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A SURVEY OF BIOMASS GASIFICATION

VOLUME III - CURRENT TECHNOLOGY

AND RESEARCH

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FOREWORD

This survey was prepared by SERI staff and a number of consultants for the Department of Energy under Contract EG-77-C-01-4042, Task 3322. Compiled in three volumes, the survey covers the technical background of biomass gasification, the present status of research and development, and recommendations for future work. Volume I, Synopsis and Executive Summary, condenses the body of the report for the more casual reader. Volume II, Principles of Gasification, discusses the properties of biomass relevant to gasification and the specific kinetics and thermodynamics of biomass gasification reactions; it is intended for the researcher or engineer. Volume III, Current Technology and Research, details the present status of biomass technology and includes specific recommendations for the future.

This survey has been compiled by a number of SERI staff members and consultants under the direction of T. B. Reed. Although many authors contributed to the survey and are listed in the Table of Contents, many others had less formal input. We would like to thank them for their efforts.

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SYNOPSIS

PURPOSE

This Survey of Biomass Gasification was written to aid the Department of Energy and the Solar Energy Research Institute Biological and Chemical Conversion Branch in determining the areas of gasification that are ready for commercialization now and those areas in which further research and development will be most productive. This summary gives a minimal amount of discussion of the technical background of gasification and focuses on conclusions and recommendations that affect policy.

The Executive Summary gives the highlights of each chapter of the survey for ready reference in condensed form. The survey itself, running to over 400 pages, presents relevant scientific background information, surveys the current status of gasification activities, and examines various questions relevant to the uses of the product gases.

TECHNICAL BACKGROUND

Solid fuels such as biomass (any material derived from growing organisms) and coal have a limited field of direct use because of problems of distribution, combustion, and emissions. Gaseous fuels, on the other hand, have been used for 150 years because they are clean burning and easy to distribute. In addition, the gases can be converted to liquid fuels or chemicals:

Thus gasification can continue to supply the "convenience" liquid and gaseous fuels that we have come to depend on during the age of low-cost fossil fuels. While there are dozens of gasifiers and routes to gas production, they all fall into the following categories:

Pyrolysis is the breakdown of matter, especially biomass or coal, by heat. By its nature it produces some gas, some oil, and some char (charcoal from biomass and coke from coal). In some pyrolytic processes the char and oil are valued products; in pyrolytic gasification they are a nuisance, and extensive subsequent processing, generally at higher temperatures, is needed to convert char and oil to gas. Pyrolysis and pyrolytic gasification produces a medium energy gas (MEG). The gas contains a wide variety of products including CO, H₂, methane, and other hydrocarbons.

Air gasification, while requiring a pyrolytic step, uses a minimal quantity of air and steam to convert the char to gas in a single unit. Air gasification of biomass is particularly simple, and about a million air gasifiers were built during World War II to operate cars and trucks or generate power. The gas produced is called "low energy gas" (LEG) because it is diluted by the nitrogen of the air. While not suitable for pipeline distribution, it can be used in retrofitting existing boilers now using oil or natural gas, as well as to drive engines for transportation or power generation.



Oxygen gasification is also a relatively simple process that produces a medium energy gas composed primarily of CO and H₂. While quite satisfactory for burning, it can also be used for chemical synthesis to make methanol, ammonia, H₂, CH₄, or gasoline and is called "synthesis gas" or "syngas."

Hydrogasification, in which H₂ gas is added under high pressure, is also being studied and has the potential for high, direct yields of methane.

Anaerobic digestion produces methane and carbon dioxide biologically from manure or sewage. While it is, by strict definition, a gasification method, it is not generally referred to as "gasification" and will not be considered in this survey.

Biomass gasifiers occur in a bewildering variety depending on the heat input form (air, oxygen, or pyrolytic); gas-solid contact method (updraft, downdraft, fluidized bed, or suspended flow); feedstock form (residues, pellets, powders); gasification temperature (dry ash or slagging); product (low or medium energy gas, char, or pyrolysis oil), heating rate and residence time (slow and fast pyrolysis).

CONTENT OF REPORT

The main report was structured to serve as an introductory handbook on topics relevant to gasification, as well as providing reviews of past and current activities of use to both the generalist and specialist.

CHAPTER 1 contains an introduction and history of biomass gasification.

CHAPTER 2 briefly summarizes the potential biomass resource base.

CHAPTER 3 discusses the <u>properties of biomass</u> relevant to gasification, including tables and compilations of useful data.

CHAPTER 4 reviews the <u>treatment processes</u> that may be needed to prepare biomass feedstocks for use in different gasification schemes.

CHAPTER 5 contains a literature review of <u>pyrolysis</u> of biomass, under both slow and fast heating conditions.

CHAPTER 6 presents new calculations of equilibrium compositions of biomass under conditions relevant to a wide variety of gasification schemes.

CHAPTER 7 details the kinetics and mechanism of gas-char reactions, leaning heavily on experience with coal chars.

CHAPTER 8 is a survey of gasifier types.

CHAPTER 9 consists of a <u>directory</u> of current manufacturers of gasifiers and <u>gasifier</u> development programs.

CHAPTER 10 is a sampling of <u>current gasification R&D programs</u> and their unique features.



CHAPTER 11 compares air gasification for the conversion of existing gas/oil boiler systems to biomass feedstocks with the price of installing new biomass combustion equipment.

CHAPTER 12 treats gas conditioning as a necessary adjunct to all but close-coupled gasifiers, in which the product is promptly burned.

CHAPTER 13 evaluates, technically and economically, synthesis-gas processes for conversion to methanol, ammonia, gasoline, or methane.

CHAPTER 14 compiles a number of comments that have been assembled from various members of the gasifier community as to possible roles of the government in accelerating the development of gasifier technology and commercialization.

CHAPTER 15 includes recommendations for future gasification research and development.

CONCLUSIONS AND RECOMMENDATIONS

This survey has been written to outline the value of gasification, the technical base on which future work can proceed, and the activities now underway. Various people reading this information will draw different conclusions. We give here the conclusions on which we will base our work at SERI and toward which we recommend guiding the national program. None of these conclusions is immutable and we invite comment as to their validity.

