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TECHNICAL, ECONOMIC ASSESSMENT OF THE PRODUCTION
OF FUELS FROM BIOMASS

Final Research Report

Conversion Process Analysis

By
Edward I. Wan
John A. Simmons
Joseph D. Price
Tien D. Nguyen

July 12, 1979

Work Performed Under Contract No. ET-78-C-01-3002

Science Applications, Inc.
McLean, Virginia

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Technical-Economic Assessment of
the Production of Methanol from Biomass

Final Research Report

Volume III - Conversion Process Analysis

DOE Contract ET-78-C-3002

Work Performed for:

Biomass Energy System Branch
U.S. Department of Energy

Prepared by:

Edward I. Wan
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July 12, 1979

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1. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Science Applications, Inc. (SAI) has conducted a comprehensive engineering system study to assess various thermochemical processes suitable for converting biomass to methanol. This volume presents a summary of the conversion process study results, delineating the technical and economic feasibilities of producing methanol fuel from biomass resources utilizing the currently available technologies.

The overall objectives of the conversion process study are:

- Evaluate the State-of-the-Art of biomass based methanol processes
- Perform alternative process analyses and develop process models
- Conduct process sensitivity and parametric analysis
- Develop recommendations for an RD&D plan.

1.2 SIGNIFICANT FINDINGS AND RECOMMENDATIONS

- Methanol production from biomass is technically feasible using existing technology. However, the economic attractiveness of such liquid fuel production routes will be significantly affected by:
 - Feedstock availability and cost
 - Conversion plant size
 - Selection of a specific production method and end use of the methanol
 - Future technological and process improvements

- Methanol production from biomass could become both technically and economically attractive if used in gasoline blends. The margin of this attractiveness could be further enhanced by future technological improvements and by implementing an accelerated methanol fuel demonstration programs.
- In the near term (1985), methanol production costs from biomass using existing technology are estimated to be between \$0.66 and \$0.91 per gallon (in 1979 dollars) corresponding to 2000 TPD and 430 TPD methanol production capacities with a \$1.5 per MMBTU biomass feedstock cost. At these scales of production, biomass-to-methanol processes can not compete with methanol production from other feedstocks (\$.40 to \$.65 per gallon) unless economic incentives are introduced or innovative process schemes are implemented such as:
 - Federal policy and economic assistance such as federal sales tax exemption and capital investment tax credits. The current promulgated federal sales tax laws gives an effective \$.40 per gallon of methanol tax credit for a 10 percent methanol-gasoline blend. This tax incentive would help to bring the methanol-gasoline blend to within \$.01 per gallon of the projected price of no-lead gasoline.
 - Use of hybrid feedstocks in existing methanol production facilities such as biomass with natural gas or with hydrogen. These biomass alternatives can reduce the methanol production costs to approximately \$.45 per gallon for a biomass methane hybrid production scheme utilizing an existing methanol facility.
- In the long term (1990 and on), methanol production from biomass could become economically competitive contingent upon the following developments:
 - Large scale and low cost biomass production from energy farms. A target of \$1 per MMBtu is envisioned for a 5000 TPD size biomass production farm.
 - Large scale methanol production based on dispersed conversion plant concepts such as pipeline transport of synthesis gas. This could potentially reduce the biomass transportation costs.
 - Technological improvements in gasification and methanol technology such as a single stage

catalytic gasification process for methyl fuel production. The potential utilization of advanced gasification technology would reduce the methanol production to approximately \$.38 per gallon.

- Multiple product conversion such as to methanol and ethanol, or to methanol and gasoline.

1.3 RECOMMENDATIONS FOR FURTHER RESEARCH AND DEVELOPMENT EFFORTS

1.3.1 Research and Development Opportunities

In view of the potential for technological improvements, it is recommended that future research and development be directed toward five types of efforts:

1. Fundamentals of Gasifications Processes and Properties: Pursue the research and development of biomass gasification processes which take advantage of the high reactivity and low sulfur and ash content of biomass. The goal should be to develop a gasifier which can produce a gas directly suitable for methanol and other catalytic conversion processes.
2. Materials and Mechanical Systems: Develop new and improved concepts for economically reliable systems for continuous feed of biomass and removal of ash from gasifier.
3. Catalyst Development: Perform research, on laboratory and pilot plant scales, to develop improved catalysts for efficient utilization of biomass synthesis gas.
4. Methanol Fuel Hybrid Production Alternatives: Develop and evaluate conceptual process designs and strategies for implementation of hybrid feedstocks for methanol synthesis including methane-hybrid and hydrogen-hybrid alternatives.
5. New and Innovative Processes: Perform technical and economic feasibility studies of new and improved catalytic processes for liquid fuel production from synthesis gas.

1.3.2 Methanol Demonstration Program

The program to exploit these opportunities and demonstrate a practical biomass-to-methanol process would involve three explicit demonstration phases and a pre-demonstration study phase.

Pre-demonstration phase. This phase would require about 1 year. The key objectives would be to:

- a. Select appropriate existing methanol plant sites, compatible with biomass feedstocks and markets, for biomass-methane hybrid methanol production.
- b. Evaluate and develop conceptual process which utilize new and innovative gasification and subsequent conversion technologies for production of alcohol fuels and gasoline from biomass.

Phase I demonstration program. This phase would require about 1-1/2 to 2 years. The major objective of this phase would be to:

- a. Demonstrate the technical and economic feasibility of a biomass-methane hybrid methanol facility using a commercially available biomass gasifier in the plant size range of 100 to 150 TPD.
- b. Demonstrate the economies of the collection and transport of 500 TPD biomass to a central gasification system to supply a retrofitted small-scale methanol plant (200 TPD capacity).

Phase II demonstration phase. This phase would require about 2-3 years. The key objectives would be to:

- a. Demonstrate one or more advanced biomass gasifiers for producing a synthesis gas with H₂ to CO ratio equal to 2, in the plant size range of 100 to 150 TPD.
- b. Demonstrate advanced methanol synthesis processes using new catalysts or innovative process concepts in a 200 TPD plant size.

Phase III demonstration program. This phase would require approximately 3 to 4 years. The key objective of this phase would be to:

- a. Demonstrate an integrated advanced biomass to-methanol production technology, together with the feedstock collection and product distribution, at a methanol capacity of 2000 TPD.

- b. Demonstrate the economic and operational advantages of a commercial-scale biomass-to-methanol plant compared with other methanol production technologies.

1.4 SUMMARY AND DISCUSSION OF RESULTS

This section summarizes the detailed study results of biomass based methanol processes, which are presented in subsequent sections. The major thrust of the study was the analysis of conceptual conversion processes and the development of detailed process and economic models. This summary discussion will cover the following topics (reference is made to the major section of the body of this report in which topic is presented in detail):

- Evaluation of the state-of-the-art of biomass based methanol technology (section 2).
- Development of biomass-to-methanol production concepts and process configuration analysis (section 3).
- Process optimization and sensitivity analysis (section 4).
- Detailed description of baseline process designs (section 5).
- Economic analysis of methanol production from biomass (section 6).
- Prospectives of advanced processing technology (section 8).

1.4.1 State-of-the-Art of Biomass Based Methanol Technology

1.4.1.1 Synthesis Gas Production Technology

- In the near term commercial application (before 1985), opportunities exist to transfer existing coal gasification or solid waste gasification technologies

to biomass gasification. Among those existing gasification processes, oxygen-blown entrained-bed gasifiers such as the Koppers-Totzek gasifier, oxygen-blown fixed-bed gasifier such as the Wellman-Galusha and the Purox gasifiers appear to have the greatest potential for producing synthesis gas from biomass for methanol synthesis.

- For longer term application, advanced catalytic gasification processes such as those being developed by Battelle Northwest Laboratory, and Wright-Malta, may offer a potential for significantly improving the production of methanol synthesis gas from biomass.

1.4.1.2 Synthesis Gas Modification

- Gas cleaning steps such as mist elimination and particulate removal will be required. The design requirements will vary with gasification characteristics and designs. The most suitable system for methanol synthesis will be one of the following depending upon the gasification temperatures:
 1. A combined cyclone and electrostatic precipitator system - for a high-temperature biomass gasification process which produces a minimum amount of oil and tar mist.
 2. A combined wet scrubber, oil-char separator, and wet electrostatic precipitator system - for a low-temperature biomass gasification process which produces a significant amount of oil and tar mist.
- Acid gas treatment steps will be necessary in the removal of H_2S and CO_2 prior to methanol synthesis. The most suitable acid gas removal unit will be a combined system consisting of a hot carbonate absorption unit for bulk removal of CO_2 and H_2S , followed by a ZnO guard bed for the final cleaning of H_2S . Among the hot carbonate absorption units commercially available, Benfield and Catacarb processes are judged to be most suitable for biomass application.
- The H_2 to CO molar ratio present in the exit gas from biomass gasifiers is less than 2.0, which is the theoretical lower limit for methanol production. Consequently, the H_2 to CO ratio must be raised. Two basic approaches can be considered for increasing hydrogen content in synthesis gas: (1) to convert CO to H_2 and CO_2 via the water gas shift reaction, and (2) to add a hydrogen rich gas. A commercially

available high temperature shift reactor, utilizing chromia-promoted iron oxide catalyst, will be suitable to adjust the H_2/CO ratio of the synthesis gas.

- Biomass, because of its volatile carbon component, may produce a higher fraction of hydrocarbons in the synthesis gas. These must be (1) separated for use as fuel gas, or (2) converted to CO and H_2 in order to achieve higher methanol conversion. Commercially available processes such as cryogenic separation may be used to process the hydrocarbons.

1.4.1.3 Methanol Synthesis Technology

- It is generally recognized that existing technology is readily transferable to synthesize methanol from a synthesis gas suitably prepared from biomass. The synthesis can be accomplished economically by an ICI or Lurgi-type low-pressure process utilizing copper containing catalysts.
- Older methanol synthesis processes, which utilized zinc oxide catalysts, require operation at temperatures above $300^{\circ}C$. This necessitates high synthesis pressures, 200 to 400 atm, in order to achieve an acceptable degree of conversion. Because of the extra compression required, the high pressure process is not economically competitive, especially for biomass derived methanol.
- The conversion of synthesis gas to methanol is an exothermic reaction, and hence the reactor temperature must be carefully controlled to prevent deactivation of the copper catalysts (which usually occurs at temperatures above $300^{\circ}C$) and unfavorable equilibrium conditions. The major difference between the ICI and Lurgi processes is in the manner by which temperature is controlled. In the Lurgi reactor, the catalyst is cooled with water (catalyst inside tubes immersed in water), whereas in the ICI reactor, temperature is controlled by introducing cold synthesis gas at appropriate locations. The choice of ICI-type reactor is in part due to the simplicity of the reactor design, which therefore has a relatively low reactor cost for small-scale methanol synthesis from biomass.
- Present commercial methanol processes typically include two distillation columns to remove light ends, and heavy ends and water from the crude methanol. For fuel grade methanol, much of this process appears to be unnecessary except for removal of the water, since its concentration is excessive.

- In addition, although commercially unproven, the three-phase reactor concept of Chem Systems, Inc. is unique, and this type of reactor must be considered for advanced biomass-to-methanol development. Because of its high degree of temperature control, it may give methanol synthesis at greater efficiency and lower cost than any presently commercial processes.

1.4.2 Biomass-to-Methanol Production Concepts and Process Configuration Analysis

- Four basic methanol production concepts are considered as follows:
 - A. Conventional Integrated Methanol Production Concept. This production concept involves integrating the gasification, gas cleaning and methanol synthesis processes into a new central processing plant.
 - B. Advanced Integrated Methanol Production Concept. This production system involves a new barge-mounted central processing plant concept. The advantages of such a concept might include reduction of feedstock transportation distance, and plant construction and site preparation costs.
 - C. Conventional Dispersed Methanol Production concept. This concept involves the operation of gasifiers near sources of the biomass, to produce medium-Btu gas. These gasifiers are connected to a new methanol facility via a new pipeline systems.
 - D. Advanced Dispersed Methanol Production Concept. This concept involves the dispersed gasifier operation and further production of SNG in the field. The SNG produced is then transported to an existing methanol production facility via an existing pipeline system.
- Based on preliminary system analysis, production concept A was selected for process configuration development. Four basic configurations of concept A were developed further:
 1. Synthesis gas, directly produced from a biomass gasifier with a H_2/CO ratio of less than 2, is passed to a once-through methanol synthesis reactor giving only a partial conversion of the synthesis gas to methanol.

2. Synthesis gas produced from a biomass gasifier with a H_2/CO ratio of less than 2 is shifted to a H_2/CO ratio of 2. This stoichiometric gas then enters a methanol synthesis loop with recycle to achieve a complete conversion to methanol.
 3. Synthesis gas produced from a biomass gasifier with a H_2/CO ratio equal to 2, is passed to a methanol synthesis loop with recycle, to achieve a complete conversion to methanol.
 4. Synthesis gas directly produced in a biomass gasifier, with a H_2/CO ratio of less than 2, is mixed with additional H_2 from external sources, to a H_2/CO ratio of 2. This stoichiometric gas then enters a methanol synthesis loop with recycle to achieve a complete conversion to methanol.
- Based upon the comparison of carbon utilization efficiencies, methanol production in configuration 1 appears to be at least 50 percent lower than that which can be obtained from a methanol synthesis configuration which employs recycle (configurations 2, 3, and 4). Furthermore, process configurations 2 and 3 are limited thermodynamically to approximately 41 percent carbon utilization efficiency, while configuration 4 can achieve higher efficiencies.
 - Analyses of individual process configurations further narrowed the configurations to the following:
 - a. Gasification process: (1) high temperature K-T gasifier system, and (2) low temperature Wellman-Galusha and Purox gasifier systems.
 - b. Gas conditioning and preparation process: synthesis gas from a biomass gasifier is passed to a CO_2 absorber and then followed by a series of two high temperature CO shift converters and another CO_2 absorber
 - c. Methanol synthesis process: a cold gas quench, multiple bed, adiabatic methanol reactor. (e.g., an ICI reactor)

1.4.3 Process Optimization and Sensitivity Analyses

- Detailed models of the thermochemical gasification, shift conversion, CO_2 removal, and methanol

synthesis processes were developed. The particular systems selected for modeling were chosen, based upon economic considerations and material property characteristics of biomass conversion processes. The significant aspects of these models are high-lighted in Appendix A.

1.4.3.1 Gasification Process Analysis

- Four types of gasifiers for conversion of biomass to a synthesis gas were selected for analysis as being representative of those commercially available and adaptable to biomass feedstocks:
 1. Purox gasifier,
 2. Koppers-Totzek gasifier,
 3. Wellman-Galusha, oxygen blown, gasifier,
 4. Wellman-Galusha, air blown, gasifier
- Analysis of the gasification processes indicated that the Koppers-Totzek gasifier gives the highest yield of synthesis gas per unit mass of wood. It also has the highest energy efficiency. However, it is the most expensive system, and consequently, detailed analyses of biomass-to-methanol conversion processes, considering all of the gasifiers, must be made in order to select the most cost effective system.
- For entrained bed and fluidized bed gasifiers, the highest yields of synthesis gas are attained at low biomass moisture contents and gasification temperatures in the range of 1000 to 1200°K. On the other hand, a high moisture content, above 35 percent, favors formation of a gas with a H₂:CO ratio of 2 or more.

1.4.3.2 Gas Conditioning and Preparation Process Analysis

- Detailed simulation of the hot carbonate acid gas removal system has been employed for acid gas removal analysis.
- The dependence of absorber column height and carbonate solution flow rate on specified degree of CO₂ removal has been established. The tray requirement increases rapidly as exit CO₂ level is decreased below 2 mole percent.

Calculation of the dependence of absorber tray requirement on operating pressure for several levels of exit synthesis gas CO₂ concentration has shown that operating pressures in excess of 400 psia are preferred.

- Absorber exit gas CO₂ level has been identified as a major process parameter, with 1 mole percent the lowest practical exit concentration which can be achieved with this process.
- Modeling of adjustment of synthesis gas H₂ to CO ratio through use of the shift conversion reaction has been employed in system analysis.
- Shift convertor operating temperature and pressure have been established through design calculations as 640°F and 30 atmospheres, respectively.
- Shift conversion loop configuration analysis has demonstrated that a by-pass arrangement is not warranted. The calculation involved minimization of total cost: balancing of equipment and steam addition costs.
- Shift loop inlet H₂ to CO ratio, typically 0.65 to 0.85 for biomass synthesis gases, and shift loop exit H₂ per CO ratio, generally 2.0 for methanol synthesis, have been identified as major process parameters.

1.4.3.3 Methanol Synthesis and Purification Process Analysis

- A detailed methanol synthesis process model has been employed for process analysis.
- Representative operating temperature, 225-260°C, and pressure, 50 atmospheres, have been identified.
- Calculations investigating the dependence of methanol loop CO conversion on recycle flow rate have been completed for 90, 95, and 97 percent conversion of CO.
- The dependence of recycle rate and reactor volume on inerts concentration level has been established for inerts levels of 1, 2, and 3 mole percent.
- Methanol loop CO conversion, feed H₂ to CO ratio, feed CO₂ concentration, and feed inerts concentration have been identified as major process parameters.

1.4.3.4 Over-all Process Sensitivity Analysis

- Configuration of the necessary biomass-to-methanol process elements has been established using the sensitivity analysis summarized above.
- The dependence of the unit cost of methanol on methanol loop CO conversion has been established. Nearly complete, greater than 97 percent, conversion of CO is favored.
- The dependence of relative capital costs and methanol production capability on methanol loop feed H₂ to CO ratio has been determined. For synthesis gases initially deficient in H₂, an H₂ per CO ratio of 2.0 maximized production and minimized unit production costs.
- The dependence of relative capital costs on methanol loop feed CO₂ level has been established. Concentration levels of the order of 1 mole percent have been shown to be favored.

1.4.3.5 Development of Over-all System Algorithms and Selection of Baseline Processes

- An algorithm which formed the basis of over-all process design has been developed.
- A baseline process, characterized by the process configurations and major process parameters established earlier, has been proposed for comparison of candidate systems. Total biomass input to the baseline systems is 1000 tons per day of oven dried wood.

1.4.4 Detailed Description of Baseline Process Designs

- Comparative description of three baseline biomass to methanol processes are presented in terms of major processing steps. These processes are:

Process A - Koppers-Totzek gasification and low pressure ICI methanol synthesis

Process B - Purox gasification and low pressure ICI methanol synthesis

Process C - Wellman-Galusha gasification and low pressure ICI methanol synthesis

- A comparison of the overall process efficiencies shows that the Koppers-Totzek gasification system would give the highest process efficiency (49.4%). The production of methane in the Wellman-Galusha and Purox gasification systems decreases the process carbon conversion and increases the power requirements and therefore lowers the process efficiency to approximately 40 percent.
- In each baseline process examined a significant amount of biomass must be burned in order to provide the steam required for power generation.

1.4.5 Economic Analysis of Methanol Production from Biomass

- A reference case economic analysis for each baseline process design showed that the methanol product prices range from \$0.88 to \$1.00 per gallon (\$ 1979), assuming a \$1.5 per MMBtu biomass feedstock costs for the 1000 ODT per day plant. For the 5000 ODT per day plant, the methanol prices range from \$0.61 to \$0.74 per gallon.
- The product prices are highly sensitive to feedstock costs, varying from \$0.46 to \$0.86 per gallon for the 5000 ODT per day plant when feedstocks increases from \$1 to \$3 per MMBtu. It appears that a doubling of feedstock cost can be offset by increasing plant size from 1000 to 5000 ODT per day.
- The relative importance of capital related costs, feedstock costs, and operating and utility costs, as components in the overall production cost, depends on the size of the plant, the type of gasification process and, most importantly, the cost of the feedstock. For smaller plants, 1000 ODT per day, and for feedstock costs of \$1.5 per MMBtu, capital related costs comprise 70 percent of the production cost.
- The estimated capital costs for baseline biomass to methanol processes were compared with methanol production from other feedstocks as follows:
 - It is estimated that in 1985, the average biomass to methanol economics will be competitive with methanol produced from residual oil or coal to methanol plant, using existing KT gasifiers, but will be approximately 20 percent higher than those of the large scale new coal or natural gas processes.

- In 1995, biomass based methanol economics will be comparable to all other methanol production technologies, including the new large-scale coal gasification process.
- The market values and product prices of methanol were compared in 1985 and 1995. The results show that the 10 percent gasoline blend will permit rapid market penetration because of the positive values of the differences between market values and selling prices. For the other end uses, it appears that larger tax credit will be required to equate selling prices with market values.

1.4.6 Prospective of Advanced Processing Technology

- Several new alternative methanol production concepts have been suggested, which could alleviate the resource constraint problem, and reduce the methanol production costs. Of particular interest are the concept of dispersed gasifier process, hybrid syngas process and hybrid product process.
- A preliminary economic comparison of dispersed gasifiers versus centralized gasifiers indicates a marginal economic disadvantage for dispersed gasifiers. This is due to the large capital investment required in a dispersed gasifier system. The high capital requirements stem from the relatively short average pipeline transport distance, and the fact that trucks must still be used to load and collect biomass feedstocks at each gasifier location. However, this economic disadvantage might be reversed for feedstock transportation over longer distances (i.e., greater than 100 miles).
- Preliminary analysis of material conversion indicated that the economics of methanol production from biomass feedstock could be greatly enhanced through implementation of a hybrid syngas process. The most attractive hybrid syngas process involves the addition of steam reformed methane or hydrogen to the biomass derived syngas.

- From the preliminary synthesis gas analysis, the economic potential of producing multiple products from biomass derived synthesis gas has been narrowed down to coproduction of methanol and acetic acid and the production of methyl tert-butyl ether.
- Several new technologies could have potential in improving the methanol production economics and can also provide conversion alternatives for the production of higher alcohols and gasoline products. These new technologies include:
 1. Advanced biomass gasification technologies
 2. Advanced methanol synthesis technology
 3. Higher alcohols synthesis
 4. Gasoline and related product synthesis
- Advanced gasification technology specially developed for producing synthesis gas suitable for methanol should aim at the following objectives:
 1. Avoidance of the use of oxygen
 2. Use of catalysts to achieve high gasification rate at low temperatures
 3. Use of catalysts to tailor the composition of the gas
 4. Gasification at high pressure
 5. Design of the gasification process to minimize pretreatment of the biomass
- In terms of utilizing the biomass feedstocks, there are three primary areas in which the advanced methanol synthesis technology might be desired:
 1. A new methanol synthesis catalyst suitable for low pressure operation (<30 atm). The economic advantages of this technology is apparent due to the match of the pressure of methanol synthesis loop with the output pressure of CO₂ scrubber. This would reduce the synthesis gas compression energy requirement.

2. A new methanol catalyst selectively designed for biomass feedstocks can increase the methanol yield (i.e., conversion per pass) and therefore require smaller methanol plants for dispersed biomass resources.
 3. An improved waste heat recovery and methanol reactor cooling schemes which allows a higher conversion and energy efficiency.
- There are basically three process concepts that have shown promise for the production of ethanol from synthesis gas:
 1. High pressure (300 atm) homologation of methanol to ethanol over cobalt hydrocarbonyl.
 2. Low pressure (1-50 atm) homologation of methanol to ethanol over soluble or anchored rhodium complexes with alkyl iodides, and
 3. Low pressure (1-50 atm) direct synthesis of ethanol over rhodium catalysts, supported on TiO_2 , La_2O_3 , and ZrO_2 , or over rhodium alloys
 - The recently developed Mobil methanol-to-gasoline process offers a new route for the conversion of biomass to high octane gasoline and other desirable products. The composition of the raw gasoline product is 30 to 50 percent aromatics, 45 to 55 percent isoparaffins and the balance olefins, with an unleaded research octane number of over 90.
 - Alternative gasoline conversion processes utilizing biomass may include:
 1. A two stage conversion of synthesis gas through dimethyl ether to gasoline products.
 2. Conversion of synthesis gas to methanol followed by carbonylation.

2. EVALUATION OF THE STATE-OF-THE-ART OF BIOMASS BASED METHANOL TECHNOLOGY

The current thermochemical technology for the production of methanol consists essentially of catalytically reacting hydrogen and carbon monoxide, at elevated pressures and temperatures. Production of methanol from biomass employing existing technology requires integration of three essential processing steps:

- production of synthesis gas via gasification
- synthesis gas modification
- methanol synthesis and purification

In the following, a summary of the current technology suitable for biomass feedstocks is presented. A detailed parametric analysis of these processing steps will be presented in sections 4.1 through 4.3.

2.1 SYNTHESIS GAS PRODUCTION

Synthesis gas can be produced from various solid hydrocarbons such as coal, biomass, and solid wastes etc. via thermochemical gasification technologies(1-4). The manufacturing of synthesis gas from solid organic compounds had dominated the market until the early 1930's(5), when natural gas became readily available at relatively low cost throughout the U.S. Although major technological development efforts in coal and wood gasification were discontinued in the U. S. after World War II, they continued in Europe where the only modern commercial gasification processes, such as Lurgi, Winkler, Wellman-Galusha, and Koppers-Totzek, were developed. Renewed interest in technological advancement has recently developed in the U.S., primarily because

of the dwindling supply of natural gas and oil, and the environmental constraints on burning most coals directly. The gasification of renewable resources such as woody biomass presents one of the greatest potentials for further technological advancement⁽⁶⁾. In this section, a summary evaluation of various thermochemical gasification technologies suitable for production of synthesis gas from biomass feedstock will be presented.

2.1.1 Gasification Technology Overview

Conversion of biomass to gaseous products may be accomplished by either thermochemical or biological processes. Each has potential applications depending on the type of biomass involved and economic factors. For the purposes of this study, the discussion is limited to thermochemical gasification routes, since these processes appear to be more efficient and versatile for producing a variety of synthesis gases suitable for methanol synthesis^(7,8).

At the present time, thermochemical gasification processes specifically developed for biomass are still in various stages of development⁽⁹⁾. In contrast, the coal gasification technology has been developed and several commercially proven processes are available⁽¹⁰⁾. The gasification of municipal solid waste has also been successfully demonstrated^(11,12). In spite of feedstock differences among coal, biomass, and municipal refuse, many of the thermochemical approaches to gasifying biomass have involved technologies similar to those used for coal and solid waste.

The following discussions focus on the chemical and thermodynamic considerations for biomass gasification, and the basic gasification concept.

2.1.1.1 Chemical and Thermodynamic Consideration of Gasification of Biomass

The process chemistry associated with the production of synthesis gas by biomass gasification is reasonably complex and dependent on reactor design, operating conditions, and feedstock characteristics. The first step of biomass gasification can be considered as the conversion of the cellulose to carbon and water by pyrolysis. Then the following reactions may proceed(14):

Reactions (2.1) through (2.4) involve the gasification of the fixed carbon in the biomass. Reaction (2.1) is the combustion of carbon to carbon dioxide which is highly exothermic (95 kcal/g-mol) and complete. The carbon is further gasified by CO_2 and steam via reactions (2.2) and (2.3). These reactions are reversible and endothermic, requiring roughly 40 and 30 kcal/g-mol respectively. Finally, the carbon may be gasified by hydrogen to produce methane. Reaction (2.4) is exothermic (20 kcal/g-mol) and unfavorable at high temperatures.

The oxidation reactions (2.5) and (2.7) are exothermic, 67 and 60 kcal/g-mol respectively, and essentially irreversible. Reaction (2.6), the water-gas shift reaction, is reversible and exothermic (8 kcal/g-mol). Upon rapid heating, volatile matter in the biomass decomposes to release methane and higher hydrocarbons as in reaction (2.8). Methane and higher hydrocarbons may be steam reformed to carbon monoxide and hydrogen as shown in reaction (2.9).

Figure 2.1 shows the effects of temperature and pressure on the equilibrium concentrations of gas components (15). As noted, the major effects with increasing temperature beyond 600°F are the rapid reduction of CO₂, H₂O, and CH₄ and the increase of CO and H₂. The increase of temperature beyond 1800°F essentially eliminates the formation of CH₄. The effects of pressure on gas composition are reduced at higher temperature. In reality, chemical equilibrium probably will not be achieved in reactors, especially in those operating at low temperatures. The actual product gas composition will vary somewhat from that shown in Fig. 2.1(16).

2.1.1.2 Basic Gasification Concepts

Thermochemical gasification processes can be classified according to the type of bed used, the type of reactor vessel, whether the systems use air or oxygen, and whether or not the system operates under pressure.

There are primarily three basic types of reactor beds: fixed bed, fluidized bed, and entrained bed.

Figure 2.1 The Effect of Temperature and Pressure on Equilibrium Gas Composition (C-H-O System), Solid Carbon is Assumed to be Present

Source: Reference 15

In a fixed-bed process the feed is supported by a grate. Gases pass through the supported feed, and the hot product gas exits from the top of the reactor. Heat can be supplied internally or from an outside source. The fluidized-bed system uses finely sized feed particles. A fluidized bed is a mass of suitably-sized solid particles which exhibits fluid-like characteristics when a gas flows upward through the bed. Gas flowing through the feed produces turbulent lifting and separation of particles. The result is an expanded bed having a greater feed surface area to promote the chemical reaction. An entrainment system uses finely sized particles blown into the gas stream prior to entry into the reactor. Combustion takes place with the feed particles suspended in the gas phase; the product gas and residual ash are drawn off separately. Table 2.1 presents the relative advantages and disadvantages of these three types of gasifiers.

Gasification reactor vessels can be designed to operate at either high or atmospheric pressure. High pressure maximizes the gasification reaction, improves the quality of the product gas, reduces the required size of the reactor vessel, and eliminates the need to pressurize the gas before it is introduced into methanol synthesis steps. However, working at high pressure creates problems involving the method of introducing the feedstock into the reactor. Also, design and materials requirements are much more stringent for pressurized systems. At the present time, most biomass gasification processes are developed for low pressure operation.

Table 2.1 Comparison of Commercially Available Gasifiers

Gasifier Type	Fixed Bed	Fluid Bed	Entrained Bed
Significant Characteristics	<ul style="list-style-type: none"> o Discrete gasification zones such as <ul style="list-style-type: none"> - Preheating-drying-devolatilization - Gasification - Combustion - Ash o Temperature gradient exist 	<ul style="list-style-type: none"> o Uniform temperature and composition throughout fluidized zone 	<ul style="list-style-type: none"> o Upflow suspension gasification o High temperature, high rate process
Advantages	<ul style="list-style-type: none"> o High carbon conversion efficiency o Low ash carryover o Low temperature operation o Highest turndown capability 	<ul style="list-style-type: none"> o High turndown capability o High degree of process uniformity o Excellent solids/gas contact o Lower residence time than fixed bed gasifier (higher coal throughput per unit volume of reactor) 	<ul style="list-style-type: none"> o Handles all type feedstock, no pretreatment required o Excellent solids/gas contact o No tar formation o Highest capacity per unit volume of reactor o Produces inert ash
Disadvantages	<ul style="list-style-type: none"> o Low capacity-largest number of gasifiers required o Low temperature gas produced, seriously restricted waste heat steam generation pressure o Present experience based on discharging dry ash 	<ul style="list-style-type: none"> o Requires dry feed for feeding o Requires size reduction of feed o Requires complicated gas distributor o Fluidization requirement sensitive to fuel characteristics o Single stage o High carbon loss with ash o Low pressure 	<ul style="list-style-type: none"> o Requires oxygen o Single stage o Low pressure o Low fuel inventory (control and safety considerations) o Poor turndown capability o Air-blown and two-stage gasification still under development

The principal advantages of employing oxygen instead of air in a gasification process is to eliminate the large amount of nitrogen in the product gas. For the purpose of methanol synthesis this advantage is particularly important, since an increased size of gasifier, compressor and duct, etc., must be needed if an air system is employed.

2.1.1.3 Effect of Process Variables

Process variables have a profound effect on gasifier performance. These process variables include pressure, temperature, residence time, steam to biomass, and air or oxygen to biomass ratios. In general, gasification rates tend to increase with increasing pressures. Increasing the gasification temperature will generally increase the reaction rates. However, to operate at higher temperatures requires more oxygen for the heat generating reactions. The gasification temperature must be determined by considering both the gas composition desired and the amount of oxygen required.

Residence time must be considered separately for two types of gasification processes: entrained-bed gasifiers in which the solid and the gases have the same residence time, and the fluidized-bed and fixed-bed gasifiers in which the solid has a much longer residence time than the reactant gases.

The steam-oxygen to biomass ratio is the most complex variable to quantify. Increasing the oxygen to biomass ratio tends to increase the amount of carbon gasified. Additionally, if the steam to biomass ratio is too low, not enough hydrogen will be produced. The product gas specification plays an important role in determining whether air or oxygen is to be used. If the objective is to produce a high-Btu product,

the oxygen supplied to the gasifier will be obtained from an oxygen plant while a low-BTU process may use oxygen in the form of air, thus reducing operating costs. If the addition of the nitrogen diluent will not adversely affect the downstream process, economic savings may be realized.

The method whereby biomass is fed to a high pressure gasifier may have a substantial impact on overall gasification cost. Several methods for feeding pressurized gasifiers have been investigated. These include slurry methods, lock hopper systems, and piston pumping systems. Lock hopper systems have a distinct disadvantage of loss of pressure in high-pressure systems. Recently, a project was funded by DOE to investigate the feasibility of utilizing a modified extruders for feeding fine-ground cellulosic slurries to pressurized systems. Preliminary results show that cellulosic/oil slurries in excess of 50 percent by weight can be handled by extruder, compared to about 30 percent by piston pumps. In another development, Pullman Swindell, a division of Pullman, Inc., has announced a plan to convert forest waste into fuel pellets. As claimed, these wood pellets can be used in existing coal gasifiers without equipment modifications(17).

All of the above factors can affect the operation and economics of a biomass gasification system. All factors should be considered in order to produce the desired product gas for the least possible cost. There are other factors which will affect the biomass gasification process, but those discussed play major roles in selecting the feasible gasification process for biomass.

2.1.2 Potential Application of Existing Gasification Technologies to Biomass Feedstock

This section deals with the technical aspects of application of existing gasification technologies to biomass feedstocks. The technologies considered include coal gasification, solid waste gasification, and biomass gasification systems.

Table 2.2 summarizes the operating characteristics of gasification systems which are commercially proven, in the stage of pilot plant operation, or still under development. The compositions of gases produced from those systems are shown in Table 2.3. The process descriptions for the gasification systems considered can be found in References 18 and 19. Following is a brief discussion of the technical aspects associated with application of coal and solid waste gasification technologies to biomass feedstock.

2.1.2.1 Coal Gasification Processes

There are a number of commercially available coal gasification processes that are potential candidates for biomass gasification. For the purposes of this discussion they can be grouped by the method of feed contacting with reactant gases into three major categories: fixed-, fluidized-, and entrained-bed gasifiers.

Fixed-bed gasifier systems are characterized by a slow-moving feed bed supported by a grate. Generally, feed is added to the top of a vertical retort and the feed moves down as a packed bed through the steam and/or oxygen medium. The feed reacts and forms fuel gases which are removed at

Table 2.2 Summary of Gasification Reactors for Coal, Coke, Solid Waste, and Biomass, Developed or Under Development

<u>Process</u>	<u>Type of Reactor Bed</u>	<u>Fuel Used in Existing Design</u>	<u>Gasifying Medium Used in the Existing Design</u>	<u>Operating Pressure</u>	<u>Condition Temperature (°F)</u>	<u>Gasification Capacity</u>
<u>Commercial</u>						
Kerpely	Fixed bed	Coke; nut, and pea size	oxygen & steam	atmospheric	N/A	1.90 MM scfd
Koppers-Totzek	entrained bed	coal; 70% pass 200 μ	oxygen & steam	slight positive	3500	a two-headed unit= 430 TPD of coal, 21 MM scfd a four-headed unit= 860 TPD of coal, 43 MM scfd
Louna	Fixed bed	coke; 1/8" - 1 1/2"	oxygen & steam	atmospheric	N/A	15.1 MM scfd
Lurgi	Fixed bed	coal; 1/8" - 1 1/2"	either air or oxygen & steam	350 to 450 psig	2500	a typical commercial unit= 800 TPD of coal, 5-6 MM scfd
Moore-Canada	Fixed bed	wood	air and steam	2-8 psig	2200	60 TPD of wood chip
Purox	Fixed bed	solid waste; $\leq$ 4"	oxygen	atmospheric	3000°F	a 10 ft. I.D. and 30 ft. tall reactor processes 350 TPD of feed & produce (8,780 scf per ton of feed
Texaco partial oxidation	Entrained bed	coal/hydrocarbon feeds, pulverized	oxygen & steam	300 to 1200 psig	above ash fusion point	a typical commercial unit= 1900 TPD, 100 MM scfd
Thyssen Galocsy	Fixed bed	coke; 1 1/2" - 2 1/2"	oxygen & steam	atmospheric	N/A	3.22 MM scfd
Wellman-Galusha	Fixed bed	coal & coke; 1" - 2"	oxygen & steam	atmospheric	2400	a typical agitated gasifier= 30 to 84 TPD of coal
Winkler	Fluidized bed	coal; $\leq$ 3/8"	oxygen/or air & steam	atmospheric	1500 - 1800	a typical commercial unit= 1100 TPD of coal.
Woodall Duckham/ Gas Intergrate	Fixed bed	coal; 1/4 - 1"	air & steam	atmospheric	2200	a typical unit= 200 TPD of coal, 4×10^9 Btu/day
Babcock & Wilcox	Entrained bed	coal; 70% pass 200 mesh	oxygen	atmospheric to 300 psig	3400	a 7 1/2 ft. I.D. and 110 ft. tall unit gasifies 850 TPD of coal generates 10×10^9 Btu/day at 50 psig
<u>Demonstration/pilot plants</u>						
Battelle/carbide	Fluidized bed	coal; 100 - 8 mesh	air and steam	100 psig	1800	pilot plant= 25 TPD of coal, 1 MM scfd

*Semi-commercial

Table 2.2 Summary of Gasification Reactors for Coal, Coke, Solid Waste and Biomass, Developed or Under Development (contd)

<u>Process</u>	<u>Type of Reactor Bed</u>	<u>Fuel Used in Existing Design</u>	<u>Gasifying Medium Used in the Existing Design</u>	<u>Operating Conditions</u>		<u>Gasification Capacity</u>
				<u>Pressure</u>	<u>Temperature (°F)</u>	
BCR low Btu	Fluidized bed	coal; 60% pass 200 mesh	air and steam	up to 235 psig	2100	1.2 TPD of coal; 0.2 MM scfd
BIGAS	entrained bed	coal; 70% pass 200 mesh	oxygen & steam	500 to 1500 psig	3000	3750 TPD of coal for a single unit
CO ₂ Acceptor	Fluidized bed	coal; 100 8 mesh	air & steam	150 psig	1500	pilot plant= 30 TPD of coal, 1.35 MM scfd
COGAS	Fluidized bed	coal; $\leq 1/8"$	air & steam	15-45 psig	1000	a typical commercial unit= 5000 to 10,000 TPD of coal, 159 MM scfd
ERDA-NETC Stirred Bed	Fixed bed	coal; 50% $\leq 1/2"$	air & steam	up to 285 psig	2500	pilot plant= 20 TPD of coal, 2 MM scfd
Forster-Wheeler	entrained bed	coal; 70% pass 200 mesh	air & steam	350 psig	2800	pilot plant capacity= 480 TPD of coal
HYGAS	Fluidized bed	coal; ≤ 10 mesh	oxygen & steam	atmospheric	1850	a commercial plant= 250×10^9 Btu/day
Rockwell-AI	Molten salt	coal; $\leq 1/4"$	molten salt	up to 280 psig	1800	pilot plant= 6-12 TPD of coal
Synthane	Fluidized bed	coal; ≤ 20 mesh	oxygen & steam	1000 psig	1800	pilot plant= 72 TPD, 2 MM scfd
U-Gas	Fluidized bed	coal; $\leq 1/4"$	air & steam	50 to 350 psig	1900	a commercial unit= 3000 TPD, 360 MM scfd
Westinghouse	Fluidized bed	coal; $\leq 1/4"$	air & steam	130-2000 psig	2100	pilot unit= 1200 lb/hr of coal, 2.45 MM scfd
Wright-Malta	Rotary Kiln	Biomass; $\leq 4"$	steam	400 psig	1100	67,000 scfd of syn gas TPD of coal, 125 MM scfd
Baillie	Fluidized bed	solid waste; finely pulverized	air & steam	N/A	1400	pilot plant = 500 TPD of refuse
Combustion-Engineering	Entrained bed	coal; 70% pass 200 mesh	air & steam	atmospheric	3000	a 9 ft. I.D. and 7.8 ft. tall unit - 120 TPD - 16 MM scfd
Hydrane	Fluidized bed	coal; 70% pass 200 mesh	hydrogen	1000 psig	1800	a 14.2 ft I.D. unit = 5300
<u>Bench Scale</u>						
Battelle (Pacific N.W.)	Fluidized bed	Fluidized bed Biomass;	oxygen & steam	atmospheric	1200	a 7 in I.D. and 10 ft. tall unit - 50 lb/hr, 34 M scfd
Pullman-Kellogg	Molten salt	coal	oxygen & steam	high pressure	N/A	N/A

Sources: References (18-20)

Table 2.3 Compositions of Product Gas Produced from Various Gasification Processes

Process	Fuel Used	Product Gas Composition (mole %)						HHV (Btu/scf)
		CO	CO ₂	H ₂	CH ₄	H ₂ S+C ⁺²	N ₂ +Ar	
Commercial								
Kerpely	coke; nut, and pea size	39.9	19.6	38.7	1.8	-	-	250
Koppers-Totzek	Silesian Bituminous; 70% pass 200	51.1	12.6	34.0	0.1	0.2	1.9	275
Leuna	coke; 1/8" - 1 1/2"	66.1	1.0	31.0	0.7	-	1.2	320
Lurgi	coal; 1/8" - 1 1/2"	16.9	31.5	39.4	9.0	0.8	1.6	285
Moore-Canada	wood chips	22.8	9.2	18.3	2.5	-	45.8	132
Purox	solid waste; < 4"	40.0	24.0	24.0	5.6	5.4	1.0	370
Texaco partial oxidation	coal/hydrocarbon feeds, pulverized	37.6	20.8	39.0	0.5	1.5	0.6	253
Thyssen Galocsy	coke; 1 1/2" - 2 1/2"	70.4	2.8	23.1	0.2	-	3.4	300
Wellman-Galusha	canthracite; 1" - 2"	40.0	16.5	41.0	0.9	-	1.5	260
Winkler	coal; < 3/8"	(oxygen-blown) 48.2	13.8	35.3	1.8	-	0.9	288
Woodall Duckham/Gas Intergrate	coal; 1/4 - 1"	(oxygen-blown) 37.5	18.0	38.4	3.5	0.4	2.2	280
Sabcock & Wilcox	coal; 70% pass 200 mesh	65.3	5.0	27.9	-	0.6	1.2	301
Demonstration/pilot plants								
Battelle/Carbide	coal; 100% 8 mesh	0-38.6	3.3-28.2	47.9-66.2	1.1-6.3	0.2	-	-
BCR low Btu	coal; 60% pas 200 mesh	25.7	5.2	23.4	-	0.2	45.5	160
BIGAS	coal; 70% pass 200 mesh	29.3	21.5	32.	15.7	0.8	0.7	356
CO ₂ Acceptor	coal; 100% 8 mesh	15.5	9.1	58.8	13.7	0.0	2.9	380
COGAS	coal; < 1/8"	31.2	6.6	57.9	4.0	-	0.3	333
ERDA-MIRC Stirred	coal; 50% < 1/2"	20.4	8.7	15.5	2.4	0.5	52.5	140
Foster-Wheeler	coal; 70% pass 200 mesh	29.3	3.3	14.5	3.5	0.7	48.7	177
HYGAS	coal; < 10 mesh	23.8	24.5	30.2	18.6	1.2	0.1	370
Rockwell-AI	coal; < 1/4"	29.7	3.5	13.2	1.5	< 5 ppm	48.0	158
Synthane	coal; < 20 mesh	13.2	36.2	32.3	15.0	1.6	-	355
U-Gas	coal; < 1/4"	19.6	9.9	17.5	3.4	0.7	48.9	154
Westinghouse	coal; < 1/4"	19.2	9.3	14.4	2.7	0.1	54.3	135
Wright-Malta	Biomass; < 4"	1	45	28	18	-	-	-
Baillie Process	Bagasse	23.3	23.0	35.4	8.5	-	-	281
Combustion-Engineering	coal; 70% pass 200 mesh	22.1	7.0	17.0	0.03	0.6	53.3	127
Hydrane	coal; 70% pass 200 mesh	6.0	1.7	21.7	08.2	0.6	1.4	784
Bench Scale								
Battelle (Pacific N.W. Lab)	wood chips	40.5	24.6	21.2	11.4	-	-	282
Fullman-Kellogg	bagasse (37% H ₂ O)	24.9	33.9	34.0	7.1	0.0	0.1	181

Sources: References (18-20)

Table 2.3 Compositions of Product Gas Produced from Various Gasification Processes (continued)

Process	Fuel Used	Product Gas Composition (Mole %)						HHV (Btu/scf)
		CO	CO ₂	H ₂	CH ₄	H ₂ S+CO ₂	H ₂ +Ar	
BIGAS	coal; 70% pass 200 mesh	29.3	21.5	32.	15.7	0.0	0.7	356
CO ₂ Acceptor	coal; 100 " 8 mesh	15.5	9.1	50.8	13.7	0.0	2.9	300
COGAS	coal; < 1/8"	31.2	6.6	57.9	4.0	-	0.3	335
ERDA-MIRC Stirred	coal; 50% < 1/2"	20.4	8.7	15.5	2.4	0.5	52.5	140
Foster-Wheeler	coal; 70% pass 200 mesh	29.3	3.3	14.5	3.5	0.7	48.7	177
HYGAS	coal; < 10 mesh	23.8	24.5	30.2	18.6	1.2	0.1	370
Rockwell-AI	coal; < 1/4"	29.7	3.5	13.2	1.5	< 5 ppm	48.0	158
Synthane	coal; < 20 mesh	13.2	36.2	32.3	15.0	1.6	-	355
U-Gas	coal; < 1/4"	19.6	9.9	17.5	3.4	0.7	48.9	154
Westinghouse	coal; < 1/4"	19.2	9.3	14.4	2.7	0.1	54.3	135
Wright-Malta	Biomass; < 4"	1	45	28	18	-	-	-
Baillie Process	Bagasse	23.3	23.0	35.4	8.5	-	-	401 (dry)
Combustion-Engineering	coal; 70% pass 200 mesh	22.1	7.0	17.0	0.03	0.6	53.3	127
Hydrane	coal; 70% pass 200 mesh	6.0	1.7	21.7	08.2	0.6	1.4	784
Bench Scale								
Battelle (Pacific H.W. Lab)	wood chips	40.5	34.6	21.2	11.4	-	-	262
Pullman-Kellogg	bagasse (37% H ₂ O)	24.9	33.9	34.0	7.1	0.0	0.1	181

Sources: References (18-20)

the top of the system. Ash is removed through the grate at the bottom. A fixed-bed gasifier can be operated with counter-current and/or cross-current flow. The commercially-proven processes in this category are the Wellman-Galusha Gasifier, Lurgi Gasifier, and Woodall Duckham/Gas Intergrate Process(18).

