1. Introduction

This project is a combination of process simulation and catalyst development aimed at identifying the most economical method for converting coal to syngas to linear higher alcohols to be used as oxygenated fuel additives. There are two tasks. The goal of Task 1 is to discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas, and to explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products. The goal of Task 2 is to simulate, by computer, energy efficient and economically efficient processes for converting coal to energy (fuel alcohols and/or power). The primary focus is to convert syngas to fuel alcohols. The results of Task 1 are to be incorporated into Task 2 simulations to determine the best holistic combination of chemistry, catalyst, reactor, and total process configuration. The goal is to achieve economic optimization for the conversion of syngas to liquid products, i.e., to achieve the maximum cost effective transformation of coal to energy equivalents. This latter concept is called an "Energy Park." Additionally, Task 2 contains a component to evaluate the combustion, emission, and performance characteristics of fuel alcohols and blends of alcohols with petroleum-based fuels, which is not covered in this report.

This report contains results from Task 2. The first step for Task 2 was to develop computer simulations of alternative coal to syngas to linear higher alcohol processes, to evaluate and compare the economics and energy efficiency of these alternative processes, and to make a preliminary determination as to the most attractive process configuration. A benefit of this approach is that simulations will be debugged and available for use when Task 1 results are available. 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 alcohol fuel additives as primary products and as by-products of a power generation facility. Texaco, Shell, and Lurgi gasifier designs were used to test gasifying coal. Steam reforming of natural gas, sour gas shift conversion, or pressure swing adsorption were used to alter the H_2/CO ratio of the syngas. In addition, a case using only natural gas was prepared to compare coal and natural gas as a source of syngas.

This report is organized as follows. Section 2 contains a brief history of the use of alcohol fuel additives. Section 3 contains a discussion of the research approach and the rationale for the approach. Section 4 contains discussions of the methodology for the design calculations, the methodology for evaluation of process alternatives, and how alternatives were screened. Section 5 contains process descriptions of the cases, and Section 6 contains the results of and discussion of the alternative cases. Section 7 contains a summary of the conclusions, and Section 8 includes recommendations and future work. Finally, Section 9 contains the references, and Section 10 consists of eight appendices that contain detailed process descriptions and data not presented in the main body of the report.

All numbers found in this report are current as of 9/1/95 and, where discrepancies occur, supersede those contained in previous quarterly technical progress reports. All costs and prices are in 1992 dollars unless otherwise stated.

2. 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 C_4 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 C_4 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.

3. 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.

3.1 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 OCTAMIX™.[5] These blends contain <5% (vol) methanol and >2.5% (vol) higher alcohols (C_2-C_4 for DuPont, C_2-C_8 for OCTAMIX™) 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.

3.2 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.

