak due to elemental sulfur was found in the S 2p XPS spectrum. The Mo and S binding energies for A1, A2, and

A4 matched those expected for MoS₂ (S 2p: 162.1 eV, 163.2 eV; Mo 3d: 229.2 eV, 232.4 eV).¹⁷ The carbon composition for each of these compounds was less than 0.05 %, whereas surface oxygen was detected by XPS at levels ranging from 7-28%. Therefore, on the basis of the elemental analyses, the XRD powder diffraction patterns, and the XPS data, the only identifiable products were surface oxygen, elemental sulfur, and 2H-MoS₂.¹⁸

Mo(CO)₆/H₂S Decompositions with Reactor Configuration B. This second series of GPD reactions focused on investigating the influence of specific reactor variables on the properties of the products. Specifically, variations in the furnace temperature, the Mo(CO)₆ partial pressure, or the inert gas flow rate produced significant changes (Table 3) in the surface

Table 3. Analytical Data for the MoS₂ Samples Prepared by the GPD of Mo(CO)₆ and H₂S with Reactor Configuration B.

Run	T _f ^a	Binding Energies (ev)				S/Mo (XPS)	Yield %	XRD ^b FWHH	Surface Area (m ² /g)	Sulfur % (Carbon %)
		Mo 3d _{3/2}	Mo 3d _{5/2}	S 2p _{1/2}	S 2p _{3/2}					
B1	300	231.5	228.5	162.8	161.9	0.88	26.7	5.4	21.4	22.6 (0.21)
B2	400	232.1	229.0, 228.2	162.9	162.0	0.86	45.2	5.6	47.3	22.4 (0.09)
B3	500	232.4	229.3	163.2	162.2	1.30	82.7	3.7	76.5	37.85 (0.04)
B4	600	232.5	229.3	163.3	162.2	1.59	88.6	2.6	75.4	42.61 (0.01)
B5	700	232.5	229.3	163.3	162.2		95.0	2.1	78.0	45.95 (<0.01)
B6	800	232.5	229.3	163.3	162.2		94.6	1.8	72.5	45.56 (0.06)
B7	900	232.5	229.3	163.3	162.2		98.2	1.5	66.2	46.03 (<0.01)

^a T_f = furnace temperature.

^b Full width at half height measurement in 2 θ for the Bragg powder diffraction peak for the(0 0 2) reflection.

area, chemical composition, and crystallite grain size of the product.

The influence of the reaction temperature on the product surface area was evaluated by decomposing Mo(CO)₆/H₂S mixtures at temperatures ranging from 300-900 C (B1 - B7) and determining the surface areas of the isolated products with BET methods. The surface areas for these samples reached a maximum (75.4-78.0 m²/g) within the temperature range of 500-700 C and then decreased at higher and lower temperatures. Molybdenum 3d and sulfur 2p binding energies for samples B1 - B4 were measured by X-ray photoelectron spectroscopy to monitor product composition. The sulfur 2p and the molybdenum 3d binding energies increased as the furnace temperature was elevated from 300 to 500 C and then remained unchanged for samples prepared at or above 600 C. The narrowing of the XRD peak widths observed in the XRD patterns (Figure 5) indicates that the reactor temperature also has a significant effect on the

crystallinity of the GPD product. As the reactor temperature increased from 300 to 900 C, the Bragg diffraction peaks due to MoS_2 ¹⁷ emerged and continued to sharpen.

Figure 5. X-ray powder diffraction patterns of MoS_2 formed by the thermal decomposition of $\text{Mo}(\text{CO})_6$ and H_2S at 300 (B1), 400 (B2), 500 (B3), 600 (B4), 700 (B5), 800 (B6), and 900 C (B7).

The influence of the $\text{Mo}(\text{CO})_6$ partial pressure on the surface area, composition, and crystallinity of the molybdenum sulfide products was examined by varying the temperature used to heat the $\text{Mo}(\text{CO})_6$ reservoir while keeping the reactor temperature constant at 500 C. Three compounds were prepared with the $\text{Mo}(\text{CO})_6$ sample reservoir heated to 93 (B8), 98 (B3) and 104 C (B9). Sample B9 exhibited the lowest surface area ($55.4 \text{ m}^2/\text{g}$), whereas sample B8 showed the highest surface area ($95.1 \text{ m}^2/\text{g}$). The Mo 3d

and S 2p binding energies varied only slightly (0.1 to 0.3 eV). Although the product yields were essentially the same, the crystallinity of these three samples noticeably increased with an increase in the temperature used to sublime Mo(CO)₆.

The effect of varying the Ar flow rate through the inner tube of the water-cooled injector used for reactor configuration B was also examined. Three separate reactions were conducted. For reaction B10 the Ar flow rate was set at 0 with the H₂S flow rate at 15 mL/min. This reaction produced a molybdenum sulfide product with the highest surface area (120.5 m²/g). Increasing the Ar flow rate from 0 mL/min to 220 mL/min (B3) led to a decrease in the surface area to 76.5 m²/g and a significant increase in the product yield from <20 % to 82.7 %. For reaction B11 the small increase in the Ar flow rate resulted in decreases in the product surface area and product yield. The Mo 3d and S 2p binding energies were comparable for samples B10 and B11.

Mo₂S₃ Preparations. By lowering the H₂S flow rate (i.e., raising the Mo:S ratio) relative to those used to produce samples A1-B11, a lower valent molybdenum sulfide phase, Mo₂S₃, was produced. For reaction C1, the GPD of Mo(CO)₆ and H₂S (5 mL/min) at 1000 °C afforded a material containing both MoS₂ and Mo₂S₃. These two phases were the only ones observed in the XRD patterns. For reaction C2, the lowering of the H₂S rate to 2.5 mL/min led to the observation of Mo₂S₃, MoS₂, and Mo. Not only was elemental molybdenum identified in the XRD, but the MoS₂:Mo₂S₃ ratio decreased, as indicated by the relative intensities of the Bragg diffraction peaks assignable to these two phases.

Discussion of Results

Influence of Furnace Temperature on Product Composition. The furnace temperature used to perform the GPD reactions Mo(CO)₆ and H₂S significantly influences the product composition, surface area, and crystallite size. Over the temperature range of 300-1100 °C, the formation of MoS₂ is favored thermodynamically. In fact, due to the high thermodynamic stability of MoS₂, substitution of Mo(CO)₆ with a different molybdenum precursor, such as Mo₂C, MoC, MoO₂, Mo₂N, or MoN, still favors MoS₂ formation. The fact that MoS₂ is not produced at or below 400 °C indicates that higher reaction temperatures are required to provide the activation energy needed to promote the production of MoS₂.

The two molybdenum sulfide materials, B1 and B2, prepared at 300 and 400 °C, respectively, differ significantly in their chemical composition and molybdenum valency relative to sample B3 produced at 500 °C. Whereas samples B1 and B2 exhibit an average bulk % sulfur of 22.5 %, corresponding to a S:Mo ratio near 1:1, sample B3 has a bulk % sulfur of 37.8 %, corresponding to a S:Mo ratio of 1.8. The Mo 3d binding energies measured for B1 (3d_{5/2}=228.5 eV; 3d_{3/2}=231.5 eV) and B2 (3d_{5/2}=228.2 eV and 229.0 eV; 3d_{3/2}=232.1 eV) are intermediate to those found for MoS₂ (3d_{5/2}=229.5 eV; 3d_{3/2}=232.6 eV)¹⁷ and Chevrel phase compounds, M'Mo₆S₈, where M'=Fe, Ni, Co, Pb, Sn and Ag (227.3 eV Mo 3d_{5/2} 228.2 eV).¹⁹ In contrast, the Mo 3d binding energies measured for B3 (3d_{5/2} = 229.3 eV; 3d_{3/2}=232.4 eV) are in close agreement with the values reported for MoS₂. On the basis of these Mo 3d binding energies measured for B1 and B2, the corresponding formal Mo oxidation state in these samples lies between +2 (highly reduced Chevrel phase compounds) and +4 (MoS₂).

An initial concern was that the molybdenum sulfide compounds formed by Mo(CO)_6 decomposition might contain copious amounts of carbon and oxygen from inclusion of the carbonyl ligand. Based on the results of our compositional analyses, this did not occur. The highest carbon content found for these materials was 0.21% for sample B1.

In addition to the lower sulfur content and the lower formal Mo oxidation state associated with B1 and B2, the XRD data for these samples indicate the presence of limited atomic ordering. Estimates of the grain size in B1 (or B2) and B3 were obtained by application of the Scherrer equation for XRD peak broadening due to particle size effects. Using a Scherrer constant of unity, the sizes of the crystallite particles in B1 and B3 are estimated to be 1.6 and 3.2 nm, respectively. These dimensions are calculated with the assumption that the crystallite grain size is the primary factor contributing to the peak broadening. However, if appreciable lattice strain is present in these compounds, the grain size contribution to peak broadening is less.

The reaction temperature also has a strong influence on the surface areas of the GPD products, with the higher surface areas being obtained for the MoS_2 formed within the temperature range of 500 to 700 °C. Although elemental sulfur was identified by XPS and XRD in bulk samples prepared at temperatures above 500 °C, MoS_2 was the only molybdenum sulfide compound present. The Mo 3d and S 2p binding energies of the materials prepared at or above 500 °C are consistent with the Mo and S binding energies found for MoS_2 . Although the relative peak intensities do not match those found in the JCPDS file for 2H- MoS_2 ,¹⁷ the XRD peak positions match exactly those for this hexagonal phase of MoS_2 . The intensity differences are primarily observed for the (0 0) planes, suggesting the apparent discrepancy may be a consequence of preferred orientation effects. In view of the observed broadening of the XRD peaks, the co-existence of the 3R- MoS_2 ¹⁸ phase, however, cannot be ruled out.

As the decomposition temperature is raised from 500 to 1100 °C, the surface area of the resultant product generally decreases with a concomitant increase in the crystallinity. Although similar property trends are observed for MoS_2 produced with reactor configurations A and B, the difference in the magnitude of the surface area variation with reaction temperature for these two configurations is worth noting. For reactor configuration A, the surface area decreases from 82.0 (A1 , 500 °C) to 16.7 m^2/g (A4 , 1100 °C), respectively. This inverse correlation between the MoS_2 surface area and the furnace temperature is complicated by the additional sulfur present in samples A2 , A3 , and A4 as rhombohedral S_8 . However, the XRD pattern measured for these samples indicates that S_8 in these samples is highly crystalline, thereby suggesting that the sulfur contribution to the surface area measurements is minimal (i.e., less than 1 m^2/g). Thus, the observed reduction in the measured surface area is probably not due to the excess sulfur present, but actually reflects the lower surface areas of the MoS_2 present in these four samples.

Whereas a significant decrease in the surface area was observed with increasing reactor temperature for the samples prepared using reactor configuration A, the surface areas of the corresponding MoS_2 materials generated using reactor configuration B remained fairly constant, ranging from 78.0 m^2/g at 500 °C to 66.2 m^2/g at 900 °C. This modest surface area variation is attributed almost entirely to the changes in the MoS_2 surface area and not to the presence of excess elemental sulfur. The residual sulfur

present in samples B6-B9 ranges from three to nine weight percent, therefore suggesting that the actual surface areas of the MoS₂ in these samples may be somewhat higher than the experimental values reported in Table 3.

In these GPD reactions there are at least three fundamental process variables that directly influence the product surface area. These factors include the relative rate of the GPD reaction, the degree of annealing of the solid particles formed, and the initial composition of the Mo(CO)₆/H₂S mixture in the gas phase. The furnace temperature obviously affects the first two process variables, whereas the third can be altered by changing the Mo(CO)₆ reservoir temperature, the H₂S flow rate, and the inert gas flow rates over the Mo(CO)₆. One might expect that increasing the reactor temperature will increase both the rate of the GPD reaction and the degree of annealing of the MoS₂ particles. The higher rate of decomposition associated with a higher furnace temperatures should afford more finely divided material, analogous to liquid precipitation reactions where the particle size is controlled by the kinetics of the decomposition.²⁰ On the other hand, because these products are comprised of agglomerated particles (Figure 3), an increase in the reactor temperature would also be expected to increase the solid state diffusion rates, thus producing larger particles with lower surface areas. Consequently, these two opposing effects directly influence the bulk surface area as the reactor temperature is increased.

Reactor configurations A and B further differ in the way the gaseous reactants are introduced into the hot zone and the distance through which the solid particulate is heated. With reactor configuration A, the gaseous reactants after they exit the injector inlet are exposed to a significant temperature gradient within the tube furnace prior to reaching the reactor's process temperature. In contrast, reactor configuration B facilitates the introduction of reactant vapors into the central section of the furnace hot zone where the temperature gradient over a six inch length is 5 C. This alternative configuration provides better control over the temperature of the decomposition event and the heating length. By taking into consideration the differences in the gas flow rates and the heating distances used for these two reactor configurations, the annealing time for configuration A is estimated to be approximately three times longer than that for configuration B. This reduction in heating/annealing time may be the primary reason why the surface areas of the MoS₂ samples prepared with reactor configuration B do not vary significantly with reaction temperature.

A significant reduction in the heating/annealing time during a gas phase decomposition reaction has been realized when laser excitation is used to initiate the reaction.²¹ Because the effective reaction volume is limited by the dimensions of the laser beam, products pass quickly out of the reactor, thereby minimizing annealing effects on the particle size. Although resistive heating methods cannot easily duplicate the decomposition event produced by lasers, the results of this study show that simple modifications of the reactor configuration can reduce significantly post-decomposition heating effects and increase the reaction yields to those approaching the theoretical limit.

Influence of Mo(CO)₆ Reservoir Temperature and Carrier Gas Flow Rates on Product Composition. The Mo(CO)₆ reservoir temperature and the carrier gas flow rate over the Mo(CO)₆ can be used to modify the product composition and bulk properties. An increase in either the temperature used to heat the Mo(CO)₆ reservoir or the rate of Ar flow through the reactor resulted in lowering the surface area and

crystallinity of the molybdenum sulfide product(s) at a given reactor temperature. Although the limits of these process variables remain to be investigated, the analytical data summarized in Tables 4 and 5 demonstrate that the surface area of the MoS₂ can be doubled by making relatively small changes in the Mo(CO)₆ temperature and the Ar flow rate.

Table 4. Analytical Results for the MoS₂ Samples Prepared by Varying the Mo(CO)₆ Reservoir Temperature.

Run	T _{Mo} ^a	Binding Energies (ev)				S/Mo Ratio (XPS)	Yield %	XRD ^b FWHH	Surface Area	Sulfur % (Carbon %)
		Mo 3d _{3/2}	Mo 3d _{5/2}	S 2p _{1/2}	S 2p _{3/2}					
B8	93	232.6	229.4	163.2	162.3	1.68	82.8	3.2	95.1	41.32 (<0.01)
B3	98	232.4	229.3	163.2	162.2	1.30	82.7	3.7	76.5	37.85 (0.04)
B9	104	232.3	229.2	163.1	162.1	1.04	82.8	5.7	55.4	32.70 (0.04)

^a Temperature of the Mo(CO)₆ reservoir.

^b Full width at half height measurement in 2 θ of the Bragg diffraction peak for the (0 0 2) reflection.

Table 5. Analytical Results for the MoS₂ Samples Prepared by Varying Argon Gas Flow Rate.

Run	Ar _i ^a Rate	H ₂ S Rate	Binding Energies (ev)				S/Mo Ratio (XPS)	Yield %	XRD ^b FWHH	Surface Area	Sulfur % (Carbon %)
			Mo 3d _{3/2}	Mo 3d _{5/2}	S 2p _{1/2}	S 2p _{3/2}					
B10	0	15						<20		120.5	N/A
B3	220	11	232.4	229.3	163.2	162.2	1.30	82.7	3.7	76.5	37.85 (0.04)
B11	250	11	232.3	229.2	163.1	162.2	1.01	75.5	5.3	64.0	34.09 (<0.01)

^a Argon flow rate through the inner tube of reactor configuration B.

^b Full width at half height measurement in 2 θ for the Bragg powder diffraction peak of the (0 0 2) reflection.

Mo₂S₃ Preparations. We have shown by the use of a low H₂S flow rate (i.e., at or below 5 mL/min) that it is possible to produce the reduced phase, Mo₂S₃, at 1000 °C by a GPD reaction. Alternatively, when the H₂S flow rate equals or exceeds the stoichiometric amount needed to produce MoS₂, the only molybdenum containing phase observed in the XRD is 1H-MoS₂.¹⁸ However, it should be pointed out that due to the nature of the reactor geometry the amount of Mo(CO)₆ in the reactive gas stream decreases as the Mo(CO)₆ in the reservoir is consumed during the course of the reaction. Consequently, at fixed H₂S flow rates at or below 5.0 mL/min, Mo₂S₃ (C1) or Mo₂S₃ and Mo metal (C2) are formed primarily at the beginning of the reaction when the Mo(CO)₆ concentration is high. However, as this concentration decreases, more MoS₂ is generated during the latter stages of these reactions.

The results for reactions C1 and C2 further suggest that it may be possible to obtain pure phase Mo₂S₃ by modifying the Mo(CO)₆ section of the reactor to facilitate a constant introduction of Mo(CO)₆ vapor. Further, the controlled introduction of another volatile metal carbonyl, such as Fe(CO)₅, into the reactive gas stream containing Mo(CO)₆ and H₂S, may provide the opportunity to produce other molybdenum sulfide phases, such as Chevrel phase compounds, M'Mo₆S₈ (M'=Fe, Ni, Co, etc.), some of which are also known to catalyze hydrodesulfurization reactions.¹⁸ However, due to the conventional solid state methods employed to produce these compounds, their surface areas are typically close to 1 m²/g. Chevrel and his co-workers have speculated about the viability of preparing supported Chevrel phase compounds from soluble precursors.²² However, lower reaction temperatures will be necessary to avoid subsequent reduction in the surface area of the support by sintering processes. Therefore, the major hurdles that must be overcome in order to prepare high surface area Chevrel phase compounds via a GPD reaction are the precise control of the composition of the reactive gas stream and the minimization of annealing effects induced by heating at high temperatures.

The feasibility of using our continuous flow gas phase reactor to prepare bimetallic ternary materials, however, has been demonstrated recently in our laboratories. Preliminary studies have demonstrated that the thermal decomposition of gaseous mixtures of Fe(CO)₅, Mo(CO)₆, and ammonia lead to the production of solid solutions in

which the Fe in $\gamma\text{-Fe}_3\text{N}$ is partially substituted by molybdenum, as verified by EDS measurements and the expanded dimensions of its hexagonal lattice.²³

Concluding Remarks

A continuous flow reactor has been developed for the production of molybdenum sulfide compounds by the gas phase decomposition of Mo(CO)_6 and H_2S . Nanoscale MoS_2 solids with surface areas ranging from 16 to $120\text{ m}^2/\text{g}$ were generated over the temperature range, 500-900 °C, while lower valent molybdenum sulfides were obtained at 300 and 400 °C. Three critical catalyst properties - the surface area, the chemical composition, and the crystallographic phase - were controlled by varying the furnace temperature, the carrier gas flow rate, and the partial pressure of the Mo(CO)_6 used in these GPD reactions. By modifying the original reactor with a water-cooled injector to induce laminar gas flow around the reactive gases, product yields were increased from 40-64 % to 75-98%. In addition to MoS_2 , microcrystalline Mo_2S_3 was produced by lowering the H_2S flow rate. These high surface area MoS_2 materials, when promoted with alkali, have been subsequently shown²⁴ to exhibit high catalytic activity for the selective production of linear alcohols from synthesis gas. Although this study focuses on the preparation of molybdenum sulfides, molybdenum nitrides and mixed metal nitrides have been prepared in this continuous flow reactor by the decomposition of $\text{Mo(CO)}_6/\text{NH}_3$ vapors and by the introduction of Fe(CO)_5 into this reactive gas stream, respectively.²³

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Chapter 3

SCREENING OF ALKALI-PROMOTED VAPOR-PHASE-SYNTHESIZED MOLYBDENUM SULFIDE CATALYSTS FOR THE PRODUCTION OF ALCOHOLS FROM SYNTHESIS GAS

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ABSTRACT

A series of molybdenum sulfide catalysts has been prepared using vapor-phase decomposition of molybdenum hexacarbonyl in an atmosphere of hydrogen sulfide. The effect of the decomposition conditions on the properties of the molybdenum sulfides formed has been studied over a temperature range of 300-900°C. These materials, when promoted with alkali, have been found to have a high activity for the production of alcohols from synthesis gas. The effects of the catalyst preparation temperature (*i.e.*, decomposition temperature) and reaction conditions (temperature, flow rate) have been studied, as well as the effect of the type and concentration of the alkali promoter. In all cases, the alcohols formed are primarily straight-chain, terminal -OH compounds. The variations in preparation procedure have only small effects on the conversion and the selectivity to higher alcohols. Increasing the reactant flow rate increases the selectivity to methanol at the expense of the hydrocarbons and the higher-molecular-weight alcohols. Increasing the reaction temperature changes the selectivity towards higher alcohols but also changes the selectivity towards hydrocarbons. A maximum in selectivity to higher alcohols with the reaction temperature is observed for all catalysts tested.

INTRODUCTION

Alcohols as well as other oxygenates derived from alcohols are viewed as desirable gasoline additives both to improve octane and to reduce engine emissions. Alcohols were certainly present in the liquid product of the original BASF-patented process (BASF, 1913) whereby CO was hydrogenated at high pressures and temperatures over an iron-based catalyst. However, current processes for making alcohols (other than methanol) from synthesis gas, a mixture of carbon monoxide and hydrogen, are limited by the sulfur stability and the selectivity of present-day catalysts.

Catalysts used for the production of higher alcohols from synthesis gas have been extensively reviewed by Klier *et al.* (1988a). Ponc (1992) recently speculated on the active centers of many of these catalysts. The catalysts can be divided into four categories. The first of these is a soluble Ru complex used as a homogenous catalyst. The second can loosely be described as modified methanol catalysts. This type of catalyst may operate at high pressure (*i.e.*, greater than 100 atm) or lower pressures, corresponding to the individual progenitor methanol-synthesis catalyst. Examples include alkali-doped ZnO/chromia catalysts and CuO-based catalysts respectively. The third category of higher-alcohol synthesis (HAS) catalysts comprises mixed-metal catalysts, *e.g.*, Rh and Fe on a support. The final category is chalcogenide-based, typically alkali-promoted MoS₂. This category of higher-alcohol synthesis catalyst is the focus of the present work.

Molybdenum sulfide catalysts promoted by alkali-metal compounds were discovered to be active for higher alcohol synthesis by research groups at Dow (see, *e.g.*, Murchison *et al.*, 1988) and Union Carbide (*e.g.*, Kinkade, 1984). Academic research groups such as those led by Klier (see, *e.g.*, Santiesteban *et al.*, 1988) and Somorjai (*e.g.*, Youchang *et al.*, 1986) have also studied molybdenum sulfide catalysts. Recently, the role of the promoter has been discussed by Lee *et al.* (1994). These catalysts are characterized by water-gas-shift capability and a very high tolerance for sulfur -- in fact, a pretreatment with H₂S is generally required.

The types of alcohols produced depend strongly upon the type of catalyst used. Typically, the MoS₂-based catalysts produce mainly linear alcohols, while certain lower-pressure modified methanol-synthesis catalysts (such as the K/CuO/Zn/Cr material used in the Lurgi process) produce mainly branched alcohols. The higher-pressure modified methanol-synthesis catalysts typically produce branched alcohols and linear alcohols. The temptation is therefore to assume two different mechanisms and two different types of reaction sites. This is analogous to the situation in the formation of hydrocarbons from synthesis gas by the Fischer-Tropsch process, where Lox and Froment (1993) hypothesized two different types of sites.

It is reasonable to expect that the nature of the MoS₂-based catalyst is governed by the morphology of the molybdenum sulfide, and that would depend upon the mode of preparation of the material. Molybdenum disulfide, MoS₂, has been prepared by thermolysis of MoS₃ (Eggersen and Roberts, 1959; Klier *et al.*, 1988) and of (NH₄)₂MoS₄ (Eggersen and Roberts, 1959; Wildervanck and Jellinek, 1964), by CVD (Suhr *et al.*, 1990), laser pyrolysis (Oyama *et al.*, 1989, 1994), and liquid- or vapor-phase decomposition (Chatzitheodorou *et al.*, 1988; Rice *et al.*, 1992). The size of the particles, as well as their crystallographic phase and their chemical composition, can be altered by varying the decomposition variables. In the present work, we use a continuous-flow vapor-phase technique where molybdenum hexacarbonyl, Mo(CO)₆, is decomposed in hydrogen sulfide to produce molybdenum sulfides of varying characteristics. We

then use the sulfides formed, with and without promoters, as catalysts for HAS from synthesis gas.

Below, we first describe the apparatus for the formation of the sulfides and the catalytic reactor system. The characterization of the sulfides, in terms of surface area, amount of sulfur, x-ray diffraction, and product yield is briefly provided. The results of the catalytic screening runs are then presented, along with specific experiments focussing on the alkali metals added as promoters.

EXPERIMENTAL

Sulfide Synthesis Apparatus. This is shown in Figure 1. Separate reservoirs are available in parallel for molybdenum hexacarbonyl and iron pentacarbonyl, so either single- or mixed-metal sulfides or carbides can be prepared. Here we are concerned only with the pure molybdenum sulfides. The inert gas, typically argon, is purified through molecular sieve and copper catalyst sections before being mixed with reactant H_2S . Flow rates of all gases are controlled by Matheson rotameters which were calibrated in-house. A Lindberg split furnace, controlled by a Eurotherm 818 programmable controller, is used for the thermolysis. The main tube through the furnace is fabricated from 0.9m (3 ft) of 25-mm quartz tubing. At the furnace entrance, a water-jacketed injection tube reduces the amount of molybdenum plating on the interior of the main tube. The injection tube, shown in greater detail in Figure 2, extends halfway into the 0.45m (1.5ft)-length hot zone. The injection tube is formed by three concentric Pyrex tubes, of inner diameter 4mm, 12mm and 17mm, with the 4-mm tube sealed to the 17-mm tube at the injector tip. Water flows in through the annulus formed by the 4- and 12-mm tubes, and out through the annulus formed by the 12- and 17-mm tubes. Argon gas is introduced between the main tube (25mm) and the 17-mm tube. The reactive gases pass through the innermost (4-mm diameter) tube. The flow pattern thus established keeps most of the molybdenum hexacarbonyl vapor away from the hottest surfaces, where it would thermally decompose to form unneeded products. At the furnace exit, the main tube is connected to an isolation unit where the powder products are collected in tubes constructed of coarse-porosity (P8) filter paper.

Figure 1. Schematic of apparatus used for synthesis of molybdenum sulfide by vapor-phase reduction of molybdenum carbonyl.

Figure 2. Detail of injector tube cooled by water and argon as used in the apparatus of Figure 1.

Catalytic Reaction Apparatus. The reactor system is shown in Figure 3. The system is extensively controlled by a personal computer (PC), using the commercial software package InTouch by Wonderware. Almost all operating conditions are set directly from the PC, the one exception being the reactor pressure, which must be set manually. Data are logged by the PC at operator-determined intervals. The unit is designed to operate from atmospheric pressure up to 1500psig, and at temperatures up to 500°C.

Figure 3. Schematic of apparatus for catalytic reactions. SV, sample valve; MFC, mass flow controller; P, pressure gauge; T, thermocouple; B, back-pressure regulator.

The unit has four lines for gas feed, each independently controlled by a Brooks mass-flow controller, and one line for a liquid feed, using a HPLC pump. (The liquid-feed line was not used in this work.) The reactor is a stainless-steel tube of nominal outer diameter 13mm (0.5 in.) and nominal length 0.6m, placed in a 0.45m (18 in.) single-zone furnace from Applied Test Systems. Typically, 0.5g of catalyst and 3g of crushed quartz are mixed together and placed in the center of the reactor with pyrex beads upstream and downstream of the catalyst-quartz mixture. The product stream is sampled immediately downstream of the reactor using a Valco 6-port gas-sampling valve at the pressure of the reactor and at a minimum temperature of 250 C. Analysis of the products is accomplished on-line by a Hewlett-Packard 5890 gas chromatograph (GC) using two columns and two detectors in parallel. The GC is controlled (using HP Chemstation software) by the same PC in a multitasking MS Windows environment. In the GC, the flow is split between two columns: a HayeSep-DB packed column, 9m x 3.1mm (30ft x 1/8in), and a J&W DBWax capillary column, 20m x 0.1mm ID. The oven temperature for both

columns is programmed from 40 to 230 C. The packed column is connected to a thermal conductivity detector (TCD) which provides quantitative analysis for N₂ (an internal standard) as well as CO, CO₂, and H₂O; H₂ is separated but cannot be measured satisfactorily. The capillary column is connected to a flame-ionization detector (FID) and separates all of the C₁-C₅ alcohols, and separates the C₁-C₆ hydrocarbons as a single peak. The reactor effluent that is not passed through the GC is separated by phase. The liquid phase is collected and the vapor phase is vented after passing through an H₂S scrubber.

The entire unit is located in a walk-in hood. The PC monitors alarms for CO and H₂S, and for flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, reactor pressure, compressed-air supply, and electric power. The unit automatically shuts down in the event of hood failure, fire, power- or air-supply failure, CO or H₂S leak detection, or if gas flows or reactor temperature exceed pre-set operating ranges.

Chemicals. The molybdenum hexacarbonyl, Mo(CO)₆, was obtained from Strem Chemical Company and was purified by sublimation prior to use. H₂S for catalyst synthesis was obtained from Matheson Gas Products and was used as received. Blended gases of 4% N₂ in CO and 10% H₂S in H₂ for use in the catalytic pretreatment and reaction were also obtained from Matheson and were also used as received. Other gases were Airco products obtained from West Virginia Welding Supply Company. A commercially available molybdenum sulfide (99% MoS₂) was obtained from Aldrich Chemical Company and used in a few runs for comparison purposes.

Sulfide Synthesis and Characterization. In a typical preparative procedure, 3g Mo(CO)₆ in a quartz boat was added to the materials synthesis unit shown in Figure 1 at ambient temperature under flowing inert gas. The isolation unit for product collection unit was then connected to the main tube, and the entire system was purged for 30min. At this point, the flow of H₂S was initiated, and continued for 15-20 min. After the flow of H₂S was stopped, the main tube was heated under a flow of 800-1000 ml/min of inert gas to the desired temperature. At this point, the flow of H₂S was re-started, the water-cooled injection tube was maintained at 85°C with a recirculating water bath, and the tube containing the Mo(CO)₆ was heated to 98°C (external temperature) with a heating tape. The reaction was completed after about 2h when all of the Mo(CO)₆ had sublimed. The products were collected on P8 coarse-porosity filter paper. Since none of the molybdenum sulfides appeared to be air sensitive, the product was isolated and analyzed in air. A typical yield of product, based on MoS₂, was 90%. Lost material either passed through the filter or deposited on reactor walls.

For characterization studies, the material was used as synthesized. Characterization included N₂ BET surface area measurement, x-ray powder diffraction (XRD) for phase identification, and sulfur composition by combustion analysis. Nitrogen adsorption surface areas were measured with a Coulter Omnisorp 360 instrument, x-ray powder diffraction studies were carried out on a Phillips PW 1800 diffractometer, while sulfur was analyzed with a Leco SC-432DR instrument. Many of these and other measurements have been reported earlier (Close *et al.*, 1995) and will be only briefly described here.

For use as a catalyst in the CO hydrogenation unit, the material was promoted by alkali metals as follows. The acetate salt of the alkali metal and 3ml of methanol were added to nominally 500mg of the sulfide material. The mixture was allowed to dry in air at room temperature. The mixed powder was pressed into a pellet at 4000psi and broken into smaller fragments. The size range 20-40 mesh was used in the catalytic evaluations.

Physically mixing the fine-particle molybdenum sulfide with silica caused the molybdenum powder to disappear into the silica. This “supported” catalyst (more correctly, “diluted” catalyst) was promoted by the following procedure. The acetate was added to nominally 125mg of the sulfide material. This was followed by the addition of 400mg of silica (of surface area 144m²/g) and 3ml of methanol. Mixing (grinding), drying, and pressing steps followed as above.

Catalytic Reaction. Pretreatment of the catalyst consisted of temperature-programmed sulfidation followed by hydrogen purging. During the presulfiding, a mixture of 10% H₂S in H₂ was used while the temperature was increased linearly from 200-400°C at a steady rate of 10°C/h, and then held at 400°C for 1h. This was followed by purging in H₂ while the temperature was lowered to 200°C. This pretreatment follows the general procedure used by Duchet *et al.* (1983) for carbon-supported hydrodesulfurization catalysts, except that a slower heating rate was used in the present case. After pretreatment, the system was pressurized to 750psig and the gas flows adjusted to the desired values. Typical values were 25sccm H₂ and 25sccm CO.

The screening reactions reported here were carried out as follows. In all cases, the operating pressure was 750psig. Starting with a reactor temperature of 200°C, the temperature was increased linearly at a steady rate of 10°C/h until the reactor temperature was 400°C. The temperature was then decreased, also at a steady rate of 10°C/h, until the reactor temperature was once again 200°C. The reaction products were typically sampled every 2h and were analyzed by the GC.

Alcohol products in the GC analysis were identified by matching retention times of known standards. Alcohols with up to 4 carbons were identified this way. Linear or methyl-branched alcohols were the predominant products. Hydrocarbons with up to 6 carbons eluted together as the first peak off the GC column. Hydrocarbons with 8 or more carbons were mixed with the alcohol peaks on the GC trace. Any GC peak that was not positively identified as an alcohol was assumed to be a hydrocarbon. This assumption will bias catalytic screening data toward unwanted hydrocarbon products, making conservative the reported rates of alcohol formation.

RESULTS AND DISCUSSION

Characterization: Tables 1 and 2 summarize the characterization of the sulfides prepared by continuous-flow vapor-phase decomposition of molybdenum hexacarbonyl, in terms of the furnace temperature. The other parameters for the synthesis are kept at the “standard” values noted earlier: the temperature of the Mo(CO)₆ reservoir, T_{Mo}, at 98°C; the water jacket temperature, T_w, at 85°C, the flow rate of Ar in the innermost (and outermost) tube of the injector, V_i (and V_o), at 220 (and 700) sccm/min.; and the H₂S flow rate, V_{H₂S}, at 11 sccm/min.

From Table 1, the sample prepared at 300°C shows a low yield of recovered product, a low surface area, and a poorly crystalline structure. However, the yield of the material increases monotonically with increasing furnace temperature. As summarized in Table 1, the materials prepared at lower temperatures have XRD lines that are characterized by broad bands. For furnace temperatures above 500°C, however, lines of MoS₂ and perhaps S are notable. The surface area measurements of Table 1 indicate that this parameter also increases monotonically with furnace temperature until 500°C. Between 500-700°C, the surface area is essentially

constant. However, at higher furnace temperatures, the surface-area values actually decrease. The amount of sulfur in these materials increases with increasing furnace temperature. At 300 and 400°C, the samples are sulfur-deficient, suggesting that oxygen and/or carbon from the Mo(CO)₆ is present. Between 500-600°C, the samples are stoichiometric, within error bounds. (The stoichiometric amount of sulfur in MoS₂ corresponds to 40.06wt%.) Samples produced above 500°C show excess sulfur, possibly as elemental S from the thermal decomposition of H₂S.

TABLE 1. EFFECT OF FURNACE TEMPERATURE ON PROPERTIES OF SULFIDE.

Other parameters of synthesis apparatus are at “standard” conditions: temperature of Mo(CO)₆ reservoir = 98°C, water jacket temperature = 85°C, Ar flow in inner (outer) tube of injector = 220 (700) sccm/min., H₂S flow rate = 11 sccm/min.

T _f [°C]	YIELD	XRD RESULTS (a)	SURFACE AREA [m ² /g]	SULFUR CONTENT [%]	SAMPLE #
300	26.7	5.4	21.4	22.6	2MRC128A
400	45.0	5.6	47.3	22.2	2MRC129A
500	82.7	3.7	76.5	37.9	2MRC115A
600	88.6	2.6	75.4	42.6	2MRC116A
700	95.0	2.1	78.0	46.0	2MRC116C
800	94.6	1.8	72.5	45.6	2MRC118A
900	98.2	1.5	66.2	46.0	2MRC119A

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

The decrease in surface area with increasing furnace temperature (above 700°C, at least) can be understood on the basis of faster grain growth by annealing, and this is consistent with the XRD data as well. However, the increase in surface area with increasing furnace temperature (below 500°C at least) reverses this trend. This anomaly can perhaps be explained by a crystallographic phase modification, from an amorphous material with composition and short-range order corresponding to MoS₂ (at the lowest furnace temperature) to crystalline MoS₂

(above 500°C). This interpretation is also consistent with XPS data on related samples as described by Close *et al.* (1995).

Accordingly, it is reasonable to believe that the material formed at the lowest furnace temperature is an amorphous material with short-range order corresponding to a reduced molybdenum sulfide phase. At higher temperatures, the more crystalline MoS₂ material is formed. At very high furnace temperatures, the material contains crystalline MoS₂ as well as elemental S formed by the decomposition of the H₂S.

The effects of some of the other process variables are summarized in Tables 2 and 3. Increasing the temperature, T_{Mo}, of the molybdenum carbonyl reservoir increases the concentration of molybdenum compound in the vapor phase in the furnace. Hence, larger sizes may be expected. Table 2 shows that the surface area correspondingly decreases but the XRD peaks are somewhat broader, indicating less crystallinity. Increasing the flow rate of inert argon over the reservoir and into the innermost tube of the injector provides less time in the furnace (increases the flux) and may decrease the concentration of molybdenum, if conditions are not in thermodynamic equilibrium in the reservoir. Table 3 shows that the surface area of the product decreases somewhat, but the crystallinity increases.

TABLE 2. EFFECT OF CARBONYL RESERVOIR TEMPERATURE ON PROPERTIES OF SULFIDE.

Other parameters of synthesis apparatus are at “standard” conditions: furnace temperature = 500°C, water jacket temperature = 85°C, Ar flow in inner (outer) tube of injector = 220 (700) sccm/min., H₂S flow rate = 11 sccm/min.

T _{Mo} [°C]	YIELD	XRD RESULTS (a)	SURFACE AREA [m ² /g]	SULFUR CONTENT [%]	SAMPLE #
93	82.8	3.2	95.1	41.3	2MRC113A
98	82.7	3.7	76.5	37.9	2MRC115A
104	82.8	5.7	55.4	32.7	2MRC113B

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

TABLE 3. EFFECT OF CARRIER GAS FLOW ON PROPERTIES OF SULFIDE.

Other parameters of synthesis apparatus are at “standard” conditions: furnace temperature = 500°C, temperature of Mo(CO)₆ reservoir = 98°C, water jacket temperature = 85°C, Ar flow in outer tube of injector = 700 sccm/min., H₂S flow rate = 11 sccm/min.

V _i [sccm/min]	YIELD	XRD RESULTS (a)	SURFACE AREA [m ² /g]	SULFUR CONTENT [%]	SAMPLE #
220	82.7	3.7	76.5	37.9	2MRC115A
250	75.5	3.5	64.0	34.1	2MRC115C

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

Catalytic Reactions with Synthesis Gas: The discussion above indicates that intermediate values of the furnace temperature and the cooling rates may represent an optimum flux of molybdenum for synthesis, and an optimum material for a catalyst. Hence the bulk of the reactions of synthesis gas over these materials or their derivatives as catalysts were carried out with the sulfide prepared at a furnace (synthesis) temperature of around 500°C. Most of the catalytic reactions reported below were carried out in the form of temperature-ramped screening tests using synthesis gas with a H₂/CO ratio of around unity and a gas-hourly space velocity of 6 m³(STP)/kg/h. The (reaction) temperatures were between 200-400°C. In some cases, the temperature cycle was repeated. In every repeat run, the second cycle most nearly reproduced the data obtained from the decreasing-temperature leg of the first cycle.

Figure 4(a) shows a baseline screening run for an unpromoted MoS₂ catalyst, *i.e.*, with no dopants added. The catalyst was made at 500°C with an older-style injector under conditions similar to those used to produce sample 2MRC115A. The space-time yield (STY) of hydrocarbons is excessive. The selectivity to C₂-to-C₄ alcohols is vanishingly small. These results illustrate that unpromoted MoS₂ is not a suitable catalyst for the synthesis of higher alcohols, consistent with the results of Youchang *et al.* (1986).

A similar screening run was carried out using a commercially available sample of molybdenum sulfide. The results can be seen in Figure 4(b). Note the change in scale compared to Figure 4(a). The commercially available molybdenum sulfide shows a smaller production rate of hydrocarbons, and a greater selectivity to C₁-to-C₄ alcohols.

Figure 4.(a) Results of baseline screening run on undoped molybdenum sulfide synthesized by VPR at the “standard” conditions ($T_f = 500^\circ\text{C}$ and other conditions of Table I). Reaction conditions: 0.48g catalyst, $P = 750\text{psig}$, $\text{GHSV} = 6000\text{ l/kg/h}$, $\text{H}_2/\text{CO} = 1$. Upward-pointing and downward-pointing triangles are the data for the temperature-increasing and temperature-decreasing legs respectively. Filled and open symbols refer to alcohols and hydrocarbons respectively.(b) Results of baseline screening run on commercially available molybdenum sulfide. Symbols and reaction conditions are as in (a) except that 0.50g catalyst was used.

Figure 5 illustrates the beneficial effect of alkali promotion. The sulfide was synthesized at 500°C , as was the catalyst used in Figure 4(a), but now potassium has been added such that $\text{K/Mo} = 0.7$. At intermediate temperatures, the STY of C₁-to-C₄ alcohols greatly exceeds that of hydrocarbons. Further, selectivities to C₂-to-C₄ alcohols are appreciable. Qualitatively similar improvements upon alkali promotion were found when using the commercially available molybdenum sulfide in a screening run. Similar effects have been reported by other workers using other molybdenum sulfide catalyst preparations (Youchang *et al.*, 1986, Murchison *et al.*, 1988).

Figure 5. Results when the molybdenum sulfide of Figure 4a is doped with potassium ($K/Mo = 0.7$). Reaction conditions are as in Figure 4a except that the weight of catalyst used is 0.53g. Symbols are as in Figure 4a.

Figure 5 exhibits the four features typical of the temperature-dependence of the catalytic performance of alkali-doped molybdenum sulfides prepared in this fashion -- a monotonic increase in the STY of hydrocarbons with temperature (also seen in Figures 4a and 4b); a

maximum for the STY of C_1 -to- C_4 alcohols; a maximum (corresponding to a higher temperature) for the CO_2 -free selectivity towards C_2 -to- C_4 alcohols; and an improvement in performance with respect to these three parameters after the catalyst has been run at $400^\circ C$. It is worth noting that, while the molybdenum sulfide has already been exposed to $400^\circ C$ during pretreatment with 10% H_2S in H_2 , it still changes at $400^\circ C$ under reaction conditions.

Figure 6 shows the product distribution of alcohols measured under decreasing temperature conditions for the screening run illustrated in Figure 5. The effect of temperature on product distribution shows that the (CO_2 -free) selectivity to methanol monotonically decreases with increasing temperature, while that to the hydrocarbons monotonically increases. The selectivity to C_2 -to- C_4 alcohols passes through a maximum around $350^\circ C$ (as also shown in Figure 5). Among the higher alcohols, it can be seen that ethanol comprises the largest fraction, in the temperature range of interest. The amount of ethanol in the alcohol fraction passes through a maximum around $370^\circ C$. The maximum point corresponds to the point of steepest rise for the propanol fraction, while butanol is smallest but increasing. Figure 6 is consistent with a sequential formation of higher alcohols, with methanol converting to ethanol and thence to propanol and butanol, in turn, as noted by Santiesteban *et al.* (1988) and others.

Figure 6. Selectivities of the K-doped molybdenum sulfide catalyst of Figure 5.

The effect of the nature of the alkali dopant is shown in Figure 7, where we compare doping with K, Rb and Cs, each to a molar ratio of 0.7, as before. The molybdenum sulfide was prepared at 500°C, as before. The same qualitative features are found for each dopant. The Cs-doped material has the lowest STY of C₁-to-C₄ alcohols, and the lowest selectivity to C₂-to-C₄ alcohols, and is also least affected by reaction at 400°C. The K-doped material has the highest selectivity to C₂-to-C₄ alcohols, but the K- and the Rb-doped materials are virtually indistinguishable in terms of their total alcohol STY's at all temperatures considered. The performances of both the K- and the Rb-doped material improve appreciably after reaction at the highest temperature. There are no appreciable changes in the optimal temperatures for formation rate and for selectivity with changes in the alkali metal after the high-temperature reaction.

Figure 7. Catalytic performances of the molybdenum sulfide catalyst of Figure 4a when doped with various alkali metals. (Alkali/Mo = 0.7). Symbols used for increasing-temperature and decreasing-temperature legs respectively: K-doped, open upward triangle, open downward triangle; Rb-doped, I, D; Cs-doped, filled upward triangle, filled downward triangle. Amounts of catalysts used: K-doped, 0.53g; Rb-doped, 0.51g; Cs-doped, 0.51g. Other reaction conditions are as in Figure 4a.

Figure 8, when compared with Figure 7, shows the effect of changing the concentration of the alkali dopant. At the lower value of the Cs/Mo ratio (0.22, Figure 8), there are marked and favorable changes in the STY of C_1 -to- C_4 alcohols (increases), the hydrocarbon STY (decreases), and the values of these parameters after reaction at the highest temperatures. However, the selectivity to C_2 -to- C_4 alcohols is not significantly affected, and the optimum temperature for selectivity appears to decrease, approaching the optimum temperature for the alcohol STY. The promoter level of 0.22 was recommended by Klier *et al.* (1988b) as the optimum value for Cs promotion. The improved performance at this ratio is confirmed by this study.

Figure 8. Catalytic performance of the alkali-doped molybdenum sulfide when Cs/Mo = 0.22. Symbols and reaction conditions are as in Figure 4a. Amount of catalyst used is 0.4g.

It is worth comparing Figure 8 with Figure 9, which is similar except that the sulfide was synthesized at a furnace temperature (T_f) of 400°C. From Table 1, this material has a smaller surface area and a less-crystalline structure than the sulfide in Figure 8, for which $T_f = 500^\circ\text{C}$. However, there is relatively little difference between the two catalysts, except that Figure 8 exhibits perhaps a somewhat greater STY of C_1 -to- C_4 alcohols. However, the selectivity towards C_2 - C_4 alcohols is similar, implying perhaps a somewhat greater production of methanol.

Figure 9. Performance of Cs-doped catalyst similar to that in Figure 8, except that the molybdenum sulfide was synthesized at a furnace temperature, T_f of 400°C (Sample 2MRC129A in Table I).

Analogously, Figure 10 can be compared with Figure 5 for the case of the K-doped catalysts. The sulfide of Figure 10 was synthesized at $T_f = 600^\circ\text{C}$, and has a better-developed

crystalline structure but approximately the same surface area as that of Figure 5 (for which $T_f = 500^\circ\text{C}$). The maximum selectivity towards $\text{C}_2 - \text{C}_4$ alcohols and the maximum STY of C_1 -to- C_4 alcohols is greater in Figure 5. Further, the optimum temperatures for these two parameters are greater in Figure 10 than in Figure 5. Hence, there would appear to be a slight incentive towards using the sulfide prepared at $T_f = 500^\circ\text{C}$ as the basis of the catalyst for the synthesis of higher alcohols.

Figure 10. Performance of K-doped catalyst similar to that in Figure 5 except that the molybdenum sulfide was synthesized at a furnace temperature, T_f , of 600°C .

Figure 11 illustrates the effect of introducing the silica diluent to a K-doped catalyst. Comparing these curves with those of Figure 5, we note decreases in the maximum STY of C_1 -to- C_4 alcohols (from 200 to 120 g/h/kg catalyst) and the corresponding hydrocarbon STY (from 40 to 20 g/h/kg catalyst), and a sharp decrease in the selectivity of $\text{C}_2 - \text{C}_4$ alcohols (from 47 to 20

33%). The decreases in the STYs must take into consideration that the mass of Mo per mass of catalyst has decreased in the diluted catalyst, from a loading of 41.9% Mo in Figure 5 to 13.6% Mo in Figure 11. On a molybdenum basis, using the silica results in an increase in the maximum alcohol STY from 477 to 882 g/h/kg Mo, but also results in an increase in the corresponding hydrocarbon STY from 95 to 147 g/h/kg Mo. In this regard, it should be pointed out that the sulfides used for the two catalysts are not identical: that for the unsupported catalyst corresponded to a synthesis T_f of 500°C, while that for the diluted catalyst corresponded to a synthesis T_f of 400°C. However, considering that the results of Figure 8 and 9 were not markedly different, it would appear that the changes noted between Figures 5 and 11 can be ascribed more to the introduction of the silica than to the slightly different sulfide material used.

Figure 11. Performance of K-doped catalyst essentially similar to that in Figure 5 after dilution with silica. Symbols as in Figure 4a.

Other synthesis parameters exhibit less of an effect on the catalytic properties than does the furnace temperature, T_f . For example, consider the role of the Mo reservoir in Figure 1. Samples 2MRC113A and 2MRC113B described in Table 2 were doped with potassium ($K/Mo = 1$) and diluted with silica to correspond to a loading of 25.5% Mo. Runs using these materials as catalysts yielded virtually identical results, with a maximum STY of C_1 -to- C_4 alcohols of 160g/h/kg catalyst (at 320°C), a corresponding hydrocarbon STY of 20g/h/kg, and a maximum selectivity to $C_2 - C_4$ alcohols of 40% (at 350°C).

In summary, the results indicate that molybdenum sulfide prepared by vapor-phase reaction at a furnace temperature of 500 C (and other standard conditions of Table 1) and promoted by an alkali metal to a value of the alkali/Mo ratio of 0.7 is a suitable catalyst for the synthesis of higher alcohols. This catalyst was considered in Figures 5-7.

SUMMARY AND CONCLUSIONS

Vapor-phase synthesis yields molybdenum sulfide materials with consistent structures and in sufficient yields to be suitable for the production of catalysts for higher-alcohol synthesis. These materials have been characterized by XRD, elemental analysis and BET surface area, and show distinct trends which can be correlated with the parameters of the synthesis process used. While the molybdenum sulfides themselves are inactive for the formation of higher alcohols, doping these sulfides with alkali results in materials which can be used for this purpose.

These materials, both unsupported as well as diluted with silica, have been used in a plug-flow microreactor operated in a screening mode, *i.e.*, by increasing the temperature gradually from 200°C to 400°C and back again to 200°C, with synthesis gas having a H_2/CO ratio of unity. In all cases, the main alcohols formed are straight-chain compounds, containing from one to four carbon atoms, and with the -OH group at a terminal carbon atom. Methanol is formed in the greatest amounts at low temperatures, while ethanol is formed and passes through a maximum at intermediate temperatures; propanol and butanol increase monotonically with temperature in the range considered here.

Changing the nature of the sulfide in the catalyst leads to at best small changes in the catalytic performance. Using a furnace temperature of 500°C in the synthesis procedure appears to result in an acceptable material.

The alkali metals used, K, Rb and Cs, all appear to have similar promoting effects. At an alkali/Mo ratio of 0.7, the performances of K and Rb are superior to those of Cs. For Cs, the performance can be improved by decreasing the ratio from 0.7 to 0.22.

Maxima with respect to temperature are observed both for the space-time yields (STYs, amounts/time/mass catalyst) of C_1 -to- C_4 alcohols and for selectivity towards $C_2 - C_4$ alcohols. The optimum temperature for selectivity is generally higher than that for the STY. Hence, by varying the temperature, and the type and amount of the alkali metal, optimum conditions for the STY or selectivity can be achieved.

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Chapter 4

HIGHER ALCOHOLS FROM SYNTHESIS GAS USING CARBON-SUPPORTED DOPED MOLYBDENUM-BASED CATALYSTS

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ABSTRACT

A series of carbon-supported molybdenum-based catalysts was prepared by incipient wetness impregnation. The materials, when promoted with potassium and additionally with cobalt, were screened for the selective production of mixed higher-molecular-weight alcohols from syngas. The effects of the catalyst preparation parameters (Mo precursor, Mo loading, doping levels of K and Co, and calcination) and of the reaction conditions (temperature, space velocity) were studied. The screening procedure consisted of ramping the temperature steadily from 200 C to 400 C and back again. Adding K results in a maximum in the space-time yield (STY) of total alcohols and the ratio of higher alcohols to methanol. Increasing the reaction temperature results in a monotonic increase in the STY of hydrocarbons, a monotonic decrease in the selectivity toward alcohols and a maximum in the STY of alcohols. Increasing the space velocity increases the STY and selectivity to alcohols while decreasing the STY of hydrocarbons. Increasing the space velocity also decreases the higher alcohol fraction in the alcohol products.

INTRODUCTION

Over the last decade or so, the synthesis of mixed alcohols has drawn considerable interest due to the increasing demand for octane boosters. The incentive stems from the phasing out of lead from the gasoline pool by legislation and the reduction of volatile compounds. Higher alcohols (ethanol and those of higher molecular weight) are preferable to methanol because of their lower volatility and higher solubility in hydrocarbons.

It is widely recognized that higher alcohols together with methanol (MeOH) can be produced from syngas, a mixture of carbon monoxide and hydrogen, by appropriate modification of MeOH-synthesis catalysts and the reaction conditions^{1,2}. Italian researchers³⁻⁷ have worked extensively with Cu- and Zn-based oxide catalysts, especially those with spinel-like structures, although their performance for alcohol synthesis has not been so good. The Lehigh group⁸⁻¹¹ has emphasized the direct synthesis of isobutanol over Cu-based catalysts. These researchers have found that Cs doping significantly

enhances the selectivity and productivity to isobutanol, and have studied the mechanisms and kinetics of alcohol formation over these catalysts.

Other catalyst types have also been used for the synthesis of higher alcohols. In the 1980s, Rh- and Ru-based catalysts have been explored^{12,13} for the synthesis of higher oxygenates. Classical Fischer-Tropsch (F-T) catalysts have also been modified, by addition of alkali or by nitridation, to improve the selectivity toward alcohols¹⁴. The Institut Francais du Petrole has claimed that mixtures of light alcohols could be produced over a series of catalysts consisting of MeOH synthesis catalysts and F-T catalysts¹⁵.

The final category of catalysts for the synthesis of higher alcohols is promoted Mo-based materials, which is the focus of the present work. Research groups at Dow Chemical^{16,17} and Union Carbide¹⁸ discovered that molybdenum sulfide catalysts promoted by cobalt or/and alkali compounds are active for production of C₁-C₅ alcohols. Xie *et al.*¹⁹ have reported the effect of pressure on alcohol synthesis over K₂CO₃-promoted MoS₂ catalysts prepared by thermolysis of ammonium tetrathiomolybdate. The Lehigh research group has worked extensively with alkali-doped unsupported MoS₂ catalysts as well, with special emphasis on the effect of promoters²⁰. Tatsumi *et al.*²¹ reported the effect of potassium promoter on alcohol synthesis over reduced oxide-supported molybdenum catalysts. The role of the alkali promoter has also been studied by Jiang *et al.*²² and by Lee *et al.*²³.

Most of the previous work on molybdenum-based catalysts used for alcohol synthesis deals with unsupported materials with alkali promoters. It is reasonable to expect that catalytic performance on supported catalysts would be different from that on unsupported ones. It is also expected that the catalytic performance depends, to a certain extent, on the support used. Carbon-supported catalysts have been claimed to have some potential advantages over oxide-supported ones, such as lower tendencies of carbon deposition²⁴ and less dehydration. In the present work, we prepared a series of activated carbon-supported molybdenum-based catalysts by incipient wetness impregnation. The materials were then used as catalysts for synthesis of mixed alcohols. The effects of catalyst preparation parameters and reaction conditions on the catalytic performance were studied using a temperature-scanning screening technique as described below.

EXPERIMENTAL

Chemicals

The activated carbon used for the catalyst support was obtained from Aldrich Chemical Company, Inc. The activated carbon has a granule size of 20 to 40 mesh, a total BET surface area of 660 m²/g and a total pore volume of 1.00 ml/g. To remove soluble impurities, the activated carbon was treated in boiling water for 1h. This was followed by filtering and drying in air at 100°C for 2h.

Ammonium heptamolybdate [AHM, (NH₄)₆Mo₇O₂₄·4H₂O], potassium carbonate [K₂CO₃] and cobalt nitrate [Co(NO₃)₂·6H₂O] were obtained from Fisher Scientific and were used as received. Oxalic acid [H₂C₂O₄] was from Aldrich and was also used as received. All gases used for catalyst pretreatment and testing were obtained from Matheson; except for CO, all gases were used as received. The CO was passed through an activated carbon scrubber to remove metal carbonyls.

Preparation of Catalysts

The incipient wetness technique was used to prepare carbon-supported Mo-based catalysts. The “standard” source of Mo was AHM. Generally, Mo was impregnated first onto the carbon support, followed by Co (if applicable), with the alkali (K) being the last one to be impregnated. Each impregnation step was usually followed by drying, first in air for 4h at room temperature, and then overnight at about 100°C. Multiple impregnation steps for one component were needed for the preparation of catalysts with relatively high metal loadings. In these cases, the drying steps were not carried out between each impregnation step.

For comparison, other procedures were also employed for the preparation of the catalyst. In one, a different impregnation sequence was used: K was impregnated first onto the C support, followed by Mo and Co. In a second alternative procedure, molybdenum oxalate $[\text{Mo}(\text{C}_2\text{O}_4)_3]$ was used as the Mo precursor instead of ammonium heptamolybdate. The molybdenum oxalate was made by reacting ammonium heptamolybdate with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). In a third alternative, after the impregnation steps were completed, the material was calcined in flowing N_2 at 500 C for 2h. In this procedure, the Mo source was also the oxalate. The final alternative was the use of a co-impregnation procedure: the three components (Mo, Co and K) were added simultaneously onto the support using a mixed solution. Multiple impregnation steps were used in this procedure.

Table 1 lists all the catalysts used in this study. Note that the sequence of elements in the catalyst designation code represents the sequence of impregnation, with the exception of the co-impregnated catalyst

Table 1 List of Catalysts Used in This Study

Catalyst No.	Designation Code	Mo Precursor	Mo Loading (wt%)	K Precursor	K/Mo Molar ratio	Co/Mo Molar ratio	Calcination
I	Mo/C	AHM	18	N/A	N/A	N/A	NO
II	Mo-K/C	AHM	18	K ₂ CO ₃	0.3	N/A	NO
III	Mo-K/C	AHM	18	K ₂ CO ₃	0.5	N/A	NO
IV	Mo-K/C	AHM	18	K ₂ CO ₃	0.7	N/A	NO
V	Mo-K/C	AHM	18	K ₂ CO ₃	1.0	N/A	NO
VI	Mo-K/C	AHM	18	K ₂ CO ₃	1.3	N/A	NO
VII	Mo-K/C	AHM	18	K ₂ CO ₃	3.0	N/A	NO
VIII	Mo-K/C	AHM	3	K ₂ CO ₃	1.0	N/A	NO
IX	Mo-K/C	AHM	6	K ₂ CO ₃	1.0	N/A	NO
X	Mo-Co-K/C	AHM	18	K ₂ CO ₃	1.3	0.34	NO
XI	K-Mo-Co/C	AHM	18	K ₂ CO ₃	1.3	0.34	NO

XII	Co-impregnated Mo-Co-K/C	AHM	18	K ₂ CO ₃	1.3	0.34	NO
XIII	Mo-Co-K/C	Mo(C ₂ O ₄) ₃	18	K ₂ CO ₃	1.3	0.34	NO
XIV	Mo-Co-K/C	Mo(C ₂ O ₄) ₃	18	K ₂ CO ₃	1.3	0.34	YES

AHM, Ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄·4H₂O

Catalytic Reaction

The reactor system is shown in Figure 1. Since the apparatus has been described elsewhere in detail ²⁵, only a brief description is provided here. The unit is designed to operate from atmospheric pressure to 1500psig, and at temperatures up to 500°C. Almost all operating conditions are set directly from a personal computer (PC), the one exception being the reactor pressure, which must be set manually. Data are logged by the PC at operator-determined intervals. The entire unit is located in a walk-in hood. The PC monitors alarms for CO and H₂S, and for flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, reactor pressure, compressed-air supply, and electric power. The unit automatically shuts down in the event of hood failure, fire, power- or air-supply failure, CO or H₂S leak detection, or if gas flows or reactor temperature exceed pre-set operating ranges.

Figure 1. Schematic of reactor system. B, back-pressure regulator; MFC, mass-flow controller; P, pressure gauge; SV, sample valve; T, thermocouple.

The unit has four lines for gas feed, each independently controlled, and one line for a liquid feed. (The liquid-feed line was not used in this work.) The reactor is a stainless-steel tube placed in a single-zone furnace. Typically, 0.5g of catalyst and 3g of crushed quartz are mixed together and placed in the center of the reactor, with pyrex beads upstream and downstream of the catalyst-quartz mixture. The product stream is sampled immediately downstream of the reactor at the pressure of the reactor and at a minimum temperature of 150°C. The products are analyzed on-line, using a gas chromatograph (GC) containing two columns and two detectors in parallel. The oven temperature for both columns is programmed from 40 to 240°C. The packed column is connected to a thermal conductivity detector (TCD) which provides quantitative analysis for N₂ (an internal standard) as well as CO, CO₂, and H₂O; H₂ is separated but cannot be measured satisfactorily. The capillary column is connected to a flame-ionization detector (FID) and separates all of the C₁-C₅ alcohols, and separates the C₁-C₆ hydrocarbons as a single peak. The reactor effluent that is not passed through the GC is separated by phase. The liquid phase is collected and the vapor phase is vented after passing through an H₂S scrubber.

Prior to reaction, the catalyst was first presulfided *in situ* in a flowing mixture of 10% H₂S in H₂ (50 cc/min for 0.5 g catalyst) at 400°C and atmospheric pressure for 1h, followed by purging in H₂ (50 cc/min) at the same temperature for 0.5h. After this pretreatment procedure, the temperature was lowered to about 190°C (slightly lower than the starting value of the temperature scan), and the system was then pressurized to the desired value, normally 750 psig. Finally, the gas flows were adjusted to the preset values, typically 25 cc(STP)/min for H₂ and 25 cc(STP)/min for CO. This corresponds to a gas-hourly space velocity of 6 m³(STP)/h/kg-cat.

The reactions were carried out in a temperature-ramping process as follows. The pressure was kept constant, usually 750 psig. The temperature was increased linearly from 200°C to 400°C at a steady rate of 10°C/h. After the temperature reached 400°C, it was then decreased at the same steady rate until it was 200°C once again. Some isothermal runs were also carried out. Here the temperature was raised rapidly to the required temperature and maintained at that value. In all cases, the reaction products were sampled every 2h and were analyzed by the GC.

RESULTS AND DISCUSSION

Screening of Catalysts

Preliminaries. During our screening runs, the reaction temperature was usually cycled from 200°C to 400°C, as described in the experimental section. In our previous study²⁵, for runs in which the temperature cycle was repeated, we found that the second cycle most nearly repeated the data obtained from the decreasing-temperature leg of the first cycle. It is therefore reasonable to believe that the decreasing-temperature leg of the first cycle accurately represents the temperature dependence of the catalytic performance. Therefore, only those data from the decreasing-temperature leg are reported and discussed in this paper.