In the fixed-bed process, the feed move down through a gas stream as a packed bed, while in the fluidized bed system the gas velocity is increased to the point where the particles are suspended and no longer in continuous contact. In this way, the feeds are in better contact with reactant gases resulting in higher specific gasification rate than with a fixed-bed reactor. The Winkler process is a commercially proven coal gasification system in this category(18).

In the entrained bed system, feeds are carried fully entrained in the steam or oxygen medium. The entrained flow gasifier operates at a relatively high temperature which allows processing of almost any rank of coal in addition to a variety of hydrocarbon liquids and gases. Because of the high temperature, gasification of the coal is almost complete and instantaneous, and the product gas is relatively free of tars or oils. Its atmospheric operation also minimizes mechanical complexity leading to a high degree of reliability. Because of its small quantity of feed in the reactor, the turndown capacity is relatively limited. The Koppers-Totzek gasifier is a commercially-proven system in this category, while the Babcock and Wilcox gasifier is a semi-commercial system. The Texaco partial oxidation process is another commercial process. However, this system was originally developed for hydrocarbon fuels, and its application to coal is not yet commercially proven(18).

As shown in Table 2.2, the operating characteristics are quite different for each of these three categories of gasifier. There will be different technical considerations in their application to biomass feedstocks. Table 2.4 summarizes the technical factors to be considered in evaluation of application of three selected commercial coal gasification processes to biomass feedstock.

2.1.2.2 Solid Waste Gasification Process

Research and development activities have been in existence for several years in the area of gasifying municipal solid waste. Table 2.5 presents the operating characteristics and product distribution for existing waste gasification processes. Among those commercially-available systems, only the Purox system produces synthesis gas suitable for methanol production. The Purox process was developed by the Union Carbide Corporation. A demonstration plant with 200 TPD capacity has been successfully tested at South Charleston, West Virginia, using the municipal solid waste collected in that area. This Purox system can convert either "as received" or processed refuse to a raw synthesis gas. Based on the published information, this process appears attractive for biomass gasification.

In the Purox gasifier system, the shredded and classified refuse is injected via a lock hopper into the top of the reactor and slowly descends as a moist feed. Hot combustion gases from the hearth rise through the descending feedstock, decomposing the organic materials to gases, liquids and char. The oxygen supplied by an onsite cryogenic air separator unit is injected into the hearth to provide partial oxidation. The operating conditions and other major features of the Purox system can be found in Tables 2.4 and 2.5.

Table 2.4 Factors to be Considered in Application of Selected Commercial Gasifiers to Biomass Feedstock

<u>Gasification System Component</u>	<u>Coal Gasifiers</u>			<u>Solid Waste Gasifier</u>
	<u>Fixed-Bed Reactor: Wellman-Galusha Gasifier</u>	<u>Fluidized-Bed Reactor: Winkler Gasifier</u>	<u>Entrained Bed Reactor Koppers-Totzek Gasifier</u>	<u>Purox Reactor (fixed bed reactor)</u>
Feed handling and storage	<ul style="list-style-type: none"> Due to the relatively low bulk density of biomass, the manpower and space required to handle a given volume may be higher than coal; moist biomass such as crop residue need to be dried to the level that permits storage; highly moist biomass presents difficulty in handling process; most biomass can not be stored in open area during raining seasons. 	<ul style="list-style-type: none"> Same as for fixed-bed reactor 	<ul style="list-style-type: none"> Same as for fixed-bed reactor 	<ul style="list-style-type: none"> Same as for coal Gasifiers
Feed pretreatment (sizing and predrying)	<ul style="list-style-type: none"> Most raw biomass has a moisture content ranging from 40 to 70% and has to be predried to 35% or less of moisture before feed-into the reactor. Large chunks of biomass have to be reduced to less than 2" in size; size reduction may be difficult for fluffy, or fibrous biomass; fines may be required to remove from the feed. 	<ul style="list-style-type: none"> Predrying is needed to reduce feed's moisture content to 25-30% Feeds must be sized less than 3/8"; size reduction may be difficult for fluffy or fibrous biomass; requirement for close sizing of feed and removal of fines. 	<ul style="list-style-type: none"> Feed must be dried to 2-8% of moisture, high cost of drying for biomass Biomass feed has to be reduced to 70% pass 200 mesh; this will be difficult for most fibrous biomass; sawdust needs little pretreatment. 	<ul style="list-style-type: none"> Moisture content up to 45% is acceptable. Required predrying is relatively limited. Can handle relatively large chunks (< 4") of biomass; pretreatment is relatively simple.

Table 2.4 Factors to be Considered in Application of Selected Commercial Gasifiers to Biomass Feedstock (continued)

<u>Gasification System Component</u>	<u>Coal Gasifiers</u>			<u>Solid Waste Gasifier</u>
	<u>Fixed-Bed Reactor: Wellman-Galusha Gasifier</u>	<u>Fluidized-Bed Reactor: Winkler Gasifier</u>	<u>Entrained Bed Reactor Koppers-Totzek Gasifier</u>	<u>Purox Reactor (fixed bed reactor)</u>
Reactor performance	<ul style="list-style-type: none"> • Biomass will have a higher reactivity than coal because of its larger volatile component; the residence time required may be shorter for biomass. • Biomass feed may not have enough ash to support the feed over the grate. 	<ul style="list-style-type: none"> • Due to the low bulk density of biomass, the fluidization conditions may be difficult to achieve and maintain. • Channeling will occur if the feed is not uniformly sized 	<ul style="list-style-type: none"> • Some types of biomass tend to mat, thus impairing the performance efficiency • It may be difficult to feed biomass feed stock through feeding nozzle. 	<ul style="list-style-type: none"> • Due to the slugging operation, there will be a problem with pure biomass feed. Biomass feed will not properly form slag in the hearth zone to prevent feeds from falling into the slag pit.
Gas Cleaning	<ul style="list-style-type: none"> • Raw Gas will contain less amount of particulates due to relatively low ash content in biomass. 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for coal gasifiers
Desulfurization	<ul style="list-style-type: none"> • Less amount of sulfur oxides will be generated because of low sulfur content in biomass 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for coal gasifiers
Residue disposal	<ul style="list-style-type: none"> • Less amount of ash will be generated when compared with coal 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for fixed bed reactor 	<ul style="list-style-type: none"> • Same as for coal gasifiers • Existing slag quenching operation may complicate the ash disposal.

Table 2.5 Summary of Existing Waste Gasification Processes

Pyrolysis Reactor Type	Description	Input Feed Requirements	Product Distribution			Reactor Temperature °F	Development Status		
			Solid (Stu/lb)	Liquid (Stu/lb)	Gas (Stu/ft ³)		PDS	Pilot (TPD)	Comm. (TPD)
I. Vertical Shaft									
Garrett	Adiabatic fluid bed reactor. Operates on presorted refuse at 500°C. Produces fuel oil, char, and gas. Gas is used for process heat. The process is known as "flash pyrolysis."	Dry, Fine (0.014 in.) shredded, combustible, relatively free of glass.	9,700	10,500	550	900	—	4	200
Union Carbide	Gasification is shaft furnace with oxygen to produce 300 Stu/scf gas and slag.	Mixed municipal refuse — 4 ft. gaseous oxygen.	—	—	300	3,000	—	5	200
Urban Research and Development	Gasification with air heated to 900°F in metal heat exchanger fired with gas generated on site.	Mixed municipal refuse — 4 ft.	—	—	150	2,600	—	120	—
Torrax	Gasification with air heated to 2200°F in ceramic heat exchanger fired with supplementary fuel.	Mixed municipal refuse — 4 ft. auxiliary fuel.	—	—	150	3,000	—	75	—
Battelle	Gasification with air and steam.	Not yet defined.	—	—	170	1,800	—	2	—
II. Horizontal Shaft									
Barber-Colman	Closed horizontal shaft with a circulating molten lead bed as the heat transfer media.	Fine shredded material to 2 inches.	—	—	500	1,200	—	1	—
III. Rotary Kiln									
Monsanto	Rotary kiln with internal heating by counter current flow of deficient air plus supplementary fuel. Requires presorted refuse. The process is known as "Landgard".	Shredded refuse to 4 inch. Supplementary oil fuel.	2,500	—	130	1,800	—	35	1,000
IV. Fluid Bed									
W. Virginia University	Fluid bed reactor with heat addition. 1500°F operating temperature to produce gas.	Dry, finely pulverized, noncombustible, free refuse. Make up sand 30 tons/day.	—	—	450	1,400	—	—	500

Although Purox has not yet conducted any significant tests on feeding of biomass, it is anticipated that this process can be used successfully for biomass gasification. The Purox system has several advantages over most existing coal gasifiers. These include its ability to handle relatively large chunks of feed (4-8") and to accept moist feed (up to 45% moisture). The cost of feed pretreatment, including predrying and size reduction, will be less than with most coal gasification systems(20). The only potential problem of the Purox system for biomass feedstock is the slagging operation of the reactor. The proper formation of slag at the hearth zone is necessary to prevent unreacted organic materials from falling into the slag quench water below the hearth. A small proportion of slagging material may be required to add to the biomass feeds to provide proper formation of slag. An alternative to this is to combine biomass feed with municipal refuse so that proper formation of slag can be achieved. Another alternative is the modification of the reactor shape, particularly in and around the higher temperature hearth zone, to prevent excessive loss of organics into the slag pit.

2.1.2.3 Biomass Gasification Technology

Commercial gasification technology for wood biomass had been developed and followed a path of improvement up until the petroleum era commencing around 1920. Most commercial gasifier units available then were designed to produce low-BTU gases having a heating value of around 150 BTU/SCF(21). Table 2.6 summarizes the composition of product gases from various early wood gasifiers. As can be seen, all of these product gases contain up to 50 percent nitrogen, this is because all gasifiers use air as oxidant. It appears that significant modification to most of the early

Table 2.6 Producer Gases from Wood

<u>Reactor Type</u>	<u>Compositions</u>					
Up Draught	CO ₂ (%)	N ₂ (%)	CO (%)	H ₂ (%)	CH ₄ (%)	Unsaturation (%)
"Suction Gas"	13.7	52.1	17.4	9.8	4.6	2.4
"Westwood Polygas"	11.5	47.0	22.0	16.0	2.5	1.0
Down Draught						
"Imbert"	11.2	49.3	20.5	17.0	2.0	--
"Fouchet"	16.0	46.8	13.3	21.0	2.6	0.3
Fluid Bed						
"BC Res"	11.2	53.3	15.8	13.1	3.7	1.6

Source: Reference 22

developed gasifiers are needed so that those gasifiers can produce gases suitable for methanol synthesis.

Renewed interest in converting biomass into useful fuels and chemical products has prompted an accelerated developmental effort in several advanced biomass gasification processes in the U. S.

Advanced gasification processes are in various stages of bench scale and pilot plant development. These gasification processes emphasize catalytic gasification or steam gasification of biomass as opposed to the early air-blown gasification processes. Not until recently has the role of a catalyst in the conversion of biomass been examined in detail. There have been some efforts in the wood and pulp industry to upgrade some of the by-products of paper production, particularly in terms of hydrogenation of lignin to phenol and phenol derivatives. However, efforts to catalytically enhance thermochemical biomass conversion to fuels have been limited to the use of alkaline compounds such as sodium carbonate and calcium oxide in the PERC and Battelle work. Perhaps the most important effect of catalyst is to enhance the reactivity of the feedstock. From an economic standpoint, this is particularly important for biomass due to its lower energy content relative to coal. This difference in energy content, and the low bulk density of biomass, increases the reactor size necessary for a given amount of product relative to that for coal.

There are several gasification processes which are currently under development:

- Battelle Columbus Process
- Battelle Northwest Process
- Texas Tech University Process
- IGT Process
- University of California Process
- Wright-Malta Process
- Moore Canada
- University of Missouri

Prospects of these advanced biomass gasification processes are discussed in Section 7.2. A summary of two most promising gasification systems for methanol synthesis is presented in the following paragraphs:

Wright-Malta Process

The Wright-Malta process is characterized by a combination of catalytic pyrolysis and hydro (steam) gasification²³. Figure 2.2 depicts the schematic flow diagram of the Wright-Malta gasification process. The main gasifier consists of a rotary kiln suitable for gasifying coarsely-shredded biomass feedstocks. Experimental work at Wright-Malta has shown that the presence of steam with an alkaline catalyst (Na_2CO_3) under pressure can reduce the formation of char in biomass pyrolysis, and that it can also reform the volatile liquid products into fuel gas. Under typical reaction conditions (400 psi and 1100°F), the conversion of biomass produces a medium-Btu gas having these compositions: CH_4 (18%), H_2 (28%), C_2 (8%), CO (1%), and CO_2 (45%). Note that the CO has shifted almost entirely to CO_2 , while the methane and higher hydrocarbons were unaffected. The reported gas composition does not appear to be directly useable for methanol synthesis, since the product gas is extremely deficient in carbon monoxide and contains excessive methane. It is estimated

W-M Biomass Gasifier Schematic

Figure 2.2 Wright-Malta Gasification Process

that with six tons per day of green biomass (50% moisture), the daily output from a pilot-scale Wright-Malta gasifier will be 67,000 SCF of fuel gas with heating values of 750 BTU/SCF (after CO₂ scrubbing)(23).

The experimental work performed using a variety of biomass materials has confirmed the following:

- Presence of an alkaline catalyst (e.g., Na₂CO₃) can significantly increase the gasification rate of biomass
- Increasing steam pressure and temperature can reduce the amount of char residue
- Reaction of steam with the char commenced at about 900°F and increases rapidly with increasing temperature.

Experimental work to date at Wright-Malta has basically been performed on a bench-scale rotary kiln. The limited heat and mass transfer associated with this type of reactor has resulted in a long residence time and may also pose reactor wall material problems for heat transfer consideration. However, the simplicity of the process also offers promise for the commercial production of medium-Btu gas useable for industry purposes at about \$2.50/MM Btu.

Battelle Columbus Process

The Battelle Columbus process under development involves a multi-solid fluid bed gasifier utilizing a chemically incorporated calcium oxide catalyst with biomass(24). Figure 2.3 depicts the schematic diagram of the Battelle Columbus process. The gasification reactor is comprised of a dense-phase fluid bed of inert particles into which an entrained phase of finer particles is fed to provide heat and improve solid-gas contacting. The Battelle study indicated that in order to exploit the very high reactivity

Figure 2.3 Battell Columbus Gasification Process Flow Diagram for Intermediate-BTU Gas from Wood Plant

of wood biomass, a reactor system capable of operating at very high velocities (usually 10 times those for other fluid bed reactors) is required.

The Battelle catalysis concept is based on the finding that chemically incorporated calcium oxide was a much more effective coal gasification catalyst than calcium oxide which is simply physically mixed with the coal. The chemical incorporation of calcium oxide in wood can be accomplished by treating the wood in an aqueous slurry of CaO at a temperature approximately 250°C and at pressures above the vapor pressure of the water at the treatment temperature. In addition to the CaO catalyst, the following catalyst systems have also been evaluated using wood biomass as feedstock:

- Sodium carbonate incorporated from a high-temperature slurry
- Mixtures of sodium carbonate and calcium oxide incorporated from a high-temperature slurry
- Calcium acetate from an ambient slurry
- Calcium nitrate from an ambient slurry
- Potassium carbonate from an ambient slurry
- Calcium oxide dry mixed with the wood
- Wood ash sprayed on the wood

Based on the above evaluation, the best catalysts found thus far have been calcium oxide and wood ash itself. It was also discovered that the wood ash can be applied by simply spraying a solution of it on wood chips and the calcium oxide can be simply mixed with the wood chips and still be as effective as when incorporated from a high temperature aqueous slurry.

Battelle estimated that an intermediate-Btu (300 BTU/SCF) gas can be produced at approximately \$2.90/MM BTU (average utility selling price) for a 500 TPD gasification plant with wood chips available at \$1.00/MM Btu.

2.1.3 Experimental Data on Synthesis Gas Production from Biomass

Very few experimental results of syngas production from biomass have been reported in the literature. However, some available biomass gasification data are presented in Table 2.7(26-31). The data provides a basis for examining the approach of the gasification process to equilibrium. It also helps to determine the extent of gas cleaning and conditioning processes required for the subsequent methanol synthesis process.

A comparison of the product gas composition with the equilibrium data shown in Fig. 2.1 indicates that most processes do not achieve equilibrium conditions in the reactors. The composition of product gas will depend upon the reaction temperature, pressure, residence time, feedstock composition and moisture content, and other factors. The data shown in Table 2.7 also indicates that a gas cleaning and conditioning process will be needed to convert the product gases to the composition ($H_2/CO=2$) required for methanol synthesis.

2.1.4 Current Available Gasification Technology Suitable for Biomass Based Methanol Production

There are a number of factors which should be considered in selecting an appropriate process for producing synthesis gas from biomass for methanol production. Ideally,

Table 2.7 Experimental Data on Biomass Gasification

Process	Reactor Type	Status	Feedstock	Gas composition (vol %)								Net heating value	
				CO	H ₂	CO	CH ₄	C ₂ H ₂	H ₂	H ₂ S	H ₂ /CO	H ₂ /CO	(BTU/SCF)
Puron ⁽²⁶⁾	fixed bed	process, originally developed for municipal solid waste	bagasse (6% moisture)	41.9	28.9	19.0	5.0	5.1	0.1	-	0.69	357	
Pullman-Kellogg ⁽²⁶⁾	molten salt	process development unit originally developed for coal	bagasse (37% moisture)	24.9	34.0	33.9	7.1	0.0	0.1	0.0	1.36	181	
Baillie ⁽²⁶⁾	fluidized bed	PDU originally developed for solid waste	dry bagasse	23.3	35.4	23.0	8.5	9.8	-	-	1.52	401(dry)	
Battelle-Northwest ⁽²⁷⁾	fixed bed	pilot plant reactor developed for biomass	wood waste	24.1	20.6	13.4	2.1	0.3	38.9	-	0.85	300 (gross heating value)	
Moore-Canada ⁽²⁵⁾	fixed bed	full scale PDU in operation	wood waste	22.8	18.3	9.2	2.5	0.9	45.8	-	0.79	132	
Battelle-Northwest ⁽²⁹⁾	fluidized bed	Bench-scale reactor developed for biomass	wood waste + catalyst	40.5	21.2	24.6	11.4	2.0	-	-	0.52	262	
Wallman-Galuska ⁽²⁹⁾	fixed bed	commercial process originally developed for coal	wood	44.4	30.2	20.0	4.0	-	1.4	-	0.68	279	
Koppers-Totzek ⁽²⁸⁾	entrained bed	commercial process originally developed for coal	wood	44.4	36.1	19.1	0.3	-	0.1	-	0.81	-	
Texas-Tech	fluidized bed	process development unit	wood	22.7	3.4	37.2	13.4	-	18.1	-	0.15		
Davy Power gas.	fixed bed	commercial process originally developed for wood	wood										

a gasification process suitable for biomass application should meet most of the criteria shown in Table 2.8. Although there is no ideal biomass gasification process existing which meets all these criteria, it is hoped that some of the discussions presented here will lead to future development in biomass gasification technology. From the standpoint of development status, only Koppers-Totzek, Wellman Galusha, Davy Power, and Purox processes can be considered as commercial technology. Based on the processes analyzed in this section, the following conclusions with regard to the current available gasification technology suitable for biomass based methanol production are drawn:

- In the near-term commercial application (before 1985), opportunities exist to transfer existing coal gasification technologies or solid waste gasification technology to biomass gasification. Among those existing gasification processes, oxygen-blown entrained-bed gasifiers such as the Koppers-Totzek Gasifier, oxygen-blown fixed bed gasifiers such as the Wellman-Galusha Gasifier, and the PUROX gasifier appear to have the greatest potential for producing synthesis gas from biomass for methanol synthesis.
- For longer term application, advanced catalytic gasification processes such as Battelle, Battelle Columbus, Texas Tech, Battelle Northwest Laboratory, and Wright-Malta processes may offer a potential for improving the production of synthesis gas from biomass.

Table 2.8 Major Factors/Criteria to be Considered in the Selection of a Process for Biomass Gasification

- Raw Gas Produced

- composition (H_2/CO ratio) and pressure of the raw gas being as close as possible to the requirements of the methanol synthesis process
- contain little undesirable components including particulates, sulfur, chlorine, hydrocarbons, and inerts-
- no undesirable byproducts such as oil or tar

- Process Performance

- high gasification capacity
- high carbon conversion efficiency and gas production rate
- thermal and energy efficient
- potential for waste heat recovery

- Ability to Handle Biomass Feedstock

- accept moist biomass feeds
- gasify large chunks of biomass
- not require uniform sizing of feed
- handle a variety of biomass including wood, crop residues, mill wastes, and others

- Simple Operation and Low Maintenance

- Competitive Synthesis Gas Production Cost

- Development Status and Capitalize Commercial Experience.

2.2 SYNTHESIS GAS MODIFICATION

To be suitable for methanol synthesis via present technology, the synthesis gas should consist mainly of hydrogen and carbon monoxide in a molar ratio exceeding 2 to 1, and should contain a small amount of CO₂. All other gaseous and particulate components either are inert or may contaminate the methanol synthesis catalyst. The available methanol synthesis catalysts can potentially be poisoned by many trace compounds in synthesis gas including sulfur, ash, tars, oils, and chlorine compounds. A survey of existing literatures on the methanol catalyst tolerances show that very little information is available about the potential catalyst poisoning by various hydrocarbons and aromatics which may also be produced from biomass gasification. Table 2.9 summarizes the potential poisoning capabilities of various components in synthesis gas. In order to achieve the maximum methanol production efficiencies, a synthesis gas modification step is required prior to methanol synthesis conversion.

The gasification of biomass can produce a wide range of synthesis gas compositions as shown previously in Table 2.3. From these data, several requirements for synthesis gas modification are apparent:

- Gas cleaning and the removal of particulates will be required. The design requirements will vary with gasification characteristics and feed type. Commercially available particulate removing and scrubbing technology can be easily transferred to this application.

Table 2.9 Potential Methanol Synthesis Catalyst Contamination

<u>Synthesis Gas Component</u>	<u>Contamination Level and Potential</u>
C ₂ H ₂	potential poison @ > 3 ppm for Cu-Zn catalyst
C ₂ H ₄ , higher olefin	presently unknown but possibly poisonous at higher concentration
CH ₄ , higher paraffin	inert
Sulfur (H ₂ S, COS, CS ₂)	poison @ > 0.2 ppm for Cu catalyst poison @ > 10 ppm for Zn catalyst
Chlorides	poison @ > 0.2 ppm for Cu-Zu-Cr catalysts
NH ₃ , HCN	possible poison at modest concentration
Particulate	possible poison and affect catalyst life
Oil mist	possible poison at modest amount

- H₂S removal may be required in order to assure long catalyst life in the methanol synthesis. Typical allowable sulfur content of .2 ppm for Cu catalysts and 10 ppm for Zn catalysts can be handled in methanol synthesis without adverse effects. The ranges of H₂S shown in Table 2.3 range up to 500 ppm.
- The H₂/CO molar ratio present in the exit gas from biomass gasifiers is less than 2.0 which is the theoretical lower limit for methanol production. Consequently, the H₂/CO must be raised. Two basic approaches can be considered for increasing hydrogen content in synthesis gas: (1) to convert CO to H₂ and CO₂ via the water gas shift reaction, and (2) to add a hydrogen rich gas. All these processes use commercially-available technology and should present no specific problems when applied to biomass synthesis gas.
- Biomass, because of its volatile carbon component, may produce a higher fraction of hydrocarbons in synthesis gas which must be (1) separated for use as fuel gas or (2) converted to CO and H₂ in order to achieve higher methanol synthesis conversion. Commercially available processes such as steam reforming, and cryogenic separation may be used to process the hydrocarbons.
- An acid gas treatment step will be necessary in the removal of the majority of CO₂ prior to methanol synthesis. Some CO₂ is advantageous from a reaction kinetics standpoint, but CO₂ exceeding 5 molar percent is a detriment. The removal of CO₂ is usually accomplished in an acid gas removal system to remove H₂S and CO₂ simultaneously.

2.2.1 Gas Cleaning

Various potential process technologies suitable for cleaning synthesis gas produced from biomass are summarized in Table 2.10. Depending upon the gasification temperature and gasifier types, the gasification products may consist of oil, tar, and char in addition to the synthesis gas products. However, these products are generally recycled in the gasification system as gasifier fuels. The major undesirable constituents in the synthesis gas are particulate matter, CO₂, N₂, and gaseous hydrocarbons. Specific technologies for accomplishing these gas cleaning functions are reviewed in the following sections.

Table 2.10 Potential Process Technology for Cleaning
Synthesis Gas Derived from Biomass

<u>Syngas Constituent</u>	<u>Concentration</u>	<u>Potential Process</u>
H ₂ S, CO ₂	H ₂ S $\leq$ 500 ppm CO ₂ $\leq$ 20%	Acid gas scrubbing process
COS, CS ₂	trace	Selectively removed by acid gas process
NH ₃ , HCN	trace	Water scrubbing and condensing
Char	$\leq$ 0.3%	Recycled as gasifier, steam or utility fuels
Oils & tar	Vary, depending on gasifier	Mist elimination or condenser separated; recycled in gasifier as combustible; residual treated in waste water
Particulate matter	low	Cyclone separators, fabric filters, wet scrubbers, electrostatic precipitators
Gaseous hydrocarbon	Vary, depending on gasifier	Steam reforming, cryogenic separation

2.2.1.1 Acid Gas Removal

There are numerous commercial acid gas removal processes available for removing primarily H_2S and CO_2 (18,32). These processes, which are summarized in Table 2.11, employ at least one of three techniques:

- Absorption into a solvent
- Chemical conversion into another compound
- Adsorption on solids.

Solvents for the first category include amines, methanol, or hot carbonate. Reagents for chemical conversion include zinc oxide, ferric oxide, calcium oxide, and vanadium pentoxide. Adsorbents include iron sponge, charcoal, and active carbon.

The majority of the commercial processes for H_2S removal are solvent absorption systems. These are the most economical at present. Good absorber efficiency comes from operating at low temperatures and high pressures (100-2000 psia). Chemical absorption (as in one of the amines or hot carbonate processes) is best suited for operations at low acid gas partial pressures; and physical absorption (as in Selexol--dimethyl ether or polyethylene glycol) is most suitable when the partial pressures are high. Thermal efficiency is an important criterion in process selection. Extremely low H_2S concentrations are difficult to obtain by absorption alone and solvent regeneration is required.

Chemical conversion processes can operate at higher temperatures than absorption systems. This improves the overall gasification thermal efficiency. The reagents are solids and require regeneration. Typical reagents are zinc oxide (ZnO) and ferric oxide (Fe_2O_3) operating at 600-650°F.

Table 2.11 Summary of Commercial Acid Gas Removal Processes

Process	Inventor + Vendor	What Treated	Purpose	Method	Level Removed	Other Things Removed	Operating Conditions
ADIP	Shell	Industrial gases	H ₂ S + CO ₂ removal	Gas/liquid absorption in aqueous solution of di-isopropanol amine	5 ppm in natural gas 100 ppm in fuel gas 10 ppm in LPG	COS	Absorber: 100°F 0-1000 psig Regenerator: 250°-275°F 1 atm Variable to handle feed contents
ALKAZIO	BASF Corp. (Germany)	Synthesis gas, watergas, natural gas	H ₂ S and/or CO ₂ removal	Gas liquid absorption in aqueous solution of alkali salts of weak nonvolatile amino acids	65 ppm H ₂ S in absence of CO ₂ at low pressure 320 ppm H ₂ S in presence of high CO ₂ at low pressure 5 ppm H ₂ S at low CO ₂ /H ₂ S ratio at high pressure		Variable to meet feed & purified gas requirements 0-1000 psig (stripper 5 psig) Near ambient temperature (may be cooler)
CLAUS	Black, Sivalis & Bryson; Ford, Bacon and Davis Texas; Ralph M-Parsons	Industrial gas	Convert H ₂ S to S	Combustion and Catalytic Conversion	Conversion of 94% of sulfur (94% removed)		near atmospheric pressure first converter 700°F second converter lower 20% H ₂ S requires additional O ₂ or fuel
Benfield	U.S. Bureau of Mines	Industrial gas natural gas Purification, synthesis gas	CO ₂ + H ₂ S removal	gas-liquid absorption scrubbing with hot potassium-carbonate	H ₂ S-90-98% CO ₂ -10-40%	COS, CS ₂	High pressure favors absorp/desorp scheme and lowers utility requirements 280°F practical limit of operating temperature variable

Table 2.11 Summary of Commercial Acid Gas Removal Processes (contd)

Process	Inventor + Vendor	What Treated	Purpose	Method	Level Removed	Other Things Removed	Operating Conditions
MDEA	Fluor Corp.	Industrial gases	H ₂ S removal	gas-liquid absorption in aqueous solution of methyl-diethanol-amine	< 4 ppm H ₂ S 99% H ₂ S removes CO ₂ to lesser extent 30-55%	CO ₂	absorber: 80-125°F stripper: 240-250°F redistillation unit: 250-300°F feed gas: 60-120°F absorber 0-1000 psig stripper redist 7-10 psig variable
PURISOL	LURGI	Natural gas, Synthesis gas	acid gas & CO ₂ removal H ₂ S removal	physical absorption in N-Methyl-2-Pyrrolidone	H ₂ S < 4 ppm CO ₂ < 2-3% can be as low as H ₂ S = 2 ppm CO ₂ = 10 ppm		absorber regenerator 80-105°F low press-1000 psig variable
SCOT	Royal Dutch/ Shell Laboratories	Plant tail gases & off-gases containing up to 30,000 ppm sulfur components	removal of S, H ₂ S, COS, CS ₂ , SO ₂	catalytic chemical reaction the gas-liq. absorption using di-isopropanolamine	H ₂ S < 200-300 ppm	CO ₂ 10/30%	absorption: 60-100°F 1 atm. stripper: 250°F 7-10 psig hydrogenation 575°F 3-5 psig
SELEXOL SOLVENT	Allied Chemical Corp.	Industrial gases	removal of H ₂ S and CO ₂	gas-liquid physical absorption with either di-methyl ether or polyethylene glycol.	< 1 ppm H ₂ S < 1 ppm COS CO ₂ any level required	other acid gases	absorber 20-100°F 500-1000 psig stripper 0-5 psig

Table 2.11 Summary of Commercial Acid Gas Removal Processes (contd)

Process	Inventor + Vendor	What Treated	Purpose	Method	Level Removed	Other Things Removed	Operating Conditions
STRETFORD	British Gas Corp.	Commercial gases	H ₂ S removal and S recovery	chemical absorption	H ₂ S < 1 ppm	SO ₂ , HCN	absorber 1 atm-100 psig solution oxidizer sulfur recovery 1 atm feed gas: 80-120°F 300 ppm-95% H ₂ S any amount. CO ₂ up to 2000 ppm HCN
RECTISOL	American Lurg. Corp.	fuel gas and synthesis gas	H ₂ S & CO ₂ removal	physical absorption using methanol	reduces gas containing 1% H ₂ S & 35% CO ₂ to less than 0.1 ppm H ₂ S & 1 ppm CO ₂		absorbers: -100-0 °F regenerator: up to 150°F 300 - 2000 psig variable
SULFIBAN	Black, Sivalle and Bryson, Inc.	Industrial gases	H ₂ S removal	gas-liquid chemical absorption in mono-ethanol-amine	H ₂ S < 1 ppm	COS, CS ₂ , HCN, CO ₂	absorber 100°F stripper 200-250 °F redistillation 250-300 °F feed gas 60-100 °F absorber 0-1000 psig stripper redist 7-10 psig variable
SULPINOL	Shell Development Corp.	Industrial fuel gases and natural gases	H ₂ S, CO ₂ removal	Organic physical absorption di-isopropanol-amine	H ₂ S < 2 ppm CO ₂ < 50 ppm	COS, mercaptans	absorber > 1 atm-1000 psig stripper 1 atm lean solvent 100-125°F rich solvent higher variable

Table 2.11 Summary of Commercial Acid Gas Removal Processes (contd)

Process	Inventor + Vendor	What Treated	Purpose	Method	Level Removed	Other Things Removed	Operating Conditions
Cryogenic	Union Carbide Corp. and Air Products and Chemicals, Inc.	purif. of H ₂ , CO, other synthesis gases	remove H ₂ S, CO ₂ , NH ₃ , light- HC	adsorption onto solid media (act. carbon, mol-sieves) at refig. temps. and condensation at low temperature	H ₂ S, CO ₂ , NH ₃ <1 ppm	H ₂ O, aromatics higher hydrocarbon acid gases	hydrogen purification 100-600 psig <0°F H ₂ conc. are commonly 30-90%
Activated Carbon Adsorption	Calgon Corp., Girdler Chemical, Inc.	Industrial gases	H ₂ S removal	adsorption onto solid activated carbon	<.2 ppm S	COS, mercaptans	apparently no pressure limit feed gas < 150 °F bed temp. during regeneration 350 - 500 °F Feed < 30 ppm H ₂ S and low MWS accomp.
Iron Oxide	Connelly-GPM, Inc.	Industrial gases	H ₂ S removal	chemical absorption on a solid bed of feric oxide	H ₂ S < 2 ppm		100-1000 psig (1 atm for earlier plants) 80 - 120 °F Feed 60-1200 ppm H ₂ S
Molecular Sieves	Union Carbide Corp.	Industrial gases	H ₂ S removal	adsorption on Zeolite based solid sieves	H ₂ S < 4 ppm	COS mercaptans	200-1200 psig 60-120 °F Feed 8 ppm - 1 vol% H ₂ S
Zinc oxide	Girdler Chemical, Inc., Catalysis and Chemicals, Inc. The New Jersey Zinc Corp.	Natural gas	H ₂ S removal	Chemical adsorption onto Zinc Oxide	H ₂ S < 2 to .5 ppm	mercaptans	660-840 °F though may be as low as 70 °F 1 atm - 50 + atm

Solid adsorption involves the capture of H_2S on the surface of a solid adsorbent such as iron sponge, charcoal, etc. usually at high pressures and low temperatures. Adsorption works best for low concentrations. It is usually used to further reduce H_2S levels following a solvent absorber and at the same time removes traces of organic absorption solvents.

The most economic process for removing acid gases in biomass gasification products are dependent upon the partial pressure and the selective removal requirements of the acid gases in the feed to the removal unit⁽³³⁾. Examination of various synthesis gas compositions produced from biomass gasification show that:

- The H_2S , COS , and CS_2 are in trace amount: The highest H_2S concentration is reported to be 500 ppm. and the requirement for methanol synthesis is below 1 ppm.
- The inlet CO_2 concentrations are ranging between 15 and 20 percent and the requirements for methanol synthesis are to reduce the CO_2 concentration to 1-2 percent level.

Based on the above specifications, the most suitable acid gas removal units will be a combined system consisting of an absorption type unit for bulk removal of CO_2 and H_2S followed by a chemical conversion (ZnO) guard bed unit for the final cleaning of H_2S . A recent study comparing conventional absorption type removal units show so that the Selexol process is the most economic when the partial pressure of acid gas is above 200 psi, and that the hot carbonate process is preferred when the partial pressure is lower than 200 psi⁽³³⁾.

Among the hot carbonate absorption units, the Benfield and Catacarb processes are judged to be most suitable for biomass

application. Both the Benfield (Fig. 2.5) and Catacarb (Fig. 2.5a) processes use hot potassium carbonate to remove acid gas⁽³²⁾. Steam stripping and pressure reduction release the hydrogen sulfide and carbon dioxide. If the synthesis gas also contains appreciable amounts of aromatics and carbonyl sulfide, an active carbon unit should be included. From the economic view point, the Benfield and Catacarb designs are very competitive and either process can show some economic advantages depending upon the degree of optimization of the design⁽³⁴⁾. However, in the subsequent process modeling analysis, a Benfield process was selected in order to assure compatability with the biomass gasifiers' heat recovery and gas cleaning equipment.

2.2.1.2 Particulate and Mist Elimination

Several types of commercial equipment can be employed for collection and removal of particulates and oil mist from a synthesis gas stream⁽³⁵⁻³⁷⁾. These include settling chambers, inertial separators, cyclones, filters, electrostatic precipitators, and scrubbers. Table 2.12 summarizes the characteristics of various particulate and mist collection equipment. The advantages and disadvantages of several types of equipment are presented in Table 2.13. The optimum selection of a specific equipment or a combination of equipment suitable for biomass gasification depends on the following considerations.

- The synthesis gas produced from high temperature biomass gasifier may exceed 1000°F. Therefore, a heat recovery step is necessary prior to particulate and mist elimination.
- Experimental data on particle size distribution show that biomass gasification produces average particulate and drop size smaller than 10 microns. This reveals a requirement of high energy device such as wet scrubbers, fabric filters, or electrostatic precipitators.
- The gas cleaning equipment selected should be compatible with the subsequent gas conditioning process such as shift conversion and acid gas removal.

Figure 2.4 Benfield Process Flow Chart. Source: Reference 32

Figure 2.5 Catacarb CO₂ Removal Process Flow Chart. Source: Reference 32

Table 2.12 Approximate Characteristics of Dust and Mist Collection Equipment

Equipment Type	Relative Cost Index ^a	Smallest Particle Collected (μ) ^b	Space	Pressure Drop (Inches H ₂ O)	Power Used ^c		Max. Temp., °C, Standard Construction	Remarks
					kW	1000 ft ³ /min		
A. Settling Chamber			Moderate				400°	
1. Simple	1	40		0.1-0.5		0.1		Large, low pressure drop, precleaner
2. Multiple Tray	2-6	10		0.1-0.5		0.1		Difficult to clean, warpage problem
B. Inertial Separators			Moderate				400°	
1. Baffle Chamber	1	20		0.5-1.5		0.1-0.5		Power plants, rotary kilns, acid mists
2. Orifice Impaction	1-3	2		1.3		0.2-0.6		Acid mists
3. Louver Type	1-3	10		0.3-1		0.1-0.2		Fly ash, abrasion problem
4. Gas Reversal	1	40		0.1-0.4		0.1		Precleaner
5. Rotating Impeller	2-6	5		---		0.5-2		Compact
C. Cyclones							400°	
1. Single	1-2	15	Small	0.5-3		0.1-0.6		Simple, inexpensive, most widely used
2. Multiple	3-6	5	Large	2-10		0.5-2		Abrasion and plugging problems
D. Filters			Large				400° ^d	
1. Tubular	3-20	0.1		2-6		0.5-1.5		High efficiency, temperature and humidity levels
2. Reverse Jet	7-12	0.1	Moderate	2-6		0.7-1.5		More compact, constant flow
3. Envelope	3-20	0.1		2-6		0.5-1.5		Limited capacity, constant flow possible
E. Electrical Precipitators			Large				650°	
1. One-Stage	6-30	0.1		0.1-0.5		0.2-0.6		High efficiency, heavy duty expensive
2. Two-Stage	2-6	0.1		0.1-0.3		0.2-0.4		Compact, airconditioning service
F. Scrubbers							Unlimited ^e	
1. Spray Tower	1-1	10	Moderate	0.1-0.5		0.1-0.2		Common, low water use
2. Jet	4-10	2	---	---		2-10		Pressure gain, high velocity liquid jet
3. Venturi	4-12	1	Moderate	10-15		2-10		High velocity gas stream
4. Cyclonic	3-10	5	Moderate	2-8		0.6-2		Modified dry collector
5. Inertial	4-10	2	Small	2-15		0.8-8		Abrasion problem
6. Packed	3-6	5	Large	0.5-10		0.6-2		Channeling problem
7. Rotating Impeller	4-12	2	Small	---		2-10		Abrasion problem

Notes: a- Including necessary auxiliaries. b- With 90-95% efficiency by weight. c- Includes pressure loss, water pumping, electrical energy. d- Glass 400°C, cotton fabric 85°C, synthetic fabrics up to 135°C, Nomex 220°C. e- Pre-cooling of high temperature gases will be necessary to prevent rapid evaporation of fine droplets.

Table 2.13 Collection Equipment Advantages and Disadvantages

Particle Collection Device	Advantages	Disadvantages
Electrostatic Precipitators	<ol style="list-style-type: none"> 1. High efficiency (up to 99%). 2. No lower limit to the size of particles that can be collected. 3. Pressure and temperature drops are small. 4. Can collect tar mists if present. 5. Large gas flow rates can be handled. 	<ol style="list-style-type: none"> 1. Temperature limit of about 1300°F. 2. Initial cost is high (usually higher than any other method) 3. Not easily adaptable to variable conditions. 4. Large space requirements. 5. Cannot remove materials in gaseous phase.
Inertial Separators (cyclones)	<ol style="list-style-type: none"> 1. Good for medium and coarse sized particles. 2. Costs lower than other types of collectors. 3. Can handle wide range of conditions. 	<ol style="list-style-type: none"> 1. Bad for fine particulates (<15u) 2. Agglomeration starts to occur at particulate concentrations >100grams/ft³. 3. High velocities reduce efficiency.
Scrubbers	<ol style="list-style-type: none"> 1. Constant pressure drop. 2. Can handle high temperatures and moisture laden gases. 3. Small space requirement. 	<ol style="list-style-type: none"> 1. Cools gas (if desired). 2. Disposal or clarification of waste water may be expensive. 3. Decline rapidly in efficiency for particles between 10u and 1u.
Baghouses (Fabric Filters)	<ol style="list-style-type: none"> 1. Collection efficiency up to 99%. 2. Pressure drop 2-6 in. H₂O. 3. Annual cost \$1.05/cfm. 4. Recovered material recovered dry 5. No liquid waste. 6. Can capture submicrongaseous matter. 	<ol style="list-style-type: none"> 1. Acid or alkaline particles reduce fabric life. 2. Temperatures of gas should be <500°F. 3. Gas must be dry.