- We recommend that both coal and biomass gasification be developed rapidly, because these two technologies will be required soon to supplement fuel supplies as oil and gas become increasingly costly or unavailable. Gasification can provide not only the gas needed for clean heat and power in our cities, but also the basis for synthesis of liquid fuels, SNG, ammonia, and olefins.
- Air gasifiers may find a place in domestic and commercial heating, but they
 certainly will be used in process heating and producing power for the biomass
 industries. Although research in progress may improve air gasification, we
 recommend immediate commercialization at the present level of development.
- Large-scale oxygen gasifiers may play a prominent role in the conversion of municipal waste. If small oxygen gasifiers and plants could be developed (50 tons/day), they could play a crucial role in energy self-sufficient farms, manufacturing ammonia and methanol or gasoline from residues at the farmers' cooperative level to eliminate the heavy dependence on fossil fuels that makes our farms vulnerable to inflating fuel costs and uncertain supply. We recommend development of a 50 ton/day to 100 ton/day pressurized oxygen gasifier to operate on farm or forest residues. From preliminary operation of a downdraft gasifier on oxygen, and from the thermodynamics presented in the survey, we believe that it will be possible to design an oxygen gasifier that produces clean synthesis gas in one step, eliminating the need for costly gas conditioning. In this regard we recommend that support be provided for research on energy efficient methods to separate oxygen from air.
- Pyrolytic gasifiers are not as well developed as oxygen gasifiers, but the majority
 of the research supported by EPA and DOE has been in this area. We recommend



continuing research and pilot work on many of these systems because they promise higher efficiencies and lower costs than oxygen gasification in production of medium energy gas. However, because it is not clear to what degree medium energy gas will be distributed in the United States, full-scale development of pyrolytic gasifiers must wait on decisions concerning the gas infrastructure in the United States. These decisions hinge on the costs of converting gas to methane for distribution versus distribution of lower energy and lower cost gas. One possible development would be the use of medium energy gas in captive installations and industrial parks but conversion of coal to methane for domestic distribution.

- We recommend top priority development of fast pyrolysis processes that give a high yield of olefins which can be converted directly to gasoline or alcohols. This seems to be the one truly new development in gasification since World War II. We recommend evaluating various feedstocks and particle size options at the bench level, combined with bench and engineering studies of process designs giving the very high heat transfer and short residence times necessary to produce these products. We also recommend evaluation of processes for reducing particle size at reasonable costs, since this appears to be a necessary adjunct to fast pyrolysis.
- Finally, we recommend a continuing effort to determine the molecular details of pyrolysis under carefully controlled but realistic laboratory conditions, to provide a firm foundation for understanding and thus improving all gasification processes.

A number of systems studies should be performed as adjuncts to the technical program.

- We recommend that the scale of gasification plants be studied immediately and, where appropriate, that programs be initiated to overcome scale limitations. In particular, coal is likely to supply gas heat for our cities, where large plants can clean the gas sufficiently and make methane for distribution. Because biomass is much cleaner it can be used on a smaller scale, a fact which is compatible with its wider distribution. If biomass residues must be processed at the 1,000 ton/day level or greater to be economically viable, very little biomass will be used as an energy source in this country. If it can be processed economically at the 100 ton/day level, it can be used more widely.
- We recommend a systems study of biomass energy refineries to be used in conjunction with farming and forestry operations, taking residues and converting them to the ammonia and fuel required to operate the farm and forestry operation, and shipping any surplus energy to the cities in the form of gaseous or liquid fuels.

For the longer term, and for biomass conversion plants of larger scale, economic analyses should be performed to identify suitable hybrid schemes. These include:

- production of methanol using a combination of biomass (low hydrogen/carbon ratio) and natural gas (high hydrogen/carbon ratio);
- joint electrolytic/gasification systems in which waste generates hydrogen and oxygen electrolytically, the oxygen is consumed in gasification, and the hydrogen increases the hydrogen/carbon ratio; and
- solar fast pyrolysis, in which the high intensity heat is supplied by solar collectors.



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Types of Gasifiers and Gasifier Design Considerations

T. B. Reed

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CHAPTER 8

TYPES OF GASIFIERS AND GASIFIER DESIGN CONSIDERATIONS

8.1 INTRODUCTION

Gasifiers come in a seemingly bewildering variety. The principal types are shown in Fig. 8-1. This chapter explains why the various types exist and delineates the factors needed to choose among them or to design a new one. Later chapters give a comprehensive list of biomass and other gasifiers and discuss in some depth the work of a number of groups engaged in gasifier research or development.

8.2 GENERAL CONSIDERATIONS FOR GASIFIER DESIGN

The development of gasifiers has been and continues to be largely empirical. Inventors study existing gasifiers and design improvements to fit specific concepts and needs. Initial models generally do not work well and require a great deal of effort and learning to become operational. Many problems are mechanical and can be solved by trial and error. Other problems are conceptual or chemical, or involve nonobvious heat transfer problems that remain unidentified—yet which fundamentally determine allowable conditions for practical operation. It would be presumptuous to claim that all the areas that must be considered in designing or choosing a gasifier are identified in Chapter 8, but it does offer a framework in which to consider the most important factors contributing to successful operation of gasifiers.

8.2.1 Chemistry of Biomass Gasification

The central problem in gasification is the conversion of a solid fuel (biomass, MSW, coal, peat, lignite, etc.) to a gaseous fuel, as can be seen from studying Figs. 8-1, 8-2, and 8-3.

The chemical composition of solid and gaseous fuels, along with the various processes of converting solid fuels to gaseous fuels, are shown in the ternary diagram of Fig. 8-2. The atomic compositions of the biomass, coal, and char samples from Tables 3-4 and 3-7 (Chapter 3, Volume II) are plotted, and they define the practical range of variation of these solid fuels. It is interesting to note that the composition of biomass ranges between that of lignin (L) and that of cellulose (C). The average composition of the biomass used in the calculations of Chapter 6 (Volume II) is shown with the larger point marked B (biomass) with composition CH_{1.4}O_{0.6}. The chart also shows the wide variation of char compositions, overlapping the composition (but not the physical structure) of coals. These compositions are especially arbitrary. Chars formed at low temperatures (between say 500 C and 800 C) have a surprisingly high H and O content. The compositions of three peats have been included (Punwani 1979), and it is seen that peats are very close in composition to lignin.