The reactor tube packed with only Pyrex beads (*i.e.*, without any catalyst) was first tested, to determine the reactivity of the stainless steel reactor. From Figure 2, the CO conversion is vanishingly small. Also shown in Figure 2 are values of the space-time yield (STY) for the total hydrocarbons and the total alcohols separately as products. A (dummy) amount of 0.5 g of inert (catalyst) was used to calculate the values of the STYs; this allows a comparison with actual

catalytic runs, and also allows us to estimate errors for the calculation of the STYs for the actual catalytic runs.

Figure 2. Reactivity of the reactor tube packed with Pyrex beads. Reaction conditions: $P = 750$ psig, flow rate of H_2 and $CO = 25$ cc(STP)/min each.

Mo/C Catalyst The performance of the Mo/C catalyst (Catalyst I in Table 1) is shown in Figure 3. While the catalyst is clearly very active for CO hydrogenation, the predominant products are light hydrocarbons. Methanol and ethanol are the only two alcohol products observed, and they are present in very small amounts compared to the hydrocarbons. We return to this below. These observations are consistent with earlier results from our laboratory²⁵ and from other laboratories^{16, 18-20, 29} when unsupported MoS_2 was used.

Figure 3. Results of screening run on a Mo/C catalyst with Mo loading of 18% by weight. Reaction conditions: 0.51g catalyst, other conditions as in Figure 2. This corresponds to a GHSV of $6\text{m}^3/\text{h/kg-catalyst}$.

Mo-K/C Catalysts Figure 4 gives the catalytic performances of catalysts which have been doped with varying amounts of K. The catalysts labelled I through VII in Table 1 were used in this portion of the work. With increasing temperature, the following features are typical for all of the K loadings used: a monotonic increase in the overall CO conversion and in the STY of hydrocarbons, a maximum for the STY of total alcohols, a monotonic increase of CO_2 selectivity with temperature (except perhaps for K/Mo ratios of 0.5-0.7 at low temperatures), a monotonic decline in the CO_2 -free selectivity to total alcohols, and a maximum in the molar ratio of higher alcohols (ethanol and higher) to methanol. (Recall that the decreasing-temperature leg was used to obtain these data.) These results are consistent with those from other laboratories using sulfide catalysts²⁹ as well as oxide catalysts²⁶. It has been postulated that the activation energy for methanol synthesis is lower than that for the formation of hydrocarbons and higher alcohols.

Figure 4. Catalytic performances of Mo-K/C catalysts with different K/Mo molar ratios. The following parameters are reported: X_{CO} , the conversion of CO; Y_{HC} and Y_{alc} , space-time yields of hydrocarbon and total alcohol, respectively; S_{CO_2} and S_{Alc} , selectivities of CO_2 and total alcohols (CO_2 -free basis), respectively; and $C_{2+}OH/MeOH$, the molar ratio of higher alcohols to methanol. The different catalysts all have the same Mo loading, 18 wt%. Amounts of catalysts used: 0.51 g for catalysts with K/Mo molar ratio of 0 and 0.3; 0.50 g for the remaining catalysts. Other reaction conditions are the same as in Figure 2.

The catalytic performances for different K/Mo molar ratios are also compared in Figure 4. Obviously, K-doping causes dramatic changes in the catalytic performance. First, the overall CO conversion decreases significantly upon the first addition of K_2CO_3 into the catalyst (K/Mo =

0.3). Even if the activity is based on the amount of Mo in the catalyst, *i.e.*, if the “specific” activity is considered, the value still decreases. As the K/Mo ratio increases further, the overall CO conversion keeps decreasing, but proportionately not as much as for the initial addition of K.

Second, the STY of hydrocarbons shows a parallel decline, from about 900 g/h/kg-catalyst (K/Mo = 0) to around 300 g/h/kg-catalyst (for K/Mo = 0.3) at the highest temperature studied. Again, as the K/Mo ratio increases further, the STYs of hydrocarbons decrease further, but not as dramatically as for the initial addition.

Third, the formation of alcohols is greatly promoted by the K-doping. For the undoped catalyst, the STY of total alcohols is essentially zero, if the reactivity of the reactor itself is taken into account. However, for the catalyst with a K/Mo molar ratio of 0.3, the highest STY of total alcohols (at approximately 300°C) approaches 100 g/h/kg-catalyst. Further, the maximum in the STYs increases with increasing K/Mo, up to values of unity. At higher values, the maximum STY decreases with increasing K/Mo ratio. Finally, the location of the maximum STY seems to be more-or-less independent of K/Mo for values of the ratio less than or equal to unity. At higher values of K/Mo, the optimum temperature increases slightly, to about 320°C, but then appears to be unchanged, at least up to values of K/Mo = 3.

Fourth, the CO₂ molar selectivity increases slightly with the initial addition of K. The molar selectivity toward CO₂ increases further with increasing K/Mo molar ratio up to the value of unity. For dopant values greater than unity, the selectivity decreases with increasing K/Mo.

Finally, as can be seen from Figures 4f and 5, the addition of K₂CO₃ not only shifts the products towards higher alcohols, it also changes the distribution of alcohols. Figure 4f shows the ratio of higher alcohols to methanol as functions of T and K/Mo. At low (but non-zero) values of K/Mo, there is a sharp increase in the molar ratio of higher alcohols at lower temperatures, a maximum value of approximately 0.5 at around 300°C, and then a falling off. At increasing values of K/Mo, the low-temperature increase is attenuated, the maximum ratio increases, and it occurs at a higher temperature.

Some more insight into this behavior is obtained from Figure 5, in which are plotted the distributions of the individual alcohols for a few values of K/Mo. For the undoped catalyst of Figure 5a, as noted earlier, the absolute amounts of alcohols are low. In fact, only MeOH and EtOH can be detected at all, and the molar distribution of these is probably independent of temperature, within the expected error bars. For large values of K/Mo, of which Figure 5c (with K/Mo = 3) is an example, increasing the temperature leads to a generally monotonically decreasing distribution of MeOH, with successive maxima observed for EtOH, PrOH and BuOH in turn. However, for intermediate values of K/Mo, of which Figure 5b (with K/Mo = 1) is a typical example, a minimum in the methanol fraction is noted around 350°C.

Figure 5. Distribution of alcohols formed as functions of temperature over three of the Mo-K/C catalysts used for Figure 4. In all cases the Mo loading is 18 wt%. K/Mo values are: (a) 0; (b) 1.0; (c) 3.0.

It is worth discussing briefly the role of the alkali dopant. Alkali compounds are widely used as promoters in heterogeneous catalysis, particularly for CO hydrogenation. They have been reported either to increase the chain-growth probability or to promote the selective formation of oxygenates in CO hydrogenation. Various, sometimes controversial, explanations have been proposed for the observed effects^{27, 28}. Klier and co-workers²⁹ have studied the catalytic performances of CsOOCH-promoted MoS₂ catalysts, and suggest that the catalysts are bifunctional: MoS₂ dissociatively activates H₂, while the alkali component activates CO and decreases the availability of active hydrogen atoms.

For the present catalysts, bifunctionality can also explain the observed promotional effect of K₂CO₃ toward the formation of higher alcohols. With increasing K₂CO₃ levels, the number of CO-activating centers increases, thereby resulting in a greater rate of alcohol formation. When the concentration of K₂CO₃ exceeds a certain value (K/Mo = 1 in our case), the hydrogenation of the activated intermediates is depressed, due to the decreased availability of active hydrogen atoms, thereby leading to a drop in the STY of total alcohols. That is to say, the balance of the two opposite effects of K₂CO₃ doping determines the alcohol formation rate.

The decreasing rate of formation of hydrocarbon with the addition of K₂CO₃ may also be a result of the decreased availability of hydrogenation active centers. For the production of hydrocarbons, the availability of active hydrogen atoms plays a more important role, since the formation of hydrocarbons demands stronger hydrogenation centers. Therefore, it is not

surprising that the STY of hydrocarbons decreases monotonically with an increase in the K-doping level.

For classical iron Fischer-Tropsch catalysts, the CO₂ selectivity usually passes through a maximum with increasing alkali concentration³⁰. For alkali-promoted MoS₂ catalysts, no one (to our knowledge) has reported the effect of alkali doping on CO₂ selectivity. However, Tatsumi *et al.*³¹ report that CO₂ selectivity decreases with an increasing K/Mo molar ratio for mixed-alcohol synthesis over reduced Mo-based catalysts.

As mentioned earlier, alkali promoters act either to increase the chain-growth probability or to promote the formation of oxygenates. Lee *et al.*²³ claim that the two effects are mutually exclusive. But Jiang *et al.*²² report that alkali compounds not only promote the formation of alcohols, but also change the distribution of alcohol products. A maximum in the ratio of higher alcohols to methanol was usually observed with changing alkali concentration. It was also reported³² that the ratio of higher alcohols to methanol can be adjusted by introducing a sulfur-releasing substance in the feed gas. Our earlier work²⁵ on alkali-doped MoS₂ prepared by vapor-phase reaction yielded a product distribution consistent with Figure 5c. Such a product distribution can be attributed to a series progression of the formation of the higher alcohols. However, the existence of a minimum in methanol mole fraction at intermediate values of K/Mo (Figure 5b) is different from that observed earlier. Coupling the data of Figure 5 and 4c, we see that the minimum mole fraction of methanol is not due to an increasing STY of methanol at the highest temperatures. Rather, the methanol STY is decreasing, as are the STYs of the other individual alcohols. This leads us to believe that the increase in the methanol mole fraction is due to a decrease in the formation of higher alcohols from methanol under these conditions, and is not due to the existence of an additional pathway for methanol formation from CO and hydrogen. It should be noted that the catalysts used earlier²⁵ were unsupported, or supported on silica, while the catalysts of Figure 5 are supported on activated carbon.

The effect of loading on the performance of the Mo-K/C catalyst is shown in Figure 6. Here the catalysts are doped to the same value of the molar ratio K/Mo, equal to unity, and the amounts of both are increased. The catalysts used are labelled V, VIII and IX in Table 1. The overall CO conversion increases significantly with increasing loading, as seen in Figure 6a. This indicates an increase of the overall activity, and is apparently because of the increasing of the concentration of the active component (Mo). Moreover, the STYs of both total hydrocarbons and total alcohols increase with increasing Mo content.

Figure 6. Catalytic performances of Mo-K/C catalysts with different Mo loadings. Catalyst parameters are as defined in Figure 4. Each catalyst was doped with K to the same K/Mo molar ratio of unity. In each case, 0.50g of catalyst was used. Other reaction conditions are as in Figure 2.

Increasing the Mo loading also causes a slight increase in the CO₂ selectivity. In terms of selectivity toward total alcohols, changing the loading does not cause much difference, as shown in Figure 6e. Clearly, increasing the amount of Mo increases the formation of both hydrocarbons and alcohols in approximately equal amounts. However, increasing the Mo content enhances the relative formation of higher alcohols among the alcohol products, as indicated in Figure 6f. Figure 7 indicates that this change arises as a consequence of the decreasing mole fraction of methanol and the increasing (and no longer negligible) mole fractions of propanol and alcohols of even higher molecular weight.

Figure 7. Distribution of alcohols formed as functions of temperature over the Mo-K/C catalysts used for Figure 6. In all cases, K/Mo = 1. The Mo loadings are: (a) 3; (b) 6 (c) 18 wt %.

Mo-Co-K/C Catalysts Figure 8 compares the catalytic performance of a doubly promoted Mo-Co-K/C catalyst (Catalyst X in Table 1) with that of a similar catalyst but without Co-doping (Mo-K/C, Catalyst VI in Table 1). The addition of Co causes a decrease of the overall CO conversion and a decline of the hydrocarbon production rate. The Co causes a shift to the right (higher-temperature) side for the curve for the total alcohol STY, so that the STYs decrease at low temperatures but increase at high temperatures: the maximum STY increases, as does the temperature at which the maximum occurs. Also noted is a suppression of CO₂ formation. The selectivity to total alcohols is increased. However, the molar ratio of higher alcohols to methanol decreases. Figure 9 indicates that this decrease is due to a drop in the mole fraction of propanol and other higher-molecular-weight alcohols. Figure 9b also indicates that the presence of Co may remove, or at least diminish, the minimum in the methanol mole fraction at high temperatures.

Figure 8. Effect of Co doping on catalyst performance. Catalyst parameters are as defined in Figure 4. Both catalysts contain 18 wt% Mo and a molar ratio of K/Mo = 1.3; 0.50g catalyst was used for both catalysts. In addition, the Mo-Co-K/C catalyst is doped with Co to a Co/Mo molar ratio of 0.34. Other reaction conditions are as in Figure 2.

Figure 9. Distribution of alcohols formed as functions of temperature over the catalysts used for Figure 8. (a) Mo-K/C; (b) Mo-Co-K/C.

Stevens³³ disclosed that the preparation method of MoS₂ catalysts doubly promoted by K and Co may strongly affect the distribution of the alcohol products: co-precipitated Co/Mo sulfide catalysts favor the production of C₂ to C₅ alcohols, while an impregnated Co-MoS₂ catalyst favors the production of methanol. Further, Murchison *et al.*³⁴ reported that the addition of Co to an alkali-doped MoS₂ catalyst shifts the selectivity in favor of ethanol. It was postulated that Co promotes the homologation of methanol to form ethanol. Further, the alcohol composition is a strong function of conversion, with higher conversions coinciding with lower methanol contents. However, Murchison *et al.* provided little detail about the preparation of the catalyst. Our result confirm that the addition of Co enhances the formation of higher alcohols while depressing the production of hydrocarbons and CO₂. Further, the promotional effect of Co is consistent with the observations of Stevens³³.

It is clearly worth investigating the effect of preparation techniques for the present family of catalysts. Figure 10 summarizes the performances of catalysts X, XI and XII which were prepared using three different impregnation procedures: Mo first, K first, and co-impregnated, respectively. Note that the three catalysts have the same composition, 18 wt% Mo, K/Mo = 1.3, Co/Mo = 0.34.

Figure 10. Comparison of the catalytic performances of C-supported K- and Co-promoted catalysts prepared using different impregnation procedures. Catalyst parameters are as described in Figure 4. The three catalysts all contain 18 wt% Mo and have the same K/Mo molar ratio of 1.3 and the same Co/Mo molar ratio of 0.34. Amounts of catalysts used: 0.50g for the Mo-Co-K/C (molybdenum impregnated first) catalyst and for the K-Mo-Co/C (potassium impregnated first) catalyst; 0.51g for the co-impregnated catalyst. Other reaction conditions are as in Figure 2.

The impregnation sequence Mo-Co-K results in higher activities to both hydrocarbons and alcohols, and a lower CO₂ selectivity, than does sequence K-Mo-Co. For the co-impregnated catalyst, the overall activity and the activity for hydrocarbon formation are almost the same as those for impregnation sequence Mo-Co-K. But the co-impregnated catalyst exhibits a higher CO₂ selectivity, thus showing a lower selectivity toward total alcohol formation. In terms of the ratio of higher alcohols to methanol, the co-impregnated catalyst works best at low and medium temperatures. However, the Mo-Co-K sequence may be advantageous at higher temperatures. From Figure 11, the superior performance of the co-impregnated catalyst at the low temperatures can be ascribed to the diminution of the the methanol component, especially at low

temperatures, while the superior performance of the Mo-Co-K sequenced catalyst is due to the larger amounts of the butanol-plus components. The presence of the cobalt component appears to suppress the minimum in the methanol mole fraction, especially if impregnated last (Figure 11b); however, the co-impregnated catalyst (Figure 11c) exhibits this minimum.

Figure 11. Distribution of alcohols formed as functions of temperature over the catalysts used for Figure 10. (a) Mo-Co-K/C; (b) K-Mo-Co/C; (c) co-impregnated catalyst.

Figure 12 illustrates the effect of Mo precursor. From this figure, we note that the catalyst from the ammonium molybdate precursor (Catalyst X) gives a slightly better performance than does that from the oxalate precursor (Catalyst XIII). The distributions of the higher alcohols from these two catalysts are not shown as they are qualitatively similar.

Figure 12. Comparison of the catalytic performances of Mo-Co-K/C catalysts prepared from different Mo precursors. Catalyst parameters are as described in Figure 4. The two catalysts have the same composition: Mo loading of 18% by weight, K/Mo molar ratio of 1.3 and Co/Mo molar ratio of 0.34. The same amount of catalyst (0.50g) was used for the reactions. Other reaction conditions were the same as in Figure 2.

The effect of calcination (in N_2 at 500°C for 2h) on the catalytic performance is demonstrated in Figure 13, using Catalysts XIII and XIV. Calcination causes a slight increase in the overall CO conversion and an enhancement of hydrocarbon production, both more marked at high temperatures. The STY of total alcohols shifts to the left (lower-temperature) side: the maximum value of the STY is slightly increased, and the maximum occurs at a slightly lower temperature. Calcination decreases the CO_2 -free selectivity to total alcohols, and also decreases the ratio of higher alcohols to methanol. Figure 14 indicates that the decrease in the ratio is due to calcination increasing the methanol mole fraction at the expense of the mole fractions of propanol and higher alcohols. Figure 14 also indicates that calcination results in the re-

appearance, at high reaction temperatures, of the minimum in the methanol fraction that was removed by the addition of Co.

Figure 13. Effects of calcination on the performance of the Mo-Co-K/C catalyst. Catalytic parameters are described in Figure 4. The two catalysts have the same composition: Mo loading of 18% by weight, K/Mo molar ratio of 1.3 and Co/Mo molar ratio of 0.34. One catalyst is calcined in flowing N_2 at 500 C for 2 hours while the other is uncalcined. Amounts of catalysts used: 0.51g for the calcined catalyst and 0.50g for the uncalcined catalyst. Other reaction conditions are as in Figure 2.

Figure 14. Distribution of alcohols formed as functions of temperature over the Mo-Co-K/C catalysts used for Figure 13. (a) uncalcined catalyst; (b) calcined catalyst.

Isothermal Performance of a Mo-Co-K/C Catalyst

The Mo-Co-K/C catalyst performs better than Mo-K/C or Mo/C catalysts for higher-alcohol synthesis. Therefore, the best Mo-Co-K/C catalyst we have tested (Catalyst X in Table 1) was chosen for a series of isothermal runs. Our screening results showed that the catalyst had a maximum STY to total alcohols at temperatures around 350°C at a space velocity of 6m³ (STP) /h/kg-catalyst. Hence, the reaction was carried out isothermally at 350°C at space velocities of 6, 12, 18, and 21.6 m³(STP)/h/kg-catalyst. The results are plotted in Figure 15.

Figure 15. Isothermal performances of a Mo-Co-K/C catalyst at 350 C and 750 psig with increasing GHSV: (a) 6, (b) 12, (c) 18, (d) 21.6 m³/h/kg-catalyst. The corresponding flow rates of H₂ and CO are in units of cc(STP)/min. The catalyst contains 18 wt% Mo and has a K/Mo molar ratio of 1.3 and a Co/Mo molar ratio of 0.34; 0.51 g catalyst was used. Catalyst parameters are as described in Figure 4.

As shown in this figure, higher space velocities result in higher STY values for total alcohols, lower STY values for hydrocarbons, and lower overall CO conversions. In terms of selectivity, a higher space velocity gives a slightly lower CO₂ selectivity, a higher CO₂-free selectivity to alcohols, but a lower fraction of higher alcohols in alcohol products. Increasing the space velocity enhances the production of methanol, while suppressing the formation of hydrocarbons and higher alcohols. Since a higher space velocity is associated with a lower residence time, and a lower residence time results in a larger fraction of the primary product and

smaller fractions of secondary products, the above results confirm that methanol is a primary product while hydrocarbons and higher alcohols are secondary products. This conclusion is consistent with the theory²⁹ that higher alcohols are formed by a classical mechanism that proceeds *via* stepwise CO insertion in alkyl-metal center bonds and that hydrocarbons are produced by decomposition of alcohols.

The individual distributions of alcohols are depicted in Figure 16, as an Anderson-Schulz-Flory (ASF) plot. Clearly, the carbon-number distributions of alcohols over the Mo-Co-K/C catalyst follow the ASF distribution. Quantitatively, the ASF distribution can be written as:

$$M_n = p^{n-1} (1-p) \quad (1)$$

where M_n is the mole fraction of the product with carbon number of n , and p is the chain-growth probability. The values of p , calculated using the last data point for each space velocity, are shown in Figure 16, along with the corresponding values of the space velocity. The value of the chain-growth probability decreases with increasing space velocity. This is obviously consistent with the product distribution described earlier.

Figure 16. Anderson-Schulz-Flory plots for alcohol products at different GHSV values using the catalyst of Figure 15.

Effect of Sulfur in Feed

Two isothermal runs were carried out with the same Mo-Co-K/C catalyst to evaluate its performance in the presence of H_2S . In both cases, the reaction temperature was $350^\circ C$, a space velocity of $6 m^3/h/kg\text{-catalyst}$ was used, and the molar ratio of H_2/CO in the feed was 1. In one run, 13.5 ppm H_2S was introduced into the feed at the beginning of the reaction. These results are summarized in Figure 17. For the other run (Figure 18), the same level of impurity, 13.5 ppm H_2S , was introduced after a reaction time of 16h. The presence of H_2S at this level seems to have

no effect on the catalytic performance. This is consistent with the known sulfur resistance of molybdenum-sulfide-based catalysts.

Figure 17. Catalytic performance of the catalyst of Figure 15 in a feed containing H_2S . The sulfur impurity is introduced into the feed for the fresh catalyst and maintained for 65h. Reaction conditions are as in Figure 15 except that 0.50g catalyst is used. Catalyst parameters are as described in Figure 4.

Figure 18. Effect of sulfur on the performance of the catalyst of Figure 15. The H₂S-containing feed is now introduced after the catalyst has been on stream for 16 hours. Reaction conditions are as in Figure 17. No significant drop in catalyst performance is seen after the introduction of the sulfur impurity. Catalyst parameters are described in Figure 4.

CONCLUSION

The production of mixed alcohols from synthesis gas (CO and H₂) was investigated on a series of C-supported Mo-based catalysts. The screening results indicate that carbon-supported sulfided molybdenum promoted by K, optionally promoted by Co, is a suitable material for higher-alcohol synthesis. Calcination of the catalyst has relatively little effect, but is not particularly helpful. Preparation parameters, such as the type of Mo precursor, the Mo loading and the K doping level, affect the catalytic performance to different extents. The catalyst is resistant to sulfur in the feed.

Increasing the space velocity enhances the production of methanol while suppressing the formation of hydrocarbons and higher alcohols. The observations can be well explained by the bifunctionality of the catalyst and by a classical step-wise CO-insertion mechanism. Increasing the reaction temperature increases the selectivity toward hydrocarbons while decreasing the selectivity to alcohols. A maximum in the STY of total alcohols with the reaction temperature is observed for all catalysts tested. The distribution of the individual alcohol products is as follows:

increasing temperatures lead to a decreasing mole fraction of methanol, and progressive maxima in the mole fractions of higher alcohols. This, too, is consistent with a CO-insertion mechanism. However, at high temperatures, a minimum in the methanol mole fraction is sometimes noted, after which the methanol mole fraction increases with temperature. This implies a decrease in the insertion of CO. The minimum is observed for the case of the C-supported catalyst, small Mo loadings, small levels of K dopings, an absence of Co (or co-impregnation of Co with K and Mo), and if the catalyst is calcined.

The screening results indicate that the catalyst with K/Mo around unity, with Co/Mo around 0.34 is worthy of further study for this process. Typical reaction conditions are expected to be: temperatures around 350 C, pressures around 750 psi, CO/H₂ ratios around unity, and space velocities around 20 m³(STP)/h/kg-catalyst. In a separate work³⁵, we obtain the reaction kinetics of such a catalyst around these reaction conditions.

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Chapter 5

A Kinetic Model for the Synthesis of High-Molecular-Weight Alcohols over a Sulfided Co-K-Mo/C Catalyst

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ABSTRACT

A statistically-designed set of experiments was run in a recycle reactor to evaluate the kinetics of the formation of higher alcohols and total hydrocarbon byproducts from synthesis gas (hydrogen and carbon monoxide) in a range of experimental conditions that mirrors the limits of commercial production. The alkali-promoted, C-supported Co-Mo sulfide catalyst that was employed in this study is well known for its sulfur resistance. The reaction was carried out in a gradientless Berty-type recycle reactor. 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 alcohols of higher carbon number were also detected, and analysis of the liquid product revealed also the presence of trace amounts of ethers in the products. Yields of hydrocarbons were non-negligible. The alcohol product distribution followed an Anderson-Schultz-Flory distribution. 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 are 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, including CO-insertion, H₂-cleavage and hydrogenation steps do not appear to affect the rate correlations.

INTRODUCTION

The modification of Fischer-Tropsch (FT) synthesis catalysts by adding an alkali promoter produces a variety of oxygenated compounds including alcohols. The direct synthesis of higher-molecular-weight alcohols from CO and H₂ has been practiced since the mid 1920's (Fischer, 1925; Frolich and Lewis, 1928; Frolich and Cryder, 1930; Morgan *et al.* 1932). These higher alcohols can be used as gasoline additives to improve octane number. Catalysts used for the production of higher alcohols are classified into the following three categories: (i) Modified High-Pressure Methanol-Synthesis catalysts (alkali-doped Zn-Cr oxides); (ii) Modified Low-Pressure Methanol-Synthesis catalysts (alkali-doped Cu/ZnO/Al₂O₃); and (iii) Alkali-Doped Molybdenum Sulfide (ADM) catalysts. The modified methanol synthesis catalysts have been characterized and the reaction mechanisms over these catalysts have been identified (Smith and Anderson, 1983, 1984; Vedage *et al.*, 1983; Nunan *et al.*, 1989). Kinetic models for higher-alcohol synthesis over Cs-Cu/ZnO, K-Cu/ZnO/Cr₂O₃, K-CuO/ZnO/Al₂O₃, and Zn-Cr-K catalysts have been reported (Smith *et al.*, 1991; Calverly and Smith, 1992; Boz *et al.*, 1994; Tronconi *et al.*, 1987; Tronconi *et al.*, 1992). These catalysts are not considered in this work.

ADM catalysts are of particular interest since they are tolerant of sulfur compounds in the feed stream. The use of such catalysts saves the considerable costs of ultra-desulfurization of the syngas feed stream. The patents from the Dow Chemical Company first describe a promoted molybdenum sulfide catalyst that produces higher alcohols (Conway *et al.*, 1987; Stevens, 1988) and is sulfur tolerant. The major oxygenated products over these catalysts are found to be linear alcohols following an Anderson-Schultz-Flory distribution (Santiesteban *et al.*, 1988; Klier *et al.*, 1988). The isotopic studies of Santiesteban (1989) suggest that higher alcohols are formed by a CO-insertion mechanism.

Herman *et al.* (1990) developed a kinetic model for higher-alcohol synthesis over a K-MoS₂/C catalyst. But the literature still lacks a kinetic model developed from a set of statistically designed experiments. In the present study, a kinetic model for higher-alcohol synthesis over a Co-K-MoS₂ catalyst has been developed from a set of fractional-factorial experiments. The advantages of such a statistically designed experiment are two-fold. First, all of the several variables in the study have been investigated simultaneously, and over the entire range of their respective conditions. This affords a much greater opportunity for interactions between variables to exert influence on observed rates, leading to the development of a more-robust kinetic model. Second, we have been able to examine the statistical significance of each variable before any model is developed. If the average reaction rates at the high level of the variable are not significantly different from the rates at the low level of the variable, the variable is considered to have no real influence, and is eliminated. The early elimination of non-influential variables is a very real advantage of this approach.

Further, most of the kinetic studies reported in the literature were performed in plug-flow reactors. These reactors may be limited by external mass- and heat-transfer rates, and may not yield the intrinsic kinetics of the reaction of interest. In the present work, a Berty-type internal

recycle reactor was used for kinetic testing. Owing to the high linear velocities that are achievable in recycle reactors, it is possible to overcome external mass- and heat-transfer limitations. Hence it is possible to obtain better and more-reliable kinetic data.

The catalyst used in the present work was a C-supported, K-promoted Co-Mo sulfide. In earlier work (Liu *et al.*, 1997), we have compared related supported catalysts to unsupported catalysts. Addition of a support results in an increase in the yields of both alcohols and hydrocarbons, on a Mo basis. The clearly beneficial effect of K on (unsupported) MoS₂ catalysts was also reported.

EXPERIMENTAL

Catalyst Preparation

The C-supported, K-promoted Co-Mo sulfide catalyst was prepared by an incipient-wetness technique. Mo was impregnated first, followed by Co and K. The activated carbon support (20-40 mesh size, BET surface area of 655m²/g, pore volume of 0.93ml/g) was obtained from Aldrich Chemical Company (Lot # 00915PX). The soluble impurities on the activated carbon were removed by boiling it in water for about an hour. An aqueous solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was prepared by dissolving 4.3g of ammonium heptamolybdate in approximately 10cc of water. This solution was used to impregnate 10g of washed activated carbon support. The sample thus obtained was dried at room temperature for four hours and then dried again at 100°C overnight in an oven. The dried material was impregnated with a cobalt nitrate solution prepared by dissolving 2.2g of cobalt nitrate (Co(NO₃)₂·6H₂O) in approximately 10cc of water. After the impregnation, the sample was again dried at room temperature for four hours and then dried again at 100°C overnight. Finally, the material was impregnated with 5cc of 3.2M potassium carbonate (K₂CO₃) solution and dried at 100°C overnight. This results in a catalyst containing 18% Mo by weight, and with a Co/Mo ratio of 0.34 and a K/Mo ratio of 1.3. The weight of catalyst used in all the runs was 2.0g.

The catalyst was then reduced to the sulfide form inside the reactor using 100cc/min (STP) of a gas mixture containing 10% H₂S and 90% H₂ for one hour at 400°C and 1atm pressure. After the sulfidation the catalyst was purged in 100cc/min (STP) of pure H₂ for 90 minutes at 400°C.

Catalytic Testing

The catalyst was tested in the experimental unit shown in Figure 1. The heart of the unit is a gradientless Berty reactor (PPI Inc., Model # 93U-00006-B) used as an internal recycle reactor to measure the catalyst performance. The unit is further equipped with four mass-flow controllers, a back-pressure regulator, a liquid pump, a gas chromatograph (GC) and a personal computer (PC). The PC is used to set all flow rates and temperatures, and to collect and log all data, using commercial software (Wonderware, InTouch 4.1). The carbon monoxide stream enters the system after passing through a trap of activated charcoal (not shown in Figure 1) in order to remove any iron carbonyl impurities. The inlet flow rates of carbon monoxide, hydrogen, helium and hydrogen sulfide are regulated individually by one of four mass-flow controllers (Brooks Model 5850E, range 0-500cc/min). A HPLC pump (ISCO model 2350) is used to inject

liquids such as methanol directly into the reactor. An on-line GC (HP-5890 Series II) samples the exit gases at regular intervals, using a sampling valve (VICI 6-port) located downstream of the reactor. The inorganic gases (CO, N₂ and CO₂) are separated by a packed HayeSep DB packed-bed column, 30ft x 1/8in in column size and 100-120 mesh in particle size, and are analyzed using a thermal conductivity detector. The organic gases (hydrocarbons and alcohols) are separated by a capillary column (DB Wax, 20m x 0.1mm) and are analyzed using a flame ionization detector. The total CO conversion was calculated using nitrogen as internal standard. A pressurized trap at room temperature is placed downstream of the reactor to collect the liquid products of the reaction. A gas-chromatograph/mass-spectrometer (GC/MS, Varian, Saturn-3) is used off-line to identify the liquid products collected in the the trap.

Figure 1. Catalyst testing unit. MFC, mass flow controller; P, pressure gage; T, thermocouple; SV, sampling valve; B, back-pressure regulator; C, check valve; TV, three-way valve; HPLC, liquid pump; R, relief valve.

Experimental design

The variables considered for the kinetic study were temperature, and partial pressures of carbon monoxide, hydrogen, inerts and methanol. A fractional-factorial experimental design for these

five variables was used in this study. The range of conditions used in the experimental design (and in which the kinetic expressions obtained are valid) was determined as follows. During catalyst screening runs in a plug-flow reactor (Liu *et al.*, 1996), the catalyst activity showed a maximum in the temperature range of 300-350°C. Hence, the kinetic runs were performed in this temperature range. The range of total pressure was chosen to be 400-1000 psi, and the ratio of CO/H₂ was varied from 0.5 to 2. These ranges for the two variables are expected to define the limits of commercial operation. All the experiments were performed at a gas hourly space velocity (GHSV) of 9000 l/hr/kg-catalyst, measured on a fresh-feed basis at 25°C and 1atm. This flow rate has been shown to result in measurable values of products being formed in the experimental range of conditions used. As a necessary characteristic of the experimental design, methanol reaction rates were measured on both sides of chemical equilibrium for the formation of methanol. Hence every run was repeated with and without the introduction of liquid methanol at a flow rate of 0.02 ml/min, measured at 25°C.

The experiments performed in this study are listed in Table 1. The factorial experiments were performed in a random order, as shown in Table 1, so as to make the catalyst age an additional independent variable. The center-point experiment was repeated after every four runs, in order to obtain a measure of the deactivation of the catalyst.

Table 1. Fractional-Factorial Experimental Design.^a

LABEL	Temp [K]	Pressure [psig]	Vapor Flow Rates ^b [cc /min]			CH ₃ OH Flow Rate ^c [cc/min]	SEQUENCE
			CO	H ₂	He		
A	573	600	100	100	100	0	13
B	573	600	100	100	100	0.02	4
C	573	600	200	100	0	0	11
D	573	600	200	100	0	0.02	12
E	573	600	100	200	0	0	20
F	573	600	100	200	0	0.02	19
G	573	1000	120	120	60	0	18
H	573	1000	120	120	60	0.02	17
I	623	400	150	150	0	0	5
J	623	400	150	150	0	0.02	16
K	623	800	150	75	75	0	7
L	623	800	150	75	75	0.02	15
M	623	800	75	150	75	0	8
N	623	800	75	150	75	0.02	10
O	623	800	150	150	0	0	2
P	623	800	150	150	0	0.02	3
CP	598	700	128.5	128.5	43	0.01	1,6,9,14,21

^a Weight of catalyst used = 2.0 g^b Measured at 25°C and 1 atm^c Liquid-phase, measured at 25C

Each run was conducted for about twelve hours. The product rates and CO conversion were measured every two hours. Only when the rates were reasonably constant for at least three successive 2-hour periods was it assumed that the reactor had reached a steady state. Between the runs, when it was needed to shut down the reactor, the catalyst was kept under a constant inert gas flow of 50 cc/min.

RESULTS

Product Distribution Calculations

Both hydrocarbons and oxygenated products are observed with this catalyst. The major oxygenated products are found to be the linear alcohols methanol, ethanol, n-propanol, n-butanol and n-pentanol. In addition, occasional analysis of the liquid product by GC/MS revealed the presence of trace amounts of dimethyl ether and diethyl ether, as well as hydrocarbons and alcohols. All the individual hydrocarbons are not quantified in this study, but the major hydrocarbon product was found to be methane. Ethers and other oxygenates not explicitly identified as alcohols were lumped with the hydrocarbon fraction.

As mentioned earlier, the overall conversion of CO was obtained by using inert (nitrogen) as an internal standard. The rates of formation for CO₂ and for the individual linear alcohols were directly measured. A carbon balance was then used to obtain the total hydrocarbons. (Recall that this lump includes all products not explicitly identified as alcohols.) Finally, a hydrogen balance was used, along with the assumption that the water-gas shift reaction:

is in equilibrium, to estimate the amounts of hydrogen and water in the outlet stream. The detailed results from each run can be found in Gunturu (1997) and are summarized in Tables 2 and 3.

Table 2. Rates of Production of Hydrocarbons and Alcohols for Factorial Experiments

Sequence	Label	Observed rate of production (g/hr/kg-cat)				Catalyst Age (hr)
		Hydrocarbons	Methanol	Ethanol	Propanol	
1	CP	40.96	-79.23	40.00	5.52	12.00
2	O	43.09	50.86	26.60	6.03	25.50
3	P	94.04	-241.21	72.12	11.66	34.50
4	B	21.11	-97.98	44.24	1.14	55.50

		Observed rate of production (g/hr/kg-cat)				
5	I	21.69	34.95	11.95	1.84	69.00
6	CP	27.72	-70.22	40.34	5.08	79.50
7	K	23.36	20.95	11.43	2.76	91.50
8	M	13.41	21.23	7.55	1.39	103.50
9	CP	43.67	-83.60	37.92	5.20	12.00
10	N	83.45	-237.82	43.03	8.59	27.00
11	C	2.49	9.78	4.18	0.59	37.50
12	D	18.41	-100.19	36.59	1.52	49.50
13	A	3.49	16.00	4.98	0.75	61.50
14	CP	27.90	-70.14	36.31	4.53	73.50
15	L	87.12	-286.84	49.58	12.79	84.00
16	J	67.67	-195.69	41.22	6.79	97.50
17	H	25.41	-89.15	63.21	1.13	113.00
18	G	0.46	3.29	0.96	0.10	122.00
19	F	16.73	-55.99	47.11	0.57	131.00
20	E	0.96	11.33	1.96	0.15	140.00
21	CP	26.90	-46.56	34.47	4.31	149.00

Table 3. Partial Pressures of Products in the Outlet Stream for Factorial Experiments

Sequence	Label	Partial Pressures (atm)								
		CO	CO ₂	H ₂	N ₂	He	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₇ OH
1	CP	19.234	0.795	18.844	0.848	7.095	0.028	0.663	0.117	0.0124
2	O	25.538	0.692	26.711	1.130	0.000	0.036	0.244	0.089	0.0154
3	P	25.659	1.857	24.297	1.165	0.000	0.088	1.152	0.248	0.0308
4	B	13.213	0.391	10.844	0.572	14.292	0.008	1.370	0.112	0.0022
5	I	12.969	0.114	13.468	0.555	0.000	0.006	0.082	0.020	0.0023
6	CP	19.438	0.575	18.872	0.844	7.058	0.020	0.698	0.117	0.0113
7	K	25.845	0.328	13.150	1.108	13.848	0.008	0.099	0.037	0.0069
8	M	12.589	0.355	27.024	0.551	13.775	0.038	0.099	0.025	0.0035
9	CP	19.288	0.741	18.876	0.848	7.092	0.027	0.645	0.111	0.0117
10	N	12.374	1.336	24.441	0.575	14.369	0.132	1.153	0.146	0.0224
11	C	26.115	0.039	13.524	1.093	0.000	0.001	0.034	0.010	0.0011
12	D	26.814	0.489	10.888	1.141	0.000	0.005	1.359	0.093	0.0029
13	A	12.992	0.035	13.490	0.547	13.683	0.001	0.056	0.012	0.0014
14	CP	19.420	0.591	18.894	0.843	7.052	0.021	0.697	0.106	0.0101
15	L	25.868	1.593	10.390	1.144	14.302	0.032	0.910	0.168	0.0332
16	J	13.227	0.483	12.166	0.574	0.000	0.022	0.678	0.070	0.0088
17	H	26.505	0.721	22.660	1.149	14.365	0.016	2.348	0.268	0.0037
18	G	25.994	0.122	27.178	1.090	13.620	0.003	0.019	0.004	0.0003

		Partial Pressures (atm)								
19	F	13.300	0.281	25.012	0.573	0.000	0.014	1.526	0.120	0.0011
20	E	12.993	0.052	27.180	0.546	0.000	0.003	0.039	0.005	0.0003
21	CP	19.480	0.522	18.798	0.845	7.066	0.018	0.798	0.100	0.0100

The results of a typical run (Label O from Table 1) are used to illustrate the distribution of alcohols in the products. If the alcohols follow an Anderson-Schultz-Flory distribution, as observed previously by Santiesteban (1989), then the following relationship applies between the mole fraction of an alcohol y_n , and its carbon number n :

$$\log[y_n] = \log[1-\alpha] + (n-1) \log[\alpha] \quad (2)$$

Figure 2 indicates that such a relationship is obtained for this typical run. From the value of the intercept, the value of the chain-growth probability (α) is found to be 0.18, and the value of α is found to be 0.20 from the value of the slope. Hence an average value of 0.19 can be assumed for α .

Figure 2. Product distribution of alcohols over Co-K-MoS₂/C catalyst after Run Label O. Experimental conditions: 350°C; 800 psi; 2g catalyst; flow rates - CO, 150 ml/min; H₂, 150 ml/min; He, 0 ml/min; CO conversion, 0.058.

Effect of Methanol in Feed

To study the effect of products in the feed stream, methanol was injected into the reactor, along with CO and H₂. Results of typical experiments with and without methanol in the feed (Labels P and O from Table 1 respectively) are shown in Figure 3. The fraction of CO converted increases from 0.058 to 0.082 when methanol is present in the feed. Methanol in the feed seems to increase the productivities of both higher alcohols and hydrocarbons. The increase in higher-alcohol productivities indicate that higher alcohols are generated from secondary reactions involving

methanol. This result too is consistent with the work of Santiesteban (1989) using isotopic labeling experiments.

Figure 3. Comparison of rates of production of hydrocarbons and alcohols with and without methanol in the feed. Experimental conditions: 350°C; 800 psi; 2g catalyst; flow rates - CO, 150 ml/min; H₂, 150 ml/min; He, 0 ml/min. Unshaded data: Run Label O, no MeOH in feed. Shaded data: Run Label P, 0.02 ml/min MeOH in feed.

Methanol Decomposition over the Co-K-MoS₂/C Catalyst

In order to test the hypothesis that higher alcohols may be formed from the condensation of lower alcohols, additional runs were carried out in which only methanol and helium were fed into the reactor. In the product stream from this experiment, no higher alcohols were found, as shown in the unshaded points in Figure 4. If the mechanism of higher-alcohol production involves only the condensation of lower alcohols, then significant amounts of ethanol would have been found in the product stream. The absence of ethanol in the products rules out the possibility of a condensation mechanism.

Figure 4. Comparison of methanol decomposition with and without CO in the feed. Experimental conditions: 350°C; 700 psi; 2g catalyst; methanol flow rates, 0.02 ml/min; hydrogen flow rates, 0 ml/min. Unshaded data: flow rates - CO, 0 ml/min; He, 300 ml/min; MeOH conversion, 0.92. Shaded data: flow rates - CO, 171 ml/min; He, 128 ml/min; MeOH conversion, 0.73.

When carbon monoxide was fed along with the methanol, with all other conditions maintained constant, then appreciable rates of production of ethanol and propanol were found. See the shaded points in Figure 4. This supports a mechanism in which CO is inserted into a lower-carbon-number alcohol to form an alcohol with a higher carbon number, the so-called CO-insertion mechanism.

Effect of Catalyst Age

As mentioned earlier, several runs were carried out at the conditions of the center point of the matrix of experimental ranges (CP in Table 1). These repeated runs are plotted in Figure 5 as a function of the catalyst time on stream. The results indicate qualitatively that there is no significant effect of catalyst age on the production of higher alcohols. We return to this later.

Figure 5. Effect of catalyst age on rates of production of alcohols and hydrocarbons after runs at center-point conditions, Run Label CP.

Reaction Scheme

Santiesteban (1989) suggested a detailed mechanism for the production of alcohols over MoS_2 catalysts. A reaction network involving all the steps of this model would be very complicated, and it is difficult to obtain a statistically valid model for such complicated reaction schemes. So, the simplified reaction scheme shown below is assumed:

In this reaction scheme, the production of methanol from CO and H₂ is reversible. The subsequent steps proceed mainly via a CO-insertion mechanism and are assumed to be irreversible. The water-gas shift reaction, Equation (1), is assumed to be in thermodynamic equilibrium. Further, it is assumed that hydrocarbon products are composed exclusively of methane and are produced from methanol. As noted earlier, all products that were not identified as linear alcohols were also included in the hydrocarbon lump.

The reactions involved in the above scheme are sequential, that is, ethanol is produced from methanol by the insertion of CO, propanol is produced from ethanol by the insertion of another molecule of CO, and so on (although alcohols of carbon number higher than propanol are formed in quantities small enough to be neglected for present purposes). Further, methane is produced from reactions involving methanol. Hence the gross rate of production of methanol is equal to the sum of the observed (or net) rates of production of methane, methanol, ethanol and propanol, with all rates expressed in mol/hr/kg-cat to satisfy the carbon balance. Similarly, the gross rate of production of ethanol is equal to the sum of the observed (net) rates of production of ethanol and propanol. The gross rates of production, rather than the observed rates, are used for developing the kinetic models for the sake of simplicity. Kinetic models for the observed (net) rates are later back-calculated from the gross-rate models using the relationships above.

Analysis of Kinetic Data

Since reactions occur at discharge conditions in recycle reactors, partial pressures at the outlet conditions have been chosen as the independent variables. It is necessary to ensure that the partial pressures of CO, H₂, He and CH₃OH, temperature and catalyst age at outlet conditions are indeed independent. Hence, a correlation analysis is used (Cropley, 1987a). The determinant of the correlation matrix is a useful measure to judge the independence of the corresponding set of variables. Values of the determinant close to unity indicate that the variable set is independent. The correlation matrix for the present study is shown in Table 4. Using the values of Table 4, the determinant of the correlation matrix is found to be 0.79. This is sufficiently close to unity that a regression analysis can be performed on the data of Table 3.

Table 4. The SAS System Correlation Analysis

X1 refers to outlet temperature; X2, X3, X4 and X5 refer to the partial pressures of CO, H₂, He and CH₃OH respectively in the products; and X6 refers to the catalyst age.

Correlation matrix with catalyst age						
	X1	X2	X3	X4	X5	X6
X1	1.0000	-0.0368	0.0080	0.0038	-0.2087	-0.2366
X2	-0.0368	1.0000	-0.0674	0.0287	0.1276	-0.1501
X3	0.0080	-0.0674	1.0000	-0.0442	-0.0235	0.2183
X4	0.0038	0.0287	-0.0442	1.0000	0.1119	0.0834
X5	-0.2087	0.1276	-0.0235	0.1119	1.0000	0.0216
X6	-0.2366	-0.1501	0.2183	0.0834	0.0216	1.0000
Determinant value = 0.79						

Two kinds of models were developed from the kinetic data: exponential models and Langmuir-Hinshelwood (LH) models. The form of the exponential models and of the LH models are given later. In the exponential models, parameters were estimated by minimizing the sum of the squares of the differences between experimental and predicted natural logarithms of the rates for each component:

$$\min \sum_{i=1}^N \left(\ln[r_i^{\text{exp}}] - \ln[r_i^{\text{mod}}] \right)^2$$

where N is the total number of observations (21 in this case), r_i^{exp} is the experimental rate of the component during observation i, and r_i^{mod} is the predicted rate of the component during observation i. Then Student's t test was used to test the statistical significance of the parameter estimates. The variables that were determined to be statistically significant in the exponential models were used in LH models. For the LH models, the parameters were estimated by using

DBCPOL, an optimizing subroutine from IMSL. The two types of models are discussed further below.

Exponential Model

Exponential rate equations of the following form were developed for the rates of production of ethanol, propanol and hydrocarbons:

$$r_{C_2H_5OH}^{gross} = A_1 e^{-(E_1/R)(1/T - 1/T_{cp})} \left[\frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_1} \left[\frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_1} \left[\frac{P_I}{P_I^{cp}} \right]^{c_1} \times \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]^{d_1} \left[\frac{t}{t^{cp}} \right]^{l_1} \quad (6)$$

$$r_{C_3H_7OH}^{gross} = A_2 e^{-(E_2/R)(1/T - 1/T_{cp})} \left[\frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_2} \left[\frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_2} \left[\frac{P_I}{P_I^{cp}} \right]^{c_2} \times \left[\frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right]^{d_2} \left[\frac{t}{t^{cp}} \right]^{-l_2} \quad (7)$$

$$r_{HC}^{gross} = A_3 e^{-(E_3/R)(1/T - 1/T_{cp})} \left[\frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_3} \left[\frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_3} \left[\frac{P_I}{P_I^{cp}} \right]^{c_3} \times \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]^{d_3} \left[\frac{t}{t^{cp}} \right]^{-l_3} \quad (8)$$

In the above equations, the A_i terms refer to pre-exponential factors in rate constants and E_i terms represent activation energies, *i.e.*, the temperature dependencies of the rate constants. Partial pressures of components i are denoted by P_i , and t refers to the catalyst age; P_i^{cp} refers to the value at the center-point condition, while t^{cp} refers to the mean catalyst age. Component I denotes the inert. As mentioned earlier, a log-linear regression was used to estimate the parameters in these equations.

Note that an exponential rate equation cannot be developed for the rate of methanol. The overall rate of formation of methanol is negative for those runs where methanol is a reactant, and

positive where methanol is not a reactant. Values which are both positive and negative cannot be accounted for in expressions of the form of Equations (6)-(8).

The results of the regression for Equations (6)-(8) are shown in Table 5. The values of the t-statistic for the rate of ethanol and the rate of hydrocarbons indicate that only the activation energy term and the exponent of the partial pressure of methanol are statistically significant, since only those values of the t-statistic are greater (in absolute magnitude) than the critical value of 3.0. For the rate of propanol, the statistically significant variables are found to be the activation energy and the exponent of ethanol. In all cases, the value of the exponent of the catalyst age is not statistically significant. This is consistent with the qualitative result noted earlier. Only the variables that are statistically significant (using the t-test) are retained in the LH models developed below.

Table 5. Parameter Estimates for Exponential Models

Exponential Model for Ethanol			Exponential Model for Propanol			Exponential Model for Hydrocarbons		
Parameter	Estimate	t-statistic	Parameter	Estimate	t-statistic	Parameter	Estimate	t-statistic
$\ln(A_1)$	-0.0420	-0.31	$\ln(A_2)$	-2.4035	-10.43	$\ln(A_3)$	0.9866	7.79
E_1	38.252	-5.11	E_2	97.852	-7.39	E_3	106.478	-15.23
a_1	0.1242	0.69	a_2	0.0893	0.29	a_3	-0.0273	-0.16
b_1	-0.3067	-1.89	b_2	-0.6406	-2.32	b_3	-0.5212	-3.43
c_1	-0.0411	-1.02	c_2	0.0216	0.31	c_3	-0.0123	-0.33
d_1	0.7307	19.06	d_2	0.5642	6.73	d_3	0.6636	18.53
λ_1	-0.1511	-1.96	λ_2	-0.3226	-2.43	λ_3	-0.2684	-3.74

A_1 , A_2 , and A_3 are in [mol/hr/kg-catalyst]; E_1 , E_2 , and E_3 are in [kJ/mol]; all other parameters are dimensionless.

LH Expression for Methanol Gross Rate

A LH rate expression of the following form can be used for methanol synthesis:

$$r_{CH_3OH}^{gross} = \frac{A_m e^{-(E_m/R)(1/T - 1/T_{cp})} \left(\left[\frac{P_{CO}}{P_{CO}^{cp}} \right] \left[\frac{P_{H_2}}{P_{H_2}^{cp}} \right]^2 - \frac{1}{K_{eq}} \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)}{\left(1 + K_1 \left[\frac{P_{CO}}{P_{CO}^{cp}} \right] + K_2 \left[\frac{P_{H_2}}{P_{H_2}^{cp}} \right]^2 + K_3 \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_m}} \quad (9a)$$

The form of Equation (9a) is widely used in the literature for methanol synthesis; see, *e.g.*, Cropley (1989). Note that this relation allows both positive and negative rates of formation to be obtained, by accounting for both forward and reverse rates of the reaction of Equation (3). Again, the gross rate of production of methanol (the sum of the observed rates of hydrocarbons, methanol, ethanol and propanol) is used instead of the observed rate, as discussed earlier. The parameters K_1 , K_2 and K_3 , in the denominator represent adsorption coefficients. The non-dimensional equilibrium constant K_{eq} in the numerator can be given by:

$$K_{eq} = K_a / (K_z K^{cp}) \quad (9b)$$

The parameter K_z is a fugacity correction factor which is estimated from the nonlinear regression. The equilibrium constant, K_a , is obtained as a function of temperature from software CHEMEQ.BAS developed by Sandler (1989). Table 6 shows the results of the calculation of K_a at the temperature values used here. Finally, the nondimensionalizing term K^{cp} is given by the ratio of the partial pressures at the central point:

Table 6. Values of the Equilibrium Constant K_a ^a

T (K)	$K_a \times 10^5$
573	20.83
598	8.686
623	3.868

^a Sandler (1989)

$$K^{cp} = \frac{P_{CH_3OH}^{cp}}{P_{CO}^{cp} [P_{H_2}^{cp}]^2} (9c)$$

For simplicity, the only temperature dependencies employed in Equation (9a) are that of K_a and that of the rate constant in the numerator, as given by the activation energy term E_m . This is consistent with previous uses of this type of kinetic relation (see, *e.g.*, Cropley, 1987b)

The results of the non-linear parametric estimation of Equation (9) are summarized in Table 7. Additional details can be found in Gunturu (1997). The coefficient of determination for the above model is 0.8148, that is, more than 80% of the variation in the rate data is explained by the model.

Table 7. Parameter Estimates for Methanol Synthesis Model

Parameter	Estimate
A_m [mol/hr/kg-cat]	4.9047
E_m [kJ/mol]	117.733
K_z [dimensionless]	0.3359
K_1 [dimensionless]	0.0696
K_2 [dimensionless]	0.6400
K_3 [dimensionless]	0.6940
n_m	2
Coefficient of determination	0.8148
F-statistic	10.1160

LH Expressions for Gross Rates for Ethanol, Propanol and Hydrocarbons

Recall that the catalyst age and partial pressures of carbon monoxide, hydrogen and inerts are statistically insignificant for the gross rates of ethanol, propanol and hydrocarbons. Hence the following forms of the LH rate expressions are selected:

$$r_{C_2H_5OH}^{gross} = \frac{A_e e^{-(E_e/R)(1/T - 1/T_{cp})} \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]}{\left(1 + K_e \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_e}} \quad (10)$$

$$r_{C_2H_5OH}^{gross} = \frac{A_p e^{-(E_p/R)(1/T - 1/T_{cp})} \left[\frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right]}{\left(1 + K_p \left[\frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right] \right)^{n_p}} \quad (11)$$

$$r_{HC}^{total} = \frac{A_h e^{-(E_h/R)(1/T - 1/T_{cp})} \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]}{\left(1 + K_h \left[\frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_h}} \quad (12)$$

In the above rate expressions, A_e , A_p and A_h represent pre-exponential terms; E_e , E_p and E_h represent temperature dependence terms; and K_e , K_p and K_h represent adsorption coefficients.

The results of the non-linear parametric estimations are shown in Table 8. Additional details are given in Gunturu (1997). The coefficients of determination for the models are also given in Table 8. These values range from 0.92 to 0.97, *i.e.*, over 92 percent of the variation in the rate data is explained by the models.

Table 8. Parameter Estimates for Langmuir-Hinshelwood Models

LH Model for Ethanol		LH Model for Propanol		LH Model for Hydrocarbons	
Parameter	Estimate	Parameter	Estimate	Parameter	Estimate
A_e	1.5259	A_p	0.1101	A_h	4.6928
E_e	24.986	E_p	89.943	E_h	95.416
K_e	0.7367	K_p	0.2502	K_h	1.2472
n_e	1	n_p	1	n_h	1
Coefficient of determination	0.92	Coefficient of determination	0.92	Coefficient of determination	0.97
F-statistic	67.53	F-statistic	65.30	F-statistic	157.31

A_e , A_p and A_h are in [mol/h/kg cat]; E_e , E_p and E_h are in [kJ/mol]; all other parameters are dimensionless.

Note that partial pressures of CO and H₂ do not appear in Equations (10)-(12). The absence of the partial pressures of CO and H₂ in the LH rate expressions suggest that the CO-insertion, H₂-cleavage, and hydrogenation steps implicit in Equations (3)-(5) do not effect the rates, at least in the range of conditions used here. A possible rate-limiting step might be a surface reaction of an adsorbed alcohol, perhaps a dehydration. However, we note that it is not advisable to infer mechanisms from kinetics obtained in this limited range of experimental conditions.

The values of the activation energy terms for methanol, ethanol and propanol are gathered in Tables 7 and 8. It is not very clear why the term for ethanol is so low compared to those for methanol and propanol. Perhaps ethanol could be forming oxygenated products such as esters and ethers at high temperatures in the actual reaction network. Since these compounds are not considered in this study, the temperature dependence of the gross rate of ethanol production could be lower than the actual value.

Observed Rates of Formation

Equations (10)-(12) describe the gross rates of formation of methanol, ethanol, propanol and total hydrocarbons over the catalyst under the given conditions. Gross rates are used for ease in the fitting procedure, but expressions for the net (observed) rates are more convenient for reactor design. These expressions can be obtained from the sequential reaction scheme of Equations (3)-(5):

$$r_{HC} = r_{HC}^{gross} \quad (13)$$

$$r_{C_3H_7OH} = r_{C_3H_7OH}^{gross} \quad (14)$$

$$r_{C_2H_5OH} = r_{C_2H_5OH}^{gross} - r_{C_3H_7OH}^{gross} \quad (15)$$

$$r_{CH_3OH} = r_{CH_3OH}^{gross} - r_{C_2H_5OH}^{gross} - r_{HC}^{gross} \quad (16)$$

The gross reaction rates are given by Equations (10)-(12).

It is of interest to compare the experimental values of the rates with the values of the net rates obtained from Equations (13)-(16) and the model parameters. A comparison diagram for each of the species methanol, ethanol, propanol and total hydrocarbons is given in Figures 6 through 9. The fit of the models is generally good.

Figure 6. Comparison plot for net rates of methanol production.

Figure 7. Comparison plot for net rates of ethanol production.

Figure 8. Comparison plot for net rates of propanol production.

Figure 9. Comparison plot for net rates of hydrocarbon production.

CONCLUSIONS

The formation of higher-molecular-weight alcohols over a sulfided Co-K-Mo/C catalyst was evaluated. Both hydrocarbons and oxygenated products were observed over this catalyst. The major oxygenated products were found to be linear alcohols such as methanol, ethanol, n-propanol and n-butanol. The major hydrocarbon product was methane. For the sake of simplicity, all oxygenates other than alcohols were lumped with the total hydrocarbon products. The alcohol product distribution follows an Anderson-Schultz-Flory distribution. Alcohol chain growth seems to occur via a CO-insertion mechanism, as suggested by Santiesteban (1989). A Langmuir-Hinshelwood type of kinetic model was developed to quantify the gross rates of

synthesis of each of the higher alcohols, and of the total hydrocarbons (as methane), in the temperature range of 300-350°C and in the range of partial pressures of CO and H₂ of 200-400 psi. The kinetic models suggest that, in the above temperature and partial pressure ranges, the rate-limiting step in the chain growth of the alcohols may be a surface reaction of the corresponding precursor alcohol. Other steps, including CO insertion, hydrogen cleavage, and hydrogenation, do not effect the rate correlations in the ranges used here. The models can be manipulated to predict the net (or observed) rates of formation of the higher alcohols. The predictions agree well with the experimental data.

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Chapter 6

A TEMPERATURE PROGRAMMED REDUCTION (TPR) STUDY ON ALKALI - PROMOTED, CARBON-SUPPORTED MOLYBDENUM CATALYSTS

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Abstract

The reducibility of a series of carbon-supported, molybdenum-based catalysts with or without a potassium promoter was investigated using temperature-programmed reduction (TPR). The Mo loading and the K-doping level influence the reducibility of the K-Mo/C catalysts. The TPR spectra of both Mo/C and K-promoted Mo/C catalysts generally consist of four peaks. Two of these (located around 350°C and 440°C) are attributed to the reduction of octahedrally coordinated Mo [Mo(O)], and a third peak (located around 740°C) is attributed to the reduction of tetrahedrally coordinated Mo [Mo(T)]. The fourth peak (located around 850°C) is assigned to CO desorption from the decomposition of the oxidized carbon support. The distribution of the different Mo species is greatly affected by the Mo loading and the K-doping level. In the absence of the K promoter, Mo(O) species predominate at relatively low metal loadings while Mo(T) species predominate at higher loadings. The reducibility of both species, quantified by the hydrogen consumed, or the average Mo valence, decreases with increasing Mo loadings. Mo carbides (or other more-refractory compounds) may be formed in Mo/C catalysts, either during the catalyst preparation process or in the TPR experiments. The K/C runs indicate that K is not itself reduced, but it may modify the reducibility of other metal compounds. A small amount of K, when added to the Mo/C, increases the area of the low-temperature Mo(O) peaks at the expense of the high-temperature Mo(T) peak. Under these conditions, the Mo(T) is significantly more reduced than is the Mo(O). Larger amounts of K decrease the Mo(T) peak area and cause less reduction in both the Mo(T) and Mo(O) species. K and Mo interact in K-promoted Mo/C catalysts, with the interaction being most pronounced for molar ratios of K/Mo between 0.2 and 1.

Introduction

Molybdenum-based catalysts are active for many kinds of catalytic reactions, including hydrogenation, hydrogenolysis, hydrocracking, hydrodesulfurization, and hydrodenitrogenation. The catalytic performance depends, to a certain extent at least, on the support used, since the surface properties of the catalyst vary with the support.

Alumina, silica, and silica-alumina are commonly used for hydrotreating and hydrocracking catalysts. A carbon support has been used for hydrocarbon synthesis (1) and higher-alcohol synthesis (2-5) from carbon monoxide and hydrogen. A carbon support possesses advantages over oxide supports for some reactions because of its inactive surface, which could lead to a weak interaction between the support and the active components, thus preferentially forming active phases and making them more effective (6). Further, specially pretreated carbon supports can prevent coke formation on the surface of catalyst so that the life of the catalyst increases (6,7).

Alkali promoters and modifiers are important in heterogeneous catalysis. For example, molybdenum-based catalysts promoted by potassium or cesium have been used for the synthesis of mixed alcohols from syngas (2-5,8-10), while unpromoted molybdenum catalysts produce mainly light hydrocarbons (1). The mechanism of the promotional effect of alkali still remains open to question. Some researchers (10) believe that the catalysts are bifunctional, while others (11) suggest that alkali atoms modify the local electron density of the transition metal, either directly or indirectly *via* the support. Generally, the nature, the doping level and the counter-anion of the alkali affect the activity and selectivity of catalytic reactions (12-14).

Mo-based catalysts generally need to be reduced or sulfided prior to reaction, in order to achieve the desired performance. The relative amount of different molybdenum species on the surface of the catalyst after pretreatment dramatically affects catalyst performance (15). Therefore, the reducibility of molybdenum-based catalysts is an interesting and important aspect for study. For this purpose, temperature-programmed reduction (TPR) is a useful technique (16). It has been widely applied to oxide-supported Mo-based catalysts. Most previous work has dealt with the effects of oxide supports on the reducibility of the active metal of the catalysts (17-19), while very few researchers (to our knowledge) have been concerned about the reduction behavior of carbon-supported, molybdenum-based catalysts. In the present work, we use TPR to study the reduction behavior of carbon-supported, molybdenum-based catalysts, both with and without a potassium promoter. In particular, we investigate the effects of molybdenum loading and potassium doping on the reducibility of the catalysts.

Experimental

Materials

Activated carbon was obtained from Aldrich Chemical Company. The granule size of the activated carbon is 20-40 mesh, the surface area is 660 m²/g, and the pore volume is 1.0 ml/g. A sample of this carbon was sent to Galbraith Laboratories for elemental analysis. ICP results for metals present indicate 8.0% Si, 0.87% Al, 0.28% Fe, 0.18% Ca, 0.074% Mg and 0.069% Ba, smaller amounts of Sr and Ti, and measurable values in the ppm range of at least six other metals. The high concentration of silicon by elemental analysis is consistent with x-ray powder diffraction data, which show strong lines for the cristobalite phase of SiO₂. Copper oxide (99.9999% CuO) and commercial molybdenum oxide (MoO₃) were also obtained from Aldrich Chemical Company. Ammonium heptamolybdate ([NH₄]₆Mo₇O₂₄•4H₂O) and potassium nitrate (KNO₃), used as the sources of molybdenum and potassium for catalyst preparation, were obtained from Fisher Scientific. All were used as received. Gases argon (high purity, 99.995%)

and a mixture of 10% hydrogen in argon were obtained from Matheson and used as received.