Based on the above considerations, the most suitable particulate and mist elimination system for a biomass system will be the following systems depending upon the gasification temperatures.

1. A combined cyclone and electrostatic precipitation system - For a high temperature biomass gasification process which produces with a minimum amount of oil and tar mist.
2. A combined wet scrubber, oil-char separator, and wet electrostatic precipitator system - For a low temperature biomass gasification processes producing a significant amount of oil and tar mist.

2.2.2 Carbon Monoxide Shift Conversion

The synthesis gas from the gasification process is generally sent to what is known as a shift converter to convert the CO content of the gas to hydrogen by CO shift reaction:

The CO shift reaction is slightly exothermic. The reaction is limited by thermodynamic equilibrium, lower temperatures favoring more complete conversion of CO.

Until recently, catalyst limitations have prevented the use of lower temperatures in the shift reaction⁽³⁸⁾. The catalyst in general use for the high temperature shift conversion is chromium promoted iron formed by co-precipitation of the oxides of the two metals. These catalysts normally operate in the range of 650° - 1000°F⁽³⁹⁾. The high temperature CO shift conversion system has normally been operated in two stages, with an intermediate CO₂ removal step, to obtain more

complete conversion. Lower carbon monoxide contents in the exit gas can be obtained by using an excess of steam, and the steam/gas ratios are determined in part by the overall heat balance of the plant. The shift reaction is exothermic and heat requirements are at a minimum. The gas leaving the converter passes through a heat exchanger, giving up heat to the incoming gases, and is combined with a recirculating water system in order to minimize heat consumption.

Recent developments in catalyst technology have made changes in shift conversion design. Both Girdler, and Catalysts and Chemicals have developed low temperature catalysts with high activity. These catalysts are mixtures of the oxides of zinc, chromium and copper. These new catalysts permit operation of the shift conversion unit at temperatures of 350°-550°F, with resulting savings in both construction and operating costs. These low temperature and the high activity catalysts may allow the use of only one stage of shift conversion instead of two. It is claimed that one stage low temperature shift conversion with this new catalyst can reduce the CO content in the exit gases to 0.2 percent or possibly less. Normally, a renewable bed of zinc oxide is installed just before the catalyst to prevent sulfur poisoning. Table 2.14 compares the high temperature CO shift catalyst and low temperature CO shift catalyst(57).

For a biomass gasification product, the objective of the water gas shift reaction is to adjust the H_2/CO ratio to a range above 2:1. Therefore, it is not desirable to convert all the CO in synthesis gas to H_2 . The selection of a single-stage high temperature shift reaction will be a preferable choice.

Table 2.14 Comparison of CO-Shift Catalyst Characteristics

<u>Composition</u>	<u>High Temp Catalyst Chromia-promoted Iron Oxide</u>	<u>Low Temperature Catalyst Copper- zinc Oxide</u>
Maximum operating temp., °F	890	500-550
Tablet size (in.)	$\frac{1}{4} \times \frac{1}{4}$	$\frac{1}{4} \times \frac{1}{8}$
Bulk density (lb/cu ft)	70	90
Particle density (lb/cu ft)	126	155
Cost (\$/cu ft)	20.00	75.00
Catalyst poisons	Inorganic salts, boron, oils, or phosphorous compounds, liquid H ₂ O is a temporary poison. Sulfur compounds in an amount greater than 50 ppm	Sulfur and halogen compounds, and un- saturated hydro- carbons
Catalyst life	3 yr. and over depending on care in startup and operation (Use times up to 15 yr. have been reported)	2-3 yr.

2.2.3 Conversion of Hydrocarbon Gases

Depending on the gasifier type and operating conditions, potential production of methane and higher hydrocarbons can be realized. Methane and most higher saturated hydrocarbons will act as inert gases in methanol conversion and could be used as a fuel gas by-product in a methanol synthesis plant. However, if a higher carbon utilization efficiency is desired, a process which reforms the hydrocarbons may be utilized. For biomass gasification, two approaches may be considered for handling the hydrocarbon problems. These two choices are, (1) to operate the gasifier at a high temperature: a condition that minimizes methane production and (2) to operate the gasifier at a condition that produces moderate amounts of methane and to process the product stream through a hydrocarbon conversion step.

Two major commercial technologies developed for separation and processing of hydrocarbon gases, are judged to be suitable for biomass applications(38-40):

- steam reforming
- cryogenic separation

2.2.3.1 Steam Reforming Technology

The steam-hydrocarbon reforming process is very highly developed and has been used extensively in industry to prepare synthesis gases for the production of methanol from a natural gas feedstock(38).

The reaction for reforming is:

Methane is reacted with steam to obtain carbon monoxide and hydrogen for methanol synthesis. In the normal production of methanol from natural gas, the reformer feed also contains carbon dioxide. Since excess hydrogen is available from reforming, carbon dioxide is added to the reformer feed to lower the hydrogen to carbon ratio in the reformed gas so that it is stoichiometrically appropriate for methanol synthesis.

The steam reforming is conducted over a catalyst that is nickel based (such as oxide on alumina). The catalyst is arranged in a long multi-vertical tube fashion and the reactions take place at 1400° to 1700°F. This type of catalyst can be purchased in quite similar composition from a number of catalyst vendors who have some variations in manufacturing procedure or composition which are purportedly advantageous to the catalyst life, avoiding carbon deposition, avoiding disintegration or, giving more rapid approach to equilibrium.

The recovery of waste heat from the reforming unit is an important part of the process design. The energy of the reformed gas stream is used to heat boiler feed water and to generate steam. The steam thus produced (900 psig. and 500°F of superheat) provides the motive power for the synthesis gas compressor and for the recycle gas circulator. The exhaust steam from the compressor turbines (400 psig.) is used both as process steam for the reformer and as a source of heat in the purification section of the process.

In the more efficient two stage reformer design, the unreacted methane and some of the gas produced in the primary reformer is reacted with air over a nickel catalyst. Thus, a methane content as low as 0.3 percent in product gas can be obtained(38).

If steam reforming is applied to a gasified biomass feed, several potential modes of operation are available in order to prepare the gas for methanol synthesis. Table 2.7 shows that the biomass gases have hydrogen carbon ratios of 0.5 to 0.8 which are below that required for methanol synthesis.

Alternatives to feeding the biomass gas to the reformer directly are:

1. Pass all the synthesis gas through a reformer and use the product gas in the methanol synthesis loop.
2. Separate CH_4 and use it as a fuel gas for some other plant operation or process.

Another potential use of reforming could be for hybrid synthesis gas production. A separate source of methane could be reformed without or with limited CO_2 addition and the hydrogen rich product could be combined with the biomass gas to adjust the gas to the CO/H_2 ratio required for methanol synthesis. More detailed discussion of hybrid synthesis gas production schemes will be discussed in Section 7.

2.2.3.2 Cryogenic Separation Process

Although cryogenic separation processes have wide application, the most desirable process for biomass will be the one similar to hydrogen purification used in refinery operation⁽¹⁸⁾. Several process variations are available for the cryogenic purification of hydrogen depending on the total gas flow, pressure and temperature of the feed.

Figure 2.6 pictures a simplified cryogenic system, which illustrates the basic principles involved. Feed gas is compressed to at least 100 psig, cooled, and separated from the condensed moisture in a knockout drum. It then passes through a fixed bed dryer, where water and any H_2S , CO_2 , or NH_3 present in the feed gas are reduced to less than 1 ppm. The absorbent generally used for drying is activated carbon or a suitable molecular sieve. Dry gas is precooled in a refrigerator unit and then cooled to less than $0^{\circ}F$ by interchange with the purified hydrogen and light hydrocarbon products. If further cooling is required for the desired separation, the stream passes through another refrigeration unit.

Compact, high efficiency countercurrent heat exchange equipment is normally employed in cryogenic processing units. The processes are characterized by near reversible heat exchange (very close temperature approach between feed and return streams) to achieve maximum utilization of available refrigeration and minimum external refrigeration supply requirement.

Hydrocarbons in the feed gas are condensed in the cooling train and the two-phase mixture is separated. Purified hydrogen passes overhead while the liquid hydrocarbons are expanded isenthalpically to provide refrigeration for the feed gas via the Joule-Thompson effect. More than one separating stage is often used if separation of the light hydrocarbons into fractions is desired.

When feed gas concentration is greater than 25 percent light hydrocarbons, precooling in a refrigeration unit is not required, since sufficient cooling is provided by the Joule-Thompson effect. In most biomass gasification processes, however, the gas produced is too low in light hydrocarbons to eliminate precooling entirely.

Figure 2.6 Simplified Cryogenic System Flow Diagram

The selection of an appropriate hydrocarbon removal process for biomass gasification applications depend primarily on several factors:

- overall process economics
- process energy consumption
- potential for integration with other biomass to methanol processing steps

Based on these considerations, it is judged that a cryogenic separation unit will be most suitable for low temperature biomass gasification processes. The utilization of waste heat generated by other biomass to methanol processes poses an economic advantage for suppling the compression energy required for the cyrogenic unit. The steam reforming process on the other hand required substantial fuel inputs.

2.3. METHANOL SYNTHESIS TECHNOLOGY

2.3.1 Technology Overview

The synthesis of methanol dates back to the early years of this century when methanol was produced along with numerous other alcohols, aldehydes, ketones, acids and hydrocarbons in what is referred to as Fischer-Tropsch synthesis (44). This synthesis is accomplished at elevated temperatures and pressures over catalysts containing Ni, Cr, Ag, Fe, Co, Cu and other metals and metal oxides. Methanol is a relatively minor product of Fischer-Tropsch synthesis and over the years selective catalysts were developed for it.

During the 1920s and the 1930s, catalysts containing the oxides of zinc, chromium, copper and other metals were developed (44). The first commercial catalysts were a mixture primarily of zinc and chromium oxides, the latter being a promoter. With this catalyst, methanol is produced at temperatures of 300 to 400°C and at pressures of 200 to 300 atmospheres (atm). An example of a commercial process using this technology is that offered by Vulcan-Cincinnati, Inc. During 1960's, more active and selective catalysts containing copper and zinc oxides have been developed which permit synthesis of methanol at lower temperatures, 200 to 300°C, and at lower pressures, 50 to 100 atm. This technology has gradually superseded the previous high pressure technology and is embodied in processes offered by the Imperial Chemical Corporation, Ltd. (ICI) and by Lurgi. A novel liquid phase methanol process developed recently by Chem Systems Inc., has the potential to further improve the methanol conversion economics(43).

2.3.2 Catalyst Development and Evolution of Process Technology

In the early 1920's, ZnO was used as the first catalyst for the conversion of carbon monoxide and hydrogen into methanol(44). This was soon followed by the development of ZnO-Cr₂O₃ mixtures, which were improved catalysts. These catalysts were immediately employed in the commercial production of methanol, where the reactors were usually operated at 250-350 atmospheres and 350°-400°C.

It was found that the presence of copper in the methanol catalysts seemed to initially increase the activity of the catalyst. However, the synthesis gas always contained quantities of sulfur-containing impurities, and the copper-containing

catalysts were rather quickly poisoned. Several decades later, the means became available to purify the synthesis gas such that less than 0.1 ppm of sulfur was present. This allowed the use of copper catalysts, which, because of their high activity, were able to convert the synthesis gas to high-quality methanol at the same rate as previously but at lower pressures and lower temperatures, e.g., 50-100 atmospheres and 250°C. Thus, during the middle 1960's, a push was underway to improve the copper-containing catalysts. Most of these were ZnO-Cr₂O₃ catalysts that contained copper in the form of CuO before reduction. Table 2.15 compares the commercial methanol catalyst compositions and yields.

The catalysts generally used for the low pressure commercial production of methanol are the CuO-ZnO-Al₂O₃ preparations in which the ratios of the components can be varied over a wide range but usually Al₂O₃ is the compound present in lowest concentration. These catalysts provided a much more economical method of synthesizing methanol. The savings result from both decreased equipment costs and decreased operating costs of the methanol plant, which arise from a decrease of the reactor pressure from 300-350 atm to 50-100 atm. A major part of plant investment cost is pipework, especially flanges, valves, and fittings, and it is found that equipment costs increase disproportionately with increasing pressure rating of an installation. In addition, the low pressure process can make use of steam-turbine-driven centrifugal compressors, while the high pressure route generally requires electrically driven reciprocating compressors. The low pressure process is also advantageous for potential small scale applications in biomass conversion. Steam can be generated internally since the conversion of carbon monoxide and hydrogen into methanol is an exothermic process which releases approximately 700,000 kcal of heat per ton of methanol produced. In contrast to reciprocating

Table 2.15 Methanol Synthesis Catalysts Composition and Yield Using H₂ + CO Synthesis Gas

CuO/ZnO/Cr ₂ O ₃	Temp. (°C)	Pres. (atm)	H ₂ / CO	GHSV (hr ⁻¹)	% CO Con- version	Yield (kg/l/hr)	Yield (kg/kg/hr)
15:48:37	270	145	2.8	10,000	-	-	1.95
20:70:10	250	75	2.3	7,800	2.3	0.08	0.10
31:38:5	230	50	4.5	10,000	-	0.755	-
31:38:5 (a)	230	50	4.5	10,000	-	1.275	-
60:30:10	250	75	2.5	4,700	7	0.15	0.14
60:30:10	250	100	3.5	6,800	4	0.06	0.05
60:30:10 (b)	250	100	3.0	7,100	60	1.17	1.05
60:30:10 (c)	260	100	2.3	5,000	66	1.87	1.61

- (a) Synthesis gas contained 1% (by vol.) O₂
 (b) Small amount of O₂ added to the synthesis gas
 (c) Synthesis gas consisted of H₂/CO/CO₂ = 65/28/7

Source: Reference 45

compressors, double streaming is eliminated with turbine compressors. Thus, a 40 percent reduction in compression costs can be realized by reducing synthesis pressure from 350 atm to 50 atm, which is also reflected in the capital costs.

It has been customary to design commercial methanol plants so that only 2.5-6.5 percent methanol appears in the reactor effluent(46,47). The unconverted reactants are recycled so that methanol is essentially the only escaping component of the system. These principles were incorporated into the first low pressure methanol plant that was put into operation by ICI in December 1966. The plant was designed to produce 300 tons of methanol per day while running at a reactor pressure of 50 atm. The content of methanol in the effluent was approximately half that in a high pressure plant, and when operated at 25 percent of full output, it was necessary to employ external heaters to maintain catalyst temperatures. These data indicate that a more active catalyst will be desirable. This is especially true since the catalyst cost per ton of methanol produced is higher with the low pressure process than with the high pressure technology.

2.3.3 Commercial Methanol Synthesis Process

A description of current commercial methanol synthesis processes is presented in four categories: (1) the high pressure process, (2) the low pressure process(48,50), (3) the medium pressure process, and (4) the liquid-phase process(51).

2.3.3.1 High Pressure Process

This process, representing a large fraction of the methanol production capacity at the present time, was used exclusively up to 1966, until Imperial Chemical Industries introduced its low-pressure process. The high-pressure process operates at 300-350 atm (4400-5100 psig) and at a temperature of 300-400°C (570-750°F). The catalyst, a ZnO-Cr₂O₃ mixture, is mounted in a fixed-bed reactor. The product stream is cooled to condense and remove the methanol, and the unconverted synthesis gas is recycled to the reactor. Small amounts of dimethyl ether (light ends) and higher alcohols (high-boilers) are formed as by-products and are removed by distillation; the light ends may be burned in the reformer, and the high boilers are either recovered or burned.

2.3.3.2 Low Pressure Process

The low-pressure process, originally introduced by Imperial Chemical Industries of the United Kingdom (ICI) in 1966, is now available in a number of variations. All of these processes use a copper-based catalyst and depend on a low temperature and a sulfur and chlorine-free feed to maintain catalyst activity. The original ICI process operates at temperatures below 300°C (570°F) and at a pressure near 50 atm (750 psig).

The various low pressure processes now used operate at pressures ranging between 450 to 1500 psig, and temperatures ranging from 210 to 290°C. The ICI low-pressure process, differs from high-pressure processes in several respects.

A highly active Cu/Zn/Cr catalyst is used in a multi-bed converter, and the reaction temperature is controlled by introducing cold synthesis gas through specially designed spargers between the beds. The crude methanol produced by this process is purer than the methanol produced in the high-pressure plants since the low temperatures reduce the rate of the side reactions. There are several cost advantages to using the low-pressure process for producing methanol. Production costs are lowered because of reduced compression requirements, maintenance costs and reduced downtime of the turbine driven centrifugal compressors.

Several other low-pressure processes currently available are compared with low ICI process in Table 2.16. Lurgi has introduced a tube-in-shell reactor designed to closely control catalyst temperature, while Topsoe employs a radial-flow converter with a copper-based catalyst capable of operation up to 350°C. A flow sheet for the Lurgi process is shown in Fig. 2.7.

2.3.3.3 Medium-Pressure Processes

Although several companies have developed medium-pressure processes, no U.S. plant is now using a medium-pressure process. These companies include Vulcan-Cincinnati, Inc., ICI, Nihon Suiso Kogyo of Japan, and Haldor Topsoe A/S of Denmark (52,53).

The medium-pressure process of Vulcan-Cincinnati, Inc., operating in the range of 150-180 atmospheres (2,205-2,645 psi), is essentially the same as a high-pressure process except that the improved zinc-chromite catalyst used enables utilization of pressures significantly

Table 2.16 Typical Low-Pressure Methanol Catalysts and Synthesis Techniques

<u>Vendor</u>	<u>Catalyst Type</u>	<u>Pressure (atm)</u>	<u>Temperature (°C)</u>	<u>Reactor Type</u>	<u>Cooling Method</u>
ICI	Cu-Zn-Al	50-100	220-290	Fixed, Multiple Bed	Multiple Gas Quench
Lurgi	Supported Cu	30-50	235-280	Tube in Shell	Steam Generation
Haldor Topsoe	Cu-Zn-Cr	50-100	220-350	Radial Flow	

Source: Reference (49)

Source: Lurgi Brochure 1053/12.76

Figure 2.7 Methanol Synthesis and Distillation in the Lurgi Low Pressure Methanol Synthesis Process

lower than those used in high-pressure processes. The zinc-chromite catalyst also has the advantage of not needing to be replaced as frequently as the ZnO catalyst. The overall efficiency of the new system is thus improved with a consequent reduction in plant energy requirements and capital cost. The converter embodies the principles of Vulcan's prior high-pressure process technology, and steam-turbine driven centrifugal compressors may be applied rather than reciprocating compressors at commercially viable capacities in plants.

ICI also is offering a medium-pressure process commercially. A flow sheet for this process is shown in Fig. 2.8. This is beneficial since it increases the reaction rate, degree of conversion and carbon utilization efficiency, and permits a reduced reactor size for the same throughput. The latter is important for large plants to be located outside the U.S. where there may be problems fabricating and transporting very large items of equipment. The catalyst for the plant is based on copper, but it is prepared in a different way from that used in the ICI low-pressure process, so that it is more resistant to deactivation.

Nihon Suiso Kogyo (NSK) of Japan and Haldor Topsoe A/S of Denmark have developed a medium-pressure process which operates between 700 and 4,500 psi and at a temperature of about 500°F. It uses a copper catalyst and centrifugal compressors.

The advantages of the medium-pressure process, then, are higher-per-pass conversion of carbon oxides to methanol (hence a reduction in interchanger head load and size, and a lower circulation rate) higher carbon conversion (which reduces synthesis gas rate and reformer size) smaller converter

Figure 2.8 The ICI Medium Pressure Process for the Synthesis of Methanol

and catalyst volume, and smaller diameter loop pipework. The disadvantages of the medium-pressure process compared to the low-pressure process are the higher design pressure for loop equipment and piping, and the greater power needed for compression.

2.3.3.4 Liquid-Phase Methanol Synthesis Process

This process concept is presently under development by Chem Systems, Inc. but deserves discussion since published economic analyses indicate significantly reduced costs(51). A flow sheet for this process is shown in Fig. 2.9. This concept addresses one of the major problems in methanol synthesis, efficient removal of the reaction heat and maintenance of near isothermal conditions in the reactor. By fluidizing the catalyst in an inert liquid phase, the reaction heat is readily absorbed by the high heat capacity of the liquid with a minimal temperature rise. Also circulation of the process liquid permits efficient external heat removal. Several advantages are claimed for this concept(51);

- Because of improved temperature control, a greater conversion towards equilibrium can be achieved;
- Because of the fluidization smaller catalyst particles are used which provide increased reaction rates; and
- Because of higher conversion, reduced recycle compressor size and operating costs are realized.

Problem areas can include deterioration of the heat-transfer fluid, inhibition of the catalyst by the fluid, and insufficient solubility of the synthesis gas in this fluid.

Initial comparison of the economics of this process with the ICI process shows a cost advantage of approximately 15 percent in the methanol produced(43,51). This reactor concept is unproven commercially.

Figure 2.9 Chem Systems Three-Phase Methanol Synthesis Process

Source: Reference 51

2.3.4 Methanol Production Efficiency

The efficiency of methanol production generally has been based on the thermodynamic first law(54,55): the combustion enthalpy of the products divided by the energy of the feedstocks plus energy losses. The energy efficiency of three most promising methanol synthesis loop are compared in Table 2.17. As can be seen, the methanol synthesis loop has process efficiencies between 81.7 percent to 93.8 percent. The process efficiency are dependent upon the methanol operating pressure, and recovery heat. In all three processes compared, the high pressure process have an average of 3 percent lower efficiency than those of low pressure design. The low pressure (500 psi) Chem System appears to have the highest process efficiency of 93.8 percent.

2.3.5 Methanol Purification

Crude methanol obtained following condensation will contain non-condensable gases, water, dimethyl ether, higher alcohols and hydrocarbons(56). The non-condensable gases are removed as the product is "let down" from the synthesis pressure to atmospheric pressure. The liquid phase produced during this flash operation contains side products, such as, dimethyl ether and ethyl alcohol in addition to water and methanol. Fractional distillation employing one or more columns is the only process employed commercially for separation of methanol from this solution but extraction and absorption processes have been proposed. In a typical distillation purification scheme, one column is employed for removal of low boiling impurities, such as, dimethyl ether, while a second column produces essentially pure methanol as distillate and water and higher alcohols as residue.

Table 2.17 Comparison of Methanol Synthesis Technology

	ICI Multi-Bed Adiabatic Quench System		Lurgi Tube-wall Isothermal Reactor System		Chem System Liquid Phase Reactor System	
Operating Pressure, PSI	<u>750</u>	<u>1500</u>	<u>500</u>	<u>500</u>	<u>500</u>	<u>1100</u>
Energy Balance, MMBtu/ ton MeOH						
① Synthesis gas	23.52	23.52	23.52	23.52	23.52	23.52
② System horsepower requirements						
Feed compression (1)	0.80	2.48	-	2.48	-	1.70
Gas recycle	0.92	0.25	1.39	0.27	0.55	0.14
Oil circulation	-	-	-	-	0.27	0.12
Total energy input	25.24	26.25	24.91	26.27	24.34	25.48
③ Methanol	19.28	19.28	19.28	19.28	19.28	19.28
④ Recovery heat	1.15	1.17	2.35	2.40	2.57	2.58
⑤ Purge gas	0.99	1.00	0.99	1.01	0.99	1.19
Total energy output	21.42	21.45	22.62	22.69	22.84	23.05
Process efficiency, %	84.9	81.7	90.8	86.4	93.8	90.5

(1) Assume synthesis gas available at 500 psig

2.3.6 Applicability of Present Methanol Technology to Biomass Processing

It is generally recognized that existing technology is readily transferable to synthesize methanol from a synthesis gas suitably prepared from biomass. The synthesis can be economically accomplished by an ICI or Lurgi type low pressure process utilizing copper containing catalysts. The principle reasons of utilizing such synthesis processes for biomass processing are based on:

- Older methanol synthesis processes which utilized zinc oxide catalysts require operation at temperatures above 300°C, which necessitate high synthesis pressures, 200 to 400 atm, in order to achieve an acceptable degree of conversion. Because of the extra compression required, the high pressure process is not economically competitive, especially for biomass methanol.
- Medium pressure processes may be practicable and even desirable. However, it must be kept in mind that they must be built large enough to use centrifugal compressors in order to be economical. This would require a methanol production rate of about 600 TPD, corresponding to 1500 to 1800 TPD of dry biomass.
- Methanol synthesis catalysts are easily poisoned by sulfur-containing contaminants in the synthesis gas. Zinc catalysts can maintain their activity in gases with a sulfur content as high as 10 ppm. Copper catalysts are more sensitive; the sulfur level must be less than 0.2 ppm to avoid loss of activity⁽⁹⁾. This requirement poses a unique advantage for the biomass synthesis of methanol, since most biomass materials contain little sulfur and small amounts of sulfur may be easily removed by a zinc oxide "guard bed" or activated carbon placed ahead of the methanol catalyst beds.
- The conversion of synthesis gas to methanol is an exothermic reaction and hence the reactor temperature must be carefully controlled to prevent deactivation of copper catalysts (which usually occurs at temperatures above 300°C) and unfavorable equilibrium conditions. The major difference between

ICI and Lurgi reactors is in the way in which the temperature is controlled. The Lurgi reactor design cools the catalyst with water (catalyst inside tubes immersed in water, whereas ICI obtains cooling by introducing cold synthesis gas at appropriate locations. The preferable choice of ICI type reactor is due in part on the simplicity of the reactor design and therefore relative low reactor cost for a small scale methanol synthesis from biomass

- Present commercial methanol processes typically include two distillation columns to remove light ends, heavy ends, and water from the crude methanol. For biomass fuel grade methanol much of this process appears to be unnecessary except for removal of the water, since its concentration is excessive.
- In addition, although commercially unproven, the fluidized bed concept of Chem Systems, Inc. is unique, and this type of reactor must be considered for advanced biomass to methanol development. Because of its high degree of temperature control, it may give synthesis at greater efficiency and lower cost than any commercial processes.

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3. BIOMASS TO METHANOL PRODUCTION CONCEPTS AND PROCESS CONFIGURATION ANALYSIS

This section presents analyses and discussion on various alternative process configurations that have been synthesized during the course of the study. It outlines a system approach and screening procedure whereby a selection of the most promising conversion process configuration is made.

3.1 BASIC BIOMASS TO METHANOL PRODUCTION CONCEPTS

In evaluating alternative biomass to methanol production concepts, four basic approaches as shown in Fig. 3.1 are considered. These are:

- A. Conventional integrated methanol production concept. This production concept involves integrating the gasification, gas cleaning and methanol synthesis processes into a new central processing plant.
- B. Advanced integrated methanol production concept. This production system involves a new barge-mounted central processing plant concept. The advantages of such a concept might include reduction of feedstock transportation distance and plant construction and site preparation costs.
- C. Conventional dispersed methanol production concept. This concept involves the dispersed gasifier operation to produce medium-Btu gas interconnecting with a new pipeline system to a new methanol facility.
- D. Advanced dispersed methanol production concept. This concept involves the dispersed gasifier operation and further production of SNG in the field. The SNG produced is then transported to an existing methanol production facility via existing pipeline system.

Based on preliminary system analyses, production concept A is selected for process configuration development. The exclusion of other production concepts are based on the following reasons:

- The production concept B is considered a novel shipbuilding and plant engineering design undertaking. It is not anticipated that such a production concept will become economically attractive in the U.S. before 1990.

Figure 3.1 Alternative Biomass to Methanol Production Concepts

- The production concept C, which is based on the economic transport of synthesis gas, is a site-specific concept and requires detailed pipeline transportation study and is beyond the scope of our current study.
- The production concept D, which appears to have economic advantages based upon use of existing pipeline and methanol facilities is significantly dependent upon the technological advancement of synthesis gas methanation processes, and is beyond the scope of our current study.

3.2 DEVELOPMENT OF INTEGRATED CONCEPTUAL PROCESS CONFIGURATIONS

The development of an integrated biomass to methanol process can start with the evaluation of process configurations synthesized from a group of individual process elements. The basic processing steps utilized in the conventional methanol technology consists of: (a) gasification for synthesis gas production; (b) synthesis gas cleaning and conditioning; and (c) methanol conversion from synthesis gas.

3.2.1 Preliminary Process Screening

A screening analysis of each of the above mentioned processing steps shows that various process alternatives exist, as follows (1,2):

- Gasification Step
 1. Gasification processes which produce a synthesis gas with a H_2/CO ratio of less than 2
 2. Gasification processes which produce a synthesis gas with a H_2/CO ratio equal to 2.
- Synthesis Gas Cleaning and Conditioning Step
 1. With or without CO shift conversion
 2. With or without CO_2 removal
 3. With or without H_2S removal.

● Methanol Conversion Step

1. Methanol synthesis loop with recycle to achieve complete conversion
2. Once-through methanol synthesis converter achieving partial conversion.

Based on the above analyses, four basic process configurations can be developed:

1. Synthesis gas directly produced from a biomass gasifier with a H_2/CO ratio of less than 2 is passed to a once-through methanol synthesis converter for a partial methanol conversion.
2. Synthesis gas produced from a biomass gasifier with a H_2/CO ratio of less than 2 is shifted to a H_2/CO ratio of 2 and then enters a methanol synthesis loop with recycle to achieve a complete methanol conversion.
3. Synthesis gas produced from a biomass gasifier with a H_2/CO ratio equal to 2, is passed to a methanol synthesis loop with recycle to achieve a complete methanol conversion.
4. Synthesis gas produced directly from a biomass gasifier with a H_2/CO ratio of less than 2, is mixed with additional H_2 from external sources, to a H_2/CO ratio of 2, and then enters a methanol synthesis loop with recycle to achieve a complete methanol conversion.

These configurations are depicted in Figure 3.2. In process configuration 1, which is the simplest process, no CO shift and acid gas removal steps are included. The process configuration 2 is the most complete conversion process, and process configuration 3 which eliminates the CO shift step can be considered as a special case of configuration 2. The configuration 4 can be regarded as another alternative means to adjusting H_2/CO ratio.

Although the comparative advantages and disadvantages of each of these configurations depend upon the final economics associated with methanol production cost, it is nevertheless

Figure 3.2 Basic Alternative Biomass to Methanol Process Configurations

possible to quantify the relative advantages and limitations of various processes considered. For example, it is possible to quantify the conversion efficiency of biomass to methanol processes by using a carbon utilization efficiency. The carbon utilization efficiency is defined as the ratio of total moles of methanol produced to the moles of carbon originally contained in biomass. Comparison of the efficiencies associated with different process configurations establishes the potential usefulness of the processes as systems for production of methanol from biomass.

Table 3.1 compares the carbon utilization efficiencies for the four types of process configurations described above. These analyses are based upon the attainment of thermodynamic equilibrium in a system composed of the ideal gases formed during gasification of biomass. Table 3.1 shows the basic effect of temperature on the equilibrium concentrations of various gas components. As noted, the major effects of increasing temperature between 1267° and 2030°F are the reduction in concentration of CO₂, H₂, and CH₄, and the increase in concentrations of CO and H₂O. The increase of temperature beyond 1422°F essentially eliminates the formation of CH₄. It is also noted that the ratio of H₂ to CO decreases from 2.0 to 1.0 as temperature increases from 1267° to 2030°F. The stoichiometric H₂/CO ratio of 2 required for methanol synthesis corresponds to a gasification temperature of approximately 1267°F.

Based upon the carbon utilization efficiencies shown in Table 3.1 methanol production in configuration 1 appears to be at least 50 percent lower than that which can be obtained from a methanol synthesis configuration which employs recycle (configurations 2, 3, and 4). Furthermore, process configurations 2 and 3 will be limited thermodynamically to approximately 41 percent carbon utilization efficiency, while configuration 4 can

Table 3.1 Comparison of Carbon Utilization Efficiencies for
Selected Process Configurations
(Wood, 35% H₂O, Gasified with 95% Pure O₂)

Gasification Temperature (°F)	Moles of CO and H ₂ Per Mole of Wood C	Equilibrium Gas Composition (Mole Percent)					H ₂ :CO Ratio	Process Carbon Utilization Efficiency (Percent)			
		H ₂	H ₂ O	CH ₄	CO	CO ₂		1 ²	2 ³	3 ³	4 ³
1267	1.23	32.3	27.2	0.2	16.2	23.2	2.00	29	41	41	41
1422	1.20	29.3	30.2	0	17.5	21.7	1.67	27	40	--	45
1670	1.13	25.2	34.3	0	19.0	20.1	1.33	24	38	--	49
1800	1.10	23.4	36.2	0	19.6	19.6	1.19	23	37	--	50
2030	0.99	20.2	39.3	0	20.2	19.0	1.00	19	33	--	50

¹ Balance is N₂.

² Single pass methanol equilibrium conversion, assuming 227 °C and 50 atm.

³ Multipass methanol conversion, 100 percent conversion.

achieve higher efficiencies as gasification temperature continues to increase beyond 1267°F. The carbon efficiency calculated for process 4 employing this simple procedure does not include a penalty for H₂ addition and consequently is deceptively high.

It should be mentioned that the carbon utilization efficiency data presented so far assumes a complete thermodynamic equilibrium condition. In reality, many gasification processes never approach the true equilibrium condition. In particular, the product gas compositions of fixed-bed type gasification processes operated at low temperature cannot be predicted based on equilibrium considerations. As a matter of fact, the hypothetical gasification process which produces synthesis gas with a H₂/CO ratio of 2, has not been demonstrated. The intensive study in recent years to incorporate the catalyst into fluidized-bed gasification, may prove to be a viable approach to achieve equilibrium at low gasification temperature.

Based on the above analyses, process configuration 2 is selected for further conversion process analyses. The exclusion of other process configurations is based on the following reasons:

- The once-through methanol conversion process has exceedingly low carbon utilization efficiency.
- The process configuration 3, which assumes a hypothetical gasification process capable of producing synthesis gas with a H₂/CO of 2, is still in the early developmental stage.
- The process configuration 4, although it demonstrates a potential higher carbon utilization efficiency than process configuration 2, is beyond the scope of our current study. A proposed second phase study will cover the analyses of this configuration.

3.2.2 Individual Process Configuration

Gasification Process Configuration Analysis

Various thermochemical gasification systems are currently being developed for converting biomass into synthesis gas. These gasification processes can be categorized in terms of three basic considerations: (1) gasifier type, (2) type of oxidant used, and (3) catalytic or non-catalytic reaction. However, the commercially available gasification systems are low pressure, two-phase, oxygen blown, non-catalytic processes and may be further classified according to operating temperature. Figure 3.3 shows two alternative biomass gasification system configurations: (1) high temperature gasifier systems and (2) low temperature gasifier systems. In the subsequent process analysis, three relatively well-developed gasifiers and one hypothetical gasifier for converting biomass into a synthesis gas were selected for process analysis.

- Koppers-Totzek,
- Purox,
- Wellman-Galusha (oxygen-blown),
- Wellman-Galusha (air-blown).

Gas Conditioning and Preparation Process Configuration Analysis

Production of methanol from synthesis gases is favored when the primary reactants, H_2 and CO , are present in the stoichiometric ratio, that is, with two moles of H_2 present for each mole of CO . The carbon efficiency analysis presented above has demonstrated that adjustment of the synthesis gas H_2/CO ratio is required in a biomass-to-methanol system since the synthesis gas is deficient in H_2 . Removal of H_2S is

1. High Temperature Gasifier System

2. Low Temperature Gasifier System

Figure 3.3 Alternative Biomass Gasification Systems Configurations

considered an absolute requirement but is not a factor in configuration analysis due to the low level of H_2S encountered in biomass synthesis gases. Removal of large amounts of CO_2 from synthesis gas deficient in H_2 results in increased shift conversion and methanol conversion efficiencies and is consequently economically favored. The large amounts of CO_2 generated in gasification and shift conversion require two separate processing stages of approximately equal size of the hot carbonate absorption system selected for this application. The calculations involved in reaching these latter two conclusions are discussed in detail in Section 4 and in Appendix A of this report. These considerations indicate that separate CO_2 removal systems should follow the gasification and shift conversion process elements.

Gas conditioning and preparation process analysis may then be limited to the following configurations:

- G-1. Synthesis gas from a biomass gasifier is passed to a CO_2 absorber and then splits into two streams: a) a by-passed stream, and b) a high temperature CO shift convertor stream followed by a CO_2 absorber.
- G-2. Synthesis gas from a biomass gasifier is passed to a CO_2 absorber and then splits into two streams: a) a by-passed stream followed by a CO_2 absorber, and b) a high temperature CO shift convertor stream.
- G-3. Synthesis gas from a biomass gasifier is passed to a CO_2 absorber and then splits into two streams: a) a by-passed stream, and b) two high temperature CO shift convertors stream followed by a CO_2 absorber.
- G-4. Synthesis gas from a biomass gasifier is passed to a CO_2 absorber and then followed by a series of two high temperature CO shift convertor and another CO_2 absorber.

Figure 3.4 depicts the alternative gas conditioning process configurations. In the optimization procedure, the key parameters are (1) inlet H_2/CO ratio, r_1 , (2) the fraction

Figure 3.4 Gas Conditioning Process Configurations

Legend:

r = H_2/CO mole ratio

A = CO_2 mole percent

H.S = High temperature shift reactor

CO_2 = CO_2 absorber

of CO shift feed stream, k_{sp} , (3) desired outlet H_2/CO ratio, r_3 and (4) H_2O/CO ratio, and hence the steam consumption. Design calculations indicated that the CO_2 concentration level, A_1 , and A_2 , in the absorber synthesis gas exit stream should be approximately one mole percent. The details of the design calculation are described in Section 4 and Appendix A and involve balancing the cost of equipment with the cost of the addition of the steam necessary for conversion of CO. The results of the calculation, which are presented in Table 3.2, indicate that the straight-through shift conversion loop is the optimum processing configuration. Therefore, process configuration G-4 was selected for detailed process design and cost analysis.

Methanol Synthesis Configuration Analysis

All commercial methanol synthesis processes are essentially similar and require recycle for complete conversion. The copper based catalyst is subject to deactivation at temperatures above $300^{\circ}C$, and consequently control of maximum temperature is prominent in reactor design. In this study a cold gas quench multiple bed adiabatic methanol convertor, which is used in large ICI plants, is adopted in the methanol process development. The catalyst is contained in four beds placed in series in the convertor as shown in Fig. 3.2. Each bed is operated adiabatically, and thus the temperature of the gases increases along the length of the bed. Cold synthesis gas is injected between each catalyst bed to cool the reaction mixture, maintaining the temperature below a specified maximum. Gas space velocities are high, typically a few tens of thousands of volumes of synthesis gas per volume of catalyst per hour. After leaving the reactor, the gases are passed through a heat exchanger for energy recovery, and then into a water cooled condenser where water, products of side reactions, and methanol are condensed. A portion of the condenser exit gas stream is purged to allow removal of inerts and unconverted reactants, and the balance is recycled through the convertor.

Table 3.2 Summary of Gas Conditioning Process Sensitivity

k_{sp}	$C_{Equip} (\frac{M\$}{yr})$	$C_{Cat} (\frac{M\$}{yr})$	Steam Cost ($\frac{M\$}{yr}$)	Total Cost ($\frac{M\$}{yr}$)
1.0	34.8	3.5	48.5	86.9
0.75	31.0	1.77	63.5	96.3
0.65	24.6	1.46	94.6	120.7

REFERENCES (Section 3)

- (1) Catalytic Associates, Inc., Evaluation of Sulfur - Tolerate Catalytic Processes for Producing Peak - Sharing Alcohol Fuels. EPRI Report AF-687, Prepared for The Electric Power Research Institute, February 1978.
- (2) S. Strelzoff, "Methanol: It's Technology and Economics". CEP Symposium, Methanol Technology and Economics, No. 98, Vol. 66, 1977.

4. PROCESS OPTIMIZATION AND SENSITIVITY ANALYSES

In this section, detailed process optimization and sensitivity analyses results are presented. In carrying out the analyses, a series of conversion process models and system algorithms were developed. These detailed models, which represent the behavior of individual process elements, have been combined as necessary to allow completion of the following tasks:

- Gasification process analysis
- Gas conditioning and preparation process analysis
- Methanol synthesis process analysis
- Over-all process sensitivity analysis
- Selection of baseline processes

A baseline process is one in which representative values of all process variables have been selected and which may be subjected to extensive economic analysis.

4.1 GASIFICATION PROCESS ANALYSIS

In this analysis, four commercially available gasifiers were selected for detailed comparative gasification analyses. These gasifiers are:

- Koppers-Totzek,
- Purox,
- Wellman-Galusha (oxygen-blown)
- Wellman-Galusha (air-blown)

The Purox gasifier, designed to gasify refuse, is considered to be easily adaptable to a biomass feed, since the major constituents of refuse (paper, food wastes and yard wastes), are very similar to biomass. The Wellman-Galusha gasifier,

commercially used for coal, has been operated successfully with biomass (wood with 35 percent moisture). The K-T gasifier evidently has not been operated with a wood feed. Commercial experience for the operation of other gasifiers with a biomass feed are unavailable. However, the above four gasifiers are considered reasonably representative of those gasifiers which have been proven commercially and have been shown to be adaptable to a biomass feed.

4.1.1 Product Gas Characteristics

The yield and compositions of the product synthesis gas from the four gasifiers are summarized in Table 4.1. For the fixed-bed gasifiers, Wellman-Galusha and Purox, the synthesis gas contains a spectrum of hydrocarbons from methane to oil and tars from the volatilization zone, in addition to the gasification products from the steam-oxygen zone (i.e., H_2 , CO and CO_2). In these gasifiers, the oil and tars are recovered and recycled to extinction. In the entrained-bed Koppers-Totzek gasifier, the gas leaves at a higher temperature ($1800^{\circ}F$) and contains insignificant amounts of methane (0.3 percent). According to the biomass gasification data presented by Koppers-Totzek, no hydrocarbons heavier than methane are produced.

The data presented in Table 4.1 for the K-T and the Wellman-Galusha gasifiers were calculated from data furnished by the vendors. No such data were available for the Purox gasifier, and the data presented were estimated using SAI's gasification model (see appendix A), based on data for refuse^(1,2). The gas yield per dry weight of wood was assumed to be the same as the yield from the dry weight of organic material in the refuse feed. The oxygen requirements and the product gas composition for a refuse feed were modified to reflect the fact that the biomass feed (wood) contains little

Table 4.1 Operational Characteristics of Selected Gasifiers with a Wood Feed

Mole % (Dry Basis)	Purox		Koppers-Totzek		Wellman-Galusha (Oxygen Blown)		Wellman-Galusha (Air Blown)	
	Generator Gas	After Acid Gas Removal	Generator Gas	After Acid Gas Removal	Generator Gas	After Acid Gas Removal	Generator Gas	After Acid Gas Removal
CO	41.9	51.7	44.4	54.9	44.4	55.5	25.0	27.2
CO ₂	19.0	-	19.1	-	20.0	-	8.0	-
H ₂	28.9	35.7	36.1	44.6	30.2	37.7	12.7	13.8
CH ₄ +	10.1	12.5	0.3	0.3	4.0	5.0	3.0	3.3
N ₂	0.1	0.1	0.1	0.2	1.4	1.8	51.3	55.7
H ₂ S	nil	-	nil	-	nil	-	nil	-
Total	100	100	100	100	100	100	100	100
Total SCF/lb dry wood	18.91	15.32	23.11	18.69	20.91	17.94	39.63	36.46
SCF of H ₂ + CO per lb of dry wood	13.39	-	18.60	-	15.59	-	14.94	-
H ₂ /CO	-	0.691	-	0.812	-	0.679	-	0.507
CO/CO ₂	2.21	-	2.32	-	2.22	-	3.13	-
Tars and oils lb/lb dry wood	0.03	-	nil	-	0.03	-	0.03	-
Oxygen, lb/lb dry wood	0.30	-	0.56	-	0.52	-	-	-
Steam lb/lb dry wood	0	-	0.026	-	0.41	-	0.41	-

ash and none of the metal-glass materials that refuse contains. When the Purox gasifier is operated with a refuse feed (which typically contains 15 percent of inorganic materials), enough heat must be generated at the bottom of the gasifier to "slag" the inorganic materials (i.e., heat them to $\sim 3000^{\circ}\text{F}$). Since this is not necessary with a wood feed, less organic material must be burned, and hence, less oxygen is required. The result is an increase in the amount of CO and H_2 relative to the amount of CO_2 and H_2O in the product gas.