In this diagram, fuel gases lie to the right of the line defined by the composition CO and C_2H_4 . At high temperatures, only CO and H_2 are stable, defining the gas fuel range to be to the right of the H-CO line. However, at lower temperatures, CH_4 becomes stable and CO becomes unstable, so there is no exact position for the line separating gas fuels from solid fuels unless thermodynamic and kinetic conditions are specified. Finally, the products of complete combustion are CO_2 and H_2O , so that this line defines the low

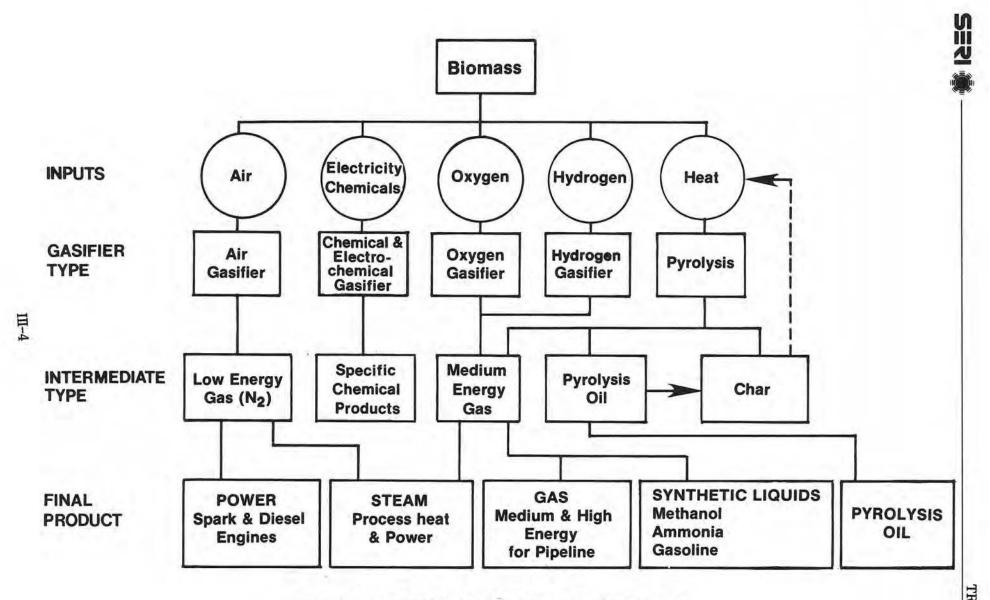


Figure 8-1. Gasification Processes and Their Products



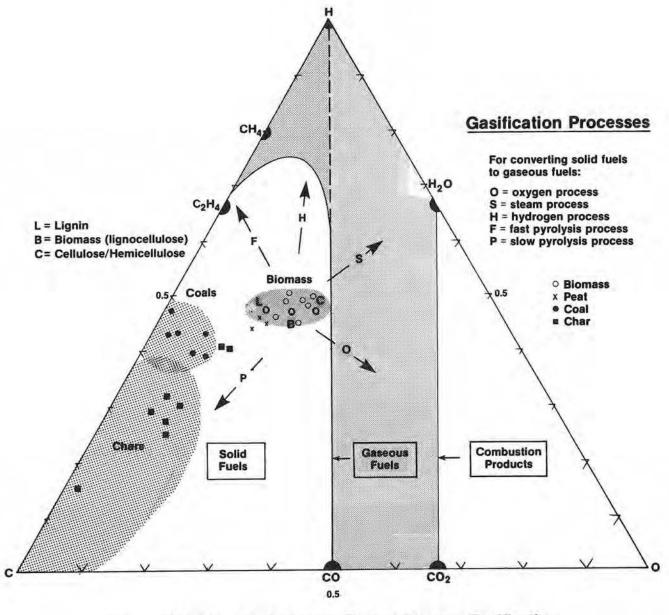
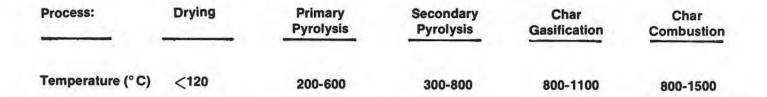


Figure 8-2. Chemical Changes During Biomass Gasification



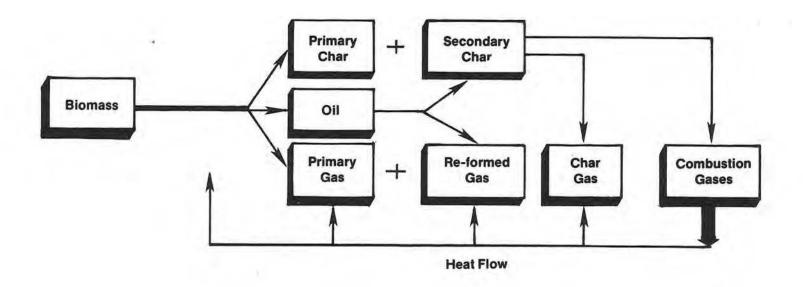


Figure 8-3. Heat and Mass Flows in Pyrolysis and Gasification Processes



energy limit of gaseous fuels. Compositions to the right of this line represent combustion with excess air or oxygen.

Thus, the problem of gasification becomes the problem of shifting the composition of the solid fuels of the left side of Fig. 8-2 along one or more of the arrows to a gaseous composition. A simple equation for high-temperature biomass pyrolysis to gas and char,

$$\text{CH}_{1.4}\text{O}_{0.6} \longrightarrow 0.7 \text{ H}_2 + 0.6 \text{ CO} + 0.4 \text{ C (solid)},$$

suggests that with heat alone char must result and that there must be a change in composition if biomass is to be completely gasified (with the possible exception of flash pyrolysis). The arrows of Fig. 8-3 show the various methods of accomplishing this. Pyrolysis is the disproportionation of biomass to yield some gases (typically methane, CO, and H₂) and the arrow P shows that in addition there will be a char formed. Oxygen/air gasification is mechanically the simplest method of producing gas because the initial reaction is exothermic (arrow O), and by far the largest number of the gasifiers of Chapters 9 and 10 use this method. Oxygen gasification is quite exothermic; in many cases, steam is used in conjunction with the oxygen to conserve energy and produce a fuel higher in hydrogen (arrow S). Steam can be used alone for biomass gasification, producing a gas high in methane, but the temperature of operation must be kept relatively low (see the Wright-Malta process and Fig. 6-10b in Volume II).