Catalyst Preparation

The incipient-wetness impregnation method was employed. The Mo/C samples were prepared by impregnating the activated carbon with an aqueous solution of ammonium heptamolybdate. This was followed by drying in air at 100°C overnight and then calcining in flowing N₂ at 500°C for 2 hours. K/C samples were prepared by impregnating activated carbon with a solution of potassium nitrate, again followed by drying in air at 100°C overnight and calcining in flowing N₂ at 300°C for 2 hours. For the Mo/C and K/C samples, loadings are given as the weight percent relative to the activated carbon support. The process used to prepare Mo-K/C catalysts was the same as that for the K/C samples, except that Mo/C was used in place of the activated carbon. For the Mo-K/C materials, nominal Mo percentages are based on the weight of activated carbon support, while potassium-doping levels are given as the molar ratios of potassium to molybdenum.

Temperature-Programmed Reduction

The equipment used for temperature-programmed reaction was constructed from a Hewlett Packard 5890 gas chromatograph and an external furnace with a temperature programmer. The sample to be analyzed was placed in a quartz U-tube reactor and surrounded with quartz chips. The reactor was heated using a furnace and temperature programmer obtained from Automated Test Systems (Butler, PA). Either high-purity Ar or the 10% H₂-Ar mixture flowed through the reactor. The exit stream from the reactor passed through a cold trap filled with a mixture of dry ice and acetone (to remove water from the exit stream) and thence to a thermal conductivity detector (TCD) in the gas chromatograph, where the H₂ content of the stream was monitored. A Hewlett-Packard personal computer and HP ChemStation Software were used for data acquisition and processing.

Approximately 120 mg of catalyst was used for each TPR experiment. The sample was first preheated in the high-purity Ar at 250°C for 1 h with a flow rate of 30 cc/min, to remove any absorbed volatile impurities. During this time, the reactor was isolated from the TCD, and separate streams flowed to the detection and reference arms of the TCD. Thus the TCD was uncontaminated by the exit stream from the reactor during pretreatment. The sample was then cooled down to room temperature in flowing Ar and the TPR experiment was started. Typically, a TPR experiment was conducted in the 10% H₂ - Ar gas mixture flowing at 30 cc/min, the same flow rate used in the pretreatment. The temperature was usually ramped from room temperature to 850°C at a fixed rate of 10°C/min. The furnace was held at 850°C for 30 min. The H₂ consumption was monitored by the TCD. The TPR profiles of the samples were analyzed by deconvoluting them using PeakFit software from Jandel Scientific.

Results

Reduction of CuO

In a calibration experiment, TPR data were collected using the high-purity CuO sample. This experiment was used to quantify the H₂ consumption during the reduction,

and thus to calibrate the response of the TCD. The results allow us to obtain an average valence of Mo for the catalysts after reduction, assuming the initial oxidation state of the Mo to be +6.

Figure 1(a) shows the TPR spectrum of the CuO. Only one peak of H₂ consumption is observed. The peak is symmetric and occurs at a temperature of around 260°C. After the first TPR run, the sample was cooled to room temperature in flowing Ar, and a second TPR experiment was conducted, following exactly the same procedure as used in the first run. A very flat line was obtained (not shown in Figure 1). In other words, no more H₂ was consumed in this second run. This indicates that CuO can be completely reduced at a relative low temperature in a single step. This experiment was readily repeatable. Therefore, the TCD response may be reliably calibrated by assuming stoichiometric reduction of the CuO.

Figure 1. TPR spectra when the sample is ramped from room temperature to 850°C , then held at 850°C for 30 min. Samples are as follows: (a), CuO; (b) commercial MoO_3 ; (c) in-house MoO_3 .

Reduction of Unsupported Molybdenum Oxides

Figure 1(b) shows the TPR spectrum from the commercially obtained MoO_3 , and Figure 1(c) that from unsupported MoO_3 made in-house by calcining ammonium heptamolybdate in flowing N_2 at 500°C for 2 hours. The TPR profiles of both the purchased MoO_3 and the prepared MoO_3 show two peaks of H_2 consumption: one at a temperature around 660°C , and the other at 850°C . The shape and location of the two peaks are very similar for the two samples. This suggests that the ammonium heptamolybdate is converted to MoO_3 after calcination in N_2 at 500°C .

TPR of Activated Carbon

For the activated carbon, four experiments have been carried out. The first one was a TPR of the activated carbon. For the second run, a sample of activated carbon that had been calcined in flowing N_2 at 500°C for 2 h was used for the TPR experiment. After this second run, the same sample was cooled to room temperature in flowing Ar. The third run was also a TPR, but with the same sample used in run (b), without exposing the sample to air. In the final run, a fresh sample of activated carbon was calcined in N_2 , like the sample used in run (b), and was then heated using pure Ar (rather than in a mixture of H_2 and Ar) following the same temperature program. In other words, this was a temperature-programmed desorption run, rather than TPR. These four spectra are shown in Figure 2.

Figure 2. Spectra for activated carbon support material: (a) TPR of fresh sample; (b) TPR of N_2 -calcined sample; (c) repeated TPR of sample used for curve (b); (d) TPD of fresh sample.

Both the carbon sample (Figure 2a) and the N₂-calcined carbon sample (Figure 2b) exhibit a positive peak at a temperature around 570°C and a negative peak at around 850°C. Clearly, the N₂ calcination procedure has no significant effect on the TPR profile for the activated carbon. In the third run, where the TPR procedure was repeated for the same calcined carbon sample, only small fluctuations in the baseline are observed (Figure 2c) -- there are no significant positive or negative peaks. Clearly, the reduction is complete after the first TPR run. In the TPD experiment without hydrogen (Figure 2d), only one peak is obtained. This is the same negative peak observed in Figures 2a and 2b. The presence of this peak even in the absence of hydrogen implies that the peak is unrelated to TPR. We return to this later.

The runs with CuO, unsupported Mo oxides, and the activated carbon support may be summarized as follows. The positive peaks observed correspond to hydrogen consumption due to reduction of the sample. The reduction is complete after the first TPR experiment. The negative peak seen at 850°C is not relevant to TPR.

K/C Samples

The TPR profiles of K/C samples are presented in Figure 3, curves (b) through (e), with the TPR profile of the carbon support alone presented as curve (a). Qualitatively, one positive peak, one shoulder, and one negative peak are observed for all the K/C samples. At low loadings of K (less than 6 wt%), the temperature position of the positive peak is nearly the same as that for the carbon support alone, and the impregnation of potassium makes the positive peak sharper. At the low loadings, a broad shoulder is observed at around 450°C, a temperature lower than the main (C-based) peak. When the potassium loading is relatively high (greater than 6 wt%), the broad shoulder narrows and is converted to a narrow peak, while the sharp main peak broadens into a shoulder. Further, the total area under the TPR spectrum, corresponding to the amount of H₂ consumed, increases significantly even when only 3 wt% K is added. However, addition of over 11 wt% K does not appear to increase the consumption of H₂ significantly beyond the initial increase.

Figure 3. TPR spectra for K/C samples. Loadings of K are as follows, in wt%, as weight of elemental K divided by weight of support: (a) 0; (b) 2.9; (c) 5.8; (d) 8.8; (e) 11.6.

These results imply that the potassium itself is not reduced, but may influence the reduction of (impurities in) the carbon support. Further, the effect of K appears to change somewhere between loadings of 6 and 8 wt% K. Quantitative descriptions of the TPR peaks are given in the Discussion Section.

Mo/C Catalysts

Figure 4 shows the TPR profiles of Mo/C catalysts with different Mo loadings. At 3% and 6% molybdenum loadings, curves (b) and (c), three major peaks are observed. Two are positive peaks at temperatures around 440°C and 720°C; the third is the negative peak at around 850°C, as observed in the TPD profile of the carbon support and determined to be irrelevant. On increasing the Mo loading to 9%, curve (d), the position of the peak at around 720°C apparently shifts to a higher temperature, while that of the peak around 440°C moves slightly to a lower temperature. When the Mo loading reaches 9 wt%, a small shoulder develops near 300°C. The location of this fourth peak shifts to lower temperatures with increasing Mo loading. The areas of the peaks vary with Mo loading, with the higher-temperature peak accounting for a larger percentage of the total area as the loading increases. These peaks are quantitatively described in the Discussion Section.

Figure 4. TPR spectra for Mo/C samples. Loadings of Mo are as follows, in wt%, as weight of elemental Mo divided by weight of support: (a) 0; (b) 3; (c) 6; (d) 9; (e) 12; (f) 18; (g) 21; (h) 24.

Mo-K/C Catalysts

Figure 5 gives the TPR profiles of Mo-K/C catalysts containing 18 wt% Mo with varying K-promotion level. Curve (a) is the TPR profile for the support alone, while curve (b) represents the TPR profile of the Mo/C catalyst without potassium, also shown in Figure 4(f). Qualitatively, at least three major peaks are seen for each catalyst: at least two positive peaks and one negative peak. This is analogous to the behavior of the Mo/C materials. Note that the peak at the lowest temperature (around 320°C) vanishes with the addition of even a small amount of K. Further, the presence of even the smallest loading of K dramatically alters the relative areas of the two major positive peaks. Increasing the K/Mo molar ratio from 0.2 to 1.6 does not cause much qualitative change in the TPR profiles, but the relative areas of the positive peaks do show small changes. Quantitative discussions of the TPR peaks are given below.

Figure 5. TPR spectra for Mo-K/C catalysts. Curve (a), activated carbon support alone; for curves (b)-(h), Mo loadings are 18 wt% relative to the support, and K/Mo values are as follows, in molar ratio: (b) 0; (c) 0.2; (d) 0.6; (e) 1.0; (f) 1.2; (g) 1.4; (h) 1.6.

Discussion

Unsupported Mo Oxide

Table 1 shows quantitative results from the TPR of the commercial MoO₃ and the MoO₃ prepared in-house, Figures 1b and 1c. The locations of the low-temperature maximum (T_L) and the high-temperature maximum (T_H) are taken directly from the figure and are seen to be very close, but not identical, for the two materials. The small difference in the positions of the peaks might be caused by different amounts or different particle sizes of the MoO₃ used in the two experiments.

Table 1. TPR Results Of Unsupported MoO₃ *

Sample	Location of Maximum, (°C)		H ₂ Consumption h (mol H ₂ / mol MoO ₃)		Mo Valence, V _{Mo}	
	T _L	T _H	L	H	L	H
Commercial	660	>850	1.07	3.13	3.86	-0.26
In-House	676	>850	1.04	3.10	3.92	-0.20

* L: low-temperature reduction, H: high-temperature reduction.

In Table 1, the hydrogen consumption entries (h) refer to the area of the corresponding peak, calibrated by TPR with CuO, assuming that the CuO is fully reduced to the metal. (As shown above, this is a reasonable assumption.) The Mo valence values (V_{Mo}) are calculated by assuming that the hydrogen is consumed by a stoichiometric reaction of the type:

where h is the hydrogen consumption (mol H₂ / mol MoO₃); the valence of Mo is then given by:

$$V_{\text{Mo}} = 2(3-h) \quad (2)$$

According to Table 1, the ratio of the area of the high-temperature peak to the area of the low-temperature peak is approximately 3. Further, for both purchased and self-prepared MoO₃, the Mo valence value V_{Mo} after the low-temperature reduction (corresponding to the first peak) is close to +4, while V_{Mo} ≈ 0 after the whole TPR run, *i.e.*, metallic Mo is formed after the high-temperature reduction. These results suggest that the reduction of bulk MoO₃ under our TPR experimental conditions consists of two distinct steps. The MoO₃ is reduced to MoO₂ in the first step, while the MoO₂ is further reduced to metallic Mo at higher temperatures. This is consistent with other results (20,21).

Activated Carbon Support

For the activated carbon support, Table 2 lists the locations of the peaks as well as the integrated areas of the TPR curves and of the TPD curve, all based on Figure 2. The parameters for the N₂-calcined samples and the fresh carbon samples are very similar to each other. This is an indication of similar reducibility.

Table 2. TPR and TPD Curves for Activated Carbon Support

Experiment *	Location of Maximum (°C)		Area (a.u.) x 10 ⁻⁶	
	Positive Peak	Negative Peak	Positive Peak	Negative Peak
(a)	583	>850	6.76	1.04
(b)	573	>850	6.12	1.21
(d)	---	>850	---	3.76

* Letters correspond to curves of Figure 2: (a), TPR of fresh sample; (b) TPR of N₂-calcined sample; (d) TPD of N₂-calcined sample.

The positive peak observed must be the reduction of the oxidized surface of the activated carbon support and/or some of its impurities. For the negative peak, there are two major possibilities. The first possibility is the decomposition of one or more impurities in the carbon, leading to the release of gases with higher thermal conductivity than that of the reducing gas (10% H₂ in Ar). The second possibility is the gasification of the carbon support, due to methanation in the H₂ atmosphere (22,23).

However, recall that the negative peak was also observed in the TPD experiment with the carbon support, *i.e.*, in the absence of hydrogen, and the position of the negative peak is basically the same as that in the TPR curves, whether for the fresh carbon sample or for the N₂-calcined carbon sample. This rules out the possibility of methanation of the activated carbon as the source of the negative peak. Moreover, no distinguishable peak, positive or negative, was observed in the repeated TPR run, where the same calcined carbon sample was used after being cooled to room temperature following the first TPR run. This also shows that methanation of the carbon support is not important during TPR runs.

Studies by Mims and coworkers have shown that graphite and glassy carbon surfaces are oxidized when exposed to air or water vapor (24,25). This oxidation occurs primarily on the edges rather than on the basal planes of graphite. Mims and coworkers found that oxygen is lost as CO in the temperature range 650 - 800°C when the carbon is heated in vacuum. Any CO released from the decomposition of the activated carbon would pass through the dry-ice/acetone trap. Since the thermal conductivity of CO is greater than that of argon, the thermal conductivity of the gas mixture would increase, causing a negative peak in the TPR or TPD spectrum. Therefore, it is likely that the negative peak is produced by CO in the gas phase released by the decomposition of an oxygen impurity in the activated carbon support.

The difference in the area of the negative peak between the TPD spectrum and the TPR spectrum can be attributed to two causes. First, differences in thermal conductivity for the Ar and 10% H₂ in Ar gas streams will produce different responses for a fixed

amount of CO. Hence, the same response would not be expected in both TPD and TPR experiments, even if the amount of CO desorbed were the same. Second, in the TPR experiment, some of the oxygen on the support reacts with H_2 at lower temperatures, giving positive peaks. Less oxygen remains at higher temperatures for activated carbon decomposition to form CO. Hence, less CO should be produced in a TPR experiment.

K/C Samples

The TPR spectra for the K/C samples were shown in Figure 3. It is reasonable to deconvolute these spectra into two positive peaks. One deconvolution for the 2.9 %K sample is shown in Figure 6. Note that only positive peaks have been fitted. The spectrum appears to be fitted well using a Gaussian-type function. The two peaks are denoted as R (at 494°C) and S (at 570°C). These two peaks indicate that there are two reducible species in a K/C sample.

Figure 6. Analysis of TPR spectrum for K/C sample (K loading = 5.8wt%). Top, experimental curve and composite curve from analysis. Bottom, individual peaks from analysis.

The location and area for each peak are summarized in Figure 7 as a function of the amount of K present. The areas of Peak R and Peak S change with the loading of K, but in a more-or-less complementary fashion. Peak R decreases with increasing K, while Peak S increases. The total area of the two peaks is nearly constant over the entire range of K loadings. That implies that K itself cannot be reduced under our experimental conditions for TPR. Kelemen and Mims drew similar conclusions from UPS measurements studying KOH adsorbed on graphite surfaces (25,26).

Figure 7. Quantitative results from TPR of K/C samples as functions of K loading: (a) peak areas; (b) peak positions. Peak nomenclature as in Figure 6.

From Figure 3, the total peak area is considerably greater than the area obtained for the carbon support alone. Further, Peak S is fairly close to the peak for the carbon support alone. Hence, Peak S is most probably from the reduction of the oxidized surface of the carbon support and/or its impurities itself. The addition of (even a small amount of) K probably modifies the reducibilities of other metal oxides in the carbon support considerably. Hence, it is possible that Peak R is from the reduction of a (second) impurity oxide in the carbon support, made more reducible by the presence of K.

Finally, Figure 7 shows that the positions of both Peak R and Peak S shift to lower temperatures with increasing K-doping level. Hence the higher the K-doping level, the easier is the reduction of the two reducible species.

Mo/C Samples

Figure 8 shows the typical fitting result of a TPR profile for a Mo/C catalyst. Again, only positive peaks have been fitted, and a Gaussian-type function can be used. For the Mo/C samples, a closer examination of the TPR curves shows that the profiles can be generally deconvoluted into four positive peaks, not three as qualitatively estimated earlier. (At Mo loadings above 9 wt%, an additional low-temperature peak may be observed. This is not considered here, as the magnitude of the corresponding area can be seen to be very small.) Of the four peaks, the next-to-highest, denoted as Peak S, is again most probably from the reduction of the oxidized surface of the carbon support itself, and/or its impurities, as that peak is also shown in the case of the carbon support alone. The other three peaks are designated as X, Y and Z as shown. Even though Peak Y is close to the position of Peak R in Figures 6 and 7, Peak Y is not ascribed to incremental reduction of an impurity by the presence of Mo. This is because Mo has not been reported to improve the reducibility of other species; we return to this later. Instead, Peak Y, as well as Peaks X and Z, correspond to the reduction of different Mo species on carbon support. Peaks X and Y (which occur below peak S) are grouped together as low-temperature peaks, with Peak Z (which occurs above Peak S) being the high-temperature peak.

Figure 8. Analysis of TPR spectrum for Mo/C sample (Mo loading = 9 wt%). Top, experimental curve and composite curve from analysis. Bottom, individual peaks from analysis.

The positions and areas of the deconvoluted peaks are shown in Figures 9a and 9b as functions of Mo loading. In performing the deconvolution, the reducibility of the impurities in the carbon support was assumed to remain unchanged when Mo is impregnated. In other words, the “specific” area of peak S, *i.e.*, the area per mole of carbon in the samples, was constrained to stay the same during the deconvolution of all the samples, as shown in Figure 9. However, the location of peak S, as given by the temperature corresponding to the maximum point of the peak, was allowed to change during the deconvolution procedure. The location of the peak is found to decrease with increased Mo loading, consistent with the behavior observed in Figure 7.

We define specific areas of Peaks X, Y and Z based on moles of Mo in the sample. The specific areas of Peaks X and Y decrease monotonically with Mo loading.

The positions of these two peaks also decrease monotonically with loading. However, the specific area of Peak Z passes through a maximum within the Mo loading range studied, and the location of Peak Z shifts to higher temperatures with increasing Mo loading.

Figure 9. Quantitative results from TPR of Mo/C samples as functions of Mo loading: (a) peak areas; (b) peak positions; (c) after-reduction valences of Mo and peak area ratio. Peak nomenclature as in Figure 8.

It should be noted that, while the specific area of Peak Y decreases somewhat with Mo loading, the actual area of this peak increases. This is in contrast to the behavior of Peak R in Figure 7, which stays constant or decreases with K loading. Clearly, any reduction of support impurity that occurs in this region of the TPR spectrum of Mo/C is negligible, and all of Peak Y may reasonably be ascribed to the reduction of a Mo species.

Shown in Figure 9c are the calculated values of Mo valences after low- and high-temperature reductions. In both cases, the Mo valences increase with Mo loading. This indicates that the extents of reduction decrease with Mo loading. Consistent with this, Figure 9c also shows that the ratio of the area of the high-temperature peak (Z) to the total area of the two low-temperature peaks (X and Y) increases with Mo loading. (This was also qualitatively noted in the Results.) Accordingly, varying the Mo loading changes not only the total amount of Mo in the catalyst, but also the distribution of the different Mo species.

It is widely recognized that the distribution of Mo species on supported Mo-based catalysts is influenced by the preparation method of the catalyst, such as the nature of support employed, the Mo precursor, and the drying and calcination conditions. For example, after drying a Mo/Al₂O₃ catalyst, Mo was found to be converted from an octahedral coordination [Mo(O)] in paramolybdate ion to a tetrahedral coordination [Mo(T)]. Mo(T) was attributed to Al₂(MoO₄)₃, either as a surface complex or as a bulk phase; whereas Mo(O) has been assigned to a surface complex such as Al₂(Mo₇O₂₄) or to bulk MoO₃. Upon calcination, both Mo(O) and Mo(T) species exist (27). Mo(T) and Mo(O) species have also been found in SiO₂-supported Mo catalysts (28).

A lower-temperature reduction peak in the TPR profiles has normally been assigned to the partial reduction of Mo and the reduction of readily reducible Mo species such as Mo(O), while a higher-temperature reduction peak has usually been attributed to the deep reduction of Mo, and the reduction of refractory Mo species such as Mo(T) (29). Hence, for our Mo/C samples, Peak Z might arise because of the deep reduction of Mo species and/or the reduction of refractory Mo(T) species on the carbon support, while Peaks Y and X may correspond to the partial reduction of Mo and/or the reduction of readily reducible Mo(O) species on the support.

The Mo(O) and Mo(T) species behave differently on the activated carbon support, in the present case, than has been reported for these materials on Al₂O₃ or SiO₂ supports. On Al₂O₃ or SiO₂ supports (28,30,31), the Mo(T) species (or the more-refractory Mo species) is dominant when the Mo loading is relatively low, but decreases in significance at higher loadings. However, for our Mo/C catalysts, the ratio of the area of the high-temperature peak to the total area of the two low-temperature peaks is greater than 1 only at a Mo loading of greater than 4-6 wt%; see Figure 9c. In other words, the Mo(O) species predominates only at loadings of less than 4 wt%: at loadings of greater than 6 wt%, the amount of Mo(T) species on activated carbon is more than the amount of Mo(O) species.

Further, consider the effect of the support on low-temperature reductions as a function of metal loading. For Al₂O₃- and SiO₂-supported Mo-based catalysts, Rajagopal et al. (28) found that, when the reduction temperature is programmed to no higher than 550°C, the extent of reduction of Mo increases with increasing Mo loading. However, for

our Mo/C catalysts at low temperatures, the extent of reduction of Mo decreases with Mo loading, and the Mo valence increases, as indicated by Figure 9c.

Differences between the activated-carbon support and alumina or silica supports are observed also during the high-temperature reduction. For Mo/Al₂O₃ and Mo/SiO₂ catalysts, when the temperature of a TPR experiment was ramped to 900°C, the Mo was found to be almost completely reduced to the metal (28). In the present work, while complete reductions of unsupported MoO₃, both commercial and in-house, were achieved at high temperature, complete reduction of Mo was not observed for the supported Mo/C catalysts even at 850°C, the highest temperature used here. Further, for Mo/C, the extent of reduction of Mo after high-temperature reduction decreases with Mo loading. This trend too is completely different from that observed on Mo/Al₂O₃ and Mo/SiO₂ catalysts. Consistent with these observations, the increase in the ratio of the area of the high-temperature peak to the total area of the two low-temperature peaks with Mo loading is also totally different from that for Mo/Al₂O₃ and Mo/SiO₂ catalysts. For the latter catalysts, the ratio of Mo(T) (or Mo species reducible only at high temperature) to Mo(O) (or low-temperature reducible Mo species) decreases with Mo loading.

The reasons for these differences may be related to the surface properties of the support used. Note that the surface of Al₂O₃ contains mostly basic -OH groups, but it also contains some neutral -OH groups and some weakly acidic -OH groups (32, 33). The basic -OH groups are expected to react preferentially with MoO₄²⁻ ions, where the Mo coordination is tetrahedral, while the neutral or weakly acidic -OH groups react with Mo₇O₂₄⁶⁻, where the Mo coordination is octahedral (27,32-35). On alumina, for low Mo loading, much of the adsorbed Mo species retains tetrahedral coordination in a highly dispersed state, even after calcination. With increasing Mo loading, the interaction between Mo and the support becomes weaker, because of a decreased dispersion, thus leading to a smaller fraction of Mo(T) species upon drying and calcination. Heptamolybdate ions, attached to neutral or slightly acidic -OH groups, probably do not retain their identity upon calcination. Instead, they form multilayers of Mo oxide, in which Mo is believed to be present as Mo(O). Consistent with the isoelectric point of SiO₂ being lower than that of Al₂O₃, neutral and weakly acidic -OH groups are the major groups on the surface of SiO₂. That leads to a smaller fraction of the Mo species being present as Mo(T) on a SiO₂-supported catalyst than on an Al₂O₃-supported catalyst. This was confirmed by Rajagopal et al. (28). When activated carbon is used as the support, as in our case, the almost inert surface of the carbon support could give rise to very weak interactions between the support and Mo. Therefore, upon calcination, multilayers of Mo oxide are expected to be formed predominantly, even at relatively low Mo loadings. For low-temperature reduction of C-supported catalysts, therefore, the extent of Mo reduction is deeper than when using Al₂O₃, or even SiO₂, as the support.

All these effects could also be explained by the formation of one or more less-easily reducible (or non-reducible) Mo species and/or Mo species inside the structure of carbon support, either during the TPR experiment or during the preparation of the samples. A molybdenum carbide could be such a species. Oyama et al. (36) report that some carbides can consume H₂ to form bulk hydrides. Hence some of the Mo carbides could chemically adsorb H₂ to form hydrides, leading to higher H₂ consumption (compared with Al₂O₃- or SiO₂-supported Mo-based catalysts) at high temperatures. Further, the higher the Mo loading, the larger the amount of carbides formed; therefore,

the extent of reduction of Mo after high-temperature reduction decreases with Mo loading. That explains why the ratio of the area of the high-temperature peak to the total area of the two low-temperature peaks increases with Mo loading for our Mo/C catalysts; again, different from the behavior of Mo/Al₂O₃ or Mo/SiO₂ materials.

While carbides can be produced by contacting molybdenum oxide with solid carbon, the carburization has to be carried out at a high temperature for a relative long period of time (35), in order to allow carbon atoms to diffuse into the matrix of the oxide and thereby to replace oxygen atoms. Although our Mo/C catalysts neither were treated at a very high temperature nor were heated for a long time in our experiments, Mo could be very well dispersed onto the surface or into the pore of the carbon support. This is because we used a liquid-phase Mo solution and an activated carbon with a high surface area during catalyst preparation; hence, the contacting area between Mo and carbon in Mo/C catalysts might be much larger in our experiments than it might be for reacting bulk MoO₃ with solid carbon. Therefore, Mo carbides could be formed at relatively low temperatures in our experiments. The amounts and the properties of carbides formed should depend on the Mo loading, the carbon support and the conditions used in the catalyst preparation and TPR experiments. There should also be a competition between the formation of Mo carbides and the forming of Mo(O) and Mo(T) species.

Mo-K / C Catalysts

We have shown earlier that K itself cannot be reduced under our experimental conditions; K as a promoter modifies the reducibilities of other compounds in the catalyst. Therefore, similar to those for Mo/C catalysts, the TPR spectra for Mo-K/C catalysts are also deconvoluted into four peaks. Figure 10 illustrates a typical TPR spectrum and the deconvoluted peaks for a Mo-K/C catalyst. The designation and the definition of those peaks are as in the case of the Mo/C samples. The results from the fitted TPR data are collected in Figure 11, as a function of the K-doping level, quantified as the molar ratio K/Mo.

Figure 10. Analysis of TPR spectrum for Mo-K/C sample (Mo loading = 18 wt%, K/Mo = 1.2). Top, experimental curve and composite curve from analysis. Bottom, individual peaks from analysis.

Figure 11. Quantitative results from TPR of Mo-K/C samples with 18 wt% Mo loading as functions of K/Mo: (a) peak areas; (b) peak positions; (c) after-reduction valences of Mo and peak area ratio. Peak nomenclature as in Figure 10.

As in Figure 9, the specific area of Peak S, *i.e.*, the area per mole of carbon in the samples, was constrained to stay the same during the deconvolution of all the samples, while the location of Peak S, as given by the temperature corresponding to the maximum point of the peak, was allowed to fluctuate. In this case, however, the location of Peak S does not change with increasing K/Mo. For both the low-temperature peaks, X and Y, the specific areas, *i.e.*, the areas per mole of Mo, increase greatly upon the addition of a small amount of K (K/Mo = 0.2); correspondingly, the specific area of the high-temperature peak, Peak Z, decreases. With an increase in K/Mo, the specific area of Peak X decreases, with a small local minimum around K/Mo = 1.2. Correspondingly, the specific

area of Peak Y continues to increase, but to a much smaller extent, with an increase in K/Mo. The total area of the low-temperature peaks, (X+Y), increases initially, then passes through a small local minimum around K/Mo = 1. On the other hand, the specific area of the high-temperature peak (Peak Z) decreases monotonically with increasing K/Mo. The change of the total specific areas of the three positive peaks passes through a maximum around K/Mo = 0.4, with a local minimum around K/Mo = 1.2.

These results indicate that the initial addition of K greatly promotes the formation of a Mo species reducible at low-temperature (a Mo(O) species), and retards the generation of Mo species that are reducible only at high-temperature (Mo(T) or other difficult-to-reduce Mo species). This means that Mo can be more easily reduced at low temperatures for catalysts with K than for those without K.

This trend can also be observed from the changes in the calculated Mo valences after low- and high-temperature reduction with increasing K/Mo values. The valence after low-temperature reduction decreases drastically with increasing K/Mo at low K/Mo values, then appears to level off around K/Mo = 1.4. The valence after high-temperature reduction also decreases rapidly at low K/Mo values, but then increases, again leveling off around K/Mo = 1. Similar to Mo/C catalysts, complete reduction of Mo was not observed for Mo-K/C catalysts under our TPR conditions.

The effects of the K promoter on the properties of unsupported or supported Mo-based catalysts have been investigated by many researchers. Xie and co-workers (12) verified that a new phase, consisting of K, S, Mo and O, is formed on the surface of K₂CO₃-doped MoS₂ catalysts, and this phase enhances the performance of catalysts for the synthesis of higher alcohols (ethanol and higher). The amount of the new phase increases with increasing K concentration until the weight ratio K₂CO₃ / MoS₂ reaches 0.6, corresponding to a K/Mo molar ratio of about 1.4. Jiang et al. (37) also confirmed the formation of a K-Mo interacting species, this one originating from the interaction between a KCl promoter and an alumina-supported molybdenum catalyst. In the case of Jiang et al., the amount of the interacting species is saturated at a K/Mo molar ratio of 0.8. Jiang et al. also claimed that the formation of Mo(T) species is greatly suppressed by the addition of potassium.

Analogously, a new species could also be formed on the surface of the Mo-K/C catalysts considered in the present work, due to the interaction between the K promoter and the Mo component. The effect of the formation of the new phase on the reducibility of the Mo-K/C catalyst may be quantified by the changes in the average Mo valence. After both high- and low-temperature reductions, these changes are most pronounced for the initial addition of K, while saturation occurs at a K/Mo molar ratio of 1.0-1.4 in our case. This threshold value at which saturation is achieved probably depends on the potassium salt, the support, and other catalyst-preparation variables.

It should be noted that the addition of K does not always enhance the reduction of Mo at low-temperature; some literature references note the contrary. Tatsumi et al. (38) reported that K inhibits the reduction of Mo(VI) on K-Mo/SiO₂ catalysts. DeCanio et al. (39) observed that the reduction of Mo(VI) is depressed by the K promoter in Mo/ γ -Al₂O₃. The reason for these differences is not clear.

Summary and Conclusions

A series of Mo-K/C catalysts were evaluated by means of TPR, and the results can be compared to unsupported catalysts as well as to catalysts supported on silica or alumina. First, the loading of Mo was increased, from 0 to 24 wt% of the activated carbon support. Then, for a fixed value of the Mo loading (18 wt%), the amount of the K dopant was increased from none to a value corresponding to a molar ratio $K/Mo = 1.6$. A few runs were carried out with K/C samples as well. The TPR data were obtained by ramping from room temperature to 850°C at 10°C/min using a mixture of 10% H_2 in Ar at 30 cc/min.

For the Mo/C species, three major peaks were observed, in addition to a peak attributable to the reduction of the oxidized surface of the support and/or of impurities in the support. Of the three major peaks, the two peaks which are found at lower temperatures than the support peak are interpreted as being due to the reduction of Mo species with octahedral coordination, denoted as Mo(O). The third, high-temperature, peak is interpreted as being due to the reduction of tetrahedrally coordinated Mo, Mo(T). Analogous results have been observed for catalysts supported on alumina and on silica in the literature, except that generally only two peaks are observed. Contrary to what is found in Mo/Al_2O_3 and Mo/SiO_2 catalysts, Mo(O) species are predominant only at relatively low Mo loadings in the present case. Further, the reducibility of Mo decreases with increasing Mo loading. Finally, while unsupported Mo can be reduced to the zero-valent metal at high temperature, this is not possible for the C-supported material. The differences between the activated carbon support and alumina or silica are probably because of the inert surface of the activated carbon. The decreased reducibility could be due to the formation of one or more less-easily reducible Mo species, such as the carbide, during the catalyst preparation process or in the TPR experiment itself. Some of the Mo carbides could adsorb hydrogen at high temperatures, resulting in a higher consumption of hydrogen for Mo/C, compared with Mo supported on Al_2O_3 or on SiO_2 .

The runs using K/C indicate that potassium itself can not be reduced; as a promoter, it modifies the reducibility of the oxidized surface of the support or of other impurity oxide components present. The addition of a small amount of potassium to Mo/C increases the area of the low-temperature peaks and decreases the area of the high-temperature peak. Larger amounts of potassium decrease the high-temperature peak area but have correspondingly little effect on the low-temperature peaks. Hence the presence of K enhances the formation of low-temperature reducible Mo species, or octahedrally coordinated Mo(O), while retarding the generation of Mo species that are reducible only at high temperatures, or tetrahedrally coordinated Mo(T). At low values of the molar ratio K/Mo , the Mo after high-temperature reduction is significantly more reduced than after low-temperature reduction, as evidenced by the much-lower value of the Mo valence for the high-temperature reduction. As the molar ratio K/Mo is increased, the Mo valence increases, but more so for the high-temperature reduction than for the low-temperature case. At a value of K/Mo around 1, the values of the Mo valence level off to approximately the same value for both high- and low-temperature reductions. The results are consistent with a K-Mo interacting species being formed at low K/Mo values, saturating at around $K/Mo = 1$. This is analogous to what has been observed in other cases.

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Chapter 7

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Background

The exact composition of the mixed alcohol product produced by a facility is dependent upon the catalysts and reactor conditions employed. Since the catalyst and reactor conditions are only imprecisely known at the present stage of the research, the actual composition of the mixed alcohol product can only be hypothesized. Therefore, the actual demand and value of this product cannot be determined until decisions are made regarding the product composition. However, some insight may be gained into the potential demand and market value for the proposed mixed alcohol fuel by examining the market for individual alcohols.

The near-term potential of methanol as a fuel oxygenate or neat fuel in the United States is questionable. Its use in this capacity is marred by numerous problems ranging from consumer and industry acceptance to its lack of economic competitiveness. Despite its relative abundance, consumption of methanol in gasoline has declined steadily from its high point of 400 million liters (106 MM gallons) in 1985 to less than 15 million liters (4 MM gallons) in 1987 [1]. By 1988, the demand for methanol as an octane enhancer had virtually disappeared.

Historically, this trend has been attributed to methanol's acceptance problems and its recent lost cost advantage over other octane enhancers. Many of the acceptance problems are a result of adverse publicity as well as mechanical problems. In the 1980's, several automobile manufacturers stated warranties would not be honored if owners used methanol enhanced gasoline blends in their cars. While these manufactures discouraged the use of gasoline containing methanol as an octane enhancer, they warranted the use of gasoline blends containing up to 10% ethanol. Methanol's acceptance was further eroded by technical problems such as fuel foaming, aldehydes emissions, vapor locking in hot weather, and starting problems in cold weather, along with numerous corrosion problems in the engine and fuel system. Reports of these problems prompted the EPA to limit the amount of neat methanol in unleaded gasoline to 0.3% by volume despite the fact that

neat methanol concentrations of up to 3% (vol) have been used in Germany for several years without any reported problems [1].

The use of ethanol was met with less resistance due in part to the efforts of the corn lobby from the Midwest. Initially instituted as a means of conserving crude oil in the late 1970's, a mixture of 10% ethanol and 90% gasoline was used in place of straight gasoline. The manufacture of ethanol soon became profitable as a result of government subsidies, and demand for ethanol continued to grow through the 1980's at the subsidized prices. However, these subsidies only apply to fermentation ethanol and are dependent on legislative support. Without these subsidies, its use as a fuel additive would be no longer economically viable, since, from a pure manufacturing cost perspective, it is the most expensive of all currently used blending agents. Synthetic ethanol is also relatively expensive in comparison to other blending agents, which accounts for its lack of use in this market.

The most promising alcohol fuel additive, from cost and technical viewpoints, appears to be tertiary-butyl alcohol (TBA) which is currently approved by an EPA interpretative rule that permits blends approaching 16% by volume for straight TBA. However, ARCO Chemical Company appears to have a monopoly on the production of TBA since 1986. TBA may also be used as a cosolvent with methanol, although its use in this capacity has declined since methanol blending was stopped because of problems stated previously. The features that make this product so attractive are that it can be used in its original form or it can be further refined to produce high purity isobutylene, which can be reacted with methanol to produce methyl tertiary butyl ether (MTBE).

Isobutanol was once considered to be an unwanted by-product generated in the production of oxo-chemicals derived from propylene. This may, in part, explain its growth as a fuel additive in the early 1980's. A number of companies under the United States Environmental Protection Agency's (EPA) Petrocoal waiver [2] began to use alcohols as octane enhancers during this time period. Under this waiver, the addition of up to 15 volume percent alcohol could be used as a blending agent in gasoline. However, the composition of the alcohol was limited to a maximum of 12 percent methanol and a maximum methyl to butyl alcohol ratio of 6.5 to 1. Consumption of isobutanol and n-butanol peaked under this waiver at approximately 9100 metric tons and 4500 metric tons, respectively, in 1983, after which the market essentially collapsed due in part to the EPA's efforts to rescind the Petrocoal waiver.

Continued growth in the propylene-based oxo-chemicals industry has forced producers of oxo-chemicals to rely on virtually any source of C₄ oxo-molecules, causing the conventional price spread between n-butanol and isobutanol to decrease significantly. As a result of this significant price inducement, isobutanol was adopted as a substitute for n-butanol in many markets. However, the overall tightening of C₄ feedstocks also decreased the economic viability of adding butanols to gasoline. Currently, butanols are more valuable as chemical feedstocks than fuels. Estimates suggest that butanol may be economical if it can be produced for less than \$0.37 per liter (\$1.40/gal) provided that the

pre-tax gate cost of gasoline is in the range of \$ 0.19 to \$0.21 per liter (\$0.72-0.79/gal) [2].

Although the Petrocoal waiver permitting the use of butyl alcohols was revoked in 1984, legislation as of September 1990 permits the use of butanol as an octane enhancer. Currently aliphatic alcohols (other than methanol) may be added to gasoline so long as there is no more than 2.7 percent oxygen by mass. There are specific EPA waivers for various blends of alcohols with gasoline, but all strictly limit methanol. Since the fuel product is likely to be a blend of various alcohols, it should be emphasized that methanol appears to be an undesirable product from the standpoint of EPA regulations. Therefore, to avoid complications of obtaining waivers for the use of this alcohol product, it may be advisable to eliminate methanol from the mixed alcohol fuel.

The potential local annual market (West Virginia and a surrounding seven-state area) is approximately 6.4 billion liters (1700 million gallons) used as a 10% blend. The potential problems from the marketing aspect may be regulatory if the alcohol fuel product does not fall into one of the approved categories.

Chapter 8

Approach and Rationale

Coal-derived transportation fuels can be generated by indirect liquefaction in which coal is first converted to syngas and the syngas is then upgraded to motor fuels. The commercial feasibility of this conversion method depends upon the net cost of the syngas, the cost of syngas conversion, and the value of the finished products relative to existing competing products, such as gasoline, ethanol, and MTBE. In addition, the relative environmental costs of producing and using these competing fuels must also be compared.

Our approach is to study a series of cases (with the goal of producing gasoline oxygenate additives from coal-derived syngas), each characterized by discrete process choices. For cases that show distinct advantages, we would proceed to more detailed process analysis and optimization. The objective functions used to discriminate between alternatives are manufacturing cost per unit of mixed alcohol product and overall energy efficiency. The economies of scale for the cases are studied relative to both technical and market constraints. We have made several process choices, which are described in this section. These methodologies are described in more detail in Section 4.

8.1 Target Blends

To provide a production goal for the designs, target products were identified. All fuels for light-duty gasoline vehicles must be certified by EPA. Two blends already certified (i.e., granted waivers) are the DuPont blend [3,4] and OCTAMIXTM. [5] These blends contain <5% (vol) methanol and >2.5% (vol) higher alcohols (C₂-C₄ for DuPont, C₂-C₈ for OCTAMIXTM) plus 40 mg/liter of a corrosion inhibitor necessitated because water is soluble enough in methanol to corrode automobile gasoline distribution systems. We chose these certified blends as standards for this study for two reasons. First, the anticipated product slate from our process should satisfy the requirements of these certified blends without major purification. Second, this approach is also a conservative strategy. As future environmental regulations are largely unpredictable, we chose not to design around a less restrictive standard that might prove to be unacceptable under future regulations. All products produced would meet existing regulations.

8.2 Choice of Cases

Given the goals of the economic evaluation, a number of technological cases must be designed and tested. Five concerns guide the choice of cases.

1. A comparison of the manufacturing cost of syngas from coal with that from natural gas is needed. Since natural gas is the current lowest-cost source for all

manufactured syngas, this case is used as a benchmark by which to measure all projects using coal gasification. Hybrid cases are also investigated in order to uncover possible synergies between the two raw materials available to produce syngas.

2. An investigation of by-product production in coal gasification is needed since this requirement presents a number of production and marketing constraints that seriously impact the net cost of syngas and the resultant transportation fuels. For example, processes that convert coal to syngas without by-products can be economical only if their costs are less than the net costs of processes that co-produce syngas and by-products. Also, the production of by-products can present serious marketing problems. Lastly, the social costs of coal must be considered when the net costs of syngas process alternatives are compared.
3. A comparison of alternative modern gasifier technologies is essential.
4. A case is considered in which the higher alcohol fuel additives are by-products of a power generation facility.
5. Economic models must recognize present environmental regulation and the possibility of future changes.

Seven cases are chosen to the test range of possible technological and economic configurations identified as being important. The seven cases are shown in Table 3.1.

Table 3.1 Summary of Designs		
Case Number	Gasifier	H₂/CO adjustment
1	Texaco	steam reforming of natural gas
2	Lurgi	pressure swing adsorption to separate excess H ₂
3A/3B [†]	None (natural gas reformation only)	pressure swing adsorption to separate excess H ₂
4	Texaco	sour gas shift converter
5	Shell	sour gas shift converter
6	Shell	steam reforming of natural gas
7 [‡]	Texaco	sour gas shift converter
[†] The difference between these sub-cases is the price of natural gas. [‡] In this case, higher-alcohols are a by-product of a power production facility.		

They represent a broad range of cases, the details of which are given in Section 5 and in the Appendices. Our overall approach to these cases is that the alcohol synthesis and separation portion of the flowsheet is decoupled from the syngas production portion. This scheme is shown in Figure 3.1. Thus, the characteristic features of the various cases are their gasifier design and method for H₂/CO adjustment. For each case, the design downstream of the syngas cleaning is identical.

The natural gas case (Case 3) and IGCC case (Case 7) are chosen as a benchmarks. Although the goal of the study was to identify opportunities using coal-derived synthesis gas, such syngas is presently (for all gasifier types) more expensive than syngas produced from natural gas. Thus, Cases 3 and 7 present frames of reference for all case analyses. The Lurgi gasifier case (Case 2) was also chosen as a point of reference. This gasifier technology is proven, yet not state-of-the-art. This case allowed us to study the potential of producing additional by-products, as well as to quantify the improvements obtained by advances in gasifier design. The other five cases involve modern gasifiers (Texaco and Shell), each with H₂/CO adjustment by either water-gas shift or natural gas reformation. The slurry-fed Texaco design was chosen because it is a proven technology with many

commercial installations. The Shell gasifier, with gas-conveyed feed, is representative of newer designs that are only now being built on a commercial scale.

8.3 Energy Park

The range of cases allowed us to use a holistic approach, which we call the *Energy Park* concept. An energy park is a combination of facilities that utilizes one or more types of fuel in one or more types of conversion technologies to produce more than one product with the goal of reducing costs through the production of by-products, increased energy efficiency, and reduced pollution. This means that all types of fuels, including coal and natural gas, should be considered as inputs. In fact, hybrid cases, such as Cases 1 and 6, were investigated to study potential synergies between raw materials. In addition, the co-production of power, alcohol fuel, coal chemicals, and useful steam must be considered as a means to increase energy utilization efficiencies and to decrease overall costs.

If energy is used more efficiently, not only are costs lowered, but pollution is also reduced. For example, a conventional steam-electric generation plant converts only 35 percent of the energy from combustion to usable electric energy. For the quantity of power produced, a proportional amount of pollutants is also produced. If the energy in the waste heat is captured, the overall efficiency can be improved. This increase in efficiency results in a decline in pollution per usable energy unit output. Thus, energy efficiency as well as costs can be used to determine the feasibility of a process. Therefore, more usable energy is obtained from the same amount of fuel.

Figure 3.1: Alternative Syngas and Alcohol Production Pathways

Chapter 9

Methodology

9.1 Design

9.1.1 Case Studies

There were seven case studies developed in this work, which are presented in this report. Each of the first six case studies uses a different front-end configuration of process blocks to produce essentially the same amount of synthesis gas feed, with the same composition, to the alcohol production block. The mixed alcohol product is the same for each of the cases. The main difference between the case studies lies in what material is used as the source of the carbon and hydrogen for the synthesis gas production. Cases 4 and 5 use only coal as the raw material, and each case uses a different gasifier. Cases 1 and 6 use a mixture of coal and natural gas as the raw material, with each case using a different gasifier. Case 7 is a power production facility with a base-load of 500 MW and a peaking load of 100 MW for two two-hour periods per day, with higher alcohols produced as by-products. The peaking power is produced by burning methanol produced in the synthesis reactor, with the higher alcohols sold as fuel additives. For all these cases, we assume a Pittsburgh coal. Case 3 uses natural gas only and serves as a baseline economic comparison for the other cases. Two subcases are considered. For Case 3A, we assume a natural gas cost of \$106/1000 std m³. For Case 3B, we assume \$61.8/1000 std m³. The cost used in Case 3A represents a typical industrial natural gas price in West Virginia. The Case 3B cost is the corresponding Gulf Coast price.

The optimal synthesis gas feed to a process to produce C-1 and higher alcohols should contain a hydrogen to carbon monoxide ratio (H_2/CO) of 1.1/1 [6, 7]. Since neither coal nor natural gas can be used directly to produce a synthesis gas with this H_2/CO ratio, additional processing of the gas is required. Two basic approaches were taken in this regard when considering coal. The first approach was to supplement the hydrogen-deficient synthesis gas from a coal gasifier with the hydrogen-rich gas produced by reforming natural gas. By adjusting the ratio of coal and natural gas feeds to the plant, the desired composition and flow of synthesis gas was produced by directly blending the cleaned gases from both processes. The second approach was to adjust the H_2/CO ratio of the gas produced in the coal gasifier by shifting some of the carbon monoxide to carbon dioxide via the water-gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$.

This second approach has the disadvantage of requiring a much larger coal feed and hence requires larger (or more) gasifiers to produce the required amount of synthesis gas. In Case 3 the synthesis gas is produced by the steam reformation of natural gas followed by the removal of excess hydrogen via pressure swing adsorption. The relative benefits and economic potentials of each of these cases are considered further in Section 5.

9.1.2 Scale of Operation

The choice of the size of plant to be considered depended upon a combination of process and economic constraints. Upper and lower bounds on the size of the production facility were set using the rationale outlined below.

The lower bound on the size of the production facility was set by considering economically reasonable lower bounds on both coal and oxygen feed rates to the plant. Since the main thrust of this work was to concentrate on the gasification of coal to produce synthesis gas, it was decided to focus mainly on modern oxygen-blown gasifiers such as the Texaco and Shell processes. A reasonable lower bound on coal feed was considered to be one unit train of coal (~9100 metric tons (10,000 tons)) per week (1270 metric tons/day, 1400 tons/day). We used cryogenic separation of air, since this is the best way to produce the corresponding quantities (~2000 metric tons/day) of high purity oxygen [8]. For the purposes of discussion, we are assuming that this coal-to-alcohol-fuels plant would be located in southern West Virginia.

If the minimum sized plant were scaled-up by a factor of eight, 5.1 billion liters/yr (32 MM bbl/yr) of alcohol fuel additive would be produced, which is about 8% of the total gasoline sold in a seven-state area surrounding West Virginia. This scale seems a reasonable upper limit on plant size if the alcohol fuel is to be used as an additive comprising <10% (vol) in gasoline. Finally, for most cases, this limit resulted in plant scales up to 20 unit trains of coal per week (about 10 million tons/year). This represents the output of three of the largest mines in West Virginia. The coal supply pattern also indicates that this is a maximum size of plant. The facility must be located near mines of this size so that transportation costs do not significantly increase the delivered cost of coal to the alcohol plant. Because it uses more coal per unit of alcohol product, Case 2 reaches this coal constraint at a higher alcohol production rate of only 2.5 billion liter/yr (16 MM bbl/yr).

There are also limits to plant size because of natural gas supply limitations. Case 6, for example, uses approximately 220 million standard cubic meters (7.8 billion cubic feet) of natural gas a year to produce approximately 640 million liters/yr (4 MM bbl/yr) of alcohol. This is equivalent to roughly 16 percent of the industrial gas consumption for the state of West Virginia. If this facility's capacity is increased by a factor of eight, the amount of natural gas consumed by this facility would be equivalent to approximately 60 percent of the *total* natural gas consumption of this state. The possibility of supplementing commercial natural gas with coal bed methane in West Virginia was examined as a means of circumventing this potential constraint. Since there are no reliable statistics on coal bed methane reserves for West Virginia, an estimate was made using different sources of data [9, 10]. Although there appear to be sufficient reserves to meet the requirements of the proposed facility, collection and quality problems overshadow any potential benefits that coal bed methane may offer.

Since large scale facilities using steam reformation of natural gas for the production of syngas, such as Case 3A at x4 and x8 scales, would not be feasible for this region, an

alternative natural gas case (Case 3B) has been added for comparison purposes. Case 3B uses the same process design as Case 3A; however, it assumes a lower natural gas price that would be indicative of regions capable of supplying large quantities of natural gas on contract to a facility of this nature.

9.1.3 Available Technology

The rationale for selecting specific process modules is as follows. The choice of modern, efficient, oxygen-blown gasifiers (Shell and Texaco) was addressed previously. A Lurgi gasifier was also used in one case (Case 2) in an attempt to produce a suite of profitable coal-liquid by-products. This approach proved to be economically unattractive and was not pursued further.

Cryogenic oxygen separation was preferred to pressure swing adsorption or membrane separation because of the large scale of oxygen production required for this process. Rectisol was chosen because of its wide-spread use in the removal of acid gases from coal-derived synthesis gas. UCarSol, a proprietary Union Carbide solvent process, was also considered. However, this process does not work because of a “temperature bulge” caused by heat generated in the exothermic absorption of acid gases leading to unfavorable equilibrium conditions for the absorption. The Claus and Beavon processes were chosen for sulfur removal because they are proven technologies. While there are alternatives, the costs of these modules are very small compared to the cost of the entire process; hence, there is little benefit to investigating alternatives.

The alcohol synthesis reactor using an MoS_2 catalyst and producing linear $\text{C}_1\text{-C}_5$ alcohols was chosen because of the published information available on product distributions [7] and reactor costs and because Task 1 of this project is focused on developing novel MoS_2 catalysts.

9.2 Economics

9.2.1 Assumptions

Equipment costs were obtained from previous designs [6, 7, 11-13]. Costs were assigned to a module (e.g., Rectisol) rather than by evaluating each piece of equipment within the module. To determine the appropriate cost for a module of the desired size, exponential scaling was used within a train, and linear scaling was used for multiple trains.

The prices assumed for reactants, products, and by-products are shown in Table 4.2. It was assumed that all by-products such as sulfur and slag could be sold at the indicated price.

A method using MTBE as a reference was used to assign values to higher alcohol fuel products. The method is based upon RVP and octane number, and a similar method has been used previously to determine the value of other fuel additives [14]. The results are presented in Table 4.3. The value of unleaded gasoline {50 kPa (7.2 psia) RVP, 87 octane ((RON+MON)/2)} was chosen as \$0.170/liter (\$0.644/gal). N-butane was valued at \$0.085/liter (\$0.321/gal), and MTBE was valued at \$0.223/L (\$0.845/gal). These values are the means of the weekly spot prices during 1992 [15, 16]. The relationship used was

$$value(\$ / L) = 0.023 - 0.0037(RVP \text{ in } kPa) + 0.00237(octane \text{ number})$$

Table 4.2
Price of Reactants, Products, and By-products

Item	Price
Coal	\$33/metric ton delivered
Power	\$0.05/kWh
Peaking Power	\$0.10/kWh
Slag	\$5.5/metric ton
Sulfur	\$300/metric ton
Coal Tar/Liquid*	\$99.1/metric ton
Hydrogen [†]	\$35.3/1000 std m ³ (Case 3A)
	\$20.6/1000 std m ³ (Case 3B)
Natural Gas [†]	\$106/1000 std m ³ (Case 3A)
	\$61.8/1000 std m ³ (Case 3B)

*Based on its fuel value at \$3/MM BTU

[†] Case 3A prices are for West Virginia
Case 3B prices are for Gulf Coast

Table 4.3
Estimated Value of Alcohol Fuel Additives

Component	Blending Value (\$/liter)	Blending Value (\$/gal)
methanol	0.148	0.561
ethanol	0.235	0.893
n-propanol	0.185	0.699
n-butanol	0.183	0.693
n-pentanol	0.180	0.681
mixed alcohol product*	0.197	0.747
MTBE	0.223	0.845

*value obtained based upon product distribution
from alcohol synthesis reactor [7]

These values do not recognize the effects of substitution on the MTBE price should a less expensive competitive product be placed on the oxygenate market. The lowest price for which MTBE could be sold has not been determined. However, we have estimated the marginal producer's cost of MTBE as \$0.159/liter (\$0.600/gal). If the price of MTBE declines, so would the relative values of the other blending agents.

9.2.2 Measures of Economic Feasibility

The alcohol production process has been divided into two stages. The first stage entails those steps required to produce synthesis gas, while the second stage deals with the steps involved with the transformation of the synthesis gas into the alcohol fuel and waste. Since the alcohol product can be manufactured from synthesis gas derived from either coal or natural gas, the price of the synthesis gas derived from its respective source becomes a critical factor in determining the choice of feed stock. Thus, the prices for the respective syngases must be derived because they are intermediate products that are not marketed. Consequently, price data do not exist.

The manufacturing cost is defined as the sum of the raw materials and operating costs plus a capital recovery annuity, minus by-product credits. This model simply amortizes the installed capital investment over the anticipated life of the plant (which in this case is assumed to be twenty years) at a given interest rate (which we have assumed to be 10%, given current economic conditions). Besides utilities, the operating costs also include maintenance, insurance, plant overhead, and sustaining capital charges. These latter costs are estimated to be 1.5 times the annualized capital investment [11] (which is approximately equivalent to 17.6 percent of the total installed capital [17]).

9.3 Screening of Alternatives

Two screening mechanisms have been employed for the purpose of eliminating and ranking technologies. The first process entails the calculation of the manufacturing cost for the mixed alcohols produced by the various technologies. These costs (in 1992 dollars) are current, identifiable and are calculated to include all by-product credits. Therefore, the process with the lowest manufacturing cost represents the best technology. The second screening alternative that was considered was overall energy efficiency. This method was considered to ensure that the optimal technology was selected given the level of uncertainty of future costs and prices. The thermal efficiencies were calculated based upon the total energy input in relation to the total energy output. Energy flows were also analyzed to determine which process provided the best alcohol conversion. This was measured by analyzing the total energy input in relation to the total energy content (heats of combustion) of the various products produced. The results of these methods are given in Section 6 of this report.

Chapter 10

Description of Cases

10.1 Process Concept

A generic process for converting coal to syngas to higher alcohol fuel additives is outlined in Figure 5.1. The oxygen plant provides oxygen for the gasifier. The sour gas shift converter adjusts the H_2/CO ratio to the desired ratio of 1.1/1 using the water gas shift reaction, with the necessary steam provided by vaporization of water used to slurry the coal. An alternative process might employ steam reforming of natural gas ($CH_4 + H_2O \leftrightarrow CO + 3H_2$) to adjust this ratio. Acid gas treatment and sulfur removal precede alcohol synthesis. The alcohol synthesis reactor is a shell-and-tube design with the MoS_2 catalyst in the shell. Use of the MoS_2 catalyst yields a product that is primarily C_1 - C_5 linear alcohols [7]. Table 5.1 gives a typical reactor yield.

Table 5.1 Typical Product Yields from MoS_2 Catalyst based on 40% CO Conversion		
carbon dioxide	32.00%	(mol)
methane	9.45%	
ethane	0.75%	
methanol	13.46%	
ethanol	28.08%	
propanols	9.32%	
butanols	3.13%	
C_5 alcohols	1.63%	
methyl acetate	1.16%	
ethyl acetate	<u>1.02%</u>	
total	100%	

10.2 Designs

The features of the seven cases were shown in Table 3.1. Detailed descriptions of each case (with flowsheet and flow tables) are included in the appendices. A very brief overview of each case is given below.

Case 1 is shown in the Appendix A, Figure A.1. The Texaco gasifier is oxygen blown, operates at high temperature ($1300^\circ C$ ($\sim 2400^\circ F$), 8 MPa (80 atm)), and is fed a coal-water slurry. This down-flow entrained design is currently being used in over 90

commercial applications world-wide. For larger scales we assume multiple trains. To enhance the H_2/CO ratio, natural gas is steam reformed.

Case 2 (Appendix B, Figure B.1) incorporates a Lurgi (dry-bottom) gasifier design. This gasifier is oxygen blown and operates at moderate temperatures (400°C (750°F), 2.8 MPa (28 atm)). It is the design used at the Great Plains Gasification Plant [11] and produces phenolic and related by-products. To reduce the H_2/CO ratio, pressure swing adsorption is used to separate the excess H_2 .

Cases 3A and 3B (Appendix C, Figure C.1) are benchmark cases with natural gas as the feed. Through steam reformation, a syngas that is too rich in H_2 is produced. Pressure swing adsorption is used to separate the excess hydrogen. Some of the excess hydrogen is used to balance process power needs, and the remaining hydrogen is given a

value based on its heating value relative to that of natural gas (Table 4.2). The difference between Cases 3A and 3B are that the former uses a West Virginia natural gas price (\$106/1000 std m³, \$3.00/10⁶ BTU) and the latter uses a Gulf Coast natural gas price (\$61.8/1000 std m³, \$1.75/10⁶ BTU).

Case 4 is shown in the Appendix D, Figure D.1. As in Case 1, a Texaco gasifier is used. However, the hydrogen deficit is corrected by producing more syngas from the coal and then using a water-gas shift reactor to produce more hydrogen. Thus, more gasifiers are required in Case 4 than in Case 1.

Case 5 (Appendix E, Figure E.1) incorporates a Shell gasifier. As with the Texaco design, this gasifier is oxygen blown. It operates at high temperature and moderate pressure (1300°C (~2400°F), 2.8 MPa (28 atm)). However, the pulverized coal is conveyed to the gasifier in a gas stream (CO₂ in this case). This down-flow entrained design is not in current commercial use for coal gasification. However, it has been proven on pilot scale, and an integrated, combined-cycle, coal gasification power plant using this technology is under construction in The Netherlands [18]. For larger scales we assume multiple trains. To enhance the H₂/CO ratio, more syngas is produced from coal and a water-gas shift reactor is used.

Case 6 is shown in the Appendix F, Figure F.1. As in Case 5, a Shell gasifier is used. However, the hydrogen deficit is corrected by steam reformation of natural gas. Thus, fewer gasifiers are required in Case 6 than in Case 5.

Case 7 is shown in the Appendix G, Figure G.1. It is an IGCC power plant with a net base load capacity of 500 MW and an additional 100 MW of peaking capacity (for 2 two-hour periods per day) derived from burning methanol separated from the mixed alcohol produced in the alcohol synthesis loop. Approximately 112 million liters/yr (30 million gallons/yr) of higher alcohols can be produced as a by-product of this process for use as oxygenates.

In all of the designs, the purge from the alcohol synthesis loop is used to generate power. Additionally, steam produced by recovering heat from the gasifier outlet is also used to generate power.

Chapter 11

Results and Discussion

11.1 Economics of Designs

Table 6.1 is a summary of capital costs for the seven cases at all scales. Individual unit costs are tabulated in Appendix H.

Table 6.1 Capital Costs for Cases (in millions of dollars)				
Case #	x1	x2	x4	x8
1	562.80	958.96	1,778.88	3,311.88
2	1,817.14	3,438.22	--	--
3	335.89	562.28	981.88	1,748.10
4	650.27	1,182.33	2,171.06	4,076.87
5	629.92	1,138.72	2,066.51	3,926.76
6	416.61	734.38	1,347.78	2,488.20
7	999.63	--	--	--

Figure 6.1 shows the manufacturing cost of higher alcohols for Cases 1-6 at different scales. The lowest scale (x1) produces 636 million liters/yr (4 MM bbl/yr). It is apparent that the most attractive option is to produce higher alcohols from synthesis gas produced by the steam reformation of natural gas available at Gulf Coast prices. The main reason for this result is the low capital investment associated with the natural gas reformation process. From Table 6.1, it can be seen that this investment is significantly lower than that for the other cases considered for the same alcohol output. Of the cases using coal as a raw material, the Shell Gasifier with natural gas is the best case, and can be better than natural gas, as long as the natural gas price is above \$2.45/MM BTU. The best coal case also involves a Shell Gasifier, and can be better than Shell coal/natural gas hybrid case, if the natural gas price exceeds \$4.94/MM BTU. Furthermore, the economic advantages of a Shell or Texaco gasifier over a Lurgi gasifier are clear. The manufacturing costs in Figure 6.1 represent a 10% real rate of return on capital over a 20 year plant life without considering the effects of taxes. If a plant life of 10 years is used, which is more typical in the chemical process industry, then all of the curves in Figure 6.1 using coal gasification will shift upwards, making natural gas the clearly superior option. The effects of differential inflation rates on coal and natural gas are discussed later in this section.

On Figure 6.1, the curves labeled Case 3A and Case 3B reflect the sensitivity of manufacturing costs to changes in natural gas prices. In Case 3A, the cost of natural gas

used is \$106/1000 std m³, which is a typical industrial price in West Virginia. In Case 3B, the cost is a typical Gulf Coast price of \$61.8/1000 std m³. In both cases, excess hydrogen is assigned a credit of approximately one-third that of natural gas, based on the respective heating values. These cases are detailed in Appendix C.