Table 4.1 shows the composition both before and after removal of the acid gas (mainly CO_2 in this case). The resulting synthesis gases for all gasifiers do not contain the desired $\text{H}_2:\text{CO}$ ratio of 2. Indeed, it is less than unity. Also, the Purox and the Wellman-Galusha gases contain appreciable amounts of methane and higher hydrocarbons, especially the former gasifier. The presence of these materials reflect the fact that these gasifiers were designed to produce an intermediate Btu gas. For a synthesis gas, these species are undesirable since the carbon and hydrogen they contain are unavailable for conversion to methanol without added, expensive gas cleaning steps.

The Purox gas has the highest hydrocarbon content, and this is a reflection of its relatively low requirement for oxygen. The Wellman-Galusha gasifiers require considerably more oxygen, primarily used for heating the steam (by combustion) and oxidatively converting the hydrocarbons to CO and hydrogen. The K-T gasifier requires slightly more oxygen, primarily to convert all the hydrocarbons and to raise the temperature of the gas to 1800°F . It may be noted that the K-T gasifier was originally developed to produce a synthesis gas from coal.

One of the more important figures of merit for the gasifiers is the yield of synthesis gas, moles of H_2 and CO , per unit weight of wood. Table 4.1 shows that by this measure

the Koppers-Totzek ranks the highest, whereas the Purox gasifier ranks the lowest and the Wellman-Galusha gasifiers are intermediate. Although the air-blown Wellman-Galusha gasifier produces a good yield of H_2 and CO , the gas contains a large amount of nitrogen which makes it unsuitable for methanol synthesis.

4.1.2 Gasification Energy Efficiency

From the point of view of energy utilization, the Koppers-Totzek gasifier also ranks well. Table 4.2 shows the steam production and consumption for the four gasifiers. The Wellman-Galusha gasifier produces all of its steam requirement from the cooling of the gasifier's walls. The Purox neither consumes nor produces any usable steam. Because of the high temperature of its product gases, the Koppers-Totzek gasifier produces a significant quantity of steam, most of it at 900 psig (532°F). A small amount of steam (at 25 psig) is consumed by the K-T gasifier. The value of recovering the heat in this steam depends on the ability of the remainder of the methanol conversion process to utilize it effectively.

Table 4.3 is a comparison of the energy efficiency of the four gasifiers. The efficiencies are considered in three different ways. The first is the ratio of the heating value of the syntheses gas to that of the dry wood. As expected from Table 4.1, the K-T gasifier ranks the best. The second measure of efficiency includes the heating value of the hydrocarbons. By this measure the Purox gasifier ranks highest and confirms its high performance as a producer of an intermediate Btu gas.*

*However, if the energy required to produce the required oxygen were accounted for, the air-blown Wellman-Galusha gasifier would rank highest for this type of application

Table 4.2 Comparison of Steam Production and Consumption of Four Gasifiers

	<u>Eurox</u>	<u>Koppers-Totzek</u>	<u>(oxygen blown)</u> <u>Wellman-Galusha</u>	<u>(air blown)</u> <u>Wellman-Galusha</u>
Off-gas temperature, °F	290-400	1800	279	248
HP steam recovered, T/T wood ^{1/}	0	0.895 ^{2/}	0	0
Jacket steam recovered, T/T wood ^{1/}	0	0.368 ^{3/}	0.41 ^{4/}	0.41 ^{4/}
Steam used, T/T wood ^{1/}	0	0.026 ^{3/}	0.41 ^{4/}	0.41 ^{4/}
Net steam export, T/T wood ^{1/}	0	1.237	0	0
Net waste heat recovery, MMBtu/T wood ^{1/}	0	2.93	0	0

1/ on dry wood basis

2/ 900 psig saturated steam

3/ 25 psig saturated steam

4/ 0 psig

Table 4.3 Comparison of Gasification Energy Efficiency (First Law)

		(oxygen blown)	(air blown)
	<u>Purox</u>	<u>Koppers-Totzek</u>	<u>Wellman-Galusha</u>
E_1^a , CO and H ₂ heating efficiency, %	53.6	74.6	62.6
E_2^a , Total gas heating efficiency, %	77.5	75.3	72.9
E_3^a , Process efficiency, %	77.5	83.0	72.9
E_4 , Process efficiency, %	75.1	78.3	69.0

where:

$$E_1 = \frac{\text{Heating value of H}_2 \text{ Plus CO produced}}{\text{Heating value of biomass}}$$

$$E_2 = \frac{\text{Heating value of H}_2, \text{CO and C}_1 + \text{C}_2 \text{ produced}}{\text{Heating value of biomass}}$$

$$E_3 = \frac{\text{Heating value of H}_2, \text{CO, C}_1 + \text{C}_2 \pm \text{net steam exported}}{\text{Heating value of biomass}}$$

a = efficiencies do not include energy consumed in making O₂.

$$E_4 = \frac{\text{Heating value of H}_2, \text{CO, C}_1 + \text{C}_2 \pm \text{net steam exported}}{\text{Heating value of biomass plus energy consumed in making O}_2}$$

The third measure includes the energy contained in any steam which can be exported from the gasifier. In this case the K-T gasifier ranks highest. It should be noted that this evaluation has not included consideration of the energy required to produce the oxygen necessary for gasification. The last efficiency takes into account the energy consumed in making the oxygen for the gasifiers.

On the basis of the analysis presented above, the K-T gasifier ranks highest on both the basis of yield of synthesis gas and overall energy conservation. However, the gasifier is more expensive. For this and other reasons, all the gasifiers should be considered in a complete biomass-to-methanol conversion process and economic analysis. Without investigating many of the possible technical and economic trade-offs, it is premature at this point to decide which gasifier will be the best for methanol synthesis.

4.2 GAS CONDITIONING AND PREPARATION PROCESS ANALYSIS

4.2.1 Introduction

Efficient utilization of the available carbon for methanol synthesis, protection of synthesis catalysts, and attention to environmental standards require that the synthesis gas be subjected to conditioning processes. The selection of gas conditioning process elements for detailed analysis and modeling was based upon evaluation of economic factors as well as considerations of process suitability and efficiency. The gas preparation process elements which required the detailed analysis presented below were:

- Acid gas removal
- Shift conversion of CO

Once the individual process models had been developed, an economic and design analysis which incorporated Guthrie's Rapid Costing Method(3) was employed to identify the major process parameters and to identify the optimum processing configuration. A detailed discussion of the construction of the models is presented in Appendix A. In this section, the essential features of the models are summarized and use of the models for process analysis is described.

4.2.2 Acid Gas Removal

Synthesis gases produced from biomass contain low concentrations of sulfur compounds and relatively high concentrations of carbon dioxide. Under these conditions removal of acid gases by absorption in carbonate solutions is favored over other conventional processes(4). The primary elements of a carbonate absorption system are a column in which acid gases in the synthesis gas stream are dissolved at elevated pressure into lean carbonate solution and a regenerating column in which acid gases are steam stripped from the rich carbonate solution at low pressure. The system is represented schematically in Fig. 4.1.

Operating conditions may be classified as those determined by the nature of the carbonate solution, and those which may remain as independent variables. The carbonate solution flow rate is established by the maximum carrying capacity of the solution and the total amount of gas to be absorbed. The operating temperature of the absorber is constrained by the solution properties to a range of 200° to 240°F. The outlet gas mole fraction of CO₂ and the absorber operating pressure remain as significant, independent variables associated with the absorber. The regenerator operating temperature and pressure are determined by the

LEGEND

- I Absorption Column
- II Energy Transfer System
- III Flash Chamber
- IV Partial Condenser
- V Regenerator Column

Figure 4.1 Diagram of Potassium Carbonate Acid Gas Removal Process

solution regeneration requirements, and remain in the ranges of 215° to 230°F, and 1.0 to 1.1 atmospheres, respectively. The flow rate of steam employed for stripping the CO₂ from solution remains as an independent variable associated with regenerator operation. The principle features of the model developed for the hot carbonate acid gas removal system are presented in Table 4.4. The model can be employed for equipment sizing given a set of operating conditions, or for the parametric analysis described in the following paragraph.

The results of a design calculation and sensitivity analysis will be discussed for the absorber operating conditions summarized in Table 4.5.

Firstly, the relation of column height and liquid solution flow rate to the specified degree of removal of CO₂ was established and is presented in Fig. 4.2. It is seen that as the exit mole fraction of CO₂ is decreased from 0.05 to 0.01 the column tray requirement increases by 100 percent while the carbonate solution flow rate requirement increases by 25 percent. Secondly, the sensitivity of the column height to operating pressure level was determined for several exit gas CO₂ concentrations. The results of this calculation are presented in Fig. 4.3. As demonstrated, the sensitivity to exit gas CO₂ mole fraction is evident. In addition, it is seen that the tray requirement is a strong function of pressure at the lower operating pressures. This dependence on pressure coupled with the enhanced reaction rate obtained in the shift convertor at high pressures dictates that absorber operating pressure should be in excess of 400 psia. At this level the tray requirement and absorber design is not a strong function of pressure. Hence, the analysis indicates that the major process variable associated with absorber operation is the specified exit mole fraction of CO₂ in the synthesis gas and that an absorber operating pressure of 30 atmospheres is favored.

Table 4.4 Characteristics and System Algorithms
of CO₂ Absorption Process Model

-
- Tray to tray calculation employing material and energy balances for each tray
 - CO₂ equilibrium solubility in potassium carbonate solutions employing a correlation fit to Bureau of Mines data(5)
 - Published tray efficiencies used for calculation of actual gas composition(6)
 - Iterative calculation of the number of trays based upon estimation of exit gas temperature
 - Prediction of column diameter based on correlations of carrying capacity dependence on liquid and gas flow rates
-

Table 4.5 Representative Absorber Operating Conditions

Inlet gas flow rate:	39.6	$\frac{\text{lb mole}}{\text{min}}$	
Inlet gas temperature:	200°F		
Inlet gas composition, mole fraction:	CO	.428	
	CO ₂	.193	
	H ₂	.292	
	CH ₄	.053	
	H ₂ O	.034	
Liquid Inlet temperature:	230°F		
Initial concentration of K ₂ CO ₃ in liquid, wt %:	25.0		

Legend:

operating pressure = 500 psig
inlet CO₂ mole fraction = 0.19
inlet gas flow rate = 39.6 lb mole/min
inlet gas temperature = 200°F
liquid inlet temperature = 230°F
liquid outlet temperature = 240°F

Figure 4.2 CO₂ Absorption Requirements

Figure 4.3 Dependence of Tray Requirement on Pressure

The model may be employed to demonstrate the importance of steam rate in regenerator design. A minimum steam rate is required for any specified regeneration load, and as this minimum is approached the regenerator tray requirement increases without limit. This effect is evident in the results of sample calculations employing varying steam rates. Tray requirement, for a specified regeneration load at varying values of the ratio of regenerator liquid to gas flow rate, is presented in Fig. 4.4. As the ratio of L/G approaches a value of 22 an inordinately tall column is required for regeneration. For this reason, a L/G of 16 will be chosen for use in design calculations. This value, and the steam stripping efficiency, which is equal to the standard cubic feet of CO₂ stripped per pound of feed steam, are in agreement with values reported in the literature⁽⁷⁾.

4.2.3 Shift Conversion Analysis

Production of methanol from synthesis gases is favored when the primary reactants, H₂ and CO, are present in the stoichiometric ratio, i.e., two to one. Synthesis gases produced from biomass are, however, deficient in H₂ and consequently require adjustment of the H₂/CO ratio. The process which has been chosen for use for this purpose is the shift conversion process. In this process, the reaction of water with carbon monoxide in the presence of a catalyst produces hydrogen and carbon dioxide. In this manner, hydrogen is produced at the expense of loss of carbon monoxide and a desired H₂/CO ratio can be obtained. Of the catalyst available for this process, a rugged (sulfur tolerant), high temperature catalyst is favored since complete conversion of CO is not required. Steam is required for this reaction and is

Inlet liquid temperature: 216°F
Outlet liquid temperature: 230°F
Inlet liquid flowrate: 433 lb mole/min
Outlet liquid flowrate: 442 lb mole/min
Inlet steam temperature: 230°F

Figure 4.4 Effect of Regenerator Liquid-Gas Ratio on Tray Requirement

added to the reaction gases upstream of the shift reactor. Since steam generation costs represent a significant expense, selection of the reactor inlet steam to CO ratio is based upon an equilibrium criterion which minimizes steam usage. A 50°F approach to equilibrium is generally suggested by a catalyst manufacturer for reactor design purposes. The shift convertor is modeled as an adiabatic plug flow reactor in which the temperature increases in the axial direction. The reaction rate increases with pressure due to mass transfer effects up to 20 atmospheres, at which point the rate becomes independent of pressure⁽⁸⁾. For this reason, and to insure capatability of the shift loop with the acid gas removal system, reactor operating pressure of 30 atmospheres will be employed.

Identification of the optimum operating conditions and process configuration requires analysis of the by-pass shift conversion loop represented schematically in Fig. 4.5. Generally, the H₂/CO ratio of the loop inlet stream is established by the gasifier characteristics, and the H₂/CO ratio of the loop outlet stream is established by the methanol synthesis requirements. When the shift loop inlet and outlet H₂/CO ratios have been specified, the required conversion of the loop feed stream CO is also established. When only a portion of the shift loop inlet stream is fed to the reactor, a greater fractional conversion of the CO in the reactor feed stream must be obtained, since the total CO conversion has been specified. Mass balances have been used to develop relationships between the fraction of the loop inlet stream fed to the reactor, represented by k_{sp} , and the loop inlet H₂/CO ratio, represented by r_1 , the loop outlet H₂/CO ratio, represented by r_4 , the reactor outlet H₂/CO ratio, represented by r_3 , and the reactor inlet steam/CO ratio, represented by s_4 . Specification of each of these variables and the reactor inlet temperature allows calculation of the reactor volume and outlet temperature through integration of the reactor differential mass and energy

Figure 4.5 Shift Conversion Process Flow Diagram

balances. The primary features of the reactor model are summarized in Table 4.6. Analysis of shift loop characteristics will be discussed for a loop inlet stream whose properties are presented in Table 4.7.

Firstly, results which locate the minimum acceptable reactor inlet temperature will be considered. Reactor volumes required to increase the H_2/CO ratio from $r_2=0.68$ to $r_4=2.0$ were calculated for two values of k_{sp} and a series of inlet temperatures. The results are presented in Fig. 4.6. To simplify the analysis, a constant inlet steam/ CO ratio of 3.0 was used in this set of calculations. The results demonstrate that use of a lower fraction of synthesis gas for reactor feed requires operation nearer to equilibrium conditions and results in lower reaction rates and higher reactor volumes. In both cases, the results indicate that a rate limitation is encountered when the reactor feed temperature is below $640^{\circ}F$ ($1100^{\circ}R$), and consequently this temperature was chosen as the reactor inlet temperature for all subsequent calculations.

Secondly, analysis which establishes the optimum fraction of the loop inlet stream to be fed to the reactor will be considered. The shift loop inlet stream treated in the analysis has the properties listed in Table 4.7, but the calculational algorithm summarized in Fig. 4.7 was employed in this design procedure. The relations required for the sequential calculations are presented graphically in Fig. 4.8. For specified values of r_2 , r_4 , and k_{sp} , the plots yield values for overall CO conversion, X_{CO} , reactor outlet H_2/CO ratio, r_3 , reactor inlet steam/ CO ratio, s_4 , and catalyst volume, V . For a given r_1 and r_4 , the optimum k_{sp} will be that value which yields the lowest total loop cost. This cost includes that associated with feed preheating, energy recovery, steam and catalyst usage and reactant conversion. For a feed

Table 4.6 Characteristics and System Algorithms
of CO Shift Reactor Model

- Simultaneous solution of material and energy balances for an adiabatic plug flow shift reactor using fourth order Runge-Kutta integration allows calculation of reactor volume and temperature and conversion profiles
- Rate form for disappearance of CO in shift reactor includes description of intraparticle mass transfer as well as reaction kinetic effects
- Steam addition required for reaction based upon a 50°F approach to equilibrium in the reactor outlet.
- Fraction of the synthesis gas stream passed through the shift reactor determined by minimization of cost: balance of reactor equipment cost and steam addition cost

Table 4.7 Representative Shift Convertor Loop Inlet Gas

Inlet gas flow rate: 39.6 lb mole/min

Inlet gas composition, mole fraction:	CO	0.428
	CO₂	0.193
	H₂	0.292
	CH₄	0.053
	H₂O	0.034

Pressure: 30 atmospheres

Figure 4.6 Catalyst Volume Required for Shift Conversion
 Inlet $\frac{H_2}{CO} = .69$, methanol synthesis feed $\frac{H_2}{CO} = 2.0$
 total synthesis gas inlet flow rate = $2391 \frac{\text{lb mole}}{\text{hr}}$
 K_{sp} = fraction of synthesis gas sent to shift reactor

Figure 4.7 CO Shift Conversion System Optimization Algorithms

Figure 4.8 Parametric Sensitivity of Shift Conversion System

stream with the properties listed in Table 4.7, the cost of adjusting the H_2/CO ratio from 0.68 to 2.0 was calculated for a series of values of k_{sp} . The results, presented in Table 4.8, indicate that a straight-through (no by-pass) shift-loop is economically favored.

The process analysis has shown that the operating pressure should be approximately 30 atmospheres and that the reactor inlet temperature should be $640^{\circ}F$ ($1100^{\circ}R$). In addition, the optimum process configuration was found to be one in which a shift convertor by-pass loop is not employed, but one in which the entire loop inlet stream is passed through the reactor. The major process parameters associated with the shift loop have been found to be the loop inlet and outlet H_2/CO ratios.

4.3 METHANOL SYNTHESIS AND PURIFICATION PROCESS ANALYSIS

The methanol synthesis process chosen for modeling is represented schematically in Fig. 4.9. Process units include heat exchangers for feed preheating and energy recovery, a heterogeneous gas-solid catalytic reactor, a condenser for crude methanol separation and distillation columns for production of chemical grade methanol. The reactor itself is modeled as a cold gas quench multiple-bed adiabatic convertor in which catalyst is contained in four beds placed in series in the convertor. The highly exothermic nature of the methanol synthesis reaction requires a mode of operation which maintains the gas temperature below the level at which catalyst damage is sustained. Gas space velocities are high, typically on the order of a few tens of thousands of volumes of synthesis gas per volume of catalyst per hour. After leaving the reactor, the gases are passed

Table 4.8 Summary of Gas Conditioning Process Sensitivity

k_{sp}	C_{Equip} ($\frac{M\$}{yr}$)	C_{Cat} ($\frac{M\$}{yr}$)	Steam Cost ($\frac{M\$}{yr}$)	Total Cost ($\frac{M\$}{yr}$)
1.0	34.8	3.5	48.5	86.9
0.75	31.0	1.77	63.5	96.3
0.65	24.6	1.46	94.6	120.7

Figure 4.9 Methanol Synthesis and Distillation in the Lurgi Low Pressure Methanol Synthesis Process

through heat exchangers for energy recovery, and then into a condenser where water, products of side reactions, and methanol are condensed. A portion of the condenser exit gas stream is purged to allow removal of inerts and unconverted reactants, and the balance is recycled through the convertor. Recycle of reactants and inerts after removal of products allows nearly complete conversion of CO in the synthesis gas feed even though conversion within the reactor itself is limited by equilibrium constraints.

The reactor, represented schematically in Fig. 4.10, is modeled using differential mass and energy balances. The primary features of the reactor modeling procedure are summarized in Table 4.9.

Specification of the inlet temperature, the maximum operating temperature (i.e., the temperature of the gas as it leaves each catalyst bed in the reactor), and the desired conversion of CO in the make-up gas stream allows calculation of the required catalyst volume, the recycle gas flow rate, and the fraction, q_L , of the reactor inlet gas stream diverted for quenching. However, the relation between CO conversion, temperature, and recycle gas flow rate is implicit, and an iterative solution procedure is required. In this calculation, a recycle constant, K_r , defined as equal to the fraction of CO in the condensor exit gas stream which is recycled, is employed to represent the variation in recycle gas flow rate. A value of K_r of 0 indicates no recycle while a value of 1.0 indicates complete recycle. Since the commercial low pressure methanol synthesis process is well established, the normally employed operating temperature and pressure conditions of 435° to 500°F and 50 atmospheres will be used in the process analysis and design calculations.

Legend:

- I - Feed Gas Compressor
- II - Methanol Synthesis Reactor
- III - Crude Methanol Separator

Figure 4.10 Methanol Synthesis Loop Process Diagram
(Multiple Adiabatic Reactor with Cold Gas Quench)

Table 4.9 Characteristics and System Algorithms
of Methanol Synthesis Reactor Model

- Simultaneous solution of material and energy balances in each bed of the adiabatic methanol synthesis reactor employing fourth order Runge-Kutta integration allows calculation of catalyst bed volumes and of temperature and conversion profiles
- Rate form employed for description of methanol production consistent with published methanol synthesis characteristics (10)
- Iterative calculation of the fraction of the reactor feed gas flow rate required for quenching the reaction gas mixture exiting each bed based upon specification of the temperature of the gas exiting each bed
- Iterative calculation of the recycle gas flow rate required to obtain a desired percent conversion of CO in the make-up gas stream
- Primary process parameters:
 - o temperature of gas exiting each bed within the reactor
 - o recycle gas flow rate
 - o percent conversion of CO in make up gas stream

Extensive process calculations identified CO conversion, inerts concentration level, CO₂ concentration level, and synthesis feed gas H₂/CO ratio as significant variables in determining methanol synthesis loop performance. Increased conversion of CO is obtained through recycle of larger fractions of the non-condensed reactants and inerts. Results of calculations demonstrating this effect are presented in Table 4.10 for a make-up gas stream containing a H₂/CO ratio of 2.0, 1.0 mole per cent CO₂ and 0.5 mole percent inerts. As expected, the CO conversion increases with the fraction of non-condensed products recycled, K_r , and the yield decreases as the conversion increases. The difficulties involved in reaching generalized conclusions, regarding system behavior in a recycle system characterized by interacting equilibrium and kinetic effects, is demonstrated by consideration of the effects of increasing inerts levels in a make-up gas stream with a H₂/CO ratio of 2.0. At each level of inerts concentration the make-up stream CO conversion is maintained at 97 percent, but different recycle rates are required to obtain this conversion. The results of design calculations are presented in Table 4.11, where F_0 and F_r are the make-up and recycle gas flow rates, respectively, and V/V_0 is the normalized reactor volume. The equilibrium constant of the primary methanol synthesis reaction increases with the square of the total number of moles present in the reaction mixture, and consequently increasing the inerts level in this case allows a decrease in the recycle flow rate while the CO conversion remained constant. This beneficial equilibrium effect is counterbalanced by a kinetic effect in which decreasing reactant concentrations result in lowered yield and increased reactor volume.

The analysis has established that CO conversion can be employed as the major process parameter characterizing methanol synthesis for a given make-up gas stream and that

Table 4.10 Dependence of CO Conversion of Recycle Rate

Percent CO Conversion	K_r	$V(\text{ft}^3)$	Space Velocity (hr^{-1})	Yield ($\frac{\text{lb mole}}{\text{hr ft}^3}$)
90	0.9856	1100	14049	1.17
95	0.9919	1330	10845	1.03
97	0.9940	1530	9090	0.92

Table 4.11 Dependence of Methanol Convertor Volume on Inerts Concentration

Mole percent inerts	K_r	F_r/F_o	V/V_o
1.0	0.9949	8.91	1.00
2.0	0.9932	8.42	1.26
3.0	0.9919	7.87	1.56

the inerts level should be maintained as low as possible to limit synthesis convertor costs. The role of CO₂ concentration levels, and of the H₂/CO ratio in the make-up gas stream will be discussed in the following section. The nature of the methanol separation and purification processes is such that optimizing of operating conditions in this area does not impact significantly on the over-all process.

4.4 OVER-ALL PROCESS SENSITIVITY ANALYSIS

4.4.1 Introduction

Selection of the optimum configuration and operating conditions for the integrated biomass-to-methanol plant would constitute an intractable mathematical problem if all combinations of all process variables were to be considered. It is not the intent of this program to produce a solution to this complex optimization problem, but rather to identify those process parameters of prime importance in a biomass-to-methanol system, and to locate the values of these parameters which form a reasonable baseline for economic analysis. Implementation of this approach involved division of the integrated process into process elements, analysis of the performance of these process elements for identification of the major process parameters, selection of operating conditions of those variables which are not significant to plant operation beyond the level of the process element, and, finally, analysis of the sensitivity of the integrated process to variations in the major process parameters. The discussion presented in this section will describe the following analyses:

- Configurational analysis
- Over-all systems sensitivity to variations in major process parameters

Preliminary analysis demonstrated that the individual gasification system, a hot carbonate acid gas removal system, a high temperature shift conversion system, and an ICI low pressure methanol synthesis system were the process elements which could be combined to form a representative biomass-to-methanol production process. Further investigation demonstrated that the ratio of H_2/CO and the CO_2 concentration level in the streams entering and leaving each process element, and the CO conversion obtained in the methanol convertor, were the major parameters which determined the performance of the individual process elements. An effort was made to maintain high material and energy efficiencies throughout the process through use of detailed reactor design and use of energy recovery systems.

4.4.2 Configurational Analysis

Few flow sheet arrangements of the four primary process elements are possible, due to the nature of the biomass gasification and methanol synthesis processes. The large amount of CO_2 produced in biomass gasification and shift conversion requires use of at least two stages of the hot carbonate system. Equipment sizes in the shift loop will be minimized if one stage of acid gas removal precedes the shift loop while the second stage must then follow, preceding the methanol loop. Detailed analysis of the shift loop demonstrated that a bypass arrangement is not favored and therefore the straight-through configuration will be employed. Methanol system analysis demonstrated that high inerts levels are not acceptable, and consequently the Wellman-Galusha and Purox gasification systems will require cryogenic removal of methane. The cryogenic unit requires low feed levels of CO_2 and therefore will be placed prior to the methanol loop following the second stage acid gas removal system.

4.4.3 Sensitivity to Major Process Parameters

The methanol synthesis requirements and the levels of CO₂ concentrations encountered does not vary significantly among the three gasification systems analyzed in this program and consequently the sensitivity analysis of the Koppers-Totzek system will be presented as representative of all systems. Relative costs were employed to represent the over-all system dependency on the variation of the following major process parameters:

- methanol loop CO conversion
- methanol loop inlet H₂/CO ratio
- methanol loop inlet CO₂ level

4.4.3.1 Sensitivity to Methanol Loop CO Conversion

The dependence of unit cost of methanol on methanol loop CO conversion will be discussed for a feed stream with a H₂/CO ratio of 2.0 and a CO₂ concentration level of one mole percent. As methanol loop CO conversion is increased, reactor, separation, and heat recovery costs increase while the combustion energy recoverable in the purge stream decreases. The increase in energy recoverable in the purge stream as CO conversion decreases from 97 percent to 90 percent amounts to 0.24 percent of the total system energy requirement. An economic analysis involving detailed costing of methanol loop equipment, inclusion of other capital costs, fixed capital charges and unit production costs, was employed to calculate the normalized unit costs presented in Table 4.12. The results demonstrate that optimum operation of the biomass-to-methanol system with the specified feed stream H₂/CO

Table 4.12 Dependence of Methanol Unit Cost on CO Conversion

CO Conversion (mole %)	90	95	97
Methanol Production (TPD)	496	524	535
Relative Unit Costs	1.047	1.003	1.000

ratio and CO₂ concentration level, is characterized by nearly complete conversion of the CO entering the methanol loop.

4.4.3.2 Sensitivity to Methanol Loop Inlet H₂/CO Ratio

The equilibrium characteristics of methanol synthesis are such that feed streams having a H₂/CO of 2.0 are favored. Since biomass synthesis gases are deficient in hydrogen, adjustment of the H₂/CO ratio through shift conversion directly affects three process elements. As the H₂/CO ratio is increased through shift conversion, additional CO₂ is produced and acid gas removal load increases, shift reactor costs increase, and methanol synthesis loop performances changes. An economic analysis involving calculation of capital cost effects for shift conversion, CO₂ removal, and methanol synthesis was conducted for a Koppers-Totzek synthesis gas upgraded to three H₂/CO ratios. A constant methanol production rate of 496 TPD was selected along with a CO₂ level of one mole percent. The results of the calculations are presented in Table 4.13.

Table 4.13 Dependence of Capital Costs on H₂/CO Ratio

H ₂ /CO Ratio	1.8	2.0	2.2
Shift reactor volume, ft ³	851	800	912
Total CO ₂ absorber tray requirement	140	144	148
Methanol reactor volume, ft ³	1210	1100	1180
Relative capital cost	1.0025	1.000	1.049

The results indicate that at this level of methanol production the H₂/CO ratio of 2.0 is favored. Mass balance considerations further support this conclusion, demonstrating that the maximum methanol conversion is obtained with a H₂/CO ratio of 2.0. This is due to the fact that when the H₂/CO ratio is less than 2.0, methanol production is limited by the amount of H₂ available and excess unreacted CO is purged from the methanol loop. Similar considerations apply when the H₂/CO ratio exceeds 2.0 and conversion to methanol is limited by the available CO. These considerations are a consequence of the hydrogen deficiency of biomass synthesis gas produced in conventional gasification systems.

4.4.3.3 Sensitivity to CO₂ Concentration Level

The presence of high levels of CO₂ concentrations in methanol reaction mixtures which do not contain an excess of H₂ has a deleterious effect on the equilibrium yield of methanol.

In addition, the rate of the primary methanol synthesis reaction may be decreased if the mole fraction of CO and H₂ are lowered by the inclusion of CO₂ in the reaction mixture. However, the contribution of the reverse shift conversion reaction and the reduced absorption costs associated with tolerance of elevated CO₂ levels in the synthesis gas, requires analysis of the sensitivity of the cost of methanol production to CO₂ concentration level. In the methanol loop, capital and operating costs required for a given methanol production rate will increase while capital and operating costs for CO₂ removal will decrease. Calculation of relative capital costs for production of 535 TPD of methanol for a methanol loop feed stream having a H₂/CO ratio of 2.0 at three levels of CO₂ concentration were performed and the results are presented in Table 4.14. The results indicate that CO₂ concentration levels greater than 2 percent, will impose unacceptable capital cost penalties.

Table 4.14 Dependence of CO₂ Absorption and Methanol Synthesis Capital Costs on CO₂ Level

Mole % CO ₂	1.0	2.0	5.0
Relative methanol loop costs	1.00	1.20	1.82
Relative absorption costs	1.70	0.71	0.47
Synthesis & absorption costs	1.00	1.002	1.24

The relation of these three sensitivities will be discussed in the following section where a base line process is selected based upon these results.

Comparison of alternative systems has been facilitated through selection of a baseline process, which incorporated all the process elements required for the production of methanol from a specified biomass feedstock. The selection of the baseline process is based upon the results of the preceding sections, in which process sensitivity to specification of the major operating variables was investigated. The baseline process may be characterized by the configuration of the process elements, and by the values assigned to the major process parameters. A series arrangement was selected for the baseline process configuration in which the gasifier will be followed by the number 1 acid gas removal system, the shift conversion process, the number 2 acid gas removal system, the cryogenic separation unit, and the methanol synthesis and purification system. The synthesis gas feed streams, to all process elements downstream of the gasifier, will be at thirty atmospheres pressure except, for the methanol synthesis loop feed stream which will be at 50 atmospheres pressure. The carbon dioxide concentration level of the synthesis gas streams exiting each acid gas removal system will be one mole percent, and the H_2/CO ratio of the methanol synthesis loop feed stream will be 2.0. The inerts concentration level entering the methanol loop will be less than one mole percent, and nearly complete ($> 97\%$) conversion of the CO fed to the methanol loop will be obtained. Once these operating conditions have been established, the description of the baseline process is completed by specification of the basis of the calculation. The complete system has been designed to supply all power requirements internally through biomass - fired generation of steam. Consequently, a biomass feed stream of 1000 oven dry tons per day, which includes the gasifier biomass feed and the steam generator biomass feed, was chosen as the basis of the baseline process design.

The development of an over-all system algorithm established a reasonable basis for calculations, which provided the information necessary for comparison of candidate systems. The over-all system algorithm employed is presented in Fig. 4.11. An iterative procedure is required as the process energy requirements associated with a given gasifier, can not be predicted in advance. The material and energy flows through the process elements are determined by the gasifier biomass feed rate, which can be adjusted to fit the 1000 TPD total feed requirement once the process energy requirement is known. The steam flow through the process elements is represented schematically in Fig. 4.12. Steam at pressure levels of 900, 450, and 40 psig is employed in the process. The 40 psig steam is required in the CO₂ removal and methanol distillation process elements, and is supplied by internal recovery of waste heat and by the exhaust of non-condensing turbines. A small amount of 450 psig steam is required in the shift loop, and is provided by extraction from a back-pressure turbine. The balance of the system compression and power requirement is provided by condensing turbines.

Figure 4.11 Overall System Design Algorithm

Figure 4.12 Over-all System Steam Flow Diagram

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5. DETAILED DESCRIPTION OF BASELINE PROCESS DESIGNS

In this section, comparative description of three baseline biomass to methanol processes is presented. The designs of these baseline processes are based upon the results of detailed process modeling and sensitivity analyses presented in Section 4. The three baseline processes are:

Process A - Koppers-Totzek gasification and low pressure ICI methanol synthesis

Process B - Purox gasification and low pressure ICI methanol synthesis

Process C - Wellman-Galusha gasification and low pressure ICI methanol synthesis.

5.1 OVERALL PROCESS CONFIGURATION AND MATERIAL BALANCE

Grass-roots biomass-to-methanol plants based on oxygen blown gasifiers of the Koppers-Totzek, Purox, and Wellman-Galusha designs integrated with low-pressure ICI methanol processes, are shown schematically on the block flow diagrams of Fig. 5.1, 5.2, and 5.3, respectively. This plant consumes 1000 TPD (dry) of wood biomass and produces fuel grade methanol. The material balance data for each process are shown also in Fig. 5.1 through 5.3. The main plant consists of feedstock preparation, oxygen production, gasification, compression, acid gas removal, CO shift, cryogenic separation, and methanol synthesis and storage. In addition to the main processing trains, the plant includes necessary offsites, and utility and environmental facilities. These shall include the raw water treating, steam generation, cooling water and effluent water treating equipment. A discussion of major processing steps is presented in Section 5.2 through Section 5.9.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	Total Biomass	Gasifier Biomass	Steam	Oxygen	Methanol Product	Total Slag/Ash	Mole Fraction	Raw Gas	Steam	CO ₂ Vent	Shift Feed	Boiler Feed Water	Steam Addition	Shift Effluent	Steam	CO ₂ Vent	MeOH Feed	Purge
Biomass, TPD (oven dry)	1008.0	804.5					CO	0.4101			0.5259			0.2624			0.3172	0.2089
Oxygen, TPD				450.0			CO ₂	0.1764		0.200	0.0100			0.1810		0.20	0.0100	0.2196
Methanol, TPD					430.2		H ₂	0.3337			0.4275			0.5268			0.6368	0.4711
Slag/Ash, TPD						3.00	CH ₄	0.0023			0.0025			0.0024			0.0029	0.0640
Steam, TPD			21.0				H ₂ O	0.0762	1.00	0.800	0.0316	1.00	1.00	0.0260	1.00	0.80	0.0315	0.0
							H ₂ -A	0.0013			0.0017			0.0014			0.0016	0.0359
							H ₂ B	Trace		Trace						Trace		
							MeOH											0.0005
							Total, Wet (lb mole/hr)	4671.2	3451.0	4010.5	3642.6	464.2	378.5	4402.5	3139.0	3872.5	3641.9	166.0
							Temp (°F)	105	230	218.1	640	50	460	200	230	218.1	240	90
							Pres (atm)	1.0	1.097	1.097	30	30	30	30	1.097	1.097	50.0	50.0
Sensible Heat MBTU/hr	1.71	1.38			4.78			2.570			15.6			5.521			5.314	0.074
HHV MBTU/hr	708.3	569.9			150.0			429.0			428.9			429.9			429.9	17.9

Figure 5.1 Koppers-Totzek Gasification and ICI Methanol Process Flow Diagram with Material Balance

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	Total Biomass	Gasifier Biomass	Steam	Oxygen	Methanol Product	Total Slag/Ash	Mole Fraction	Raw Gas	Steam	CO ₂ Vent	Shift Feed	Boiler Feed Water	Steam Addition	Shift Effluent	Steam	CO ₂ Vent	MeOH Feed	Purge
Biomass, TPD (oven dry)	1000.0	905.0					CO	0.387			0.496			0.230		0.316	0.316	
Oxygen, TPD				271.5			CO ₂	0.176		0.19	0.010			0.186		0.20	0.011	0.236
Methanol, TPD					349.2		H ₂	0.267			0.342			0.459		0.633	0.630	
Slag/Ash, TPD						3.0	CH ₄	0.093			0.119			0.098		0.003	0.003	
Steam, TPD			0				H ₂ O	0.076	1.00	0.81	0.032	1.00	1.00	0.026	1.00	0.80	0.036	
							H ₂ -A	0.001			0.001			0.001		0.001	0.001	0.030
							H ₂ S	Trace		Trace						Trace		
							MeOH											0.001
							Total, Wet (lb mole/hr)	4299.2	2975.6	3647.2	3357.4	487.8	305.0	4084.5	2997.4	3698.1	2965.1	131.0
							Temp (°F)	105	230	218	640	80	460	200	230	215	240	90
							Pres (atm)	1.0	1.097	1.097	30	30	30	30	1.097	1.097	50.0	50.0
Sensible Heat MBTU/hr	1.71	1.55			0.63			2.427			14.9			5.276		4.332	0.059	
EHV MBTU/hr	708.3	641.0			224.1			496.9			496.9			498.2		348.3	13.8	

Figure 5.2 Purox Gasification and ICI MeOH Synthesis Process Diagram

S-4

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	<u>Total Biomass</u>	<u>Gasifier Biomass</u>	<u>Steam</u>	<u>Oxygen</u>	<u>Methanol Product</u>	<u>Total Slag/Ash</u>	<u>Mole Fraction</u>	<u>Raw Gas</u>	<u>Steam</u>	<u>CO₂ Vent</u>	<u>Shift Feed</u>	<u>Boiler Feed Water</u>	<u>Steam Addition</u>	<u>Shift Effluent</u>	<u>Steam</u>	<u>CO₂ Vent</u>	<u>MeOH Feed</u>	<u>Purge</u>
Biomass, TPD (oven dry)	1000.0	737.5					CO	0.416			0.541			0.245			0.317	0.222
Oxygen, TPD				388.1			CO ₂	0.187		0.20	0.010			0.200		0.20	0.010	0.234
Methanol, TPD					331.7		H ₂	0.283			0.368			0.459			0.635	0.444
Slag/Ash, TPD						3.0	CH ₄	0.037			0.048			0.039			0.003	0.070
Steam, TPD			302.7				H ₂ O	0.076	1.00	0.80	0.032	1.00	1.00	0.026	1.00	0.80	0.034	
							N ₂ -A	0.001			0.001			0.001			0.001	0.030
							H ₂ S	Trace		Trace								
							MeOH									Trace		
							Total, Wet (lb mole/hr)	3824.1	2843.8	3510.3	2939.9	143.9	320.4	3639.9	2883.3	3561.4	2805.8	120.0
							Temp (°F)	105	230	218	640	80	460	200	230	218	240	90
							Pres (atm)	1.0	1.097	1.097	30	80	30	30	1.097	1.097	50.0	50.0
Sensible Heat MBTU/hr	1.71	1.26			0.60			2.134			12.773			4.519			4.096	0.054
HHV MBTU/hr	708.3	522.4			269.9			381.00			380.7			381.8			330.6	13.0

Figure 5.3 Wellman-Galusha Gasification and ICI MeOH Synthesis Process Diagram

5.2 FEEDSTOCK HANDLING AND PREPARATION

5.2.1 Koppers-Totzek Gasifier System

An extensive front end feedstock preparation system is required due to the entrained bed mechanism of the Koppers-Totzek gasifier. Figure 5.4 depicts the process arrangement of equipment in this system.(1)

Wood feedstock is received at the plant site by trucks to form a storage pile. Wood is reclaimed from this pile by front-end loader and delivered via a surge hopper and conveyor to a surge bin that feeds a hammer mill (hogger) which reduces the wood to a 70% minus 2 inch product. The hogged wood is conveyed to a surge bin which feeds four rotary drum dryers via belt feeders and conveyors. The drum dryers utilize air, heated by 200 psig saturated steam as the drying medium and reduce the moisture content of the wood from 52.4 percent to 10 percent. The dried wood is airveyed to two surge bins which in turn each feed three wind swept grinding mills where the wood is reduced to a minus 30 mesh product. Pulverizing and drying facilities are capable of producing a day's supply of minus 30 mesh, 10 percent moisture gasifier wood feedstock in 20 hours. The ground, dried wood is airveyed to a 4 hour capacity product bin and necessary cyclones, bag filters, and fans, are provided with the hogging, drying and pulverizing systems.

5.2.2 Purox and Wellman-Galusha Gasifier Systems

Since the Purox(2) and Wellman-Galusha(3) gasifiers are both of fixed bed design, the front end handling and preparation system will be essentially identical and will be simpler than that of the Koppers-Totzek system.

Figure 5.4 Koppers-Totzek Feedstock Preparation System

Wood feedstock is received at the plant site by trucks to form a storage pile. The major components of the system are front-end loader, surge bin, hammer mill, storage bin and conveyors.

Wood is reclaimed from this pile by front end loader and delivered via a surge hopper and conveyor to a surge bin which feeds a hammer mill (hogger) which reduces the wood to a minus 2 inch product. The hogged wood is conveyed to a surge bin that feeds to the gasifier and conveyors.

5.3 GASIFICATION AND GAS COOLING

5.3.1 Koppers-Totzek Gasification System

Figures 5.5 and 5.6 show the overall K-T gasification and gas cooling process scheme. Wood from the product bin is delivered via a Fuller-Kinyon type pneumatic (N₂) pump and a N₂ conveying system to two service bins, one located at each end of Koppers' 2-headed gasifier. Each service bin delivers via a rotary feeder to a feed bin which in turn feeds two screw conveyors. The four screw conveyors feed two pairs of burners located 180° apart and directed toward the center of the gasifier. Steam and preheated oxygen carry the wood through the burners into the gasifier.

The K-T gasifier is ellipsoidal in shape, with two heads shaped as truncated cones mounted on the ends, and a boiler mounted on the top which recovers heat from the hot effluent gases.

Figure 5.5 Koppers-Totzek Gasification Flow Diagram

Figure 5.6 Koppers-Totzek Gas Cleaning Flow Diagram

The two-headed gasifier has a set of two adjacent burners installed in each of the heads. Wood, steam, and oxygen are injected through the four burners. The gasifier shell has a double-walled construction, and the inner shell is protected from the high temperatures of gasification by a castable refractory lining.

The oxygen, steam, and wood react to convert the carbon and volatile matter in the wood to gaseous products. Since the reaction temperature is only about 1800°F, no slag will be formed, and virtually all the ash will be entrained with the gas. An ash quenching tank is provided to catch any ash that drops through the bottom gasifier outlet or from the bottom section of the waste heat boiler. Water is circulated through this tank to maintain a temperature below the boiling point, and continuous blowdown is pumped to the gas cleaning and cooling system clarifier.

Low pressure steam is produced in the jacket of the gasifier from waste heat which passes through the refractories and through the ducts below the gasifier and waste heat boiler.

The gas and entrained particles of ash pass through a waste heat boiler in which 1,000 psig saturated steam is produced. The gas leaves the waste heat boiler at about 450°F and enters a saturator-cooler where it is adiabatically saturated with the effluent water of disintegrators located down stream. Discharge water from the saturator-cooler flows to a clarifier.

Gas leaves the saturator-cooler and enters two series arranged Theisen type disintegrators in which entrained particulates are reduced to less than 0.002 grains per SCF (dry

basis). From there the gas passes through a mist eliminator for removal of entrained water droplets and then enters a final cooler in which it is indirectly cooled with plant cooling water. Condensate from the gas is removed from the base of the final cooler and pumped to the boiler feedwater system. The mist eliminator and final cooler are contained in the same vessel.