Hydrogen has been used in the past for the liquifaction and gasification of coal, and it can be seen from the arrow H in Fig. 8-2 that this shifts the composition of solid fuels toward high-methane and high-energy content fuels. However, the reaction with hydrogen requires high pressures, high temperatures, and a source of hydrogen—a fuel in its own right. Furthermore, at the low temperatures at which biomass volatilizes (200-500 C) it is not clear that there is any primary reaction between the biomass and the hydrogen, while the high temperatures required for coal volatilization make primary reactions more likely. Several groups are working on hydrogen gasification, but the processes are not ready for commercial demonstration.

A new area of biomass gasification involves the production of ethylene and higher olefins such as ethylene, propylene and butylene. These molecules are relatively unstable compared to methane or CO at high temperatures, yet their decomposition is slow, so that they can be formed in high yields by the <u>flash</u> pyrolysis of hydrocarbon feedstocks at temperatures of 750-1000 C. Recent experiments have shown that the rapid pyrolysis of biomass also gives high yields of these olefins with correspondingly low char yields (see Table 5-6, Section 5.3.2, Volume II). Fast pyrolysis of biomass to ethylene is shown diagrammatically by the arrow F on Fig. 8-2.

8.2.2 Energetics of Biomass Gasification

The thermodynamics of gasification was discussed in Chapters 3 (Heats of Combustion and Formation) and 6 (Thermodynamics of Gas-Char Reactions), both in Volume II. The energy requirements for idealized cellulose reactions to form gases, liquids, and chars are shown in Table 8-1. The increase or decrease in energy content of the products is illustrated diagrammatically in Fig. 8-4 (Reed 1978). These reactions show that the energy involved in conversion to gas, liquid, or solid products runs from -5 to 5 kJ/g (-5 to 5 MBtu/ton), which is small compared to the heat released on combustion (18 kJ/g or 16 MBtu/ton). In any practical gasifier, however, it is necessary to heat the biomass to

Table 8-1. ENERGY CHANGE FOR IDEALIZED CELLULOSE THERMAL CONVERSION REACTIONS

					Energy consumed ^a			
Chemical Reaction			$\Delta H_{r}(kcal/m)$	$\Delta h_{\mathbf{r}}(kJ/g)$	Products	Process		
1. C	H ₁₀ O ₅		→	6 C + 5 H ₂ + 5/2 O ₂	+229.9b	+5.94	Elements	Dissociation
2.	11		+	6 C + 5 H ₂ O (g)	-110.6	-2.86	Charcoal	Charring
3.	n		+	0.8 C ₆ H ₈ O + 1.8 H ₂ O (g) + 1.2 CO ₂	-80.3°	-2.07	Pyrolysis oil	Pyrolysis
1.	n n		+	$2 C_2 H_4 + 2 CO_2 + H_2 O (g)$	+6.2	+0.16	Ethylene	Fast Pyrolysis
	n	+ 1/2 O ₂	→	6 CO + 5 H ₂	+71.5	+1.85	Synthesis gas	Gasification
3.	11	+ 6 H ₂	+	6 "CH ₂ " + 5 H ₂ O (g)	-188.0 ^d	-4.86	Hydrocarbons	Hydrogenation
7.	***	+ 6 O2	→	6 CO ₂ + 5 H ₂ O (g)	-677.0	-17.48	Heat	Combustion

 $^{^{8}}$ 1 kJ/g = 0.239 kcal/g = 430 Btu/lb = 0.860 MBtu/ton.

^bThe negative of the conventional heat of formation calculated for cellulose from the heat of combustion of starch.

^cCalculated from the data for the idealized pyrolysis oil C_6H_8O ($\Delta H_c = -745.9$ kcal/mol, $\Delta H_f = -149.6$ kcal/g).

 $^{^{}d}$ Calculated for an idealized hydrocarbon with ΔH_{c} = -149.6 kcal/mol. Note H_{2} consumed.



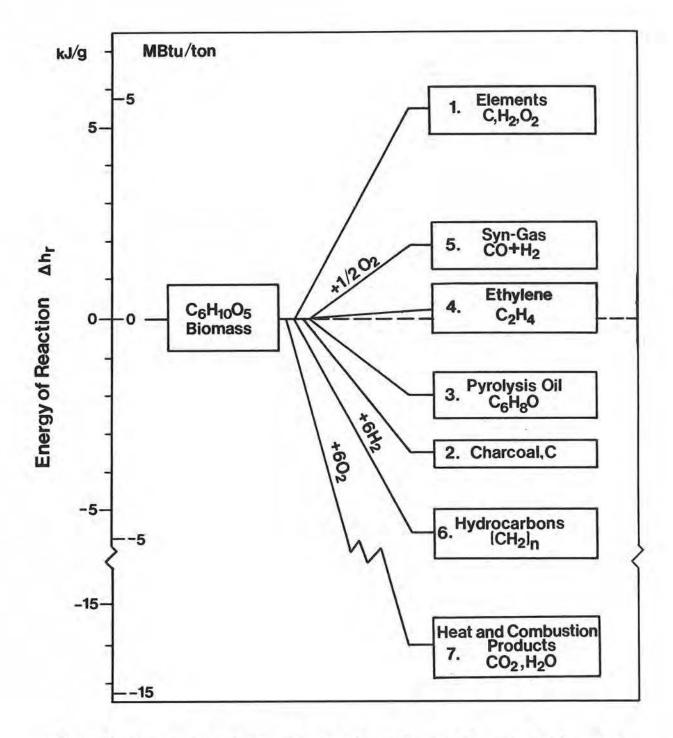


Figure 8-4. Energy Change for the Cellulose Thermal Conversion Reactions Shown in Table 8-1



the required reaction temperature (typically 500-1100 C) and then add the necessary energy for reaction, if any.

There is little reliable experimental data on the amount of energy necessary for the gasification reactions. Laboratory work on pyrolysis (see Fig. 5.5, Volume II) suggests that during very slow reactions with high char formation (Fig. 8-4) pyrolysis can be mesothermic or exothermic, but faster pyrolysis, producing a higher proportion of gases, is endothermic.