Considering the cases that use coal as a raw material, the process based around the Lurgi Gasifier (Case 2) is by far the worst option and is not considered further in this discussion. Of the remaining cases, all of which use modern oxygen-blown gasifiers, the cases which utilize a mixed feed of coal and natural gas (Cases 1 and 6) are superior, in terms of unit cost of product, to their respective counterparts (Cases 4 and 5) which use coal as the only feed material. Again the main reason for this result is the reduced capital investment associated with the cases using natural gas which in turn is mainly due to the reduced cost of the gasifier and oxygen plant. Comparisons between the Texaco and

Shell Gasifiers, with or without a natural gas feed, (Case 1 vs. 6 and Case 4 vs. 5), show the Shell to be slightly superior to the Texaco. For the hybrid cases (1 and 6), the substantial difference in manufacturing costs results from the increased natural gas requirement for Case 6 (Shell). This case, therefore, benefits from the fact that natural gas is a less expensive source of hydrogen than is syngas shifting.

In all of the cases, light hydrocarbon gases are separated from the alcohol fuel product, with a fraction recycled to the reactor and the remainder used to produce power in combustion turbines. The methane in the recycle was held constant at 21%, as in previous designs [7]. Optimization of the fraction recycled for each case does not appreciably alter the results in Figure 6.1, except for the Lurgi gasifier. For this case, the manufacturing cost is reduced by about \$0.35/gal at the optimum recycle fraction. The Lurgi gasifier is still the worst case, but not by as large a margin as in Figure 6.1.

From Figure 6.1, it is clear that natural gas is superior to coal as a source of alcohol fuels, as long as the price of natural gas is less than \$2.45/MM BTU (based on Case 6). However, it has been reported that natural gas suppliers are reluctant to provide long term contracts at this price, even with built-in inflation clauses [19]. The manufacturing cost of the alcohol derived from natural gas is a strong function of the raw material cost. The two cases, 3A and 3B, represent reasonable bounds for the cost of natural gas and clearly illustrate the sensitivity to raw material costs. Additional savings could be achieved in both cases 3A and 3B if the pressure-swing adsorption unit were replaced with a separation process that delivered the hydrogen-stripped syngas at close to the pressure of the feed to that process, e.g., membrane separation.

The cost of producing syngas from coal or from coal and natural gas is currently greater than 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. The effects of both are illustrated in Figures 6.2 and 6.3. 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 relative profitability of higher alcohol fuel additives with respect to MTBE depends upon both the initial manufacturing costs and the rate of change of these costs with time. Figures 6.2 and 6.3 show the results of an analysis of the relative costs of higher alcohol fuel additives assuming the following initial costs: coal, \$33/metric ton; oil, \$0.116/liter (\$18.45/bbl); MTBE, \$0.223/liter (\$35.49/bbl). The difference between Figures 6.2 and 6.3 is the different starting price of natural gas in Case 3. The starting price of natural gas in Case 6 is the West Virginia price, since the desired comparison is between a West Virginia hybrid plant and either a West Virginia or a Gulf Coast natural

gas only process. Table 6.2 shows the assumed inflation rate for each component of the economic analysis.

Figure 6.3
Projected Manufacturing Costs
and Blending Values

Table 6.2 Assumed Inflation Rates	
coal [20]	1.7%
natural gas [20]	3.5%
equipment and labor [21]	3.9%
hydrogen [20]	3.5%
slag [21]	3.2%
electricity [20]	0.55%
sulfur (estimated)	0.09%
alcohol fuel product*	3.2%
*assumed to be the same as the inflation rate of crude oil [20]	

As can be seen in Figures 6.2 and 6.3, the cheapest source of higher alcohol fuel additives depends upon the assumed starting price for natural gas. Different relative cost increases will change the ranking over time. From Figure 6.2 (natural gas at \$106/1000 m³), it appears that the hybrid case may be the most profitable relative to the alcohol blending value until 2003. After 2003, it appears that none of these cases will be profitable. From Figure 6.3 (natural gas at \$61.8/1000 m³), the hybrid case the natural gas case appears to be the most profitable until 2008. However, we have estimated the marginal producer's cost of MTBE as \$0.159/liter (\$0.600/gal). If the price of MTBE declines, so would the relative values of the other blending agents. Therefore, if the alcohol fuel product must compete with MTBE at the marginal producer's cost of MTBE, then none of the cases (neither coal, natural gas, nor a hybrid) would be profitable.

11.2 Energy Efficiency of Designs

Using the Energy Park concept, it is suggested that overall energy efficiencies may be used as a screening mechanism. Therefore, the overall thermal efficiencies and distribution of energy flows for the various cases are calculated to assess the viability of the various processes. These calculations are based upon the original design capacities of approximately 1.9 million liters of mixed alcohol/day (12,000 bbl/day). The total energy inputs and outputs for these cases are summarized in Table 6.3 and illustrated graphically in Figures 6.4 and 6.5. The most efficient processes are those which involve the use of natural gas or produce the least amount of electric power. Of these processes, the steam reformation of natural gas (Case 3) yields the best overall efficiency assuming full credit is given to the energy contained as H_2 . Closer examination of this process, however, reveals that only 22.5 percent of the total energy input actually goes to the production of alcohol. Given that the objective is to produce as much alcohol as possible, and that, at best, only half of the energy contained in H_2 can actually be recovered, Case 6 may provide better results. Case 6 has the highest efficiency with respect to alcohol conversion at 44.2 percent. However, the amount of natural gas consumed by these processes may impose a series of logistical problems if these facilities are located in remote areas not accessible to major natural gas distribution lines.

Figure 6.4
Overall Efficiency & Distributions

Figure 6.5
Energy Production and Consumption

Table 6.3
Overall Energy Efficiencies and Distributions for Designs

Case	1	2	3	4	5	6	7
Energy Input GJ/hr							
Coal	3501.48	17994.19	0.00	4757.02	4593.03	2159.17	6417.04
Natural Gas	871.81	0.00	7670.86	0.00	0.00	1750.43	0.00
Total	4373.29	17994.19	7670.86	4757.02	4593.03	3909.60	6417.04
Energy Output GJ/hr							
Alcohol	1728.00	1728.00	1728.00	1728.00	1728.00	1728.00	345.76
Electricity	352.44	2808.00	150.12	375.12	374.40	302.40	1919.77
H ₂	0.00	1771.78	4289.32	0.00	0.00	0.00	0
Light Coal Oil Mix	0.00	2026.93	0.00	0.00	0.00	0.00	0
Total	2080.44	8334.72	6167.44	2103.12	2102.40	2030.40	2265.53
Losses	2292.84	9659.48	1503.42	2653.89	2490.63	1879.20	4151.51
Energy Flows							
conversion to alcohol	39.51%	9.60%	22.53%	36.33%	37.62%	44.20%	5.39%
conversion to electricity	8.06%	15.61%	1.96%	7.89%	8.15%	7.73%	29.92%
conversion to H ₂	0.00%	9.85%	55.92%	0.00%	0.00%	0.00%	0.00%
conversion to coal oil	0.00%	11.26%	0.00%	0.00%	0.00%	0.00%	0.00%
conversion loss	52.43%	53.68%	19.60%	55.79%	54.23%	48.07%	64.70%
TOTAL EFFICIENCY	47.57%	46.32%	80.40%	44.21%	45.77%	51.93%	35.30%

Confronted with these potential problems, it appears that one of the less efficient technologies, which relies entirely on coal, may ultimately provide a feasible solution. Case 5, which uses a Shell gasifier in conjunction with a sour gas shift converter, appears to be only slightly less efficient than its counterpart Case 6, which uses steam reformation of natural gas to increase the hydrogen content of the syngas. The difference between the overall efficiencies of these two cases is approximately 6 percentage points.

However, the most efficient case, by wide margin, is Case 3, which uses only natural gas. If pollution credits based on CO₂ 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.

11.3 Fugitive Emissions

To construct a plant such as the one being designed here, current environmental regulations must be followed, and anticipated environmental regulations must be considered. Therefore, a preliminary environmental analysis of the sulfur removal portion of Case 1, at the smallest scale, has been completed. This case includes fugitive emissions and stack emissions. The sulfur portion of the process is emphasized because all of the sulfur compounds along with a major part of the process's CO, volatile organic contaminants (VOCs) which are precursors to ozone formation, and two hazardous air pollutants (methanol and COs) are found in this portion of the process. The results indicate that, for SO_x compounds, there will be no trouble meeting environmental regulations. However, for reduced sulfur compounds (H₂S and COS) and for ozone producing VOCs, the process is over the current threshold values. This requires application of BACT (Best Available Control Technology) which could significantly increase the cost of construction and operation of a coal to syngas to higher alcohols process. Details of this analysis are in Appendix A.

Chapter 12

Conclusions

- 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, 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 CO₂ 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.

Chapter 13

Recommendations and Future Work

13.1 Optimization

A solution methodology to maximize the profitability of alcohol synthesis, separation, and blending has been developed. The temperatures, pressures, flowrates, and key component recoveries in the separation steps are the optimization variables. This methodology is robust and flexible; therefore, a wide-range of processing conditions can be investigated yielding consistent and accurate results. This methodology is in the process of being applied to the alcohol synthesis and separation portion of the process.

13.2 Sensitivity Analysis

13.2.1 Process

A methodology, using Monte Carlo simulation, to determine the effects and influences of process variable uncertainties on the performance of a design has been developed [22]. Input variables in the model to be considered include the reaction product distribution, the operating temperatures of equipment (e.g., gasifiers, separators, etc.), and the estimates in the thermodynamic model used in the computer aided design simulation of the process. The output variables are the manufacturing cost and the energy efficiency of the plant. Determination of the parameters that may cause uncertainty in the process will be accomplished by choosing those parameters that are probabilistic in value and those which are not correlated to other more significant parameters. The result will be a range of expected operating conditions for the process and an indication of which variables' uncertainties are most likely to affect process operating conditions.

13.2.2 Cost and Price

Costs and prices are not known with certainty, and the expected ranges may be sufficiently large to affect the relative rankings of the tested options as well as their absolute economics. In addition to the costs and prices of the inputs and outputs, prices of substitutes, such as MTBE and gasoline, also affect process economics. The relative expected growth rate in natural gas, oil, and coal prices determine the time in which coal-derived alcohol fuels may become economical.

To explore the effects that changing input and product prices have on the process economics, sensitivity analysis (Monte Carlo simulation) will be used. The results will

indicate which processes have the most economic promise given the uncertainties of prices and costs.

13.3 Energy Park

The potential exists for an integrated approach to produce mixed alcohols and energy (with an emphasis on electric power) given the various technologies currently under consideration. Each technology has its own strengths and weaknesses. By taking advantage of the strengths of these various technologies, the overall economics of alcohol production may be improved. This integration may be achieved in the context of an Energy Park, as described in Section 3.3. Future efforts will focus on taking advantage of this possibility.

13.4 Possible Additional Case Studies

The present results of this work indicate that a facility to produce higher alcohols for use as transportation fuel additives from coal is currently uneconomical. This situation may, of course, change if significant savings can be found in gasifier technology or if the price of natural gas increases significantly. Possible alternative processing schemes may be sought to identify potentially profitable alternatives in this area. Examples of alternative processing schemes include:

1. Economically disadvantaged feedstocks (EDF's) such as vacuum residuum and petroleum coke should be considered as potential substitutes for coal. The surplus of these refinery derived materials gives rise to a potential window of opportunity and may offset some of the economic disadvantages of solid-based feed materials.
2. The possibility of converting methanol (and other higher alcohols) to ethers via condensation type reactions should be considered. For example, dimethyl ether (DME) has potential as a diesel fuel additive [23].

Consideration may be given to such alternatives in the future.

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Chapter 14

Appendices for chapters 7-13

The appendices that follow contain details of the six cases analyzed, for the smallest scale process considered. The appendices are as follows:

Appendix A	Case 1: Texaco gasifier and steam reforming of natural gas (including fugitive emissions study)
Appendix B	Case 2: Lurgi gasifier
Appendix C	Case 3: Natural gas only
Appendix D	Case 4: Texaco gasifier and sour gas shift converter
Appendix E	Case 5: Shell gasifier and sour gas shift converter
Appendix F	Case 6: Shell gasifier and steam reforming of natural gas
Appendix G	Case 7: Texaco gasifier and power production facility (higher alcohols as by-products and methanol burned to provide peaking power)
Appendix H	Scale-up and comparison of design cases

Appendices A-G are organized as follows:

Process description, equipment sizing, and cost

Flow Sheet

Flow Table

Energy Analysis

In addition, Appendix A contains the results of the fugitive emissions analysis. Finally, Appendix H contains a tabular comparison of the cases, a tabular summary of the capital costs for the scaled-up cases, and a tabular summary of the manufacturing cost.

Appendix A

Case 1: Texaco gasifier and steam reforming of natural gas (including fugitive emissions study)

CASE 1

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 0.96 million metric tons of coal, 0.82 million metric tons of oxygen, 0.18 billion standard cubic meters of natural gas, and produces 0.50 million metric tons of mixed alcohols per year.

SYNGAS PRODUCTION FROM NATURAL GAS

Compressed natural gas (stream 14) and steam (stream 15) are reacted in the Steam Reformation Block. The cooled output gas (stream 17) goes to the Rectisol Block. The cost for this unit was estimated from data found for a hydrogen production facility, with a scaling exponent of 0.8 [2]. The fuel gas usage for this block is estimated to be 30% of the natural gas feed.

COAL PREPARATION

Coal (stream 10) and water (stream 12), are sent to the Coal Preparation Block. The coal is crushed, mixed with the water, and pumped to the gasifier as a ~60% solids mixture by weight (stream 13). The Coal Preparation Block is composed of four plants from the Houston report. Plant 01 is the Coal Slurry Preparation Plant. The cost of this plant was scaled linearly due to its multiple train format; where each train can handle up to 1,150 tons of coal per day. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen

(stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not include the inlet air compressors or the outlet oxygen compressors. In the cryogenic system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. We also assume that some scale down is possible for this system, so the capital investment has been calculated linearly for the reduction in trains, and exponentially for throughput reduction per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas streams (streams 17 and 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A $\text{CO}_2\text{-N}_2$ mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

TEXACO GASIFIER

The coal slurry (stream 13) is mixed with compressed oxygen (stream 9) and burned at 1,200-1,400°C and 8,000 kPa in the Texaco Gasifier Block. The hot, raw gas (stream 8) is sent to the Syngas Heat Recovery Block, and the slag (stream 33) is sent to the Slag Handling Block. The equivalent of the Texaco Gasifier Block is Plant 03 in the Houston report, and each train can handle up to 958.3 tons of coal per day.

SLAG HANDLING

Molten slag from the Texaco Gasifier Block (stream 33) is direct quenched with water and sent to slag disposal (stream 37). A small amount of water (stream 36) is purged from the closed loop and is replaced by water make-up (stream 34). This block is the same as Houston Plant 63. The cost for this plant was estimated by exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

SYNGAS HEAT RECOVERY

The raw gas stream from the Texaco Gasifier Block (stream 8) at 1,300°C and 8,000 kPa enters the Syngas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 71). The raw gas stream exits at 300°C (stream 18), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 68). It is assumed that the raw gas stream is cooled further prior to entering the Rectisol Block. This block is part of Houston Plant 04.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 41) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [3].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [4].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. Its power requirements are included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [9]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [10].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [10]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Syngas Heat Recovery Block and the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [10]. This is a 3-stage steam turbine system. The high pressure stage inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be outlined. Also, there are alternatives that have not been fully considered which will be considered in more detail later. They are listed below along with the reasons behind them.

- Catalytic steam/methane reformation used to adjust the $H_2:CO$ ratio upwards. The ratio from coal gasification is less than 1. Since the optimal ratio for higher alcohol synthesis is approximately 1.1 - 1.2, an additional source of hydrogen was required. The reformer was assumed to operate at equilibrium, as suggested in the literature [8]. Other alternatives to this block are available and will be considered.

- The traditional method for purifying high quantities of pure oxygen is by cryogenics, which is used for this case. However, recent reports suggest that membrane and catalytic processes are becoming economically competitive with cryogenics. Therefore, we will examine these alternatives.
- The Rectisol system was chosen for this case for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that quantities of H₂S are beneficial if the reaction involves the MoS₂ catalyst. If this is so, then a system such as the Benfield acid gas removal process might be more suitable. The Benfield system does not remove as much H₂S and has lower capital and operating costs.
- The operating pressure for the Texaco gasifiers has been set at 8,000 kPa. This is the highest pressure indicated in the literature at which a Texaco gasifier has been run. Since the pressure required at the reactor is 14,000 kPa, we would of course like to run the gasifiers at as high a pressure as possible. Another limiting factor is the oxygen feed pressure. According to various sources, the highest pressure available with conventional centrifugal compressors is around 80 atmospheres. It is assumed that, because of the size of this case, a higher cost for the oxygen compressor would be acceptable in return for savings on feed gas compression. In addition, other gasification systems will also be investigated.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Synthesis Gas via Natural Gas	15.9
Coal Preparation	40.8
Texaco Gasifier	156.7
Slag Handling	3.0
Gas Turbines	45.0
Steam Turbines	22.1
Exhaust Gas Heat Recovery	9.9
Synthesis Gas Heat Recovery	4.6
Cryogenic Oxygen Production	89.3
Rectisol (Acid Gas Separation)	34.9
Claus (Sulfur Recovery)	10.3
Beavon	2.2
Alcohol Synthesis Loop	47.2
CO2 Removal	26.9
Other Compressors	54.1

TOTAL 562.8

(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)	562.8
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)	149.6
Coal (\$33/metric ton delivered)	31.8
Natural Gas (\$106/1000 cubic meters)	18.7
Other Expenses	99.2
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)	46.6
Power (\$0.05/kWh)	39.2
Slag (\$5.5/metric ton) (6)	0.6
Sulfur (\$300/metric ton) (7)	6.9

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 5 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (5). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-31.1	28.3
O2 Prep	2	500	9	8136	-10.8	10.1
Reform Comp	17C	1400	17	8106	-6.4	5.8
Rxtr Prep	22	8106	26	14000	-7.1	6.2
Recy Comp	56A	12666	56B	14000	-3.6	3.6
Total compressor needs					-58.9	
Other in plant needs					-10.1	
Total produced in steam and gas turbines					167.0	
Net power output					98.0	
Total installed compressor costs (1992 dollars)						54.1

REFERENCES

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9. Report TR-101789, Houston Lighting and Power Company's Evaluation of Coal Gasification Coproduction Energy Facilities, EPRI Project 3226-04, 1992.
10. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure A.1 : Block Flow Diagram for Case 1

Table A.1 Case 1 Flow Table

	001	001A	002	003	004	006	008	009	010	012
Ar	142.5	142.5				142.5				
C									6646.6	
CH3OH										
C2H5OH										
C3H7OH										
C4H9OH										
C5H11OH										
CO							4770.4			
CO2	4.9	4.9					1861.6			
COS							8.9			
CaCO3										
H2							3649.6		2716.0	
H2O	368.3	368.3					3098.6		76.5	4061.1
H2S							80.4			
N2	11933.5	11933.5		11933.5	11694.5		54.3		58.8	
NH3							9.1			
O2	3208.2	3208.2	3208.2					3208.2	523.5	
S									89.3	
Al2O3									124.4	
C3H6O2										
C4H8O2										
CH4							5.7			
C2H6										
kmol/hr	15657.5	15657.5	3208.2	11933.5	11694.5	142.5	13538.5	3208.2	10235.2	4061.1
kg/hr	449349.1	449349.1	102664.0	334137.8	327447.3	5700.1	283586.3	102664.0	120516.7	73098.9
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	1300.0	225.0	25.0	25.0
Press. (KPA)	500.0	101.3	500.0	500.0	500.0	500.0	8135.8	8135.8	101.3	101.3

Table A.1 Case 1 Flow Table (cont'd)

	013	014	015	017	017A	017B	017C	018	019	020	022
Ar											
C	6646.6										
CH3OH										0.9	
C2H5OH											
C3H7OH											
C4H9OH											
C5H11OH											
CO				611.7			611.7	4770.4			5382.1
CO2				143.1			143.1	1861.6			
COS								8.9			
CaCO3											
H2	2716.0			2407.5			2407.5	3649.6			6057.1
H2O	4137.6		1785.3		3098.6	887.3		3098.6			
H2S								80.4			
N2	58.8							54.3	238.9		
NH3								9.1			
O2	523.5										
S	89.3										
Al2O3	124.4										
C3H6O2											
C4H8O2											
CH4		755.4		0.6			0.6	5.7			5.7
C2H6											
kmol/hr	14296.2	755.4	1785.3	3162.9	3098.6	887.3	3162.9	13538.5	238.9	0.9	11444.9
kg/hr	193615.7	12086.3	32134.7	28248.8	55773.9	15972.2	28248.8	283586.3	6690.6	29.3	162904.7
Temp. (C)	25.0	25.0	300.0	25.0	25.0	25.0	25.0	300.0	25.0	25.0	25.0
Press. (KPA)	8135.8	1480.0	1480.0	8106.0	8106.0	1400.0	1400.0	8106.0	500.0	101.3	8106.0

Table A.1 Case 1 Flow Table (cont'd)

	023	024	025	026	026A	027	028	033	034	036
Ar										
C										
CH3OH										
C2H5OH			0.9		628.3					
C3H7OH					655.4					
C4H9OH					145.0					
C5H11OH					36.5					
CO					15.2					
CO2	1202.8	701.6	100.2	5382.1	7001.9	714.2				
COS			8.9		1493.7	152.4	4.9			
CaCO3										
H2										
H2O				6057.1	7880.0	803.8				
H2S			80.4		140.1		368.3		7689.1	7689.1
N2		293.2								
NH3			9.1							
O2										
S										
Al2O3										
C3H6O2					18.0			124.4		
C4H8O2					11.9					
CH4				5.7	4380.8	446.8				
C2H6					171.6	17.5				
kmol/hr	1202.8	994.8	199.5	11444.9	22578.5	2134.7	373.3			
kg/hr	52923.7	39082.0	7861.0	162904.7	420678.3	35983.3	6847.1	124.4	7689.1	7689.1
Temp. (C)	25.0	25.0	25.0	98.0	310.0	25.0	25.0	12693.4	138404.0	138404.0
Press. (KPA)	8106.0	8106.0	8106.0	14000.0	12666.0	12666.0	500.0	1300.0	25.0	25.0
								101.3	101.3	101.3

Table A.1 Case 1 Flow Table (cont'd)

	037	041	042	045	046	047	050	051	054	056	056A
Ar											
C											
CH3OH		0.9		0.9			0.9				
C2H5OH											
C3H7OH											
C4H9OH											
C5H11OH											
CO										6287.7	6287.7
CO2		109.1		109.1			109.1			1341.4	
COS											
CaCO3											
H2										7076.3	7076.3
H2O				84.8					89.3		
H2S		89.3		4.5							
N2			159.6	159.6		21.1	180.6				
NH3		9.1		9.1			9.1				
O2			42.4			5.6	3.4				
S					84.8			4.5			
Al2O3	124.4										
C3H6O2											
C4H8O2											
CH4										3933.9	3933.9
C2H6										154.1	154.1
kmol/hr	124.4	208.4	202.0	368.0	84.8	26.7	303.1	4.5	89.3	18793.3	17452.0
kg/hr	12693.4	8020.7	5826.1	11131.8	2715.1	768.7	10149.9	142.9	1607.6	316794.0	257773.6
Temp. (C)	25.0	25.0	25.0	200.0	125.0	25.0	100.0	125.0	50.0	25.0	25.0
Press. (KPA)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	12666.0	12666.0

Table A.1 Case 1 Flow Table (cont'd)

	056B	057	059	063	064	065	067	068	070	071
Ar										
C										
CH3OH					628.3					
C2H5OH					655.4					
C3H7OH					145.0					
C4H9OH					36.5					
C5H11OH					15.2					
CO	6287.7		7001.9							
CO2		1341.4	1493.7						1348.4	
COS										
CaCO3										
H2	7076.3		7880.0							
H2O				140.1		967.2		10615.6	2717.1	10615.6
H2S										
N2							20422.1		20422.1	
NH3										
O2							5428.7		3714.7	
S										
Al2O3										
C3H6O2				18.0						
C4H8O2				11.9						
CH4	3933.9		4380.8							
C2H6	154.1		171.6							
kmol/hr	17452.0	1341.4	20928.0	170.1	1480.4	967.2	25850.8	10615.6	28202.4	10615.6
kg/hr	257773.6	59020.4	352777.2	4905.1	62996.0	17409.0	745536.0	191080.1	798928.2	191080.1
Temp. (C)	45.0	25.0	25.0	25.0	25.0	25.0	25.0	535.0	590.0	25.0
Press. (KPA)	14000.0	12666.0	12666.0	12666.0	12666.0	10000.0	101.3	10000.0	101.3	10000.0

Table A.1 Case 1 Flow Table (cont'd)

	073	074	075	076	077	078
Ar						
C						
CH3OH						
C2H5OH						
C3H7OH						
C4H9OH						
C5H11OH						
CO						
CO2			1348.4			
COS						
CaCO3						
H2						
H2O	3600.0	3600.0	2717.1	14215.6	14215.6	14215.6
H2S						
N2			20422.1			
NH3						
O2			3714.7			
S						
Al2O3						
C3H6O2						
C4H8O2						
CH4						
C2H6						
kmol/hr	3600.0	3600.0	28202.4	14215.6	14215.6	14215.6
kg/hr	64800.6	64800.6	798928.2	255880.7	255880.7	255880.7
Temp. (C)	25.0	535.0	200.0	40.0	380.0	535.0
Press. (KPA)	10000.0	10000.0	101.3	7.4	3000.0	3000.0

Table A.2 Case 1 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	2.0	0.0
Cryogenic Oxygen Plant	4.3	0.0
Rectisol Plant	2.3	0.0
Texaco Gasifier	0.6	0.0
Syn. Gas Heat Recovery	0.9	0.0
Claus Plant	0.1	0.0
Gas Turbine	0.0	80.7
Steam Turbine	0.0	86.3
Compressor 1	31.1	0.0
Compressor 2	10.8	0.0
Compressor 3	6.4	0.0
Compressor 4	7.1	0.0
Compressor 5	3.6	0.0
Total	69.1	167.0

EMISSIONS FROM THE SULFUR REMOVAL PROCESS

BASE CASE 1

Base Case 1 is primarily a model of a process that will turn coal into an alcohol based fuel additive. This plant is very large, and will have a production of roughly 0.5 million metric tons of mixed alcohols per year. In order to properly design this Plant, it is important to compare the emissions of this facility with the Threshold Emission levels allowed by the government before Best Available Control Technology (BACT) is required. If BACT is required it will significantly affect the cost of our plant. The emissions were estimated from the Sulfur Removal portion of the plant because all of the sulfur compounds, along with a major part of the plant's CO, ozone producing compounds (VOC's that are precursors to ozone formation), and two Hazardous Air Pollutants (HAP's), methanol and COS, are found in this part of the process. After the estimations were completed, it was found that the H₂S, Total Reduced Sulfur (including H₂S), Reduced Sulfur Compounds (including H₂S and COS), Ozone producing VOC's, and the HAP's were all above the Threshold Values.

If the size of the plant increases, the total emissions will also increase. The stack emissions will go up with any raise in production. However, the fugitive emissions will grow only if the amount of equipment increases, for example, more trains are added.

The estimation of emissions for the sulfur removal process, which includes four blocks from Base Case 1 ; the Rectisol, COS Hydrolysis, Claus, and Beavon blocks (see Figure A.1), includes stack emissions and an estimation of the fugitive emissions for the blocks. The stack emissions were taken from the Base Case 1 flowsheet (see Figure A.1 and Tables A.1), while the fugitive emissions had to be estimated.

The fugitive emissions were estimated by using average emission factors.

$$E_{ij} = m_j F_i N_i$$

i = a type of equipment

j = a component

E_{ij} = Emissions of component j in equip. i (kg/hr)

m_j = mass fraction of component i

F_i = SOCFI Emission Factor for equipment i (kg/hr/source)

N_i = number of equipment i

The average emission factors (F_i) were taken from the Average Emission Factors for Synthetic Organic Chemical Manufacturing Industry (SOCMI) Fugitive Emissions (see Table A.1), which was taken from the U.S. Environmental Protection Agency, Emission Factors for Equipment Leaks of VOC and HAP, EPA-450/3-86-002, Research Triangle Park, NC, 1986.

Table A.3

EQUIPMENT	SERVICE	EMISSIONS FACTOR, kg/hr/source
Valves	Gas	0.0056
	Light Liquid	0.0071
	Heavy Liquid	0.00023
Pumps	Light Liquid	0.0494
	Heavy Liquid	0.0214
Compressors	Gas	0.228
Pressure Relief Valves	Gas	0.104
Flanges and Other Connectors	All	0.00083
Open-Ended Lines	All	0.0017
Sampling Connectors	All	0.015

A "light liquid" is defined by SOCMI as any fluid that is a liquid at the operating conditions and that either:

- (1) Has a vapor pressure greater than 0.3 kPa at 20°C, or
- (2) Contains at least 20% (by weight) of any component that has a vapor pressure greater than 0.3 kPa at 20°C.

A "heavy liquid" is any fluid that is a liquid at the operating conditions and that is not a "light liquid."

The mass fractions for each component in every stream were estimated from actual flowsheets and process specifications. The last estimation made was the quantity of each type of equipment that released fugitive emissions. This estimation involved a classification of each piece of equipment. For example, a reactor would be classified as a vertical vessel (see Table A.4). From these classifications, the total number of valves could be calculated, by using the Valve Estimations provided by the Chemical

Manufacturers Association, Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment, p. 25, Washington, DC, January 1989, along with a correlation of the quantity of valves to the number of open-ended lines and flanges.

Table A.4

VALVE ESTIMATION	
Flow Sheet Predicting Item	Estimating Factor Valves per Item
Pressure Relief Valves	3
Flow Transmitter	6
Storage	13
Pump	11
Turbine Meter and Prover Connection	14
Vertical Vessel (reactor)	23
Horizontal Vessel (settler)	21
Heat Exchanger-Heated Side	8
Heat Exchanger-Cooled Side	17
Loading or Unloading Point	4

Number of open ended lines = 50% of the number of valves

Number of flanges = 420% of the number of valves

After the estimations and calculations were completed, the total emissions for the sulfur removal process were compared to the West Virginia Administrative Regulations, Air Pollution Control Commission, Chapter 16-20, Series 14, p. 14-5, 1984. If the quantity of a substance released is above its threshold value, then BACT applies. Table A.5 shows the comparison.

Table A.5

SIGNIFICANT EMISSIONS FROM THE SULFUR REMOVAL PROCESS

CLASSIFICATION	COMPONENTS EMITTED	THRESHOLD VALUES (ton/yr)	TOTAL EMISSIONS (ton/yr)
CO	CO	100	42.8
NO _x	n/a	40	0
SO _x	SO ₂	40	3.52
H ₂ S	H ₂ S	10	20.49
Total Reduced Sulfur Including H ₂ S	H ₂ S	10	20.49
Reduced Sulfur Compounds Including H ₂ S	H ₂ S, COS	10	21.39
Ozone (VOC excluding non-reactives)	CH ₃ OH	40	73.69

The total emissions for the sulfur removal process were compared to the 1990 Clean Air Act Amendment, Section 301. Any plant that emits 25 tons per year of any combination of HAP's, or more than 10 tons per year of any HAP compound is classified as a "major source" and is subject to stringent air pollution control. This portion of the plant has two HAP's: methanol and COS. The COS emitted is 0.9 tons per year, which is well below the limit. However, the methanol is well above the limit, 73.69 tons per year, which pushes the plant over the combined 25 tons per year limit by 49.59 tons per year. Thus, the plant is a major source of HAP's.

The conclusion is that for SO_x compounds, we will have no trouble meeting regulations because no other place in our plant has any SO_x. However, H₂S, Total Reduced Sulfur Including H₂S, Reduced Sulfur Compounds Including H₂S, and Ozone (VOC excluding non-reactives) are above the thresholds for BACT. The threshold value is not just for a particular part of the plant, it is a cumulative value that includes the entire plant. Therefore it is a possibility that CO emissions will surpass the threshold, along with an increase in the Ozone (VOC) emissions because all of the alcohols (which are VOC's) are produced in the other portion of the plant. Also the plant is well over the HAP's limit, due to the large amount of methanol going up the stack.

The following tables (A.6-A.8) contain a summary of the emissions from the Stack, the fugitive emissions, and the total emissions for the sulfur removal process.

Table A.6

STACK EMISSIONS FROM THE SULFUR REMOVAL PROCESS

COMPONENT	STACK EMISSIONS FROM:		TOTAL STACK EMISSIONS (kmol/hr)	TOTAL STACK EMISSIONS (ton/yr)
	Rectisol Plant (kmol/hr)	Beavon Plant (kmol/hr)		
CO ₂	1535	84.2	1619	560983
N ₂	247.5	152.8	400	88255
CH ₃ OH	0	0.19	0.19	48
NH ₃	0	8	8	1111

Table A.7

ESTIMATED FUGITIVE EMISSIONS FROM THE SULFUR REMOVAL PROCESS

COMPONENT	SULFUR REMOVAL EMISSIONS FROM:				TOTAL SULFUR REMOVAL EMISSIONS (ton/yr)
	Rectisol (kg/hr)	COS Hydrolysis (kg/hr)	Claus (kg/hr)	Beavon (kg/hr)	
CH ₃ OH	3.28	0	0	0	25.82
CH ₄	0.03	0	0	0	0.21
CO	4.06	1.37	0	0	42.80
CO ₂	4.54	0.77	2.65	1.76	76.50
COS	0.07	0.05	0	0	0.90
H ₂	0.33	0	0	0	2.58
H ₂ O	1.28	0	0.48	4.66	50.52
H ₂ S	0.81	0.53	0.79	0.48	20.49
N ₂	0.65	0.08	2.31	3.31	49.99
NH ₃	0.01	0.03	0.1	0.06	1.63
O ₂	0	0.02	0	0.07	0.74
SO ₂	0	0	0.45	0	3.52

Table A.8

TOTAL (stack plus fugitive) EMISSIONS FROM THE SULFUR REMOVAL PROCESS

CLASSIFICATION	COMPONENTS EMITTED	THRESHOLD VALUES (ton/yr)	TOTAL EMISSIONS (ton/yr)
CO	CO	100	42.8
NO _x	n/a	40	0
SO _x	SO ₂	40	3.52
H ₂ S	H ₂ S	10	20.49
Total Reduced Sulfur Including H ₂ S	H ₂ S	10	20.49
Reduced Sulfur Compounds Including H ₂ S	H ₂ S, COS	10	21.39
Ozone (VOC excluding non-reactives)	CH ₃ OH	40	73.69

RECTISOL PLANT

The flowsheet for the Rectisol Plant was taken from the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide (Further references to this will be referred to as Houston). The information needed for the flow estimations was taken from Houston as well as the Gas Process Handbook '92, Hydrocarbon Processing, April 1992, p. 125.

Table A.9

RECTISOL PLANT OVERALL FUGITIVE EMISSIONS FOR TWO TRAINS

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Vdves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Vdves (kg/hr)	Flanges (kg/hr)	Open- Ended Lines (kg/hr)	
CO	2.02E+ 00	0	4.22E-01	1.76E-01	1.16E+ 00	2.83E-01	4.06
CO ₂	2.45E+ 00	0	0	4.56E-01	1.32E+ 00	3.21E-02	4.54
COS	4.02E-02	2.79E-03	0	1.34E-03	2.01E-02	4.90E-03	0.07
H ₂	1.63E-01	0	3.42E-02	1.42E-02	9.37E-02	2.28E-02	0.33
H ₂ O	6.80E-01	0	0	1.48E-01	3.65E-01	8.89E-02	1.28
H ₂ S	4.67E-01	3.24E-02	0	1.55E-02	2.33E-01	5.69E-02	0.81
N ₂	3.67E-01	0	0	8.17E-03	2.25E-01	5.48E-02	0.65
NH ₃	8.42E-03	0	0	9.02E-04	4.36E-03	1.06E-03	0.01
CH ₄	1.43E-02	0	0	2.78E-03	7.73E-03	1.88E-03	0.03
CH ₃ OH	1.87E+ 00	2.61E-01	0	9.13E-03	9.18E-01	2.24E-01	3.28

The following tables (A.10-A.25) are the actual estimations made for the Rectisol Plant in Base Case 1.

Table A.10

ESTIMATION OF FUGITIVE EMISSIONS FOR THE RECTISOL PLANT

RECTISOL PLANT	
QUANTITY	EQUIPMENT TYPE
3	Pumps
7	Vertical Vessles
0	Horizontal Vessles
0	Storage Tanks
4	Pressure Relief Valves
3	Heat - Exchangers (Heating Side)
6	Heat - Exchangers (Cooling Side)
0	Loading or Unloading Point
37	Flow Transmitters
0	Turbine Meter and Prover Connection

QUANTITY	ACTUAL EQUIPMENT
3	Separators (Knockout Drums)
4	Towers
4	Heat Exchangers
3	Pumps
1	Compressor
4	Pressure Relief Valves
37	Flow Transmitters

QUANTITY	ESTIMATED EQUIPMENT
623	Valves
312	Open - Ended Lines
2617	Flanges

QUANTITY	EQUIPMENT WITH FUGITIVES
623	Valves
3	Pumps
1	Compressors
4	Pressure Relief Valves
2617	Flanges
312	Open - Ended Lines

Table A.11

INLET STREAM (gas)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	4673	130630	4.56E-01
Vertical Vessels	0	CO ₂	1619	71245	2.48E-01
Horizontal Vessels	0	COS	4	210	7.31E-04
Storage Tanks	0	H ₂	5260	10520	3.66E-02
Pressure Relief Valves	0	H ₂ O	3893	70074	2.44E-01
Heat - Exchangers (Heating Side)	0	H ₂ S	72	2448	8.52E-03
Heat - Exchangers (Cooling Side)	0	N ₂	46	1277	4.45E-03
Loading or Unloading Point	0	NH ₃	8	141	4.91E-04
Flow Transmitters	2	CH ₄	27	434	1.51E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	1	22	7.80E-05
		TOTAL FLOW	15602	287201	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	12	0	0	0	50	6

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	3.06E-02	0	0	0	1.91E-02	4.65E-03	5.43E-02
CO ₂	1.67E-02	0	0	0	1.04E-02	2.53E-03	2.96E-02
COS	4.91E-05	0	0	0	3.06E-05	7.46E-06	8.72E-05
H ₂	2.46E-03	0	0	0	1.53E-03	3.74E-04	4.37E-03
H ₂ O	1.64E-02	0	0	0	1.02E-02	2.49E-03	2.91E-02
H ₂ S	5.73E-04	0	0	0	3.57E-04	8.69E-05	1.02E-03
N ₂	2.99E-04	0	0	0	1.86E-04	4.53E-05	5.30E-04
NH ₃	3.30E-05	0	0	0	2.06E-05	5.01E-06	5.86E-05
CH ₄	1.01E-04	0	0	0	6.32E-05	1.54E-05	1.80E-04
CH ₃ OH	5.24E-06	0	0	0	3.26E-06	7.96E-07	9.30E-06

Table A.12

FEED HEAT EXCHANGER AND KNOCKOUT VESSEL (gas)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	3071	85991	5.19E-01
Vertical Vessels	1	CO ₂	810	35622	2.15E-01
Horizontal Vessels	0	COS	2	105	6.33E-04
Storage Tanks	0	H ₂	3425	6850	4.13E-02
Pressure Relief Valves	0	H ₂ O	1947	35037	2.11E-01
Heat - Exchangers (Heating Side)	0	H ₂ S	36	1224	7.38E-03
Heat - Exchangers (Cooling Side)	1	N ₂	23	638	3.85E-03
Loading or Unloading Point	0	NH ₃	4	71	4.26E-04
Flow Transmitters	2	CH ₄	14	217	1.31E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	0	11	6.76E-05
		TOTAL FLOW	9331	165766	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	52	0	0	0	218	26

COMPONENT	EMISSIONS (kg/hr) FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.51E-01	0	0	0	9.40E-02	2.29E-02	2.68E-01
CO ₂	6.26E-02	0	0	0	3.90E-02	9.50E-03	1.11E-01
COS	1.84E-04	0	0	0	1.15E-04	2.80E-05	3.27E-04
H ₂	1.20E-02	0	0	0	7.49E-03	1.83E-03	2.14E-02
H ₂ O	6.15E-02	0	0	0	3.83E-02	9.34E-03	1.09E-01
H ₂ S	2.15E-03	0	0	0	1.34E-03	3.26E-04	3.82E-03
N ₂	1.12E-03	0	0	0	6.98E-04	1.70E-04	1.99E-03
NH ₃	1.24E-04	0	0	0	7.71E-05	1.88E-05	2.20E-04
CH ₄	3.81E-04	0	0	0	2.37E-04	5.78E-05	6.76E-04
CH ₃ OH	1.97E-05	0	0	0	1.22E-05	2.99E-06	3.49E-05

Table A.13

GAS ABSORBER WASH TOWER (gas)

ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	4673	130830	4.56E-01
Vertical Vessels	1	CO ₂	1619	71245	2.48E-01
Horizontal Vessels	0	COS	4	210	7.31E-04
Storage Tanks	0	H ₂	5260	10520	3.66E-02
Pressure Relief Valves	0	H ₂ O	3893	70074	2.44E-01
Heat - Exchangers (Heating Side)	0	H ₂ S	72	2448	8.52E-03
Heat - Exchangers (Cooling Side)	0	N ₂	46	1277	4.45E-03
Loading or Unloading Point	0	NH ₃	8	141	4.91E-04
Flow Transmitters	1	CH ₄	27	434	1.51E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	1	22	7.80E-05
		TOTAL FLOW	15602	287201	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	29	0	0	0	122	15

COMPONENT	EMISSIONS (kg/hr) FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	7.40E-02	0	0	0	4.61E-02	1.12E-02	1.31E-01
CO ₂	4.03E-02	0	0	0	2.51E-02	6.11E-03	7.15E-02
COS	1.19E-04	0	0	0	7.39E-05	1.80E-05	2.11E-04
H ₂	5.95E-03	0	0	0	3.70E-03	9.03E-04	1.06E-02
H ₂ O	3.96E-02	0	0	0	2.47E-02	6.01E-03	7.03E-02
H ₂ S	1.38E-03	0	0	0	8.62E-04	2.10E-04	2.46E-03
N ₂	7.22E-04	0	0	0	4.49E-04	1.10E-04	1.28E-03
NH ₃	7.98E-05	0	0	0	4.97E-05	1.21E-05	1.42E-04
CH ₄	2.45E-04	0	0	0	1.53E-04	3.72E-05	4.35E-04
CH ₃ OH	1.27E-05	0	0	0	7.88E-06	1.92E-06	2.25E-05

Table A.14

GAS ABSORBER WASH TOWER (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			mass fraction
Pumps	0	CO	0	0	0
Vertical Vessels	1	CO ₂	0	0	0
Horizontal Vessels	0	CO ₂	0	0	0
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	0	0	0
Heat - Exchangers (Cooling Side)	0	N ₂	0	0	0
Loading or Unloading Point	0	NH ₃	0	0	0
Flow Transmitters	1	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	50	1600	1
		TOTAL FLOW	50	1600	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0	0.00083	0.0017
QUANTITY	29	0	0	0	122	15

COMPONENT	EMISSIONS (kg/hr) FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0	0
N ₂	0	0	0	0	0	0	0
NH ₃	0	0	0	0	0	0	0
CH ₄	0	0	0	0	0	0	0
CH ₃ OH	0.21	0	0	0	0.10	0.02	3.32E-01

Table A.15

H2, CO RECLAIMER #1 (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	350	9811	4.30E-01
Vertical Vessels	1	CO2	270	11876	5.21E-01
Horizontal Vessels	0	COS	0	0	0.00E+00
Storage Tanks	0	H2	398	795	3.49E-02
Pressure Relief Valves	1	H2O	0	0	0.00E+00
Heat - Exchangers (Heating Side)	0	H2S	0	0	0.00E+00
Heat - Exchangers (Cooling Side)	1	N2	8	213	9.34E-03
Loading or Unloading Point	0	NH3	1	23	1.03E-03
Flow Transmitters	3	CH4	5	72	3.17E-03
Turbine Meter and Prover Connection	0	CH3OH	0	0	0.00E+00
		TOTAL FLOW	1031	22790	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0.104	0.00083	0.0017
QUANTITY	61	0	0	1	256	31

COMPONENT	EMISSIONS (kg/hr) FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.86E-01	0	0	4.48E-02	9.15E-02	2.23E-02	3.45E-01
CO2	2.26E-01	0	0	5.42E-02	1.11E-01	2.70E-02	4.18E-01
COS	0	0	0	0	0	0	0
H2	1.51E-02	0	0	3.63E-03	7.42E-03	1.81E-03	2.80E-02
H2O	0	0	0	0	0	0	0
H2S	0	0	0	0	0	0	0
N2	4.04E-03	0	0	9.71E-04	1.99E-03	4.84E-04	7.48E-03
NH3	4.46E-04	0	0	1.07E-04	2.19E-04	5.34E-05	8.25E-04
CH4	1.37E-03	0	0	3.30E-04	6.75E-04	1.65E-04	2.54E-03
CH3OH	0	0	0	0	0	0	0

Table A.16

H₂, CO RECLAIMER #2 (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	350	9811	4.14E-01
Vertical Vessels	1	CO ₂	270	11876	5.02E-01
Horizontal Vessels	0	CO ₂	1	70	2.96E-03
Storage Tanks	0	H ₂	398	795	3.36E-02
Pressure Relief Valves	1	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	24	816	3.45E-02
Heat - Exchangers (Cooling Side)	1	N ₂	8	213	8.99E-03
Loading or Unloading Point	0	NH ₃	1	23	9.91E-04
Flow Transmitters	3	CH ₄	5	72	3.05E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	0	0	0
		TOTAL FLOW	1056	23677	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0.104	0.00083	0.0017
QUANTITY	61	0	0	1	256	31

COMPONENT	EMISSIONS (kg/hr) FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.79E-01	0	0	4.31E-02	8.81E-02	2.15E-02	3.32E-01
CO ₂	2.17E-01	0	0	5.22E-02	1.07E-01	2.60E-02	4.02E-01
CO ₂	1.28E-03	0	0	3.08E-04	6.30E-04	1.54E-04	2.38E-03
H ₂	1.45E-02	0	0	3.49E-03	7.14E-03	1.74E-03	2.69E-02
H ₂ O	0	0	0	0	0	0	0
H ₂ S	1.49E-02	0	0	3.58E-03	7.33E-03	1.79E-03	2.76E-02
N ₂	3.89E-03	0	0	9.35E-04	1.91E-03	4.66E-04	7.20E-03
NH ₃	4.29E-04	0	0	1.03E-04	2.11E-04	5.14E-05	7.94E-04
CH ₄	1.32E-03	0	0	3.18E-04	6.50E-04	1.58E-04	2.45E-03
CH ₃ OH	0	0	0	0	0	0	0

Table A.17

H₂, CO RECYCLE STREAM (gas)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	701	19622	9.25E-01
Vertical Vessels	0	CO ₂	0	0	0
Horizontal Vessels	0	CO ₂	0	0	0
Storage Tanks	0	H ₂	795	1590	7.50E-02
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	0	0	0
Heat - Exchangers (Cooling Side)	1	N ₂	0	0	0
Loading or Unloading Point	0	NH ₃	0	0	0
Flow Transmitters	5	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	0	0	0
		TOTAL FLOW	1496	21212	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0.228	0	0.00083	0.0017
QUANTITY	47	0	1	0	197	24

COMPONENT	EMISSIONS (kg/hr) FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	2.43E-01	0	2.11E-01	0	1.52E-01	3.70E-02	6.43E-01
CO ₂	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
H ₂	1.97E-02	0	1.71E-02	0	1.23E-02	2.99E-03	5.21E-02
H ₂ O	0	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0	0
N ₂	0	0	0	0	0	0	0
NH ₃	0	0	0	0	0	0	0
CH ₄	0	0	0	0	0	0	0
CH ₃ OH	0	0	0	0	0	0	0

Table A.18

PURIFIED GAS STREAM
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			
Pumps	0	CO	2336	kg/hr	mass fraction
Vertical Vessels	0	CO ₂	0	65416	9.26E-01
Horizontal Vessels	0	COS	0	0	0
Storage Tanks	0	H ₂	2630	5260	7.44E-02
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	2	H ₂ S	0	0	0
Heat - Exchangers (Cooling Side)	0	N ₂	0	0	0
Loading or Unloading Point	0	NH ₃	0	0	0
Flow Transmitters	2	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	0	0	0
		TOTAL FLOW	4966	70676	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	28	0	0	0	118	14

COMPONENT	EMISSIONS (kg/hr) FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.45E-01	0	0	0	9.03E-02	2.20E-02	2.58E-01
CO ₂	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0
H ₂	1.17E-02	0	0	0	7.26E-03	1.77E-03	2.07E-02
H ₂ O	0	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0	0
N ₂	0	0	0	0	0	0	0
NH ₃	0	0	0	0	0	0	0
CH ₄	0	0	0	0	0	0	0
CH ₃ OH	0	0	0	0	0	0	0

Table A.19

UNSHIFTED GAS METHANOL - WATER SEPARATION TOWER (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	0	0	0
Vertical Vessels	1	CO ₂	540	23747	2.41E-01
Horizontal Vessels	0	CO ₂	1	70	7.12E-04
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	1	H ₂ O	3900	70200	7.12E-01
Heat - Exchangers (Heating Side)	0	H ₂ S	24	816	8.27E-03
Heat - Exchangers (Cooling Side)	0	N ₂	15	426	4.31E-03
Loading or Unloading Point	0	NH ₃	3	47	4.77E-04
Flow Transmitters	3	CH ₄	9	144	1.46E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	100	3214	3.26E-02
		TOTAL FLOW	4592	98665	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0.104	0.00083	0.0017
QUANTITY	44	0	0	1	185	22

COMPONENT	EMISSIONS (kg/hr) FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	0	0	0	0	0	0	0
CO ₂	7.52E-02	0	0	2.50E-02	3.69E-02	9.00E-03	1.46E-01
CO ₂	2.22E-04	0	0	7.40E-05	1.09E-04	2.66E-05	4.32E-04
H ₂	0	0	0	0	0	0	0
H ₂ O	2.22E-01	0	0	7.40E-02	1.09E-01	2.66E-02	4.32E-01
H ₂ S	2.58E-03	0	0	8.60E-04	1.27E-03	3.09E-04	5.02E-03
N ₂	1.35E-03	0	0	4.49E-04	6.62E-04	1.61E-04	2.62E-03
NH ₃	1.49E-04	0	0	4.96E-05	7.32E-05	1.79E-05	2.90E-04
CH ₄	4.57E-04	0	0	1.52E-04	2.25E-04	5.48E-05	8.89E-04
CH ₃ OH	1.02E-02	0	0	3.39E-03	5.00E-03	1.22E-03	1.98E-02

Table A.20

UNSHIFTED GAS STRIPPING COLUMN (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY				mass fraction
Pumps	0	CO	0	kg/hr	0	0
Vertical Vessels	1	CO ₂	540	23756	8.84E-01	
Horizontal Vessels	0	COS	1	70	2.61E-03	
Storage Tanks	0	H ₂	0	0	0.00E+00	
Pressure Relief Valves	0	H ₂ O	0	0	0	
Heat - Exchangers (Heating Side)	0	H ₂ S	24	816	3.04E-02	
Heat - Exchangers (Cooling Side)	0	N ₂	15	426	1.58E-02	
Loading or Unloading Point	0	NH ₃	3	47	1.75E-03	
Flow Transmitters	2	CH ₄	9	145	5.39E-03	
Turbine Meter and Prover Connection	0	CH ₃ OH	50	1600	5.96E-02	
		TOTAL FLOW	642	26859		

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0	0.00083	0.0017
QUANTITY	35	0	0	0	147	18

COMPONENT	EMISSIONS (kg/hr)				FROM :			TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)		
CO	0	0	0	0	0	0		0
CO ₂	2.20E-01	0	0	0	1.08E-01	2.63E-02		3.54E-01
COS	6.49E-04	0	0	0	3.19E-04	7.78E-05		1.05E-03
H ₂	0.00E+00	0	0	0	0.00E+00	0.00E+00		0.00E+00
H ₂ O	0	0	0	0	0	0		0
H ₂ S	7.55E-03	0	0	0	3.71E-03	9.04E-04		1.22E-02
N ₂	3.94E-03	0	0	0	1.93E-03	4.71E-04		6.34E-03
NH ₃	4.34E-04	0	0	0	2.13E-04	5.20E-05		6.99E-04
CH ₄	1.34E-03	0	0	0	6.57E-04	1.60E-04		2.16E-03
CH ₃ OH	1.48E-02	0	0	0	7.27E-03	1.77E-03		2.38E-02

Table A.21

UNSHIFTED GAS STRIPPING COLUMN (gas)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			
Pumps	0	CO	0	kg/hr	mass fraction
Vertical Vessels	1	CO ₂	0	0	0
Horizontal Vessels	0	CO ₂	0	0	0
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	0	0	0
Heat - Exchangers (Cooling Side)	0	N ₂	101	2828	1
Loading or Unloading Point	0	NH ₃	0	0	0
Flow Transmitters	1	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	0	0	0
		TOTAL FLOW	101	2828	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	29	0	0	0	122	15

COMPONENT	EMISSIONS (kg/hr) FROM :					TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)
CO	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0
H ₂	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0
N ₂	1.62E-01	0	0	0	1.01E-01	2.47E-02
NH ₃	0	0	0	0	0	0
CH ₄	0	0	0	0	0	0
CH ₃ OH	0	0	0	0	0	0

Table A.22

UNSHIFTED METHANOL REGENERATION TOWER (gas feed)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			
Pumps	0	CO	0	kg/hr	mass fraction
Vertical Vessels	1	CO ₂	270	11876	9.30E-01
Horizontal Vessels	0	COS	1	35	2.77E-03
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	1	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	12	408	3.19E-02
Heat - Exchangers (Cooling Side)	1	N ₂	8	213	1.67E-02
Loading or Unloading Point	0	NH ₃	1	23	1.84E-03
Flow Transmitters	3	CH ₄	5	72	5.66E-03
Turbine Meter and Prover Connection	0	CH ₃ OH	5	145	1.13E-02
		TOTAL FLOW	301	12772	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	61	0	0	1	256	31

COMPONENT	EMISSIONS (kg/hr)						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	0	0	0	0	0	0	0
CO ₂	3.18E-01	0	0	9.67E-02	1.98E-01	4.82E-02	6.60E-01
COS	9.47E-04	0	0	2.88E-04	5.89E-04	1.44E-04	1.97E-03
H ₂	0	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0	0
H ₂ S	1.09E-02	0	0	3.32E-03	6.79E-03	1.66E-03	2.27E-02
N ₂	5.69E-03	0	0	1.73E-03	3.54E-03	8.64E-04	1.18E-02
NH ₃	6.27E-04	0	0	1.91E-04	3.91E-04	9.52E-05	1.30E-03
CH ₄	1.93E-03	0	0	5.89E-04	1.20E-03	2.94E-04	4.02E-03

Table A.23

UNSHIFTED METHANOL REGENERATION TOWER (liquid feed)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			mass fraction
Pumps	1	CO	0	0	0
Vertical Vessels	1	CO ₂	0	0	0
Horizontal Vessels	0	COS	1	70	2.82E-02
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	24	816	3.28E-01
Heat - Exchangers (Cooling Side)	1	N ₂	0	0	0
Loading or Unloading Point	0	NH ₃	0	0	0
Flow Transmitters	3	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	50	1600	6.44E-01
		TOTAL FLOW	75	2486	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0.0494	0	0	0.00083	0.0017
QUANTITY	69	1	0	0	290	35

COMPONENT	EMISSIONS (kg/hr)				FROM :			TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)		
CO	0	0	0	0	0	0		0
CO ₂	0	0	0	0	0	0		0
COS	1.38E-02	1.39E-03	0	0	6.79E-03	1.66E-03		2.37E-02
H ₂	0	0	0	0	0	0		0
H ₂ O	0	0	0	0	0	0		0
H ₂ S	1.61E-01	1.62E-02	0	0	7.89E-02	1.92E-02		2.75E-01
N ₂	0	0	0	0	0	0		0
NH ₃	0	0	0	0	0	0		0
CH ₄	0	0	0	0	0	0		0
CH ₃ OH	3.15E-01	3.18E-02	0	0	1.55E-01	3.77E-02		5.40E-01

Table A.24

METHANOL RECYCLE STREAM (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY				mass fraction
Pumps	2	CO	0	kg/hr	0	0
Vertical Vessels	0	CO ₂	0	0	0	0
Horizontal Vessels	0	CO ₂	0	0	0	0
Storage Tanks	0	CO ₂	0	0	0	0
Pressure Relief Valves	0	H ₂	0	0	0	0
Heat - Exchangers (Heating Side)	1	H ₂ O	0	0	0	0
Heat - Exchangers (Cooling Side)	0	H ₂ S	0	0	0	0
Loading or Unloading Point	0	N ₂	0	0	0	0
Flow Transmitters	4	NH ₃	0	0	0	0
Turbine Meter and Prover Connection	0	CH ₄	0	0	0	1
		CH ₃ OH	100	3200		
		TOTAL FLOW	100	3200		

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0.0494	0	0	0.00083	0.0017
QUANTITY	54	2	0	0	227	27

COMPONENT	EMISSIONS (kg/hr) FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0	0
H ₂ S	0	0	0	0	0	0	0
N ₂	0	0	0	0	0	0	0
NH ₃	0	0	0	0	0	0	0
CH ₄	0	0	0	0	0	0	0
CH ₃ OH	3.83E-01	9.88E-02	0	0	1.88E-01	4.59E-02	7.16E-01

Table A.25

H₂S , COS RICH STREAM (gas)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE UNSHIFTED RECTISOL TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			mass fraction
Pumps	0	CO	0	0	0
Vertical Vessels	0	CO ₂	81	3555	5.59E-01
Horizontal Vessels	0	COS	4	210	3.30E-02
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	0	H ₂ O	0	0	0
Heat - Exchangers (Heating Side)	0	H ₂ S	72	2448	3.85E-01
Heat - Exchangers (Cooling Side)	0	N ₂	0	0	0
Loading or Unloading Point	0	NH ₃	8	141	2.22E-02
Flow Transmitters	2	CH ₄	0	0	0
Turbine Meter and Prover Connection	0	CH ₃ OH	0	6	9.56E-04
		TOTAL FLOW	165	6360	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0	0.0083	0.0017
QUANTITY	12	0	0	0	50	6

COMPONENT	EMISSIONS (kg/hr)			FROM :			TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	0	0	0	0	0	0	0
CO ₂	4.76E-02	0	0	0	2.34E-02	5.70E-03	7.67E-02
COS	2.81E-03	0	0	0	1.38E-03	3.37E-04	4.53E-03
H ₂	0	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0	0
H ₂ S	3.28E-02	0	0	0	1.61E-02	3.93E-03	5.28E-02
N ₂	0	0	0	0	0	0	0
NH ₃	1.89E-03	0	0	0	9.28E-04	2.26E-04	3.04E-03
CH ₄	0	0	0	0	0	0	0
CH ₃ OH	8.14E-05	0	0	0	4.00E-05	9.75E-06	1.31E-04

COS HYDROLYSIS PLANT

The flowsheet for the COS hydrolysis along with the information needed for the stream estimations were taken from the Gas Process Handbook '84, Hydrocarbon Processing, April 1984, p. 78.

Table A.26

COS HYDROLYSIS PLANT OVERALL FUGITIVE EMISSIONS

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open- Ended Lines (kg/hr)	
CO	6.65E-01	0	0	1.93E-01	4.14E-01	1.01E-01	1.37
CO ₂	3.74E-01	0	0	1.08E-01	2.33E-01	5.67E-02	0.77
COS	2.21E-02	0	0	6.40E-03	1.37E-02	3.50E-03	0.05
H ₂	7.36E-04	0	0	2.13E-04	4.58E-04	1.12E-04	0
H ₂ S	2.57E-01	0	0	7.47E-02	1.60E-01	3.91E-02	0.53
N ₂	3.65E-02	0	0	1.06E-02	2.27E-02	5.54E-03	0.08
NH ₃	1.48E-02	0	0	4.30E-03	9.23E-03	2.25E-03	0.03
CH ₃ OH	6.39E-04	0	0	1.85E-04	3.98E-04	9.70E-05	0
O ₂	1.11E-02	0	0	3.22E-03	6.91E-03	1.68E-03	0.02

The following tables (A.27-A.29) are the actual estimations made for the COS Hydrolysis Plant in Base Case 1.

Table A.27

ESTIMATION OF FUGITIVE EMISSIONS FOR THE COS HYDROLYSIS PLANT

COS HYDROLYSIS	
QUANTITY	EQUIPMENT TYPE
0	Pumps
1	Vertical Vessles
0	Horizontal Vessles
0	Storage Tanks
1	Pressure Relief Valves
1	Heat - Exchangers (Heating Side)
0	Heat - Exchangers (Cooling Side)
0	Loading or Unloading Point
5	Flow Transmitters
0	Turbine Meter and Prover Connection

QUANTITY	ACTUAL EQUIPMENT
1	Preheater
1	Hydrolysis Reactor
1	Pressure Relief Valves
5	Flow Transmitters

QUANTITY	ESTIMATED EQUIPMENT
64	Valves
32	Open - Ended Lines
269	Flanges

QUANTITY	EQUIPMENT WITH FUGITIVES
64	Valves
0	Pumps
0	Compressors
1	Pressure Relief Valves
269	Flanges
32	Open - Ended Lines

Table A.28

MIXER - PREHEATER
ESTIMATION OF FUGITIVE EMISSIONS FOR COS HYDROLYSIS

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	3.5	98	9.28E-01
Vertical Vessels	0			3555	5.21E-01
Horizontal Vessels	0	COS	4	210	3.08E-02
Storage Tanks	0	H2	4	7	1.03E-03
Pressure Relief Valves	0	H2S	72	2448	3.59E-01
Heat - Exchangers (Heating Side)	1	N2	12	347	5.09E-02
Heat - Exchangers (Cooling Side)	0	NH3	8	141	2.07E-02
Loading or Unloading Point	0	CH3OH	0	6	8.91E-04
Flow Transmitters	3	O2	3	106	1.55E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	184	6820	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	26	0	0	0	109	13

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.35E-01	0	0	0	8.41E-02	2.05E-02	2.40E-01
CO2	7.59E-02	0	0	0	4.72E-02	1.15E-02	1.35E-01
COS	4.48E-03	0	0	0	2.79E-03	6.80E-04	7.95E-03
H2	1.49E-04	0	0	0	9.30E-05	2.27E-05	2.65E-04
H2S	5.23E-02	0	0	0	3.25E-02	7.93E-03	9.27E-02
N2	7.41E-03	0	0	0	4.61E-03	1.13E-03	1.32E-02
NH3	3.01E-03	0	0	0	1.88E-03	4.57E-04	5.34E-03
CH3OH	1.30E-04	0	0	0	8.08E-05	1.97E-05	2.30E-04
O2	2.25E-03	0	0	0	1.40E-03	3.42E-04	4.00E-03

Table A.29

HYDROGENATION / HYDROLYSIS REACTOR
ESTIMATION OF FUGITIVE EMISSIONS FOR COS HYDROLYSIS

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO	0	0	0
Vertical Vessels	1	CO ₂	87	3846	5.57E-01
Horizontal Vessels	0	COS	0	0	0
Storage Tanks	0	H ₂	0	0	0
Pressure Relief Valves	1	H ₂ S	76	2567	3.72E-01
Heat - Exchangers (Heating Side)	0	N ₂	12	347	5.03E-02
Heat - Exchangers (Cooling Side)	0	NH ₃	8	141	2.04E-02
Loading or Unloading Point	0	CH ₃ OH	0	6	8.80E-04
Flow Transmitters	2	O ₂	0	0	0
Turbine Meter and Prover Connection	0	TOTAL FLOW	184	6907	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	38	0	0	1	160	19

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO	1.97E-01	0	0	9.65E-02	1.23E-01	3.00E-02	4.47E-01
CO ₂	1.11E-01	0	0	5.42E-02	6.91E-02	1.68E-02	2.51E-01
COS	6.55E-03	0	0	3.20E-03	4.08E-03	9.95E-04	1.48E-02
H ₂	2.18E-04	0	0	1.07E-04	1.36E-04	3.32E-05	4.94E-04
H ₂ S	7.64E-02	0	0	3.73E-02	4.75E-02	1.16E-02	1.73E-01
N ₂	1.08E-02	0	0	5.29E-03	6.74E-03	1.64E-03	2.45E-02
NH ₃	4.40E-03	0	0	2.15E-03	2.74E-03	6.68E-04	9.96E-03
CH ₃ OH	1.90E-04	0	0	9.27E-05	1.18E-04	2.88E-05	4.29E-04
O ₂	3.29E-03	0	0	1.61E-03	2.05E-03	5.00E-04	7.46E-03

CLAUS PLANT

The flowsheet for the Claus Plant was taken from Houston. The information needed for the flow estimations was taken from Houston as well as the Gas Process Handbook '84, Hydrocarbon Processing, April 1984, p. 74.