A special quick-closing, water-sealed valve is provided in the gas line after the final cooler so that the gasifier along with its associated gas cleaning and cooling equipment can be isolated from the equipment downstream. The valve also maintains a positive pressure on the system. The gas then enters a blower which boosts its pressure to about 15 psig and delivers it to a water-irrigated type electrostatic precipitator which reduces the particulate content to about 0.0001 grains per SCF (dry), to permit subsequent compression and catalytic conversion to methanol. A floating roof-type gas holder rides on the fan discharge line to dampen surges in gas production, to provide a constant 15 inches of water pressure, and to provide a means of regulating the speed of the downstream compressor.

Particulate laden waters from the ash quenching tank, the saturator-cooler, and the precipitator, are delivered to a clarifier. The clarified water is recirculated to the disintegrators and to the precipitator, while the underflow containing the removed solids is pumped to a vacuum filter. The filter cake is conveyed to a pit for disposal via front-end loader and truck. The gas cleaning-water handling system uses vented pumping tanks and a covered clarifier to prevent dissolved gases from being released to the atmosphere. All of these vents are exhausted to a flare stack, which is connected to the gas system to permit venting of gas during start-up and emergencies. Nitrogen is used for continuously venting the flare stack, and is also used on demand to automatically purge the gas processing equipment.

Clean gasifier effluent from the particulate removal equipment is cooled to approximately 105°F in a series of exchangers. Heat is recovered in the exchangers by generating saturated 25 psig steam. The effluent, after separation of condensate in the knockout drum, is further cooled with water to approximately 105°F in a trim cooler.

5.3.2 Purox Gasification System

Figure 5.7 shows the overall Purox gasification and gas cooling system.(2)

The major pieces of equipment and their purposes are as follows:

- Inclined feed conveyor and bin feeder
- Gasifier reactor to convert the wood to syngas
- Water quench tank to solidify and shatter the slag into a frit
- Water spray scrubber, with knock-out tank, to cool and remove char, tar, and ash from reactor off-gas
- Cooler for recycled scrubber water
- Wet electrostatic precipitator to remove fly ash, char and oil and tar mist from the cooled and scrubbed reactor off-gas
- Solid-liquid separator system to remove water from the char, oil, tar, and ash mixture which is recycled to the reactor.
- Condenser to further reduce moisture content
- Combustor flare for emergency disposal of the synthesis gas

Figure 5.7 Train of Equipment for Purox Gasifier System

- Waste water treatment to condition water for acceptance into local sewage systems (required only if a Sanitation District does not allow high BOD discharge into sewage lines)

The Purox gasifier is an oxygen-blown, wet bottomed, vertical shaft furnace operated slightly above atmospheric pressure. Moist feedstock is introduced at the top of the bed.

Relatively pure oxygen is preheated and admitted through tuyeres into a combustion zone near the bottom of the furnace, maintaining a hearth temperature of 2900-3000°F. At this temperature, the ash generated is fused completely and flows to the bottom, forming a liquid seal. Wood-ash requires a fluxing agent to perform this function. Glass scrap serves well for this purpose and may be introduced along with the wood feed. Besides forming a seal, the slag also serves to coat the refractory lining of the furnace with a protective layer. As the slag collects, it overflows a weir and is quenched in a water tank, forming a glassy frit, which is scraped from the bottom by a drag conveyor.

In the partial combustion section of the bed, the descending tars, oils, and char are converted chiefly to CO, H₂, and CO₂. The rising hot gases pyrolyze and dry the feed in the upper sections of the bed, and filter out most of the particulates and oils formed.

Approximately 3 weight percent of the feed is converted to an oil mist which exits with the gas. It is estimated that 10 percent of the ash introduced in the wood feed is entrained. The oil and ash removed in the gas cleaning train are recycled to the furnace.

5.3.3 Wellman-Galusha Gasification System

The overall gasification and gas cooling system design for the Wellman-Galusha system is identical to that of the Purox system (Fig. 5.7) because of the great similarity of fixed-bed gasifier mechanism and product characteristics. Figure 5.8 shows the detailed Wellman-Galusha agitated gasifier design.

The gasifier itself is water-jacketed. Water in the jacket completely surrounds the gasifier and also covers the top. The inner wall of the gasifier is steel plate and does not require a refractory lining. The agitator has a revolving horizontal arm which also spirals vertically below the surface of the wood bed to retard channeling and maintain a uniform fuel bed. The agitator arm and its vertical drive shaft are made of water-cooled heavy steel tubing. The arm can be revolved at varying speeds, and its position within the fuel bed may be changed as desired for different feedstocks and operating rates. A revolving step-type grate, which distributes the air-stream blast into the wood bed and forces the ash formed into the ash bin, is mounted eccentrically at the bottom of the gasifier on a center post.

Sized wood feedstock is fed into an elevated bin from which it flows into the feeding compartment by gravity. The feeding compartment continuously feeds the wood into the gasifier by gravity through the vertical feed pipes. Four slide valves control the flow of wood into and out of the feeding compartment. The upper valves are always closed except when refilling for brief intervals; and, the lower valves are always open except when refilling. Continuous flow of wood into the gasifier is highly desirable because it assists in maintaining the wood bed and gas quality in a stabilized condition.

A blower supplies the oxygen required for gasification. Oxygen is passed over the top of the water in the jacket, and,

Figure 5.8 Wellman-Galusha Agitated Gasifier

Source: Dravo Corporation, "Handbook of Gasifiers and Gas Treatment Systems", 1976.

as it does, it picks up steam required for the blast. Saturation of the blast is regulated by adjusting the jacket water temperature, estimated at approximately 359°F as it leaves the gasifier.

5.4 ACID GAS REMOVAL

The acid gas removal systems employ a hot potassium carbonate process similar to the Benfield process(4). Figure 5.9 depicts the basic process configuration suitable for use in all three baseline process systems. Tables 5.1 through 5.6 present the material and energy flow information for the two CO₂ removal systems required for each of the baseline processes A., B., and C., respectively.

Both the absorber and regenerator operate at a temperature of about 230°F. The recommended maximum practical operating temperature is 280°F. Synthesis gas to be purified is introduced into the absorber below a packed section. As it flows upward through the column, it is contacted with lean carbonate solution flowing counter-currently downward. Purified gas is collected at the absorber top, and rich carbonate solution is withdrawn at the base of the absorber. The rich solvent from the bottom of the absorber flows to the flash drum where some of the dissolved gases flash off. The rich carbonate solution from the flash drum flows to the top of the regenerator, where the balance of the absorbed CO₂ is stripped from the solution.

The rich carbonate solution is regenerated while passing downward through the second tower against a rising flow of steam. Direct process steam and/or the reboiler vapors are used as the stripping media. Steam is condensed and separated from the regenerated acid gas and refluxed to the stripper.

LEGEND

- I Absorption Column
- II Energy Transfer System
- III Flash Chamber
- IV Partial Condenser
- V Regenerator Column

Figure 5.9 Diagram of Potassium Carbonate Acid Gas Removal Process

Table 5.1 Material Balance for No.1 CO₂ Removal, Koppers-Totzek System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.432					0.526
CO ₂	0.186				0.196	0.010
H ₂	0.352					0.428
CH ₄	0.003					0.004
H ₂ O	0.026	0.946	0.931	1.00	0.804	0.031
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	4430.3	52013	52013	3251.0	4010.5	3642.6
Temp. (°F)	200	230	242	230	218	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	0.0	24.092	23.332	0.489	0.149	0.770

Table 5.2 Material Balance: No.2 CO₂ Removal, Koppers-Totzek System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.262					0.317
CO ₂	0.181				0.189	0.010
H ₂	0.527					0.637
CH ₄	0.003					0.003
H ₂ O	0.026	0.946	0.931	1.00	0.811	0.031
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	4402.5	50220	50220	3139.0	3872.5	3641.9
Temp. (°F)	200	230	242	230	218	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	0.0	23.262	22.496	0.472	0.143	0.766

Table 5.3 Material Balance: No.1 CO₂ Removal, Purox System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.408					0.496
CO ₂	0.185				0.191	0.010
H ₂	0.282					0.342
CH ₄	0.098					0.119
H ₂ O	0.026	0.946	0.931	1.00	0.809	0.032
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	4078.6	47610	47610	2975.6	3647.2	3357.4
Temp. (°F)	200	230	242	230	218	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	0.0	22.053	21.319	0.447	0.135	0.735

Table 5.4 Material Balance: No.2 CO₂ Removal, Purox System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.230					0.279
CO ₂	0.186				0.197	0.010
H ₂	0.459					0.558
CH ₄	0.098					0.120
H ₂ O	0.026	0.946	0.931	1.00	0.803	0.032
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	4084.5	47954	47954	2997.4	3698.1	3357.5
Temp. (°F)	200	230	242	230	215	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	D.C	22.212	21.479	0.450	0.107	0.733

Table 5.5 Material Balance: No.1 CO₂ Removal, Wellman-Galusha System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.438					0.541
CO ₂	0.198				0.194	0.010
H ₂	0.298					0.368
CH ₄	0.039					0.048
H ₂ O	0.026	0.946	0.931	1.00	0.804	0.032
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	3627.8	45493	45493	2843.8	3510.3	2939.9
Temp. (°F)	200	230	242	230	218	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	0.0	21.072	20.442	0.427	0.130	0.630

Table 5.6 Material Balance: No.2 CO₂ Removal, Wellman-Galusha System
-Reference Figure 5.9

Stream No.	101	102	103	104	105	106
	Syn Gas Feed	Lean Carbonate Solution	Rich Carbonate Solution	Steam	CO ₂ Vent	Clean Syn Gas
Mole Fraction						
CO	0.245					0.303
CO ₂	0.200				0.196	0.010
H ₂	0.489					0.606
CH ₄	0.039					0.048
H ₂ O	0.026	0.946	0.931	1.00	0.804	0.032
N ₂ -A	0.001					0.001
CH ₃ OH						
K ₂ CO ₃		0.029	0.014			
KHCO ₃		0.025	0.055			
Total Flow (LB Mole/hr)	3639.9	46135	46135	2883.3	3561.4	2940.3
Temp. (°F)	200	230	242	230	218	230
Pres (atm)	30	30	30	1.097	1.097	30
Enthalpy Flow (MMBTU/hr)	0.0	21.370	20.742	0.433	0.132	0.628

5.5

CO SHIFT CONVERSION

The basic process flow diagram of the CO shift conversion design for all three baseline processes is shown in Fig. 5.10. Since the temperature of the synthesis gas after the acid gas removal unit is lower than the desired inlet temperature (640°F) for shift conversion, a preheater is incorporated in the system. The synthesis gas, after preheating and admixing with 450 psig saturated steam, is then introduced to the reactor in which the molar ratio of hydrogen to carbon monoxide is adjusted to 2:1. The reactor effluent exits at 800°F and passes through a preheater and waste heat boiler for generating 450 psig saturated steam. The exit syngas gas temperature is estimated to be 200°F. Table 5.7 summarizes the material balance data for the three baseline processes.

5.6

METHANOL SYNTHESIS CONVERSION

The flow diagram for methanol synthesis conversion is shown in Figure 5.11. The major processing equipment consists of a zinc oxide guard chamber, syn-gas compressors and the methanol synthesis unit(5). Methanol synthesis gas is delivered from the acid gas removal units at 450 psig and 230°F. The synthesis gas then flows from a preheater through the zinc oxide guard chamber for the removal of to remove traces of H₂S that may contaminate the methanol synthesis catalyst. Recycled gas is combined with the synthesis gas downstream of the guard chamber, and is fed to a methanol converter. The converter effluent is then sent to a methanol condenser. The two-phase mixture from the condenser is separated in a condensate knockout drum, where the gas flow is split into two streams. The bulk of the gas is compressed by a recycle gas compressor and returned to the synthesis gas preheater. The remaining gas from the condensate knockout drum is purged from the system in order to prevent the buildup of

Figure 5.10 Shift Conversion Loop Flow Diagram

Table 5.7 Shift Conversion Material Balances, Koppers-Totzek, Wellman-Galusha, and Purox Systems - Reference Figure 5.10

Stream No.	201			202		
	Syn Gas Feed			Steam Addition		
	K-T	W-G	Purox	K-T	W-G	Purox
Mole Fraction						
CO	0.526	0.541	0.496			
CO ₂	0.010	0.010	0.010			
H ₂	0.428	0.368	0.342			
CH ₄	0.003	0.048	0.119			
H ₂ O	0.032	0.032	0.032	1.00	1.00	1.00
N ₂ -A	0.001	0.001	0.001			
Total Flow (LB Mole/hr)	3642.6	2939.9	3357.4	842.7	764.3	792.8
Temp (°F)	230	230	230	460	460	460
Pres (atm)	30	30	30	30	30	30

Table 5.7 con't

Stream No.	203			204		
	Convertor Feed Stream			Boiler Feed Water		
	K-T	W-G	Purox	K-T	W-G	Purox
Mole Fraction						
CO	0.427	0.429	0.401			
CO ₂	0.008	0.008	0.008			
H ₂	0.347	0.292	0.277			
CH ₄	0.003	0.038	0.097			
H ₂ O	0.214	0.232	0.216	1.00	1.00	1.00
N ₂ -A	0.001	0.001	0.001			
Total Flow (LB Mole/hr)	4485.3	3704.2	4150.2	464.2	443.9	487.8
Temp (°F)	279	283	278	80	80	80
Pres (atm)	30	30	30	30	30	30

Table 5.7 con't

Stream No.	205			206		
	Syn Gas Effluent			Condensate Water		
	K-T	W-G	Purox	K-T	W-G	Purox
Mole Fraction						
CO	0.263	0.245	0.230			
CO ₂	0.181	0.200	0.186			
H ₂	0.526	0.489	0.459			
CH ₄	0.003	0.039	0.098			
H ₂ O	0.026	0.026	0.026	1.00	1.00	1.00
N ₂ -A	0.001	0.001	0.001			
Total Flow (LB Mole/hr)	4402.5	3639.9	4084.5	82.8	64.3	65.7
Temp (°F)	200	200	200	200	200	200
Pres (atm)	30	30	30	30	30	30

Table 5.7 con't

Stream No.	207			208		
	Steam Generated			Steam Addition		
	K-T	W-G	Purox	K-T	W-G	Purox
Mole Fraction						
CO						
CO ₂						
H ₂						
CH ₄						
H ₂ O	1.00	1.00	1.00	1.00	1.00	1.00
N ₂ -A						
Total Flow (LB Mole/hr)	464.2	443.9	487.8	378.5	320.4	305.0
Temp (°F)	460	460	460	460	460	460
Pres (atm)	30	30	30	30	30	30

Legend:

- I ZnO Guard Bed
- II Methanol Converter
- III Crude Methanol Separator

Figure 5.11 Methanol Synthesis Loop Flow Diagram

inerts within the synthesis unit. The liquid methanol (methanol fuel) phase in the condensate knockout drum containing water and dissolved inerts is flashed to a flash drum where the two phase mixture is separated. Tables 5.8, 5.9, and 5.10 summarize the methanol loop material balance data for the K-T, W-G, and Purox baseline processes, respectively.

5.7 STEAM GENERATION PLANT

A portion of the steam required for the process plant is generated within the various process units by heat recovery at two pressure levels: 25 psig and 450 psig. High pressure steam (900 psig and 900°F) which powers the air separation, cryogenic separation, and other syn-gas compressors, is generated in wood-fired utility steam boilers. Waste heat recovered from the process streams is utilized for saturated steam generation, superheating steam, and preheating BFW, as represented in Fig. 5.12. The steam and power requirements and steam and energy balance for the process plant complex are summarized in Table 5.11 to Table 5.16 for baseline processes A, B, and C, respectively.

5.8 OXYGEN PLANT

The oxygen plant consists of three parts; one air compressor, one air separation plant, and one oxygen blower⁽⁴⁾. Atmospheric air is compressed to 96 psig in a two stage centrifugal machine, and the heat of compression is rejected to air in an interchange airfan cooler. The horsepower required by the air feed compressor is supplied by a steam turbine. The compressed air is processed in an air separation unit which produces 98 percent pure oxygen. Liquid oxygen storage of approximately three days of rated capacity is

Table 5.8 Methanol Synthesis Loop Material Balance, Koppers-Totzek System,
Reference Figure 5.11

Stream No.	401	402	403	404	405	406	407
Mole Fraction							
CO	0.318	0.2217	0.2000	0.2090	0.2090	0.2090	
CO ₂	0.010	0.1950	0.2101	0.2195	0.2195	0.2195	
H ₂	0.637	0.4906	0.4512	0.4714	0.4714	0.4714	
CH ₄	0.003	0.0568	0.0612	0.0639	0.0639	0.0639	
H ₂ O	0.031	0.0037	0.0040				0.0927
N ₂ -A	0.001	0.0318	0.0343	0.0358	0.0358	0.0358	
CH ₃ OH		0.0004	0.0392	0.0004	0.0004	0.0004	0.9073
CH ₃ -O-CH ₃							
C ₂ H ₅ OH							
Total Flow Rate LB mole hr	3641.9	31165.0	28912.7	27677.8	27511.8	166.0	1234.9
Temp. (°F)	240.	440.	500.	100.	100.	100.	100.
Pres (atm)	50	50	50	50	50	50	50

Table 5.9 Methanol Synthesis Loop Material Balance, Wellman-Galusha System,
Reference Figure 5.11

Stream No.	401	402	403	404	405	406	407
Mole Fraction							
CO	0.3174	0.2341	0.2122	0.2223	0.2223	0.2223	
CO ₂	0.010	0.2059	0.2229	0.2337	0.2337	0.2337	
H ₂	0.6346	0.4676	0.4236	0.4440	0.4440	0.4440	
CH ₄	0.0030	0.0618	0.0669	0.0701	0.0701	0.0701	
H ₂ O	0.0337	0.0042	0.0046				0.0987
N ₂ -A	0.0013	0.0260	0.0282	0.0295	0.0295	0.0295	
CH ₃ OH		0.0004	0.0416	0.0004	0.0004	0.0004	0.9013
CH ₃ -O-CH ₃							
C ₂ H ₅ OH							
Total Flow Rate LB Mole hr	2805.8	22684.0	20956.4	19998.1	19878.1	120.0	958.3
Temp. (°F)	240.	440.	500.	100.	100.	100.	100.
Pres (atm)	50	50	50	50	50	50	50

Table 5.10 Methanol Synthesis Loop Material Balance, Purox System,
Reference Figure 5.11

Stream No.	401	402	403	404	405	406	407
Mole Fraction							
CO	0.3162	0.2270	0.2052	0.2148	0.2148	0.2148	
CO ₂	0.0113	0.2270	0.2450	0.2564	0.2564	0.2564	
H ₂	0.6324	0.4545	0.4110	0.4303	0.4303	0.4303	
CH ₄	0.0030	0.0599	0.0647	0.0677	0.0677	0.0677	
H ₂ O	0.0358	0.0043	0.0047				0.1045
N ₂ -A	0.0013	0.0269	0.0291	0.0304	0.0304	0.0304	
CH ₃ OH		0.0004	0.0402	0.0004	0.0004	0.0004	0.8955
CH ₃ -O-CH ₃							
C ₂ H ₅ OH							
Total Flow Rate LB mole hr	2965.1	24656.7	22838.1	21822.6	21691.6	131.0	1015.5
Temp. (°F)	240.	440.	500.	100.	100.	100.	100.
Pres (atm)	50	50	50	50	50	50	50

Figure 5.12 Overall System Steam Flow Diagram

Table 5.11 Steam and Power Requirements for Baseline Process A - Koppers-Totzek System

Steam Requirements

	<u>In</u>				<u>Out</u>			
<u>Pressure Level, psig</u>	900	450	25	5	900	450	25	5
<u>Steam, M lb/hr</u>								
Reactor Gasifier				2	60		25	
Turbine								
Condensing	47							
Non-condensing	99					7	92	
No 1 Hot Carbonate				59				
No 2 Hot Carbonate				56				
Shift Convertor		7						
<u>Power Requirement, hp</u>								
Gasification & Gas Cleaning					3220			
Syn Gas Compression					12340			
Oxygen Plant Compression					8170			
Methanol Recycle Compression					260			
Electricity Generation					720			
Total Horsepower					24710			

Table 5.12 Steam and Power Energy Balance - Baseline Process A -
Koppers-Totzek System

In:

<u>By-Product Heat Generation</u>	MM BTU/day
Methanol Purge Stream	280
Hydrocarbons from Gas Separation System	
Distillation By-Products	<u>210</u>
Sub-Total	490
<u>Biomass Combustion Heat</u>	
195 TPD	<u>2820</u>
Total	3310

Out:

Steam Generation

$2065 \times 10^3 \frac{\text{LB}}{\text{d}}$ steam at 900 psia & 900°F 2890

Gasifier Steam Superheating

$1450 \times 10^3 \frac{\text{LB}}{\text{d}}$ steam at 900 psia & 900°F 420
Total 3310

Table 5.13 Steam and Power Energy Balance for Baseline Process B -
Purox System

<u>Steam Requirements</u>									
	<u>In</u>					<u>Out</u>			
<u>Pressure Level, psig</u>	900	450	25	5		900	450	25	5
<u>Steam, M lb/hr</u>									
Reactor Gasifier									
Turbine									
Condensing	50								
Non-condensing	113						5	108	
No 1 Hot Carbonate				54					
No 2 Hot Carbonate				54					
Shift Convertor			5						
<u>Power Requirement, hp</u>									
Gasification & Gas Cleaning									3060
Syn Gas Compression									11200
Oxygen Plant Compression									4920
Methanol Recycle Compression									200
Cryogenic Separation									6910
Electricity Generation									560
Total Horsepower									26850

Table 5.14 Steam and Power Energy Balance - Baseline Process B -
Purox System

In:	MM BTU day
<u>By-Product Heat Generation</u>	
Methanol Purge Stream	210
Hydrocarbons from Gas Separation System	3140
Distillation By-Products	<u>170</u>
Sub-Total	3520
<u>Biomass Combustion Heat</u>	
95 TPD	<u>1960</u>
Total	5480
Out:	
<u>Steam Generation</u>	
$3910 \times 10^3 \frac{\text{LB}}{\text{d}}$ steam at 900 psia & 900°F	5480

Table 5.15 Steam and Power Requirements Balance for Baseline Process C -
Wellman-Galusha System

Steam Requirements

	<u>In</u>				<u>Out</u>			
<u>Pressure Level, psig</u>	900	450	25	5	900	450	25	5

Steam, M lb/hr

Reactor Gasifier				25				25
------------------	--	--	--	----	--	--	--	----

Turbine

Condensing	48							
Non-condensing	108					6	102	

No 1 Hot Carbonate				51				
No 2 Hot Carbonate				51				
Shift Convertor			6					

Power Requirement, hp

Gasification & Gas Cleaning	1500
Syn Gas Compression	10030
Oxygen Plant Compression	6960
Cryogenic Separation	6530
Methanol Recycle Compression	180
Electricity Generation	560
Total Horsepower	<u>25760</u>

Table 5.16 Steam and Power Energy Balance - Baseline Process C -
Wellman-Galusha Systems

In:	MM BTU d
<u>By-Product Heat Generation</u>	
Methanol Purge Stream	200
Hydrocarbons from Gas Separation System	1100
Distillation By-Products	<u>160</u>
Sub-Total	1460
<u>Biomass Combustion Heat</u>	
262 TPD	<u>3790</u>
Total	5250
Out:	
<u>Steam Generation</u>	
$3746 \times 10^3 \frac{\text{LB}}{\text{d}}$ Steam at 900 psia & 900°F	5250

provided. The air separation plant produces oxygen at 2 psig and 90°F and the oxygen is blown into gasifier. The oxygen plant compression requirement is supplied by a condensing type steam turbine. The inlet steam condition is 385 psig, 1000°F with back pressure at 2 1/2" Hg ab.

5.9 GENERAL AND SUPPORT FACILITIES

The general and support facilities provided for a complete biomass to methanol process are similar for all three baseline processes and include the following:

- Electrical supply and distribution
- Buildings
- Site development
- Fire protection
- Water supply system
- Security and communication
- Mobile equipment
- Cooling water piping distribution
- Steam distribution
- Sewer and drainage system

All the above items will be included for a complete plant. However, many of these facilities are site dependant items and therefore can not be specified at this time.

5.10 SUMMARY OF MATERIAL AND ENERGY BALANCE DATA FOR BASELINE PROCESSES

A comparison of the overall process efficiencies and flow rates for Baseline Processes A, B, and C are presented in Table 5.17. In each case a significant amount of biomass must be burned in order to provide the steam required for

Table 5.17 Comparison of Biomass to Methanol Processes

	Baseline Process A Koppers-Totzek	Baseline Process B Purox	Baseline Process C Wellman-Galusha
Biomass Input to Gasifier, TFD	805	905	738
Biomass Input to Boilers, TPD	195	95	262
Total Biomass Input, TPD	1000	1000	1000
Oxygen Requirement, TPD	450	272	388
Total System Water Requirement			
Methanol Production, TPD	430	349	332
Process Efficiency ⁽¹⁾ , %	49.4	40.0	38.1
<u>Heat and Steam Generated, MM BTU PD</u>			
Gasification	2370	0	0
Fuel Gas By-Products	490	3520	1416
Biomass Boilers	3315	1515	4454
<u>Large Steam Turbine Requirements, HP</u>			
Syn Gas and Cryogenic Compressor	15560	21170	18060
Oxygen Plant Compressor	8170	4920	6960
Methanol Recycle Compressor	260	200	180

$$(1) \text{ Process Efficiency} = \frac{\text{Heating Value of Methanol Product}}{\text{Total Heating Value of Biomass}}$$

power generation. In the Koppers-Totzek system a large amount of energy is recovered from the gasifier exit gases while in the Wellman-Galusha and Purox systems a large amount of energy is recovered through combustion of the methane produced in these gasifiers. As can be seen, the Koppers-Totzek gasification system would give the highest process efficiency (49.4%). The production of methane in the Wellman-Galusha and Purox gasification systems lowers the overall process carbon conversion and increases the process horsepower requirement through addition of cryogenic compressors. As a consequence the overall process efficiency of these systems will be significantly lower than that of the Koppers-Totzek system.

REFERENCES

1. Preliminary Engineering Study for Koppers Gasification Process to Produce Synthesis Gas from Wood for the Production of Methanol. Koppers Company, Inc. to Science Applications, Inc., August 11, 1978.
2. E.M. Wilson et al. "Engineering and Economic Analysis of Waste to Energy Systems". Prepared for EPA by the Ralph M. Parsons Co., Pasadena, California, June 1977.
3. "Preliminary Analysis of Wellman-Galusha Gasification Process to Produce Synthesis Gas from Wood". McDonald-Wellman Co. to Science Applications, Inc., August 14, 1978.
4. "Economic Studies of Coal Gasification Combined Cycle Systems for Electric Power Generation". EPRI AF-642. Prepared by Fluor Engineers and Constructors, Inc., Irvine, California, January 1978.
5. "Screening Evaluation Synthetic Liquid Fuels Manufacture". EPRI AF-523. Prepared by The Ralph M. Parsons Co., Pasadena, California, August 1977.

6. ECONOMIC ANALYSIS OF METHANOL PRODUCTION FROM BIOMASS

This section presents the economics of methanol production based on the detailed process analysis and designs derived in Section 5. A base case cost estimation is performed for each gasification technology.

The sensitivities of methanol production cost are next assessed in terms of feedstock price, conversion plant size, and financing method. Last, the base case costs are compared with methanol productions costs from conventional feedstocks.

6.1 PLANT CAPITAL INVESTMENT COSTS

6.1.1 Cost Data Sources

The capital costs are derived from published data with proper escalation, and from discussions with equipment suppliers. The capital costs of all major equipment, except the gasifiers, are estimated based on Guthrie's Cost Method (see Appendix B), and compared with published and vendor supplied data. The major data sources available in that analysis include the following:

<u>Equipment Item</u>	<u>Sources</u>
● gasifier -	
Purox	R.M. Parsons(1)
Koppers-Totzek	Koppers(2)
Wellman-Galusha	McDowell Wellman(3)
● Front end process	SAI, Guthrie(4)
● Shift conversion	SAI, Guthrie, C.F. Braun(5)
● Acid gas removal	SAI, Guthrie, R.M. Parsons

● Compressor	SAI, Guthrie
● Oxygen plant	Exxon-Chem Systems (6)
● Methanol synthesis	Exxon-Chem Systems, Guthrie
● Steam plant	SAI, Guthrie

6.1.2 Capital Investment Costs

Table 6.1 summarizes the capital costs for three baseline biomass to methanol processes. The capital costs are broken down into battery limit capital costs (BLCC), off-site costs, and working capital. Among the battery limits capital costs, the largest cost items are associated with the oxygen plant, gasifier, cryogenic separation, and methanol synthesis and purification. BLCC costs range from approximately 45 million for the Wellman-Galusha system to 76 million for the Koppers-Totzek system.

Since insufficient design data are available to directly estimate off-site costs, all off-site estimates are based on approximate facility designs. Among the off-site costs, the largest capital expenditure is associated with the steam power plant.

Working capital is required mostly for payments on feedstock purchases and arrangements for product sales, and on storage quantities maintained for both. In the analysis, working capital is assumed to be 10 percent of fixed investment (BLCC + off-sites). Estimated total investment costs for a 1000-TPD biomass to methanol plant range from 74 million for the Wellman-Galusha system to 113 million for the Koppers-Totzek system.

Table 6.1 Comparison of Capital Investment Costs
of Conceptual Biomass to Methanol Processes.
(1979 Dollars)

	Process A Koppers Totzek	Process B Purox	Process C Wellman Galusha
Total biomass feed, TPD (dry)	1000	1000	1000
Biomass feed to gasifier (dry)	805	905	738
Methanol production, TPD	430	350	330
Battery Limits Capital Cost (BLCC) MM\$			
Front end	14.54	3.38	2.86
Oxygen plant	9.42	6.84	8.56
Gasifier	37.04*	26.29	10.72
Gas cleaning and cooling	-	4.07	3.68
Gas compression	4.10	3.92	3.48
Shift conversion	0.28	0.28	0.25
Acid gas removal	1.80	1.85	1.73
Cryogenic separation	-	6.73	6.05
Methanol synthesis and purification	8.61	7.44	7.17
BLCC subtotal	75.79	60.80	44.50
Off-sites, MM\$			
Steam generation	5.84	3.68	7.05
Electricity generation	1.13	1.08	0.74
Water treating	0.43	0.68	0.65
Cooling towers	1.44	2.01	0.79
Storage and shipping	1.35	1.16	1.12
Utility distribution	1.54	2.39	2.31
Building and Structure	1.46	1.22	0.96
Site deveopment	0.64	0.62	0.48
Off-site subtotal	13.93	12.84	14.10
Subtotal BLCC and off-site	89.72	73.64	58.60
Contingencies and Engineering @ 15%	13.46	11.04	8.79
Fixed investment	103.18	112.00	67.39
Working capital @ 10%	10.31	8.47	6.74
TOTAL INVESTMENT COST	113.49	93.26	74.13

*Costs include gas cleaning and cooling

6.2 OPERATING AND MAINTENANCE COSTS

The biomass to methanol plant is assumed to operate on a continuous basis of 330 days per year with an annual shutdown period of 35 days for maintenance. The operating requirements, in addition to wood feedstock, will include a variety of process supplies and energy inputs. Tables 6.2-6.4 summarize the various operating and maintenance requirements for the three baseline processes (see Section 5.0). As pointed out in Section 5.1, the design philosophy of the baseline process is such that a minimum amount of materials and energy input from outside sources will be required. In these designs, water consumption has been reduced by means of recycling and use of cooling towers. Electricity requirements has also been reduced by use of waste steam and biomass generated steam. In order to be consistent, the following assumptions are made for operation and maintenance cost analysis:

6.2.1 Utility, Maintenance and Plant Overhead Costs

The following utility costs are used for the analysis:

<u>Item</u>	<u>Unit</u>	<u>1979 ¢/unit</u>
Electricity	kWh	2.5
Cooling water	kGal	5.0
Boiler feed water	kGal	80
Process water	kGal	50

The maintenance and plant overhead costs are assumed directly related to the plant investment as follows:

<u>Items</u>	<u>Cost Estimate</u>
Maintenance	4% of battery limits capital cost (BLCC)

Table 6.2 Annual Operating and Maintenance Costs
for Baseline Process A - Koppers-Totzek
Gasification(430 TPD Methanol)

Battery Limits Capital Costs*				87.16
Off-site Capital Costs*				16.02
Fixed Investment				103.18
Working Capital				10.31
Total Investment				113.49

<u>Raw Materials</u>	<u>Annual Quantity</u>	<u>Unit</u>	<u>Price</u>	<u>MM\$ Annual Cost</u>
Wood biomass (HHV=8500 Btu/lb)	330,000	Ton, oven dry	25.5	8.42
Catalyst and chemicals				0.15
Subtotal				8.57
<u>Utilities</u>				
Power	23,180,000	kWh	0.025	0.58
Cooling water	227,000	kGal	0.05	0.01
Process water	19,000	kGal	0.50	0.01
Fuel	-	-	-	-
Steam	1,227,000	kLb	internal	-
Subtotal				0.60
<u>Labor Related</u>				
Labor, L	32	Man-yr	20,000	0.64
Supervisor, S	8/1	Man-yr	22500/ 27000	0.21
Labor Overhead @ 100%(L&S)				0.85
Subtotal				1.70
<u>Capital Related**</u>				
Maintenance	4% BLCC			3.49
General plant overhead	2.6% BLCC			2.27
Extraordinary expenses at start- up year				2.27

* Includes contingencies and engineering

**Other capital related costs are discussed in Section 6.3
together with the discounted cash flow product price esti-
mation because they are calculated by the DCF computer code.

Table 6.3 Annual Operating and Maintenance Costs
for Baseline Process B - Purox Gasification
(350 TPD Methanol)

Battery Limits Capital Costs*	69.92
Offsite Capital Costs*	14.77
Fixed Investment	84.69
Working Capital	8.47
Total Investment	93.16

<u>Raw Materials</u>	<u>Annual Quantity</u>	<u>Unit</u>	<u>Price</u>	<u>Annual Cost</u>
Wood biomass (HHV=8500 Btu/lb)	330,000	Ton	25.5	8.42
Catalyst and chemicals				0.11
Subtotal				8.53
<u>Utilities</u>				
Power	21,400,000	kWh	0.025	0.54
Cooling water	157,000	kGal	0.050	0.01
Process water	155,000	kGal	0.50	0.08
Fuel	-	-	-	-
Steam	844,000	kLb	internal	-
Subtotal				0.63
<u>Labor Related</u>				
Labor, L	40	Man-yr	20000	0.80
Supervisor, S	8/1	Man-yr	22500/ 27000	0.21
Labor overhead @ 100% (L&S)				1.01
Subtotal				2.02
<u>Capital Related</u>				
Maintenance	4% BLCC			2.79
General plant overhead	2.6% BLCC			1.82
Extraordinary expenses at start-up year				1.86

* Include 15% contingency

** Other capital related costs are discussed in Section 6.3, together with the discounted cash flow product price estimation because they are computed by the DCF computer code

Table 6.4 Annual Operating and Maintenance Costs
for Baseline Process C - Wellman-Galusha
Gasification (330 TPD Methanol)

Battery Limits Capital Costs*	51.18
Off-site Capital Costs*	16.21
Fixed Investment	67.39
Working Capital	6.74
Total Investment	74.13

<u>Raw Materials</u>	<u>Annual Quantity</u>	<u>Unit</u>	<u>Price</u>	<u>Annual Cost</u>
Wood biomass (HHV=8500 Btu/lb)	330,000	Ton, oven dry	25.5	8.42
Catalyst and chemicals				0.12
Subtotal				8.54
<u>Utilities</u>				
Power	12,098,000	kWh	0.025	0.30
Cooling water	146,000	kGal	0.050	0.01
Process water	14,700	kGal	0.50	0.01
Fuel	-	-	-	-
Steam	97,000	kLb	internal	-
Subtotal				0.32
<u>Labor Related</u>				
Labor, L	48	Man-yr	20000	0.96
Supervisor, S	8/1	Man-yr	22500/ 27000	0.21
Labor Overhead @ 100% (L&S)				1.17
Subtotal				2.34
<u>Capital Related**</u>				
Maintenance	4% BLCC			2.05
General plant overhead	2.6% BLCC			1.33
Extraordinary expenses at start-up year				1.48

* Includes 15% contingency

** Other capital related costs are discussed in Section 6.3,
together with the DCF product price estimation because they
are computed by the DCF computer code.

General plant overhead 2.6 percent of battery limits
capital cost (BLCC)

6.2.2 Labor and Related Costs

Labor related costs include two parts: direct labor charges, and labor overhead at 100 percent of direct labor costs. The following annual salaries have been assumed (\$1979):

<u>Position</u>	<u>Annual Salaries</u>
Operator	\$20,000
Foreman	\$22,500
Supervisor & Manager	\$27,000

6.3 METHANOL PRODUCTION COST - BASELINE PROCESS DESIGNS

A reference case economic analysis has been performed for each baseline process design to determine the most likely methanol production costs. Next, sensitivity studies were performed with respect to feedstock cost, and venture type (regulated or non-regulated).

6.3.1 Methanol Production Costs - Reference Case

A discount cash flow (DCF) computer program (detailed in appendix B) was used for estimating the base case

cost for the three process designs. The major assumptions made in the economic analyses are:

- All costs in \$1979
- 9% annual interest rate on debt
- 15% after tax return on equity
- 46% Federal income tax rate
- 3% state income tax rate
- 1% local property tax rate
- 1% property insurance rate
- 15% investment tax credit, carry-forward 7 years
- Tax loss carry-forward 5 years
- 4 years construction and 20 years operation
- 60% plant factor at start-up year, and 90% thereafter.
- Biomass at \$1.5/MM Btu for the reference cases. This represents a cost lying in the range of both biomass farm products and biomass residues, as shown in Section 2.1.2, Volume II.

In addition, the following applies:

	<u>Regulated Utility Venture</u>	<u>Private Non-regulated Venture</u>
Debt capital	65%	-
Equity capital	35%	100%
Depreciation tax life	20 years	20 years
Depreciation method	straight line	sum of the years' digits
Interest rate during construction on debt capital	10%	-

Table 6.5 shows the base case economic results using the DCF computer program. Tables 6.6 - 6.8 present the detailed DCF results for the three baseline processes. The DCF

Table 6.5 Economics of Methanol Conversion via Biomass Gasification.
(\$1979, 90% plant factor)

	Koppers-Totzek		Purox		Wellman-Galusha	
	1000 ODT/day	5000 ODT/day	1000 ODT/day	5000 ODT/day	1000 ODT/day	5000 ODT/day
Biomass feed rate						
Methanol capacity, S. Tons/yr.	142070	710380	115270	576370	109500	547500
S. Tons/day	430	2150	350	1740	330	1660
Investment, \$ Millions	113.49	373.42	93.16	306.53	74.13	217.92
Biomass cost, \$/CDT	25.5	25.5	25.5	25.5	25.5	25.5
\$/MM Btu	1.5	1.5	1.5	1.5	1.5	1.5
Production cost, \$/gallon methanol						
Feedstock	0.197	0.197	0.243	0.243	0.256	0.256
Utilities, chemicals, labor	0.057	0.033	0.107	0.071	0.084	0.040
Capital charges*	0.654	0.431	0.652	0.428	0.537	0.315
TOTAL	0.91	0.66	1.00	0.74	0.88	0.61

* Capital charges include maintenance, overhead, insurance, property taxes, and 15% annual after tax return on equity. Financing is 65% by debt, 35% equity.

Table 6.6 Detailed DCF Analysis - Koppers-Totzek Baseline Process Design

PAYOUT TABULATION

FEED PRICE = 25.5C

TRIAL 1 PRICE = 272.7100 DEBT AT 9.00 % RATE OF RETURN ON EQUITY = 15.000 % D/E = 0.65/0.35

	1	2	3	4	5	6	7	8	9	10	11
	CPSTRT	EFFNCY	INCOME	PLTEXP	SILTAX	TXCRDT	FEDTAX	CASHFL	TOTRTN	AMORTZ	CAPEND
1	135.4096	0.6000	25.8202	16.3355	1.2510	0.0	0.0	8.2337	15.0305	-6.7968	142.2064
2	142.2064	0.9000	38.7302	17.5927	1.4554	0.0	0.0	19.6821	15.7849	3.8972	138.3092
3	138.3092	0.9000	38.7302	17.5927	1.4623	2.4138	0.0	19.6752	15.3523	4.3229	133.9663
4	133.9663	0.9000	38.7302	17.5927	1.4659	2.6797	0.0	19.6676	14.8725	4.7952	129.1911
5	129.1911	0.9000	38.7302	17.5927	1.4783	2.8049	0.0	19.6592	14.3402	5.3190	123.8720
6	123.8720	0.9000	38.7302	17.5927	1.4876	2.9437	0.0	19.6499	13.7498	5.9001	117.9719
7	117.9719	0.9000	38.7302	17.5927	1.4980	3.0977	0.0	19.6395	13.0949	6.5447	111.4272
8	111.4272	0.9000	38.7302	17.5927	1.5094	3.2686	0.0	19.6281	12.3684	7.2596	104.1676
9	104.1676	0.9000	38.7302	17.5927	1.5222	0.0	3.4581	16.1572	11.5626	4.5946	99.5730
10	99.5730	0.9000	38.7302	17.5927	1.5303	0.0	3.5780	16.0293	11.0526	4.9767	94.5963
11	94.5963	0.9000	38.7302	17.5927	1.5390	0.0	3.7079	15.8906	10.5002	5.3904	89.2058
12	89.2058	0.9000	38.7302	17.5927	1.5484	0.0	3.8486	15.7405	9.9018	5.8386	83.3672
13	83.3672	0.9000	38.7302	17.5927	1.5587	0.0	4.0010	15.5778	9.2538	6.3240	77.0432
14	77.0432	0.9000	38.7302	17.5927	1.5698	0.0	4.1661	15.4016	8.5518	6.8498	70.1933
15	70.1933	0.9000	38.7302	17.5927	1.5818	0.0	4.3449	15.2108	7.7915	7.4194	62.7740
16	62.7740	0.9000	38.7302	17.5927	1.5948	0.0	4.5386	15.0041	6.9679	8.0362	54.7377
17	54.7377	0.9000	38.7302	17.5927	1.6089	0.0	4.7483	14.7802	6.0759	8.7044	46.0334
18	46.0334	0.9000	38.7302	17.5927	1.6242	0.0	4.9755	14.5378	5.1097	9.4281	36.6053
19	36.6053	0.9000	38.7302	17.5927	1.6408	0.0	5.2216	14.2751	4.0632	10.2119	26.3934
20	26.3934	0.9000	38.7302	17.5927	1.6587	0.0	5.4882	13.9906	2.9297	11.0610	15.3324

THE LAST ENTRY IN THE FINAL YEAR SHOULD BE EQUAL TO THE WORKING CAPITAL INVESTMENT PLUS SALVAGE VALUE

WORKING CAPITAL RECOVERED INTACT AT END OF PROJECT LIFE = 10.31000
 SALVAGE VALUE RECOVERED INTACT AT END OF PROJECT LIFE = 5.02000
 TOTAL 15.33000

KEY TO CALCULATIONS IS AS FOLLOWS.