As mentioned previously, the gasification of biomass and char with oxygen or air is exothermic, while the oxidation by decomposition of steam is highly endothermic. Thus, practical gasifiers sometimes use mixtures of oxygen/steam to maintain proper reaction temperature. Similarly, the production of methane and CO₂ at lower temperatures can be exothermic, but it proceeds relatively slowly and may require a catalyst.

Each gasification process has its own energy requirements—some are exothermic, some endothermic, and all have process heat losses that have to be accounted for. The adiabatic reaction temperature (ART) is, of course, a measure of the degree of energy production in any process, and Fig. 8-5 shows the ART for pyrolysis, air, and oxygen gasification as a function of the amount of air or oxygen added relative to that required for combustion (the equivalence ratio). These results were calculated assuming equilibrium among the products, a fairly good assumption for downdraft gasification. Results of calculations for other conditions are given in Chapter 6, Volume II. In many other processes, the products are far from equilibrium (see Chapters 6 and 7, Volume II).

8.2.3 Pyrolysis and Char Gasification Reactions

Although the mechanics of gasification vary widely in different processes, each particle of biomass must undergo some or all of the stages shown in Fig. 8-3.

The first stage, <u>drying</u>, occurs below about 110 C, and locally the temperature cannot rise above this until all physical water has been driven off. Due to the low thermal conductivity of biomass (0.05-0.1 Btu/ft-h-F) and the even lower conductivity of char (0.03 Btu/ft-h-F), larger pieces can be burning on the outside while there is still moisture inside.

Once dry, <u>pyrolysis</u> converts the biomass to oil vapors, primary char, and primary gas (cellulose typically produces very little primary char, whereas the lignin and hemicellulose components produce higher char yields).

For small particles, the oil vapors are generated near the surface and can escape into the gas phase before being cracked to secondary char. These oil vapors can be condensed for use, burned with the gases, or cracked at higher temperatures to form re-formed gas. Recent experiments show that this re-forming only occurs at temperatures over 600 C (see Section 5.3, Volume II). For larger particles, the longer escape path provides more time for cracking the oil vapors, thus resulting in higher char production.

Char gasification and combustion are the most difficult tasks in gasifier design. The gasification of char proceeds relatively slowly even at temperatures high enough to require special construction materials. Combustion of char, on the other hand, is rapid and exothermic. Again, materials of construction will set the upper temperature limits. In some biomass gasifier designs, these reactions are carried out in the same vessel as the pyrolysis and drying; in other processes, the char may be gasified or burned separately.



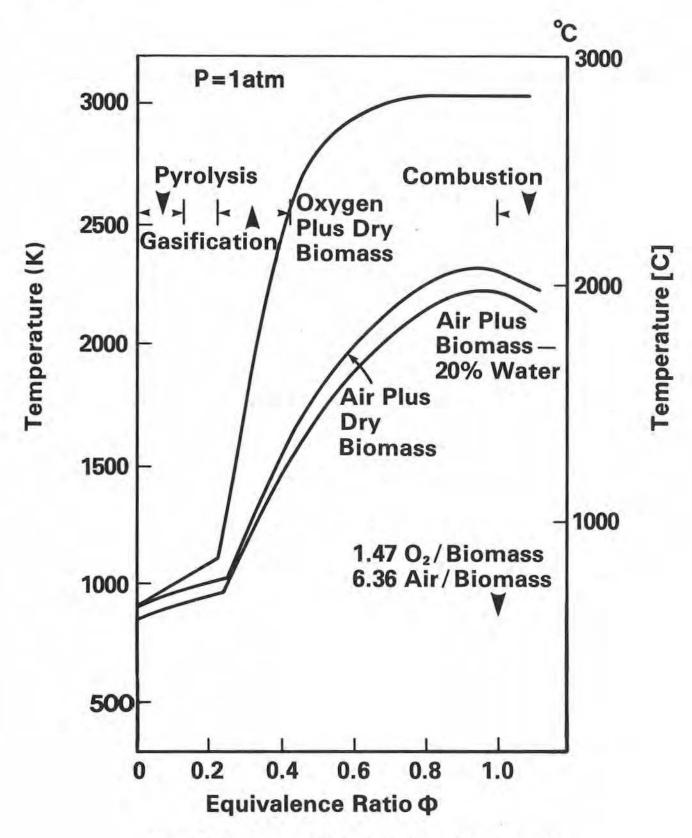


Figure 8-5. Biomass Adiabatic Reaction Temperatures



In coal gasification, the char reactions are even more difficult, because there is a higher proportion of char and it is much less reactive.

8.2.4 Heat Transport and Heat Transfer in Gasification

The micro- and macroscopic paths of heat transfer to the biomass suggested in Fig. 8-3 must be a central consideration in the design of any gasifier. Both the heat flow within the biomass particle and the heat flow to its surface from other parts of the gasifier must be examined.

In general, heat will flow within the biomass particle by conduction from its externally heated surface. The thermal conductivity of wood, and even more so of char, is especially low relative to most other materials (see Section 3.4.1, Volume II); for large pieces of biomass, it may require minutes, even hours, before the pyrolysis is complete at the core, despite the outer surface being maintained at 1000 C. Early charcoal manufacture required reaction times in excess of weeks! Thus, it is necessary to consider that there can be very steep temperature gradients inside the particle, with microzones of drying, pyrolysis, and char gasification from the center to the surface of the biomass particle undergoing external heating.

It is also possible to conceive of a biomass particle being uniformly heated throughout, either by solar radiation for small particles or by microwave radiation, but this is not likely to be important at higher temperatures after char coats the surface. Heat is transported and transferred, in general, by conduction, natural and forced convection, radiation, and change of state (as in a heat pipe); all of these mechanisms are active in gasification.

Conduction through a solid metal wall was used in early gas generators to heat a retort, producing gas, char, and oil. This has the advantage of yielding a relatively high Btu gas, since there is no dilution by air. However, it also produces the maximum char yield, because of the slow transfer of heat through the biomass volume. Indirect heating can be made more efficient by increasing the surface to volume ratio, for instance by using a multitude of small heat exchange tubes as is done for fast pyrolysis.