Table A.30

CLAUS PLANT OVERALL FUGITIVE EMISSIONS FOR TWO TRAINS

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open- Ended Lines (kg/hr)	
CO ₂	1.33E+ 00	0	0	2.93E-01	8.25E-01	2.01E-01	2.65
H ₂ O	2.33E-01	0	0	6.51E-02	1.45E-01	3.54E-02	0.48
H ₂ S	4.07E-01	0	0	6.44E-02	2.53E-01	6.18E-02	0.79
N ₂	1.12E+ 00	0	0	3.23E-01	6.97E-01	1.70E-01	2.31
CH ₃ OH	2.10E-03	0	0	4.65E-04	1.31E-03	3.19E-04	0.00
S	3.39E-03	0	0	2.77E-03	2.11E-02	5.15E-03	0.06
SO ₂	2.11E-01	0	0	7.21E-02	1.32E-01	3.21E-02	0.45
O ₂	0	0	0	0	0	0	0.00
NH ₃	4.87E-02	0	0	1.08E-02	3.03E-02	7.39E-03	0.10

The following tables (A.31-A.37) are the actual estimations made for the Claus Plant in Base Case 1.

Table A.31

ESTIMATION OF FUGITIVE EMISSIONS FOR THE CLAUS PLANT

CLAUS PLANT	
QUANTITY	EQUIPMENT TYPE
0	Pumps
6	Vertical Vessles
6	Horizontal Vessles
0	Storage Tanks
8	Pressure Relief Valves
8	Heat - Exchangers (Heating Side)
0	Heat - Exchangers (Cooling Side)
0	Loading or Unloading Point
28	Flow Transmitters
0	Turbine Meter and Prover Connection

QUANTITY	ACTUAL EQUIPMENT
2	Separators (Knockout Drums)
2	Thermal Incinerators
2	Boilers
6	Reheaters
2	3 - Staged Catalytic Reactors
2	Sulfur Condensers
8	Pressure Relief Valves
28	Flow Transmitters

QUANTITY	ESTIMATED EQUIPMENT
520	Valves
260	Open - Ended Lines
2184	Flanges

QUANTITY	EQUIPMENT WITH FUGITIVES
520	Valves
0	Pumps
0	Compressors
8	Pressure Relief Valves
2184	Flanges
260	Open - Ended Lines

Table A.32

SEPARATOR
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUSTRATION TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			
Pumps	0	CO ₂	kgmol/hr	kg/hr	mass fraction
Vertical Vessels	0	H ₂ O	87	3846	5.57E-01
Horizontal Vessels	1	H ₂ S	76	2567	3.72E-01
Storage Tanks	~0	N ₂	12	347	5.03E-02
Pressure Relief Valves	0	CH ₃ OH	0	6	8.80E-04
Heat - Exchangers (Heating Side)	0	S	0	0	0
Heat - Exchangers (Cooling Side)	0	SO ₂	0	0	0
Loading or Unloading Point	0	O ₂	0	0	0
Flow Transmitters	5	NH ₃	8	141	2.04E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	184	6907	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	51	0	0	0	214	26

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	1.59E-01	0	0	0	9.90E-02	2.41E-02	2.82E-01
H ₂ O	0	0	0	0	0	0	0
H ₂ S	1.06E-01	0	0	0	6.61E-02	1.61E-02	1.88E-01
N ₂	1.44E-02	0	0	0	8.94E-03	2.18E-03	2.55E-02
CH ₃ OH	2.51E-04	0	0	0	1.56E-04	3.82E-05	4.46E-04
S	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	0	0
NH ₃	5.83E-03	0	0	0	3.63E-03	8.86E-04	1.04E-02

Table A.33

THERMAL INCINERATOR AND BOILER
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUS TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO ₂	29	1282	2.81E-01
Vertical Vessels	0	H ₂ O	12	222	4.86E-02
Horizontal Vessels	1	H ₂ S	11	385	8.43E-02
Storage Tanks	0	N ₂	67	1883	4.12E-01
Pressure Relief Valves	1	CH ₃ OH	0	2	4.49E-04
Heat - Exchangers (Heating Side)	0	S	2	61	1.33E-02
Heat - Exchangers (Cooling Side)	1	SO ₂	11	685	1.50E-01
Loading or Unloading Point	0	O ₂	0	0	0.00E+00
Flow Transmitters	0	NH ₃	3	47	1.03E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	135	4566	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	41	0	0	1	172	21

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	6.45E-02	0	0	2.92E-02	4.01E-02	9.78E-03	1.44E-01
H ₂ O	1.12E-02	0	0	5.06E-03	6.95E-03	1.69E-03	2.49E-02
H ₂ S	1.94E-02	0	0	8.77E-03	1.20E-02	2.94E-03	4.31E-02
N ₂	9.47E-02	0	0	4.29E-02	5.89E-02	1.44E-02	2.11E-01
CH ₃ OH	1.03E-04	0	0	4.66E-05	6.41E-05	1.56E-05	2.29E-04
S	3.06E-03	0	0	1.38E-03	1.90E-03	4.64E-04	6.81E-03
SO ₂	3.44E-02	0	0	1.56E-02	2.14E-02	5.23E-03	7.67E-02
O ₂	0.00E+00	0	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NH ₃	2.37E-03	0	0	1.07E-03	1.47E-03	3.59E-04	5.27E-03

Table A.34

FIRST REHEATER AND FIRST REACTOR STAGE
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUS TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY				mass fraction
Pumps	0	CO ₂	44	1923		3.40E-01
Vertical Vessels	1	H ₂ O	12	222		3.92E-02
Horizontal Vessels	0	H ₂ S	24	813		1.44E-01
Storage Tanks	0	N ₂	69	1940		3.43E-01
Pressure Relief Valves	1	CH ₃ OH	0	3		5.37E-04
Heat - Exchangers (Heating Side)	1	S	0	0		0
Heat - Exchangers (Cooling Side)	0	SO ₂	11	685		1.21E-01
Loading or Unloading Point	0	O ₂	0	0		0.00E+00
Flow Transmitters	3	NH ₃	4	71		1.25E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	164	5656		

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	52	0	0	1	218	26

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	9.90E-02	0	0	3.54E-02	6.16E-02	1.50E-02	2.11E-01
H ₂ O	1.14E-02	0	0	4.08E-03	7.11E-03	1.73E-03	2.44E-02
H ₂ S	4.18E-02	0	0	1.49E-02	2.60E-02	6.35E-03	8.92E-02
N ₂	9.99E-02	0	0	3.57E-02	6.22E-02	1.52E-02	2.13E-01
CH ₃ OH	1.57E-04	0	0	5.59E-05	9.74E-05	2.38E-05	3.34E-04
S	0	0	0	0	0	0	0
SO ₂	3.53E-02	0	0	1.26E-02	2.19E-02	5.35E-03	7.51E-02
O ₂	0.00E+00	0	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NH ₃	3.63E-03	0	0	1.30E-03	2.26E-03	5.51E-04	7.74E-03

Table A.35

SECOND REHEATER AND SECOND REACTOR STAGE
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUS TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	0	CO ₂	44	1923	3.93E-01
Vertical Vessels	1	H ₂ O	28	509	1.04E-01
Horizontal Vessels	0	H ₂ S	8	271	5.55E-02
Storage Tanks	0	N ₂	69	1940	3.97E-01
Pressure Relief Valves	1	CH ₃ OH	0	3	6.21E-04
Heat - Exchangers (Heating Side)	1	S	0	0	0
Heat - Exchangers (Cooling Side)	0	SO ₂	3	175	3.58E-02
Loading or Unloading Point	0	O ₂	0	0	0.00E+00
Flow Transmitters	2	NH ₃	4	71	1.44E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	156	4893	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	46	0	0	1	193	23

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	1.01E-01	0	0	4.09E-02	6.30E-02	1.54E-02	2.20E-01
H ₂ O	2.68E-02	0	0	1.08E-02	1.67E-02	4.07E-03	5.84E-02
H ₂ S	1.43E-02	0	0	5.77E-03	8.89E-03	2.17E-03	3.11E-02
N ₂	1.02E-01	0	0	4.12E-02	6.36E-02	1.55E-02	2.23E-01
CH ₃ OH	1.60E-04	0	0	6.46E-05	9.96E-05	2.43E-05	3.49E-04
S	0	0	0	0	0	0	0
SO ₂	9.23E-03	0	0	3.73E-03	5.75E-03	1.40E-03	2.01E-02
O ₂	0.00E+00	0	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NH ₃	3.71E-03	0	0	1.50E-03	2.31E-03	5.64E-04	8.09E-03

Table A.36

THIRD REHEATER AND REACTOR STAGE
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUS TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			
Pumps	0	CO ₂	kgmol/hr	kg/hr	mass fraction
Vertical Vessels	1	H ₂ O	44	1923	3.97E-01
Horizontal Vessels	1	H ₂ S	33	585	1.21E-01
Storage Tanks	- 0	N ₂	4	128	2.63E-02
Pressure Relief Valves	1	N ₂	69	1940	4.01E-01
Heat - Exchangers (Heating Side)	1	CH ₃ OH	0	3	6.28E-04
Heat - Exchangers (Cooling Side)	0	S	0	0	0
Loading or Unloading Point	0	SO ₂	3	192	3.97E-02
Flow Transmitters	2	O ₂	0	0	0.00E+00
Turbine Meter and Prover Connection	0	NH ₃	4	71	1.46E-02
		TOTAL FLOW	156	4841	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0.104	0.00083	0.0017
QUANTITY	67	0	0	1	281	34

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	1.49E-01	0	0	4.13E-02	9.28E-02	2.26E-02	3.06E-01
H ₂ O	4.53E-02	0	0	1.26E-02	2.82E-02	6.88E-03	9.30E-02
H ₂ S	9.88E-03	0	0	2.74E-03	6.15E-03	1.50E-03	2.03E-02
N ₂	1.50E-01	0	0	4.17E-02	9.36E-02	2.28E-02	3.09E-01
CH ₃ OH	2.36E-04	0	0	6.53E-05	1.47E-04	3.58E-05	4.83E-04
S	0	0	0	0	0	0	0
SO ₂	1.49E-02	0	0	4.12E-03	9.26E-03	2.26E-03	3.05E-02
O ₂	0.00E+00	0	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NH ₃	5.47E-03	0	0	1.52E-03	3.40E-03	8.30E-04	1.12E-02

Table A.37

SULFUR CONDENSER
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE CLAUS TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY				mass fraction
Pumps	0	CO ₂	160	kg/hr	7050	3.58E-01
Vertical Vessels	0	H ₂ O	95		1714	8.71E-02
Horizontal Vessels	1	H ₂ S	28		939	4.77E-02
Storage Tanks	0	N ₂	275		7704	3.91E-01
Pressure Relief Valves	0	CH ₃ OH	0		11	5.67E-04
Heat - Exchangers (Heating Side)	0	S	34		1086	5.52E-02
Heat - Exchangers (Cooling Side)	0	SO ₂	14		924	4.69E-02
Loading or Unloading Point	0	O ₂	0		0	0.00E+00
Flow Transmitters	4	NH ₃	15		259	1.31E-02
Turbine Meter and Prover Connection	0	TOTAL FLOW	622		19687	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	45	0	0	0	189	23

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	9.02E-02	0	0	0	5.62E-02	1.37E-02	1.60E-01
H ₂ O	2.19E-02	0	0	0	1.37E-02	3.33E-03	3.89E-02
H ₂ S	1.20E-02	0	0	0	7.48E-03	1.82E-03	2.13E-02
N ₂	9.86E-02	0	0	0	6.14E-02	1.50E-02	1.75E-01
CH ₃ OH	1.43E-04	0	0	0	8.90E-05	2.17E-05	2.54E-04
S	1.39E-02	0	0	0	8.65E-03	2.11E-03	2.47E-02
SO ₂	1.18E-02	0	0	0	7.36E-03	1.80E-03	2.10E-02
O ₂	0.00E+00	0	0	0	0.00E+00	0.00E+00	0.00E+00
NH ₃	3.31E-03	0	0	0	2.06E-03	5.03E-04	5.88E-03

BEAVON PLANT

The flowsheet for the Beavon Plant along with the information needed for the stream estimations were taken from the Gas Process Handbook '84, Hydrocarbon Processing, April 1984, p. 88.

Table A.38

BEAVON PLANT OVERALL FUGITIVE EMISSIONS

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open- Ended Lines (kg/hr)	
CO ₂	9.91E-01	8.12E-02	0	0	5.53E-01	1.35E-01	1.76
O ₂	3.77E-02	0	0	1.00E-02	1.85E-02	4.51E-03	0.07
S	1.46E-01	0	0	2.56E-02	7.17E-02	1.75E-02	0.26
H ₂ O	2.61E+ 00	2.58E-02	0	4.06E-01	1.30E+ 00	3.17E-01	4.66
H ₂ S	2.65E-01	5.39E-03	0	4.00E-02	1.35E-01	3.29E-02	0.48
N ₂	1.86E+ 00	8.20E-02	0	1.42E-01	9.82E-01	2.39E-01	3.31
NH ₃	3.64E-02	2.98E-03	0	0	2.03E-02	4.95E-03	0.06
CH ₃ OH	1.57E-03	1.28E-04	0	0	8.75E-04	2.13E-04	0.00

The following tables (A.39-A.48) are the actual estimations made for the Beavon Plant in Base Case 1.

Table A.39

ESTIMATION OF FUGITIVE EMISSIONS FOR THE BEAVON PLANT

BEAVON PLANT	
QUANTITY	EQUIPMENT TYPE
4	Pumps
16	Vertical Vessles
6	Horizontal Vessles
2	Storage Tanks
6	Pressure Relief Valves
2	Heat - Exchangers (Heating Side)
2	Heat - Exchangers (Cooling Side)
0	Loading or Unloading Point
42	Flow Transmitters
0	Turbine Meter and Prover Connection

QUANTITY	ACTUAL EQUIPMENT
2	Preheater
2	Hydrolysis Reactor
4	Boilers
4	Pumps
2	Desuperheater Contact Condenser
2	Venturi Scrubber-Stripper
8	Pressure Relief Valves
4	Oxidizer Tanks
2	Slurry Tank
2	Balance Tank
2	Separation Wash and Reslurry
2	Sulfur Collector Drum
46	Flow Transmitters

QUANTITY	ESTIMATED EQUIPMENT
442	Valves
221	Open - Ended Lines
1856	Flanges

QUANTITY	EQUIPMENT WITH FUGITIVES
442	Valves
4	Pumps
0	Compressors
8	Pressure Relief Valves
1856	Flanges
221	Open - Ended Lines

Table A.40

FEED COOLER
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	0
Horizontal Vessels	0
Storage Tanks	0
Pressure Relief Valves	0
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	1
Loading or Unloading Point	0
Flow Transmitters	2
Turbine Meter and Prover Connection	0

FLOW SUMMARY			
CO2	kg/hr	mass fraction	
O2	1923	4.11E-01	
S	0	0.00E+00	
H2O	0	0	
H2S	34	1.31E-01	
N2	128	2.73E-02	
NH3	1942	4.16E-01	
CH3OH	71	1.51E-02	
TOTAL FLOW	3	8.50E-04	
	155	4677	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	29	0	0	0	122	15

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	6.88E-02	0	0	0	4.16E-02	1.01E-02	1.18E-01
O2	0.00E+00	0	0	0	0.00E+00	0.00E+00	0.00E+00
S	0	0	0	0	0	0	0
H2O	2.12E-02	0	0	0	1.32E-02	3.22E-03	3.77E-02
H2S	4.43E-03	0	0	0	2.78E-03	6.72E-04	7.88E-03
N2	6.74E-02	0	0	0	4.20E-02	1.02E-02	1.20E-01
NH3	2.45E-03	0	0	0	1.53E-03	3.72E-04	4.35E-03
CH3OH	1.08E-04	0	0	0	6.57E-05	1.60E-05	1.87E-04

Table A.41

DESUPERHEATER CONTACT CONDENSER (liquid lines)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
Pumps	2	CO2	44	1823	4.11E-01
Vertical Vessels	1	O2	0	0	0.00E+00
Horizontal Vessels	0	S	0	0	0
Storage Tanks	0	H2O	34	611	1.31E-01
Pressure Relief Valves	0	H2S	4	128	2.73E-02
Heat - Exchangers (Heating Side)	1	N2	69	1942	4.15E-01
Heat - Exchangers (Cooling Side)	0	NH3	4	71	1.51E-02
Loading or Unloading Point	0	CH3OH	0	3	6.50E-04
Flow Transmitters	5	TOTAL FLOW	155	4677	
Turbine Meter and Prover Connection	0				

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0.0484	0	0	0.00083	0.0017
QUANTITY	83	2	0	0	349	42

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	2.42E-01	4.06E-02	0	0	1.19E-01	2.90E-02	4.31E-01
O2	0.00E+00	0.00E+00	0	0	0.00E+00	0.00E+00	0.00E+00
S	0	0	0	0	0	0	0
H2O	7.70E-02	1.29E-02	0	0	3.78E-02	9.22E-03	1.37E-01
H2S	1.61E-02	2.89E-03	0	0	7.89E-03	1.92E-03	2.86E-02
N2	2.45E-01	4.10E-02	0	0	1.20E-01	2.93E-02	4.36E-01
NH3	8.89E-03	1.49E-03	0	0	4.38E-03	1.06E-03	1.58E-02
CH3OH	3.83E-04	6.42E-05	0	0	1.88E-04	4.59E-05	6.81E-04

Table A.42

DESUPERHEATER CONTACT CONDENSER (vapor lines)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	1
Horizontal Vessels	0
Storage Tanks	0
Pressure Relief Valves	0
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	0
Loading or Unloading Point	0
Flow Transmitters	2
Turbine Meter and Prover Connection	0

FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
CO ₂	44	1923	4.11E-01
O ₂	0	0	0.00E+00
S	0	0	0
H ₂ O	34	611	1.31E-01
H ₂ S	4	128	2.73E-02
N ₂	69	1942	4.15E-01
NH ₃	4	71	1.51E-02
CH ₃ OH	0	3	6.50E-04
TOTAL FLOW	155	4677	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	36	0	0	0	147	18

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	8.06E-02	0	0	0	5.02E-02	1.22E-02	1.43E-01
O ₂	0.00E+00	0	0	0	0.00E+00	0.00E+00	0.00E+00
S	0	0	0	0	0	0	0
H ₂ O	2.56E-02	0	0	0	1.59E-02	3.89E-03	4.54E-02
H ₂ S	5.34E-03	0	0	0	3.33E-03	8.11E-04	9.48E-03
N ₂	8.14E-02	0	0	0	5.07E-02	1.24E-02	1.44E-01
NH ₃	2.96E-03	0	0	0	1.84E-03	4.49E-04	5.25E-03
CH ₃ OH	1.27E-04	0	0	0	7.93E-05	1.93E-05	2.26E-04

Table A.43

VENTURI SCRUBBER / STRIPPER (vapor line)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	2
Horizontal Vessels	0
Storage Tanks	0
Pressure Relief Valves	0
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	0
Loading or Unloading Point	0
Flow Transmitters	0
Turbine Meter and Prover Connection	0

FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
CO ₂	44	1923	4.11E-01
O ₂	0	0	0.00E+00
S	0	0	0
H ₂ O	34	611	1.31E-01
H ₂ S	4	128	2.73E-02
N ₂	69	1942	4.15E-01
NH ₃	4	71	1.51E-02
CH ₃ OH	0	3	6.50E-04
TOTAL FLOW	155	4877	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0056	0	0	0	0.00083	0.0017
QUANTITY	46	0	0	0	193	23

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO ₂	1.06E-01	0	0	0	6.59E-02	1.81E-02	1.88E-01
O ₂	0.00E+00	0	0	0	0.00E+00	0.00E+00	0.00E+00
S	0	0	0	0	0	0	0
H ₂ O	3.37E-02	0	0	0	2.10E-02	5.11E-03	6.87E-02
H ₂ S	7.02E-03	0	0	0	4.37E-03	1.07E-03	1.25E-02
N ₂	1.07E-01	0	0	0	6.66E-02	1.62E-02	1.90E-01
NH ₃	3.89E-03	0	0	0	2.42E-03	5.90E-04	6.89E-03
CH ₃ OH	1.67E-04	0	0	0	1.04E-04	2.54E-05	2.97E-04

Table A.44

VENTURI SCRUBBER / STRIPPER (liquid lines)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY	FLOW SUMMARY			mass fraction
Pumps	0	CO2	0	0	0
Vertical Vessels	2	O2	0	0	0
Horizontal Vessels	0	S	0	0	0
Storage Tanks	0	H2O	20	360	5.81E-01
Pressure Relief Valves	0	H2S	1	34	5.49E-02
Heat - Exchangers (Heating Side)	0	N2	8	225	3.64E-01
Heat - Exchangers (Cooling Side)	0	NH3	0	0	0
Loading or Unloading Point	0	CH3OH	0	0	0
Flow Transmitters	5	TOTAL FLOW	29	819	
Turbine Meter and Prover Connection	0				

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0	0.00083	0.0017
QUANTITY	78	0	0	0	319	38

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0
H2O	3.14E-01	0	0	0	1.54E-01	3.75E-02	5.05E-01
H2S	2.98E-02	0	0	0	1.45E-02	3.55E-03	4.77E-02
N2	1.96E-01	0	0	0	9.84E-02	2.35E-02	3.18E-01
NH3	0	0	0	0	0	0	0
CH3OH	0	0	0	0	0	0	0

Table A.46

**OXIDIZER TANK (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN**

EQUIPMENT TYPE	QUANTITY	kgmol/hr	kg/hr	mass fraction
Pumps	0	0	0	0
Vertical Vessels	2	2	69	4.82E-02
Horizontal Vessels	0	0	0	0
Storage Tanks	0	0	0	0
Pressure Relief Valves	1	54	971	6.81E-01
Heat - Exchangers (Heating Side)	0	5	162	1.13E-01
Heat - Exchangers (Cooling Side)	0	8	225	1.58E-01
Loading or Unloading Point	0	0	0	0
Flow Transmitters	0	0	0	0
Turbine Meter and Prover Connection	1	69	1427	0
TOTAL FLOW				

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	2
Horizontal Vessels	0
Storage Tanks	0
Pressure Relief Valves	1
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	0
Loading or Unloading Point	0
Flow Transmitters	0
Turbine Meter and Prover Connection	1
	0

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0.104	0.00083	0.0017
QUANTITY	55	0	0	1	231	28

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	0	0	0	0	0	0	0
O2	1.88E-02	0	0	5.01E-03	9.25E-03	2.25E-03	3.53E-02
S	0	0	0	0	0	0	0
H2O	2.86E-01	0	0	7.08E-02	1.30E-01	3.18E-02	4.99E-01
H2S	4.42E-02	0	0	1.18E-02	2.17E-02	5.29E-03	8.30E-02
N2	6.17E-02	0	0	1.64E-02	3.03E-02	7.39E-03	1.16E-01
NH3	0	0	0	0	0	0	0
CH3OH	0	0	0	0	0	0	0

Table A.46

SLURRY TANK AND WASH (liquid)
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY	kgmol/hr	kg/hr	mass fraction
Pumps	0	0	0	0
Vertical Vessels	0	0	0	0
Horizontal Vessels	1	5	173	1.23E-01
Storage Tanks	1	64	971	6.92E-01
Pressure Relief Valves	1	1	34	2.42E-02
Heat - Exchangers (Heating Side)	0	8	226	1.01E-01
Heat - Exchangers (Cooling Side)	0	0	0	0
Loading or Unloading Point	0	0	0	0
Flow Transmitters	2	0	0	0
Turbine Meter and Prover Connection	0	0	0	0
TOTAL FLOW		68	1403	

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	0
Horizontal Vessels	1
Storage Tanks	1
Pressure Relief Valves	1
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	0
Loading or Unloading Point	0
Flow Transmitters	2
Turbine Meter and Prover Connection	0

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0.104	0.00083	0.0017
QUANTITY	49	0	0	1	206	26

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0
S	4.28E-02	0	0	1.28E-02	2.10E-02	5.13E-03	8.18E-02
H2O	2.41E-01	0	0	7.20E-02	1.18E-01	2.88E-02	4.60E-01
H2S	8.43E-03	0	0	2.62E-03	4.14E-03	1.01E-03	1.61E-02
N2	5.59E-02	0	0	1.67E-02	2.74E-02	6.69E-03	1.07E-01
NH3	0	0	0	0	0	0	0
CH3OH	0	0	0	0	0	0	0

BALANCE TANK (liquid)

ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY
Pumps	0
Vertical Vessels	0
Horizontal Vessels	1
Storage Tanks	0
Pressure Relief Valves	1
Heat - Exchangers (Heating Side)	0
Heat - Exchangers (Cooling Side)	0
Loading or Unloading Point	0
Flow Transmitters	1
Turbine Meter and Prover Connection	0

FLOW SUMMARY	kgmol/hr	kg/hr	mass fraction
CO ₂	0	0	0
O ₂	0	0	0
S	0	0	0
H ₂ O	20	360	6.81E-01
H ₂ S	1	34	5.49E-02
N ₂	8	225	3.84E-01
NH ₃	0	0	0
CH ₃ OH	0	0	0
TOTAL FLOW	29	619	

EQUIPMENT WITH FUGITIVES		Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR		0.0071	0	0	0.104	0.00083	0.0017
QUANTITY		30	0	0	1	128	15

COMPONENT	EMISSIONS FROM:						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0
H2O	1.24E-01	0	0	0	0	0	0
H2S	1.17E-02	0	0	6.04E-02	6.08E-02	1.48E-02	2.80E-01
N2	7.75E-02	0	0	5.71E-03	5.74E-03	1.40E-03	2.45E-02
NH3	0	0	0	3.78E-02	3.81E-02	9.28E-03	1.63E-01
CH3OH	0	0	0	0	0	0	0

Table A.48

WATER - SULFUR SEPARATOR
ESTIMATION OF FUGITIVE EMISSIONS FOR ONE BEAVON TRAIN

EQUIPMENT TYPE	QUANTITY	kg/hr	mass fraction
Pumps	0	0	0
Vertical Vessels	0	0	0
Horizontal Vessels	1	173	1.09E-01
Storage Tanks	0	1151	7.27E-01
Pressure Relief Valves	0	34	2.15E-02
Heat - Exchangers (Heating Side)	0	225	1.42E-01
Heat - Exchangers (Cooling Side)	0	0	0
Loading or Unloading Point	0	0	0
Flow Transmitters	3	0	0
Turbine Meter and Prover Connection	0	1583	0
TOTAL FLOW		78	

EQUIPMENT TYPE	QUANTITY	kg/hr	mass fraction
Pumps	0	0	0
Vertical Vessels	0	0	0
Horizontal Vessels	1	173	1.09E-01
Storage Tanks	0	1151	7.27E-01
Pressure Relief Valves	0	34	2.15E-02
Heat - Exchangers (Heating Side)	0	225	1.42E-01
Heat - Exchangers (Cooling Side)	0	0	0
Loading or Unloading Point	0	0	0
Flow Transmitters	3	0	0
Turbine Meter and Prover Connection	0	1583	0
TOTAL FLOW		78	

EQUIPMENT WITH FUGITIVES	Valves	Pumps	Compressors	Pressure Relief Valves	Flanges	Open - Ended Lines
EMISSION FACTOR	0.0071	0	0	0	0.00083	0.0017
QUANTITY	39	0	0	0	164	20

COMPONENT	EMISSIONS FROM :						TOTAL EMISSIONS (kg/hr)
	Valves (kg/hr)	Pumps (kg/hr)	Compressors (kg/hr)	Pressure Relief Valves (kg/hr)	Flanges (kg/hr)	Open - Ended Lines (kg/hr)	
CO2	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0
S	3.02E-02	0	0	0	1.48E-02	3.82E-03	4.87E-02
H2O	2.01E-01	0	0	0	9.88E-02	2.41E-02	3.24E-01
H2S	5.85E-03	0	0	0	2.82E-03	7.12E-04	9.58E-03
N2	3.94E-02	0	0	0	1.94E-02	4.72E-03	6.35E-02
NH3	0	0	0	0	0	0	0
CH3OH	0	0	0	0	0	0	0

Appendix B

Case 2: Lurgi gasifier

CASE 2

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 5.0 million metric tons of coal, 2.1 million metric tons of oxygen, and produces 0.50 million metric tons of mixed alcohols per year.

COAL PREPARATION

Coal (stream 10) is sent to the Coal Preparation Block. The coal is crushed and conveyed to the lockhopper on top of the gasifier. The Coal Preparation Block is composed of three plants from the Houston report. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

LURGI GASIFIER

The coal enters the Lurgi gasifier through a lockhopper at the top. The coal flows down in the gasifier, counter-current to the gases. The ash settles to the conical bottom of the gasifier. The compressed oxygen (stream 9) and steam (stream 12) enter beneath the surface of the ash bed, which is supported by a rotating grate. Ash exits from the bottom of the gasifier. The syngas exits near the top of the gasifier at 400°C and 2,800 kPa. The raw syngas is quenched, some heat is recovered, and the heavy by-products condense and are removed. Economic data for this block was obtained from a report on the Great Plains Gasification Project, and the cost for this plant was estimated by using exponential scaling, where each train can handle up to 958.3 tons of coal per day [5].

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen (stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not

include the inlet air compressors or the outlet oxygen compressors. In the cryogenic system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. The capital investment has been calculated linearly for the reduction in trains, and exponentially for throughput change per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas stream (stream 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A CO_2 - N_2 mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 25) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [2].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [3].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. The power requirement for this unit has been included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [7]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [8].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [8]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [8]. This is a 3-stage steam turbine system. The high pressure stage

inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

PRESSURE SWING ADSORPTION

The clean syngas (stream 22A) is sent to PSA for selective hydrogen removal and purification. The adjusted syngas (stream 22AA), which leaves the PSA unit at 200 kPa, is compressed and sent on to the reactor while the purified excess hydrogen is sent to the plant battery limits for sale if possible.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be pointed out. Also, there are alternatives that have not been fully considered which should be viewed in more detail. They are listed below along with the reasons behind them.

- The traditional method of producing large quantities of pure oxygen is by cryogenics, which is used for this case. However, recent reports have suggested that membrane and catalytic processes are becoming economically competitive with cryogenics. Therefore, we suggest that more research be done in this area.
- The Rectisol system was chosen for this case for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that substantial quantities of H₂S are beneficial in the reaction stages of this case. If this is so, then a system such as the Benfield Acid Gas removal process might be more suitable. The Benfield system does not remove as much H₂S and has lower capital and operating costs.
- The operating pressure for the Lurgi Gasifiers has been set at 2,800 kPa. No data have been found on the maximum pressure that a Lurgi Gasifier can be run. Since the pressure required at the reactor is 14,000 kPa, we would of course like to run the gasifiers at as high a pressure as possible.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Pressure Swing Adsorption	20.6
Coal Preparation	77.5
Lurgi Gasifier	653.4
Gas Turbines	356.4
Steam Turbines	46.8
Exhaust Gas Heat Recovery	29.6
Cryogenic Oxygen Production	212.7
Rectisol (Acid Gas Separation)	115.5
Claus (Sulfur Recovery)	29.7
Beavon	6.4
Alcohol Synthesis Loop	47.2
CO ₂ Removal	4.5
Other Compressors	216.6
TOTAL	1817.1

(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)	1817.1
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)	483.7
Coal (\$33/metric ton delivered)	163.5
Other Expenses	320.2
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)	430.2
Power (\$0.05/kWh)	312.0
Sulfur (\$300/metric ton) (7)	35.2
Coal Tar/Liquid By-Products (\$99.1/metric ton)	43.4
Hydrogen (\$35.31/1000 cubic meters)	39.5

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 4 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (4). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-81.4	71.4
O2 Prep	2	500	9	2800	-16.0	15.0
Rxtr Prep	22AA	200	26	14000	-148.0	129.8
Recy Comp	56A	12666	56B	14000	-0.2	0.4
Total compressor needs					-245.6	
Other in plant needs					-39.5	
Total produced in steam and gas turbines					1065.1	
Net power output					780.1	
Total installed compressor costs (1992 dollars)						216.6

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3.* Prepared by the Linde Division of Union Carbide Corporation, June 1982.
2. "Beavon Sulfur Removal Process," *Hydrocarbon Processing*, April 1984, p. 78.
3. Frank, Marshall E. "Methanol: Emerging Uses, New Syntheses," *Chemtech*, June 1982, pp. 358-362.
4. Baasel, William D., *Preliminary Chemical Engineering Plant Design, 2nd edition*, Van Nostrand Reinhold, New York, 1990, pp. 529-530.
5. Miller, W. R., F. I. Honea, R. A. Lang, T. E. Berty, R. C. Delaney, R. W. Hospodarec, and P. F. Mako, "Great Plains Gasification Plant Start-Up and Modification Report," U.S. Dept. of Energy report no. DOE/CH/10088-2018, March 1986.
6. *Chemical Marketing Reporter*, August 31, 1992.
7. Report TR-101789, Houston Lighting and Power Company's Evaluation of Coal Gasification Coproduction Energy Facilities, EPRI Project 3226-04, 1992.
8. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure B.1 : Block Flow Diagram for Case 2

Table B.1 Case 2 Flow Table

	001	001A	002	003	004	006	009	Q10
Ar	372.8	372.8				372.8		
C								34157.0
CH3OH								
C2H5OH								
C3H7OH								
C4H9OH								
C5H11OH								
CO								
CO2	12.9	12.9						
CO3								
CaCO3								
H2								13957.8
H2O	963.5	963.5						393.3
H2S								
N2	31216.9	31216.9		31216.9	29708.1			302.1
NH3								
O2	8392.5	8392.5					8392.5	2690.0
S								459.0
Al2O3								639.5
C3H6O2								
C4H8O2								
CH4								
C2H6								
kmol/hr	40958.6	40958.6	8392.5	31216.9	29708.1	372.8	8392.5	52598.7
kg/hr	1175455.8	1175455.8	268559.6	874073.8	831826.2	14911.0	268559.6	619338.9
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	140.0	25.0
Press. (kPa)	500.0	101.3	500.0	500.0	500.0	500.0	2800.0	101.3

Table E.1 Case 2 Flow Table (cont'd)

	012	017A	018	019	020	022	027AA	023
Az								
C								
CH3OH					5.8			
C2H5OH								
C3H7OH								
C4H9OH								
C5H11OH								
CO			11,261.9			11261.9	11261.9	
CO2			12,559.6					7595.2
CO3								
CaCO3								
H2			18,922.4			18922.4	12674.3	
H2O	37985.6	23964.8	23,964.8					
H2S			459.0					
N2			299.9	1508.8				
NH3			4.4					
O2								
S								
Al2O3								
C3H6O2								
C4H8O2								
CH4								
C2H6			3,787.8			3787.8	3787.8	
kmol/hr	37985.6	23964.8	71828.3	1508.8		469.4	469.4	
kg/hr	583741.0	431366.8	1440290.1	42247.6	5.8	34441.6	28193.5	7595.2
Temp. (C)	400.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Press. (kPa)	3900.0	2800.0	2800.0	500.0	101.3	2800.0	200.0	2800.0

Table B.1 Case 2 Flow Table (cont'd)

	024	025	026	026A	027	027A	028	029	034
Ar									
C								944.6	4,565.2
CH ₃ OH		5.8		628.3					
C ₂ H ₅ OH				655.4					
C ₃ H ₇ OH				145.0					
C ₄ H ₉ OH				36.5					
C ₅ H ₁₁ OH				15.2					
CO			11281.9	7001.9	6594.0				
CO ₂	4430.5	632.9		1493.7	1406.7		12.9		
COS									
CaCO ₃									
H ₂			12674.3	7880.0	7421.0	6248.1			
H ₂ O				140.1			963.5		
H ₂ S		459.0							
N ₂	1809.8								
NH ₃		4.4							
O ₂									
S									
Al ₂ O ₃								639.5	
CH ₃ CO ₂				18.0					
C ₄ H ₈ O ₂				11.9					
CH ₄			3787.8	4490.5	4228.9				
C ₂ H ₆			469.4	517.1	486.9				
kmol/hr	6239.3	1102.1	28193.5	23033.7	20137.5	6248.1	976.4	1584.2	4565.2
kg/hr	248588.7	43713.7	415369.9	432797.5	343640.2	12496.2	17911.5	76567.4	54781.9
Temp. (C)	25.0	25.0	240.0	310.0	25.0	25.0	25.0	25.0	25.0
Press. (KPa)	2800.0	2800.0	14000.0	12666.0	12666.0	2800.0	500.0	101.3	101.3

Table B.1 Case 2 Flow Table (cont'd)

	042	045	046	047	050	051	054	056	056A
Ar									
C									
CH3OH		5.8			5.8				
C2H5OH									
C3H7OH									
C4H9OH									
C5H11OH									
CO									
CO2		632.9			632.9			407.9 87.0	407.9
COS									
CaCO3									
H2								459.0	459.0
H2O		436.0					459.0		
H2S		22.9							
N2	820.1	820.1		109.6	929.7				
NH3		4.4			4.4				
O2	218.0			29.1	17.7				
S			436.0			22.9			
Al2O3									
C3H6O2									
C4H8O2									
CH4								261.6	261.6
C2H6								30.1	30.1
kgol/hr	1038.2	1922.2	436.0	138.7	1590.9	22.9	459.0	1245.6	1158.6
kg/hr	29940.6	59701.4	13952.9	4000.3	54705.8	734.4	8261.6	21256.2	17477.6
Temp. (C)	25.0	200.0	125.0	25.0	100.0	125.0	50.0	25.0	25.0
Press. (kPa)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	12666.0	12666.0

Table B.1 Case 2 Flow Table (cont'd)

	056a	057	059	063	064	065	067	070
Ar								
C								
CH ₃ OH					628.3			
C ₂ H ₅ OH					655.4			
C ₃ H ₇ OH					145.0			
C ₄ H ₉ OH					36.5			
C ₅ H ₁₁ OH					15.2			
CO	407.9		7001.9					13203.5
CO ₂		87.0	1493.7					
COS								
CrCO ₃								
H ₂	459.0		7880.0	140.1		9633.9		26973.6
H ₂ O								
H ₂ S							203424.9	203424.9
N ₂								
NH ₃							54075.0	36905.4
O ₂								
S								
Al ₂ O ₃				18.0				
C ₃ H ₆ O ₂				11.2				
C ₄ H ₈ O ₂								
CH ₄	261.6		4490.5					
C ₂ H ₆	30.1		517.1					
kmol/hr	1158.6	87.0	21383.2	170.1	1480.4	9633.9	257499.8	280507.3
kg/hr	17427.6	3828.6	364896.5	4905.1	62996.0	173411.0	7426295.3	7943346.5
Temp. (C)	45.0	25.0	25.0	25.0	25.0	25.0	25.0	590.0
Press. (kPa)	14000.0	12666.0	12666.0	12666.0	12666.0	10000.0	101.3	101.3

Table B.1 Case 2 Flow Table (cont'd)

	073	074	075	076	077	078
Ar						
C						
CH ₃ OH						
C ₂ H ₅ OH						
C ₃ H ₇ OH						
C ₄ H ₉ OH						
C ₅ H ₁₁ OH						
CO						
CO ₂			13203.5			
CO ₃						
CaCO ₃						
H ₂						
H ₂ O	43501.6	43501.6	26973.6	43501.6	43501.6	43501.6
H ₂ S						
N ₂			203424.9			
NH ₃						
O ₂			36905.4			
S						
Al ₂ O ₃						
C ₃ H ₆ O ₂						
C ₄ H ₆ O ₂						
CH ₄						
C ₂ H ₆						
kmol/hr	43501.6	43501.6	280507.3	43501.6	43501.6	43501.6
kg/hr	783028.2	783028.2	7943346.5	783028.2	783028.2	783028.2
Temp. (C)	25.0	535.0	200.0	40.0	380.0	535.0
Press. (kPa)	10000.0	10000.0	101.3	7.4	3000.0	3000.0

Table B.2 Case 2 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	10.1	0.0
Cryogenic Oxygen Plant	11.2	0.0
Rectisol Plant	14.5	0.0
Lurgi Gasifier	3.1	0.0
Claus Plant	0.6	0.0
Gas Turbine	0.0	801.1
Steam Turbine	0.0	264.0
Compressor 1	81.4	0.0
Compressor 2	16.0	0.0
Compressor 4	146.0	0.0
Compressor 5	0.2	0.0
Total	285.1	1065.1

Appendix C

Case 3: Natural gas only

CASE 3

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, have been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 1.2 billion standard cubic meters of natural gas per year and produces 0.50 million metric tons of mixed alcohols per year.

SYNGAS PRODUCTION FROM NATURAL GAS

Compressed natural gas (stream 14) and steam (stream 15) are reacted in the Steam Reformation Block. The cooled output gas (stream 17) goes to the Rectisol Block. The cost for this unit was estimated from data found for a hydrogen production facility, with a scaling exponent of 0.8 [2]. The fuel gas usage for this block is estimated to be 30% of the natural gas feed.

RECTISOL

The cooled gas stream (stream 17), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. CO₂ levels are reduced to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A CO₂-N₂ mixture (stream 24) and a CO₂ rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

PRESSURE SWING ADSORPTION

The clean syngas (stream 22) is sent to PSA for selective hydrogen removal and purification. The adjusted syngas (stream 22AA), which leaves the PSA unit at 200 kPa, is compressed and then sent on to the reactor. The purified excess hydrogen is then split into two streams. One stream (27A) sent to the plant battery limits for sale, if possible.

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [3].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. The power requirement for this unit is included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [5]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [6].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [6]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [6]. This is a 3-stage steam turbine system. The high pressure stage

inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Pressure Swing Adsorption	15.1
Syngas Reforming	90.3
Rectisol	25.8
Gas Turbines	45.0
Steam Turbines	9.9
Exhaust Gas Heat Recovery	11.1
CO2 Removal	26.9
Other Compressors	57.5
Alcohol Synthesis Loop	47.2

TOTAL	328.8
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(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant, for Case 3A.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)		335.9
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)		223.3
Natural Gas (\$106/1000 cubic meters)	164.1	
Other Expenses	59.2	
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)		112.4
Hydrogen (\$35.31/1000 cubic meters)	95.7	
	H-5	
Power (\$0.05/kWh)	16.7	

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant, for Case 3B.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)		328.8
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)		153.6
Natural Gas (\$61.8/1000 cubic meters)	95.7	
Other Expenses	57.9	
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)		72.5
Hydrogen (\$20.6/1000 cubic meters)	55.8	
Power (\$0.05/kWh)	16.7	

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 2 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (4). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Rxtr Prep	22AA	200	26	14000	-60.1	53.8
Recy Comp	56A	12666	56B	14000	-3.6	3.6
Total compressor needs					-63.6	
Other in plant needs					-1.4	
Total produced in steam and gas turbines					106.8	
Net power output					41.7	
Total installed compressor costs (1992 dollars)						57.5

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3*. Prepared by the Linde Division of Union Carbide Corporation, June 1982.
2. Baasel, William D., *Preliminary Chemical Engineering Plant Design, 2nd edition*. (Van Nostrand Reinhold, New York 1990), pp. 268-269.
3. Frank, "Methanol: Emerging Uses, New Syntheses," *Chemtech*, June 1982, pp. 358-362.
4. Baasel, pp. 529-530.
5. Report TR-101789, Houston Lighting and Power Company's Evaluation of Coal Gasification Coproduction Energy Facilities, EPRI Project 3226-04, 1992.
6. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure C.1 : Block Flow Diagram for Case 3

Table C.1 Case 3 Flow Table

	014	015	017	017A	019	020	022	022A	023
Air									
C									
CH ₃ OH						0.6			
C ₂ H ₅ OH									
C ₃ H ₇ OH									
C ₄ H ₉ OH									
C ₅ H ₁₁ OH									
CO			5382.1				5382.1	5382.1	
CO ₂			1259.2						755.5
CO ₂									
C ₆ CO ₃									
H ₂			21183.2				21183.2	6057.1	
H ₂ O		15708.1	7807.6	7807.6					
H ₂ S									
N ₂					150.1				
NH ₃									
O ₂									
S									
A1203									
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄	5646.5		5.2				5.2	5.2	
C ₂ H ₆									
kmol/hr	5646.5	15708.1	35637.3	7807.6	150.1	0.6	26520.5	11444.4	755.5
kg/hr	106344.5	282745.6	389090.1	140536.0	4202.6	18.4	193148.7	162896.6	33243.2
Temp. (C)	25.0	100.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Press. (kPa)	1480.0	1480.0	1400.0	1400.0	1400.0	101.3	1400.0	200.0	1400.0

Table C.1 Case 3 Flow Table (cont'd)

	024	026	026A	027	27A	27B	056	056A	056B
Ar									
C									
CH ₃ OH			628.3						
C ₂ H ₅ OH			655.4						
C ₃ H ₇ OH			145.0						
C ₄ H ₉ OH			36.5						
C ₅ H ₁₁ OH			16.2						
CO		5382.1	7001.9	714.2			6287.7	6287.7	6287.7
CO ₂	503.7		1493.7	152.4			1341.4		
COS									
CaCO ₃									
H ₂		6057.1	7880.0	803.8	15126.1		7076.3	7076.3	7076.3
H ₂ O			140.1						
H ₂ S									
N ₂	150.1								
NH ₃									
O ₂									
S									
Al ₂ O ₃									
C ₃ H ₆ O ₂			18.0						
C ₄ H ₈ O ₂			11.9						
CH ₄		5.2	4375.8	446.3			3929.5	3929.5	3929.5
C ₂ H ₆			171.6	17.5			154.1	154.1	154.1
kmol/hr	653.8	11444.4	22573.5	2134.1	15126.1		18788.9	17447.5	17447.5
kg/hr	26364.7	162896.6	420598.8	35975.2	30252.1		316722.5	257702.2	257702.2
Temp. (C)	25.0	240.0	310.0	25.0	25.0	25.0	25.0	25.0	45.0
Press. (kPa)	1400.0	1400.0	12666.0	12666.0	1400.0	1400.0	12666.0	12666.0	14000.0

Table C.1 Case 3 Flow Table (cont'd)

	057	059	063	064	065	067	070	073	074
Ar									
C									
CH ₃ OH				628.3					
C ₂ H ₅ OH				658.4					
C ₃ H ₇ OH				145.0					
C ₄ H ₉ OH				36.5					
C ₅ H ₁₁ OH				15.2					
CO		7001.9							
CO ₂	1341.4	1493.7					1347.9		
COS									
CuSO ₃									
H ₂		7880.0							
H ₂ O			140.1		955.8		2704.7	4298.2	4298.2
H ₂ S									
N ₂						20181.9	20181.9		
NH ₃									
O ₂						5384.8	3651.9		
S									
Al ₂ O ₃									
C ₃ H ₆ O ₂			18.0						
C ₄ H ₈ O ₂			11.9						
CH ₄		4375.8							
C ₂ H ₆		171.6							
kmol/hr	1341.4	20923.0	170.1	1480.4	955.8	25546.7	27886.4	4298.2	4298.2
kg/hr	59020.4	352697.7	4805.1	62996.0	17204.2	736757.3	789946.7	77367.5	77367.5
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	590.0	25.0	535.0
Press. (kPa)	12666.0	12666.0	12666.0	12666.0	10000.0	101.3	101.3	10000.0	10000.0

Table C.1 Case 3 Flow Table (cont'd)

	075	076	077	078
Ar				
C				
CH ₃ OH				
C ₂ H ₅ OH				
C ₃ H ₇ OH				
C ₄ H ₉ OH				
C ₅ H ₁₁ OH				
CO				
CO ₂	1347.9			
CO ₂				
CaCO ₃				
H ₂				
H ₂ O	2704.7	4298.2	4298.2	4298.2
H ₂ S				
N ₂	20181.9			
NH ₃				
O ₂	3651.9			
S				
Al ₂ O ₃				
C ₃ H ₆ O ₂				
C ₄ H ₈ O ₂				
CH ₄				
C ₂ H ₆				
kmol/hr	27886.4	4298.2	4298.2	4298.2
kg/hr	789946.7	77367.5	77367.5	77367.5
Temp. (C)	200.0	40.0	380.0	535.0
Press. (kPa)	101.3	7.4	3000.0	3000.0

Table C.2 Case 3 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Rectisol Plant	1.4	0
Gas Turbine	0	80.7
Steam Turbine	0	26.1
Compressor 4	60.1	0
Compressor 5	3.6	0
Total	65.1	106.8

Appendix D

Case 4: Texaco gasifier and sour gas shift converter

CASE 4

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 1.3 million metric tons of coal, 1.1 million metric tons of oxygen, and produces 0.50 million metric tons of mixed alcohols per year.

COAL PREPARATION

Coal (stream 10) and water (stream 12), are sent to the Coal Preparation Block. The coal is crushed, mixed with the water, and pumped to the gasifier as a ~60% solids mixture by weight (stream 13). The Coal Preparation Block is composed of four plants from the Houston report. Plant 01 is the Coal Slurry Preparation Plant. The cost of this plant was scaled linearly due to its multiple train format; where each train can handle up to 1,150 tons of coal per day. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

TEXACO GASIFIER

The coal slurry (stream 13) is mixed with compressed oxygen (stream 9) and burned at 1,200-1,400°C and 8,000 kPa in the Texaco Gasifier Block. The hot, raw gas (stream 8) is sent to the Syngas Heat Recovery Block, and the slag (stream 33) is sent to the Slag Handling Block. The equivalent of the Texaco Gasifier Block is Plant 03 in the Houston report, and each train can handle up to 958.3 tons of coal per day.

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen (stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not include the inlet air compressors or the outlet oxygen compressors. In the cryogenic

system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. We also assume that some scale down is possible for this system, so the capital investment has been calculated linearly for the reduction in trains, and exponentially for throughput reduction per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas stream (stream 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A $\text{CO}_2\text{-N}_2$ mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

SLAG HANDLING

Molten slag from the Texaco Gasifier Block (stream 33) is direct quenched with water and sent to slag disposal (stream 37). A small amount of water (stream 36) is purged from the closed loop and is replaced by water make-up (stream 34). This block is the same as Houston Plant 63. The cost for this plant was estimated by exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

SYNGAS HEAT RECOVERY

The raw gas stream from the Texaco Gasifier Block (stream 8) at $1,300^\circ\text{C}$ and 8,000 kPa enters the Syngas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 71). The raw gas stream exits at 300°C (stream 18), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 68). It is assumed that the raw gas stream is cooled further prior to entering the Rectisol Block. This block is part of Houston Plant 04.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 41) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [2].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [3].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. Its power requirement is included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [7]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [8].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [8]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Syngas Heat Recovery Block and the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [8]. This is a 3-stage steam turbine system. The high pressure stage inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

SOUR GAS SHIFT CONVERTER

Raw fuel gas (stream 8A) leaving the Heat Recovery Block is shifted to produce the desired H₂ to CO ratio needed in the alcohol synthesis reactor.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be outlined. Also, there are alternatives that have not been fully considered which will be considered in more detail later. They are listed below along with the reasons behind them.

- The traditional method for purifying high quantities of pure oxygen is by cryogenics, which is used for this case. However, recent reports suggest that membrane and catalytic processes are becoming economically competitive with cryogenics. Therefore, we will examine these alternatives.
- The Rectisol system was chosen for this system for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that quantities of H₂S are beneficial if the

reaction involves the MoS_2 catalyst. If this is so, then a system such as the Benfield acid gas removal process might be more suitable. The Benfield system does not remove as much H_2S and has lower capital and operating costs.

- The operating pressure for the Texaco gasifiers has been set at 8,000 kPa. This is the highest pressure indicated in the literature at which a Texaco gasifier has been run. Since the pressure required at the reactor is 14,000 kPa, we would of course like to run the gasifiers at as high a pressure as possible.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Sour Gas Shift	4.4
Coal Preparation	51.4
Texaco Gasifier	195.9
Slag Handling	3.7
Gas Turbines	45.1
Steam Turbines	25.4
Exhaust Gas Heat Recovery	8.9
Synthesis Gas Heat Recovery	5.6
Cryogenic Oxygen Production	109.0
Rectisol (Acid Gas Separation)	51.3
Claus (Sulfur Recovery)	12.5
Beavon	2.7
Alcohol Synthesis Loop	47.2
CO ₂ Removal	26.9
Other Compressors	60.4

TOTAL 650.3

(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)	650.3
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)	157.8
Coal (\$33/metric ton delivered)	43.2
Other Expenses	114.6
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)	51.8
Power (\$0.05/kWh)	41.7
Slag (\$5.5/metric ton) (5)	0.8
Sulfur (\$300/metric ton) (6)	9.3

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 4 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (4). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-42.3	37.4
O2 Prep	2	500	9	8136	-14.7	12.9
Rxtr Prep	22	8030	26	14000	-7.2	6.4
Recy Comp	56A	12666	56B	14000	-3.6	3.6
Total compressor needs					-67.8	
Other in plant needs					-15.2	
Total produced in steam and gas turbines					187.1	
Net power output					104.2	
Total installed compressor costs (1992 dollars)						60.4

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3.* Prepared by the Linde Division of Union Carbide Corporation, June 1982.
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3. Frank, Marshall E. "Methanol: Emerging Uses, New Syntheses," *Chemtech*, June 1982, pp. 358-362.
4. Baasel, William D., *Preliminary Chemical Engineering Plant Design, 2nd edition*, Van Nostrand Reinhold, New York, 1990, pp. 529-530.
5. T. Torries, personal communication
6. *Chemical Marketing Reporter*, August 31, 1992.
7. Report TR-101789, Houston Lighting and Power Company's Evaluation of Coal Gasification Coproduction Energy Facilities, EPRI Project 3226-04, 1992.
8. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure D.1 : Block Flow Diagram for Case 4

Table D.1 Case 4 Flow Tables

	001	001A	002	003	004	006	008	8a	009
Ar	193.6	193.6				193.6			
C									
CH3OH									
C2H5OH									
C3H7OH									
C4H9OH									
C5H11OH									
CO							6481.0	6481.0	
CO2	6.7	6.7					2529.1	2529.1	
COs							12.1	12.1	
CaCO3									
H2							4958.2	4958.2	
H2O	500.4	500.4					4209.6	4209.6	
H2S							109.3	109.3	
N2	16212.5	16212.5		16212.5	15780.1		73.7	73.7	
NH3							12.3	12.3	
O2	4358.6	4358.6	4358.6						4358.6
S									
Al2O3									
C3H6O2									
C4H8O2									
CH4							7.8	7.8	
C2H6									
kmol/hr	21271.9	21271.9	4358.6	16212.5	15780.1	193.6	18393.1	18393.1	4358.6
kg/hr	610474.5	610474.5	139476.8	453951.3	441843.2	7744.0	385273.2	385273.2	139476.8
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	300.0	300.0	225.0
Presg. (kPa)	500.0	101.3	500.0	500.0	500.0	500.0	8135.8	8106.0	8135.8

Table D.1 Case 4 Flow Tables (cont'd)

	010	012	013	017A	018	019	020	022	023
Ar									
C	9029.9		9029.9				1.7		
CH ₃ OH									
C ₂ H ₆ O									
C ₃ H ₈ O									
C ₄ H ₁₀ O									
C ₅ H ₁₂ O									
CO					5382.1			5382.1	
CO ₂					3628.0				2089.1
CO ₂ S					12.1				
CaCO ₃									
H ₂	3689.9		3689.9		6057.1			6057.1	
H ₂ O	104.0	5517.2	5621.2	3110.8	3110.8				
H ₂ S					109.3				
N ₂	79.9		79.9		73.7	432.4			
NH ₃					12.3				
O ₂	711.1		711.1						
S	121.3		121.3						
Al ₂ O ₃	169.1		169.1						
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄					7.8			7.8	
C ₂ H ₆									
kmol/hr	13905.2	5517.2	19422.5	3110.8	16393.1	432.4	1.7	11447.0	2089.1
kg/hr	163731.0	99910.4	263041.5	55993.5	385273.2	12108.1	53.0	162937.6	91918.8
Temp. (C)	25.0	25.0	25.0	25.0	300.0	25.0	25.0	25.0	25.0
Press. (kPa)	101.3	101.3	8135.8	8030.0	8030.0	500.0	101.3	8030.0	8030.0

Table D.1 Case 4 Flow Tables (cont'd)

	024	025	026	026A	027	028	033	034	036
Ar									
C									
CH3OH		1.7		628.3					
C2H6O				655.4					
C3H8O				145.0					
C4H10O				36.5					
C5H12O				15.2					
CO			5382.1	7001.9	714.2				
CO2	1269.8	269.1		1493.7	152.4	6.7			
COS		12.1							
CaCO3									
H2			6057.1	7680.0	803.8			10446.2	10446.2
H2O				140.1		500.4			
H2S		109.3							
N2	506.2								
NH3		12.3							
O2									
S							169.1		
Al2O3				18.0					
C3H6O2				11.9					
C4H8O2									
CH4			7.8	4400.9	448.2				
C2H6				171.6	17.5				
kmol/hr	1775.9	404.4	11447.0	22599.6	2136.7	507.1	169.1	10446.2	10446.2
kg/hr	70042.7	16541.9	162937.5	421000.0	36016.1	9302.4	17245.0	188032.2	188032.2
Temp. (C)	25.0	25.0	100.0	110.0	25.0	25.0	1300.0	25.0	25.0
Press. (KPa)	8030.0	8030.0	14000.0	12666.0	12666.0	500.0	101.3	101.3	101.3

Table D.1 Case 4 Flow Tables (cont'd)

	037	041	042	045	046	047	050	051	054
Ar									
C									
CH ₃ OH		1.7		1.7			1.7		
C ₂ H ₆ O									
C ₃ H ₈ O									
C ₄ H ₁₀ O									
C ₅ H ₁₂ O									
CO									
CO ₂		281.2		281.2			281.2		
CO ₂ S									
CaCO ₃									
H ₂									
H ₂ O				115.3					121.3
H ₂ S		121.3		6.1					
N ₂			216.8	216.8		33.9	250.8		
NH ₃		12.3		12.3					12.3
O ₂			57.6			9.0	6.0		
S					115.3			6.1	
Al ₂ O ₃	169.1								
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄									
C ₂ H ₆									
kmol/hr	169.1	416.5	274.5	633.3	115.3	43.0	539.6	6.1	133.7
kg/hr	17245.0	16758.9	7915.2	20985.4	3688.7	1239.1	19637.0	194.1	2393.4
Temp. (°C)	25.0	25.0	25.0	200.0	125.0	25.0	100.0	125.0	50.0
Press. (kPa)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3

Table D.1 Cave 4 Flow Tables (cont'd.)

	056	056A	056B	057	059	063	064	065	067
Ar									
C									
CH ₃ OH									
C ₂ H ₆ O							628.3		
C ₃ H ₈ O							655.4		
C ₄ H ₁₀ O							145.0		
C ₅ H ₁₂ O							36.5		
CO	6287.7	6287.7	6287.7		7001.9		15.2		
CO ₂	1341.4			1341.4	1493.7				
CO ₂									
CaCO ₃									
H ₂	7076.3	7076.3	7076.3		7880.0				
H ₂ O						140.1		967.2	
H ₂ S									
N ₂									20421.9
NH ₃									
O ₂									5428.6
S									
Al ₂ O ₃						19.0			
C ₃ H ₆ O ₂						11.9			
C ₄ H ₈ O ₂									
CH ₄	3952.0	3952.0	3952.0		4400.9				
C ₂ H ₆	154.1	154.1	154.1		171.6				
kmol/hr	18811.4	17470.0	17470.0	1341.4	20948.1	170.1	1490.4	967.2	25850.5
kg/hr	317082.8	258062.4	258062.4	59020.4	353098.9	4905.1	63996.0	17408.8	745529.1
Temp. (C)	25.0	25.0	45.0	25.0	25.0	25.0	25.0	25.0	25.0
Press. (kPa)	12666.0	12666.0	14000.0	12666.0	12666.0	12666.0	12666.0	10000.0	101.3

Table D.1 Case 4 Flow Tables (cont'd)

	068	070	071	073	074	075	076	077	078
Ar									
C									
CH ₃ OH									
C ₂ H ₆ O									
C ₃ H ₈ O									
C ₄ H ₁₀ O									
C ₅ H ₁₂ O									
CO		1350.4				1350.4			
CO ₂									
COS									
CaCO ₃									
H ₂									
H ₂ O	14422.0	2721.2	14422.0	3079.4	3079.4	2721.2	17501.5	17501.5	17501.5
H ₂ S		20421.9				20421.9			
N ₂									
NH ₃									
O ₂		3710.6				3710.6			
S									
Al ₂ O ₃									
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄									
C ₂ H ₆									
kmol/hr	14422.0	28204.2	14422.0	3079.4	3079.4	28204.2	17501.5	17501.5	17501.5
kg/hr	259596.7	798954.0	259596.7	55430.1	55430.1	798954.0	315026.7	315026.7	315026.7
Temp. (C)	535.0	590.0	25.0	25.0	535.0	200.0	40.0	380.0	535.0
Press. (kPa)	10000.0	101.3	10000.0	10000.0	10000.0	101.3	7.4	3000.0	3000.0

Table D.2 Case 4 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	2.7	0.0
Cryogenic Oxygen Plant	5.8	0.0
Rectisol Plant	4.2	0.0
Texaco Gasifier	0.8	0.0
Syn. Gas Heat Recovery	1.2	0.0
Claus Plant	0.5	0.0
Gas Turbine	0.0	80.9
Steam Turbine	0.0	106.2
Compressor 1	42.3	0.0
Compressor 2	14.7	0.0
Compressor 4	7.2	0.0
Compressor 5	3.6	0.0
Total	82.9	187.1

Appendix E

Case 5: Shell gasifier and sour gas shift converter

CASE 5

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 1.3 million metric tons of coal, 1.0 million metric tons of oxygen, and produces 0.50 million metric tons of mixed alcohols per year.