5

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	H_2/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 H_2/CO adjustment. For each case, the design downstream of the syngas cleaning is identical.
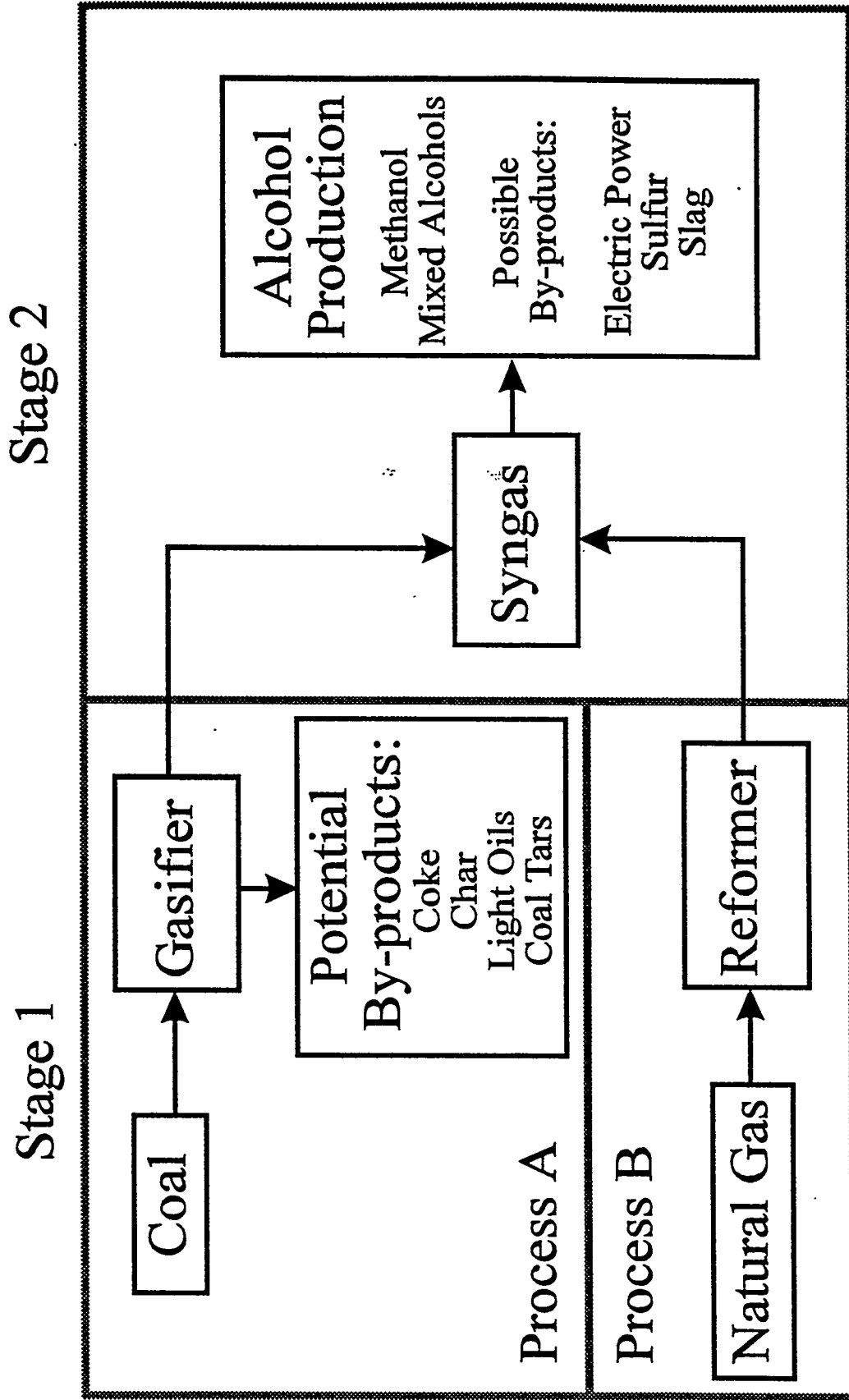
The natural gas case (Case 3) and IGCC case (Case 7) are chosen as a benchmarks. Although the goal of the study was to identify opportunities using coal-derived synthesis gas, such syngas is presently (for all gasifier types) more expensive than syngas produced from natural gas. Thus, Cases 3 and 7 present 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 H_2/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.

3.3 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

Stage 1

Stage 2

Process A

Coal → Gasifier → Syngas

Gasifier → **Potential By-products:**
Coke
Char
Light Oils
Coal Tars

Process B

Natural Gas → Reformer → Syngas

Syngas → **Alcohol Production**
Methanol
Mixed Alcohols

Possible By-products:
Electric Power
Sulfur
Slag

4. Methodology

4.1 Design

4.1.1 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 m^3. For Case 3B, we assume $61.8/1000 std m^3. 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

4.1.2 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.

4.1.3 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 C_1-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.

4.2 Economics

4.2.1 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

11

((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. ·

4.2.2 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]).

4.3 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.

5. Description of Cases

5.1 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	1.02%	
total	100%	

5.2 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°C (~2400°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.