COLUMN 1 = CAPITAL INVESTMENT OUTSTANDING AT START OF YEAR INCLUDING WORKING CAPITAL
 COLUMN 2 = UNSTREAM EFFICIENCY (PLANT OPERATING FACTOR)
 COLUMN 3 = GROSS INCOME FROM SALES
 COLUMN 4 = OPERATING EXPENSES EXCLUDING TAXES
 COLUMN 5 = STATE AND LOCAL TAXES
 COLUMN 6 = FEDERAL INVESTMENT TAX CREDIT
 COLUMN 7 = NET FEDERAL INCOME TAX PAID
 COLUMN 8 = CASH FLOW AFTER TAXES
 COLUMN 9 = INTEREST ON DEBT AND RETURN ON EQUITY BASED ON COLUMN 1
 COLUMN 10 = REDUCTION OF OUTSTANDING CAPITAL INVESTMENT, COLUMN 8-9
 COLUMN 11 = OUTSTANDING CAPITAL INVESTMENT AT END OF YEAR INCL WORKING CAPITAL, COL 1-10

COLUMN 11 PLUS NEW INVESTMENT = NEXT ENTRY OF COLUMN 1

Table 6,7 Detailed DCF Analysis - PUROX Baseline Process Design

PAYOUT TABLE

PAYOUT PERIOD = 20.00

TRIAL 1 PRICE = 100.9550 DEBT AT 5.00 % RATE OF RETURN ON EQUITY = 15.000 % D/E = 0.65/0.35

	1	2	3	4	5	6	7	8	9	10	11
	CPSTRT	EFFNCY	INCOME	PLTEXT	SLTAX	TXCRDT	FEDTAX	CASHFL	TOTRTN	AMORTZ	CAPEND
1	111.2481	0.6000	22.1237	15.3013	1.0268	0.0	0.0	6.7956	12.3374	-5.5418	116.6895
2	116.6899	0.9000	34.6855	17.3435	1.1946	0.0	0.0	16.1474	12.9526	3.1948	113.4950
3	113.4950	0.9000	34.6855	17.3435	1.2002	2.0036	0.0	16.1418	12.5979	3.5438	109.9512
4	109.9512	0.9000	34.6855	17.3435	1.2065	2.2002	0.0	16.1356	12.2046	3.9310	106.0202
5	106.0202	0.9000	34.6855	17.3435	1.2134	2.3028	0.0	16.1287	11.7682	4.3604	101.6598
6	101.6598	0.9000	34.6855	17.3435	1.2210	2.4166	0.0	16.1210	11.2842	4.8368	96.8230
7	96.8230	0.9000	34.6855	17.3435	1.2295	2.5429	0.0	16.1125	10.7473	5.3652	91.4578
8	91.4578	0.9000	34.6855	17.3435	1.2389	2.6829	0.0	16.1031	10.1518	5.9513	85.5065
9	85.5065	0.9000	34.6855	17.3435	1.2494	0.0	2.8383	13.2544	9.4912	3.7632	81.7434
10	81.7434	0.9000	34.6855	17.3435	1.2560	0.0	2.9365	13.1496	9.0735	4.0760	77.6673
11	77.6673	0.9000	34.6855	17.3435	1.2631	0.0	3.0429	13.0360	8.6211	4.4150	73.2523
12	73.2523	0.9000	34.6855	17.3435	1.2709	0.0	3.1581	12.9130	8.1310	4.7820	68.4703
13	68.4703	0.9000	34.6855	17.3435	1.2793	0.0	3.2824	12.7798	7.6002	5.1796	63.2907
14	63.2907	0.9000	34.6855	17.3435	1.2884	0.0	3.4182	12.6355	7.0253	5.6103	57.6805
15	57.6805	0.9000	34.6855	17.3435	1.2982	0.0	3.5645	12.4792	6.4025	6.0767	51.6037
16	51.6037	0.9000	34.6855	17.3435	1.3089	0.0	3.7232	12.3049	5.7280	6.5819	45.0218
17	45.0218	0.9000	34.6855	17.3435	1.3204	0.0	3.8950	12.1266	4.9974	7.1292	37.8926
18	37.8926	0.9000	34.6855	17.3435	1.3329	0.0	4.0811	11.9280	4.2061	7.7219	30.1707
19	30.1707	0.9000	34.6855	17.3435	1.3465	0.0	4.2827	11.7129	3.3489	8.3639	21.8068
20	21.8068	0.9000	34.6855	17.3435	1.3612	0.0	4.5010	11.4759	2.4206	9.0593	12.7475

THE LAST ENTRY IN THE FINAL YEAR SHOULD BE EQUAL TO THE WORKING CAPITAL INVESTMENT PLUS SALVAGE VALUE

WORKING CAPITAL RECOVERED INTACT AT END OF PROJECT LIFE = 8.47000
 SALVAGE VALUE RECOVERED INTACT AT END OF PROJECT LIFE = 4.27000
 TOTAL 12.74000

KEY TO CALCULATIONS IS AS FOLLOWS.

COLUMN 1 = CAPITAL INVESTMENT OUTSTANDING AT START OF YEAR INCLUDING WORKING CAPITAL
 COLUMN 2 = DNSTREAM EFFICIENCY (PLANT OPERATING FACTOR)
 COLUMN 3 = GROSS INCOME FROM SALES
 COLUMN 4 = OPERATING EXPENSES EXCLUDING TAXES
 COLUMN 5 = STATE AND LOCAL TAXES
 COLUMN 6 = FEDERAL INVESTMENT TAX CREDIT
 COLUMN 7 = NET FEDERAL INCOME TAX PAID
 COLUMN 8 = CASH FLOW AFTER TAXES
 COLUMN 9 = INTEREST ON DEBT AND RETURN ON EQUITY BASED ON COLUMN 1
 COLUMN 10 = REDUCTION OF OUTSTANDING CAPITAL INVESTMENT, COLUMN 8-9
 COLUMN 11 = OUTSTANDING CAPITAL INVESTMENT AT END OF YEAR INCL WORKING CAPITAL. COL 1-10

COLUMN 11 PLUS NEW INVESTMENT = NEXT ENTRY OF COLUMN 1

Table 6.8 Detailed DCF Analysis - Wellman Galusha Baseline Process

PAYOUT TABULATION

FEED PRICE = 25.50

TRIAL 1 PRICE = 263.5105 DEBT AT 9.10 % RATE OF RETURN ON EQUITY = 15.000 % D/E = 0.65/0.35

	1	2	3	4	5	6	7	8	9	10	11
	CPSTRT	EFFNCY	INCOME	PLTEXP	STLTAX	TAXCREDIT	FEDTAX	CASHFL	TOTRTN	AMORTIZ	CAPEND
1	88.4436	0.6200	19.2415	12.9295	0.8170	0.0	0.0	5.4949	9.8172	-4.3223	92.7659
2	92.7659	0.9000	28.8623	15.0758	0.9503	0.0	0.0	12.8362	10.2970	2.5392	90.2267
3	90.2267	0.9000	28.8623	15.0758	0.9548	1.6256	0.0	12.8317	10.0152	2.8166	87.4101
4	87.4101	0.9000	28.8623	15.0758	0.9597	1.7464	0.0	12.8268	9.7025	3.1243	84.2858
5	84.2858	0.9000	28.8623	15.0758	0.9652	1.8280	0.0	12.8213	9.3557	3.4656	80.8203
6	80.8203	0.9000	28.8623	15.0758	0.9713	1.9185	0.0	12.8152	8.9710	3.8442	76.9761
7	76.9761	0.9000	28.8623	15.0758	0.9780	2.0188	0.0	12.8085	8.5443	4.2641	72.7119
8	72.7119	0.9000	28.8623	15.0758	0.9855	2.1301	0.0	12.8010	8.0710	4.7300	67.9819
9	67.9819	0.9000	28.8623	15.0758	0.9938	0.0	2.2536	10.5391	7.5460	2.9931	64.9888
10	64.9888	0.9000	28.8623	15.0758	0.9991	0.0	2.3317	10.4557	7.2138	3.2420	61.7468
11	61.7468	0.9000	28.8623	15.0758	1.0048	0.0	2.4163	10.3654	6.8539	3.5115	58.2353
12	58.2353	0.9000	28.8623	15.0758	1.0109	0.0	2.5080	10.2676	6.4641	3.8035	54.4318
13	54.4318	0.9000	28.8623	15.0758	1.0176	0.0	2.6073	10.1616	6.0419	4.1197	50.3121
14	50.3121	0.9000	28.8623	15.0758	1.0248	0.0	2.7148	10.0469	5.5846	4.4622	45.8498
15	45.8498	0.9000	28.8623	15.0758	1.0327	0.0	2.8313	9.9226	5.0893	4.8332	41.0166
16	41.0166	0.9000	28.8623	15.0758	1.0411	0.0	2.9574	9.7879	4.5528	5.2351	35.7815
17	35.7815	0.9000	28.8623	15.0758	1.0503	0.0	3.0941	9.6421	3.9717	5.6703	30.1111
18	30.1111	0.9000	28.8623	15.0758	1.0603	0.0	3.2421	9.4841	3.3423	6.1418	23.9693
19	23.9693	0.9000	28.8623	15.0758	1.0711	0.0	3.4024	9.3130	2.6606	6.6524	17.3169
20	17.3169	0.9000	28.8623	15.0758	1.0827	0.0	3.5761	9.1277	1.9222	7.2055	10.1114

THE LAST ENTRY IN THE FINAL YEAR SHOULD BE EQUAL TO THE WORKING CAPITAL INVESTMENT PLUS SALVAGE VALUE

WORKING CAPITAL RECOVERED INTACT AT END OF PROJECT LIFE = 6.74000
 SALVAGE VALUE RECOVERED INTACT AT END OF PROJECT LIFE = 3.37000
 TOTAL 10.11000

KEY TO CALCULATIONS IS AS FOLLOWS.

COLUMN 1 = CAPITAL INVESTMENT OUTSTANDING AT START OF YEAR INCLUDING WORKING CAPITAL
 COLUMN 2 = ONSTREAM EFFICIENCY (PLANT OPERATING FACTOR)
 COLUMN 3 = GROSS INCOME FROM SALES
 COLUMN 4 = OPERATING EXPENSES EXCLUDING TAXES
 COLUMN 5 = STATE AND LOCAL TAXES
 COLUMN 6 = FEDERAL INVESTMENT TAX CREDIT
 COLUMN 7 = NET FEDERAL INCOME TAX PAID
 COLUMN 8 = CASH FLOW AFTER TAXES
 COLUMN 9 = INTEREST ON DEBT AND RETURN ON EQUITY BASED ON COLUMN 1
 COLUMN 10 = REDUCTION OF OUTSTANDING CAPITAL INVESTMENT, COLUMN 8-9
 COLUMN 11 = OUTSTANDING CAPITAL INVESTMENT AT END OF YEAR INCL WORKING CAPITAL. COL 1-10

COLUMN 11 PLUS NEW INVESTMENT = NEXT ENTRY OF COLUMN 1

analysis indicates that capital charges (depreciation, property taxes, maintenance, return on equity, overhead, insurance, and interest on debt) account for approximately 24 percent of total investment. Methanol product prices at the plant range from \$0.88 to \$1.00 per gallon (\$1979) for the 1000 ODT/day plant (regulated venture). Approximately 70% of the production cost can be attributed to capital related costs. Utility, labor and chemical costs account for less than 10%, and the remaining costs are attributed to biomass feedstock costs. As can be seen, the Purox process consistently has the higher methanol production cost than the K-T and Wellman Galusha processes. For the 5000 ODT/day plant, product prices range from \$0.61 to \$0.74 per gallon for the regulated venture.

6.3.2 Economic Sensitivity Analyses

For the two plant sizes examined, feedstock costs were varied from \$17 to \$51 per ODT, or \$1 to \$3 per MMBtu. The results are shown in Figure 6.1 and Table 6.9 for the reference (regulated utility) case. The product prices are highly sensitive to feedstock costs. In addition, the non-regulated venture case results in a 40 percent increase in product price, as shown in Figure 6.2 for the 1000 ODT/day plants.

In practice, the economy of scale for the conversion plant will be offset by increasing delivered biomass costs. The economics of biomass supply is site-specific, and therefore, a site for which data are available was chosen to illustrate the effect of the trade-off. The timbershed supplying the Mead mill in Escanaba, Michigan, has been investigated by the U.S. Department of Agriculture (reference 13). It is selected here for an illustrative analysis.

The above study considered tree gasifier types, hauling distances, road types, harvested acreages, harvest types (clearcut, thinning, or selection cut/relogging) and other

Figure 6.1 Methanol Conversion Economics (\$1979)

65% debt, 35% equity
 9% annual interest on debt
 15% after tax return on equity
 10% interest on construction loan

Table 6.9 Biomass to Methanol Conversion Economics: Effects of Plant Size and Feedstock Cost. (\$1979, 90% Plant Factor, Debt/Equity = 65/35, 9% Interest on Debt, 15% Return on Equity)

	Koppers-Totzek Gasification		Purox Gasification		Wellman-Galusha Gasification	
	1000 ODT/d	5000 ODT/d	1000 ODT/d	5000 ODT/d	1000 ODT/d	5000 ODT/d
Tons methanol per year	142,070	710,380	115,270	576,370	109,500	547,500
Utilities, chemicals, labor						
Annual \$MM	2.45	6.99	3.70	12.24	2.78	6.65
Capital charges including 15% return on equity, annual \$MM	27.92	91.86	22.54	74.18	17.64	51.86
Total annual costs, \$MM (without feedstock)	30.37	98.85	26.24	86.42	20.42	58.51
\$/ton methanol	213.8	13.92	227.7	149.94	186.5	106.9
\$/gallon methanol	0.71	0.46	0.76	0.50	0.62	0.36
Annual feedstock cost at \$17/ODT or \$1/MM Btu \$MM	5.61	28.05	5.61	28.05	5.61	28.05
Total annual cost, \$MM	35.98	126.9	31.85	114.47	26.03	87.01
\$/ton methanol	253.3	178.6	276.3	198.6	237.72	258.9
\$/gallon methanol	0.84	0.59	0.92	0.66	0.79	0.53
Annual feedstock cost at \$25.5/ODT or \$1.5/MM Btu, \$MM	8.42	42.1	8.42	42.1	8.42	42.1
Total annual cost, \$MM	38.79	140.9	34.66	128.5	28.84	100.6
\$/ton methanol	273.0	198.4	300.7	223.0	263.38	183.8
\$/gallon methanol	0.91	0.66	1.00	0.74	0.88	0.61
Annual feedstock cost at \$51/ODT or \$3/MM Btu \$MM	16.83	84.15	16.83	84.15	16.83	84.15
Total annual cost, \$MM	47.20	183.0	43.07	170.57	37.25	142.7
\$/ton methanol	33.2	257.6	373.6	295.9	340.2	260.6
\$/gallon methanol	1.11	0.86	1.24	0.98	1.13	0.87

Figure 6.2 Regulated vs. Non-Regulated Economics
(\$1979, 1000 ODT/day)

appropriate factors. The delivered prices were also based on opportunity values of wood as a substitute for fossil fuels, after deducting costs of retrofit and efficiency losses. Figure 6.3 shows the results derived from that study.

The trade-off between economy of scale and increased delivered biomass prices are plotted in Figure 6.4. The rate of biomass price increase will be a function of any particular site.

In addition, a few illustrative sensitivity studies were performed for assumed variations in various components of biomass costs, to determine their effects on the methanol product price. Table 6.10 shows the results.

6.3.3 Potential Cost Reduction of Methanol Production from Biomass

As shown in Table 6.5, the bulk of the methanol production costs are attributed to capital related costs. In the following section, potential reduction in capital cost areas are explored.

Examination of capital cost distribution indicated that the oxygen plant, gasifier system, gas cleaning and separation, methanol synthesis and steam power plant are the major contributors to the overall capital cost. It is evident that some of these capital costs can be substantially reduced in the near future when a properly designed advanced biomass gasification, and methanol synthesis processes are incorporated. Since the gasification process will dictate the synthesis gas cleaning and separation requirement, it is imperative that an advanced gasification system be

Figure 6.3 Supply Curve for Mead Timbershed, Escanaba, Michigan
(All Forest Types)

Reference 13

Figure 6.4 Trade-off Between Economy of Scale and Increased Feedstock Prices

Table 6.10 Sensitivity of Methanol Product Prices in \$1979/gallon
to Various Components of Feedstock Costs

(Production or Acquisition, Collection, Transportation)*

	<u>Logging Residues</u>	<u>Standing Biomass</u>	<u>Crop Residues</u>	<u>Mill Residues</u>	<u>Silvicultural Biomass</u>
Base methanol price	0.66	0.66	0.66	0.66	0.66
30 percent decrease in acquisition cost	0.0	-0.01	-0.02	-0.03	-0.05
30 percent decrease in collection cost	-0.05	-0.02	-0.04	0.0	-0.01
50 percent increase in transportation cost	+0.02	+0.04	+0.01	+0.05	+0.0

* 2000 short tons methanol per day; base feedstock price is \$1.5/MM Btu.
Base transportation distance between 20 and 50 miles.

designed with an objective of minimizing capital equipment costs. The advanced gasification process envisioned will be a pressurized steam catalytic gasification process with the following advantages:

- The steam catalytic gasification process will totally eliminate the oxygen plant requirement.
- The gasification process will produce synthesis gas with H_2 per CO = 2 and therefore totally eliminate the CO shift conversion step and also reduce the CO₂ removal system cost.
- The gasification process will minimize the CH₄ and higher hydrocarbon production and thus reducing the gas cleaning and separation system cost.
- The high pressure gasification process will reduce the syngas compression and steam power plant cost.

In addition, the advanced methanol synthesis process such as the Chem Systems liquid phase methanol process can reduce steam energy consumption, and increase conversion yield. This translates to a net reduction of steam power plant and compressor costs.

Table 6.11 summarizes the potential capital cost reduction of each major processing step. As can be seen, the total potential cost reduction amounts to about half of the capital cost. The net effect of this capital cost reduction is equivalent to nearly 35 percent decrease in overall methanol production cost.

Table 6.11 Capital Cost Reduction Potential for
Biomass Based Methanol Processes

Current Biomass to Methanol Process

<u>Processing Step</u>	<u>Percent of Capital Cost</u>	<u>Advantages of Advanced Biomass to Methanol Process</u>	<u>Potential reduction %</u>	<u>Weighted total cost reduction</u>
Front end	9.4	Reduce feedstock drying and size reduction requirements	50	4.7
Oxygen plant	11.1	Elimination of oxygen plant	100	11.1
Gasifier	33.4	Use steam gasification or catalytic fluidized bed gasification	40	13.4
Gas compression	5.2	Use pressurized gasification to reduce compression cost	80	4.1
Gas cleaning and separation	9.2	Reduce oil and tar formation and hydrocarbon separation	40	3.7
Shift and acid gas removal	2.8	Produce synthesis gas with $H_2/CO=2$ and eliminate shift conversion step	60	1.7
Methanol syn- thesis	10.5	Use Chem System methanol process to improve methanol conversion effi- ciency and production cost	50	5.2
General facility and utility	18.4	Improve waste heat recovery effi- ciency and elimination of waste disposal facility. High pressure gasification to reduce need for compressor and steam power plant facility	40	7.3
Total	100			51.2

6.4 COMPARISON WITH OTHER METHANOL PRODUCTION COSTS

6.4.1 Methanol From Biomass

Reported cost data from Intergroup Consulting Economists (reference 7), SRI (reference 16), and MITRE (reference 8) are compared with SAI's estimates in Table 6.12, using the same capital charge factor, after escalation to \$1979 at 7 percent per year. It is apparent that ICE's and SAI's estimated product prices are within 16 percent of each other. MITRE's low cost resulted from the use of too low a value for the Purox gasifiers. The SRI study, which assumes a pressurized fluidized bed gasification system, apparently has much higher (50%) methanol conversion efficiency than the others.

A plot is presented in Fig. 6.5, illustrating SAI's and others' results. From the figure, it appears that, except for MITRE, the capital cost estimates from various sources are within 20 percent of one another.

6.4.2 Comparison of Methanol Production Economics Between Biomass and Other Feedstocks

Methanol production from natural gas, coal and residual oil was assessed in a recent Exxon-Chem Systems report (reference 6) for plants producing 2000 tons of methanol per day.

A likely scenario was selected for fossil feedstock price escalation, based on a series of recent projections by the Energy Information Administration, Department of Energy (reference 12, Series C, mid demand, mid supply, high oil prices). Biomass residue price escalation is assumed by SAI to be at the same rate as that of coal, because of the potential substitutability between those two in many combustion applications. The results are summarized in Table 6-13.

Table 6.12 Comparison of Biomass to Methanol Economics: SAI, Intergroup Consulting Economists, MITRE and SRI (\$1979)

Source	Methanol S.Tons/day	Biomass ODT/day	Gasifier Type	Capital* Invest- ment \$/gallon	Operat- ing Costs \$/gallon	Product Cost (With- out Feed-) stock) \$/gallon
SAI	1000	2860	Purox	0.49	0.08	0.57
ICE (6)	1000	2300	Purox	0.58	0.08	0.66
MITRE (7)	670	1700	Purox	0.33	0.06	0.39
MITRE (7)	1340	3400	Purox	0.25	0.05	0.30
SRI (16)	570**	1000	Purox	0.35	0.14	0.49

* All capital charges are reduced to the same basis, 24 percent of total investment.

** SRI's methanol conversion efficiency is approximately 50% higher than other estimates.

Figure 6.5 Capital Costs (Fixed Investment) of Methanol Plants

Note: Numbers inside parenthesis are reference numbers

**Table 6.13 Comparison of Methanol Conversion Economics - Effects
of Various Feedstock Prices in 1985 and 1995
(\$1979, 90% Plant Factor)**

Status of Technology S. Tons Methanol Per Day	Average Case Biomass Gasification		Bituminous Coal Gasification				Residual oil Partial Oxidation	Natural Gas Reforming
	Reference (1) 2000	Improved 2000	Reference 2000	8000	Improved 2000	8000	Reference 2000	Reference 2000
Total Investment, \$ Millions								
1985	353.7	(2)	338.9	945.6	(2)	(2)	230.7	134.7
1995	353.7	179.6	338.9	945.6	300.4	835.3	230.7	134.7
Feedstock Cost (7)								
1985 (8) - \$/Unit	25.50/ODT (3)	(2)	23.2/T	23.2/T	(2)	(2)	26.41/bbl	3.21/MM Btu
- \$/MM Btu	1.50	(2)	1.02	1.02	(2)	(2)	4.19	3.21
1995 (9) - \$/Unit	31.45/ODT	25.50/ODT (4)	29.02/T	29.02/T	29.02/T	29.02/T	36.63/bbl	4.54/MM Btu
- \$/MM Btu	1.94	1.50	1.27	1.27	1.27	1.27	5.81	4.54
Production Cost, \$/gallon								
1985 - Feedstock	0.197	(2)	0.132	0.132	(2)	(2)	0.546	0.384
- Operating (5)	0.033		0.032	0.026			0.032	0.036
- Capital (6)	0.429		0.410	0.286			0.279	0.163
- By-Product Credit	0		-0.008	-0.008			-0.005	0
Total	0.659		0.566	0.436			0.852	0.583
1995 - Feedstock	0.242	0.134	0.165	0.165	0.154	0.154	0.758	0.544
- Operating	0.033	0.030	0.032	0.026	0.031	0.024	0.032	0.036
- Capital	0.429	0.218	0.410	0.286	0.363	0.253	0.279	0.163
- By-Product Credit	0	0	-0.008	-0.008	-0.008	-0.008	-0.005	0
Total	0.704	0.382	0.599	0.469	0.540	0.423	1.064	0.743

(1) Koppers Totzek gasification

(2) Technology not expected to be available in 1985

(3) Assumed forestry residues

(4) Assumed biomass farms with improved yield are operational

(5) Include utilities, chemicals and labor

(6) Include overhead, maintenance, return on investment and other capital related charges.

(7) DOE/EIA-0102/52, Series C, high oil prices, escalated to \$1979 - Coal prices adjusted to Illinois coal. Biomass residue price assumed to increase at the same rate as coal.

(8) World wide oil at \$23.22/bbl in \$1979.

(9) World crude oil at \$34.02/bbl in \$1979.

In 1985 it appears that the average biomass to methanol economics is competitive with residual oil conversion, approaching KT coal economics for the smaller plant size, but is still unfavorable with respect to the new coal process or natural gas reforming. By 1995, the improved biomass-based methanol economics appears competitive.

6.5 COMPARISON OF BASE CASE PRODUCT PRICES AND MARKET VALUES

The market values (from Table 3.6 of Volume II) and product prices of methanol (from Table 6.13) are compared in Table 6.14. For the assumptions made regarding economic conditions in 1985 and 1995, the gasoline blend end use will permit rapid market penetration for methanol because of the positive values or small negative values of the differences between market values and selling prices.

The market values of methanol fuel were also assessed in Section 3.4, assuming that a gallon of transportation fuel (whether pure or blended with gasoline) is granted a tax credit of 4 cents per gallon. The amount 4 cents is chosen because of its comparability to the present gasohol tax exemption of 4 cents per gallon. No attempt was made to assess governmental incentive policies with respect to methanol fuel from biomass, and the values shown are for sensitivity studies only. Table 6.15 shows the savings in oil imports and government subsidies required to balance selling prices and market values of methanol fuels in various markets. The cost benefit ratios, excluding R&D costs for methanol applications, also appear to favor the transportation markets.

Table 6.14 Methanol Market Values Versus Selling Prices
(\$1979/gallon Methanol)

End Use	10% in Gasoline		30% in Gasoline		Pure Auto Fuel		30% in Diesel		Home Heating		Gas Turbine	
	1985	1995	1985	1995	1985	1995	1985	1995	1985	1995	1985	1995
Market Value Without Tax Credit	1.12	1.35	0.83	1.00	0.70	0.84	0.32	0.41	0.30	0.42	0.27	0.38
Market Value With Tax Credit	1.53	1.75	0.98	1.13	0.74	0.88	-	-	-	-	-	-
Biomass Price \$/MM Btu	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Product Price at Plant(1)	0.66	0.38	0.66	0.38	0.66	0.38	0.66	0.38	0.66	0.38	0.66	0.38
Selling Price to End Users Excluding Tax(2)	0.81	0.48	0.81	0.48	0.81	0.48	0.73	0.43	0.84	0.49	0.68	0.40
Market Value Without Tax Credit-Selling Price	0.31	0.87	0.02	0.52	-0.11	0.36	-0.41	-0.02	-0.54	-0.07	-0.41	-0.02
Market Value With Tax Credit - Selling Price	0.72	1.27	0.17	0.65	-0.07	0.40	-	-	-	-	-	-

(1) Methanol capacity 2000 short tons per day.

(2) Includes 2.2 cents per gallon for methanol transportation to end user, plus 20 percent dealer's margin for use with gasoline⁽¹⁴⁾, 7 percent dealer's margin for use with diesel, and 24 percent for home heating⁽¹⁵⁾. Gas turbine fuel assumed at wholesale price, with no dealer's margin.

Table 6.15 Example of National Benefits in Terms of Reduction in Oil Imports, and Representative Costs to the Government for Equalizing Selling Prices and Market Values of Methanol Products
-(\$1979 Billions)

	<u>10% in Gasoline</u>	<u>30% in Gasoline</u>	<u>Pure Methanol Auto Fuel</u>	<u>30% in Diesel</u>	<u>Home Heating</u>	<u>Gas Turbine</u>
Savings in Oil Imports(1)						
1985-million barrels	218.5	-	-	-	-	-
-\$ billions	5.1	-	-	-	-	-
1995-million barrels	160.8	386	1100	298	375	88
-\$ billions	5.5	13.1	37.6	10.1	12.8	3.0
Cost of Methanol Subsidies(2)						
1985-billion gallons	13.44	-	-	-	-	-
-\$ billions	0	-	-	-	-	-
1995-billion gallons	9.89	23.7	69.0	19.4	24.4	7.6
-\$ billions	0	0	0	0.39	1.7	0.15
Cost/Benefit Ratio(3)						
-1985	0	-	-	-	-	-
-1995	0	0	0	0.04	0.13	0.05

(1) World oil at \$23.22 per barrel in 1985 and \$34.02 per barrel in 1995 (\$1979)

(2) Methanol volumes from Tables 3.1 and 3.4, and also from reference 12 (Table 21, p. 73). Subsidy per gallon shown in Table 6.14, in the row labeled "Market Value without Tax Credit - Selling Price."

(3) Excludes R&D costs.

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7. PROSPECTIVES OF ADVANCED PROCESSING TECHNOLOGY

Analysis of the current technology for large-scale methanol production from biomass by thermochemical gasification indicates that methanol production costs will be significantly affected by plant size, feedstock cost, waste heat utilization potentials, and future technological improvements in gasification and in methanol synthesis. Aside from probable long-term technological breakthroughs in biomass gasification and methanol synthesis, the near-term commercialization prospect of biomass to methanol processes appears to suffer from the lack of cheap biomass resources for large-scale conversion and from the high investment costs required for plant construction. However, several new and innovative concepts have been suggested which could alleviate the resource constraint problem and reduce the methanol production costs. Of particular interest are the concepts of:

1. Dispersed gasifier process (Section 7.2)
2. Hybrid syngas process (Section 7.3)
3. Hybrid product process (Section 7.4)
4. Advanced biomass gasification process (Section 7.5)
5. Advanced methanol synthesis technology (Section 7.6)
6. Higher alcohol synthesis (Section 7.7)
7. Hydrocarbon fuels and gasoline (Section 7.8)

In the longer term, new technologies may play a significant role in improving the methanol production economics, and can also provide conversion alternatives for the production of higher alcohols and gasoline products.

A review of these advanced processing technologies and their potential for converting biomass derived synthesis gas to various fuels and chemicals is presented below:

7.1 PRELIMINARY ASSESSMENT OF THE ECONOMIC MERIT OF NEW TECHNOLOGIES

Before discussing in detail the new processing technologies and processing concepts, it is worth noting their potential economic value. A preliminary assessment shows that a 50 percent reduction to approximately \$.38 per gallon for the production cost of methanol can be achieved. This is approximately \$.1 per gallon less than the estimated production cost from a new plant using natural gas, the conventional U.S. feedstock.

These results are displayed in Table 7.1, which is based on Table 6.13 in Section 6.4.2. Capital and production costs are compared for 2000 ton-per-day methanol plants. The first columns list the estimated costs for all-new totally biomass-based and natural gas-based plants, as shown in Table 6.13.

The third column lists the costs for a hybrid plant, utilizing combined biomass and natural gas feedstocks. As will be discussed in Section 7.3, the advantage of this approach is that steam reforming methane produces a synthesis gas too rich in hydrogen ($H_2:CO = 3$) for efficient methanol synthesis. On the other hand, gasification of biomass normally produces a synthesis gas which is too lean in hydrogen. Hence, in combination the proper stoichiometry for methanol synthesis can be

Table 7.1 Potential Economic Advantage of Some New Technologies and Integrated Production Concepts for the Conversion of Biomass to Methanol (Cost in \$1979, 90% Plant Factor)

	<u>New Technologies</u>				
	<u>Average Case Biomass</u>	<u>Natural Gas Reforming</u>	<u>Hybrid Plant</u>	<u>Advanced Gasification</u>	<u>Advanced Gasification and Methanol Synthesis</u>
Methanol Capacity, tons/day	2000	2000	2000	2000	2000
Total Investment, MM\$	353.7	134.7	181.4	215.0	179.6
Feedstock Requirements and Costs					
Biomass, ODT/day	4650	-	1284	4092	3160
\$/ODT	25.5	-	255	25.5	25.5
\$/MMBtu	1.50	-	1.50	1.50	1.50
Natural Gas, MMBtu/day	-	7.09 x 10 ⁴	2.36 x 10 ⁴	-	-
\$/MMBtu	-	3.21	3.21	-	-
Production Cost, \$/gal					
Feedstock	0.198	0.384	0.180	0.174	0.134
Operating	0.033	0.036	0.049	0.031	0.030
Capital	0.429	0.163	0.220	0.261	0.218
Total Cost	0.660	0.583	0.449	0.466	0.382

achieved such that the conversion efficiency of the CO, from both sources, to methanol is nearly 100 percent. This is not possible using the two synthesis gases separately. Another advantage is that on an equivalent heating value basis, biomass is projected to be less expensive than is natural gas, \$1.50 per MMBtu versus \$3.21 per MMBtu.

The reduced feedstock cost shown in Table 7.1 for the hybrid plant, compared with the natural gas-based plant, reflects both the reduced feedstock cost and the more efficient conversion to methanol. Also, it was assumed that combustion of biomass would provide the heat required by the methane steam reformer.

The estimated capital costs for the hybrid plant are intermediate between those for the biomass and natural gas-based plants. In making this estimate, it was assumed that the hybrid plant would be built to operate entirely on natural gas. The cost of an oxygen plant, gasifier and other associated processing equipment for producing a clean synthesis gas from biomass were added to the cost of the natural gas-based plant.

The last two columns in Table 7.1 show the estimated costs for biomass-based plants which might utilize advanced technologies, primarily for the gasification of biomass. The column headed "Advanced Gasification" assumes the use of a gasifier in which gasification is accomplished by indirect heating under high pressure, as discussed in Section 7.5. Hence no oxygen plant is required. This would permit a 9 percent increase in yield of methanol from biomass. Another increase in yield of 3 percent is projected from a reduction in the gasification temperature. The total of 12 percent increased yield is reflected in the reduced feedstock cost compared with the biomass plant in column one.

The capital cost of this plant was based on the estimated reductions achievable as shown in Table 6.11 of Section 6.3, which are approximately 40 percent.

The last column in Table 7.1 shows the cost of a plant in which the methanol is produced using both advanced gasification and methanol synthesis processes. In this case the total increased yield of methanol from biomass is expected to be approximately 32 percent (see Sections 7.5 & 7.6). In this case, the capital cost reductions are expected to be nearly 50 percent.

7.2 DISPERSED GASIFIER PROCESS

The current methanol production costs are significantly affected by the high cost of feedstocks and small scale conversion plants. In order to take advantage of the economy of scale, the conversion plant should produce several thousands of tons of methanol per day. However, this would require the transportation of feedstocks over long distances by truck at a high cost. On the other hand, there is no scale advantage for gasification; the size of the gasifier is limited to one or two hundred tons of wet biomass per day. Hence there is a possibility of dispersing the gasifiers, reducing the transportation costs of the biomass. A pipeline network would be used to transport the gas to the centrally located conversion site. Hence, the tradeoff to be considered is the pipeline network for a low Btu gas versus the trucking of biomass.

A preliminary economic comparison of dispersed gasifiers versus centralized gasifiers indicates a marginal economic disadvantage for dispersed gasifiers as shown in Table 7.2. This is due to the large capital investment required. In a dispersed gasifier system a 12-inch pipeline network, which could handle the outputs from all gasifiers for a 1000 ODT per day plant, would have a capital cost of 11.8 million and an additional 0.54 million for the trucks to supply the gasifiers. This is compared with only 1.6 million investment for the centralized gasifier system.

The high capital requirements stem from the relatively short average pipeline transport distance, and the fact that trucks must still be used to load and collect biomass feedstocks at each gasifier location⁽¹⁾. However, this economic disadvantage might be reversed for feedstock transportation over longer distances⁽²⁾. Further analysis is needed on the economic trade-off.

7.3 HYBRID SYNGAS PROCESS

A recent study by a Canadian group⁽¹⁾ estimated that the economics of methanol production from biomass feedstock could be greatly enhanced through implementation of a hybrid syngas process. The most attractive hybrid syngas processes employs the addition of either steam reformed methane or hydrogen to the biomass derived syngas.

7.3.1 Technical Advantages of Biomass-Methane Hybrid Methanol System

The currently proposed technology for large-scale methanol production from renewable biomass feedstocks employs thermal gasification. The synthesis gas is cleaned,

Table 7.2 Economic Comparison of Centralized versus

Dispersed Gasifiers (cost in \$1979)

Capacity: 400 tons methanol per day (1000 ODT/day),

Radius: 50 miles average

	Centralized Gasifier <u>27 Trucks</u>	<u>Dispersed Gasifier</u> <u>12-in Pipeline</u>	<u>9 Trucks</u>	<u>Total</u>
Initial investment, \$	1,580,000	11,800,000(1)	540,000	-
Annual operation & maintenance, \$	2,196,000	700,000(2)	735,000	1,435,000
Salvage value, \$	0	0	0	0
Life, years	4	20	4	-
Present worth(3)	8,540,000	17,760,000	2,990,000	-
Unacost (uniform end- of-year annual amount)	2,694,000	2,086,000	943,000	3,030,000

(1) Pipeline capital costs from Oil and Gas Journal, August 14, 1978.
Escalated at 7% per year.

(2) Assumed equal 6 percent of initial investment for pipeline. For
trucks, include tires, parts, fuel and oil, and labor.

(3) Discrete compound interest is 10 percent.

compressed and shifted to obtain the stoichiometric ratio of hydrogen to carbon monoxide required for methanol synthesis. Adjustment of the hydrogen-carbon monoxide ratio through use of the shift conversion reaction lowers the mass conversion efficiency of the overall process.

On the other hand, steam reforming of methane produces a synthesis gas rich in hydrogen. Combination of these two synthesis gas streams in the proper proportion would allow adjustment of the hydrogen-carbon monoxide ratio without shift conversion, while maximizing the amount of carbon available for conversion to methanol. Depending on the gasification process, this methane hybrid system can increase methanol outputs per unit of biomass feedstock to about 2 to 5 times the level achievable by the biomass feed alone. Table 7.3 compares the mass conversion efficiency of a simple biomass and a biomass methane hybrid methanol system. In addition, the methane hybrid methanol system, through elimination of the shift conversion, would reduce the CO₂ scrubbing requirements. Figure 7.1 illustrates a simplified flow diagram of alternative biomass-syngas hybrid methanol processes.

7.3.2 Economic Advantages of Biomass-Methane Hybrid Methanol Systems

For near-term development, a biomass-methane hybrid methanol system could be constructed in two stages (within 4 years) without a significant capital cost penalty:

- Stage one would provide (within 2 years) a natural gas methanol plant with a deliberately designed under capacity steam reforming process.
- Stage two would add the biomass gasifiers within 1 to 2 years from the time the initial methanol production commenced.

Table 7.3 Comparison of the Relative Mass Conversion Efficiency of a Simple Biomass, and a Biomass-Methane Hybrid, to Methanol System

<u>Gasification Process</u>	(Tons of Methanol per ton of dry wood feed) ^c	
	<u>Simple Gasification^a</u>	<u>Methane Hybrid^b</u>
Purox	0.464	2.09
Moore-Canada	0.505	1.86
Koppers-Totzek	0.497	1.80
Wellman-Galusha	0.462	1.91

-
- a. Gasification plus shift conversion to $H_2/CO=2$.
 - b. Gasification plus appropriate steam reformed methane addition to adjust $H_2/CO = 2$.
 - c. Estimated yields do not include fuels used for process energy or removed from the methanol reactor purge stream.

Figure 7.1 Biomass to Methanol Process Flow Diagram Using Hybrid Feed Stocks

The biomass-methane hybrid system can be viewed also as a mechanism for retrofitting existing methanol-from-natural gas plants. In this capacity, biomass gasifiers could replace up to 30 percent of the natural gas feedstock. Therefore, the only capital cost requirement will be that associated with the biomass gasifier. It is estimated that such retrofitting arrangements would not only prolong the natural gas supply in several regions, but also would reduce the methanol production cost.

For longer term development (1990 and on), methanol production from biomass could benefit economically from implementation of any of several methane gas production alternatives. These alternatives include (1) anaerobic digestion of biomass, MSW, sewage sludge, or peat, (2) SNG production from fossil fuels, and (3) SNG from petroleum sources. Other possible biomass hybrid feedstocks also are being investigated. One system augments the biomass gas stream with pure hydrogen. This hydrogen hybrid is estimated to be less cost effective than the methane hybrid systems⁽¹⁾. In the long term, the hydrogen source could be generated from (1) electrolysis of water, (2) closed-cycle thermochemical decomposition, and (3) hydrogen from fossil fuels.

All of the above-described alternative biomass hybrid feedstocks appear to offer considerable technological and economic advantages over a simple, biomass-to-methanol process.

7.4 HYBRID PRODUCT PROCESS

In this section, prospectives of producing multiple products along with methanol is examined. A generic analysis of potential application of biomass derived synthesis gas is first

screened on the basis of synthesis gas stoichiometry followed by a description of various hybrid product process concepts.

7.4.1 Synthesis Gas and its Potential Uses

The simplest aspect to explore the potential applications of biomass derived synthesis gas is through the stoichiometry of synthesis gas composition⁽³⁾. Table 7.4 compares the composition of synthesis gas derived from various carbon-hydrogen feedstocks including gas, oil, coal, and biomass. Table 7.4 shows that the raw synthesis gas derived from biomass is basically deficient in hydrogen when compared with those produced from other hydrocarbon feedstocks. These characteristics may present a unique potential of producing various chemical and fuel products. The current major use of synthesis gas, as well as potential application are listed in Table 7.5. From the preliminary synthesis gas analysis, the economic potential of producing multiple products from biomass derived synthesis gas has been narrowed down to co-production of methanol and acetic acid and the production of Methyl Tert-butyl ether. A description of conceptual processes for these co-production schemes follows.

7.4.2 Co-production of Methanol and Acetic Acid

Since the biomass derived synthesis gas contains CO and H₂ in the molar ratio of approximately 3:2 (i.e., Wellman-Galusha biomass gasification), the synthesis gas can be processed into two separate streams for the optimum co-production of methanol and acetic acid⁽⁵⁾. In this system, the front end process, gasification, is the same as for methanol production alone. Following acid gas (H₂S and CO₂) removal (hot carbonate), the gas is split into two

Table 7.4 A Comparison of the Composition of
Synthesis Gas Derived from Various
Carbon-Hydrogen Feedstocks

<u>Process</u>	<u>Feedstock</u>	<u>Synthesis gas composition</u> <u>H₂:CO mole ratio</u>
Steam-methane reforming	Natural gas	3 : 1
Steam-naphtha reforming	Naphtha	2 : 1
Partial oxidation of resid	Crude oil or resid	1 : 1
Lurgi coal gasification	Bituminous coal	2.2 : 1
K-T coal gasification	Bituminous coal	0.63 : 1
K-T biomass gasification	Wood biomass	0.81 : 1
Purox biomass gasification	Wood biomass	0.69 : 1
W-G biomass gasification	Wood biomass	0.68 : 1

Table 7.5 Major Use of Synthesis Gases and Their Composition Requirements

<u>Current Major Use</u>	<u>Stoichiometry of Synthesis Gas Composition H₂:CO</u>
Methanol	2 : 1
Ammonia	All H ₂
Acetic acid	2:1 + 1CO
Isocyanates	3H ₂ + 1CO
Oxo alcohols	1:1 + 1H ₂
Methyl Tert-butyl ether (MTBE)	1.5 : 1
 <u>Future Potential Uses</u>	
Ethylene glycol	1.5 : 1
Acetic anhydride	1 : 1
Vinyl acetate	1.25 : 1
Ethanol	2 : 1
Acetaldehyde	1.5 : 1
Ethylene & higher olefins	2 : 1
Aromatics	1.5 : 1

streams, the first routed directly to a cryogenic CO separation unit for CO recovery. The pressurized hydrogen obtained from cryogenic separation is added to the second stream to adjust the ratio of hydrogen and carbon monoxide to the level required for optimum methanol synthesis. The shift conversion step in the normal methanol synthesis process is omitted. Part of the methanol produced passes to the acetic acid plant where CO and methanol reacted catalytically.

The special advantages of this coproduction concept lies on two areas:

1. A new low pressure (30 atm) process for the production of acetic acid from methanol and CO has been developed versus the conventional high pressure (700 atm) process. This low pressure process offers significant economic advantages especially when operated in conjunction with the low pressure (40-50 atm) methanol process.
2. The biomass derived synthesis gas has the optimum stoichiometric ratios for simultaneous production of methanol and acetic acid.

7.4.3 Co-Production of Methyl Tert-Butyl Ether (MTBE)

A rapidly increasing market for methanol is the production of Methyl Tert-butyl ether, a octane booster for motor fuel. The great demand and popularity of MTBE in U.S. and world market stems from two factors⁽⁶⁾:

1. MTBE has a very high octane blending value, rated about 110 [(Research & Motor)/2]. Therefore, it has the special attraction of freeing toluene (an aromatic currently in short supply) that might otherwise be added to gasoline in order to meet unleaded octane requirements.

2. The U.S. regulatory attitude toward octane additives and blending components. MMT antiknock (methylcyclopentadienyl manganese tricarbonyl) was banned in U.S. and lead antiknock compounds are continuing their phase-down to 0.5 g/gal of gasoline.

MTBE production could be more attractive in the near future than the competing alkylate production, because the octane of unleaded gasoline made up with MTBE is higher than that containing a similar amount of isobutylene-based alkylate.

Several commercial process technologies are available for the production of MTBE, but there is not much difference between them. Basically, they all react methanol and isobutylene in the presence of a catalytic ion-exchange resin, typically a sulfonated styrene/divinyl benzene resin. The basic reaction is:

The yield is 95 percent(7).

A recent report from Chem System(6) predicts that MTBE demand will reach 8.34 million tons per year in U.S. by 1985. Table 7.6 summarizes the world production estimates for MTBE and related products.

Table 7.6 World Production Estimates for MTBE

	W. Europe		U.S.		Japan	
Million metric tons per year	1980	1985	1980	1985	1980	1985
Ethylene production*	15.0	21.05	4.81	8.34	5.4	7.58
Isobutene byproduct**	2.06	2.88	0.66	1.14	0.74	1.04
MTBE production	3.0	4.21	0.96	1.67	1.08	1.52

*From steam cracking of butanes and heavier feedstocks.