Forced convection gas heating of biomass is accomplished by passing a hot gas through the interstices in a fixed bed or around fluidized or suspended biomass particles in most gasifiers. In addition to the obvious forced flow of gases caused by the passage of the gas, currents due to natural convection and aspiration can occur unexpectedly and greatly alter the gasifier behavior.

"Solid convection" may seem like a contradiction in terms, but a fluidized bed accomplishes rapid, even, heat transfer by the movement of biomass or inert particles in a rising gas column. In a true fluidized bed, the temperature is considered to be uniform throughout, but in spouted beds and other forms there may be different temperature zones. Solid convection of particles can even be used to transfer heat alone from one vessel to another, permitting combustion of char with air in one vessel to provide heat for pyrolysis in a second vessel.

Liquid conduction and convection can provide much faster heating rates than gas convection, and baths of molten salts or metals have been used to heat biomass very rapidly. Solid and liquid convection are used in a number of the processes discussed in Chapter 10.



Radiation in gasifiers is an important heat transfer mechanism at higher temperatures between particles or with the wall, but only over short distances, since charred biomass is opaque to most radiation.

Finally, friction can be used to generate intense heat at the biomass surface. Change of state is an important mechanism of heat transfer that is generally overlooked in operating gasifiers. Oil and water vapors are generated in higher-temperature zones of reactors; if they pass to low-temperature areas, they can condense, releasing very large quantities of heat directly at the condensing surface. This is a very important heat transfer mechanism, comparable to that found in "heat pipes," and it must be considered in understanding any practical gasifier.

8.2.5 Mass Transport in Gasification

Both micro- and macroscopic aspects of mass flow are important in gasifier design as suggested by Fig. 8-3.

In a particle of biomass undergoing pyrolysis, there must be a continuous flow of gases and oil vapors to the surface and into the surrounding gas stream. This flow of gas tends to produce a boundary layer of cooler gases around the particle. As the gases pass through the char layer, there can be cracking reactions of the larger molecules, and this is probably one reason why char production is higher in larger particles.

In addition, in a fixed bed there will be a macroscopic flow of the solids (generally down), of the ash produced, of the oil vapors, and of the gas, all of which must be accounted for in the design of any gasifier.

8.2.6 Fuel and Ash Handling

A major consideration in gasifier design is the type of fuel or fuels to be used. Fixed bed gasifiers are most suitable for fuels of larger sizes (more than 1/4 in.); fluidized beds can operate with a range of sizes; suspended fuel gasifiers operate with smaller sizes (less than 1/4 in.), whereas fast pyrolysis may require very small particles to maximize heating rate and minimize internal vapor cracking.

Fuel feeding is often a major difficulty in gasifier operation, as is bridging inside the reactor. These problems can be minimized by densification (pelleting or briquetting), if this is economically justified (see Section 4.1.3, Volume II). The strength of the char is often important in the successful operation of fixed bed gasifiers since a weak char is likely to have high losses to the ash pit. Densification of the biomass increases the density and strength of the char.

Ash production is usually very low for wood fuels, higher for agricultural and aquatic biomass, and higher still for municipal wastes. In fixed bed gasifiers, provision must be made to either keep the ashes below about 1100 C to prevent aglomeration ("dry ash" operation) or heat the ash above 1300 C so the ash can be removed as a liquid ("slagging" operation). In fluidized and suspended bed gasifier operation, the ashes are typically removed after gasification by a cyclone.



8.2.7 Gasifier Pressure

In most cases, gasifiers will be operated close to 1 atmosphere of pressure in order to minimize sealing difficulties. Gasifiers designed for engine operation generally operate under slightly negative pressure and are called "suction" gasifiers. Those used to provide gaseous fuel for boilers typically operate slightly above atmospheric pressure.

Pressurized gasifiers require sturdy construction, lock hoppers, and pressurized feed gas. Nevertheless, these added requirements may be justified if the gas is subsequently to be used in a turbine, pipeline, or for chemical synthesis (to make ammonia or methanol), because of the elimination of compression costs, and commercial coal gasifiers are operated at pressures as high as 100 atmospheres.

8.3 GASIFIER TYPES

In designing, buying, or building a gasifier, one must make the following choices (discussed in the previous sections):

- Chemical change: air, oxygen, hydrogen, and slow or fast pyrolysis (5 types).
- Method of heat and mass contact—direct: updraft (counter-flow), downdraft (co-flow), fluidized bed, and suspended; and indirect: solids (fluidized bed), liquids, and gaseous recirculation (7 types).
- Fuel type and form: biomass, MSW, and pellets, powder, etc. (4 types).
- Ash type: dry ash and slagging (2 types).
- Pressure: suction, low pressure, and high pressure (3 types).

Gasifiers could also be categorized by products (gas, gas/oil, gas/oil/char, gas/char); by purpose (for power, for making steam, for pipeline distribution, for synthetic liquids); and in many other ways.

The world of gasifiers is potentially rich and varied. The possible combinations of the above five categories give over 500 types; only a few dozen are listed in Chapters 9 and 10. Figure 8-1 shows one possible simple breakdown of the major processes, and some important characteristics of the most common varieties are discussed below. Chapter 9 lists manufacturers and research groups working in these major areas, Chapter 10 gives more detail on certain specific research and development projects.

8.3.1 Air Gasification

The simplest way to produce gas is by air gasification, according to the (oversimplified) formula

$$\mathrm{CH}_{1.4}\,\mathrm{O}_{0.6}$$
 + 0.2 O_2 + 0.8 N_2 \rightarrow CO + 0.7 H_2 + 0.8 N_2 . "Air"

Unfortunately, this reaction is slightly endothermic and in practice somewhat more air must be added and some CO_2 and H_2O produced to provide the process energy. The nitrogen results in a dilute "low energy gas" of 120-200 Btu/SCF.