COAL PREPARATION

Coal (stream 10) and carbon dioxide (stream 12) are sent to the Coal Preparation Block. The coal is crushed, mixed with the carbon dioxide, and sent to the gasifier (stream 13). The Coal Preparation Block is composed of three plants from the Houston report. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

SHELL GASIFIER

The coal is conveyed by CO₂ to the gasifier, where it mixes with compressed oxygen (stream 9) and is burned at approximately 1,300°C and 2,800 kPa in the Shell Gasifier Block. The hot raw gas (stream 8) is sent to the Syngas Heat Recovery Block, and the slag (stream 33) is sent to the Slag Handling Block. Each train can handle up to 2,541 tons of coal per day, with a scaling exponent of 0.65.

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen (stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not include the inlet air compressors or the outlet oxygen compressors. In the cryogenic system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. We also

assume that some scale down is possible for this system, so the capital investment has been calculated linearly for the reduction in trains, and exponentially for throughput reduction per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas stream (stream 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A $\text{CO}_2\text{-N}_2$ mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

SLAG HANDLING

Molten slag from the Shell Gasifier Block (stream 33) is direct quenched with water and sent to slag disposal (stream 37). A small amount of water (stream 36) is purged from the closed loop and is replaced by water make-up (stream 34). This block is the same as Houston Plant 63. The cost for this plant was estimated by exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

SYNGAS HEAT RECOVERY

The raw gas stream from the Shell Gasifier Block (stream 8) at $1,300^\circ\text{C}$ and 2,800 kPa enters the Syngas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 71). The raw gas stream exits at 300°C (stream 8A), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 68). It is assumed that the raw gas stream is cooled further prior to entering the Rectisol Block. This block is part of Houston Plant 04.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 41) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [2].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [3].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. Its power requirement is included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas (7). The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [8].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [8]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Syngas Heat Recovery Block and the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [8]. This is a 3-stage steam turbine system. The high pressure stage inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

SOUR GAS SHIFT CONVERTER

Raw fuel gas (stream 8A) leaving the Heat Recovery Block is shifted to produce the desired H₂ to CO ratio needed in the alcohol synthesis reactor.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be outlined. Also, there are alternatives that have not been fully considered which will be considered in more detail later. They are listed below along with the reasons behind them.

- The traditional method for purifying high quantities of pure oxygen is by cryogenics, which is used for this case. However, recent reports suggest that membrane and catalytic processes are becoming economically competitive with cryogenics. Therefore, we will examine these alternatives.
- The Rectisol system was chosen for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that quantities of H₂S are beneficial if the reaction involves the

MoS₂ catalyst. If this is so, then a system such as the Benfield acid gas removal process might be more suitable. The Benfield system does not remove as much H₂S and has lower capital and operating costs.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Sour Gas Shift	4.3
Coal Preparation	31.9
Shell Gasifier	193.2
Slag Handling	3.6
Gas Turbines	44.9
Steam Turbines	25.8
Exhaust Gas Heat Recovery	8.7
Synthesis Gas Heat Recovery	5.4
Cryogenic Oxygen Production	103.3
Rectisol (Acid Gas Separation)	54.4
Claus (Sulfur Recovery)	12.2
Beavon	2.6
Alcohol Synthesis Loop	47.2
CO ₂ Removal	26.9
Other Compressors	65.5

TOTAL 629.9

(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)	629.9
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)	152.6
Coal (\$33/metric ton delivered)	41.7
Other Expenses	111.0
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)	51.0
Power (\$0.05/kWh)	41.3
Slag (\$5.5/metric ton) (5)	0.7
Sulfur (\$300/metric ton) (6)	9.0

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 4 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (4). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-38.9	35.0
O2 Prep	2	500	9	2834	-7.8	7.8
Rxtr Prep	22	2728	26	14000	-21.5	19.0
Recy Comp	56A	12666	56B	14000	-3.6	3.6
Total compressor needs					-71.7	
Other in plant needs					-13.9	
Total produced in steam and gas turbines					188.9	
Net power output					103.3	
Total installed compressor costs (1992 dollars)						65.5

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3.* Prepared by the Linde Division of Union Carbide Corporation, June 1982.
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4. Baasel, William D., *Preliminary Chemical Engineering Plant Design, 2nd edition*, Van Nostrand Reinhold, New York, 1990, pp. 529-530.
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8. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure E.1 : Block Flow Diagram for Case 5

Table E.1 Case 5 Flow Tables

	1	1A	2	3	4	5	6	7	8	9	10
Ar	171.8	171.8				171.8					
C											8701.0
CH ₃ OH											
C ₂ H ₅ OH											
C ₃ H ₇ OH											
C ₄ H ₉ OH											
C ₅ H ₁₁ OH											
CO								8868.6	8868.6		
CO ₂	5.7	5.7						488.1	488.1		
CO ₂								10.7	10.7		
CaCO ₃											
H ₂								2570.7	2570.7		3555.5
H ₂ O	460.1	460.1						970.8	970.8		100.2
H ₂ S								106.2	106.2		
N ₂	14911.1	14911.1		14911.1	14437.4			75.6	75.6		77.0
NH ₃								2.6	2.6		
O ₂	4009.4	4009.4	4009.4							4009.4	685.2
S											116.9
Al ₂ O ₃											162.9
C ₃ H ₆ O ₂											
C ₄ H ₈ O ₂											
CH ₄								2.0	2.0		
C ₂ H ₆											
HCN											
kgmol/hr	19558.2	19558.2	4009.4	14911.1	14437.4	171.8	13095.4	13095.4	13095.4	4009.4	11398.7
kg/hr	561219.3	561219.3	128300.5	417511.3	404246.4	6873.2	298861.2	298861.2	298861.2	128300.5	157767.4
Temp., (C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	1300.0	300.0	141.0	25.0
Press., (kPa)	500.0	101.3	500.0	500.0	500.0	500.0	2833.7	2833.7	2803.9	2833.7	101.3

Table E.1 Case 5 Flow Tables (cont'd)

	12	13	15	17A	19	20	22	23	24
AF									
C		8701.0				1.8			
CH ₃ OH									
C ₂ H ₅ OH									
C ₃ H ₇ OH									
C ₄ H ₉ OH									
C ₅ H ₁₁ OH									
CO				5382.1			5382.1		
CO ₂	668.4	668.4		3974.5				1716.3	1391.1
CO ₂				10.7					
CACO ₃							6057.1		
H ₂		3555.5		6057.1					
H ₂ O		100.2	2522.6	7.0	7.0				
H ₂ S					106.2				
N ₂		77.0			75.6	473.7			549.4
NH ₃					2.6				
O ₂		685.2							
S		116.9							
Al ₂ O ₃		162.9							
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄					2.0		2.0		
C ₂ H ₆									
HCN									
kgmol/hr	668.4	14067.2	2522.6	7.0	15618.0	473.7	11441.3	1716.3	1940.5
kg/hr	29410.2	187177.6	45406.9	125.7	344268.2	13264.9	58.1	162845.7	76590.8
Temp. (C)	25.0	25.0	25.0	25.0	300.0	25.0	25.0	25.0	25.0
Press. (kPa)	2833.7	2833.7	2803.9	2727.9	2727.9	500.0	101.3	2727.9	2727.9

Table B.1 Case 5 Flow Tables (cont'd)

	25	26	26A	27	28	33	34	36	37	41
Ar										
C										
CH ₃ OH	1.6		628.3							1.8
C ₂ H ₅ OH			555.4							
C ₃ H ₇ OH			145.0							
C ₄ H ₉ OH			36.5							
C ₅ H ₁₁ OH			15.2							
CO		5382.1	7001.9	714.2						
CO ₂	198.7		1493.7	152.4	5.7					209.4
COS	10.7									
CuCO ₃										
H ₂		6057.1	7880.0	803.8						
H ₂ O			140.1		460.1		10065.7	10065.7		
H ₂ S	106.2									116.9
N ₂										
NH ₃	2.6									2.6
O ₂										
S										
Al ₂ O ₃						162.9			162.9	
C ₃ H ₆ O ₂			18.0							
C ₄ H ₈ O ₂			11.9							
CH ₄		2.0	4344.6	443.1						
C ₂ H ₆			171.6	17.5						
HCN										
kgmol/hr	320.1	11441.3	22542.3	2131.0	465.9	162.9	10065.7	10065.7	162.9	330.8
kg/hr	13100.9	162845.7	420099.3	35924.2	8534.3	16618.8	181183.4	181183.4	16616.8	13293.8
Temp. (C)	25.0	139.0	310.0	25.0	25.0	1300.0	25.0	25.0	25.0	25.0
Press. (kPa)	2727.9	14000.0	12666.0	12666.0	500.0	101.3	101.3	101.3	101.3	101.3

Table E.1 Case 5 Flow Tables (cont'd)

	42	45	46	47	50	51	54	56	56A	56B	57
Ar											
C					1.8						
CH ₃ OH		1.8									
C ₂ H ₅ OH											
C ₃ H ₇ OH											
C ₄ H ₉ OH											
CSH ₁₁ OH											
CO								6287.7	6287.7	6287.7	
CO ₂		209.4			209.4			1341.4			1341.4
CO ₂											
CaCO ₃											
H ₂								7076.3	7076.3	7076.3	
H ₂ O		111.1					116.9				
H ₂ S		5.8									
N ₂	208.9	208.9		30.0	236.9						
NH ₃		2.6					2.6				
O ₂	55.5			8.0	5.1						
S			111.1			5.8					
Al ₂ O ₃											
C ₃ H ₆ O ₂											
C ₄ H ₈ O ₂								3901.4	3901.4	3901.4	
CH ₄								154.1	154.1	154.1	
C ₂ H ₆											
HCN											
kgmol/hr	264.5	539.7	111.1	38.0	455.2	5.8	119.6	18760.9	17419.5	17419.5	1341.4
kg/hr	7626.9	17366.4	3554.3	1095.4	16125.2	187.1	2149.5	316274.0	257253.6	257253.6	59020.4
Temp. (C)	25.0	200.0	125.0	25.0	100.0	125.0	50.0	25.0	25.0	45.0	25.0
Press. (KPA)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	12666.0	12666.0	14000.0	12666.0

Table E.1 Case 5 Flow Tables (cont'd)

	75	76	77	78
Al				
C				
CH ₃ OH				
C ₂ H ₅ OH				
C ₃ H ₇ OH				
C ₄ H ₉ OH				
C ₅ H ₁₁ OH				
CO				
CO ₂	1344.7			
CO ₂ S				
CaCO ₃				
H ₂				
H ₂ O	2703.6	17874.6	17874.6	17874.6
H ₂ S				
N ₂	20293.1			
NH ₃				
O ₂	3687.8			
S				
Al ₂ O ₃				
C ₃ H ₆ O ₂				
C ₄ H ₈ O ₂				
CH ₄				
C ₂ H ₆				
H ₂ N				
kgmol/hr	28029.2	17874.6	17874.6	17874.6
kg/hr	794050.3	321742.7	321742.7	321742.7
Temp. (C)	200.0	40.0	380.0	535.0
Press. (KPA)	101.3	7.4	3000.0	3000.0

Table E.1 Case 5 Flow Tables (cont'd)

	59	63	64	65	67	68	70	71	73	74
Ar										
C										
CH ₃ OH			628.3							
C ₂ H ₅ OH			655.4							
C ₃ H ₇ OH			145.0							
C ₄ H ₉ OH			38.5							
C ₅ H ₁₁ OH			15.2							
CO	7001.9									
CO ₂	1493.7						1344.7			
CO ₃										
CaCO ₃										
H ₂	7880.0									
H ₂ O		140.1		961.1		14890.6	2703.6	14890.6	2984.0	2984.0
H ₂ S										
N ₂					20293.1		20293.1			
NH ₃										
O ₂					5394.4		3687.8			
S										
Al ₂ O ₃										
C ₃ H ₆ O ₂		18.0								
C ₄ H ₈ O ₂		11.9								
CH ₄	4344.6									
C ₂ H ₆	171.6									
HCN										
kgmol/hr	20891.9	170.1	1480.4	961.1	25687.5	14890.6	28029.3	14890.6	2984.0	2984.0
kg/hr	352198.2	4905.1	62998.0	17299.0	740827.1	268030.8	794050.3	268030.8	53711.9	53711.9
Temp. (C)	25.0	25.0	25.0	25.0	25.0	535.0	590.0	25.0	25.0	535.0
Press. (kPa)	12666.0	12666.0	12666.0	10000.0	101.3	10000.0	101.3	10000.0	10000.0	10000.0

Table E.2 Case 5 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	2.6	0.0
Cryogenic Oxygen Plant	5.3	0.0
Rectisol Plant	4.6	0.0
Syn. Gas Heat Recovery	1.3	0.0
Claus Plant	0.1	0.0
Gas Turbine	0.0	80.4
Steam Turbine	0.0	108.5
Compressor 1	38.9	0.0
Compressor 2	7.8	0.0
Compressor 4	21.5	0.0
Compressor 5	3.6	0.0
Total	85.6	188.9

Appendix F

Case 6: Shell gasifier and steam reforming of natural gas

CASE 6

All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 0.59 million metric tons of coal, 0.48 million metric tons of oxygen, 0.35 billion standard cubic meters of natural gas, and produces 0.50 million metric tons of mixed alcohols per year.

SYNGAS PRODUCTION FROM NATURAL GAS

Compressed natural gas (stream 14) and steam (stream 15) are reacted in the Steam Reformation Block. The cooled output gas (stream 17) goes to the Rectisol Block. The cost for this unit was estimated from data found for a hydrogen production facility, with a scaling exponent of 0.8 [2]. The fuel gas usage for this block is estimated to be 30% of the natural gas feed.

COAL PREPARATION

Coal (stream 10) and carbon dioxide (stream 12) are sent to the Coal Preparation Block. The coal is crushed, mixed with the carbon dioxide, and sent to the gasifier (stream 13). The Coal Preparation Block is composed of three plants from the Houston report. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen (stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not include the inlet air compressors or the outlet oxygen compressors. In the cryogenic system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. We also assume that some scale down is possible for this system, so the capital investment has

been calculated linearly for the reduction in trains, and exponentially for throughput reduction per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas streams (streams 17 and 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A $\text{CO}_2\text{-N}_2$ mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

SHELL GASIFIER

The coal is conveyed by CO_2 to the gasifier, where it mixes with compressed oxygen (stream 9) and is burned at approximately $1,300^\circ\text{C}$ and 2,800 kPa in the Shell Gasifier Block. The hot raw gas (stream 8) is sent to the Syngas Heat Recovery Block, and the slag (stream 33) is sent to the Slag Handling Block. Each train can handle up to 2,541 tons of coal per day, with a scaling exponent of 0.65.

SLAG HANDLING

Molten slag from the Shell Gasifier Block (stream 33) is direct quenched with water and sent to slag disposal (stream 37). A small amount of water (stream 36) is purged from the closed loop and is replaced by water make-up (stream 34). This block is the same as Houston Plant 63. The cost for this plant was estimated by exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

SYNGAS HEAT RECOVERY

The raw gas stream from the Shell Gasifier Block (stream 8) at $1,300^\circ\text{C}$ and 2,800 kPa enters the Syngas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 71). The raw gas stream exits at 300°C (stream 18), and the boiler feed

exits as steam at 10,000 kPa and 535°C (stream 68). It is assumed that the raw gas stream is cooled further prior to entering the Rectisol Block. This block is part of Houston Plant 04.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 41) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [3].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor along with the syngas recycle (stream 56B). The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). Part of this stream (stream 27) is sent to power generation while the rest (stream 56) is sent to CO₂ removal. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [4].

CO₂ REMOVAL

This block is very similar to the Rectisol Block. Recycled gas from the alcohol separation block (stream 56) is the only feed. CO₂ free syngas (stream 56A) is then recompressed and sent back to the reactor. CO₂ is taken off as a product (stream 57). The cost of this block is calculated the same way as in the Rectisol block. Its power requirement is included in the Rectisol block.

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) in the Alcohol Synthesis Loop are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in

stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [9]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [10].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate up to 425 tons of steam per hour with a scaling exponent of 0.67 [10]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Syngas Heat Recovery Block and the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [10]. This is a 3-stage steam turbine system. The high pressure stage inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be outlined. Also, there are alternatives that have not been fully considered which will be considered in more detail later. They are listed below along with the reasons behind them.

- Catalytic steam/methane reformation used to adjust the $H_2:CO$ ratio upwards. The ratio from coal gasification is less than 1. Since the optimal ratio for higher alcohol synthesis is approximately 1.1 - 1.2, an additional source of hydrogen was required. The reformer was assumed to operate at equilibrium, as suggested in the literature [8]. Other alternatives to this block are available and will be considered.
- The traditional method for purifying high quantities of pure oxygen is by cryogenics, which is used for this case. However, recent reports suggest that membrane and catalytic processes are becoming economically competitive with cryogenics. Therefore, we will examine these alternatives.

- The Rectisol system was chosen for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that quantities of H₂S are beneficial if the reaction involves the MoS₂ catalyst. If this is so, then a system such as the Benfield acid gas removal process might be more suitable. The Benfield system does not remove as much H₂S and has lower capital and operating costs.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Synthesis Gas via Natural Gas	27.8
Coal Preparation	19.5
Texaco Gasifier	92.5
Slag Handling	2.2
Gas Turbines	44.9
Steam Turbines	17.9
Exhaust Gas Heat Recovery	11.0
Synthesis Gas Heat Recovery	3.3
Cryogenic Oxygen Production	49.4
Rectisol (Acid Gas Separation)	14.5
Claus (Sulfur Recovery)	7.5
Beavon	1.6
Alcohol Synthesis Loop	47.2
CO2 Removal	26.9
Other Compressors	50.6

TOTAL	416.6
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(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)	416.6
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)	130.5
Coal (\$33/metric ton delivered)	19.5
Natural Gas (\$106/1000 cubic meters)	37.6
Other Expenses	73.4
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)	38.1
Power (\$0.05/kWh)	33.6
Slag (\$5.5/metric ton) (6)	0.3
Sulfur (\$300/metric ton) (7)	4.2

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 5 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (5). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-18.2	16.6
O2 Prep	2	500	9	2834	-3.6	3.7
Reform Comp	17C	1400	17	2804	-4.9	4.7
Rxtr Prep	22	2804	26	14000	-23.9	21.9
Recy Comp	56A	12666	56B	14000	-3.6	3.6
Total compressor needs					-54.2	
Other in plant needs					-4.9	
Total produced in steam and gas turbines					143.1	
Net power output					84.0	
Total installed compressor costs (1992 dollars)						50.6

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3.* Prepared by the Linde Division of Union Carbide Corporation, June 1982.
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10. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Table F.1 Case 6 Flow Table

	001	001A	002	003	004	006	008	009	010	012
Ar	80.4	80.4								
C						80.4			4070.3	
CH ₃ OH										
C ₂ H ₅ OH										
C ₃ H ₇ OH										
C ₄ H ₉ OH										
C ₅ H ₁₁ OH										
CO							4148.7			
CO ₂	2.7	2.7					228.3			312.7
CO ₂							5.0			
CaCO ₃										
H ₂							1202.6		1663.3	
H ₂ O	215.2	215.2					454.1		46.9	
H ₂ S							49.7			
N ₂	6975.4	6975.4		6975.4	6948.2		35.4		36.0	
NH ₃							1.2			
O ₂	1875.6	1875.6	1875.6					1875.6	320.6	
S									54.7	
Al ₂ O ₃									76.2	
C ₃ H ₆ O ₂										
C ₄ H ₈ O ₂										
CH ₄							0.9			
C ₂ H ₆										
HCN										
kmol/hr	9149.3	9149.3	1875.6	6975.4	6948.2	80.4	6126.0	1875.6	6267.9	312.7
kg/hr	262536.9	262536.9	60018.6	198310.7	194548.6	3215.3	139806.5	60018.6	73803.2	13758.0
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	1300.0	141.0	25.0	25.0
Press. (KPA)	500.0	101.3	500.0	500.0	500.0	500.0	2833.7	2833.7	101.3	2833.7

Table F.1 Case 6 Flow Table (cont'd)

	013	014	015	017	017a	017b	017c	018	019	020
Ar										
C	4070.3									
CH3OH										
C2H5OH										0.1
C3H7OH										
C4H9OH										
C5H11OH										
CO				1233.4			1233.4	4148.7		
CO2	312.7			288.6			288.6	228.3		
O2								5.0		
C4CO3										
H2	1663.3			4854.6			4854.6	1202.6		
H2O	46.9		3599.8		454.1	1789.3		454.1		
N2								49.7		
NH3	36.0							35.4	27.2	
O2	320.6							1.2		
S	54.7									
Al2O3	76.2									
C3H6O2										
C4H8O2										
CH4		1523.2		1.2			1.2	0.9		
C2H6										
HCN										
kmol/hr	6580.6	1523.2	3599.8	6377.7	454.1	1789.3	6377.7	6126.0	27.2	0.1
kg/hr	87561.2	24371.0	64797.0	56961.3	8174.7	32206.7	56961.3	139806.5	762.0	3.3
Temp. (C)	25.0	25.0	300.0	25.0	25.0	25.0	25.0	300.0	25.0	25.0
Press. (kPa)	2833.7	1480.0	1480.0	2803.6	2803.9	1400.0	1400.0	2803.9	500.0	101.3

Table F.1 Case 6 Flow Table (cont'd)

	022	023	024	025	026	026A	027	028	033	034
Az.										
C										
CH ₃ OH										
C ₂ H ₅ OH				0.1		628.3				
C ₃ H ₇ OH						655.4				
C ₄ H ₉ OH						145.0				
C ₅ H ₁₁ OH						36.5				
CO	5382.1				5382.1	7001.9	714.2			
CO ₂			180.9	25.8		1493.7	152.4	2.7		
CO ₂				5.0						
CaCO ₃										
H ₂	6057.1				6057.1	7880.0	803.8			
H ₂ O						140.1		215.2		4708.7
H ₂ S				49.7						
N ₂			62.6							
NH ₃				1.2						
O ₂										
S										
Al ₂ O ₃										
C ₃ H ₆ O ₂						18.0			76.2	
C ₄ H ₈ O ₂										
CH ₄	2.1				2.1	4345.7	443.3			
C ₂ H ₆						171.6	17.5			
HCN										
kmol/hr	11441.4		243.5	81.9	11441.4	22543.4	2131.1	217.9	76.2	4708.7
kg/hr	162847.5		9713.2	3151.5	162847.5	420117.3	35926.1	3992.3	7773.3	84757.1
Temp. (C)	25.0	25.0	25.0	25.0	275.0	310.0	25.0	25.0	1300.0	25.0
Press. (kPa)	2803.9	2803.9	2803.9	2803.9	14000.0	12666.0	12666.0	500.0	101.3	101.3

Table F.1 Case 6 Flow Table (cont'd)

	Q36	Q37	Q41	Q42	Q45	Q46	Q47	Q50	Q51	Q54
Air										
C			0.1		0.1			0.1		
CH3OH										
C2H5OH										
C3H7OH										
C4H9OH										
C5H11OH										
CO			30.9		30.9			30.9		
CO2										
COS										
CaCO3										
H2					52.0					54.7
H2O	4708.7		54.7		2.7					
H2S										
N2				97.7	97.7		11.0	108.8		1.2
NH3			1.2		1.2					
O2				26.0			2.9	1.6		
S						52.0			2.7	
Al2O3		76.2								
C3H6O2										
CH3CO2										
CH4										
C2H6										
HCN										
kmol/hr	4708.7	76.2	86.9	123.7	184.6	52.0	14.0	141.3	2.7	55.9
kg/hr	84757.1	7773.3	3241.2	3567.9	5146.9	1662.7	403.2	4457.0	87.5	1005.5
Temp. (C)	25.0	25.0	25.0	25.0	200.0	125.0	25.0	100.0	125.0	50.0
Press. (KPA)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3

Table F.1 Case 6 Flow Table (cont'd)

	056	056A	056B	057	059	063	064	065	067
Ar									
C									
CH ₃ OH							628.3		
C ₂ H ₅ OH							655.4		
C ₃ H ₇ OH							145.0		
C ₄ H ₉ OH							36.5		
C ₅ H ₁₁ OH							15.2		
CO	6287.7	6287.7	6287.7		7001.9				
CO ₂	1341.4			1341.4	1493.7				
CO ₂									
C ₂ H ₄ CO ₃									
H ₂	7076.3	7076.3	7076.3		7880.0				
H ₂ O						140.1		964.2	
H ₂ S									
N ₂									20360.4
NH ₃									
O ₂									5412.3
S									
Al ₂ O ₃									
C ₃ H ₆ O ₂						18.0			
C ₄ H ₈ O ₂						11.9			
CH ₄	3902.4	3902.4	3902.4		4345.7				
C ₂ H ₆	154.1	154.1	154.1		171.6				
H ₂ O									
kmol/hr	18761.9	17420.5	17420.5	1341.4	20892.9	170.1	1480.4	964.2	25772.6
kg/hr	316290.2	257269.8	257269.8	59020.4	352216.3	4905.1	62996.0	17356.3	743282.7
Temp. (C)	25.0	25.0	45.0	25.0	25.0	25.0	25.0	25.0	25.0
Press. (kPa)	12666.0	12666.0	14000.0	12666.0	12666.0	12666.0	12666.0	10000.0	101.3

Table 7.1 Case 6 Flow Table (cont'd)

	068	070	071	073	074	075	076	077	078
Ar									
C									
CH ₃ OH									
C ₂ H ₅ OH									
C ₃ H ₇ OH									
C ₄ H ₉ OH									
C ₅ H ₁₁ OH									
CO						1344.8			
CO ₂		1344.8							
COS									
C ₆ OO3									
H ₂									
H ₂ O	6115.7	2707.0	6115.7	4200.7	4200.7	2707.0	10316.4	10316.4	10316.4
H ₂ S									
N ₂		20360.4				20360.4			
NH ₃									
O ₂		3705.5				3705.5			
S									
Al ₂ O ₃									
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄									
C ₂ H ₆									
H ₂ N									
kmol/hr	6115.7	28117.7	6115.7	4200.7	4200.7	28117.7	10316.4	10316.4	10316.4
kg/hr	110083.5	796565.1	110083.5	75612.0	75612.0	796565.1	185695.5	185695.5	185695.5
Temp. (C)	535.0	590.0	25.0	25.0	535.0	200.0	40.0	380.0	535.0
Press. (kPa)	10000.0	101.3	10000.0	10000.0	10000.0	101.3	7.4	3000.0	3000.0

Table F.2 Case 6 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	1.2	0
Cryogenic Oxygen Plant	2.5	0
Rectisol Plant	0.6	0
Syn. Gas Heat Recovery	0.5	0
Claus Plant	0.1	0
Gas Turbine	0	80.4
Steam Turbine	0	62.6
Compressor 1	18.2	0
Compressor 2	3.6	0
Compressor 3	4.9	0
Compressor 4	23.9	0
Compressor 5	3.6	0
Total	59.0	143.1

Appendix G

Case 7: Texaco gasifier and power production facility

(higher alcohols as by-products and methanol burned to provide peaking power)

CASE 7

The following report gives a brief description of each of the units in the block flow diagram. All capital cost data in this report, except where otherwise specified, has been estimated from similar installations described in the Houston Area Medium-BTU Coal Gasification Project Final Report, published in June 1982 by Union Carbide [1] (All references to material in this report will be referred to as Houston, and all scaling exponents from the Houston report are 0.65). The plant consumes 1.7 million metric tons of coal, 1.5 million metric tons of oxygen, and produces 0.089 million metric tons of mixed alcohols per year.

COAL PREPARATION

Coal (stream 10) and water (stream 12), are sent to the Coal Preparation Block. The coal is crushed, mixed with the water, and pumped to the gasifier as a ~60% solids mixture by weight (stream 13). The Coal Preparation Block is composed of four plants from the Houston report. Plant 01 is the Coal Slurry Preparation Plant. The cost of this plant was scaled linearly due to its multiple train format; where each train can handle up to 1,150 tons of coal per day. Plant 61 is the Reclaiming, Transfer, and Crushing Plant. The cost of this plant was scaled exponentially. Plant 22 is the Barge Terminal. This plant was scaled exponentially. Plant 60 is Coal Receiving and Storage and again the cost for this plant was scaled exponentially.

TEXACO GASIFIER

The coal slurry (stream 13) is mixed with compressed oxygen (stream 9) and burned at 1,200-1,400°C and 8,000 kPa in the Texaco Gasifier Block. The hot, raw gas (stream 8) is sent to the Syngas Heat Recovery Block, and the slag (stream 33) is sent to the Slag Handling Block. The equivalent of the Texaco Gasifier Block is Plant 03 in the Houston report, and each train can handle up to 958.3 tons of coal per day.

CRYOGENIC OXYGEN PLANT

Compressed air (stream 1) is cooled and sent to the Cryogenic Oxygen Plant Block, and is separated into high purity oxygen (stream 2), nitrogen (stream 3), argon (stream 6), and a water and carbon dioxide waste mixture (stream 28). A small quantity of nitrogen (stream 19) is sent to the Rectisol Block. The Cryogenic Oxygen Plant Block does not

include the inlet air compressors or the outlet oxygen compressors. In the cryogenic system, there are provisions for gaseous and liquid oxygen backups sufficient to maintain downstream plant operation in the event of a shutdown in the cryogenic facility. We also assume that some scale down is possible for this system, so the capital investment has been calculated linearly for the reduction in trains, and exponentially for throughput reduction per train. Each train can produce up to 2,000 tons of oxygen per day. The Houston plants that comprise the Cryoplant Block are 02 and 08.

RECTISOL

The cooled raw gas stream (stream 18), nitrogen gas (stream 19) for methanol regeneration, and methanol make-up (stream 20) for vapor loss all enter the Rectisol Block. H_2S levels are reduced to the ppb range and CO_2 levels to the ppm range. The clean syngas (stream 22) is sent to the alcohol synthesis loop. A $\text{CO}_2\text{-N}_2$ mixture (stream 24) and a CO_2 rich stream (stream 23) are produced as byproducts. Condensed water is also removed (stream 17A). This block is the same as Houston Plant 05. The cost for this plant was estimated by using exponential scaling.

SLAG HANDLING

Molten slag from the Texaco Gasifier Block (stream 33) is direct quenched with water and sent to slag disposal (stream 37). A small amount of water (stream 36) is purged from the closed loop and is replaced by water make-up (stream 34). This block is the same as Houston Plant 63. The cost for this plant was estimated by exponential scaling.

COS HYDROLYSIS

The sulfide rich stream from the Rectisol Block (stream 25) and steam are sent to the COS Hydrolysis Block where COS is converted to H_2S . The product gas (stream 41) is sent to the Claus Sulfur Recovery Block. The COS Hydrolysis Block cost is assumed to be negligible.

SYNGAS HEAT RECOVERY

The raw gas stream from the Texaco Gasifier Block (stream 8) at $1,300^\circ\text{C}$ and 8,000 kPa enters the Syngas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 71). The raw gas stream exits at 300°C (stream 18), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 68). It is assumed that the raw gas stream is cooled further prior to entering the Rectisol Block. This block is part of Houston Plant 04.

CLAUS PLANT

Hydrogen sulfide rich gas (stream 41) is mixed with air (stream 42) and converted in a two-step reaction to elemental sulfur (stream 46). The unreacted hydrogen sulfide (stream 45) is then sent to the Beavon Plant for further treatment. This block is the same as Houston Plant 06. The cost for this plant was estimated by exponential scaling.

BEAVON PLANT

The Claus tail gas (stream 45) and air (stream 47) go to the Beavon Block. Additional sulfur is made (stream 51), and the gas leaving (stream 50) is sufficiently free from sulfides that it can be vented to the atmosphere. A sour water stream (stream 54) is sent from the plant for treatment. The cost of this block was estimated from data collected from various sources, with a scaling exponent of 0.65 [2].

MoS₂ ALCOHOL SYNTHESIS LOOP

Clean syngas (stream 26) at 140 atmospheres enters the catalytic reactor. The products (stream 26A) are taken to the separations block where the unreacted syngas is removed (stream 59). This stream (stream 27) is sent to power generation. The cost of this block was estimated from the cost of a methanol synthesis loop, with a scaling exponent of 0.565 [3].

COMBUSTION GAS TURBINE

The light hydrocarbons extracted from the reactor recycle (stream 27) and the methanol produced (stream 102) in the Alcohol Synthesis Loop in addition to the clean synthesis gas stream from the Rectisol block (stream 101) are sent to a combustion gas turbine with hot gas heat recovery. The power from the combustion gas turbines is assumed to be 35% of the HHV of the fuel in stream 27. This is consistent with recent studies on IGCC plants using medium BTU synthesis gas [7]. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 200 MW with a scaling exponent of 0.67 [8].

EXHAUST GAS HEAT RECOVERY

The hot exhaust gas stream from the Gas Turbine Block (stream 70) at 590°C and 101 kPa enters the Exhaust Gas Heat Recovery Block and is cooled against process boiler feed water at 25°C (stream 73). The exhaust gas stream exits at 200°C (stream 75), and the boiler feed exits as steam at 10,000 kPa and 535°C (stream 74). The cost for this block was estimated from data taken from an EPRI report, where each train can generate

up to 425 tons of steam per hour with a scaling exponent of 0.67 [8]. This block also supplies the reheat between the high pressure and intermediate pressure steam turbines.

POWER GENERATION

The steam from the Syngas Heat Recovery Block and the Exhaust Gas Heat Recovery Block is let down in the steam turbines for power production. The cost for this block was estimated from data taken from an EPRI report, where each train can produce up to 500 MW with a scaling exponent of 0.67 [8]. This is a 3-stage steam turbine system. The high pressure stage inlet is 535°C, 10,000 kPa steam. The exhaust at 3,000 kPa is reheated to 535°C before entering the intermediate pressure stage. The final stage exhausts to a surface condenser at 7.4 kPa. Each turbine has an assumed efficiency of 75%.

SOUR GAS SHIFT CONVERTER

Raw fuel gas (stream 8A) leaving the Heat Recovery Block is shifted to produce the desired H₂ to CO ratio needed in the alcohol synthesis reactor.

IMPORTANT POINTS OF INFORMATION

Several decisions were made for the creation of this case that should be outlined. Also, there are alternatives that have not been fully considered which will be considered in more detail later. They are listed below along with the reasons behind them.

- The Rectisol system was chosen for this system for H₂S and CO₂ removal. The major alternative to Rectisol is Selexol. The literature indicates that Rectisol has a higher installed capital cost, but a lower fixed operating cost than Selexol. Both of these systems are capable of removing H₂S to the ppm level and beyond. However, there is some evidence that quantities of H₂S are beneficial if the reaction involves the MoS₂ catalyst. If this is so, then a system such as the Benfield acid gas removal process might be more suitable. The Benfield system does not remove as much H₂S and has lower capital and operating costs.
- The operating pressure for the Texaco gasifiers has been set at 8,000 kPa. This is the highest pressure indicated in the literature at which a Texaco gasifier has been run. Since the pressure required at the reactor is 14,000 kPa, we would of course like to run the gasifiers at as high a pressure as possible.

TOTAL ESTIMATED CAPITAL INVESTMENT (MM\$)

Sour Gas Shift	5.3
Coal Preparation	67.8
Texaco Gasifier	274.2
Slag Handling	4.4
Gas Turbines	219.2
Steam Turbines	52.6
Exhaust Gas Heat Recovery	45.8
Synthesis Gas Heat Recovery	6.8
Cryogenic Oxygen Production	152.6
Rectisol (Acid Gas Separation)	62.3
Claus (Sulfur Recovery)	15.2
Beavon	3.3
Alcohol Synthesis Loop	17.9
Other Compressors	72.2
 TOTAL	 999.6

(sum of individual block costs does not exactly equal the total due to round-off)

OVERALL ECONOMIC EVALUATION

The following table gives the totals and breakdowns for the yearly operating costs as well as the total installed cost for the plant.

TOTAL ESTIMATED INSTALLED CAPITAL COST (MM\$)		999.6
TOTAL ESTIMATED OPERATING COSTS (MM\$/YR)		234.4
Coal (\$33/metric ton delivered)	58.3	
Other Expenses	176.1	
TOTAL ESTIMATED CREDITS (EXCLUDING ALCOHOLS) (MM\$/YR)		226.9
Power (\$0.05/kWh)	213.3	
Slag (\$5.5/metric ton) (5)	1.0	
Sulfur (\$300/metric ton) (6)	12.6	

Credits for nitrogen, argon, and other rare gases have not been included because prices were not available and potential markets have not yet been identified.

STAND ALONE COMPRESSORS AND POWER SUMMARY

There are 4 compressors that are not included in any of the blocks. Their inlet, outlet, pressure change, power rating, and installed capital cost are listed below. Following that is a summary of the total plant power output/input (4). An efficiency of 70% is assumed for all compressors, with a maximum pressure ratio of 5 for a single stage of compression. Multiple compression stages with intercooling are used for services with pressure ratios greater than 5.

FUNCTION	INLET STREAM	P (kPa)	OUTLET STREAM	P (kPa)	POWER (MW)	COST (MM\$)
Air Prep	1A	101	1	500	-57.0	50.4
O2 Prep	2	500	9	8136	-19.8	17.8
Rxtr Prep	22	8030	26	14000	-4.1	4.0
Total compressor needs					-80.9	
Other in plant needs					-20.0	
Total produced in steam and gas turbines					617.5	
Net power output					516.7	
Total installed compressor costs (1992 dollars)						72.2

REFERENCES

1. *Final Report on the Houston Area Medium-BTU Coal Gasification Project, Volumes 2 and 3*. Prepared by the Linde Division of Union Carbide Corporation, June 1982.
2. "Beavon Sulfur Removal Process," *Hydrocarbon Processing*, April 1984, p.78.
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4. Baasel, William D., *Preliminary Chemical Engineering Plant Design, 2nd edition*, Van Nostrand Reinhold, New York, 1990, pp. 529-530.
5. T. Torries, personal communication
6. *Chemical Marketing Reporter*, August 31, 1992.
7. Report TR-101789, Houston Lighting and Power Company's Evaluation of Coal Gasification Coproduction Energy Facilities, EPRI Project 3226-04, 1992.
8. EPRI Report TR-100319, *Evaluation of a 510-MWe Destec GCC Power Plant Fueled With Illinois No. 6 Coal*, Prepared by Fluor Daniel, Inc., EPRI Project 2733-12, 1992.

Figure G.1: Block Flow Diagram for Case 7

Table C.1 Case 7 Flow Tables

	001	001A	002	003	004	005	008	8A	009
Ar	261.2	261.2				261.2			
C									
CH3OH									
C2H5OH									
C3H7OH									
C4H9OH									
C5H11OH									
CO							8742.6	8742.6	
CO2	9.1	9.1					3411.6	3411.6	
CO3							16.3	16.3	
CaCO3									
H2							6688.5	6688.5	
H2O	675.0	675.0					5678.6	5678.6	
H2S							147.4	147.4	
N2	21870.1	21870.1		21870.1	21286.8		99.4	99.4	
NH3							16.6	16.6	
O2	5879.7	5879.7							5879.7
S									
Al2O3									
CaH6O2									
CaH8O2									
CH4									
C2H5							10.5	10.5	
kmol/hr	28695.0	28695.0	5879.7	21870.1	21286.8	261.2	24811.5	24811.5	5879.7
kg/hr	823506.8	823506.8	188148.8	612163.0	596029.6	10446.4	519718.9	519718.9	188148.8
Temp. (C)	25.0	25.0	25.0	25.0	25.0	25.0	1300.0	1300.0	225.0
Press. (KPa)	500.0	101.3	500.0	500.0	500.0	500.0	8135.8	8135.8	8135.8

Table 6.1 Case 7 Flow Tables (cont'd)

	010	012	013	017A	018	019	020	022
Ar								
C	12181.0		12181.0					
CH3OH							2.2	
C2H6O								
C3H8O								
C4H10O								
C5H12O								
CO					7260.3			3022.5
CO2					4894.0			
COS					15.3			
CaCO3								
H2	4977.6		4977.6		8170.8			3401.6
H2O	140.3	7442.6	7582.8	4196.3	4196.3			
H2S					147.4			
N2	107.7		107.7		99.4	583.3		
NH3					16.6			
O2	959.3		959.3					
S	163.7		163.7					
Al2O3	228.1		228.1					
C3H6O2								
C4H8O2								
CH4								
C2H6					10.5			4.4
kmol/hr	18757.6	7442.6	26200.2	4196.3	24811.5	583.3		
kg/hr	220866.9	133965.9	354832.9	75533.1	519718.9	16333.4	3.2	6428.5
Temp. (C)	25.0	25.0	25.0	25.0	300.0	25.0	25.0	25.0
Press. (kPa)	101.3	101.3	8135.8	8030.0	8030.0	500.0	101.3	8030.0

Table 6.1 Case 7 Flow Tables (cont'd)

	023	024	025	026	026A	027	028	033	034
Ar									
C									
CH ₃ OH									
C ₂ H ₆ O			2.2		162.7				
C ₃ H ₈ O					169.7				
C ₄ H ₁₀ O					37.6				
C ₅ H ₁₂ O					9.5				
CO					3.9				
CO ₂	2618.1	1712.9	363.0	3022.5	1813.5	1813.5			
CO ₂			16.3		386.9	386.9	9.1		
CaCO ₃									
H ₂				3401.6	2041.0	2041.0			
H ₂ O					36.3		675.0		14091.6
H ₂ S			147.4						
N ₂		682.8							
NH ₃			16.6						
O ₂									
S									
Al ₂ O ₃								228.1	
C ₃ H ₆ O ₂					4.7				
C ₄ H ₈ O ₂					3.1				
CH ₄									
C ₂ H ₆				4.4	118.6	118.6			
kmol/hr	2818.1	2395.7	545.5	6428.5	4792.0	4364.5	684.1	228.1	14091.6
kg/hr	123995.0	94484.9	22314.3	91504.1	91504.1	73917.3	12548.5	23262.9	253648.3
Temp. (C)	25.0	25.0	25.0	100.0	310.0	25.0	25.0	1300.0	25.0
Press. (kPa)	8030.0	8030.0	8030.0	14000.0	12666.0	12666.0	500.0	101.3	101.3

Table 6.1 Case 7 Flow Tables (cont'd)

	036	037	040	041	042	045	046	047	050
Ar									
C									
CH ₃ OH				2.2		2.2			2.2
C ₂ H ₆ O									
C ₃ H ₈ O									
C ₄ H ₁₀ O									
C ₅ H ₁₂ O									
CO									
CO ₂				379.3		379.3			379.3
CO ₂									
CaCO ₃									
H ₂									
H ₂ O	14091.6		16.3			155.5			
H ₂ S				163.7		8.2			
N ₂					292.5	292.5		45.8	338.3
NH ₃				16.6		16.6			
O ₂					77.7			12.2	8.2
S							155.5		
Al ₂ O ₃		228.1							
C ₃ H ₆ O ₂									
C ₄ H ₈ O ₂									
CH ₄									
C ₂ H ₆									
kmol/hr	14091.6	228.1	16.3	561.8	370.2	854.3	155.5	58.0	727.9
kg/hr	253648.3	23262.9	292.7	22607.0	10677.3	28368.5	4975.9	1671.5	26489.6
Temp. (C)	25.0	25.0	450.0	25.0	25.0	200.0	125.0	25.0	100.0
Press. (kPa)	101.3	101.3	10000.0	101.3	101.3	101.3	101.3	101.3	101.3

Table 6.1 Case 7 Flow Tables (cont'd)

	051	054	063	064	065	067	068	070	071
Ar									
C									
CH ₃ OH									
C ₂ H ₆ O				169.7					
C ₃ H ₈ O				37.6					
C ₄ H ₁₀ O				9.5					
C ₅ H ₁₂ O				3.9					
CO									
CO ₂								6734.7	
CO ₂ S									
CaCO ₃									
H ₂									
H ₂ O		163.7	36.3		4392.3		19454.8	11791.0	19454.8
H ₂ S									
N ₂						92746.3		92746.3	
NH ₃		16.6							
O ₂						24654.1		17713.9	
S	8.2								
Al ₂ O ₃									
C ₃ H ₆ O ₂			4.7						
C ₄ H ₈ O ₂			3.1						
CH ₄									
C ₂ H ₆									
kmol/hr	8.2	180.3	44.0	220.7	4392.3	117400.4	19454.8	128985.9	19454.8
kg/hr	261.9	3228.6	1270.4	11108.8	79062.2	3385826.5	350186.0	3672306.0	350186.0
Temp. (C)	125.0	50.0	25.0	25.0	25.0	25.0	535.0	590.0	25.0
Press. (kPa)	101.3	101.3	12666.0	12666.0	10000.0	101.3	10000.0	101.3	10000.0

Table G.1 Case 7 Flow Tables (cont'd)

	073	074	075	076	077	078	101	102	103
Ar									
C									
CH3OH							162.7		162.7
C2H6O									
C3H8O									
C4H10O									
C5H12O									
CO								4237.7	6051.2
CO2			5734.7						386.9
CO8									
CaCO3									
H2								4769.2	6810.2
H2O	21007.4	21007.4	11791.0	40462.2	40462.2	40462.2			
H2S									
N2			92746.3						
NH3									
O2			17713.9						
S									
Al2O3									
C3H6O2									
C4H8O2									
CH4								6.1	124.7
C2H6									4.5
kmol/hr	21007.4	21007.4	128965.9	40462.2	40462.2	40462.2	162.7	9013.0	13540.3
kg/hr	376133.5	376133.5	3672306.0	728319.5	728319.5	728319.5	5207.5	128292.4	207417.2
Temp. (C)	25.0	535.0	200.0	40.0	380.0	535.0	25.0	25.0	25.0
Press. (kPa)	10000.0	10000.0	101.3	7.4	3000.0	3000.0	12666.0	8030.0	8030.0

Table G.2 Case 7 Energy Analysis

ELECTRICITY		
Plant	Electricity Used (MW)	Electricity Produced (MW)
Coal Preparation Plant	3.6	0.0
Cryogenic Oxygen Plant	7.8	0.0
Rectisol Plant	5.6	0.0
Taxaco Gasifier	1.1	0.0
Syn. Gas Heat Recovery	1.7	0.0
Claus Plant	0.2	0.0
Gas Turbine	0.0	372.0
Steam Turbine	0.0	245.6
Compressor 1	57.0	0.0
Compressor 2	19.8	0.0
Compressor 4	4.1	0.0
Total	100.9	617.5

Appendix H

Scale-up and comparison of design cases

Economic Comparison of the Cases

The table below is a breakdown of the installed capital cost for each of the six cases (not including the power plant, Case 7) with a fixed alcohol production requirement. The costs are for the x1 scale. The six cases are the following:

Case 1 - Texaco Gasification and Steam Reformation

Case 2 - Lurgi Gasification

Case 3 - Steam Reformation Only

Case 4 - Texaco Gasification Only

Case 5 - Shell Gasification Only

Case 6 - Shell Gasification and Steam reformation

(all Costs in MM\$)	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Cryogenic Oxygen Plant	89.3	212.7	--	109.0	103.3	49.4
Coal Preparation	40.8	77.5	--	51.4	31.9	19.5
Gasification	158.7	653.4	--	195.9	193.2	92.5
Slag Handling	3.0	--	--	3.7	3.6	2.2
Syngas Heat Recovery	4.6	--	--	5.6	5.4	3.3
Gas Turbines	45.0	356.4	45.0	45.1	44.9	44.9
Steam Turbines	22.1	46.8	9.9	25.4	25.8	17.9
Exhaust Gas Heat Recovery	9.9	29.6	11.1	8.9	8.7	11.0
Compressors	54.1	216.6	57.5	60.4	65.5	50.6
Rectisol	34.9	115.5	25.8	51.3	54.4	14.5
Claus	10.3	29.7	--	12.5	12.2	7.5
Beavon	2.2	6.4	--	2.7	2.6	1.6
Steam Reformer	15.9	--	90.3	--	--	27.8
Pressure Swing Adsorption	--	20.6	22.2	--	--	--
Sour Gas Shift Converter	--	--	--	4.4	4.3	--
Alcohol Synthesis	47.2	47.2	47.2	47.2	47.2	47.2
CO2 Removal	26.9	4.5	26.9	26.9	26.9	26.9
Total	562.8	1817.1	335.9	650.3	629.9	416.6

Table H.1 Block Cost Breakdown for Varying Plant Capacities

Case #1

<i>Scale factor</i>	1	2	4	8
Cryo. Plant	89.33	161.55	323.10	626.82
<i># trains</i>	2	3	6	11
Coal Prep.	40.80	70.08	122.07	211.08
<i># trains</i>	3	6	12	23
Texaco Gasifier	156.70	274.22	548.43	1,057.69
<i># trains</i>	4	7	14	27
Slag Hand.	3.00	4.70	7.38	11.58
SGHR	4.57	7.18	11.26	17.67
Gas Turbines	45.03	71.65	143.31	286.61
<i># trains</i>	1	1	2	4
Steam Turbines	22.14	35.22	56.04	112.08
<i># trains</i>	1	1	1	2
EGHR	9.90	15.75	25.05	50.11
<i># trains</i>	1	1	1	2
Compressors	54.08	104.74	208.16	415.05
Rectisol	34.88	54.73	85.87	134.75
Claus	10.25	16.08	25.24	39.60
Beavon	2.21	3.46	5.44	8.53
Steam Reformer	15.85	27.60	48.05	83.67
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 Removal	26.86	42.15	66.14	103.78
Total Cap. Cost	562.80	958.96	1,778.88	3,311.88

Table H.2 Block Cost Breakdown for Varying Plant Capacities

Case 2

<i>Scale factor</i>	1	2	4	8
Cryo. Plant	212.73	425.46	831.91	1,644.19
<i># trains</i>	4	8	15	29
Coal Prep.	77.53	121.66	190.91	299.57
Lurgi Gasifier	653.40	1,270.50	2,504.70	4,973.10
<i># trains</i>	18	35	69	137
Gas Turbines	356.41	688.46	1,351.19	2,675.89
<i># trains</i>	5	9	17	33
Steam Turbines	46.83	93.67	170.37	320.84
<i># trains</i>	1	2	3	5
EGHR	29.62	59.24	118.49	226.76
<i># trains</i>	1	2	4	7
Compressors	216.61	431.97	861.11	1,720.49
Rectisol	115.54	181.31	284.50	446.43
Claus	29.70	46.61	73.14	114.77
Beavon	6.40	10.04	15.75	24.72
P.S.A.	20.61	32.34	50.75	79.63
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 removal	4.54	7.12	11.18	17.54
Total Cap. Cost	1,817.14	3,438.22	6,567.31	12,696.78

Table H.3 Block Cost Breakdown for Varying Plant Capacities

Case #3				
Scale factor	1	2	4	8
Gas Turbines	45.02	71.63	143.26	286.51
# trains	1	1	2	4
Steam Turbines	9.93	15.80	25.14	40.01
# trains	1	1	1	1
EGHR	11.15	17.73	28.21	56.43
# trains	1	1	1	2
Compressors	57.47	112.68	224.02	446.69
Rectisol	25.78	40.45	63.47	99.60
Reformer	90.29	157.20	273.69	476.53
P.S.A.	22.18	34.80	54.61	85.69
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 removal	26.86	42.15	66.14	103.78
Total Cap. Cost	335.89	562.28	981.38	1,748.10

Table H.4 Block Cost Breakdown for Varying Plant Capacities

Case #4				
Scale factor	1	2	4	8
Cryo. Plant	109.02	218.04	436.09	852.70
# trains	2	4	8	15
Coal Prep.	51.38	88.70	155.32	271.33
# trains	4	8	16	31
Tex. Gasifier	195.87	391.74	744.30	1,449.43
# trains	5	10	19	37
Slag hand.	3.66	5.74	9.00	14.13
SGHR	5.58	8.76	13.74	21.56
Gas Turbines	45.10	71.75	143.51	287.01
# trains	1	1	2	4
Steam Turbines	25.45	40.49	64.42	128.83
# trains	1	1	1	2
EGHR	8.91	14.18	22.57	45.13
# trains	1	1	1	2
Compressors	60.37	119.74	238.15	476.30
Rectisol	51.28	80.47	126.27	198.14
Claus	12.51	19.63	30.80	48.33
Beavon	2.69	4.23	6.63	10.41
Sour Gas Shift	4.38	6.87	10.78	16.92
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 removal	26.86	42.15	66.14	103.78
Total Cap. Cost	650.27	1,182.33	2,171.06	4,076.87

Table H.5 Block Cost Breakdown for Varying Plant Capacities

Case #5				
Scale factor	1	2	4	8
Cryo. Plant	103.26	206.52	394.19	788.37
# trains	2	4	7	14
Coal Prep.	31.87	50.02	78.48	123.16
Shell Gasifier	193.24	386.47	737.65	1475.30
# trains	2	4	7	14
Slag hand.	3.57	5.60	8.79	13.79
SGHR	5.45	8.55	13.41	21.05
Gas Turbines	44.92	71.47	142.94	285.88
# trains	1	1	2	4
Steam Power	25.81	41.06	65.33	130.67
# trains	1	1	1	2
EGHR	8.73	13.89	22.09	44.19
# trains	1	1	1	2
Compressors	65.47	127.77	253.09	503.60
Rectisol	54.42	85.39	133.99	210.25
Claus	12.21	19.16	30.07	47.18
Beavon	2.63	4.13	6.48	10.16
Sour Gas Shift	4.27	6.71	10.53	16.52
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 removal	26.86	42.15	66.14	103.78
Total Cap. Cost	629.92	1,138.72	2,066.51	3,926.76

Table H.6 Block Cost Breakdown for Varying Plant Capacities

Case 6

<i>Scale factor</i>	1	2	4	8
Cryo. Plant	49.44	98.89	197.78	377.49
<i># trains</i>	1	2	4	7
Coal Prep.	19.45	30.52	47.90	75.16
Shell Gasifier	92.53	185.05	370.10	706.41
<i># trains</i>	1	2	4	7
Slag hand.	2.18	3.42	5.36	8.42
SGHR	3.32	5.22	8.19	12.85
Gas Turbines	44.92	71.48	142.95	285.91
<i># trains</i>	1	1	2	4
Steam Turbines	17.86	28.41	45.21	90.41
<i># trains</i>	1	1	1	2
EGHR	10.98	17.46	27.78	55.57
<i># trains</i>	1	1	1	2
Compressors	50.56	96.68	190.94	381.88
Rectisol	14.45	22.68	35.58	55.84
Claus	7.45	11.89	18.35	28.79
Beavon	1.61	2.52	3.95	6.20
Reformer	27.78	48.37	84.22	146.63
Alcohol Syn.	47.21	69.85	103.33	152.86
CO2 removal	26.86	42.15	66.14	103.78
Total Cap. Cost	416.61	734.38	1,347.78	2,488.20

Table H.7 Block Cost Breakdown

Case #7	
<i>Scale factor</i>	1
Cryo. Plant	152.63
<i># trains</i>	3
Coal Prep.	67.76
<i># trains</i>	6
Tex. Gasifier	274.22
<i># trains</i>	7
Slag hand.	4.44
SGHR	6.78
Gas Turbines	219.24
<i># trains</i>	3
Steam Turbines	52.62
<i># trains</i>	1
EGHR	45.78
<i># trains</i>	2
Compressors	72.22
Rectisol	62.30
Claus	15.20
Beavon	3.27
Sour Gas Shift	11.09
Alcohol Syn.	17.86
 Total Cap. Cost	 1,005.40

Table H.8a Manufacturing Cost for Varying Plant Capacities \$/gal

Scale	Case 1	Case 2	Case 3a	Case 3b	Case 4	Case 5	Case 6
x1	1.01	1.59	0.90	0.71	1.09	1.05	0.84
x2	0.86	1.42	0.80	0.62	0.98	0.94	0.76
x4	0.80		0.74	0.56	0.90	0.85	0.70
x8	0.75		0.69	0.52	0.84	0.80	0.66

Table H.8b Manufacturing Cost for Varying Plant Capacities \$/L

Scale	Case 1	Case 2	Case 3a	Case 3b	Case 4	Case 5	Case 6
x1	0.27	0.42	0.24	0.19	0.29	0.28	0.22
x2	0.23	0.37	0.21	0.16	0.26	0.25	0.20
x4	0.21		0.19	0.15	0.24	0.22	0.19
x8	0.20		0.18	0.14	0.22	0.21	0.17

Chapter 15

CRITICAL ECONOMICS OF COAL DERIVED ALCOHOL TRANSPORTATION FUELS¹

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ABSTRACT

The need for and the results of a broader based economic evaluation of coal derived alcohol fuels are examined in this paper. This study indicates that coal derived alcohol fuels are at least marginally competitive with MTBE for use as a gasoline blending agent, and not economically competitive as neat fuels compared to gasoline even under a broader based evaluation process. However, alcohol derived from natural gas possessing the same characteristics as their coal counterparts exhibit superior economics.

INTRODUCTION

The objective of this paper is to focus on the need for a broader based economic evaluation of coal derived (CD) alcohol transportation fuels and to identify relevant social costs and benefits that need to be examined. The current practice of evaluating the feasibility of alcohol fuels solely on their financial attributes fails to account for all the cost and benefits associated with the production and consumption of these fuels and therefore may not reflect their true economic status.

The results and conclusions of this study are based on preliminary coal gasification and CD mixed alcohol production designs developed by the Chemical Engineering Department at West Virginia University, which consist of two base cases. The first case includes indirect liquefaction of coal using a high temperature oxygen blown Texaco gasifier in conjunction with the Sour Gas Shift conversion process to obtain the desired $H_2:CO$ ratio syngas for the alcohol synthesis process. The second is a reference case based on steam reformation of natural gas with pressure swing absorption

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to adjust the $H_2:CO$ ratio of the syngas. Both cases produce approximately 1300 million gallons of mixed alcohol a year. The composition of the mixed alcohol product on a molar percentage bases is approximately 42% methanol, 43% ethanol, 10% propanol, 3% butanol and 1% pentanol.

PRODUCTION AND SOCIAL COSTS

The cost associated with the production of alcohol fuels can be divided into two broad categories, financial and social, which must be added together to obtain a true cost. Financial costs are explicit costs obtained through engineering analysis. Social costs include the difficult to measure items such as benefits and costs of air pollution control. Current studies focus primarily on production costs only. However, this type of analysis overlooks important social costs and benefits associated with production and use of these fuels. For example, the production of CD alcohol transportation fuels would inevitably result in increased mining activity at some environmental cost, while gasification may also impose some environmental cost attributed to increased CO_2 emissions. To determine the true cost of alcohol fuels these issues must be addressed.

If we assume that current mining legislation regarding acid -nine drainage and siltation is effective, potential environmental costs associated with increased mining activity should be internalized and reflected in the price of coal. The social costs associated with the gasification plant may be minimized through design alterations, which would internalize these costs. For example, CO_2 emissions may be minimized by supplementing the gasification process with hydrogen rich natural gas. In this case the cost of the natural gas could be offset by eliminating the Sour Gas Shift converter and the reduction in annual coal consumption that would accompany these changes. As a result, the production cost of alcohol fuels would represent the actual cost to society. This is significant, since it makes it possible to derive a net cost for alcohol fuels given the uncertainty surrounding the utility of these fuels.

SOCIAL BENEFITS OF MIXED ALCOHOL AND MTBE

Alcohol fuels may be used in one of two capacities, either as a neat fuel or as a blending agent with gasoline. Many blends are possible and each blend has different performance characteristics and different costs and benefits. To reduce the economic analysis of alcohol blends to manageable proportions, the commonly used commercial blend of 10 percent alcohol was selected to represent the use of coal derived alcohols in this capacity.

A comparison was made between 10 percent CD alcohol and gasoline and a similar blend using MTBE to determine if there were differences in benefits in the form of reduced hydrocarbon and/or carbon monoxide emissions. No significant differences were noted and no adjustments to equate the social costs and benefits of using MTBE versus CD alcohol were necessary in this case.

However, this is not true when CD alcohol is used as a neat fuel. Studies suggest that significant reductions in hydrocarbon, NO_x , and carbon monoxide emissions may be

obtained if neat alcohol were to replace gasoline as a transportation fuel [1][4][6]. Rather than attempt to quantify individual social benefits and costs from using neat alcohol, total net benefits may be derived indirectly by subtracting the production cost of the neat alcohol from the cost of gasoline, assuming that all relevant costs are internalized, and making adjustments to account for different performance characteristics. Adjusting the plant gate cost of \$0.65/gal according to PEP standards for the chemical industry yields an equivalent wholesale price for the CD alcohol fuel of approximately \$0.82/gal. However, since the alcohol fuel has a lower heat content, a cost adjustment must be made. Compensating for differences in heat content, the cost of the CD alcohol fuel would be approximately equivalent to gasoline at a wholesale price of \$1.28/gal. Given the current wholesale price of gasoline of \$0.76/gal [9], additional social benefits attributed to the use of neat mixed alcohol fuels would have to exceed \$0.52/gal to make their use economically feasible, provided no additional costs or negative benefits are incurred when the alcohol is used as a neat fuel.

COMPETITIVENESS OF ALCOHOL FUELS

On a price basis alone, the mixed alcohol produced by this proposed facility appears to be competitive with the popular blending agent, MTBE. The plant gate cost for the mixed alcohol would be approximately \$0.65/gal. MTBE, on the other hand, currently sells for roughly \$0.98/gal [2] on the spot market. This spread would provide producers of the mixed alcohol a considerable margin for markup and transportation cost without jeopardizing the competitiveness of the product. However, price is only one determinant influencing the demand for blending agents. Other factors, such as the practical aspects of manufacturing and distributing the CD mixed alcohols and engine performance characteristics, must be considered. Performance factors of major importance include the effects of the blending agent on Reid vapor pressure, octane rating, and oxygen content of the fuel. Blending incentives related to these factors must be determined before the final competitiveness of the mixed alcohol to MTBE can be calculated. Preliminary research suggests that the economic differences between CD mixed alcohol factors and, MTBE factors are small.

On the negative side, in order for the CD mixed alcohol plant to obtain costs that are competitive with MTBE, economies of scale in the CD alcohol plant size must be exploited. It appears that one plant producing 1336 million gallons per year may saturate local eastern United States markets, which would cause additional costs due to additional marketing risks and distribution problems. (See Table 1).

TABLE 1
Local Market Potential for Mixed Alcohol as a Fuel Oxygenant
(10% Blend)

	Total Market										
	WV	PA	MD	NJ	DC	DE	OH	KY	Local	US	a
MM gal/yr	82	449	198	327	17	33	461	180	1747	11092	1336

a-Proposed Alcohol Production from Base Case

Source: State Energy Data Report Consumption Est. 1960-1990 EIA May 1992.

While the mixed alcohol product appears to be at least marginally competitive as a fuel additive, this is not necessarily the case for its usefulness as neat fuel. Although a plant gate cost of \$0.65/gal. is less than the current refinery price of gasoline at \$0.76/gal excluding taxes, the mixed alcohol is still more expensive due to its lower heat content. This is because the mixed alcohol product is comprised of mainly methanol and ethanol, which have lower heat content, with only small amounts of higher alcohols, which have higher heat content. Given the composition of the mixed alcohol, its price in relative terms based on its heat content would be about \$1.03/gal., which is substantially more than gasoline considering that this is a plant gate or break even cost. The high concentration of methanol (see [8]&[11]) in this mixture may also present a series of engine performance problems and institute additional social costs that would otherwise be avoided if the CD mixed alcohol were to be used as an additive.