**Medium severity operation.

It is conceivable that the methanol supply may actually be a more limiting factor than isobutylene for MTBE production. Hence, it is envisioned that a future strong demand for MTBE will likely stimulate methanol production and probably provide a potential market for biomass derived methanol.

7.5 ADVANCED BIOMASS GASIFICATION PROCESSES

Most of the gasification technology considered in this study was originally developed for coal or municipal solid waste to produce either a low or medium Btu fuel gas. Because of the inherent gasification designs, these gasifiers do not take advantage of biomass feedstock properties such as high reactivity and low sulfur and ash characteristics.

Advanced gasification techniques especially for biomass are in various stages of bench scale research and pilot plant scale development(9,10). Taken together, these efforts are aimed at the following objectives:

- Avoidance of the use of oxygen,
- Use of catalysts to achieve high gasification rates at low temperatures,
- Use of catalysts to tailor the composition of the gas,
- Gasification at high pressure,
- Design of the gasification process to minimize pretreatment of the biomass.

These objectives are discussed further below. Methanol synthesis gas produced by partial oxidation requires the use of oxygen to avoid the presence of significant amounts of nitrogen. However, with indirect heating (pyrolysis), gasification could be accomplished without oxygen. Two DOE sponsored research efforts are underway to employ indirect heating(16,17). One (Battelle Columbus) uses a heated particulate material (e.g. sand) which is mixed with the biomass in a fluidized bed. The hydro-gasification process, being developed by Wright-Malta, utilized the heat from the gasification products themselves. In the Battelle gasifier, the sand is cycled between the fluidized bed gasifier and a combustor where biomass is burned with air.

Use of indirect heating and elimination of the oxygen plant could effect both a large capital investment savings and a savings in operating cost. Reference to Table 6.11 in Section 6.3 shows the oxygen plant to be approximately 11 percent of the capital investment. The savings in operating cost is the reduced energy required to operate the oxygen plant, which

is approximately 40 percent of the total process energy requirements. If all of the energy to operate the oxygen plant derives from combustion of biomass, elimination of the oxygen plant translates into a 9 percent increased yield of methanol per unit weight of biomass consumed by the plant.

The use of catalysts to increase the rate of gasification is being pursued by several research groups, including Battelle Columbus⁽¹⁷⁾ and Battelle Northwest⁽¹⁸⁾. Catalysts which have been used for coal are generally also successful for biomass. These include alkali metal carbonates, especially K_2CO_3 , and wood ash. With catalysts, satisfactory gasification has been achieved at temperatures as low as 700 to 800°C (1300° to 1470°F) in small scale fixed-bed and fluidized bed gasifiers. The objective of this is two-fold. The first is to permit a smaller gasifier for a given throughput. From Table 6.11 in Section 6.3, the cost of the gasifier is 30 percent of the total capital investment. The second, is that the biomass material does not have to be heated to a temperature which is too high for satisfactory gasification to occur. This translates into a higher mass conversion efficiency for wood-to-methanol. For an entrained bed or fluidized bed gasifier, the increase is approximately 0.7 percent for each 100°F reduction in gasification temperature in the neighborhood of 1800°F.

Besides increasing gasification rate, other catalysts may be added to tailor the gas composition. Laboratory studies at Battelle Northwest have indicated that synthesis gas yields may be enhanced by the use of cracking catalysts, such as silica-alumina⁽¹⁸⁾. This catalyst reduces the amounts of methane and other hydrocarbons in the product gas. The potential savings to be achieved is the reduction in the amount of the purge stream from the methanol synthesis loop which permits a higher conversion of synthesis gas to methanol. This is especially important

when the gasification temperature is low and significant quantities of methane otherwise are produced. If the methane content of the synthesis is reduced 1 percent (of total gas composition) by catalytic cracking to CO and H₂, the yield of methanol can be increased by 2 percent.

Gasification at high pressure, 450 psig, could substantially increase the yield of methanol from biomass. Capital investmentwise, a large synthesis gas compressor would be eliminated but this cost savings would likely be offset by an increased cost of the gasifier. The only current development of a high-pressure gasification process of biomass is being pursued by Wright Malta(16).

The increase in yield expected from gasification at high pressure stems from a significantly reduced process energy requirement. Much more energy is required to compress a gas (i.e., the synthesis gas) than to introduce the equivalent amount of solid or liquid (slurry) biomass into a pressurized gasifier. This translates into a smaller amount of biomass to be burned for process energy. Approximately 50 percent of the process energy is required for synthesis gas compression, if gasification at atmospheric pressure is used. If instead, the gasification is performed at 450 psig, the net compression energy requirements, excluding those for oxygen, are reduced to less than 25 percent of the process energy. The corresponding increase in yield of methanol per unit weight of biomass is 23 percent.

The last objective is to design a gasifier which minimizes the pretreatment of the biomass feed. According to Table 6.11 in Section 6.3, the capital equipment cost of front end is 9.8 percent of the total capital investment. Some drying of the biomass is necessary to achieve the desired

product gas composition. However, moisture content in the range of 20 to 40 percent may be acceptable, depending on the operating conditions, and these moisture contents can be achieved by field drying.

Size reduction, such as chopping and grinding also will be necessary, but at present the extent needed is dependent on the type of biomass material and the ingenuity of gasifier designer. No systematic research is being done in this area.

7.6 ADVANCED METHANOL SYNTHESIS TECHNOLOGY

Although the presently available methanol technology is considered well developed, there is still a strong incentive for improving the methanol synthesis technology. In terms of utilizing the biomass feedstocks, there are three primary areas in which the advanced methanol synthesis technology might be desired:

1. A new methanol synthesis catalyst suitable for low pressure operation (<30 atm). The economic advantages of this technology are apparent due to the match of the pressure of methanol synthesis loop with the output pressure of CO₂ scrubber. This reduces the synthesis gas compression energy requirement.
2. A new methanol catalyst selectively designed for biomass feedstock can increase the methanol yield (i.e., conversion per pass) and therefore requires smaller methanol plants for dispersed biomass resources.
3. An improved waste heat recovery and methanol reactor cooling schemes which allows a higher conversion and energy efficiency.

In the first two areas, recent research from Union Carbide(11), Lehigh University(20), and from Sagoni Chemical Co(21) in Japan, strongly indicates that such catalyst improvements can be achieved both with the conventional CU/ZnO catalyst and with catalysts containing finely dispersed Group VIII metals such as Pd, Pt, Ir, Rh, and their alloys. The yields from these new catalysts are reported to be 3 to 5 times higher than the typical ICI CU/ZnO/Al₂O₃ type catalysts.

In the third area, various reactor heat recovery and cooling systems have been developed. These include the multiple fixed-beds (ICI), tube in shell type (Lurgi), and radial flow reactor (Topsoe)(22). In addition, a novel liquid-phase methanol synthesis process has recently been developed by Chem. System Inc. as described in Section 2(23). This process employs an alternative concept for removing the methanol heat of reaction. By fluidizing the catalyst in an inert liquid phase, the reaction heat is readily absorbed by the high heat capacity of the liquid with a minimum temperature rise. Also, circulation of the process liquid permits effective external heat removal. However, this process is still in the developmental stage. Potential problem areas might include attraction of the catalyst particles, the inhibition of the catalyst activity by the fluid, insufficient solubility of synthesis gas in the fluid, and probable deterioration of the heat transfer fluid. Nevertheless, this liquid phase methanol process appears to show economic advantages and should be evaluated for biomass feedstock in the future.

7.7 HIGHER ALCOHOL SYNTHESIS

Although no commercial process has been identified in the United States to pursue ethanol and higher alcohol production from biomass materials via thermal/gasification

processes, there is ample evidence in the catalysis literature indicating the technical feasibility of producing ethanol and higher alcohols from synthesis gas.

There are basically three process concepts which have shown promise for the production of ethanol from synthesis gas. The first two concepts involve the production of methanol first from synthesis gas, followed by methanol homologation to ethanol. The third concept is the simultaneous conversion of ethanol and methanol directly from synthesis gas. Specifically these process concepts are (19,20):

1. High pressure (300 atm) homologation of methanol to ethanol over cobalt hydrido-carbonyl.
2. Low pressure (1-50 atm) homologation of methanol to ethanol over soluble or anchored rhodium complexes with alkyl iodides, and
3. Low pressure (1-50 atm) direct synthesis of ethanol over rhodium catalysts supported on TiO_2 , La_2O_3 , and ZrO_2 or over rhodium alloys.

The first process is being pursued by DOE's Pittsburgh Energy Research Center and theoretically can convert 90 percent of the reactant methanol to ethanol. However, work performed to date shows rather poor activity and selectivity, for the homogeneous cobalt catalyst. The second process appears to pose serious material problems because of the presence of highly corrosive halogens in the reaction mixture. The third process appears promising, and deserves careful examination for its potential application to biomass feedstocks.

During the past several decades, in the intensive efforts of searching for a suitable methanol catalyst, it was discovered that several metal-containing catalysts could be used to produce mixtures of alcohols directly from synthesis gas at high temperatures and pressures. These catalysts include metal pairs such as Cu-Cr₂O₃ and MnO-Cr₂O₃. It has long been recognized that these catalyst components can be added to the ZnO type methanol catalyst, if it is desirable, to make higher alcohols. Catalysts for synthesizing higher alcohols can be prepared from Cu, Zn, Mn, Mo, and a combination of an alkali or alkaline earth oxide with a metal oxide of acid character, e.g., chromates, manganates, molybdates.

Previous test results of alcohol synthesis catalysts are summarized in Table 7.7. It is noted that as the alkali ion concentration increases, the yield of methanol decreases, while the yield of higher alcohols increases. For example, with a catalyst of the following composition: Cr₂O₃/MnO/Rb₂O = 1:0.85:0.42, the synthesis gas consisting of CO and H₂ at 400°C and 200 atm was converted to liquid products consisting of 42 percent methanol, 38 percent higher alcohol (predominantly ethanol), and 15 percent aldehydes and acetals.

In addition, recent investigations show supported rhodium catalysts to be a promising means to achieve high yield of ethanol and methanol. With the addition of iron to the rhodium catalyst, it is reported (19) that a high product yield of more than 50 percent of ethanol and methanol was achieved, the remaining product being pure methane gas. Even better selectivity to ethanol and methanol over methane was recently reported for rhodium catalysts supported on TiO₂, La₂O₃, and ZnO₂ (20).

Table 7.7 Methanol Synthesis Over Alkali Metal
Oxide Catalysts at 400°C and 200 atm

<u>Catalyst</u>	<u>Ratio (wt %)</u>	<u>Product Yield (g/hr)</u>	<u>% Methanol in Product</u>	<u>% Other Liquid Compounds in Product</u>
Cr ₂ O ₃ /MnO/Li ₂ O	1:0.93:0.10	47	76.9	21.7
Cr ₂ O ₃ /MnO/Na ₂ O	1:0.93:0.08	43	63.9	32.9
Cr ₂ O ₃ /MnO/K ₂ O	1:0.93:0.12	39	60.8	38.4
Cr ₂ O ₃ /MnO/Rb ₂ O	1:0.93:0.00	62	80.5	13.0
	1:0.93:0.06	61	75.5	23.1
	1:0.93:0.13	62	67.2	33.1
	1:0.93:0.25	53	49.7	46.0
	1:0.85:0.42	50	42.0	54.0
Cr ₂ O ₃ /MnO/Cs ₂ O	1:0.93:0.11	53	82.1	18.8

The prospect of using a uniquely developed catalyst for the simultaneous production of methanol and ethanol appears to be attractive in the near future. The appropriate mixture of ethanol and methanol can form an ideal liquid fuel suitable for transportation uses. For this purpose, it is envisioned that such alternative conversion routes may eventually become more economically attractive than producing pure methanol or ethanol fuel alone. It is our opinion that such an alternative concept for simultaneous production of ethanol and methanol needs to be examined carefully, and more technical and economic information needs to be generated.

7.8 HYDROCARBON FUELS AND GASOLINE

In addition to methanol, the greatest development in CO/H₂ synthesis since the early 1920's has been the synthesis of liquid hydrocarbon fuels. Because of the flexibility in composition for these fuels, the restrictions in terms of product selectivity are not as severe as those encountered in the synthesis of methanol or ammonia. In terms of industrial application, the most desirable liquid hydrocarbon fuels are gasoline, jet fuels, diesel fuels, and gas turbine fuels.

The most notable synthesis technology for the production of these fuels from syngas is the SASOL technology based on Fischer-Tropsch reactions. This technology uses promoted iron catalysts and operates at medium pressures (10-30 atm). The product distribution is broad, including light hydrocarbons as well as waxes, and a considerable percentage of oxygenated compounds. The presence of large amounts of olefins and only a small fraction of aromatics

makes it an undesirable product for either gasoline or jet fuel without considerable product upgrading. This problem is typical of all synthesis efforts based on the conventional Fischer-Tropsch type of catalysis(11).

The only novel approach to the synthesis of hydrocarbon fuels from CO and H₂ has been pioneered by Mobil Oil Company over the last 5 years. Instead of relying on direct synthesis of fuels, the Mobil approach is first to synthesize methanol and then to dimerize the methanol to dimethyl ether, the last intermediate for the desired hydrocarbons. By utilizing a novel catalyst, the Mobil technology can achieve a high selectivity for products of interest for gasoline manufacture, including a high yield of aromatics and no oxygenated products. More recently, the Mobil efforts have included attempts to start directly with synthesis gas.

7.8.1 Mobil Gasoline Technology

Recently a certain class of crystalline zeolite catalysts has been discovered, which can induce transformation of short chain aliphatic hydrocarbons to mixtures of higher aliphatics, olefins, and alkyl substituted aromatics. Moreover, the catalysts and associated conversion processes can be tailored to give a mixture, in high yield, which shows promise as a direct substitute for high octane gasoline. The most publicized process of this kind is the Mobil gasoline-from-methanol process.(13) In this process, industrial-grade methanol is converted to hydrocarbons consisting primarily (greater than 75%) of a gasoline grade material with small amounts of LPG (C₃ and C₄) and fuel gas (C₁ and C₂). The overall gasoline yield can be increased to over 90 percent by alkylating the C₃ and C₄ olefins with the isobutane produced by the process. Figure 7.2 depicts the Mobil methanol-to-gasoline process flow scheme using a fixed-bed reactor system.

Figure 7.2

MOBIL METHANOL TO GASOLINE PROCESS FLOW SCHEME -FIXED BED OPTION

Source: Reference 13

The Mobil methanol-to-gasoline process offers a new route for the conversion of biomass to high octane gasoline and other desirable products. The composition of the raw gasoline product is 30 to 50 percent aromatics, 45 to 55 percent isoparaffins and the balance olefins, with an unleaded research octane number of over 90. Therefore, the gasoline product from the Mobil process could be used alone or blended with petroleum-derived gasoline.

7.8.2 Reaction Path and Potential Product Characteristics

The reaction path of the methanol-to-gasoline process appears to be represented by the following mechanisms:

Two versions of this process were explored by Mobil. In the first, denoted the fixed-bed process, the conversion is carried out in two stages, each employing a separate catalyst. In the first stage, methanol is dehydrated to an equilibrium mixture of methanol and dimethyl ether. In the second stage, this mixture is passed over a proprietary "conversion catalyst" to form the desired gasoline mixture. Olefins appear as intermediates.

In the second version, a mixture of both catalysts are used in a fluidized bed reactor.

Figure 7.3 shows data on the effect of space velocity on product distribution in methanol conversion to gasoline products.

Figure 7.3 Reaction Path for Methanol Conversion to Hydrocarbons (371°C)

Source: Reference 13

Since the above reaction path indicates that the primary hydrocarbon products are light olefins, it is possible, at a low oxygenate conversion per pass, to produce ethylene and/or propylene. Laboratory work⁽¹⁴⁾ has shown that, with catalyst and process modifications, it is possible to increase the level of the more desirable ethylene to about 30 percent at approximately 48 percent oxygenate conversion.

7.8.3 Alternative Gasoline Conversion Processes

Figure 7.4 shows an integrated process for converting biomass to high octane gasoline via the fluidized bed reactor version of the Mobil methanol-to-gasoline process. Referring to Fig. 7.4, biomass, oxygen, and steam are suitably reacted to produce a synthesis gas which is admixed with auxiliary synthesis gas. The synthesis gas mixture is converted to methanol via a methanol synthesis loop. The unreacted portion of the synthesis gas may be separated into a stream comprised of methane and a stream comprised of carbon monoxide and hydrogen, or it may be further processed without separation. In either case, a methane stream is steam reformed to produce auxiliary synthesis gas. The organic portion of the product is primarily methanol and is converted to gasoline via a special zeolite catalytic process. The products from this conversion include water, which is recycled either to biomass gasification or to steam reforming, or both, and a hydrocarbon product comprised of C₅+ aromatic gasoline and C₄- hydrocarbons.

In addition to the Mobil methanol-to-gasoline process described above, there are several other process alternatives which can be used to convert the biomass derived synthesis gas to gasoline products. These process alternatives are described below.

Figure 7.4 Integrated Simplified Flow Diagram of a Biomass-to-Gasoline Process

1. A two stage conversion of synthesis gas through dimethyl ether to gasoline products (U.S. patent 4,011,1275)

This two stage process for the conversion of synthesis gas (mixed CO and H₂) to gasoline involves, (1) contacting synthesis gas with a modified methanol synthesis catalyst to produce a mixture of dimethyl ether and methanol, and (2) contacting the first-stage product, in its entirety, with a crystalline aluminosilicate catalyst to convert it to high octane gasoline.

In the last stage, synthesis gas having a smaller hydrogen to carbon monoxide ratio than that required by methanol stoichiometry, i.e., 2:1, is converted over a zinc-chronium acid or copper-zinc-alumina-acid modified methanol synthesis catalyst to a mixture of methanol and dimethyl ether. The dimethyl ether and carbon monoxide is then converted to hydrocarbons in a second stage, using Zeolite catalysts operating at 700°F and a space velocity of 1 LHSV to produce a stream consisting primarily of C₅ aromatic hydrocarbons.

2. Conversion of Synthesis Gas to Methanol Followed by Carbonylation (U.S. patent 4039600)

This process involves reacting carbon monoxide and hydrogen, about 450° to 750°F in contact with a methanol synthesis catalyst, to produce a product comprised of methanol and carbon monoxide. This mixture then is reacted, at about 300° to 800°F in contact with a carbonylation catalyst, to produce a product comprised of methanol and acetic acid. Finally this last mixture is reacted, at about 500° to 1200°F in contact with an aromatizing catalyst (a zeolite), to produce a product containing gasoline-boiling-range aromatic hydrocarbons.

This process is based partly upon the discovery that the particular admixture produced by the combination of methanol synthesis followed by carbonylation is convertible to a product, which is disproportionately and unexpectedly higher in aromatic hydrocarbons than predicted from a consideration of the conversion obtainable from individual reactants.

7.9 Summary

In the near future, new technologies may play a significant role in improving the methanol-from-biomass production economics and also may provide conversion process alternatives for the production of higher alcohols and gasoline products.

These new technologies include the following categories: improved methanol synthesis processes, direct higher alcohol synthesis, conversion of methanol to gasoline (Mobil processes), and improvements in gasification technology for biomass to produce a more easily used synthesis gas.

In nearly all of these new processes, catalysis plays a key role in the chemical conversion to desirable products. Thus, the development and interaction of new catalytic processes could be one of the determining factors in the economic production of chemicals and fuels from biomass. Although many of these catalytic processes are equally suited for coal and other hydrocarbon feedstocks, it appears that biomass feedstocks can achieve higher reactivity and selectivity because of certain physical and chemical characteristics. Since biomass contains insignificant amounts of contaminants, such as, sulfur and ash, it is possible that a one-step or a two-step catalytic conversion process could be developed in the future which would be much simpler and more economical than the multistep processes required for coal.

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8. RECOMMENDATIONS FOR FURTHER RESEARCH AND DEVELOPMENT EFFORTS

As discussed in previous sections, methanol production from biomass could become both technically and economically attractive if integrated processes and Federal Tax incentives are implemented. The margin of this attractiveness could be further enhanced by future technological improvements and by implementing an accelerated demonstration program.

In the near-term, biomass derived methanol is concluded to be an economically competitive liquid transportation fuel. This can be realized by demonstrating a methanol production process which employs a biomass methane hybrid feedstock system. The technical and economic advantages of such systems allows biomass to compete with large-scale methanol production from coal and natural gas.

In the long-term, new technologies will play a significant role in improving the methanol-from-biomass production economics, and also may provide conversion process alternatives for the production of higher alcohols and gasoline products.

In the following, a summary discussion of technological development opportunities and an outline of a proposed three phase methanol demonstration program is presented.

8.1 TECHNOLOGICAL DEVELOPMENT OPPORTUNITIES

In view of the potential for technological improvements, it is recommended that future research and development be directed toward the five types of efforts described in the following subsection.

8.1.1 Fundamentals of Gasification Processes and Properties

Research and development of biomass gasification processes, which take advantage of the high reactivity and low sulfur and ash content of biomass should be pursued. The goal should be to develop a gasifier which can produce a gas directly suitable for catalytic conversion to methanol and other fuels and chemicals. Subjects for investigation would include:

- Continue investigation of mechanisms of biomass gasification reactions for methanol synthesis gas production including: (a) flash pyrolysis, (b) steam-gasification, and (c) catalytic (low temperature) gasification.
- Investigate fundamentals of solid-gas contacting in biomass gasifiers including: (a) fluidized bed, (b) entrained-bed, and (c) fixed bed.
- Develop pressurized biomass gasification processes including: (a) non-catalytic and (b) catalytic types.
- Continue development of techniques to gasify biomass without the use of oxygen, i.e., indirect heating.

8.1.2 Materials and Mechanical Systems

Improved and economically reliable systems for continuous feed and removal of solids from gasifiers should be developed.

- Investigate biomass feeding mechanisms and ash removal systems for high pressure gasifiers.
- Investigate interaction of refractories with (a) biomass-ash material (b) catalyst, and (c) process environment in order to better understand problems such as fluxing of ash and plugging of reactors.
- Develop economic means for biomass feedstock drying including: (a) open stockpile and (b) solar concentrator drying.

8.1.3 Catalyst Development

Research, on laboratory and pilot plant scales should be performed to improve catalysts for efficient utilization of biomass synthesis gas.

- Develop new methanol catalysts for biomass derived synthesis gas that are stable at high temperature and low pressure.
- Develop long-lived, active, and selective methanol catalyst for primary transportation fuel production. Of particular interest may be the Rhodium catalyst recently discovered for enhancing the synthesis of methanol and ethanol.

8.1.4 Methanol Fuel Hybrid Production Alternative

Conceptual process designs and strategies for utilization of biomass-hybrid feedstocks for methanol production, including methane-hybrid and hydrogen-hybrid alternatives, should be developed and evaluated. The sources of these hybrid feedstocks should include the following:

- Anaerobic digestion of biomass, municipal solid wastes, sewage sludge or peat,
- SNG production from fossil fuels,
- SNG from petroleum sources,
- Electrolysis of water,
- Closed-cycle thermochemical decomposition of water,
- Hydrogen from fossil fuels.

8.1.5 New and Innovative Processes

Technical and economic feasibility studies of new and improved catalytic processes for liquid fuel production from synthesis gas, should be performed.

- Improved methanol synthesis processes such as the liquid-phase methanol process,

- Direct higher alcohol synthesis processes, such as an improved Fischer-Tropsch process,
- Methanol homologation technology,
- Mobil process for converting methanol to gasoline,
- Direct synthesis of gasoline from synthesis gas.

8.2 BIOMASS-TO-METHANOL DEVELOPMENT PROGRAM

The following section outlines the sequence for a biomass-to-methanol development program. The objective would be to accelerate the near-term demonstration of production of methanol from biomass feedstocks. On this basis, initial commercial scale methanol production from biomass could commence within 6 years, and subsequent large scale methanol production would occur prior to 1990. This program would involve three explicit demonstration phases and a pre-demonstration study phase.

Pre-demonstration phase. This phase would require about 1 year. The key objectives would be to:

- a. Select appropriate existing methanol plant sites, compatible with biomass feedstocks and markets, for consideration of a biomass-methane hybrid production of methanol.
- b. Evaluate and develop conceptual processes utilizing new and innovative gasification and conversion technology for alcohol fuels and gasoline from biomass.

The major product at the end of this phase would be:

1. The identification of suitable, existing methanol production sites with a scale commensurate with local biomass resources and methanol markets.

2. Conceptual designs and specifications for new and improved biomass-based alcohol fuels and for conversion of alcohols to gasoline.
3. A recommended specific, new gasification and methanol catalytic process for process demonstrations and final economic analyses.

Phase I demonstration program. This phase would require about 1-1/2 to 2 years. The major objective of this phase would be to:

- a. Demonstrate the technical and economic feasibility of a biomass-methane hybrid methanol facility using an existing, commercially available biomass gasifier in the size range of 100 to 150 TPD.
- b. Demonstrate the economics of the collection and transport of 500 TPD biomass to a centralized gasification system retrofitted with an existing small scale methanol plant (about 200 TPD capacity).

The appropriate implementation strategy will consist of:

- a. Commissioning of engineering designs for retrofitting an existing natural gas methanol plant at a location in Northern Louisiana, or Texas Gulf region.
- b. Purchase and install commercially available (such as W-G or K-T) biomass gasifiers with a total capacity of 500 TPD.
- c. The operation of the plant would be modified such that steam reformers will be derated to accommodate biomass produced synthesis gas to balance the H₂ to CO ratio.

Besides the technical and economic results, the Phase I demonstration program also would involve the development

of an appropriate, overall institutional framework suited to subsequent alcohol fuel or gasoline developments. This phase would also provide the lead time to confirm new and innovative gasification technologies needed for Phase II demonstration.

Phase II demonstration phase. This phase would require about 2-3 years. The key objectives would be to:

- a. Demonstrate one or more advanced biomass gasifiers for producing a synthesis gas with a H_2 to CO ratio equal to 2, in the size range of 100 to 150 TPD.
- b. Demonstrate the advanced methanol synthesis process using new catalyst or innovative process concept at a 200 TPD plant size.

The implementation strategy for this phase would include:

- a. Place the advanced gasifiers in parallel with the Phase I, existing gasifiers and compare the operation of the two gasifier systems.
- b. Utilize the steam reformer and CO shift converter only for reforming any methane produced by the advanced gasifier.
- c. Operate the advanced methanol process in parallel with the existing methanol process to compare the economics and technical capabilities.

The key benefits from Phase II would be the acquisition of the data and information needed for design and construction of an advanced biomass-to-methanol plant, employing new technology for biomass gasification and methanol synthesis. It is noted that an estimated 2-1/2 to 3 years lead time is available before full-scale investment is made and construction of a new plant begun.

Phase III demonstration program. This phase would require approximately 3 to 4 years. The key objective of this phase would be to:

- a. Demonstrate an integrated, advanced biomass-to-methanol production technology, together with the feedstock collection and product distribution, at a methanol capacity of 2000 TPD.
- b. Demonstrate the economic and operational advantages of a commercial-scale biomass-to-methanol plant compared with other methanol production technologies.

The implementation strategy of this phase would include:

- a. Select the most appropriate biomass production and collection logistics to supply approximately 5000 TPD biomass feedstock. The logistics might include a dispersed gasifier concept, whereby the biomass is gasified near resource sites and the synthesis gas is transported to a centrally located methanol plant via pipelines.
- b. Gasifiers would utilize a combination of available biomass residues and biomass products from large energy farms.
- c. Design and develop a distribution network and market strategies for wide-spread use of large-scale biomass-to-methanol facilities.

APPENDIX A. PROCESS SYSTEM MODELS

A.1 INTRODUCTION

Detailed modeling of process elements, in addition to allowing calculation of equipment dimensions, provides insight into the relationships existing among process variables, and provides guidance for selection of the optimum process configuration. For these reasons, detailed process models have been constructed for the following process elements:

- Gasification
- Acid gas removal
- Shift conversion
- Methanol synthesis and purification

In order to avoid disclosure of proprietary information, all model development was based on physical data available in the open literature.

A.2 EQUILIBRIUM GASIFICATION MODEL

In the interest of better understanding the effects of oxygen-to-biomass ratio, steam-to-biomass ratio, and gasification temperature upon the production of synthesis gas (H_2 and CO), a series of chemical equilibrium calculations were made. Clearly, chemical equilibrium is not always achieved in a gasifier. In an updraft, moving-bed gasifier, chemical equilibrium probably is achieved at the bottom of the gasifier because of the high temperature there (e.g., 2500°F in the Wellman-Galusha gasifier and 3000°F in the Purox gasifier). However, at the gas outlet chemical equilibrium does not exist. In entrained-bed and fluidized-bed gasifiers, equilibrium may be achieved, especially if the temperature is sufficiently high, if the residence time is sufficiently long or if catalysts are used. Indeed, the gas composition from the K-T gasifier closely approaches chemical equilibrium. Whether or not chemical

equilibrium is achieved in every case, it still is useful to examine the effects predicted by equilibrium considerations.

The equilibrium calculations were made using a NASA computer program together with JANAF data for the thermochemical properties of the reaction products.⁽¹⁾ Table A.1 lists the products considered in the calculations. Most of the products, however, appear in insignificant amounts. The calculational procedure utilizes the minimization of the Gibbs free energy of the system. The complete procedure is described in detail in Reference 1.

The equilibrium calculations were made for a wood, containing selected quantities of water, reacted with various amounts of tonnage oxygen (95 percent pure) at constant pressure and enthalpy (i.e., equivalent to calculation of adiabatic flame temperature and composition). The properties of the wood considered are listed in Table A.2; and the wood is the same as that used in the tests with the Wellman-Galusha gasifier mentioned above. The ash content of the wood was modeled by considering it to be sodium oxide.

Figure A.1 shows the equilibrium composition at one atmosphere pressure as a function of temperature for oxygen and wood with zero moisture content. The temperature variation, of course, results from the variation in the ratio of oxygen to wood. This composition also is shown in the figure. It may be noted that as more oxygen is added, and consequently as the gasification temperature increases, more of the wood hydrogen is converted to water. In effect, it is the combustion of hydrogen which is responsible for the increase in temperature. In fact, the proportion of CO increases relative to CO₂ because the water gas equilibrium favors CO relative to CO₂ at higher temperatures.

Table A.1 Products Considered in the Equilibrium Gasification Calculations

C(s)	HNCO
C	HNO
CH	HNO ₂
CH ₂	HNO ₃
CH ₂ O	HO ₂
CH ₃	H ₂
CH ₄	H ₂ O(l)
CN	H ₂ O
CNN	H ₂ O ₂
CN ₂	N
CO	NCO
CO ₂	NH
C ₂	NH ₂
C ₂ H	NH ₃
C ₂ H ₆	NO
C ₂ H ₂	NO ₂
C ₂ H ₄	NO ₃
C ₂ N	N ₂
C ₂ N ₂	N ₂ H ₄
C ₂ O	N ₂ O
C ₃	N ₂ O ₄
C ₃ O ₂	N ₂ O ₅
C ₄	N ₃
C ₅	O
H	OH
HCN	O ₂
HCO	O ₃

Figure A.1 Chemical Equilibrium Gasification
(Wood and Tonnage Oxygen)

Table A.2 Properties of a Wood Used for Gasification

<u>Dry Basis Composition</u>	<u>Higher Heating Value</u>
49.25 percent C	7,843 Btu/lb
6.58 percent H	
43.87 percent O	or
0.30 percent Ash	
Trace S	4.357 kcal/g

Figure A.2 shows similar results for wood containing 35 percent moisture. By comparing Figs. A.1 and A.2, it is seen that the additional water (either as steam or as moisture content) provides an increase in the $H_2:CO$ ratio at the same gasification temperature. The ratio decreases with increasing temperature but increases with increasing water content. A $H_2:CO$ ratio of 2 is achieved at a wood moisture content of 35 percent and at an equilibrium gasification temperature of approximately 975°K (1300°F). Such conditions might be attainable in a fluidized-bed gasifier.

For the temperatures shown in the figures, generally above 975°K, negligible methane and no solid carbon (char) is present. At higher pressures, above 10atm, methane does become significant at temperatures below 1000°K (1340°F). At temperatures below 950°K (1250°K), equilibrium predicts the present of carbon for woods with low moisture content.

Although the $H_2:CO$ ratio can be raised to a value of 2 or greater by the addition of water, this is done at the expense of a reduced yield of synthesis gas, $H_2 + CO$. This is shown in Fig. A.3. In this figure the synthesis gas yield efficiency,

$$\frac{(CO+H_2)}{(C + \frac{1}{2}H)_{\text{Wood}}}$$

Figure A.2 Chemical Equilibrium Gasification
(Wood and Tonnage Oxygen)

derived from the equilibrium calculations, has been used as a figure of merit, representing the fraction of the carbon and hydrogen in the wood converted to synthesis gas. (The factor of 1/2 in the denominator is used to make the ratio have the value of unity if all the wood's C and H are converted to CO and H₂, respectively.) In effect, the ratio assumes that CO and H₂ are of equal value in the synthesis gas, which may be justified based on the possibility of their interconversion using the water gas reaction.

The data plotted in Figure A.3 show that the yield efficiency for synthesis gas decreases with increasing water contents. The yield also exhibits a maximum at about 1000°K (1340°F). The reason for this is that at lower temperatures the carbon and hydrogen are converted into methane and other hydrocarbons, and at still lower temperatures, into solid carbon. Both effects reduce the yield of synthesis gas.

Also shown in Figure A.3 are the yield efficiencies for the gasifiers discussed above (see Table A.1). The K-T gasifier correlates well with the equilibrium calculations because it produces an equilibrium gas mixture. The Purox and Wellman-Galusha gasifiers correlate less well because they do not produce an equilibrium gas mixture. Their yield efficiencies are plotted as an arrow, the right-hand end of which corresponds to the highest temperature in the gasifier.

It is concluded that considerable guidance for understanding the behavior of gasifiers for biomass can be obtained from the consideration of equilibrium calculations. In

Figure A.3 Chemical Equilibrium Synthesis Gas Yield Efficiency

addition, for some types of gasifiers, especially fluidized and entrained-bed gasifiers, equilibrium calculations may be used to predict their output over a range of operating variables.

A.3 ACID GAS REMOVAL MODEL

A.3.1 The Hot Carbonate System and Physical Property Information

The primary elements of a carbonate absorption system are a column in which acid gases in the synthesis gas stream are dissolved at elevated pressure into lean carbonate solution and a regenerating column in which acid gases are steam stripped from the rich carbonate solution at low pressure. The system is represented schematically in Fig. A.4. Useful work is extracted from the rich carbonate solution exiting the absorber, and the solution is flashed to the regenerator operating pressure as it is introduced into the column. Equilibrium solubility of CO₂ in potassium carbonate solutions at elevated pressures has been reported^(2,4) in the literature. The absorption equilibria may be represented by the reaction:

Wen⁽³⁾ has presented the following equation which reliably reproduced the equilibrium data:

$$P_{\text{CO}_2}^* = \frac{x_c^2}{1 - x_c} \cdot \frac{1}{S} \cdot \frac{y_s}{1 - y_s} \cdot \frac{0.03095}{\exp[6.9 y_s - (t_F/150)]} \quad (\text{A.2})$$

$$P_{\text{H}_2\text{O}}^* = \exp \left[-\frac{8932.32}{t_F + 460.} + 12.9686 + 0.5174 (x_c - .333) \right] \quad (\text{A.3})$$

LEGEND:

- I Absorption Column
- II Energy Transfer System
- III Flash Chamber
- IV Partial Condenser
- V Regenerator Column

Figure A.4 Diagram of Potassium Carbonate Acid Gas Removal Process

where:

$$S = \frac{1000 (1 + Y_S)}{[18 + (120 + 44X_C)Y_L] [2380(\exp [.0071 (t_F - 32)]) - 1600.]}$$

$$Y_L = \frac{1}{[1 + 7.67 \frac{(1 - Y_S)}{Y_S}]}$$

$$X_C = \frac{X}{Y_S}$$

and $P_{CO_2}^*$ and $P_{H_2O}^*$ are the equilibrium partial pressures of CO_2 and H_2O , respectively, in atmospheres, t_F is the solution temperature in degrees Fahrenheit, X is the mole fraction of K_2CO_3 in solution and Y_S is the initial mole fraction of K_2CO_3 in the solution. Data on heats of solution, heat capacity, density, and viscosity of solutions of varying concentrations of K_2CO_3 have been presented by Bocard and Mayland(2). Values of heat capacities reported in the literature were used in calculation of gas phase enthalpy. Equilibrium solubility of H_2S in potassium carbonate solutions has been reported to greatly exceed that of CO_2 in these same solutions. For this reason, and because the concentration of CO_2 in the synthesis gas is more than one thousand times the concentration of H_2S , it will be assumed that the column size is established by the CO_2 removal requirement. The concentration of H_2S will be assumed to be decreased in the same proportion as the concentration of CO_2 . This approach to H_2S concentration is supported by data presented by Benson and Field(4) and by Palo and Armstrong(5).

Sizing of the absorber required for reduction of CO_2 concentration to a given level, calculation of compositions resulting from an equilibrium flash, and sizing of the column required for solution regeneration are combined to produce an overall system design. The columns were assumed to be sieve tray columns with tray efficiencies of five to ten percent as reported by Palo and Armstrong(5). The column height will be established through stage to stage

calculation of the number of trays required for the given change in CO₂ concentration. Tray spacing will be established by flow, pressure drop, and maintenance requirements as described by Treybal(6). Column diameter will be selected as that diameter which produces a gas velocity equal to 0.75 times the flooding velocity. The flooding velocity is calculated from the equation:

$$U_F = C_F \left(\frac{\rho_L - \rho_G}{\rho_G} \right)^{1/2} \quad (A.4) \quad \sigma$$

where

$$C_F = a \left\{ \log \left[\frac{1}{\left(\frac{L'}{G'} \right) \left(\frac{\rho_G}{\rho_L} \right)^{.5}} \right] + b \left(\frac{\pi}{.2} \right)^{.2} \right\}^{.5} \left(\frac{A_H}{A_A} \right)^{.5}$$

$$a = 0.0062t + 0.0385$$

$$b = 0.00253t + 0.05$$

and U_F is the superficial gas velocity at flooding, ρ_L and ρ_G are the liquid and gas densities, respectively, σ is the surface tension of the liquid, A_H and A_A are areas characteristic of the tray, and L' and G' are the superficial mass velocities of the liquid and gas, respectively. Given these preliminary considerations the design of each system component will be discussed.

A.3.2 CO₂ Absorber Modeling

Absorption of CO₂ is favored by operation at high temperature due to enhanced liquid phase reaction rates, but evaporative loss of solution places a constraint on the

absorber's operating temperature. Selection of a lean carbonate inlet temperature of 230°F is adequate to minimize losses by evaporation. Given the inlet gas stream as fully determined, the problem specification is complete when the mole fractions of K_2CO_3 in the inlet and outlet liquid streams, the column operating pressure and the mole fraction of CO_2 in the outlet gas stream are chosen. The number of trays required for the specified absorption, and the temperature, and the gas and liquid compositions on each tray are computed for the given choice of initial conditions. The calculational procedure involves estimation of the outlet gas temperature, followed by tray-to-tray solution of material and energy balances beginning with the bottom tray. The material and energy balances for the n'th tray represented in Figure A.5 are:

$$x_n = x_I - \frac{G_n - G_N}{L} \quad (A.5)$$

$$T_n = T_{LI} - \left\{ \frac{13400}{LC_{PL}} \left(\frac{x_n - x_I}{C_{PL}} \right) + \frac{1}{LC_{PL}} \left\{ \sum C_{pi} G_i (T_N - T_{n-1}) + Y_N G_N C_{p2} (T_N - T_s) - Y_n G_n C_{p2} (T_n - T_s) \right\} \right\} \quad (A.6)$$

$$G_{n+1} = G_N \left(\frac{1 - Y_{N+1}}{1 - Y_{n+1}} \right) \quad (A.7)$$

where:

x_n = liquid mole fraction of K_2CO_3 on n'th tray,

x_I = liquid mole fraction of K_2CO_3 at absorber inlet,

Y_n = mole fraction of CO_2 in outlet gas stream of (n-1)st tray,

G_n = molar flow rate of gas entering n'th tray, $\frac{lb \text{ mole}}{min}$,

G_N = molar flow rate of exit gas stream, $\frac{lb \text{ mole}}{min}$,

C_{PL} = liquid heat capacity, $\frac{Btu}{lb \text{ mole } ^\circ F}$,

Figure A.5 Typical Absorber Plate

C_{pi} = heat capacity of i'th non-absorbed gas $\frac{\text{Btu}}{\text{lb mole } ^\circ\text{F}}$,

G_i = molar flow rate of non-absorbed gas i, $\frac{\text{lb mole}}{\text{min}}$,

C_{p2} = heat capacity of gaseous CO_2 , $\frac{\text{Btu}}{\text{lb mole } ^\circ\text{F}}$,

L = liquid molar flow rate, $\frac{\text{lb mole}}{\text{min}}$,

T_n = temperature on n'th tray, $^\circ\text{F}$,

T_N = temperature of exit gas, $^\circ\text{F}$,

T_{LI} = inlet liquid temperature, $^\circ\text{F}$.

The calculations are accomplished using a digital computer, and are complete when the outlet gas temperature and composition are confirmed. The procedure is iterative but converges rapidly as the temperature of the exit gas stream may be accurately estimated as nearly equal to the temperature of the inlet carbonate solution.

A.3.3 Flash Chamber Modeling

The rich carbonate solution which has exited from the absorption column is passed through a turbine for energy recovery and is then flashed to the regenerating column operating pressure. The flash chamber and regenerator are represented schematically in Figures A.6 and A.4. The regenerator pressure is chosen as the equilibrium vapor pressure of the carbonate solution at the temperature and composition specified earlier for the carbonate stream entering the absorber. Specification of the design in this manner eliminates the need for heat exchange of the liquid streams between columns. Heat loss from the flash chamber is assumed to be negligible, and since the feed solution temperature and composition are established in the absorber

Figure A.6 Flash Chamber Diagram

design, an equilibrium flash calculation may be used to model the pressure reduction process. The material and energy balances and equilibrium relations appropriate for this process are:

$$X_1 L_1 = X_O L_O - Y_{2,F} G \quad (A.8)$$

$$L_1 = L_O + Y_{w,F} G \quad (A.9)$$

$$Y_{2,F} = \frac{1}{P_T} P_{CO_2}^* (X_O, T) \quad (A.10)$$

$$Y_{w,F} = \frac{1}{P_T} P_{H_2O}^* (X_O, T) \quad (A.11)$$

$$L_O C_{PL}(T - T_S) - L_1 C_{PL}(T_I - T_S) \quad (A.12)$$

$$= - 13400 G_{w,F} - 17496 G_{2,F} - C_{pw} G_{w,F} (T - T_S) - C_{p2} G_{2,F} (T - T_S)$$

where

X = mole fraction K_2CO_3 in inlet liquid stream,

X_O = mole fraction K_2CO_3 in outlet liquid stream,

L_1 = inlet liquid flow rate, $\frac{\text{lb mole}}{\text{min}}$,

L_O = outlet liquid flow rate, $\frac{\text{lb mole}}{\text{min}}$,

G = outlet gas flow rate, $\frac{\text{lb mole}}{\text{min}}$,

$Y_{2,F}$ = mole fraction of CO_2 in outlet gas stream

$Y_{w,F}$ = mole fraction of H_2O in outlet gas stream

P_T = regenerator pressure, atm,

$P_{CO_2}^*$ = equilibrium vapor pressure of CO_2 , atm,

$P_{H_2O}^*$ = equilibrium vapor pressure of H_2O , atm,

T = flash chamber temperature, $^{\circ}F$,

T_I = inlet liquid stream temperature, $^{\circ}F$,

T_S = reference temperature, $^{\circ}F$,

C_{pL} = liquid heat capacity, $\frac{Btu}{lb \text{ mole } ^{\circ}F}$,

C_{p2} = heat capacity of CO_2 vapor, $\frac{Btu}{lb \text{ mole } ^{\circ}F}$.

An iterative procedure, employing estimation of $Y_{w,F}$ followed by simultaneous solution of four of the equations and verification of the starting estimate with the fifth equation, is employed for calculation of the flash temperature and exit stream compositions and flow rates. The flash chamber is sized using a procedure presented by Evans⁽⁷⁾.