8.3.1.1 Updraft

The simplest air gasifier is the updraft (counterflow) gasifier shown in Fig. 8-6, in which air is introduced to the biomass through grates in the bottom of the shaft furnace. Rather high temperatures are generated initially where the air first contacts the char, but the combustion gases immediately enter a zone of excess char, where any $\rm CO_2$ or $\rm H_2O$ present is reduced to $\rm CO$ and $\rm H_2$ by the excess carbon. As the gases rise to lower-temperature zones, they meet the descending biomass and pyrolyze the mass in the range of 200 C to 500 C. Continuing to rise, they contact wet, incoming biomass and dry it. The counterflow of gas and biomass exchanges heat so that the gases exit at low temperatures.

A simpler arrangement can hardly be imagined, but the updraft gasifier has several drawbacks. A wide variety of chemicals, tars, and oils is produced in the pyrolysis zone and, if allowed, will condense in cooler regions. For this reason, this gas is generally used in the "close-coupled" mode in which it is mixed immediately with air and burned completely to CO₂ and H₂O. The close-coupled mode is quite suitable for supplying a biomass gas to existing oil or gas furnaces for process heat (see Chapter 11). The high temperature at the grate may melt the ash and produce slagging on the grates with feed-stocks such as rice hulls and corn cobs. Indeed, in the Andco-Torrax solid municipal waste (SMW) gasifier, the incoming air is preheated to give slagging temperatures on the grate, which then convert the high mineral content of SMW to a clean glass frit that can be used in road building. The Purox process uses oxygen to achieve high temperatures to melt minerals.

8.3.1.2 Downdraft

The downdraft (co-flow) gasifier shown in Fig. 8-7, is designed specifically to eliminate the tars and oils from the gas. Air is introduced to the gasifier through a set of nozzles called "tuyeres" and the products of combustion are reduced as they pass through a bed of hot charcoal extending some distance down to the grate. Continuing operation pyrolyzes descending biomass, but the oil vapors also pass through the bed of hot charcoal, where they are cracked to simpler gases or char. An important result of this cracking is an effect called "flame stabilization" in which the temperature is maintained in the range from 800 C to 1000 C by these cracking reactions. If the temperature tends to rise, the endothermic reactions predominate, thus cooling the gas. If the temperature drops below this range, the exothermic reactions predominate, keeping the gas hot.

The tars and oils are reduced to less than 10% of the value produced in updraft gasifiers, and these gases can then be used with minimal filtering to fuel spark and diesel engines, the principal use of downdraft air gasifiers. Typically, the gas velocities are low in updraft and downdraft gasifiers, and the ash settles through the grate, so that very little is carried over with the gas.

8.3.1.3 Fluidized Beds

Fluidized beds have been developed over the last few decades to provide uniform temperatures and efficient contact between gases and solids in process industries. A typical fluidized bed is shown in Fig. 8-8. Because of its higher throughput, it is more compact (Section 8.4.2), but the higher velocities carry the ash and char out with the gas and they must be separated in cyclones or bag houses.

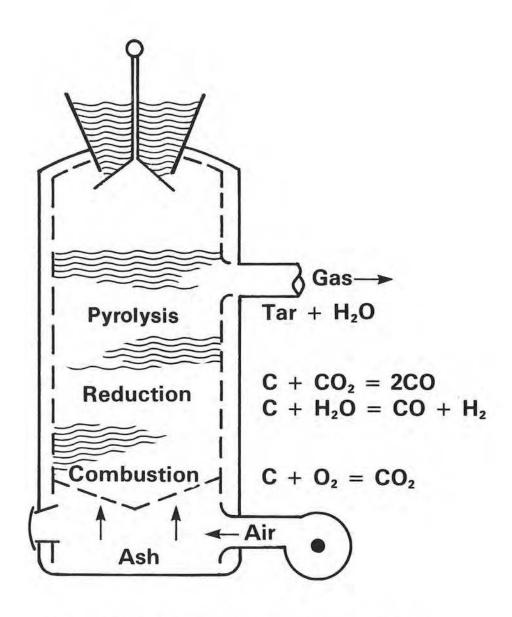


Figure 8-6. Schematic Diagram of Updraft Gasifier

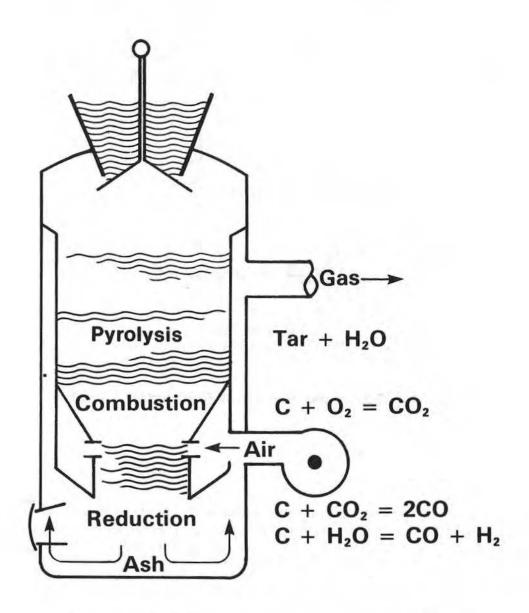


Figure 8-7. Schematic Diagram of Downdraft Gasifier



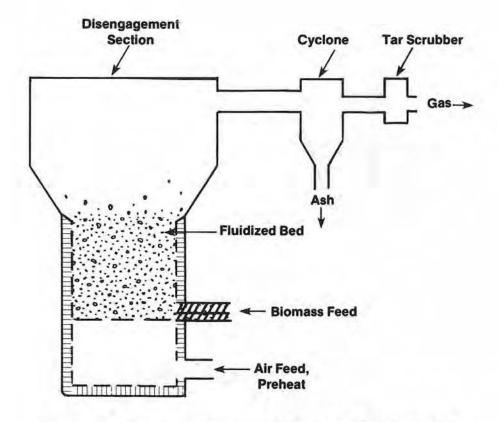


Figure 8-8. Schematic Diagram of Fluidized Bed Gasifier

Fluidized beds usually contain either inert material (such as sand) or reactive material (such as limestone or catalysts). These aid in heat transfer and provide catalytic or gascleaning action. The material is kept in suspension, simulating a "fluid," by a rising column of gas. In a true fluidized bed, the solids mix very rapidly and provide high heat transfer between all parts of the bed. In "spouted" beds and other modified gasifiers, there may be temperature gradients established and less mass exchange between the lower and upper parts.