EFFECTS OF CHANGING FEEDSTOCK PRICES AND TECHNOLOGY OVER TIME

Since natural gas can be used to obtain mixed alcohols with characteristics similar to those of CD mixed alcohols, the cost of producing alcohol from natural gas must be compared to the cost of producing alcohol from coal. Also, the price of oil must be considered in the cost of manufacturing MTBE, although MTBE prices may or may not accurately reflect the true incremental costs of producing MTBE at the refinery because of the nature of joint product pricing problems.

Figure 1.
Cost of Transportation Fuel
Oil \$22 per Barrel

The relative economics of neat alcohol fuels with respect to gasoline depends upon both the initial costs and the rate of change of these costs over time. Figure I shows the results of an analysis of the relative costs of transportation fuel assuming coal costs about \$30 per ton, natural gas costs \$3.00 per mcf, oil costs \$22 per barrel, and MTBE costs \$41.16 per barrel. Also shown are the assumptions concerning the real annual increases in costs and prices over a twenty year period.

As can be seen in Figure 1, oil is currently the cheapest source of transportation fuel, followed by natural gas and then coal. However, different relative cost increases will change the ranking over time. According to DOE estimates, coal should increase 1.7 percent per year, oil and MTBE 2.7 percent per year, and natural gas 3.5 percent per year. If coal gasification costs decrease by 0.5 percent per year, overall coal costs would increase by 1.2 percent per year. Under this scenario, oil would be the fuel of choice over the next 20 years and gas would be a cheaper source of transportation fuel than coal for the next 15 years or more.

CONCLUSIONS

This study indicates that coal derived alcohol fuels are at least marginally competitive with MTBE for use as a gasoline blending agent, and not economically competitive as neat fuels compared to gasoline even under a broader based evaluation process. In order for CD alcohol fuels to be competitive, additional cost reducing measures need to be realized. However, reducing costs of CD alcohol may be in vain because similar alcohols can be derived from natural gas at a fraction at a lower cost given the probable price relationships of coal and natural gas for the next 15 years. This situation is expected to continue, since natural gas prices are only projected to increase at about 3.5% per year according to DOE estimates.

As a blending agent, CD mixed alcohols appear to be marginally competitive with MTBE under current conditions. However, it is still cheaper to produce mixed alcohols from natural gas than coal. In fact, the natural gas derivative of this product may even have a cost advantage over MTBE, although this remains to be seen, since the price of MTBE may be artificially high like many other joint products of the petroleum refinement process. If mixed alcohols from natural gas were to be produced in competition with MTBE, MTBE prices would be expected to drop significantly, which would inevitably effect the competitiveness of CD alcohols as blending agents.

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Chapter 16

CRITICAL COSTS AND PRICES IN DETERMINING COAL DERIVED ALCOHOL FUEL ECONOMICS³

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INTRODUCTION

Although transportation fuels may be derived from coal either through direct or indirect liquefaction, this study will focus primarily on the later. It will attempt to describe the constraints and the economics associated with the use of and the production of coal derived transportation fuels in conjunction with any economic boundaries imposed by these constraints.

Coal derived transportation fuels can be generated by the indirect liquefaction of coal. The coal is heated in an entrained environment giving off a mixture of gases commonly called synthesis gas or syngas. The precise composition of this gas varies with operating conditions although the basic components remain essentially the same: carbon dioxide, methane, carbon monoxide, and hydrogen. This gas is then collected and reformed into alcohol which may serve as motor fuels. The commercial feasibility of this process thus becomes dependent upon the net cost of syngas as well as the value of the final product. Since syngas can be obtained from sources other than coal, such as natural gas, coal derived syngas must be obtainable at a cost less than any of the potential alternatives if it is to be an economical raw material. This cost may be partially offset by using alternative technologies which produce other products in conjunction with syngas.

The spectrum of potential by-products ranges from electric power to a vast array of value-added coal derivatives which are commonly used as feed stocks for the chemical industry. While the incorporation of one of these alternative technologies may provide the potential to offset production costs, it may also serve to generate numerous constraints by shifting this process into the realm of joint production. For example, marketing constraints may reduce the value of these potential by-products. The process

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may be further inhibited by the fact that external costs such as the social cost of using coal, which can be difficult to measure, must be taken into consideration.

This research suggests that if coal gasification is to be an economically viable source of syngas, the production of by-products may be inevitable. Tentative conclusions imply that in order for coal gasification to produce transportation fuels competitively, very inexpensive coal must be used, large quantities of high value by-products must be produced, or there must be significant reductions in processing costs.

NEED FOR COAL DERIVED TRANSPORTATION FUELS

The socio-economic ramifications resulting from the oil supply shocks of 1973 and 1981 should serve as a reminder of the profound linkages that exist between energy markets and the United States economy. Since the United States economy remains heavily dependant upon foreign oil, its economy remains susceptible to future supply disruptions. One way to reduce this vulnerability would be to augment alcohol fuel production with coal serving as the raw material.

Currently coal provides energy to the United States economy in two ways: directly as a primary fuel or indirectly in the form of electricity. These forms represent an important source of energy to all sectors of the United States economy except for the transportation sector. This sector accounts for approximately 26 percent of all domestic energy consumption as illustrated in Table 1. Coal's contribution to this sector for all practical purposes remains negligible. Since the United States has a limited supply of petroleum that can be produced in competition with Middle East Oil, but has large quantities of undeveloped coal reserves, a rationale exists for investigating the use of coal to supplement imported oil for transportation use. However, simply having large reserves of coal and a desire to reduce petroleum imports provides no guarantee that coal will become a substitute for oil. This substitution, for practical purposes, does not appear to be in the near future given the current price of oil and the cost of these coal derived alternatives. Even if oil was more expensive, coal derived transportation fuel would still have to compete with similar fuels derived from natural gas. However, the relatively high degree of uncertainty inherent in the entire process due to speculation of future oil and natural gas prices makes it difficult to predict this outcome. This problem is further compounded by the fact that relative environmental costs and benefits associated with the use of both coal and oil-based transportation fuel must also be quantified within an environment of uncertainty due to possible policy changes.

METHOD OF ANALYSIS

The economics of alternative transportation fuels may be approached from a two-fold perspective. The first perspective is to examine these fuels in a context relative to oil. Since numerous alternative transportation fuels have been developed, an inter-fuel analysis should also be conducted. Therefore, the second approach would be to consider the economics among the various competing alternative transportation fuels themselves. These alternatives include fuels derived from coal, natural gas, and the fermentation of

biomass materials such as grains. At this juncture, this study will primarily focus on the inter-fuel competition between coal and natural gas since the future of fermentation fuels is unclear due to expiring government subsidies. Therefore, this paper will attempt to address the question of "If alternative transportation fuels ever become economical with respect to oil, what factors will determine the economics of these products derived from coal?" Thus, a comprehensive analysis of alternative transportation fuels should include the following: (1) the cost differentials in manufacturing, storage and distribution, (2) the cost of using the fuels, including engine modifications, (3) the cost or savings associated with environmental considerations like pollution, and (4) the social and economic cost differentials resulting from the production of domestic energy as opposed to importing it.

Although the relative production and use costs of oil-based transportation fuels are essential to the economics of alternative fuels, they will not be addressed at this point due to a lack of consensus regarding their actual levels. Currently these costs are artificially low, since they fail to encompass the full realm of cost associated with using oil. Therefore the economics of alternative transportation fuels may be biased as a result of cost understatements. This makes determining the true relative economics of producing and using oil derived transportation fuels like gasoline difficult to compare with alcohol fuel in general and coal derived alcohol fuels in particular. This situation is likely to change as a result of policy implications which would cause the price of gasoline to reflect its true cost. Although the manufacturing cost of alternative fuels has been declining as result of technological improvements and operating experience, the relative economics may be influenced most through realistic pricing of gasoline. These important considerations are addressed by other researchers.

METHODS OF REDUCING THE COST OF ALCOHOL FUELS

There are a number of ways to reduce the cost of alcohol fuels. These include producing co-products at both the alcohol and syngas production stages, decreasing capital and operating costs, and increasing benefits to consumers through the reduction of hydrocarbon and nitrous oxide pollution.

Alcohol Production and Peak Power Demand

Since methods of storing energy are limited or are expensive, peaking power must be provided by generating technologies rather than power storage technologies. The question is whether or not it would be possible to produce alcohol fuel or coal-derived syngas in such a manner to take advantage of this situation.

A major problem confronting the electric power industry in the United States is how to most efficiently meet peak power demand both on a daily and on a seasonal basis. Currently, peaking plants often use natural gas fired turbines to provide the peaking power requirements. Although capital requirements of these types of plants are low, plant utilization may be only 5 percent significantly increasing the effective capital cost per kilowatt of power generated. Natural gas is also generally a more expensive fuel than coal for the generation of electric power. As a result, peaking power is much more

expensive than base-load power. However, if alcohol fuel plants were to produce both alcohol and electric power in such a manner as to produce more alcohol than electricity at night, the alcohol produced during the night could be easily stored and burned during the day in peaking units. This process would take advantage of storage potential of the alcohol thus providing relatively inexpensive means of storing power indirectly in order to meet peak demand. This arrangement would alleviate problems of using coal or natural gas for peaking power fuels, since coal cannot be easily used as a fuel for a peaking plant and natural gas cannot be easily stored in large quantities. In effect, this arrangement would allow coal to be used as a primary fuel source for peaking power and society could benefit by having access to a low cost source of energy to meet peak power demands.

Joint Use of Coal and Natural Gas

Coal is deficient in hydrogen relative to carbon for gasification purposes. Therefore, gasifying coal may result in the venting of large quantities of CO₂. Environmental concerns with regard to global warming make this an unfavorable circumstance and may even result in financial penalties if the proposed CO₂ tax were to be enacted. To avoid these potential penalties, the level of CO₂ emissions may be reduced by supplementing the process with natural gas which is rich in hydrogen. This would make it possible to make the desired adjustments in the H₂:CO ratio of the syngas without having to vent large quantities of CO₂ and this would also simultaneously increase the volume of syngas. Therefore, less coal would be required to produce the same volume of syngas. The savings in coal cost should more than offset the cost of supplementing the process with natural gas because the process would require the addition of a relatively small amount of natural gas.

Use of Coal Washer Refuse

Another alternative to reduce the cost of alcohol fuels would be to use very inexpensive coal. One source of inexpensive coal is old wash ponds. These ponds often contain significant amounts of coal left behind as a result of the coal preparation and cleaning process. This material could be fed into high temperature gasifiers in slurry form. The high operating temperatures of these gasifiers would essentially burn any combustible material and the remaining material would be discarded as slag. Coal refuse piles could also be another potential source of inexpensive coal for gasification. Although more expensive than the previous two sources, fine coal from continuous and long wall operations may also aid in this aspect of cost reduction. The coal from these operations could be screened and the fines could be used for gasification. This material could be purchased at a discount since it would not have to go through the expensive cleaning process.

While these low cost sources of coal may provide the potential to reduce alcohol fuel production cost, it is highly unlikely that they will significantly impact the overall economics of alcohol fuel production. The cost of coal is relatively small in contrast to

the overall cost of the process; therefore, a reduction in this area will have little impact on the cost of syngas and, in turn, the alcohol fuel.

Co-Product Production

The production of coal-derived alcohol fuels can be divided into two stages. Stage 1 involves the conversion of coal (process A) or natural gas (process B) to syngas while Stage 2 deals with the conversion of the syngas to alcohol fuels. By-products can be obtained from both stages; therefore, the economics of joint product production becomes a consideration in the manufacture of coal-derived alcohol fuels. Production alternatives for the two processes can be analyzed separately and together.

Process A involves the production of syngas with or without the production of by-products such as electrical power, coke, coal tar products, and other coal derived chemicals. By-product production can be in fixed or variable proportions or some combination of both. At the extreme, the proportion of syngas can vary from 0 to 100 percent of the output excluding "waste" products such as slag. In the event that no syngas is produced, all resources would be devoted to the production of the by-products. Furthermore, if by-products are manufactured, it must be at the expense of syngas production. Thus, proportions of the various by-products can vary within certain ranges which are process and stoichiometrically determined.

Stage 2 involves the conversion of syngas into the alcohol fuel and waste products (such as sulfur and CO₂) and possibly by-products, resulting from alcohol separations. Again, by-product production can be in fixed or variable proportions or some combination of both. The proportion of fuel alcohol can vary from 0 to 100 percent, just as in the case of process A and the production of syngas. Also, if by-products are manufactured (at the expense of fuel alcohol production), the proportions of the various by-products can be varied within certain ranges. Since syngas can be obtained from sources other than coal, such as natural gas, the analysis of Stage 2 can be made independently of Stage 1.

The existence of joint product production presents a number of production and marketing difficulties. First, choosing the mix of goods to be produced and their quantities is a constrained optimization problem (not necessarily linear and possibly dynamic). Second, marketing the products in proportion to their production may be difficult and usually requires the cost of stockpiling one or more of the joint products or selling the excess production at a price lower than the anticipated market price.

An estimate of the required value of by-product credits to make the production of coal-derived alcohol fuels economic from process A can be obtained by determining the current or anticipated difference between the price of gasoline and the cost of producing alcohol fuels from process B. This simplified approach ignores all costs due to externalities, such as the reduction of pollution costs, and ignores related costs, such as required modifications of the transportation fuel distribution system or engine modifications.

ENVIRONMENTAL AND SOCIAL CONSIDERATIONS

The burning of coal-derived alcohol fuels may provide some environmental benefits; unfortunately, these benefits may be offset by the social and environmental costs of mining and gasifying coal. Therefore, if the net benefits of coal-derived alcohol transportation fuels are emanately negative, producers would inevitably revert to cleaner alternative raw materials like natural gas. However, if alcohol transportation fuels were to be produced from natural gas, a question arises about the source of the natural gas for the syngas feedstock. The vast majority of proven natural gas reserves are known to lie in-conjunction with oil reserves which are predominantly located in the Middle East. Currently natural gas is considered to be a waste product of oil production in this region due to the remote well locations. Consequently this natural gas is either flared or used to enhance production through well pressurization. If alcohol fuels should become the transportation fuel of choice domestically, then this natural gas would become valuable. Alcohol synthesis plants could be built in the Middle East to convert this natural gas to alcohol which could be easily transported by essentially the same means and cost as oil. Estimates suggest that this product would have a Gulf coast port price of approximately one-half that of its domestic counterpart. Provided these estimates are accurate, competition from the Middle East would have devastating effects on the domestic production of alcohol fuels. Thus, the United States would remain dependent upon foreign sources for its energy needs. However, this need not be the case.

COST COMPARISONS

The relative economics of alcohol fuel from natural gas or coal relative to gasoline depends upon the relative initial costs and the relative rate of change of the costs over time. Figure 1 shows the results of an analysis of the relative costs of transportation fuel assuming coal costs of about \$30 per ton, natural gas cost of \$3.00 per mcf, oil at \$22 per barrel, and current prices for coal gasification by-products. Also shown are the assumptions concerning the real annual increases in costs and prices over a twenty year period.

As can be seen, oil is the cheapest source of transportation fuel, followed by natural gas and then coal. However, different relative cost increases will change the ranking over time. According to DOE estimates, coal should increase 1.7 percent per year, natural gas 3.5 percent and oil 2.7 percent per year. If coal gasification costs decrease by 0.5 percent per year, overall coal costs would increase by 1.2 percent per year. Under this scenario, oil would be the fuel of choice over the next 20 years and natural gas would be a cheaper source of transportation fuel than coal for the next 15 years or more.

Recognizing that oil prices do not fully reflect all of the costs associated with production and use of oil provides grounds to presume that the cost of oil will increase sometime in the future. If the cost of oil increases by a factor of two, as shown in Figure 3, transportation fuels from natural gas would become economical. However, this does not improve the economics of coal derived fuels.

Although the effects of CO₂ emissions on the welfare of the Earth are not known, one must consider the effects a carbon tax would have on the relative economics of transportation fuels. If a \$10 per ton carbon tax were to be levied on all fuel, the relative economics of coal, oil and natural gas would not change significantly, as shown in Figure 4. These results assume that CO₂ produced in the gasification of coal is combined with hydrogen from natural gas to prevent a large quantity of CO₂ being emitted during the production of syngas. If this were not the case, costs of using coal to produce syngas would increase dramatically, making coal uneconomical relative to natural gas until around 2040.

CONCLUSIONS

This preliminary investigation indicates that the economic production of coal derived alcohol transportation fuels will not be viable in the near future. The basic problem is that to use coal, a moderately priced commodity, for the production of transportation fuel, another moderately priced commodity, large capital and operating expenditures are required. While these fuels can be produced from coal which is in abundant domestic supply, it appears that a similar mix of final products may also be derived using natural gas at a fraction of the cost.

Therefore, it is anticipated that given the current economic and political climate, coal-derived alcohol fuels will require some form of subsidization.

If coal is to be used for alcohol fuel production, the production cost must be offset through the production of these by-products to the extent that these by-product credits equate the two alternative sources. However, the production of these by-products further complicates the issue by creating production and marketing problems. Thus, the potential cost associated with the production of the by-products may outweigh the benefits rendering the process infeasible.

While this study may not provide all of the answers to the questions surrounding the commercialization of alcohol fuels, it does make substantial progress in delineating their economic feasibility. Little information currently exists regarding the economics of alcohol fuels. Therefore, this study provides a significant contribution as a result of its identification of economic boundaries and potential constraints.

Chapter 17

Efficiency Criteria for Environmental Evaluation of Power Technologies

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ABSTRACT

The potential of using efficiency as a criteria for the development of future power generation technologies is examined within the realm of pending CO₂ limitations. Efficiency measures of CO₂ per unit of net power available for sale and overall thermal efficiency along with their effects on direct environmental benefits are used to illustrate this concept. The results of this study indicate that improvements in efficiency provide greater environmental benefits than alternative emission reduction measures. However, significant improvements in the efficiency may be required if power generation facilities are to meet the 20 percent proposed reduction in CO₂ by the year 2000.

INTRODUCTION

Advanced technologies of coal and natural gas generated electricity are designated to produce power and meet present and anticipated environmental regulations at a minimum cost. However, many externalities exists in the price of this energy, as a result of its reliance on fossil fuels. Typical evaluations often overlook external cost like the cost of energy security, future gas scarcity, and carbon emissions. Although many economist agree that externalities should be included in the price of energy to obtain socially efficient pricing, their estimates of the dollar values for these costs vary significantly. If and when these costs are internalized, current selections of technologies targeted for development may not coincide with the optimal choices. As a means of accounting for these uncertainties this paper suggest that energy efficiency measures be included in the evaluation criteria for advanced power generation technologies. Specifically, this paper will analyze efficiency measures of CO₂ per unit of net power available for sale and overall thermal efficiency along with their effects on direct environmental benefits. These principles will be illustrated with examples which will make comparisons between conventional coal fired units and combined cycle using various primary fuels.

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POTENTIAL ENVIRONMENTAL BENEFITS FROM INCREASED EFFICIENCY

Efficiency improvements in power generation can produce environmental benefits in two ways. First, benefits can be directly related to declines in energy input requirements per unit of output which ultimately translate into a reduction in the quantity of pollution generated per unit of electricity produced. The levels of reduction, however, are dependent upon the pollutants under consideration. Pollutants such as CO₂ and SO₂, for example, are fuel dependent. Therefore, emissions of these pollutants will be in direct proportion to the type and quantity of fuel used in the on process. However, other pollutants such as NO_x, CO and VOC's are technology dependent and the quantity of these pollutants emitted during the generation process depends more on the technology used rather than the amount and type of fuel used.

Second, improvements in efficiency may also generate ancillary benefits by reducing the environmental impacts caused by factors other than the combustion of fossil fuels at power generation facilities. The end use of energy at these facilities accounts for only a portion of the overall environmental impact for any given fossil fuel. Therefore, decreasing the fuel requirements for a given level of power production not only reduces the level of pollutants at the generation facility, it also reduces environmental degradation related to the production and processing of fossil fuels by reducing the need to carry out these activities. Energy efficiency can, therefore, have a strong cumulative effect on reducing environmental impacts associated with the use of fossil fuels as a result of this two fold effect.

EFFICIENCY MEASURES FOR SELECTING TECHNOLOGIES

The United States is one of a number of in of stabilizing CO₂ emissions at 1990 level by the year 2000. Some scientists, economists and environmentalists contend that this strategy is not aggressive enough and have proposed even more aggressive targets. With the increase of this attitude toward emissions, the regulation of CO₂ emissions appears to be inevitable. However, the level of abatement that will be required under these pending regulations, as well as the penalties for failure to meet these requirement have not been delineated. These pending regulations may be addressed in one of two ways either through curative or preemptive measures.

Curative measures reduce emission by treatingg and removing pollutants before they are released into the environment. Add on technologies of this nature generally reduce the overall efficiency of the facility thereby increasing fuel requirements and environmental degradation on through the ancillary effects discussed above. Depending upon the specific process and the level of CO₂ removal between 20 to 50 percent of the facility's electrical output could be consumed by the CO₂ control system [1] [2]. A summary of the effects of selected add on curative controls are presented in Table 1.

Table 1 Curative Emission Controls

FGD	SO ₂	All have a negative impact on the overall energy efficiency of the power generation facility.
Combined do-SO ₂ /NO _x FGD	SO ₂ /NO _x	
SCR	NO _x	All have been demonstrated commercially either in power generation or petrochemical facilities.
Econamine FG	CO ₂	
Selexol	H ₂ S/CO ₂	

Notes:

- (a) FDG (flue gas desulfurization), SRC (selective catalytic reaction), Econamine FG (amine flue gas scrubbing system), Selexol (flashing process – most CO₂ removed at medium pressure 50psia and the rest is removed at near atmospheric pressure)
- (b) main pollutant marked for reduction

The only curative option currently available for CO₂ control would involve a tail-gas cleanup system that could be adapted from the acid-gas removal technologies used in the petroleum and petrochemical industries. A number of variations of this process are available. However, each is comprised of essentially four basic steps: recovery, concentration, liquefaction, and disposal. Research indicates that these clean up measures would be quite expensive. Although there is a great deal of uncertainty associated with these costs, estimates for a 20 percent reduction in CO₂ emissions by the year 2000 range from \$100 to \$300 per ton of carbon reduced and an eventual GDP loss of 1 percent or more [3]. This represents an increase of 2.0 to 2.6 times the current cost of power from conventional coal fired facilities [2]. Similar reductions for IGCC plants are anticipated to increase the current cost of power by a factor approximately 1.7 [2]. Although the cost for CO₂ removal for IGCC facilities is less than that of conventional coal fired units, it is still an extremely expensive alternative method of reducing greenhouse gases when compared to preemptive options.

Preemptive options reduce emissions either by lowering the quantity of primary energy required to produce a unit of output or by substituting less polluting fuels. Fuel substitution has received considerable attention in light of mounting concerns over the effects of greenhouse gases. However, fuel substitution may provide only a temporary solution to these problems unless efficiencies are also enhanced. Because the amount of CO₂ emitted from a given facility is a linear function of the amount and type of fuel used, fuels with the lowest carbon to BTU ratio (see Table 2 for a comparison of fossil fuel properties) will be selected to reduce CO₂ emissions. Natural gas therefore provides the greatest potential for reducing CO₂ emission because it contains only 32 pounds of carbon per 10⁶ BTU's (395 8 tons per MW-yr). These cleaner burning properties have lead natural gas advocates to push for regulations mandating its use. However, natural gas may not be the savior its proponents claim due the relative scarcity that would inevitably evolve from usage of this magnitude. To offset the effects of this anticipated demand efficiencies of current natural gas fired units would have to increase significantly. Current efficiencies of natural gas GCC units range between 40 and 50 percent although it has been suggested that an additional 10 percent gain may be achieved by modifying existing

combustion turbines [4]. Even with the addition of this proposed increase in efficiency in natural gas fire GCC units, the ability of natural gas to meet anticipated demands remains questionable.

Table 2 shows that crude oil provides the second lowest carbon to BTU ratio (46 lbs per 10⁶ BTU or 7231 tons per MW-yr), however, oil is plagued by a set of scarcity problems similar to those of natural gas. Issues of energy security must also be factored into any analysis involving the uses of oil due to the United States' heavy dependence upon foreign suppliers. These factors would likely overshadow any environmental benefits gained by using oil because of the small differences that exist between the carbon to BTU ratios of coal and oil. The difference in the efficiencies of conventional coal fired units and oil fired boilers are also small, further negating any apparent advantage oil may have in reducing CO₂ emissions.

Table 2: Fossil Fuel Characteristics

Coal (1 to 3% S)	1,307.00/ton	54
Crude Oil	6.18/gal	46
Natural Gas	33.0/mcf	32

Notes: (a) Units – lbs/10⁶ BTU's

Considering the scarcity issues surrounding oil and natural gas, coal is apparently the most logical fossil fuel for the interim until alternative energy sources may be developed. However, coal has the highest level of carbon per BTU of all fossil fuels and conventional coal fired units have the lowest efficiencies of all fossil fuel generating facilities. Efficiencies of coal fired units must therefore be increased if coal is to remain the predominate fuel for power generation in light of pending legislation limiting CO₂ emissions.

Results of research and development efforts in the 1970's indicate that development of the IGCC technology is a step in the right direction. The potential of this technology to advance energy and environmental objectives goes beyond the specific reduction in pollutant emissions and energy consumption and includes opportunities for increased flexibility and diversity as well. Efficiencies of these units are approaching those of GCC natural gas units as can be seen in Table 3. However, even with the most favorable coal fueled technologies, carbon emissions per MW-yr are approximately twice those of natural gas. Although it is possible to remove this CO₂ prior to combustion, the process is relatively expensive due to the costs of liquefaction and disposal [5] [2]. The only alternative is to increase the overall efficiency of the generation facility thereby reducing the fuel requirements and in turn CO₂ emissions. Decreasing the fuel requirement of coal fired units as a result of improved efficiency would not only reduce the level of CO₂ emissions, it would also decrease the environmental impacts of related activities previously described. These impacts can be significant for coal related activities. Improving the efficiency of IGCC coal units could make them competitive with their gas counterparts since the overall environmental benefits may be higher than those of natural gas when secondary environmental benefits are factored into the analysis.

A more detailed analysis is required before any definitive conclusions can be drawn with regard to the superiority of one fuel over another. It is evident that efficiency improvements provide the greatest potential for reducing the level of pollutants generated from the production of power using fossil fuels given the short term solution of fuel switching and high costs of curative measures.

While considerable efforts have been expended in making coal a more efficient fuel, the costs remain high relative to the current benefits. If CO₂ and other externalities are included in the price of coal, it is likely that additional ways to improve coal combustion technologies would emerge.

Table 3: Efficiency Summary

Coal (1 to 3% S)	Dry Bottom Wall Fired	34	198	8792
Coal (1 to 3% S)	IGCC	40	198	7807
Resid Fuel Oil	Boiler, Opposed Wall	35	169	7231
Natural Gas	GT, Combined Cycle	45	118	3958

Source: Adapted from *Energy And The Environment: Policy Overview*

CONCLUSIONS

This study indicates that increased efficiency provides the greatest potential for reducing pollutants given the uncertainty of pending limitations on CO₂ emissions. Although other CO₂ reduction measures may be implemented they are more costly and do not have the overall impact of increased efficiency. However, significant improvements in the efficiency of all power generation facilities may be required to meet the 20 percent proposed reduction in CO₂ by the year 2000. These reductions will undoubtedly place additional burdens on even the cleanest utilities. Therefore, those technologies with the potential to substantially increase the overall efficiency of power generation facilities should be targeted for development.

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Chapter 18

THE PERFORMANCE CHARACTERISTICS OF C₁-C₅ ALCOHOL - GASOLINE BLENDS WITH MATCHED OXYGEN CONTENT IN A SINGLE CYLINDER SI ENGINE

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ABSTRACT

Alcohols with carbon numbers ranging from C₁ to C₅ were individually blended with unleaded test gasoline (UTG-96). All of the 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 pressure versus crank angle. The engine operating conditions were optimized for each (C₁-C₅) blend with two different values of matched oxygen content. Adding lower alcohols (C₁, C₂, C₃) to UTG96 improved knock resistance. Further improvement was achieved by increasing the oxygen content of the fuel blend. Blends with higher alcohols (C₄, C₅) showed degraded knock resistance when compared to neat gasoline.

INTRODUCTION

Alcohols are being used as fuel blending components to improve unleaded gasoline octane quality. Normally, methanol and ethanol are the main blending components [1]6. Addition of small amounts of alcohols, with carbon numbers greater than one, improves fuel blend water tolerance, material compatibility, and volatility characteristics [2-7]. Increasing the alcohol content, which also increases oxygen content, up to a certain concentration (when blended with gasoline) improves the blends' knock resistance. Further increase in alcohol content does not lead to any further improvements in knock resistance [2,8,9].

6 Numbers in parentheses designate references at end of paper.

The global objective of the current study is to examine individual alcohols, when blended with gasoline, with regard to engine knock. The specific objective is to determine whether the improved knock characteristics of an alcohol-gasoline blend is solely dependent on its oxygen content or if other factors are involved.

THE PHYSICAL AND CHEMICAL PROPERTIES

Selected chemical and physical properties of gasoline and alcohols are shown in table 1. When higher alcohols are blended individually with gasoline, larger amounts are needed in the blend in order to match the oxygen content of lower alcohols blends, as shown in figure 1. The changes in properties of blends with oxygen mass contents of 2.5% and 5.0%, relative to neat gasoline, are shown in figures 2 - 5. In general, as the alcohol concentration increases so does the blend's specific gravity, as shown in figure 2. Fuel blends with higher alcohols are slightly denser than those with lower alcohols for given oxygen mass contents of 2.5% and 5.0%. The energy-mass density for each blend is predicted by summing up the mass weighted heating values of the neat components[2]. The higher the oxygen content in the blend, the lower its energy mass-density value, as shown in figure 3. The decrease in the heating value is almost the same for blends with matched oxygen content. The energy-volume density for each blend is computed by multiplying its energy-mass density and its specific gravity. Blends with higher alcohols have larger energy-volume densities, when compared to those with lower alcohols for the given oxygen mass contents of 2.5% and 5.0%, as shown in figure 4. For the same operating conditions, engines burning a stoichiometric mixture need to consume more alcohol-gasoline blend than neat gasoline, as shown in figure 5. It should be noted that other important properties of gasoline-alcohol blends, such as distillation characteristics, Reid vapor pressure, and water tolerance, are not discussed.

Table 1. Comparison of selected fuel properties

	Methanol	Ethanol	N-Propanol	N-Butanol	N-Pentanol	Gasoline
Formula	CH ₃ OH	CH ₃ CH ₂ OH	CH ₃ CH ₂ CH ₂ OH	CH ₃ (CH ₂) ₂ CH ₂ OH	CH ₃ (CH ₂) ₃ CH ₂ OH	-----
Oxygen Content (Mass fraction)	0.50	0.35	0.27	0.22	0.18	0.00
Molecular weight	32.04	46.07	60.10	74.12	88.15	111.21
Specific gravity	0.79	0.79	0.80	0.81	0.81	0.74
Energy-mass density (KJ/gm)	19.93	26.75	30.94	33.22	34.84	42.91
Energy-volume density (KJ/cm ³)	15.78	21.11	24.86	26.90	28.38	31.87
Stoichiometric air/fuel ration	6.43	8.94	10.28	11.12	11.68	14.51

EXPERIMENTAL

The engine used is a Waukesha single cylinder spark ignition cooperative fuel research engine with variable compression ratio. The engine bore and stroke are 3.25 and 4.5 in; respectively, giving a displacement of 0.612 L. A DC current General Electric dynamometer is used to motor and load the engine. Unleaded test gasoline (UTG-96) and high purity straight chain (n-) alcohols are used. Table 2 lists the engine conditions which are held constant throughout this investigation.

Table 2. Engine test conditions

Speed (rev/min.)	1000
Equivalence	1.0 ± 0.02
Load	Wide open throttle
Coolant temperature (°F)	209
Oil temperature (°F)	153 ± 4
Mixture temperature (°F)	110 ± 3
Air relative humidity (%)	25 ± 4

Alcohols with carbon numbers ranging from C_1 to C_5 are individually blended with unleaded test gasoline (UTG-96). The resulting alcohol-gasoline blends have oxygen mass contents of 2.5% and 5.00%. For each fuel blend, the compression ratio (CR) is changed from a value of 7, to the high knock limiting value in increments of 0.5. The spark timing (ST) is varied from a value of 30 to 5 degrees crank angle (CA) before top dead center (BTDC) in decrements of 5.

ANALYSIS PROCEDURE

For a fixed CR, a polynomial (up to fourth order) in ST is fit to brake thermal efficiency (η) values using the least squares method. The fitted polynomial is used to determine the spark timing for maximum η .

The magnitude of the third derivative of the measured in-cylinder gas pressure is used to quantify the engine knock strength [10]. A value of 50 psia/CA³ is observed as a threshold to characterize a single pressure trace that does not exhibit any knocking. Figure 6 shows that at low knocking operations, the time-averaged knock strength value is less than the threshold value, over a set of consecutively sampled in-cylinder pressure traces for different operating conditions (CR, ST). It also shows that the percentage of traces that exhibits knocking correlates linearly with the time averaged knock strength over that range. This linear relation is used to calculate values of time averaged knock strength that corresponds to a range of that exhibit knock.

For a fixed CR, a polynomial (up to fourth order) in ST is fit to the time-averaged knock strength values using the least squares method. The fitted polynomial is used to determine the spark timing for a range (5-20%) of traces that exhibit knock.

The intersection of the knock limiting spark timing curve and that of maximum η , identifies an optimum operating point (ST, CR), as shown in figure 7. The line of maximum BMEP is shown as well. Another operating point of interest is that of the maximum possible CR within the tested range. This is the point of intersection of the 5 CA BTDC spark timing line with the knock limiting spark timing curve.

RESULTS AND DISCUSSION

For the investigated CR range, all blends with 2.5% and 5.0% oxygen content have higher maximum η values as compared to neat gasoline, with the exception of ethanol-gasoline blend with a 2.5% oxygen content, as shown in figures 8 and 9. The increase in brake thermal efficiency with increased alcohol content is attributed to the faster burning rate, and higher cylinder pressure, than those of neat gasoline [2,11]. Detailed thermodynamic analysis of the power cycle is required to explain the improvement in η values for all blends and, specifically, the degradation for the ethanol-gasoline blend with 2.5% oxygen.

Figures 10 and 11 show the knock limiting spark timing at different compression ratios for 5% traces exhibit knocking. The C_1 to C_3 alcohol-gasoline blends show a wider range of operation relative to neat gasoline. On the other hand, higher alcohol (C_4, C_5)-gasoline blends show degraded knock resistance when compared with neat gasoline. These trends are common for the 2.5% and 5.0 % oxygen blends.

In order to quantify each blend's knock resistance characteristics, the areas under the curve in figures 10 and 11 are computed and compared to that of neat gasoline, as shown in figure 12. Adding lower alcohols (C_1, C_2, C_3) to gasoline has improved knock resistance. Ethanol-gasoline blends show the highest knock resistance improvement (~20%-35%). On the other hand, blends with higher alcohols (C_4, C_5) show degraded knock resistance, when compared to gasoline. The pentanol-gasoline blend shows the highest knock tendency (~30%-60%). For the 5.0% oxygen blends, both the improvement and degradation trends of knock resistance are more pronounced when compared with the 2.5% oxygen blends.

For an engine operating at optimum conditions, the improvement in the values for η and CR for different blends relative to neat gasoline, are shown in figures 13 and 14 respectively. For the 2.5% oxygen blends, the methanol-gasoline blend shows the highest improvement in η (~2%). The ethanol-gasoline blend, however, has the highest improvement (~6.0%) for η when compared with the 5.0% oxygen blends. Blends with higher alcohols (C_4, C_5) have degraded η values, with the exception of butanol-gasoline blend with 2.5% oxygen. For the 5.0% oxygen blends, both the improvement and the degradation trends for the η values are more pronounced, when compared with the 2.5% oxygen blends with the exception of 2.5% oxygen butanol-gasoline blend. The slight improvement in η value for the butanol-gasoline blend with 2.5% oxygen, is attributed to the blend's higher η value when compared to gasoline at the same CR value. Both 2.5% and 5.0% oxygen ethanol-gasoline blends show the highest improvement (~2.5% and 10.0%, respectively) in optimum CR value, when compared with matched oxygen content blends.

For an engine operating at the maximum possible CR and ST of five degrees BTDC, all blends (with the exception of pentanol-gasoline blends) show improvement for the values of η and CR relative to neat gasoline as shown in figures 15 and 16 respectively. For the 2.5% oxygen blends, methanol-gasoline blends show the highest improvement in η (~4%). On the other hand, the propanol-gasoline blend has the highest improvement in η (~7.5%), when compared with the 5.0% oxygen blends. For the 2.5% oxygen blends, the ethanol-gasoline blend operates at the highest (~15%) CR value and the methanol-gasoline blend operates at the highest (~20%) CR value among the 5.0% oxygen blends.

CONCLUSIONS

Adding lower alcohols (C_1 , C_2 , C_3) to unleaded test gasoline improves its knock resistance from 8% to 20% for blends with a 2.5% oxygen mass content when compared to neat gasoline. The knock resistance is further improved (20% - 35% compared to gasoline) by increasing the oxygen content of the blend to 5.0%. Ethanol-gasoline blends show the highest knock resistance improvement (~20% - 35 %) among all tested blends.

Blends with higher alcohols (C_4 , C_5) show degraded knock resistance when compared to gasoline. Pentanol-gasoline blend exhibits the highest knock tendency, ~30% more, than gasoline for 2.5% oxygen blends. The knock tendency is further promoted (~60% more than gasoline) by increasing the oxygen mass content in the blend to 5.0%.

All tested alcohol-gasoline blends have a higher brake thermal efficiency than neat gasoline operating, when compared at the same compression ratio, with the exception of ethanol-gasoline blend with 2.5% oxygen mass content.

For an engine optimized for maximum brake thermal efficiency and knock limiting operating conditions, (C_1 , C_2 , C_3) alcohol-gasoline blends operate at higher efficiency (~2% for C_1 -UTG 2.5% O_2 and ~6% C_2 -UTG 5.0% O_2) when compared to neat gasoline, due to its higher optimum compression ratio. Ethanol-gasoline blends show the highest improvement in optimum compression ratio (~2.5% for 2.5% O_2 and ~10.0% for 5.0% O_2).

For an engine optimized for knock limiting operating conditions and five degrees BTDC spark timing, (C_1 , C_2 , C_3) alcohol-gasoline blends operate at higher efficiency (~4% for C_1 -UTG 2.5% O_2 and ~7.5% C_3 -UTG 5.0% O_2), when compared to neat gasoline, due to their higher compression ratios (15-20%).

Detailed thermodynamic analysis of the power-gas exchange cycle is required to explain the improved/degraded trend of different blends.

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Fig.1 Alcohol volume fraction in C₁-C₅ alcohol-gasoline blends with matched oxygen content.

Fig.6 Percentage of knocking traces versus time averaged knock strength for different operating conditions.

Fig.2 The change in specific gravity of C₁-C₅ alcohol-gasoline blends relative to neat gasoline.

Fig.7 Determination of optimum operating compression ratio and spark timing.

Fig.3 The change in energy-mass density of C₁-C₅ alcohol-gasoline blends relative to neat gasoline.

Fig.8 Maximum brake thermal efficiency at different compression ratios for blends with 2.5% oxygen.

Fig.4 The change in energy-volume density of C₁-C₅ alcohol-gasoline blends relative to neat gasoline.

Fig.9 Maximum brake thermal efficiency at different compression ratios for blends with 5.0% oxygen.

Fig.5 The change in stoichiometric air to fuel ratio of C₁-C₅ alcohol-gasoline blends relative to neat gasoline.

Fig.10 Knock limiting spark timing at different compression ratios for blends with 2.5% oxygen content.

Fig. 11 Knock limiting spark timing at different compression ratios for blends with 5.0% oxygen content.

Fig. 14 Comparison of alcohol-gasoline blends (2.5% and 5% oxygen mass content) compression ratio to neat gasoline at optimum operation.

Fig. 12 Improvement in knock resistance for alcohol-gasoline blends (2.5% and 5% oxygen mass content) relative to neat gasoline.

Fig. 15 Comparison of alcohol-gasoline blends (2.5% and 5% oxygen mass content) brake thermal efficiency to neat gasoline at maximum compression ratio.

Fig. 13 Comparison of alcohol-gasoline blends (2.5% and 5% oxygen mass content) brake thermal efficiency to neat gasoline at optimum operation.

Fig. 16 Comparison of alcohol-gasoline blends (2.5% and 5% oxygen mass content) maximum compression ratio to neat gasoline.

Chapter 19

COMBUSTION CHARACTERISTICS OF HIGHER ALCOHOL/GASOLINE BLENDS

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Abstract

An experimental investigation of combustion characteristics of higher alcohols/gasoline (UTG 96) blends is presented. Lower alcohols (methanol and ethanol) have been used in the past as fuel extenders by mixing them with gasoline, but relatively little work has been reported on higher alcohols (propanol, butanol, and pentanol). All of these alcohols can be produced from coal derived syngas. Given the abundant coal reserves in the United States, use of such higher alcohols offers an attractive alternative to alleviate the country's growing needs for transportation fuels.

Comparisons of knock limits, indicated mean effective pressure (IMEP), emissions, and fuel characteristics between higher alcohol/gasoline blends and neat gasoline were made to determine the advantages and disadvantages of blending alcohol with gasoline. All tests were conducted on a single-cylinder Waukesha Cooperative Fuel Research (CFR) engine operating at steady state conditions and stoichiometric air-to-fuel ratio. The data show that higher 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 higher 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 alcohol to gasoline. The lower alcohols (methanol and ethanol) cause the most dramatic increase in RVP and the largest depression of the distillation curve. Addition of higher alcohols (propanol, butanol, and pentanol) tend to curb the effects of methanol and ethanol on RVP and the distillation curves of the blends.

Background

Effect of Alcohol on Antiknock Performance

One of the major attractions of alcohols is their high octane blending value. Each volume percent of an oxygenate added to a typical unleaded gasoline with 87 (R+M)/2 octane rating increases blend octane rating in the range from 0.1 to 0.3 (Unzelman, 1988). In addition, Patel et al. (1987) showed that blends of methanol with higher alcohols increased antiknock performance to a greater degree than methanol alone. However, the Coordinating Research Council, Inc. (1985) and Patel and Henein (1985) have shown that the incremental gains in alcohol/gasoline blend octane rating decrease with increasing alcohol concentration in the blend and increasing octane of the base fuel. Thus, adding

alcohol to premium grade gasoline will not have as dramatic an effect on octane rating as adding alcohol to regular grade gasoline, and the change in octane rating with each volume percent addition of alcohol will become smaller. Further, as with most gasolines, oxygenated blends tend to have less knocking resistance at higher engine speeds. Brinkman et al. (1975) measured the research and motor octane numbers of methanol/gasoline blends using standard ASTM tests, as well as the road octane ratings at various engine speeds using the CRC Modified Borderline technique. Their findings showed that the road octane number, which is the octane rating of a fuel in an on-the-road vehicle, of methanol/gasoline blends decreased with increasing engine speed. However, the research and motor octane numbers, $(R+M)/2$, increased with increasing methanol in the blend, and the research octane number increased more drastically than the motor octane number with increasing methanol concentration. Their findings also highlighted the decreasing effect of methanol on octane number with increasing methanol concentration.

Alcohol Effects on Distillation, Cold Starting, and Vapor Lock

Adding alcohols to gasoline depresses the boiling temperature of individual hydrocarbons. The lower alcohols cause significant reduction in the front end distillation temperatures, thus affecting primarily the first 50% evaporated. Lower molecular weight alcohols have the greatest effect on boiling point depression. Methanol causes the largest changes; its effects can be observed even when accompanied by a co-solvent. Higher molecular weight alcohols, such as tertiary butyl alcohol (TBA), propanol, butanol, and pentanol, exert smaller changes on the distillation characteristics.

General Motors Research compared the high temperature [26.7°C - 32.2°C (80°F - 90°F)] driveability and vapor lock performance of methanol blends using six cars with closed-loop fuel control systems: three cars had carburetors, two had throttle body injection, and one car was equipped with multi-port fuel injection (Yaccarino, 1985). Four blends were tested: 3% methanol, 7% methanol, 4.75% methanol with 4.75% TBA, and 8.2% methanol with 2.7% TBA (all percentages are given on volume basis). The blends were matched with two gasolines meeting ASTM specifications for volatility classes C and D, which are fuels designed for typical summer and transitional seasons in the Midwest and Northeastern U.S., respectively. Driveability demerits, which were issued based on hot engine restart, throttle response, and smoothness of engine performance, were greatest for two of the carbureted cars when the alcohol blends were used. The fuel injected cars, and surprisingly one of the carbureted vehicles, performed similarly on the blends and with the gasolines. In the matched volatility vapor lock tests, the carbureted vehicles also performed poorly, with the worst performance from blends containing the highest methanol concentrations. The poor performance of the carbureted cars, even though they had closed-loop control, was to be expected with the alcohol blends. This was due to the fact that carburetors operate at very low pressure differentials and are unable to compensate for volume effects of partially vaporized fuel. Fuel injection systems, on the other hand, can deliver fuel to the injectors at pressure as high as 379 KPa (55 psig) and provide much greater tolerance of volatile fuels than is attainable with carbureted systems.

The property of alcohol fuels that significantly reduces cold starting ability is the heat of vaporization. Alcohols require more heat to vaporize than a typical gasoline.

Bardon et al. (1985) investigated engine response to this factor by measuring the mixture richness required for starting between temperatures of -40°C and 15.6°C (-40°F and 60°F). The starting performance of a gasoline with an RVP of 61.4 KPa (8.9 psi) was compared to a blend composed of the same gasoline splash-blended with 10% methanol by volume and an RVP of 80 KPa (11.6 psi). The starting performance was not improved with the high RVP blend and, at stoichiometric mixture ratios for each fuel, gasoline allowed the engine to be started at 5°C (41°F) whereas the blend would not allow starting below 15°C (59°F). A 10% methanol blend matching the 61.4 KPa (8.9 psi) RVP gasoline was also made by removing volatile fractions from the base gasoline. With this blend, the engine would not start at temperatures below 15°C (59°F) unless the mixture strength was enriched about 100% above the stoichiometric air-to-fuel of the blend. At -30°C (-22°F), gasoline fueled engine could be started only when the mixture was approximately eight times richer than stoichiometric, but the blend with matched RVP required a mixture strength fourteen times richer than stoichiometric. Rich mixtures are always needed to start cold engines, because enough fuel must vaporize to form a combustible air/fuel mixture. Thus, these studies only demonstrate relative difficulties in starting characteristics, not whether an engine will start when fueled with a blend. The relative cold starting difficulties largely depend on the fuel delivery system. The fuel delivery system must be able to provide a rich enough mixture to allow starting with an alcohol/gasoline blend.

EPA Guidelines for Alcohol/Gasoline Blends

The use of alcohols in unleaded gasoline must be approved by the EPA, which must ensure that emission control systems currently in place will not be affected. Thus, there are several EPA guidelines that have to be followed when blending alcohol with gasoline. The “substantially similar” ruling states that alcohol may be added to gasoline provided that the amount of oxygen in the blended fuel does not exceed 2.7% by mass. However, a number of specific proposals have been granted waivers allowing the use of alcohols in gasoline. The ruling followed throughout this research is the “DuPont Waiver.” Adopted in January 1985, the DuPont Waiver allows for methanol up to 5.0% volume plus at least 2.5% volume co-solvent (ethanol, propanol, butanol, or pentanol) plus corrosion inhibitor, with maximum oxygen content 3.7% by weight.

Test Engine and Blends

Test Engine

The engine used in this research was the ASTM Cooperative Fuel Research engine manufactured by Waukesha Engine Division, Fuel Research Department, Dresser Industries, Waukesha, WI. The complete unit is known as the “ASTM-CFR Engine*.” The Waukesha Engine has been used by several other researchers in their investigation of combustion and emissions characteristics of alcohol fuels and blends (Patel et al., 1987; Hunwartz, 1982; Harrington and Pilot, 1975; Ebersole and Manning, 1972).

The Waukesha Engine is a four stroke, single-cylinder, spark ignited, and variable compression ratio engine with specifications listed in Table 1. Engine power absorption

* The “ASTM-CFR Engine” is also known as the “Waukesha CFR Engine” or simply the “Waukesha Engine”

and engine motoring capabilities were provided by a 1250 RPM, 3.7 kW (5 HP), 230 V DC dynamometer manufactured by Louis Allis Company, Milwaukee, WI.

Test Blends

Six alcohol/gasoline blends were prepared for this research. As mentioned earlier, these blends followed the EPA DuPont Waiver for alcohol/gasoline blends. Each blend contained 90% (vol) Unleaded Test Gas 96 (UTG 96) from Phillips 66, and 10% (vol) alcohol. The alcohol component of the blends consisted of methanol, ethanol, propanol, butanol, and pentanol (see Table 3.2 for properties of the individual alcohols and UTG 96). While the total concentration was kept constant, the concentrations of individual alcohols in the mix were varied. This was done so that the effect of the individual alcohols, not the total alcohol, could be investigated. In order to decide on the concentrations of the various alcohols in the test blends, extensive tables were made which varied the concentrations of the different alcohols. Table 3 lists the volumetric composition and oxygen content of the six test blends. In addition, the net heat of combustion for each of the six test blends is given in Table 4.

Type	Water cooled-4 cycle
Bore and Stroke	8.26 cm x 11.43 cm (3.250 in x 4.500 in)
Cylinder Swept Volume	611.7 cm ³ (37.331 in ³)
Compression Ratio	4 to 16
Combustion Chamber Volume (at TDC)	176.7 cm ³ to 40.8 cm ³ (10.784 in ³ to 2.489 in ³)
Connecting Rod Length (center-to-center)	25.40 cm (10.000 in)
Piston Rings (number)	5 total (4 compression, 1 oil control)
Ignition System	Spark (coil-points-Champion D16 spark plug)
Weight of Engine (approximate)	399 kg (880 lb)
Weight of Complete Unit (approximate)	1247 kg (2750 lb)

Table 1 - Waukesha Engine Specifications

Property	UTG 96	Methanol	Ethanol	Propanol	Butanol	Pentanol
Chemical Formula	C ₈ H ₁₈ (Typical)	CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₇ OH	C ₄ H ₉ OH	C ₅ H ₁₁ OH
Molecular Weight	111.21	32.04	46.07	60.10	74.12	88.15
Oxygen Content, wt. %	0.00	49.93	34.73	26.62	21.59	18.15
Stoichiometric A/F	14.51	6.43	8.94	10.28	11.12	11.68
Specific Gravity	0.7430	0.7913	0.7894	0.8037	0.8097	0.8148
Boiling Point, °C (°F)	34-207 (94-405)	65 (149)	78.3 (173)	82.2 (180)	82.7 (181)	—
RVP, KPa (psi)	61.4 (8.9)	32.4 (4.7)	19.3 (2.8)	9.0 (1.3)	18.6 (2.7)	—
Net Ht. of Comb., kJ/L (BTU/gal)	31,913 (114,500)	15,887 (57,000)	21,183 (76,000)	23,970 (86,000)	25,921 (93,000)	26,200 (94,000)
Lat. Ht. of Vaporiz., kJ/L (BTU/gal)	223 (800)	920 (3,300)	725 (2,600)	585 (2,100)	474 (1,700)	251 (900)
RON	96.5	112	111	112	113	—
MON	87.2	91	92	—	—	—

Table 2 - Properties of Pure Alcohols and UTG 96 (Bata et al., 1989; Dorn et al., 1986; Dean, 1992; and Phillips 66, 1995)

Blend No.	Volume Percentage of						% Volume Alcohols	% wt. Oxygen in Blend
	UTG 96	Methanol	Ethanol	Propanol	Butanol	Pentanol		
1	90.00%	0.60%	2.07%	4.80%	2.40%	0.13%	10.00%	3.03%
2	90.00%	0.60%	0.22%	4.80%	2.40%	1.98%	10.00%	2.72%
3	90.00%	2.00%	2.00%	3.00%	2.88%	0.12%	10.00%	3.34%
4	90.00%	2.00%	2.00%	3.00%	0.12%	2.88%	10.00%	3.24%
5	90.00%	3.24%	2.40%	2.76%	0.13%	1.47%	10.00%	3.70%
6	90.00%	3.04%	2.40%	2.96%	1.47%	0.13%	10.00%	3.70%

Table 3 - Volumetric Composition and Oxygen Content of the Test Blends

Blend ID	kJ/kg	BTU/lb
UTG 96	42912	18448
Blend 1	42751	18379
Blend 2	42744	18376
Blend 3	42779	18391
Blend 4	42798	18399
Blend 5	42828	18412
Blend 6	42821	18409

Table 4 - Net Heat of Combustion of the Six Test Blends and UTG 96

Instrumentation

Overview

Figure 1 illustrates the instrumentation that was installed on the Waukesha Engine to monitor the engine operating parameters and the in-cylinder pressure history. The voltage output from a given sensor was related to the engineering parameter via the calibration information either given by the manufacturer of the particular sensor or generated in the laboratory. Some of the sensors required an "excitation" voltage, so a system of power supplies was constructed to provide the necessary power for the sensors. A 5-volt, a 10-volt, and a 15-volt power supply were used in the power system. Once all the sensors were installed, the voltages output by the sensors were read by an A/D data acquisition board installed in an IBM PC driven by a BASIC 7 program.

Figure 1 - Schematic of Waukesha Engine Instrumentation

Cylinder Pressure History

In order to evaluate the combustion characteristics (knock intensity, heat release, ignition delay, and burn time) of the alcohol/gasoline blends, a system was developed to capture the in-cylinder pressure history. The system consisted of a piezoelectric pressure transducer, charge amplifier, and power supply was installed on the Waukesha Engine. Piezoelectric pressure transducers contain a piezoelectric crystal, which develops a charge that is proportional to the force acting on the crystal. Then, a charge amplifier converts the induced charge on the crystal into a readable voltage. The high temperatures inside the combustion chamber and in the cylinder head where the pressure transducer was installed, made it imperative to use a water-jacketed transducer. This was necessary for two reasons: (1) piezoelectric pressure transducers experience drift in the output signal with changing temperature and (2) excess heat can destroy a piezoelectric pressure transducer.

Data Acquisition

Overview

With all the necessary transducers in place, a data acquisition system was developed to acquire and archive the test data. An RTI-835L data acquisition board from Analog Devices, which has 16 analog input channels and two digital I/O channels, was used to interface the transducers with a dedicated computer. The board was driven by means of data acquisition software developed in BASIC 7. The board was also capable of timing analog input operations with external events via triggering and pacing. The software used for driving the RTI-835L board employed a BASIC 7 software package from Analog Devices, which is a collection of subroutines that make the board perform its various functions.

Engine Operating Conditions

The voltage signals from various transducers monitoring the engine operating conditions were supplied to the data acquisition board via the analog input channels. One exception was the engine speed. Engine speed was monitored by measuring the frequency of the square wave coming from the crankshaft encoder. The data acquisition board has a counter/timer channel, which is part of the digital I/O section of the board, that can be set up to measure the frequency of an incoming signal. Once the transducers were wired into the data acquisition board, the appropriate subroutines were called from the software package to read the voltages and frequencies coming from the sensors. The calibration information was programmed into the software so that the incoming voltages and frequencies could be converted into corresponding engineering parameters.

The engine operating conditions were monitored and recorded during the blend testing program. All the measured parameters were displayed, in engineering units, on the video monitor.

Cylinder Pressure History

Although the instrumentation for measuring in-cylinder pressures operates in a manner that is similar to the other sensors (that is, converting pressure into a voltage), the initiation of pressure data acquisition had to be indexed with respect to the crank angle. Crank angle resolved in-cylinder pressure measurements (in-cylinder pressure vs. crank angle) were needed for combustion calculations. This was accomplished by a triggered and paced analog input operation. The indexing signal from a cycle position sensor was connected to the external trigger port of the data acquisition board. Thus, the data acquisition operation on the cylinder pressure history was “triggered” by the indexing signal, and the first pressure data point captured would be at the cycle position pre-set by the cycle position sensor. To keep track of the crank angle throughout the rest of the cylinder pressure data acquisition operation, the signal from the crank angle sensor was led into the external pacer port of the data acquisition board. Every fall in the crank angle signal (every half degree of rotation of the crankshaft) would result in an A/D converter command in the data acquisition board. Thus, each pressure data point would be half a degree apart.

The dual use of the crank angle sensor, both as an engine speed sensor and as an external A/D pacer, required the design and construction of an interface. The signal from the crank angle sensor could not be wired into both the frequency measurement port and the external pacer port at the same time due to the limitations of the data acquisition board. Thus, the interface had to be designed so that the signal from the crank angle sensor could be switched between the frequency measurement port and the external pacer port. The interface used signals from the digital output section of the data acquisition board to determine which port the crank angle sensor signal would go to. Thus, the path of the crank angle signal could be controlled from within the data acquisition program. In addition, the interface contained LEDs that indicated when power was available from the 5V, 10V and 15V power supplies, and it also indicated the routing of the crank angle sensor signal via LEDs.

Other Blend Properties

In addition to the combustion and performance characteristics of the blends that were studied on the Waukesha engine tests, the physical and chemical properties of the blends were also studied. These properties include the ASTM D-86 distillation curves, hydrocarbon types, net heat of combustion, Reid vapor pressure, research octane number, and motor octane number. These blend parameters were measured and reported by Core Laboratories, Long Beach, Ca, on a contract basis. Data obtained from Core Laboratories was assured to be in compliance with NIST standards and test procedures.

Data Analysis

Knock Analysis

Knock is an undesirable mode of combustion that originates spontaneously and sporadically in the engine, producing sharp pressure pulses associated with a vibratory movement of the charge and the characteristic sound from which the phenomenon derives its name (Oppenheim, 1988). Knock is associated with an abrupt increase in pressure (large positive curvature) followed by an unusually sharp pressure peak (large negative curvature) and oscillating pressure (many changes in curvature). Since curvature is the second derivative of a signal, a rapid change in curvature would be associated with a large amplitude of the third derivative of the pressure trace. Thus, the maximum amplitude of the third derivative of the pressure trace could be considered as a knock indicator (Checkel and Dale, 1986; Puzinauskas, 1992).

The value of the knock indicator that distinguishes a knocking cycle from a non-knocking cycle will be called the critical knock indicator (CKI). Currently, there is no standard for the value of the CKI; its value is arbitrary and based on experience with the engine and equipment used (Checkel and Dale, 1986). Therefore, several tests were done to determine a reasonable value for the CKI. These tests involved running the Waukesha engine on a stoichiometric mixture of UTG96, at a low compression ratio with no audible knock and spark timing of 15° BTDC. Then, the compression ratio was increased in increments of 0.1 until heavy audible knock occurred. At each compression ratio, 50 cylinder pressure traces were captured, and the severity of audible knock was noted. After studying the pressure traces for knock characteristics (sharp pressure rise, sharp pressure peak, and pressure oscillations), analyzing the first and third derivatives of those pressure traces, and comparing the pressure data with audible knock observations, a CKI of 344.7 KPa/degree³ (50 psi/degree³) was chosen. The first derivative was calculated numerically using a four-point central difference, Eq. 1, and the third derivative was calculated numerically using a 6-point central difference, Eq. 2 (Chapra and Canale, 1988):

$$f'(x_i) = \frac{-f(x_{i+2}) + 8f(x_{i+1}) - 8f(x_{i-1}) + f(x_{i-2})}{12h} \quad (1)$$

$$f'''(x_i) = \frac{-f(x_{i+3}) + 8f(x_{i+2}) - 13f(x_{i+1}) + 13f(x_{i-1}) - 8f(x_{i-2}) + f(x_{i-3})}{8h^3} \quad (2)$$

Where: h = distance between data points x_i

Figures 2 - 4 illustrate how the knock indicator changes with increasing knock intensity, and how the pressure curve begins to show definite signs of knock around a knock indicator of 344.7 KPa/degree³ (50 psi/degree³). In addition, the first derivatives

are also shown to illustrate the spike that occurs with a sharp pressure peak, which is an indication of knock. Further examination of cylinder pressure data taken from the alcohol/gasoline blends also verified that a CKI of 344.7 KPa/degree³ (50 psi/degree³) was a valid choice.

Figure 2 - Pressure trace and derivatives with a knock indicator of 145 KPa/degree³ (21 psi/degree³)

Figure 3 - Pressure trace and derivatives with a knock indicator of 345 KPa/degree³ (50 psi/degree³)

Figure 4 - Pressure trace and derivatives with a knock indicator of 1420 KPa/degree³ (206 psi/degree³)

In determining the knock limiting compression ratio (KLCR) for a particular blend at a particular spark timing, 50 pressure traces obtained via the data acquisition procedure were analyzed. The data reduction program calculated the third derivatives of the pressure traces and then kept track of how many of the 50 traces exceeded the CKI. The KLCR was set to the compression ratio (CR) immediately preceding the CR where more than 20% of the pressure curves exceeded the CKI. In other words, the KLCR is the CR corresponding to a particular spark timing where as many as 20% of the cycles are allowed to exceed the CKI, but not more than 20%. The reason for doing this was the cycle to cycle variation. Since the CKI of 344.7 KPa/degree³ (50 psi/degree³) identified light knock, there may be a few cycles which showed light knock, but the majority of the cycles were not knocking. Under these conditions, the engine was still running normally.

Indicated Mean Effective Pressure

Indicated mean effective pressure (IMEP) is a measure of the work done by the gas on the piston per unit volume of the cylinder per mechanical cycle. This allows for the comparison of engines of different sizes, because the size of the engine is scaled out. The IMEP can be calculated from a known pressure vs. volume history inside the cylinder. There are two kinds of IMEP: gross IMEP and net IMEP. Net IMEP refers to the work throughout the intake, compression, expansion, and exhaust strokes, while the gross IMEP refers only to the work during the compression and expansion strokes. All further references to IMEP shall designate the gross IMEP.