A.3.4 Regenerator Modeling

The objective of regenerator operation is the adjustment of carbonate solution flow rate, temperature, and composition to the conditions required for the absorber feed stream. A diagram of a typical regenerator tray is presented in Fig. A.7. Condensation of a portion of the saturated steam, used as a stripping agent, provides the energy required for desorption of CO_2 , as well as replacing part of the water removed during the flash process. The balance of the water removed during the flash is added by reflux of a

Figure A.7 Diagram of a Regenerator Column Plate

portion of the condensed flash gas. Material and energy balances, applied to the entire column and to each tray of the column, allow calculation of the number of trays required, the water reflux and water condensation and the temperatures and compositions at any point within the column. The material and energy balances for the n'th tray of the column are:

$$L_{n+1} + G_n = L_n + G_{n+1} - r_{d,n} \quad (A.13)$$

$$Y_{2,n+1} G_{n+1} - Y_{2,n} G_n = r_{d,n} \quad (A.14)$$

$$G_{n+1} = G_n + r_{d,n} - W_{c,n} \quad (A.15)$$

$$X_n L_n - X_{n+1} L_{n+1} = r_{d,n} \quad (A.16)$$

$$L_{n+1} C_{pL} (T_{n+2} - T_s) - [L_n C_{pL} (T_{n+1} - T_s) + \Delta H_c W_{cn} + \Delta H_d r_{d,n}] - G_n C_{p5} (T_n - T_s) - G_{n+1} C_{p5} (T_{n+1} - T_s) = 0 \quad (6.32)$$

where:

L_n = molar flow rate of liquid leaving the n'th tray, $\frac{\text{lb mole}}{\text{min}}$,

G_n = molar flow rate of gas entering the n'th tray, $\frac{\text{lb mole}}{\text{min}}$,

$r_{d,n}$ = rate of desorption of CO_2 on n'th tray, $\frac{\text{lb mole}}{\text{min}}$,

$W_{c,n}$ = rate of condensation of water on n'th tray $\frac{\text{lb mole}}{\text{min}}$,

X_n = mole fraction of K_2CO_3 in liquid exiting n'th tray

C_{pL} = liquid heat capacity, $\frac{\text{Btu}}{\text{lb mole } ^\circ\text{F}}$,

C_{p5} = heat capacity of vapor stream, $\frac{\text{Btu}}{\text{lb mole } ^\circ\text{F}}$.

The calculation procedure involves estimation of outlet gas temperature followed by tray-to-tray solution of the material and energy balances beginning with the bottom tray. Confirmation of the estimated gas temperature terminates the calculation which converges rapidly. Calculation of tray spacing and column diameter are accomplished using the procedure described above for sizing the absorption column.

A hot carbonate system design algorithm which incorporates the major steps of the column's design procedure is presented in Fig. A.8. Analysis of system operation and sensitivity to variations in operating conditions has been presented in Section IV of this volume.

A.4. SHIFT CONVERSION MODELING

Production of methanol from synthesis gases is favored when the primary reactants, H_2 and CO , are present in the stoichiometric ratio, that is, with two moles of H_2 present for each mole of CO . Synthesis gases produced from biomass are deficient in H_2 , and consequently require adjustment of the H_2/CO ratio. The shift conversion process, or the addition of H_2 produced by electrolysis of water may be employed for adjustment of the H_2/CO ratio. However, recently published estimates of the energy required for electrolytic production of hydrogen indicate that use of this process is not economically feasible at this time. In the shift conversion process, carbon monoxide reacts with steam in the presence of an appropriate catalyst producing hydrogen and carbon dioxide. While the reaction is effective in adjustment of the H_2/CO ratio it has the disadvantage of decreasing the over-all process carbon conversion efficiency. The details of incorporating a shift conversion step into the over-all process is discussed in the following sections.

Figure A.8 Hot Carbonate System Design Algorithm

A.4.1 The Shift Conversion Reaction and Equilibrium Considerations

The following reaction set has been proposed as representative of the system under consideration.

With the exception of Reaction A.17 each of these reactions is undesirable, and consequently operating conditions and mixture compositions are chosen so that these side reactions are suppressed. Particular care is taken in order that the carbon formation indicated by Reactions A.18, A.19, A.20 and A.21 is averted. Deposition of carbon on catalyst generally results in rapid loss of catalytic activity. Addition of excess water to the reaction mixture is effective in suppressing the side reactions, but operating information provided by catalyst manufacturers⁽⁸⁾ demonstrates that under normal operating conditions employing iron oxide catalysts, carbon deposition is not a significant problem.

Once the shift conversion reaction is shown to be the sole reaction taking place further analysis based upon published equilibrium constant⁽⁹⁾ data is possible. The reaction is moderately exothermic, and consequently, the equilibrium constant decreases as temperature increases. A higher conversion of CO is attainable at reduced temperatures due to this effect. This behavior is demonstrated in Figure A.9,

Figure A.9 Characteristics of Shift Conversion Under Equilibrium Conditions

where equilibrium fractional conversion of CO at 30 atmospheres is plotted as a function of temperature for a synthesis gas mixture having an initial H₂ to CO ratio of 0.68 and an initial steam to CO ratio of 3.0. Results are presented for the maximum and minimum CO₂ levels encountered with biomass synthesis gases. The effect of pressure on equilibrium conversion is not significant as the gases are nearly ideal under the relevant conditions, and the total number of moles of reactants and products does not change during the reaction.

A.4.2 Reaction and Transport Rate Considerations

Detailed information is available on the intrinsic chemical reaction rate and rate of intraparticle mass transfer in shift conversion catalysts. The reaction rate has been found to be first order in CO concentration, and dependent on pressure at low pressures, but nearly independent of pressure above 20 atmospheres. An iron oxide catalyst, useful at high temperatures, and a copper-zinc oxide catalyst, useful at lower temperatures, may be employed. The rate form which follows has been reported as reliable⁽¹⁰⁾, and will be used in the calculations.

$$-r_{CO} = k (Y_{CO}Y_{H_2O} - Y_{CO_2}Y_{H_2}/K) (379./P_B) \quad (A.25)$$

where

r_{CO} = rate of production, lb moles CO/(lb catalyst) (hr)

k = rate constant

= $\exp (19.95 - 8820/T)$ for iron catalyst

= $\exp (12.88 - 8420/T)$ for copper-zinc catalyst

K = equilibrium constant

= $\exp (-4.72 + 8640/T)$ for $760 \leq T \leq 1060$

= $\exp (-4.33 + 8240/T)$ for $1060 \leq T \leq 1360$

T = temperature, °R

Y_j = mole fraction of component j

ρ_B = catalyst bulk density, lb/cu ft

P = pressure, atm

Ψ = activity factor

$$\begin{aligned}\text{Iron catalyst } \Psi &= 0.816 + 0.184 P \text{ for } P \leq 11.8 \\ &= 1.53 + 0.123 P \text{ for } 11.8 \leq P \leq 20.0 \\ &= 4.0 \text{ for } P \geq 20.0\end{aligned}$$

$$\begin{aligned}\text{Copper zinc catalyst } \Psi &= 0.86 + 0.14P \text{ for } P \leq 24.8 \\ &= 4.33 \text{ for } P \geq 24.8\end{aligned}$$

Interphase heat and mass transfer limitations are not significant at the flow conditions normally encountered in production size shift convertors. This may be verified employing a heat-mass transfer analogy and the correlation presented by Gupta and Thodos⁽¹¹⁾ for transfer in packed beds:

$$\frac{Sh}{Re Sc} Sc^{2/3} = \frac{Nu}{Re Pr} Pr^{2/3} = \frac{2.06}{\epsilon} (Re)^{-0.575} \quad (A.25)$$

where Sh, Nu, Sc, Pr, and Re are the Sherwood, Nusselt, Schmit, Prandtl and Reynold's numbers, respectively, and ε is the void fraction of the bed. Calculation of Re requires knowledge of the diameter of the reactor which is only available as the output of a design calculation. Consequently, the correlation is most conveniently used to calculate the magnitude of the interphase concentration or temperature gradient which was neglected during the reactor design procedure. In all cases the concentration or temperature drop across the gas film surrounding the particle, was

found to be less than 1 percent of the bulk concentration or temperature. Intraparticle temperature gradients were shown to be less than 2 percent of the bulk temperature, employing the method proposed by Carberry⁽¹²⁾. Similar considerations apply in calculation of pressure drop along the bed where Ergun's equation may be applied to demonstrate that the pressure drop, due to frictional and kinetic losses, will be less than a quarter of one percent of the operating pressure. Calculations employing the dispersed plug flow model demonstrate that axial dispersion will not be significant at the space velocities encountered in this system. These results justify the use of an adiabatic, plug-flow reactor model for calculation of catalyst volume required for the specified conversion.

A.4.3 Shift Converter Modeling

The mass and energy balances for an adiabatic, plug flow reactor in which the shift conversion reaction is taking place may be written as

$$\frac{dY_{CO}}{dV} = \frac{r_{CO} \rho_B}{F_T} \quad (A.26)$$

$$\frac{dT}{dV} = \frac{\Delta H_R r_{CO}}{F_T \sum Y_k C_{Pk}} \quad (A.27)$$

where

- F_T = total molar flow rate, lb mole/hr,
- Y_k = mole fraction of component k,
- V = reactor volume, cu ft,
- r_{CO} = reaction rate, lb mole CO/(lb catalyst)(hr),
- T = temperature, °R,
- C_{Pk} = heat capacity, Btu/(lb mole °R),
- ΔH_R = heat of reaction, Btu/lb mole.

Simultaneous solution of these equations for the outlet temperature and reactor volume, given a specified conversion, are accomplished using a digital computer and Runge-Kutta integration procedures.

A.4.4 Shift Loop Design Procedure

The synthesis gas available for shift conversion does not contain the amount of water necessary for adjustment of the H_2 to CO ratio and consequently steam addition is required. The significant expense associated with steam addition requires evaluation of the performance of the shift convertor by-pass loop represented schematically in Fig. A.10. In this system only a fraction of the synthesis gas is fed to the shift reactor while the remaining portion is by-passed. In order to obtain the desired H_2 to CO ratio in the feed stream to the methanol synthesis loop, a greater fractional conversion must be obtained when only a portion of the synthesis gas is passed through the shift reactor, as the total conversion required is determined by the H_2 to CO ratios in the shift loop inlet and exit streams. A design calculation requires identification of the required CO conversion and the fraction of the loop inlet-stream to be fed to the reactor, calculation of the reactor outlet H_2 to CO ratio, and selection of a reactor inlet steam to CO ratio. Given these variables and a reactor inlet temperature, the kinetic model described above can be employed for calculation of reactor volume and outlet gas stream temperature. The details of this procedure are discussed in the following paragraphs.

Mass balances on CO and H_2 are employed to derive the following expression of X_{CO} , the fractional conversion of the CO present in the shift loop inlet stream required to raise the H_2 to CO ratio from r_1 to r_3 :

Figure A.10 Shift Conversion Process Flow Diagram

(A.28)

$$x_{CO} = \frac{r_3 - r_1}{r_3 + 1}$$

The ratio of H₂ to CO in the shift loop inlet stream r_1 , varies from 0.6 to 0.9, while the ratio of H₂ to CO in the shift loop exit stream, r_4 , is usually close to 2.0. A mass balance around the shift convertor provides the following relation among process variables:

$$r_2 = \frac{r_1 + \frac{x_{CO}}{k_{sp}}}{1 - \frac{x_{CO}}{k_{sp}}} \quad (A.29)$$

where r_2 is the H₂ to CO ratio in the reactor exit stream and k_{sp} is the fraction of the shift loop inlet stream which is fed to the shift reactor. A relation between r_2 and the inlet steam to CO ratio is provided by assuming that the r_2 attained during operation is the equilibrium conversion attained at a temperature 50°F higher than the maximum design temperature. A maximum design temperature of 790°F was chosen since the usual maximum allowable temperature for the iron oxide catalyst is specified as 890°F.

The final design calculation incorporates equipment costing and is represented by the algorithm presented in Fig. A.11. Heat exchange equipment is included for feed preheating and steam generation. The results of application of this design procedure have been presented in Section IV of this volume.

Figure A.11 CO Shift Conversion System Optimization Algorithm

A.5 METHANOL SYNTHESIS PROCESS ANALYSIS

A.5.1 Introduction

Methanol is produced commercially through the reaction of gaseous CO and H₂ in the presence of a solid phase catalyst at elevated temperatures and pressures. The first industrial catalysts were a mixture primarily of zinc and chromium oxides, the latter being a promoter. With this catalyst, methanol is produced at temperatures of 300° to 400°C and at pressures of 200 to 300 atmospheres. Recently, more active and selective catalysts containing copper and zinc oxides have been developed which permit synthesis of methanol at lower temperatures, 200° to 300°C, and at lower pressures, 50 to 100 atmospheres. This technology has gradually superseded the earlier high-pressure technology, and is embodied in the processes offered by Imperial Chemical Corporation, Ltd. (ICI) and by Lurgi. Production costs are lowered because of reduced compression requirements, maintenance costs, and equipment downtime. As a result, over 80 percent of the world's new methanol capacity built since 1967 uses low or medium pressure processes. Although new plants are generally very large, it is worth noting that the low-pressure process is particularly advantageous for small production rates (under 500 TPD of methanol), since at low pressures the gas volume is still large enough for use of centrifugal compressors, which may be driven by steam generated from waste heat. For these reasons, a low pressure (50 atm) methanol synthesis process has been selected for the detailed modeling discussed in this section.

A.5.2 Synthesis Equilibrium and Kinetic Characteristics

The major reactions involved in the synthesis of methanol are:

Side reactions which occur at elevated temperatures and pressures include:

If pure methanol is desired, reactions A.30 and A.31 and should be promoted while the side reactions should be inhibited. Catalysts for methanol synthesis are not necessarily active catalysts for the shift conversion reaction, but it is believed that this reaction may play a role at high temperatures. The enthalpy and free energy changes of these, and three additional reactions are presented in Table A.3. The formation of hydrocarbons and higher alcohols are favored thermodynamically over methanol. Moreover, the condensation of methanol to dimethyl ether is also favored thermodynamically. Consequently, production of crude methanol of 97 percent purity as is obtained commercially, requires use of a highly selective catalyst.

Methanol synthesis through reaction A.30 is a strongly exothermic process, and requires removal of heat for protection of the catalyst and for avoidance of equilibrium conversion limitations. In addition, the heat of reaction increases with pressure, lessening the benefits of operation at high pressure. The equilibrium behavior of a system involving reactions A.30 and A.32 may be investigated, employing the data presented by Sherwin and Blum⁽⁹⁾. Non-ideal gas effects are taken into

Table A.3 Enthalpy and Free Energy Changes of Some Reactions Important in the Synthesis of Methanol

Reaction	Enthalpy Change, kcal (at 1 atm pressure)			Free Energy Change, kcal (at 1 atm pressure)		
	227°C	327°C	350°C	227°C	327°C	350°C
$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$	--	--	- 24.45	+ 5.00	+ 10.80	+ 12.10
$\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	--	--	- 15.34	--	--	+ 15.80
$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	--	--	- 9.12	--	--	- 3.7
$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$	--	--	--	- 27.87	- 21.22	- 19.53
$2\text{CO} + 4\text{H}_2 = \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	--	--	--	- 11.1	- 2.67	--
$2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	--	--	- 4.5	--	--	- 1.40

Source: Reference 13

account, and solution of the following system of two simultaneous equations provides information of the dependence of equilibrium methanol production on system temperature and pressure.

The equilibrium constants can be expressed as:

$$K_1 = \frac{K_{a1} P^2}{K_{\gamma_1}} = \frac{(M + X)}{(CO - X + Y)} \frac{(Total - 2X)^2}{(H_2 - 2X - Y)^2}, \quad (A.36)$$

$$K_2 = \frac{K_{a2}}{K_{\gamma_2}} = \frac{(CO - X + Y)}{(CO_2 - Y)} \frac{(W + Y)}{(H_2 - 2X - Y)}; \quad (A.37)$$

where

$$K_{a1} = (3.27 \times 10^{-13}) \exp (11678/T),$$

$$K_{\gamma_1} = 1 - A_1 P,$$

$$A_1 = (1.95 \times 10^{-4}) \exp (1703/T),$$

$$K_{a2} = (1.17 \times 10^2) \exp (-4827/T),$$

$$K_{\gamma_2} = 1 - A_2 P,$$

$$A_2 = (4.24 \times 10^{-4}) \exp (1107/T),$$

and

- o T is temperature in degrees Kelvin,
- o P is the total pressure in atmospheres,
- o M is the number of moles of methanol in the feed,
- o X is the number of moles of methanol produced,
- o Y is the number of moles decrease in CO₂,
- o Total is the total number of moles (including all inerts) in the feed,
- o W is the number of moles of water in the feed,
- o CO is the number of moles of CO in the feed,
- o H₂ is the number of moles of H₂ in the feed,
- o CO₂ is the number of moles of CO₂ in the feed.

The results of a series of equilibrium calculations are presented in Figure A.12. The feed gas composition is typical of a synthesis gas produced from biomass. Since the primary reaction is exothermic, the equilibrium yield of methanol decreases as the reaction temperature is increased. Since the total number of moles decreases as methanol is produced, the equilibrium yield of methanol increases as the pressure is increased. The equilibrium findings indicate that operation at low temperature and high pressure is favored, and that use of a recycle flow arrangement would be useful in raising the relatively low fractional conversions obtainable in this reaction system.

Where the thermochemistry of methanol synthesis is well understood and is supported by ample data, the kinetics of the heterogeneously catalyzed reaction are little understood. A number of rate expressions have been developed for the high-pressure process, (for ZnO - Cr₂O₃ catalysts) of which the forms of Natta⁽¹³⁾ and of Bakemeier, et al.⁽¹⁴⁾, are representative. Either trimolecular surface reaction or desorption of methanol were held to be rate-determining in the development of these representations. Rate expressions have been proposed for the low-pressure process (for CuO/ZnO/Al catalyst) which are valid over limited ranges of operating conditions. Leonov, et al.⁽¹⁵⁾, found that hydrogen absorption was the rate limiting step, and that the rate of methanol production was unaffected by varying catalyst grain size from 1 x 2 to 5 x 5 mm. Intraparticle diffusion effects were found to be insignificant under steady state operation for temperatures greater than 260°C. Kotera, et al.⁽¹⁶⁾, developed the following rate form for methanol synthesis over CuO/ZnO/Al catalyst at 50 atmospheres:

$$r_{\text{CH}_3\text{OH}} = k \left\{ (P_{\text{CO}} P_{\text{H}_2}^2)^{0.3} - \frac{P_{\text{CH}_3\text{OH}}}{(P_{\text{CO}} P_{\text{H}_2})^{0.7} K} \right\} \quad \begin{matrix} \text{(A.38)} \\ \text{(6.41)} \end{matrix}$$

Figure A.12 Equilibrium Formation of Methanol in a Biomass Derived Synthesis Gas

where

$r_{\text{CH}_3\text{OH}}$ = rate of methanol production, $\frac{\text{g mole}}{\text{g cat hr}}$

P_k = partial pressure of species k, atm

k = specific rate constant, $\frac{\text{g mole}}{\text{g cat hr atm}^{0.9}}$

K = reaction equilibrium constant

The specific rate constant was adjusted so that the methanol production rates calculated from this rate form were approximately equal to the rates specified in the patent literature. Because methanol production economics are dominated by compression and operating costs, this rate expression will provide an estimate of reactor capital expenditure adequate for the establishment of the sensitivity of the methanol synthesis loop to variations in process variables.

Interphase mass and heat transfer have been shown to be unimportant at the gas flow rates employed in methanol synthesis. This may be verified through use of the correlations described above for estimation of mass transfer resistances in shift conversion. Flow and reaction conditions are such that the temperature and concentration drops across a gas film surrounding a catalyst particle do not exceed 1 percent of the bulk temperature or concentration. For this reason, interphase transport effects will be omitted from the design equations. Also, pressure drop along the length of the reactor may be shown to be a negligible fraction of the reactor operating pressure, and consequently of slight importance in the calculation of reactor volume.

A.5.3 Methanol Synthesis Modeling

All commercial methanol synthesis processes are essentially similar and may be represented by the schematic presented in Figure A.13. The copper based catalyst is subject to deactivation at temperatures above 300°C, and consequently control of maximum temperature is prominent in reactor design. In this study a cold gas quench multiple-bed adiabatic methanol convertor, which is used in large ICI plants, is simulated in the methanol process model. The catalyst is contained in four beds placed in series in the convertor as shown in Figure A.14. Each bed is operated adiabatically, and thus the temperature of the gases increases along the length of the bed. Cold synthesis gas is injected between each catalyst bed to cool the reaction mixture, maintaining the temperature below a specified maximum. Gas space velocities are high, typically a few tens of thousands of volumes of synthesis gas per volume of catalyst per hour. After leaving the reactor, the gases are passed through a heat exchanger for energy recovery, and then into a water cooled condensor where water, products of side reactions, and methanol are condensed. A portion of the condensor exit gas stream is purged to allow removal of inerts and unconverted reactants, and the balance is recycled through the convertor. Recycle of reactants and inerts after removal of methanol product allows nearly complete conversion of CO in the make-up gas feed, even though conversion within the reactor itself is limited by equilibrium constraints.

Specification of the inlet temperature, the maximum operating temperature (i.e., the temperature of the gas as it leaves each catalyst bed in the reactor), and the desired conversion of CO in the make-up gas stream allows calculation of the required catalyst volume, the recycle gas flow rate, and the fraction, q_L , of the reactor inlet gas stream diverted for

Figure A.13 Methanol Synthesis and Distillation in the
Lurgi Low Pressure Methanol Synthesis Process

Legend:

- I - Feed Gas Compressor
- II - Methanol Synthesis Reactor
- III - Crude Methanol Separator
- IV - Recycle Compressor

Figure A.14 Methanol Synthesis Loop Process Diagram
(Multiple Adiabatic Reactor with Cold
Gas Quench)

quenching. However, the relation between CO conversion, temperature, and recycle gas flow rate is implicit, and an iterative solution procedure is required. In addition, the fraction of the feed stream required for quenching is also unknown at the start of calculations, requiring a second calculational loop. The calculational procedure employed is diagrammed in Figure A.15. The details of the calculation will be discussed in the following paragraphs.

Calculation of recycle gas flow rate directly from the specified CO conversion is not possible, and consequently the starting point of a design calculation is the estimation of the recycle flow rate. In this calculation, a recycle constant, K_R , defined as equal to the fraction of CO in the condenser exit gas stream which is recycled, is employed to represent the variation in recycle gas flow rate. A value of K_R of 0.0 indicates no recycle while a value of 1.0 indicates complete recycle. Following estimation of K_R , an initial guess on q_L is developed, by assuming that equilibrium is attained in the reactor effluent gases. The molar gas flow rate entering the convertor may be derived from these initial estimates. Each of the four catalyst beds within the reactor is modeled as an adiabatic plug flow reactor with the degree of conversion obtained in each bed determined by the specified exit temperature. The mass balance on methanol and energy balance in each catalyst bed are:

$$\frac{d}{dV} N_{CH_3OH} = r_{CH_3OH} \quad (A.39)$$

$$\frac{dT}{dV} = - \frac{H_R r_{CH_3OH}}{N_k C_{pk}} \quad (A.40)$$

Figure A.15 Flowchart of Methanol Reactor Design Calculation

where

N_k = molar flow rate of species k, lb mole/hr

V = reactor volume, cu ft

T = reactor temperature, °R

r_{CHOH} = rate of methanol production, lb mole/(cu ft °R)

ΔH_r = heat of reaction, Btu/lb mole

C_{pk} = heat capacity of species k, Btu/(lb mole °R)

Simultaneous solution of the two differential equations is accomplished using a fourth-order Runge-Kutta integration procedure(17). The effect of non-ideality of the gases is accounted for through use of correction procedures developed by Gambill(18). The degree of conversion of CO₂ to methanol is estimated by assuming that the reaction mixture is in shift conversion equilibrium at the end of each integration step. The contribution of shift conversion to methanol production is negligible at low (<10%) CO₂ levels. The temperatures of the gas streams entering and leaving each catalyst bed are chosen as part of the design specification. Using these temperatures and the gas flow rate exiting the catalyst bed prior to the n'th quench, mass and energy balances around the n'th quench point allow calculation of the cold gas quench flow rate required for temperature reduction. The flow rates of the three quench streams calculated in this manner must be equal to the quench flow rate assumed at the start of the calculation. In addition, the flow rate of CO leaving the fourth catalyst bed must correspond to the specified CO conversion. When these conditions are satisfied the design calculation is complete. The results of process analysis employing this methanol synthesis model have been presented in Section IV of this volume.

A.5.4 Methanol Separation and Purification Calculations

Methanol separation and purification modeling includes the calculation of flow rates of condensed methanol and water and

non-condensed gases exiting the crude methanol condenser downstream of the methanol reactor, and calculation of the size of two distillation columns required for removal of higher alcohols and water from the methanol product stream. The condenser was assumed to be well-mixed and the exit streams were assumed to be in equilibrium. The exit temperature was chosen so that 99 mole percent of the methanol and water were condensed. An ideal vapor phase, and a non-ideal liquid phase represented by Scatchard-Hildebrand activity coefficients and a non-symmetric standard state convention were employed in the condenser calculation. Nitrogen, methane, hydrogen, and the carbon oxides were assumed non-condensable. Since the kinetic expression employed in the methanol reactor design did not predict the distribution of side products, the result can not be used directly in a distillation calculation. Instead, an approximate, conservative column design was proposed, based on the assumption that the methanol product flow rate calculated included molar flows of dimethy-ether and ethanol equal to one and two mole percent, respectively, of the total methanol flow rate. Based upon this assumption, the Fenske-Underwood-Erbar-Maddox⁽¹⁹⁾ design procedure was employed for sizing the required distillation columns.

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APPENDIX B. COST ESTIMATION AND ECONOMIC EVALUATION MODEL

B.1 SURVEY AND SELECTION OF COSTING AND ECONOMIC EVALUATION PROGRAMS

A comprehensive survey of the existing literature was performed by the SAI project team. Various authors/vendors were contacted to determine the best approach possible in terms of costing and economic models with the following criteria:

- The model should allow preliminary process configuration optimization, i.e., equipment costs can be estimated, based on parameters such as size, heat transfer area, flow rates, etc. Thus the operating/capital cost combination can be determined for each alternative configuration to come up with a reasonably economic design.
- The model should allow overall economic assessment by determining the product price at the plant.

The programs that satisfy both criteria include:

CHEEP	(University of Houston)
Economics	(CAD Center, U.K.)
Preliminary Economics Program	(Halcon Computer Tech., Inc.)
PEPCOST	(Stanford Research Institute)
PROVES	(G. Enyedy, Jr., Engineering Consultant)
PROPS	(University of Missouri - Rolla)

The programs with more limited applications include:

CFA (Kennecott Copper Corp.) for cash flow analysis
PRP (Oak Ridge National Lab.) for cash flow analysis
PDQ\$ (Gustav Enyedy, Jr.) for individual equipment cost estimation
SACDA Economics Analysis Program (SACDA, University of Western Ontario)

In addition, the survey revealed that the following process simulators include some equipment costing subroutines:

FLOWTRAN (Monsanto Company)

PDA (Phillips Petroleum Company)

The coal conversion project staff at Purdue University is developing an economic package as part of their process simulator project. However, the project is still underway at this time, with no assurance as to when it would be available to outside users. Therefore no further consideration was given to that source. FLOWTRAN⁽¹⁾ and PDA⁽²⁾ involve a complete simulator program, in addition to the costing package. Because of the lease and running costs, those programs were not used. PDA costs are also obsolete, as indicated in our telephone conversation with McAuto personnel.

The CFA program is written in BASIC⁽³⁾, and the SACDA⁽⁴⁾ program is intended for the economic evaluation of a combination of plants using a sales forecast. Therefore those two were eliminated from further consideration. PDQS⁽⁵⁾ has a data bank that contains process equipment cost. However, the availability is contingent upon subscription through a commercial computer network, and control over the resulting costs is deemed uncertain. PRP⁽⁶⁾ has good input output features and is available at no cost from Oak Ridge National Laboratory. Its use has been proven in previous synthetic fuel projects^(7,8).

The major cost elements are grouped into modules, including:

- chemical processing
- front end costs

- site development
- buildings and structures
- offsite facilities
- project indirect costs

The primary cost elements of each module include:

- equipment F.O.B. cost
- direct material
- direct field labor
- direct material and labor cost (direct cost factor)
- indirect costs
- bare module cost
- total module cost

The materials direct costs include piping, concrete, steel, instruments, insulation and paint. Indirect costs comprise construction overheads, engineering, and contractor fees and contingencies.

Instead of summing all equipment purchased cost and then multiplying by a factor to obtain the preliminary cost estimate for a plant, Guthrie divides the plant into modules. A module is a grouping of similar items such as heat exchangers, horizontal pressure vessels, steam generators, mechanical refrigerator units, docks and/or laboratories. The 1970 price of each item is then obtained, which is the F.O.B. price at the suppliers' plants. A modified Lang factor is then calculated for each module.

CHEEP(9), which was developed at the University of Houston, sizes equipment, and then costs it using Guthrie's correlations. Next, it estimates the total capital cost by the Miller's factor method, and gives the rate of return on

investment as the only profitability measure (no cash flow calculation is available). Based on on-going results of the ASPEN project at MIT(10), Guthrie's method and Hackney's method appear to give more reasonable results than Miller's method when compared with actual cost data from the Bureau of Mines. Therefore CHEEP was dropped from further consideration. PROPS(11) is based on the process simulation program CHESS which was sold to ChemShare Corporation. Hence PROPS cannot be considered for use.

The remaining programs(12) such as ECONOMIST, PEPCOST, Preliminary Economics Program, and PROVES were not considered for lease because of cost effectiveness considerations in terms of FORTRAN conversion (e.g., CDC to IBM, etc.), rental rates, and suitability to the specific tasks involved. The staff has access to extensive cost data(13,14), and thus a relatively small and efficient computer program for estimation capital cost model was developed such that the preliminary plant design can be evaluated in a cost-effective manner*.

B.2 CAPITAL COST EVALUATION MODEL

Guthrie's method(15) was employed for capital cost evaluation. In this method, estimates are built up from equipment base costs and purchased (F.O.B.) costs in the manner illustrated in Figures B.1 and B.2. This factor includes freight costs and sales taxes. It further differs from the Lang factor in that it does not include site

*Our survey revealed that the ORNL process engineering group developed a program for capital cost estimation, but the ORNL group was unwilling to make it available because it is not fully documented and user-oriented.

Figure B.1 Guthrie Modular Method for Equipment Costing

Note: 1) Total Module Cost = Bare module + Contingency and Contractor's feed.
 2) Bare Module Cost = Material and Labor (M&L) Cost (indirect factor)

Figure B.2 Module Cost Components

development or any structures, as those are figured as separate modules. By summing the costs for each module, and adding a contingency factor (13-25%) to correct for any omissions and contractors' fees, a capital cost estimate can be obtained for a plant built in mid-1970 at a Gulf Coast site. Miller claimed that if the basic equipment estimate has an accuracy of $\pm 10\%$, the most likely plant estimate by his method should have an accuracy of $\pm 14\%$ (16). Baasel, in the same reference, indicated that Guthrie's method should be more accurate than Miller's method.

Guthrie's approach can be expressed mathematically by the following equation for each equipment module:

$$\text{Bare Module Cost} = (\text{BC MF ICF}) \left[\frac{\text{FIM}}{\text{BIM}} + \frac{\text{L}}{\text{M}} \cdot \frac{\text{FIL}}{\text{BIL}} \right] + \left[(\text{EC} - \text{BC}) \frac{\text{FIM}}{\text{BIM}} \right]$$

where BC = Base equipment cost

EC = FOB equipment cost

MF = Material factor for installation

ICF = Indirect cost factor

$\frac{\text{L}}{\text{M}}$ = Labor man-hour to material cost ratio

FIM = Material index for final period

BIM = Material index for base period

FIL = Labor index for final period

BIL = Labor index for base period

In the above expression, material factor for installation (MF) indicates the relationship between total equipment base costs (BC) and total field installation materials associated with the equipment. The indirect cost factor (ICF) includes all the equipment. The indirect cost factor

(ICF) includes all the indirect cost elements associated with the module. The L/M ratio relates installation labor costs to direct material costs. The bare module cost can be multiplied by 1.2 to obtain the total module cost, assuming that contingency and contractor's fee amount to 20 percent of the bare module costs.

B.3 COST DATA FOR VARIOUS EQUIPMENT

The cost data in Guthrie are compiled from the actual field construction records of fifty major capital projects for the base year of mid-1970. The correlations are of the cost-capacity type, of the form:

$$\text{Base Cost} = A (\text{Capacity})^B$$

where A is a constant specific to each type of equipment
B is an exponent which varies between typical values between 0.50 and 0.80, as a function of equipment size.

Table B.1 shows typical cost correlations, and Table B.2 lists the equipment which is costed in the module. The following discussion will focus on the heat exchanger as a typical example. The base cost is next translated into purchased F.O.B. cost by the following relationship:

$$\text{Purchase Cost} = \text{Base Cost} \times [(F_d + F_t + F_s)F_m]$$

where: F_d is the design factor (e.g., kettle reboiler, floating head or U-tube heat exchanger), which varies with the base cost.

F_t is the tube bundle design pressure factor which varies with the tube design pressure.

F_s is the shell design pressure factor which is a function of shell pressure.

F_m is the shell/tube material factor which varies with the heat transfer area, and the material type (whether stainless shell/carbon steel tube, or stainless shell/stainless tube, or some other combination of material).

Table B.1 Typical Equipment Costs

<u>Equipment Type</u>	<u>Base 1980 Cost</u>	<u>Size Range</u>	<u>Purchased Cost</u>
Heat exchanger (U-tube)	$165.3 (\text{Area})^{0.68}$	200-5000 sq. ft.	Base cost $(F_d + F_t + F_s)F_m$
Steam Boiler	$14.72 \left(\frac{\text{lbs steam}}{\text{hr}} \right)^{0.96}$	$10^5 - 10^6$ (lbs steam/hr)	Base cost $(F_p + F_s)$
Cooling Tower	$1277 (\text{GPM})^{0.65}$	1000-50000 GPM	Base Cost (F_c)

For heat exchangers:

F_d = design factor
 F_t = tube pressure factor
 F_s = shell pressure factor
 F_m = equipment material factor

For steam boiler:

F_p = steam pressure factor
 F_s = superheat factor

For cooling tower:

F_c = cooling range factor

Table B.2 List of Equipment Included
in the Costing Program

1. Process furnaces
2. Direct-fired heaters
3. Shell and tube heat exchangers
4. Air-cooled heat exchangers
5. Process vessels and trays
6. Pumps (centrifugal, reciprocating and turbine)
7. Compressors (centrifugal and reciprocating)
8. Drivers for pumps and compressors (motor, gas turbine, condensing steam turbine)
9. Offsite equipment: cooling towers, tankage, steam plant
10. Front end equipment for wood handling

B.4. RELATIONSHIP OF THE COST OF VARIOUS MODULES TO THE
PROCESS MODULE COSTS

It is sufficient, for a conceptual costing effort, to estimate the site development, building and structures, and offsite modules by assuming that they are percentages of the process equipment module. Care must be taken, however, to take into account abnormal factors such as special steam plant requirements of certain processes. This may make a significant difference in the offsite module costs.

The ratio of each module cost to the process equipment module cost is usually inversely proportional to the process equipment cost, as shown in Figure B.3 for site preparation. The percentages for each module, as cited by Guthrie, are included in the computer model data bank. Table B.3 shows an example for process equipment cost of \$MM 10.

SITE PREPARATION

Cost Of Land

Access to site

Raw Material, Product, and Utility
Pipelines

Sewer Lines

Access Road and Railroad Spur

Right-of-Ways

Site Preparation

Site Grading, Drainage and Excavation

Roads and Parking Area

Chemical, Storm, and Sanitary Sewers

Fire Protection System

Railroad Tracks

Street Lighting

Surface Treatment (Oiling, Graveling)

Fencing

Cost of Site Preparation
Module as a Percent of
Process Equipment Module

Cost of Process Equipment Module
in Million Dollars

Figure B.3 Relationship of Site Preparation Module to Process Equipment Module

Table B.3 Cost Centers in Capital Investment.
Example for a \$MM 10.0 Process Module

Cost Center	Percent of Process Module
Site Preparation	4.3
Industrial Buildings	3.8
Storage Facilities	12.0
Utility Plants	4.3
Auxiliary Facilities	1.3
Offsite Piping	2.7

B.5 COST INDICES

Since the cost of process equipment always increases with time, it is necessary to adjust equipment costs with a cost index that would reflect this change. In the chemical process industry, four main indices are commonly used: (1) Engineering News Record (ENR) Construction Cost Index, (2) Nelson Refinery Construction Index, (3) Marshall and Stevens (M&S) Index, and (4) Chemical Engineering (CE) Plant Cost Index.

The ENR Construction Cost Index mainly measures the cost of civil structures such as dams and buildings, and is heavily dominated by construction labor costs. The Nelson Refinery Construction Index is basically an overall plant index for the petroleum refinery industry. The M&S index consists of two main indexes, one for buildings and the other for equipment. The CE plant cost index is specifically for chemical plant construction. It is a weighted average index composed of the cost of equipment, material, buildings, erection and installation labor, and engineering. Separate indices are given for equipment, machinery, supports, and construction labor in the chemical industry.

In recent years the differing rates of cost escalation has warranted separate bases for choosing the material and labor indexes. For the purpose of this study, the M&S equipment and ENR cost indices were used to reflect the adequate changes of equipment and labor costs, respectively.

The cost indices described so far are useful to correlate the past equipment cost to its present cost. Still, in performing an economic analysis of a future venture, there is a need for forecasting the cost index. A number of forecasting techniques have been proposed. However, the accuracy of these

forecasts depend largely on the degree of sophistication of economic models. The most straightforward forecast that can be made is by interpreting historical trends over a long period of time. Figure B.4 shows the equipment and labor cost indices that are used to correct equipment costs from present to future times.

B.6 VALIDATION OF THE COSTING MODEL

The validity of Guthrie's modular method has been demonstrated by Baasel(16). In Baasel's work, Guthrie's method gave a capital cost estimate which is about the median value for a chemical plant design whose high and low values (from past plant data) range between 19 and 9 million dollars. It appears that Guthrie's method and correlations give reasonable preliminary cost results.

Table B.4 shows the comparison between the results from the SAI developed costing program and previous estimates of the purchased costs for the cooling, scrubbing and organic recovery section of a wood-to-methanol plant(17). On an individual equipment basis, the SAI estimated cost is sometimes higher and sometimes lower than the published values. For example, the cooler-scrubber-absorber cost estimated by SAI is higher than the reference's cost value, while for smaller pump sizes, SAI's costs are lower than the reported values. Those differences probably arise from several factors:

- a) different design assumptions (e.g., pump type, heat exchanger design). In validating the model, SAI staff frequently had to assume certain design parameters because the specifications reported in the reference are not complete.
- b) typical variations in results of cost estimates, whenever these are from different sources. In a Ralph M. Parsons report(18), vendors' quotes for the same type of equipment are shown to differ from one another by as much as 50 percent.

Figure B.4 Commonly Used Cost Indices and Their Extrapolations

Table B.4 Comparison of Results of SAI's Costing Model and Published Purchased Costs for the Cooling, Scrubbing, Organic Recovery Section of a Wood to Methanol Plant*

Literature Description Equipment	Design	Material	1975 Cost (\$)	Additional Assumptions Used in SAI's Model	SAI 1975 Cost (\$)
Cooler-Scrubber-Absorber 16' D x 50' H	atm	304 SS	136,000	2 smaller units 304 SS clad	236,000
Liquid-Liquid Extraction Tower Baffle Trays 10' D x 80' H Trays 200 - 4" spacing	atm	316 SS	214,000	316 SS clad	205,000
Tar/Oil Tank 7' D x 7' H	atm	carbon steel	2,500		1,900
Middle Loop 5,000 gal	atm	SS	9,000		9,000
Water Layer Tank 5,000 gal	atm	SS	9,000		9,000
Absorption Water Tank 5,000 gal	atm	SS	13,000		13,000
Raffinate Storage Tank 10,000 gal	atm	SS	13,000		13,000
Extraction Storage Tank 10,000 gal	atm	SS	13,000		13,000

* Source: Raphael Katzen Associates, Chemical from Wood Wastes. (17) A few pieces of equipment are omitted from the list because their descriptions in the reference are not sufficiently detailed for costing purposes. In other cases, certain additional assumptions were made so that the cost can be estimated because the descriptions are somewhat incomplete.

Table B.4 Comparison of Results of SAI's Costing Model and Published Purchased Costs for the Cooling, Scrubbing, Organic Recovery Section of a Wood to Methanol Plant (Continued)

Literature Description Equipment	Design	Material	1975 Cost (\$)	Additional Assumptions Used in SAI's Model	SAI 1975 Cost (\$)
Oil/Tar Pump 5 hp motor	20 gpm 100' Hd	316 SS	1,800	in-line centri- fugal, general SS	800
Oil/Tar Pump 5 hp motor	20 gpm 100' Hd	316 SS	1,800	ibid	800
Lower Recirculating Pump 125 hp motor	4200 gpm 80' Hd	316 SS	8,500	ibid	7,000
Middle Recirculating Pump 125 hp motor	300 gpm 80' Hd	316 SS	8,500	ibid	7,000
Water Layer Pump 10 hp	300 gpm 80' Hd	316 SS	2,100	ibid	1,900
Water Recirculating Pump 15 hp	500 gpm 80' Hd	316 SS	2,700	ibid	2,300
Raffinate Pump 15 hp	400 gpm 80' Hd	316 SS	2,700	ibid	2,100
Extraction Pump 7.5 hp	200 gpm 80' Hd	316 SS	2,000	ibid	1,600
Extraction Reflux Pump	300 gpm 80' Hd	316 SS	2,100	ibid	1,900
Organic Pump	10 gpm 80' Hd	316 SS	1,800	ibid	700

Table B.4 Comparison of Results of SAI's Costing Model and Published Purchased Costs for the Cooling, Scrubbing, Organic Recovery Section of a Wood to Methanol Plant (Concluded)

Literature Description Equipment	Design	Material	1975 Cost (\$)	Additional Assumptions Used in SAI's Model	SAI 1975 Cost (\$)
Raffinate Reflux Pump	250 gpm 80' Hd	316 SS	2,100	ibid	1,800
Raffinate Bottoms Pump	300 gpm 80' Hd	316 SS	2,100	ibid	1,900
Bottom Loop Exchanger Plate-type A = 2350 ft ²	150 psi	304/316 SS	43,000	U-tube general SS	63,000
Middle Loop Exchanger Plate-type A = 2300 ft ²	150 psi	304/316 SS	43,000	ibid	62,000
Upper Loop Exchanger A = 500 ft ²	150 psi	310/316 SS	11,000	ibid	20,000
Extract Tower Reboiler Reboiler A = 2,700 ft ²	atm	316 SS	54,000	kettle reboiler general SS	114,000
Extract Condenser A = 5,400 ft ²	atm	316 SS	81,000	U-tube	111,000
Raffinate Tower Condenser A = 4,300 ft ²	atm	316 SS	71,000	U-tube	99,000
Total Purchased Cost			747,000		995,000

The sum of SAI's equipment cost estimates is 30 percent higher than the value from the reference, indicating that an overall degree of conservatism is built in the SAI program.

B.7 DISCOUNTED CASH FLOW ECONOMIC EVALUATION MODEL

The computer program selected for this task is the PRP program developed at Oak Ridge National Laboratory(6). Figure B.5 illustrates the working of the program. The cost of the product from a process facility is estimated when the capital investment, operating costs, interest rates, tax rates, by-product values and similar related information are supplied. The program uses a procedure that is mathematically consistent with the discounted cash flow method, and produces a table showing the cash flow history of the project. Provision is made for parametric studies in which the cost of the feedstock and the annual after-tax rate of return on equity are varied automatically over any desired range.

By doing this for several debt-equity ratios, the results can be plotted as a series of curves showing the production cost as a function of capital structure, feedstock price, and annual after-tax rate of return on equity. This type of information is especially useful in the evaluation of synthetic fuel projects, because of the marked influence of feedstock price and type of financing on the cost of the product, and because of the probability that unusual financing arrangements may have to be adopted for such plants.

Figure B.5 Parameters for Sensitivity Analysis Using the PRP program

*When the object of the calculation is the rate of return on equity for a given production cost, the unit price of the main product is specified, and all the other input requirements are essentially unchanged.

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