Figure 5.1: Generic Design Case
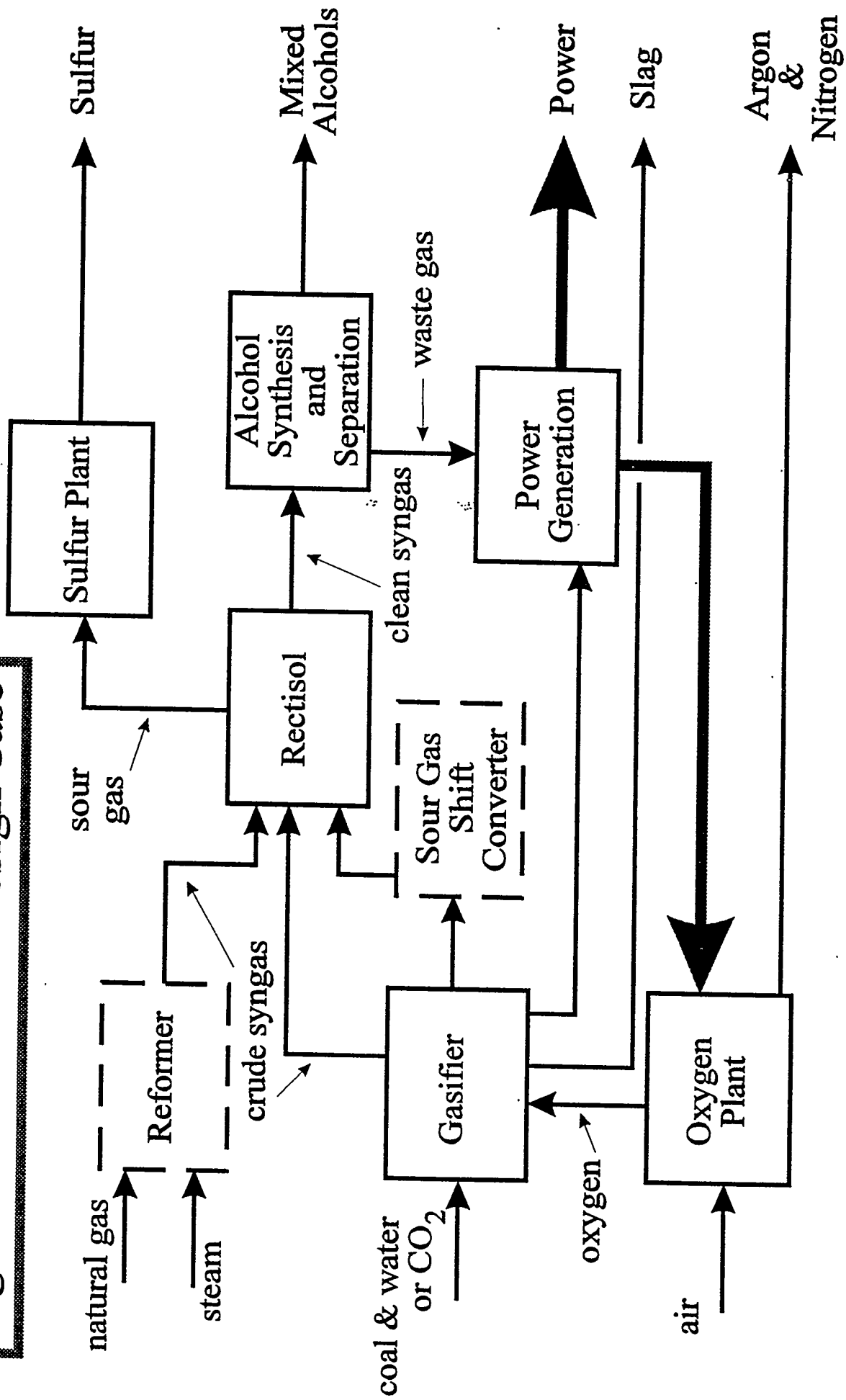
Case 2 (Appendix B, Figure B.1) incorporates a Lurgi (dry-bottom) gasifier design. This gasifier is oxygen blown and operates at moderate temperatures (400°C (750°F), 2.8 MPa (28 atm)). It is the design used at the Great Plains Gasification Plant [11] and produces phenolic and related by-products. To 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 m^3, $3.00/$10^6$ BTU) and the latter uses a Gulf Coast natural gas price ($61.8/1000 std m^3, $1.75/$10^6$ 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 (CO_2 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 H_2/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.

16