The IMEP is the net result of the positive work done by the expansion process and the negative work done through the compression stroke. IMEP is calculated by integrating the pressure-volume curve inside the cylinder and dividing by the cylinder swept volume:

$$IMEP = \frac{1}{\pi B^2 S} \int_1^2 P dV \quad (3)$$

Where: Point 1 = BDC before the compression stroke
 Point 2 = BDC after the expansion stroke
 B = cylinder bore
 S = piston stroke

Since the crank angle resolved cylinder pressure was measured directly during testing, the integral could be numerically calculated from the experimental data. Using the numerical trapezoidal integration method, Eq. 3 becomes:

$$IMEP = \frac{1}{\pi B^2 S} \sum_{i=\text{BDC before compression}}^{\text{BDC after expansion}} \frac{1}{2} (P_{i+1} + P_i) (V_{i+1} - V_i) \quad (4)$$

Volume inside the cylinder can be calculated from crank angle via Eq. 5 (Stone, 1994):

$$V = V_{TDC} + \frac{\pi B^2}{4} \left\{ \frac{S}{2} (1 - \cos \theta) + l - \sqrt{l^2 - \frac{S^2}{4} \sin^2 \theta} \right\} \quad (5)$$

Where: V_{TDC} = volume at top dead center
 θ = crank angle measured from TDC
 l = connecting rod length

Heat Release

The analysis of heat release from the combustion of the air/fuel mixture inside the cylinder of an internal combustion engine provides information on the amount of heat that should be added to the cylinder contents in order to produce the measured pressure variations. With known pressure vs. crank angle data for a particular engine, the rate of heat release from combustion can be calculated from ideal gas principles and thermodynamics. The net rate of heat release can be calculated from the following equation (for a detailed derivation of this equation, refer to Martin II, 1997)

$$\frac{dQ_{HR}^N}{d\theta} = \frac{V_\theta}{(g-1) \Delta\theta} \left(P_\theta - P_{\theta-\Delta\theta} \left[\frac{V_{\theta-\Delta\theta}}{V_\theta} \right]^g \right) \quad (6)$$

Where: $\frac{dQ_{HR}^N}{d\theta}$ = the net heat release rate (BTU/degree)
 P_θ = measured pressure at crank angle θ
 V_θ = cylinder volume at crank angle θ

$$\begin{aligned}
P_{q-\Delta q} &= \text{measured pressure at crank angle } (q - \Delta q) \\
V_{q-\Delta q} &= \text{cylinder volume at crank angle } (q - \Delta q) \\
g &= \text{ratio of specific heats} \approx 1.3
\end{aligned}$$

In order to identify the portion of the heat release curve that signifies the combustion event, a search algorithm was used to find the maximum heat release rate. The *beginning* of combustion was then set to the crank angle corresponding to the first negative or zero value for heat release *preceding* the maximum heat release. Similarly, the *end* of combustion was set to the crank angle corresponding to the first negative or zero value for heat release *following* the maximum heat release. In an effort to eliminate the effects of cycle to cycle variations, the 50 pressure curves obtained at each setpoint were averaged together to obtain an average pressure history. Heat release analysis was then performed on the average pressure curve.

Mass Fraction Burned, Ignition Delay, and Combustion Interval

Mass fraction burned (MFB) profiles for a combustion process in an internal combustion engine can be derived from the heat release data. Assuming that the amount of heat added is directly proportional to the amount of fuel burned, the MFB can be calculated by integrating the heat release curve up to the point of interest and dividing by the total heat released:

$$\text{MFB} = \frac{\sum_{i=BC}^P \left(\frac{dQ_{HR}^N}{dq} \right)_i}{\sum_{i=BC}^{EC} \left(\frac{dQ_{HR}^N}{dq} \right)_i} \quad (7)$$

Where: BC is the beginning of combustion
 EC is the end of combustion
 P is the point of interest in the combustion event

Values for MFB will range from 0% to 100%..

Ignition delay, Δq_{ID} , is defined as the crank angle interval between the spark discharge and the time when a small but significant fraction of the cylinder mass has been burned or fuel chemical energy has been released. Δq_{ID} is usually taken to be the difference between crank angles corresponding to spark discharge and 10% MFB. In addition, the combustion interval, Δq_{CI} , is defined as the crank angle interval required to burn the bulk of the charge and is usually taken as the difference between crank angles corresponding to 10% MFB and 90% MFB (Heywood, 1988).

Results and Discussion

Overview

Since the objective of this study was to evaluate the combustion characteristics of higher alcohol/gasoline blends and compare those characteristics to neat gasoline the engine was operated at steady state with certain engine operating conditions held constant. This permitted the measurement and analysis of combustion characteristics as a function of the fuel used in the engine and not the engine itself. Table 5 lists the engine operating conditions used in this study:

Engine Parameter	Specification
Speed	895 - 905 RPM
Intake Manifold Temperature	45 ⁰ C - 47.2 ⁰ C (113 ⁰ F - 117 ⁰ F)
Crankcase Oil Temperature	64.4 ⁰ C - 67.8 ⁰ C (148 ⁰ F - 154 ⁰ F)
Coolant Water Temperature	97.2 ⁰ C - 98.3 ⁰ C (207 ⁰ F - 209 ⁰ F)
Air / Fuel Ratio	Stoichiometric

Table 5 - Engine Operating Conditions During Blend Testing

The main combustion characteristic of interest with the alcohol/gasoline blends was the knock limiting compression ratio (KLCR), which is defined here as the maximum compression ratio at a given ignition timing where the engine will operate without excessive knock. To determine whether or not the engine was knocking excessively, the pressure history inside the cylinder was used. Since the KLCR is a function of ignition timing, the testing procedure consisted of capturing cylinder pressure traces at various ignition timings and compression ratios. Ignition timing was varied between 30⁰ BTDC and 0⁰ in increments of 2.5⁰. At each ignition timing, acquisition of cylinder pressure histories began at a compression ratio (CR) well below the KLCR (audible knock). Then, the CR was increased in increments of 0.1 until excessive audible knock occurred, and cylinder pressure histories were captured at each ignition timing-compression ratio setpoint. To ensure that cycle-to-cycle variation did not influence the analysis of knock, 50 pressure traces were captured at each ignition timing-compression ratio setpoint.

Once the KLCR for each ignition timing was determined, the ignition timing-KLCR combination that produced the best IMEP was identified. Similar to knock analysis, IMEP was also determined from the cylinder pressure histories. Once the best IMEP point was identified, the other combustion parameters (heat release, burn time, and ignition delay) were also compared at the point of best IMEP. It should be noted that the point of best IMEP is also the point of maximum engine power. Thus, the engine performance parameters were being compared when the engine spark timing and compression ratio were optimized for a particular blend.

Knock Limits and IMEP Trends

The knock limit curves and IMEP trends were plotted versus spark timing for each blend and UTG 96 in Figures 5 - 11. The IMEP data were generated at the corresponding spark timing/KLCR combinations. Figures 5 - 11 show, as expected, that the KLCR increased with increasingly retarded spark timing. In addition, the IMEP also increased with the spark timing/KLCR combinations from 30⁰ BTDC up to about 17.5⁰ BTDC, leveled off, and then continued to increase up to 5⁰ BTDC. Thus, the point of maximum engine power for each blend and UTG 96 was at spark timing 5⁰ BTDC and the corresponding KLCR. Table 6 summarizes the spark timing/KLCR combinations where the best IMEP was obtained for each blend. It should be noted that every blend produced a better IMEP than UTG 96. This was undoubtedly due to the better anti-knock characteristics of the blends which allowed higher compression ratios.

Blend ID	Spark Timing @Best IMEP	Compression Ratio @ Best IMEP	Best IMEP KPa (psi)
UTG 96	-5.0	8.8	275.9 (40.01)
1	-5.0	9.5	337.1 (48.89)
2	-5.0	9.4	338.1 (49.04)
3	-5.0	9.9	355.1 (51.50)
4	-5.0	9.4	338.7 (49.13)
5	-5.0	9.9	358.7 (52.02)
6	-5.0	9.9	356.9 (51.76)

Table 6 - Engine Settings for Best IMEP for Each Blend and UTG 96

Figure 5 - Knock Limits and IMEP Trend for UTG 96

Figure 6 - Knock Limits and IMEP Trend for Blend 1

Figure 7 - Knock Limits and IMEP Trend for Blend 2

Figure 8 - Knock Limits and IMEP Trend for Blend 3

Figure 9 - Knock Limits and IMEP Trend for Blend 4

Figure 10 - Knock Limits and IMEP Trend for Blend 5

Figure 11 - Knock Limits and IMEP Trend for Blend 6

At the onset of blend testing, it was hoped that a KLCR could be found for the entire range of spark timings between 30° BTDC and 0°. However, at spark timings above 5° BTDC, the KLCR could not be attained because the air/fuel mixture inside the cylinder would ignite, due to compression, before the occurrence of the spark (a phenomenon commonly called “dieseling”) and the engine would not run properly. Thus, the KLCR/IMEP data only go up to 5° BTDC spark timing.

Knock Resistance Indicator and Antiknock Index

To determine the knock resistance capability of the blends over the range of spark timings, a Knock Resistance Indicator (KRI) was calculated from the KLCR vs. spark timing curves by numerically integrating the curves via the trapezoidal rule:

$$KRI = \sum_{i=-27.5}^{-5 \text{ (by increment 2.5)}} \frac{1}{2} (KLCR_i + KLCR_{i-2.5}) \times 2.5 \quad (8)$$

Where: $KLCR_i$ = knock limiting compression ratio at spark timing i .

The KRI gives an indication of whether or not one blend allows higher compression ratios at the various spark timings than another blend, because it is the area under the KLCR vs. spark timing curve. The KRI for each blend is shown in Figure 12 along with the corresponding (RON+MON)/2 antiknock index. Figure 12 shows that both the KRI and the (RON+MON)/2 antiknock index increase with increasing oxygen content of the blend. The exceptions were blends 5 and 6, both of which contained 3.7% oxygen by mass. Blend 5 showed slightly better resistance to knock than blend 6. This indicates that lower alcohols enhance the anti-knock characteristics of the blends. Blend 5 contained 5.64% methanol/ethanol³ and 4.36% higher alcohols, whereas blend 6 contained 5.44% methanol/ethanol and 4.56% higher alcohols. The same conclusion can be drawn from blends 1 and 2. Blend 1, which contained 2.67% methanol/ethanol and 7.33% higher alcohols, showed greater anti-knock capability than blend 2, which contained 0.82% methanol/ethanol and 9.18% higher alcohols. Blends 3 and 4 further support the conclusion that the lower the order of the alcohol, the greater the anti-knock characteristics. Blends 3 and 4 contained identical quantities of methanol, ethanol, and propanol. However, blend 3, which contained 2.88% butanol and 0.13% pentanol had better anti-knock characteristics than blend 4, which contained 0.12% butanol and 2.88% pentanol. In addition, blends 1 and 2 had the least resistance to knock than any of the others and contained the least amount of methanol/ethanol and the highest amount of higher alcohols. Blends 5 and 6 that exhibited the greatest resistance to knock than any others, contained the most methanol/ethanol and the least higher alcohols.

³ A percentage of methanol/ethanol indicates the percentage of methanol and ethanol combined. For example, 5% methanol/ethanol means that methanol and ethanol made up 5% of the total blend composition.

Figure 12 - Comparison of Knock Resistance Indicator and Antiknock Index Between Blends and UTG 96

Heat Release, MFB, Combustion Intervals, and Ignition Delays

The heat release and MFB curves are presented for each blend and UTG 96 in Figures 13 - 19. The ignition delays and combustion intervals are shown in Figure 20. It should be noted that the heat release data were taken at the spark timing/KLCR combination where the engine produced the maximum power for the blend in question (summarized in Table 6).

Heat release is the amount of heat that would have to be added to the cylinder contents to produce the measured pressure variations due to combustion of the air/fuel mixture. The heat release profiles shown for all the blends and UTG 96 in Figures 13 - 19 are very similar in shape and magnitude. The MFB curves were derived from the heat release data by numerically integrating the heat release curve up to the point of interest and dividing by the total heat released. The MFB curves shown in Figures 13 - 19 are also very similar in shape.

Ignition delay and combustion interval, defined earlier, give insight into the flame speed of a particular fuel. The shorter the ignition delay, the less time it takes for the flame to develop and vice versa. The shorter the combustion interval, the faster the flame burns the bulk of the charge and vice versa.

Figure 20 shows that both the ignition delay and combustion interval decrease with increasing oxygen content of the fuel. This indicates that increasing the oxygen content results in a decrease in flame development time and an increase in the burning velocity of the fuel. Blends 5 and 6, which had the same oxygen content, have identical ignition delays, but blend 6 showed a slightly shorter combustion interval. Hence, the greater the percentage of lower alcohols in the blends, higher is the flame speed. Blend 6 contained slightly more lower alcohols than blend 5. Similar trend was observed for blends 1 and 2. Blend 1, which contained 2.67%

methanol/ethanol and 7.33% higher alcohols, experienced a shorter ignition delay and combustion interval than blend 2, which contained 0.82% methanol/ethanol and 9.18% higher alcohols. Further, blends 3 and 4 illustrate an increase in flame speed a higher percentage of a lower order alcohol. Blends 3 and 4 contained identical amounts of methanol, ethanol, and propanol. However, blend 3, which contained 2.88% butanol and 0.13% pentanol, experienced a shorter combustion interval and ignition delay than blend 4, which contained 0.12% butanol and 2.88% pentanol.

Figure 13 - Heat Release and MFB Curves for UTG 96

Figure 14 - Heat Release and MFB Curves for Blend 1

Figure 15 - Heat Release and MFB Curves for Blend 2

Figure 16 - Heat Release and MFB Curves for Blend 3

Figure 17 - Heat Release and MFB Curves for Blend 4

Figure 18 - Heat Release and MFB Curves for Blend 5

Figure 19 - Heat Release and MFB Curves for Blend 6

Figure 20 - Comparison of Ignition Delays and Combustion Intervals Between Blends and UTG 96

Reid Vapor Pressure and Distillation

The RVP for each blend and UTG 96 is shown in Figure 21. The higher the RVP, the more difficult it is to control evaporative emissions. Blend 1 (2.67% methanol/ethanol, 7.33% higher alcohols) showed only a slight increase in RVP compared to UTG 96, and blend 2 (0.82% methanol/ethanol, 9.18% higher alcohols) actually showed a small decrease in RVP compared to UTG 96. Blends 5 and 6 had the highest RVP out of all the blends, and these two blends also contained the highest amounts of the lower alcohols (5.64% methanol/ethanol for blend 5 and 5.44% methanol/ethanol for blend 6). Blends 3 and 4 also showed how higher order alcohols help control the RVP of the blend, because blend 4 had an RVP lower than blend 3. Blends 3 and 4 were identical except that blend 3 contained 2.88% butanol and 0.12% pentanol, whereas blend 4 contained 0.12% butanol and 2.88% pentanol. Another aspect of blends 5 and 6 illustrates how high order alcohols can offset the effects on RVP from lower alcohols. Blend 5 contains 3.24% methanol compared to 3.04% methanol in blend 6. However, these two blends have nearly identical RVPs. The fact that blend 5 contains 1.47% pentanol compared to 0.13% pentanol in blend 6 seems to offset the higher concentration of methanol in blend 5.

It has been shown by previous researchers that the presence of alcohols in gasoline depresses the distillation curve of the fuel, which can cause problems with cold starting and vapor lock. This expected trend was true of the six test blends. The distillation curves for each of the blends, are compared to UTG 96 in Figures 23-28. The distillation curve for each blend was significantly depressed between 0% and 60% . To determine the effects of the different alcohols on the distillation curve, the area under each curve between 0% and 60% evaporated was numerically calculated (see Figure 29). The distillation curves for blends 1 and 2 were the

least affected by the alcohols. It should be noted that these blends also contain the least methanol/ethanol. The distillation curve for blend 2 was less affected than blend 1, and, as mentioned previously, blend 2 had lower methanol/ethanol concentration than blend 1. Blends 5 and 6 showed the most pronounced effect on the distillation curve, and these blends contain the most methanol/ethanol. Thus, it becomes obvious that the lower alcohols have a more significant effect on the distillation curve than the higher alcohols.

Figure 21 - Reid Vapor Pressures of the Blends and UTG 96

Figure 22 - Percent Difference in RVP Between Blends and UTG 96

Figure 23 - Comparison of Distillation Curves Between Blend 1 and UTG 96

Figure 24 - Comparison of Distillation Curves Between Blend 2 and UTG 96

Figure 25 - Comparison of Distillation Curves Between Blend 3 and UTG 96

Figure 26 - Comparison of Distillation Curves Between Blend 4 and UTG 96

Figure 27 - Comparison of Distillation Curves Between Blend 5 and UTG 96

Figure 28 - Comparison of Distillation Curves Between Blend 6 and UTG 96

Figure 29 - Comparison of the Area Under the Distillation Curve Between 0% and 60% Evaporated for the Blends and UTG 96

Conclusions

An experimental investigation of combustion characteristics of higher alcohols/gasoline (UTG 96) blends was conducted. A single-cylinder ASTM-CFR engine was instrumented and the necessary data acquisition and corresponding data reduction computer programs were developed and implemented. Comparisons of knock limits, best IMEP, and fuel characteristics between higher alcohol/gasoline blends and neat gasoline were made to determine the advantages and disadvantages of blending higher alcohols with gasoline. All tests were conducted on the single-cylinder Waukesha CFR engine at steady state conditions and stoichiometric air-to-fuel ratio. The knock limiting compression ratio (KLCR) was found at spark timings ranging from 30° before top dead center (BTDC) and 5° BTDC by increments of 2.5°, and the corresponding indicated mean effective pressures (IMEPs) at these points were recorded. The data show that for each fuel blend tested, the best IMEP occurred at a spark timing of 5° BTDC and the corresponding KLCR. In addition, the higher alcohol/gasoline blends show a much better resistance to knock than neat gasoline, as indicated by the knock resistance indicator (KRI) and the $(RON+MON)/2$ antiknock index. The overall ability of the blends to resist knock seems to be a function of the total oxygen content of the blend; the higher the oxygen content there is in the blend, the higher the knock resistance. Ignition delay and combustion interval data show that higher alcohol/gasoline blends tend to have faster flame speeds. Here again, the oxygen content plays a role since the higher oxygen content blends tended to have faster flame speeds than the lower oxygen content blends.

The other fuel parameters, RVP and distillation curve, are affected by the addition of alcohol to gasoline. The lower alcohols (methanol and ethanol) cause the most dramatic increase in RVP and the largest depression of the distillation curve. Addition of the higher alcohols (propanol, butanol, and pentanol) seemed to curb the effects of methanol and ethanol on RVP and distillation.

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Chapter 20

EMISSIONS CHARACTERISTICS OF HIGHER ALCOHOL/GASOLINE BLENDS

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Abstract

An experimental investigation was conducted to determine the of emission characteristics of higher alcohols and gasoline (UTG96)) blends. While lower alcohols (methanol and ethanol) have been used in blends with gasoline, very little work has been done reported on higher alcohols (propanol, butanol, and pentanol).

Comparisons of emissions and fuel characteristics between higher alcohol/gasoline blends and neat gasoline were made to determine the advantages and disadvantages of blending higher alcohols with gasoline. All tests were conducted on a single cylinder Waukesha Cooperative Fuel Research (CFR) engine operating at steady state conditions and stoichiometric A/F ratio. Emissions tests were conducted at the optimum spark timing-knock limiting compression ratio (KLCR) combination for the particular blend being tested. The cycle emissions (mass per unit time; g/hr) of CO, CO₂, and organic matter hydrocarbon equivalent (OMHCE) from the higher alcohol/gasoline blends were very similar those from neat gasoline. Cycle emissions of NO_x from the blends were higher than those from neat gasoline. However, for all the emissions species considered, the brake specific emissions (g/kw-hr) were significantly lower for the higher 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 (g/hr) of higher alcohol/gasoline blends was slightly higher than neat gasoline due to the lower stoichiometric A/F ratios required by the blends. However, the brake specific fuel consumption (g/kW-hr) for the blends was significantly lower than that for neat gasoline.

Other fuel parameters, including Reid vapor pressure (RVP) and distillation curve, are affected by the addition of alcohol to gasoline. The lower alcohols (methanol and ethanol) cause the most dramatic increase in RVP and the largest depression of the distillation curve. Addition of the higher alcohols (propanol, butanol, and pentanol) seems to curb the effects of methanol and ethanol on both RVP and the distillation curve.

Background

Effect of Alcohol on Blend Vapor Pressure and Evaporative Emissions

Furey (1985) investigated RVP changes in gasoline when methanol, ethanol, and higher alcohols were added. His findings showed that very small amounts of alcohol in the blend drastically increased the RVP, and methanol seemed to have a more dramatic effect on RVP than higher alcohols. This was due to the fact that methanol forms low-boiling azeotropes with certain hydrocarbons. However, when methanol was blended in gasoline along with higher alcohols, the increase in RVP was lower compared to methanol alone. Hence, using higher alcohols as co-solvents in alcohol/gasoline blends seems to be a viable option for controlling RVP and, consequently, for controlling evaporative emissions.

Reddy (1986) compared the evaporative emissions of blends containing three levels of methanol and tertiary butyl alcohol (TBA) with gasolines of closely matched RVP. Three different fuel metering systems were tested: carburetor, throttle body injection (TBI), and multi-port fuel injection (MPI). The alcohol blends generated the same vapor levels as gasolines matched to the same ASTM D 439 volatility.

Although an alcohol/gasoline blend with an RVP close to that of neat gasoline may not produce substantially increased evaporative emissions, mixing an alcohol/gasoline blend with neat gasoline increases the RVP of the mixture. Furey (1987) investigated RVP changes when pure gasoline and an alcohol/gasoline blend of matched RVP were mixed together, as might be the case with an on-the-road vehicle. The results showed that even though a blend may have the same RVP as gasoline, a mixture of the two produces a fuel with a higher RVP. Thus, a vehicle would have to be fueled solely on neat gasoline or an alcohol/gasoline blend of matched RVP in order to avoid an increase in RVP of the tank fuel.

Alcohol Effects on Distillation, Cold Starting, and Vapor Lock

Adding alcohols to gasoline depresses the boiling temperature of individual hydrocarbons. The lower alcohols cause significant reduction in the front end distillation temperatures, thus affecting primarily the first 50% evaporated. Lower molecular weight alcohols have the greatest effect on boiling point depression. In particular, methanol causes the largest changes; its effects can be observed even when accompanied by a co-solvent. Higher molecular weight alcohols, such as Tertiary Butyl Alcohol (TBA), propanol, butanol, and pentanol, exert smaller changes on the distillation characteristics.

Yaccarino (1985) of General Motors Research compared the high temperature [26.7°C - 32.2°C (80°F - 90°F)] driveability and vapor lock performance of methanol blends using six cars with closed-loop fuel control systems: three cars had carburetors, two had throttle body injection, and one car was equipped with multi-port fuel injection. Four blends were tested: 3% methanol, 7% methanol, 4.75% methanol with 4.75% TBA, and 8.2% methanol with 2.7% TBA (all percentages by volume). The blends were matched with two gasolines meeting ASTM specifications for volatility classes C and D, which are fuels designed for typical summer and transitional seasons in the Midwest and Northeastern U.S., respectively. Driveability demerits, which were awarded based on hot engine restart, throttle response, and smoothness of engine performance, were greatest for two of the carbureted cars when alcohol blends were used. The fuel injected cars, and surprisingly one of the carbureted vehicles, performed similarly on the blends and with the gasolines. In the matched volatility vapor lock tests, the carbureted vehicles also performed poorly, with the worst performance on the blends containing the highest methanol concentrations. The poor performance of the carbureted cars, even though they had

closed-loop control, was to be expected with the alcohol blends. This was due to the fact that carburetors operate at very low pressure differentials and are unable to compensate for volume effects of partially vaporized fuel. Fuel injection systems, on the other hand, can deliver fuel to the injectors at pressure as high as 379 KPa (55 psig) and provide much greater tolerance of volatile fuels than is attainable with carbureted systems.

The property of alcohols that reduces cold starting ability the most is their higher (compared with typical gasoline) heat of vaporization. Bardon et al. (1985) investigated engine response to this factor by measuring the mixture richness required for starting between temperatures of -40°C and 15.6°C (-40°F and 60°F). The starting performance of a gasoline with an RVP of 61.4 KPa (8.9 psi) was compared to a blend composed of the same gasoline splash-blended with 10% methanol by volume and an RVP of 80 KPa (11.6 psi). The starting performance was not improved with the high RVP blend and, at stoichiometric mixture ratios for each fuel, gasoline allowed the engine to be started at 5°C (41°F) whereas the blend would not allow starting below 15°C (59°F). A 10% methanol blend matching the 61.4 KPa (8.9 psi) RVP gasoline was also made by removing volatile fractions from the base gasoline. With this blend, the engine would not start at temperatures below 15°C (59°F) unless the mixture strength was enriched about 100% above the stoichiometric A/F of the blend. At -30°C (-22°F), gasoline started the engine with a mixture eight times richer than stoichiometric, but the blend with matched RVP required a mixture strength fourteen times richer than stoichiometric. Rich mixtures are always needed to start cold engines, because enough fuel must vaporize to form a combustible air/fuel mixture. Thus, these studies only demonstrate relative difficulties in starting characteristics, not whether an engine will start when fueled with a blend. The relative cold starting difficulties largely depend on the fuel delivery system. The fuel delivery system must be able to provide a rich enough mixture to allow starting with an alcohol/gasoline blend.

Effects of Alcohol on Stoichiometry, Exhaust Emissions, and Fuel Economy

Alcohol/gasoline blends cause mixture enleanment due to the fact that alcohol requires a lower A/F ratio than gasoline. The leaning effect on the A/F ratio when low levels of oxygenates are used in vehicles without exhaust aftertreatment, results in a reduction both CO and HC emitted exhaust emissions with a slight increase in NO_x . A typical reduction in CO of 30% has been found with a fuel oxygen content of 2% (Mays, 1987). However, if the vehicle is designed to operate close to the lean limit of combustion on hydrocarbon fuels, misfire may occur when oxygenates are present under certain driving regimes with consequent increase in HC emissions (Owen et al., 1995). With vehicles equipped with catalytic converters, the effect of oxygenates found by Mays (1987) indicated reductions in CO and HC and a slight increase in NO_x . These data were obtained using 1978 to 1980 U.S. vehicles and a wide range of oxygenates.

Mixture stoichiometric effects are strongest in vehicles equipped with open-loop fuel metering systems which are calibrated to deliver a set A/F ratio without regard to fuel composition. For those vehicles calibrated richer than stoichiometric, usually older cars, the effect of operating on an alcohol/gasoline blend will be a reduction of CO and HC, and, quite likely, a modest increase in NO_x due to the leaning effect of alcohol on the A/F ratio. For non-catalyst cars with typically lean or near stoichiometric calibrations, operation on an alcohol/gasoline blend could produce a modest reduction in CO but cause the mixture to be sufficiently lean to result in poor combustion and a consequent increase in unburned HC. Catalyst-equipped vehicles with open-loop systems generally show some reduction in CO and HC and small increases in NO_x . Reductions of CO and HC emissions can be observed upstream of the catalyst but are less pronounced after the exhaust passes through a functioning (warmed-

up) catalyst. Changes in the emissions of NO_x , however, can be observed at the tailpipe in vehicles with open-loop systems. In addition, volumetric fuel economy (miles per gallon) is not likely to change in open-loop systems running on alcohol/gasoline blends due to the constant fuel delivery rate (American Petroleum Institute, 1988).

For cars equipped with closed-loop fuel metering systems, which try to keep the mixture near stoichiometric based on a reading from an oxygen sensor in the exhaust, the effect of running on alcohol/gasoline blends will only be noticed when running in open-loop mode. Closed-loop systems run in open-loop mode during warm-up after a cold start and during full power situations. A study by Furey and King (1982) showed that closed-loop systems when running in open-loop mode will show similar trends in exhaust emissions as fully open-loop systems when run on alcohol/gasoline blends. However, when the closed-loop system is functioning, little difference in exhaust emissions is noticed between blends and neat gasoline. As for volumetric fuel economy, closed-loop systems will likely show a decrease because of the capability to compensate for the lower A/F ratio required by alcohol/gasoline blends.

The exhaust from gasoline fueled vehicles commonly contains a spectrum of partially oxidized HC species known as aldehydes. Aldehydes have a very high ozone forming potential, that is, they are highly reactive. For example, formaldehyde and acetaldehyde have high Maximum Incremental Reactivity (MIR) values, 7.009 g $\text{O}_3/\text{g HC}$ and 6.322 g $\text{O}_3/\text{g HC}$, respectively. Acetaldehyde has been shown to produce laryngeal cancers in hamsters and nasal cancers in rats, and formaldehyde is a well-known carcinogen (National Institute for Occupational Safety and Health, 1991). Greater amounts of aldehydes can be generated when alcohol blends are used because the partial oxidation of methanol, ethanol, propanol, butanol, and pentanol directly produces formaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, and pentanaldehyde respectively. Exhaust oxidation catalysts can oxidize most of the aldehydes, and during closed-loop operation, three-way catalysts appear to be even more efficient at eliminating them. Aldehydes that survive the combustion process and the catalytic converter are present in the exhaust in very low concentrations relative to total hydrocarbon concentration levels (Schuetzle et al. 1981).

The Coordinating Research Council (CRC) and the EPA have investigated the trends in aldehyde emissions of alcohol/gasoline blends. In the CRC ethanol blend program (1982), tests of ethanol blends in open-loop cars showed that tailpipe aldehyde emissions averaged 0.012 grams/mile or 50% higher than with gasoline. Aldehyde emissions did not increase significantly in closed-loop vehicles with three-way catalyst technology. In the CRC methanol blend program (1984), no significant difference in aldehyde emissions was observed between any of the blends and gasoline. It is possible that the laboratory procedure used in this program could not accurately measure low levels of aldehyde concentrations. An EPA test program utilizing two 1984 model cars found that aldehyde emissions averaged 0.0043 grams/km (0.108 grains/mile), an increase of 49% over gasoline, when a blend containing 4.5% methanol by volume and 5.7% TBA by volume was used (Gabele et al., 1985). The program identified approximately 80% of the aldehyde increase, or 0.0012 grams/km (0.031 grains/mile), as formaldehyde emissions.

EPA Guidelines for Alcohol/Gasoline Blends

The use of alcohols in unleaded gasoline must be approved by the EPA, which must ensure that emission control systems, currently in place, will not be affected. Thus, there are several EPA guidelines that have to be followed when blending alcohol with gasoline. The “substantially similar” ruling states that alcohol may be added to gasoline provided that the

amount of oxygen in the finished fuel does not exceed 2.7% by mass. However, a number of specific proposals have been granted waivers allowing the use of alcohols in gasoline. The ruling followed throughout this research is the “DuPont Waiver.” Adopted in January 1985, the DuPont Waiver allows for methanol up to 5.0% volume plus at least 2.5% volume co-solvent (ethanol, propanol, butanol, or pentanol) plus corrosion inhibitor, with maximum oxygen content 3.7% by weight.

Test Engine and Blends

Test Engine

The engine used in this research was the ASTM Cooperative Fuel Research engine manufactured by Waukesha Engine Division, Fuel Research Department, Dresser Industries, Waukesha, WI. The complete unit is known as the “ASTM-CFR Engine*.” The Waukesha Engine has been used by several researchers in their investigation of combustion and emissions characteristics of alcohol fuels and blends (Patel et al., 1987; Hunwartzen, 1982; Harrington and Pilot, 1975; Ebersole and Manning, 1972).

The Waukesha Engine is a four stroke, single cylinder, spark ignited, and variable compression ratio engine with specifications listed in Table 1. Engine power absorption and engine motoring capabilities were provided by a 1250 RPM, 3.7 kW (5 HP), 230 V DC dynamometer manufactured by Louis Allis Company, Milwaukee, WI.

Test Blends

Six alcohol/gasoline blends were prepared for this research. As mentioned earlier, these blends followed the EPA DuPont Waiver for alcohol/gasoline blends. Each blend contained 90% (vol) Unleaded Test Gas 96 (UTG 96) from Phillips 66, and 10% (vol) alcohol. The alcohol portion of the blends contained methanol, ethanol, propanol, butanol, and pentanol (see Table 3.2 for properties of the individual alcohols and UTG 96). The concentrations of the individual alcohols were varied while keeping the total alcohol concentration the same. This was done so that the effect of the individual alcohols, not the total alcohol, could be investigated. In order to decide on the concentrations of the various alcohols in the test blends, extensive tables were made which varied the concentrations of the different alcohols while keeping the total O₂ less than 3.7% by weight. Table 3 lists the volumetric composition and oxygen content of the six test blends. In addition, the net heat of combustion for each of the six test blends is given in Table 4.

* The “ASTM-CFR Engine” is also known as the “Waukesha CFR Engine” or simply the “Waukesha Engine”

Type	Water cooled-4 cycle
Bore and Stroke	8.26 cm x 11.43 cm (3.250 in x 4.500 in)
Cylinder Swept Volume	611.7 cm ³ (37.331 in ³)
Compression Ratio	4 to 16
Combustion Chamber Volume (at TDC)	176.7 cm ³ to 40.8 cm ³ (10.784 in ³ to 2.489 in ³)
Connecting Rod Length (center-to-center)	25.40 cm (10.000 in)
Piston Rings (number)	5 total (4 compression, 1 oil control)
Ignition System	Spark (coil-points-Champion D16 spark plug)
Weight of Engine (approximate)	399 kg (880 lb)
Weight of Complete Unit (approximate)	1247 kg (2750 lb)

Table 1 - Waukesha Engine Specifications

Property	UTG 96	Methanol	Ethanol	Propanol	Butanol	Pentanol
Chemical Formula	C ₈ H ₁₈ (Typical)	CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₇ OH	C ₄ H ₉ OH	C ₅ H ₁₁ OH
Molecular Weight	111.21	32.04	46.07	60.10	74.12	88.15
Oxygen Content, wt. %	0.00	49.93	34.73	26.62	21.59	18.15
Stoichiometric A/F	14.51	6.43	8.94	10.28	11.12	11.68
Specific Gravity	0.7430	0.7913	0.7894	0.8037	0.8097	0.8148
Boiling Point, °C (°F)	34-207 (94-405)	65 (149)	78.3 (173)	82.2 (180)	82.7 (181)	—
RVP, KPa (psi)	61.4 (8.9)	32.4 (4.7)	19.3 (2.8)	9.0 (1.3)	18.6 (2.7)	—
Net Ht. of Comb., kJ/L (BTU/gal)	31,913 (114,500)	15,887 (57,000)	21,183 (76,000)	23,970 (86,000)	25,921 (93,000)	26,200 (94,000)
Lat. Ht. of Vaporiz., kJ/L (BTU/gal)	223 (800)	920 (3,300)	725 (2,600)	585 (2,100)	474 (1,700)	251 (900)
RON	96.5	112	111	112	113	—
MON	87.2	91	92	—	—	—

Table 2 - Properties of Pure Alcohols and UTG 96 (Bata et al., 1989; Dorn et al., 1986; Dean, 1992; and Phillips 66, 1995)

Blend No	Volume Percentage of						% Volume Alcohols	% wt. Oxygen in Blend
	UTG 96	Methanol	Ethanol	Propanol	Butanol	Pentanol		
1	90.00%	0.60%	2.07%	4.80%	2.40%	0.13%	10.00%	3.03%
2	90.00%	0.60%	0.22%	4.80%	2.40%	1.98%	10.00%	2.72%
3	90.00%	2.00%	2.00%	3.00%	2.88%	0.12%	10.00%	3.34%
4	90.00%	2.00%	2.00%	3.00%	0.12%	2.88%	10.00%	3.24%
5	90.00%	3.24%	2.40%	2.76%	0.13%	1.47%	10.00%	3.70%
6	90.00%	3.04%	2.40%	2.96%	1.47%	0.13%	10.00%	3.70%

Table 3 - Volumetric Composition and Oxygen Content of the Test Blends

Blend ID	kJ/kg	BTU/lb
UTG 96	42912	18448
Blend 1	42751	18379
Blend 2	42744	18376
Blend 3	42779	18391
Blend 4	42798	18399
Blend 5	42828	18412
Blend 6	42821	18409

Table 4 - Net Heat of Combustion of the Six Test Blends and UTG 96

Instrumentation

Overview

Figure 1 shows a schematic of the CFR engine test bed and all the instrumentation that was installed on the engine. Prior to conducting emission tests steps were taken to ensure that the engine was operating within normal limits and the repeatability of the engine operating conditions from test to test was established. The voltage output from the sensors was related to corresponding engineering parameters via calibration data. Some of the sensors required an “excitation” voltage, so a system of power supplies was constructed to provide the necessary power for the sensors. A 5-volt, a 10-volt, and a 15-volt power supply were used in the power system. Once all the sensors were installed, the voltages output by the sensors were read by an A/D data acquisition board installed in an IBM PC driven by a BASIC 7 program.

Figure 1 - Schematic of Waukesha Engine Instrumentation

Exhaust Emissions Sampling System

An exhaust emissions sampling system based on a micro-dilution tunnel (Gautam, 1994), was constructed to measure the mass emission rates of exhaust species under consideration. The system pulled raw exhaust from the exhaust pipe, through a heated line, into a heated dilution chamber. Inside the dilution chamber, the exhaust was mixed with metered zero humidity air from an air cylinder. Diluting the raw exhaust lowered the dew point temperature sufficiently to prevent water or alcohol condensation. After dilution, the exhaust was diverted into three separate lines. The first line directed a sample of the diluted exhaust to a bag which was later analyzed for CO, CO₂ and NO_x on an exhaust analysis bench in the West Virginia University's Engine Research Center. CO and CO₂ were analyzed using Rosemount Model 868 Non-dispersive Infrared (NDIR) analyzers. NO_x was analyzed on Rosemount Model 955 heated chemiluminescent analyzer. The second line led the diluted exhaust through a set of two bubblers filled with de-ionized water. Any unburned alcohol in the diluted exhaust dissolved in the bubbler water. After a test, the contents of the bubblers were analyzed for alcohols on a flame ionization detector (FID) gas chromatograph (GC). The third line directed the diluted exhaust through a DNPH (2,4-dinitrophenylhydrazine) coated silica gel cartridge. The aldehydes

in the exhaust reacted with the DNPH in the cartridge to form stable hydrazone derivatives, which were later eluted and analyzed using high performance liquid chromatography (HPLC). The analysis of the DNPH cartridges was performed by Atmospheric Analysis & Consulting, Inc., 4572 Telephone Road, Ventura, California. In addition to capturing diluted exhaust samples, the exhaust sampling system also included an in-line heated flame ionization detector (HFID) for continuous measurement of unburned HC.

The exhaust sampling system used a set of three-way valves for directing the diluted exhaust flow. The system could be operated in two distinct modes. The first mode was the warm-up/bypass mode which conditioned the lines and the dilution chamber with exhaust before any samples were drawn. The second mode was the sample mode where the diluted exhaust flows were diverted through the bubblers, through the DNPH cartridge, and into the bag. Figure 2 shows the sampling system in warm-up/bypass mode and Figure 3 shows the system in sample mode.

Figure 2 - Exhaust Emissions Sampling System in Warm-Up/Bypass Mode

Figure 3 - Exhaust Emissions Sampling System in Sample Mode

The flowrates through the various lines in the exhaust emissions sampling system were controlled by a set of four mass flow controllers (MFCs) from Seirra Instruments, Inc. In order to protect the internal components of the MFCs, a set of two filters was installed on each line. These filters labeled “DX” and “BX” are Balston® coalescing filters which remove 99.99% of particles and mist from air and other gases.

The sampling lines used in the exhaust emissions sampling system were 6.35-mm (0.250-inch) OD, 0.89-mm (0.035-inch) wall stainless steel tubing. In addition, the valves, fittings, MFC bodies, and filter bodies were also made of stainless steel.

Data Acquisition

Overview

An RTI-835L data acquisition board from Analog Devices, which has 16 analog input channels and two digital I/O channels, was used to interface all the transducers with a dedicated computer. The board was driven by means of data acquisition software developed in BASIC 7. The board was also capable of timing analog input operations with external events via triggering and pacing. The software used for driving the RTI-835L board employed a BASIC 7 software package from Analog Devices.

Engine Operating Conditions and Emissions

The voltage signals from various transducers monitoring the engine operating conditions were supplied to the data acquisition board via the analog input channels. One exception was the engine speed. Engine speed was monitored by measuring the frequency of the square wave

coming from the crankshaft encoder. The data acquisition board has a counter/timer channel, which was part of the digital I/O section of the board, that could be set up to measure the frequency of an incoming signal. Once the transducers were wired into the data acquisition board, the appropriate subroutines were called from the software package to read the voltages and frequencies coming from the sensors. The calibration information was programmed into the software so that the incoming voltages and frequencies could be converted into corresponding engineering parameters.

The engine operating conditions were monitored and recorded during the blend testing program. In addition to the engine performance data, HC emissions measured by the in-line HFID were also recorded and archived. The other emissions species (CO, CO₂, and NO_x) were analyzed from the bag sample captured by the emissions sampling system.

Other Blend Properties

These blend properties included the ASTM D-86 distillation curves, hydrocarbon types, net heat of combustion, Reid vapor pressure, research octane number, and motor octane number. These blend parameters were reported by Core Laboratories. Data obtained from Core Laboratories was assured to be in compliance with NIST standards and test procedures.

Data Analysis

Calculation of Mass Emission Rates from Diluted Exhaust Analysis

Mass emission rates were calculated from the diluted exhaust analysis by using the following equation (for a detailed derivation, refer to Martin II, 1997)

$$\dot{m}_E^i = 3.6 \times 10^{-3} \frac{(\dot{m}_A + \dot{m}_F) M_i}{M_E} \left[C_{DE}^i + d(C_{DE}^i - C_{DA}^i) \right] \quad (1)$$

Where:

- $\dot{m}_E^i$ = mass emission rate of constituent i from the engine (g/hr)
- $\dot{m}_A$ = mass flowrate of air into the engine (g/s)
- $\dot{m}_F$ = mass flowrate of fuel into the engine (g/s)
- M_i = molecular weight of constituent i (g/gmol)
- M_E = molecular weight of raw exhaust (g/gmol)
- C_{DE}^i = concentration of constituent i in the diluted exhaust (ppm)
- C_{DA}^i = concentration of constituent i in the dilution air (ppm)
- $d = \frac{\dot{V}_{DA}}{\dot{V}_{RE}} = \frac{\text{standard volume flowrate of dilution air}}{\text{standard volume flowrate of raw exhaust into sampling system}}$

Mass emission rates are usually specified in $\frac{\text{grams}}{\text{kW} \cdot \text{hr}}$ or $\frac{\text{lb}}{\text{HP} \cdot \text{hr}}$. Thus, dividing the right hand side of Eq. 1 by the engine power output, $\dot{W}$, yields:

$$\dot{m}_E^i = 3.6 \times 10^{-3} \frac{(\dot{m}_A + \dot{m}_F) M_i}{\dot{W} M_E} \left[C_{DE}^i + d(C_{DE}^i - C_{DA}^i) \right] \quad (2)$$

$\dot{m}_E^i$ calculated from Eq. 2 is expressed in terms of $\frac{\text{grams}}{\text{kW} \cdot \text{hr}}$ when $\dot{W}$ is in kW and the other parameters have the units specified in Eq. 1.

CO, CO₂, and NO_x Emissions

The concentrations of CO, CO₂, and NO_x in the diluted exhaust were measured by non-dispersive infrared analyzers (CO and CO₂) and a chemiluminescent analyzer (NO_x), respectively. The mass emission rates of these constituents were calculated directly from Equations 1 and 2. However, a humidity correction factor, K_H was included in the NO_x mass emission rate calculations:

$$K_H = \frac{1}{1 - 0.0047 \left(\frac{43.478 R_i P_d}{P_B - \left(P_d \frac{R_i}{100} \right)} - 75 \right)} \quad (3)$$

Where: R_i = relative humidity of the engine intake air, in percent

P_d = Saturated vapor pressure at the engine intake air dry bulb temperature

P_B = Barometric pressure

The NO_x emission rate obtained from Eq. 1 or Eq. 2 was multiplied by K_H (from Equation 3) to get the corrected NO_x emissions.

Unburned Alcohol Emissions

The unburned alcohol emissions were captured in the water bubblers of the emissions sampling system and were calculated from the following equation (for a detailed derivation, refer to Martin II, 1997)

$$C_{DE}^k = 8.205 \times 10^{-2} \frac{\rho_L^k V_B (C_{B1}^k + C_{B2}^k) T}{M_k P \dot{V}_{DE}^B t} \quad (4)$$

Where: C_{DE}^k = concentration of alcohol k in the diluted exhaust (ppm)

ρ_L^k = density of liquid alcohol k (g/cm³)

V_B = volume of water in each bubbler (cm³)

C_{B1}^k = concentration of liquid alcohol k in bubbler #1 (ppm)

C_{B2}^k = concentration of liquid alcohol k in bubbler #2 (ppm)

T = standard temperature set in mass flow controllers (°K)

M_k = molecular weight of alcohol k (g/gmol)

P = standard pressure set in mass flow controllers (atm)

$\dot{V}_{DE}^B$ = standard volume flowrate of diluted exhaust through bubblers (L/min)

t = amount of time exhaust sampling took place (min)

The concentration of alcohol k in the diluted exhaust calculated from Eq. 4 was substituted into either Eq. 1 or Eq. 2 to get the mass emission rate of alcohol k .

Aldehyde Emissions

Aldehyde emissions (formaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, and pentanaldehyde) were captured in the 2,4-DNPH cartridge in the emissions sampling system.

The amount of the particular aldehyde captured in the DNPH cartridge was reported in **mg** from analysis of the cartridge by another commercial analytical laboratory (Atmospheric Analysis & Consulting). Equation 5 was used to calculate aldehyde emissions (for a detailed derivation, refer to Martin II, 1997).

$$C_{DE}^k = 8.205 \times 10^{-8} \frac{m^k T}{M_k P \dot{V}_{DE}^{DNPH} t} \quad (5)$$

Where:

- C_{DE}^k = concentration of aldehyde k in the diluted exhaust (ppm)
- m^k = mass of aldehyde k captured in the DNPH cartridge (**mg**)
- T = standard temperature set in mass flow controllers ($^{\circ}\text{K}$)
- M_k = molecular weight of aldehyde k (g/gmol)
- P = standard pressure set in mass flow controllers (atm)
- $\dot{V}_{DE}^{DNPH}$ = standard volume flowrate of diluted exhaust through the DNPH cartridge (L/min)
- t = amount of time exhaust sampling took place (min)

Like the unburned alcohol concentration calculated from Eq. 4, the aldehyde concentration in the diluted exhaust calculated from Eq. 5 is substituted into either Eq. 1 or Eq. 2 to get the mass emission rate of aldehyde k .

HC Emissions

Total HC concentration was measured with an in-line heated flame ionization detector (HFID). Hydrocarbons measured by the HFID and not measured as unburned alcohols are reported as RHC (Residual Hydrocarbons). RHC is calculated from the following (Code of Federal Regulations, 1994):

$$\text{RHC} = \text{HFID} - \sum_i r_i C_i \quad (6)$$

where r_i are the HFID response factors for the particular alcohol, and C_i are the concentrations of the particular alcohol in the exhaust. The alcohol response factors were determined by analyzing a known concentration of a particular alcohol using the HFID (calibrated on propane). Hence:

$$r = \frac{\text{HFID reading in ppm}}{\text{Alcohol concentration in mixture, ppm}} \quad (7)$$

The values obtained for the response factors of the HFID to each alcohol are listed in Table 5.

Alcohol	HFID Response Factor
Methanol	0.5849
Ethanol	0.6322
Propanol	0.6345
Butanol	0.6387
Pentanol	0.6412

Table 5 - HFID Response Factors to Alcohols

Since the HC concentration is measured directly from the raw exhaust by the in-line HFID, there is no need to calculate the HC concentration in the raw exhaust. Thus, the $\left[C_{DE}^i + d(C_{DE}^i - C_{DA}^i) \right]$ term in Equations 1 and 2 can be replaced by the RHC reading (in ppm) from the HFID.

Organic Matter Hydrocarbon Equivalent

Organic Matter Hydrocarbon Equivalent (OMHCE) is commonly used to denote the total hydrocarbon mass emitted from the engine as unburned and partially burned fuel. For a fuel blend containing alcohols, the OMHCE is:

$$\begin{aligned} \text{OMHCE} = \text{RHC} &+ \frac{13.8756}{32.0420} m_{\text{CH}_3\text{OH}} + \frac{13.8756}{23.0344} m_{\text{C}_2\text{H}_5\text{OH}} + \frac{13.8756}{20.0319} m_{\text{C}_3\text{H}_7\text{OH}} + \frac{13.8756}{18.5306} m_{\text{C}_4\text{H}_9\text{OH}} \\ &+ \frac{13.8756}{17.6298} m_{\text{C}_5\text{H}_{11}\text{OH}} + \frac{13.8756}{30.0262} m_{\text{HCHO}} + \frac{13.8756}{22.0265} m_{\text{CH}_3\text{CHO}} + \frac{13.8756}{19.3599} m_{\text{C}_2\text{H}_5\text{CHO}} \\ &+ \frac{13.8756}{18.0267} m_{\text{C}_3\text{H}_7\text{CHO}} + \frac{13.8756}{17.2267} m_{\text{C}_4\text{H}_9\text{CHO}} \end{aligned} \quad (8)$$

Where: RHC = Residual Hydrocarbons calculated from Eq. 6
 m 's are mass emission of the particular constituents from Eq. 1 or Eq. 2
13.8756 = molecular weight of UTG 96 per carbon atom
32.0420 = molecular weight of CH_3OH (methanol) per carbon atom
23.0344 = molecular weight of $\text{C}_2\text{H}_5\text{OH}$ (ethanol) per carbon atom
20.0319 = molecular weight of $\text{C}_3\text{H}_7\text{OH}$ (propanol) per carbon atom
18.5306 = molecular weight of $\text{C}_4\text{H}_9\text{OH}$ (butanol) per carbon atom
17.6298 = molecular weight of $\text{C}_5\text{H}_{11}\text{OH}$ (pentanol) per carbon atom
32.0262 = molecular weight of HCHO (formaldehyde) per carbon atom
22.0265 = molecular weight of CH_3CHO (acetaldehyde) per carbon atom
19.3599 = molecular weight of $\text{C}_2\text{H}_5\text{CHO}$ (propionaldehyde) per carbon atom
18.0267 = molecular weight of $\text{C}_3\text{H}_7\text{CHO}$ (butylaldehyde) per carbon atom
17.2267 = molecular weight of $\text{C}_4\text{H}_9\text{CHO}$ (pentanaldehyde) per carbon atom

Results and Discussion

Overview

Since the objective of this study was to evaluate the emissions characteristics of higher alcohol/gasoline blends and compare those characteristics to neat gasoline, it was decided to operate the engine at steady state with certain engine operating conditions held constant. In this manner, combustion and emissions characteristics were dependent on the fuel used in the engine tests and not the engine itself. Table 6 lists the engine operating conditions used in this work.

Engine Parameter	Specification
Speed	895 - 905 RPM
Intake Manifold Temperature	45 ⁰ C - 47.2 ⁰ C (113 ⁰ F - 117 ⁰ F)
Crankcase Oil Temperature	64.4 ⁰ C - 67.8 ⁰ C (148 ⁰ F - 154 ⁰ F)
Coolant Water Temperature	97.2 ⁰ C - 98.3 ⁰ C (207 ⁰ F - 209 ⁰ F)
Air / Fuel Ratio	Stoichiometric

Table 6 - Engine Operating Conditions During Blend Testing

For each blend tested, the spark timing-compression ratio combination that produced the best Indicated mean effective pressure (IMEP) was found. Indicated mean effective pressure (IMEP) is a measure of the work done by the gas on the piston per unit volume of the cylinder per mechanical cycle. This allows for the comparison of engines of different sizes, because the size of the engine is scaled out. IMEP is calculated by integrating the pressure-volume curve inside the cylinder and dividing by the cylinder swept volume. Combustion characteristics (including measurement of in-cylinder pressures) of higher alcohols are discussed elsewhere (Gautam and Martin II, 1998).

Once the best IMEP point was found, the emissions tests were conducted at the ignition timing-KLCR (Knock limited compression ratio) combination that produced the best IMEP. KLCR is defined here as the maximum compression ratio at a given ignition timing where the engine will operate without excessive knock. To determine whether or not the engine was knocking excessively, the pressure history inside the cylinder was used. Since the KLCR is a function of ignition timing, the testing procedure consisted of capturing cylinder pressure traces at various ignition timings and compression ratios. Ignition timing was varied between 30⁰ BTDC and 0⁰ in increments of 2.5⁰. The reason for doing this was that the point of best IMEP is also the point of maximum engine power. Thus, the engine emissions were being compared when the engine spark timing and compression ratio were optimized for a particular blend. Table 7 lists the settings for best IMEP for each blend that were determined prior to conducting emissions tests (Martin II, 1997).

Blend ID	Spark Timing @Best IMEP	Compression Ratio @ Best IMEP	Best IMEP KPa (psi)
UTG 96	-5.0	8.8	275.9 (40.01)
1	-5.0	9.5	337.1 (48.89)
2	-5.0	9.4	338.1 (49.04)
3	-5.0	9.9	355.1 (51.50)
4	-5.0	9.4	338.7 (49.13)
5	-5.0	9.9	358.7 (52.02)
6	-5.0	9.9	356.9 (51.76)

Table 7 - Engine Settings for Best IMEP for Each Blend and UTG 96

Emissions and Fuel Consumption

Exhaust samples were collected for emissions analysis at the spark timing-KLCR values where the engine produced the most power. The power output of the engine at the optimum settings is given in Figure 4 for each blend and UTG 96. Mass emission rates for CO, CO₂, and NO_x are given in Figures 6 - 14; unburned alcohol and partially burned alcohol emissions are given in Figures 17 - 21; and hydrocarbon emissions are given in Figures 22 - 28. Emissions are given in terms of both mass per unit time $\left(\frac{\text{g}}{\text{hr}}, \left(\frac{\text{lb}}{\text{hr}}\right)\right)$ and mass per unit time per unit power output $\left(\frac{\text{g}}{\text{kW} \cdot \text{hr}}, \left(\frac{\text{lb}}{\text{HP} \cdot \text{hr}}\right)\right)$. Throughout the rest of the following discussion, emissions in terms of mass per unit time will be called the cycle emissions, and emissions in terms of mass per unit time per unit power output will be called the brake specific emissions.

Cycle emissions of CO and CO₂ for each blend were almost identical to UTG 96 (within 5% of each other), but the brake specific emissions of CO and CO₂ for the blends were 16% to 23% lower than UTG 96. This can be seen in Figures 6 - 11. Cycle emissions of NO_x from the blends were 12% to 16% higher than UTG 96, but the brake specific emissions of NO_x from the blends were between 5% and 11% lower than UTG 96 (see Figures 12 - 14). The higher cycle emissions of NO_x from the blends may have resulted due to higher in-cylinder temperatures. Figure 15 shows the temperatures at the exhaust port of the engine during emissions testing for each blend and UTG 96. As can be seen, the exhaust temperatures for the blends were higher than UTG 96.

Cycle emissions of alcohols and aldehydes are shown in Figures 17 - 21. These emissions were very low. All alcohol emissions were on the order of $1 \times 10^{-2} \frac{\text{g}}{\text{hr}}$ and aldehyde emissions were on the order of $1 \times 10^{-8} \frac{\text{g}}{\text{hr}}$. The alcohol emissions followed the expected trend. For each alcohol, the volume percentage in the blends is presented along with the emissions levels in Figures 17 - 21. The more of a particular alcohol there was in the blend, the higher were the emissions of that unburned alcohol. Formaldehyde emissions were virtually the same for all the blends, but formaldehyde can be formed from combustion of any of the alcohols. Acetaldehyde may only be formed from combustion of ethanol and higher alcohols. Propionaldehyde can only be formed from combustion of propanol and higher alcohols, and so on. As the order of the aldehyde got higher, the emissions of that particular aldehyde became more influenced by the concentration of the corresponding (same C number) alcohol in the fuel. In the case of pentanaldehyde, the emissions followed the exact trend of the pentanol concentration in the blend because pentanaldehyde can only be formed from combustion of pentanol.

HC emissions are reported in terms of the residual hydrocarbons (RHC) and the organic matter hydrocarbon equivalent (OMHCE). RHC emissions originate from the gasoline components of the fuel, and OMHCE emissions take into consideration both the gasoline components and alcohols/aldehydes. RHC emissions are given in Figures 22 - 24 and OMHCE emissions are given in Figures 25 - 27. The cycle emissions of RHC and OMHCE from the blends were within 3% of UTG 96. Had alcohols and aldehydes made up a more significant portion of the total HC emissions, the RHC emissions for the blends would have been lower than UTG 96. Similar to other emissions species, the brake specific emissions of RHC and OMHCE from the blends were quite a bit lower than UTG 96, ranging from 17% to 23% lower. To

determine the contribution of alcohols and aldehydes to the OMHCE emissions, the percentage of OMHCE emissions due to alcohols and aldehydes was calculated and is presented in Figure 28. For every blend, less than 1% of the OMHCE emissions were caused by alcohols and aldehydes.

Fuel consumption rates for the blends and UTG 96 are given in Figures 29 - 31. As expected, the cycle fuel consumption rates of the blends were 1.2% to 3.5% higher than UTG 96 due to the lower A/F ratios required by the blends. However, the brake specific fuel consumption (BSFC) of the blends ranged from 17% to 21% lower than UTG 96 due to the increased engine power output from the blends.

Figure 4 - Engine Power Output During Emissions Testing

Figure 5 - Percent Difference in Engine Power Output from UTG 96 During Emissions Testing

Figure 6 - Cycle CO Emissions

Figure 7 - Brake Specific CO Emissions

Figure 8 - Percent Difference in CO Emissions Between Blends and UTG 96

Figure 9 - Cycle CO₂ Emissions

Figure 10 - Brake Specific CO₂ Emissions

Figure 11 - Percent Difference in CO₂ Emissions Between Blends and UTG 96

Figure 12 - Cycle NO_x Emissions

Figure 13 - Brake Specific NO_x Emissions

Figure 14 - Percent Difference in NO_x Emissions Between Blends and UTG 96

Figure 15 - Exhaust Temperature During Emissions Testing

Figure 16 - Percent Difference in Exhaust Temperature Between Blends and UTG 96 During Emissions Testing

Figure 17 - Methanol and Formaldehyde Emissions and Volume Percentages of Methanol for the Blends

Figure 18 - Ethanol and Acetaldehyde Emissions and Volume Percentages of Ethanol for the Blends

Figure 19 - Propanol and Propionaldehyde Emissions and Volume Percentages of Propanol for the Blends

Figure 20 - Butanol and Butylaldehyde Emissions and Volume Percentages of Butanol for the Blends

Figure 21 - Pentanol and Pentanaldehyde Emissions and Volume Percentages of Pentanol for the Blends

Figure 22 - Cycle RHC Emissions

Figure 23 - Brake Specific RHC Emissions

Figure 24 - Percent Difference in RHC Emissions Between Blends and UTG 96

Figure 25 - Cycle OMHCE Emissions

Figure 26 - Brake Specific OMHCE Emissions

Figure 27 - Percent Difference in OMHCE Emissions Between Blends and UTG 96

Figure 28 - Percentage of OMHCE Emissions Coming From Alcohols and Aldehydes

Figure 29 - Cycle Fuel Consumption of the Blends and UTG 96

Figure 30 - Brake Specific Fuel Consumption of the Blends and UTG 96

Figure 31 - Percent Difference in Fuel Consumption Between Blends and UTG 96

Reid Vapor Pressure and Distillation

The RVP for each blend and UTG 96 is shown in Figure 32. RVP is a measure of the difficulty in controlling the evaporative emissions from a fuel. The higher the RVP, the more difficult it is to control evaporative emissions and vice versa. Blend 1 (2.67% methanol/ethanol, 7.33% higher alcohols) showed only a slight increase in RVP compared to UTG 96, and blend 2 (0.82% methanol/ethanol, 9.18% higher alcohols) actually showed a small decrease in RVP compared to UTG 96. Blends 5 and 6 had the highest RVP out of all the blends, and these two blends also contained the highest amounts of the lower alcohols (5.64% methanol/ethanol for blend 5 and 5.44% methanol/ethanol for blend 6). Blends 3 and 4 also show the effectiveness of higher order alcohols help in controlling the RVP of the blend. It should be noted that blend 4 had an RVP lower than blend 3. The compositions of blends 3 and 4 were identical except that blend 3 contained 2.88% butanol and 0.12% pentanol, whereas blend 4 contained 0.12% butanol and 2.88% pentanol. Blends 5 and 6 illustrate how high order alcohols can offset the effects of lower alcohols on RVP. Blend 5 contained 3.24% methanol compared to 3.04% methanol in blend 6. However, these two blends have nearly identical RVPs. The fact that blend 5 contained 1.47% pentanol compared to 0.13% pentanol in blend 6 seemed to offset the higher concentration of methanol in blend 5.

It has been shown by previous researchers that the presence of alcohols in gasoline depress the distillation curve of the fuel, which can cause problems with cold starting and vapor lock. This expected trend was true of all the six test blends. Figures 34 - 39 show the distillation curves of the blends and of UTG 96. The distillation curve for each blend was depressed between 0% and 60% points. To determine the effects of the different alcohols on the distillation curve, the area under each curve between 0% and 60% evaporated was numerically calculated

(see Figure 40). Blends 1 and 2 showed the least effects on the distillation curve from the alcohols, but it should be noted that these blends also contain the least methanol/ethanol. Blend 2 shows a lower effect on distillation than blend 1, and, as mentioned previously, blend 2 had lower methanol/ethanol concentration than blend 1. Blends 5 and 6 showed the greatest effect on the distillation curve, and these blends contained the highest amounts of methanol/ethanol. Thus, it becomes obvious that the lower alcohols have a more significant effect on the distillation curve than the higher alcohols.

Figure 32 - Reid Vapor Pressures of the Blends and UTG 96

Figure 33 - Percent Difference in RVP Between Blends and UTG 96

Figure 34 - Comparison of Distillation Curves Between Blend 1 and UTG 96

Figure 35 - Comparison of Distillation Curves Between Blend 2 and UTG 96

Figure 36 - Comparison of Distillation Curves Between Blend 3 and UTG 96

Figure 37 - Comparison of Distillation Curves Between Blend 4 and UTG 96

Figure 38 - Comparison of Distillation Curves Between Blend 5 and UTG 96

Figure 39 - Comparison of Distillation Curves Between Blend 6 and UTG 96

Figure 40 - Comparison of the Area Under the Distillation Curve Between 0% and 60% Evaporated for the Blends and UTG 96

Conclusions

An experimental investigation of emissions characteristics of higher alcohols/gasoline (UTG 96) blends was conducted. In order to carry out the experiments, a single cylinder engine was instrumented and the necessary data acquisition and data reduction computer programs were written. Comparisons of emissions and fuel characteristics between higher alcohol/gasoline blends and neat gasoline were made to determine the advantages and disadvantages of blending alcohol with gasoline. All tests were conducted on a single cylinder Waukesha CFR engine at steady state conditions and stoichiometric A/F ratio.

Emissions tests were conducted at the optimum spark timing-KLCR combination (i.e. the point of maximum power) for the particular blend being tested. The cycle emissions (mass per unit time) of CO, CO₂, and organic matter hydrocarbon equivalent (OMHCE) from the higher alcohol/gasoline blends are all within 5% of those emissions from neat gasoline. Cycle emissions of NO_x from the blends were 15% - 18% higher than those from neat gasoline. However, for all the emissions species considered, the brake specific emissions (mass per unit time per unit power output) were significantly lower for the higher alcohol/gasoline blends than for neat gasoline (16% - 20% lower CO, 18% - 23% lower CO₂, 5% - 11% lower NO_x, and 17% - 23% lower OMHCE). This is due to the fact that the blends had greater resistance to knock and allowed higher compression ratios, which increased engine power output. Thus, the brake specific emissions were lower. The contribution of alcohols and aldehydes to the overall OMHCE emissions was found to be less than 1% for every blend tested and, thus, made up a minimal amount of the total hydrocarbon emissions.

Cycle fuel consumption (mass per unit time) of higher alcohol/gasoline blends ranged from 3% to 5% higher than neat gasoline due to the lower stoichiometric A/F ratios required by the blends. However, the brake specific fuel consumption (BSFC) (mass per unit time per unit power output) for the blends ranged from 15% - 19% lower than the BSFC of neat gasoline.

The other fuel parameters, RVP and distillation curve, were affected by the addition of alcohol to gasoline. The lower alcohols (methanol and ethanol) cause the most dramatic increase in RVP and the largest depression of the distillation curve. Addition of the higher alcohols (propanol, butanol, and pentanol) seems to curb the effects of methanol and ethanol on RVP and distillation.

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