Since fluidized bed gasifiers are a newer development than updraft and downdraft, their characteristics are not as well known. It is claimed that they can produce very low tars and char with recirculation, but to date this remains to be proven. A number of fluidized beds are under development and are discussed in Chapters 9 and 10.



8.3.1.4 Suspended Gasification

Suspended combustion is quite common for coal and fine biomass, utilizing a vortex action to obtain sufficient gas-solid contact to ensure complete combustion. Smaller particles such as sawdust can also be gasified in suspension. Only one suspended gasifier has been tested to date (Fig. 8-9).

8.3.2 Oxygen Gasification

Oxygen can also be used for gasification of biomass; it has the advantage that it produces a medium energy (300-400 Btu/SCF) gas that can be used in pipelines or for chemical synthesis to make methanol, ammonia, gasoline, or methane. Reaction rates are higher and velocities are lower than with air, resulting in easier gas cleanup and handling.

Oxygen production is the second largest of that of any chemical produced in the United States (after that of sulfuric acid), and it presently sells for \$20-\$60/ton in bulk. Since it requires about 1/3 of a ton of oxygen to gasify a ton of biomass, this will add \$0.40-\$1.20/MBtu of biomass to the cost of gasification. Bulk oxygen is available in most U.S. cities.

At present, no gasifiers have been designed specifically for biomass, but the Union Carbide PUROX process (see Section 10.2.2) processes 300 ton/day of solid municipal waste using oxygen in a updraft slagging gasifier. The mineral content of the waste is converted to a clean frit, and the tars and oils are scrubbed and reinjected into the hot zone for conversion to gas. An extended analysis of a gasifier that was designed using PUROX data to work on biomass is given in Desrosiers (1979, Section 5.4). Oxygen has been tested recently in an air downdraft gasifier with biomass. The temperatures observed were surprisingly low, which suggested that downdraft gasifiers for biomass may be simpler than updraft (Solar Energy Research Institute 1979). Oxygen has not yet been demonstrated for fluidized bed or suspended operation with biomass or SMW, but it has been used with coal in these modes; there is no obvious hindrance to its use with biomass and SMW.

8.3.3 Pyrolysis and Pyrolysis Gasification

8.3.3.1 Pyrolysis Processes for Gas/Oil/Char

Air gasification has the disadvantage that it produces a low energy gas; oxygen, that it uses high-cost input (oxygen) to achieve a medium energy gas. Biomass has a high content of volatile gas relative to coal and can be pyrolyzed to form a medium energy gas containing methane and higher hydrocarbons. Unfortunately, there is also a moderate amount of char and oil produced; these are assets if they can be sold but are disposal problems if they cannot. A number of pyrolysis processes are described in Chapter 9 and 10.

8.3.3.2 Slow Pyrolysis Gasification

Pyrolysis gasification uses many ingenious schemes to recycle the energy contained in char and oil into gas energy. This recycle results in a process of greater complexity, but

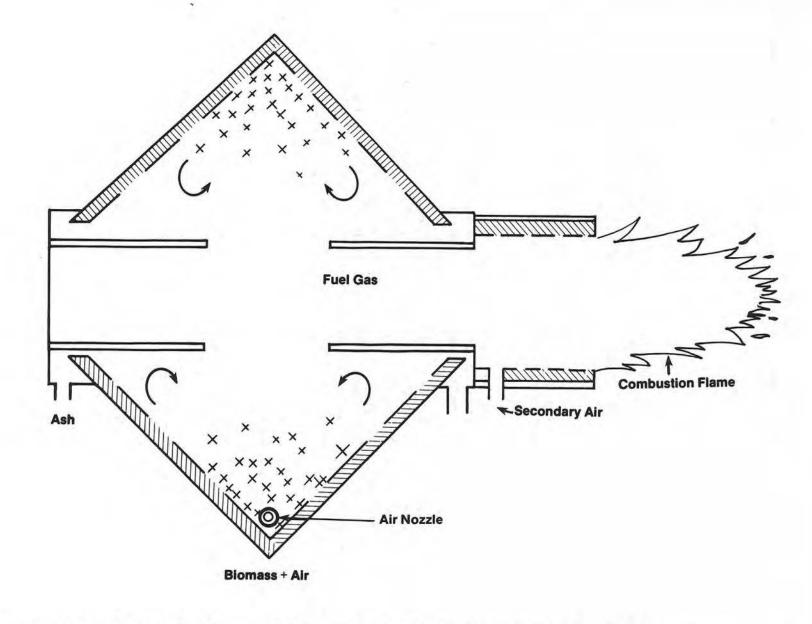


Figure 8-9. Schematic Diagram of Suspended Fuel Gasifier (After Frederick/Morback Design)



one which yields a medium energy gas with no other products. Various pyrolysis gasification processes are listed in Chapters 9 and 10.

The char energy can be recycled in a variety of ways. The char can be burned in a fluidized bed with sand. The resulting hot sand is transferred to a second bed in which the biomass is pyrolyzed. In other variations, char is burned to heat pyrolysis gas, which is then recycled to a fluidized fixed-bed pyrolysis unit, or external heat is fed to a slurry of wet biomass at high pressure.

8.3.3.3 Fast Pyrolysis Gasification

Many experiments have demonstrated that the degree of char and oil formation during pyrolysis increased with particle size, with reaction time, and with lignin content. Sufficiently rapid heating of finely divided biomass, on the other hand, need produce no char at all (see Chapter 4, Volume I).

Even more recently, it has been found that the vapor molecules generated during pyrolysis can be cracked at high temperatures to yield olefins (especially ethylene), and these products can be preserved if the gas is quenched before further reactions can occur. Since olefins form the basis of much of our chemical synthesis today, and since they can be easily converted to either gasoline-type hydrocarbons or, through hydration, to alcohols, it is understandable that there is a good deal of interest in "fast pyrolysis." Several such processes are discussed in Chapter 10.

8.3.4 Hydrogen Gasification

Hydrogen can be used at very high pressure to change the composition of biomass as shown in Fig. 8-2; this results in the formation of liquids or gasses, depending on the reaction conditions. This approach will be most attractive where hydrogen is readily available. Several projects in hydrogen gasification are described in Chapter 10.

8.3.5 Chemical and Electrochemical Gasification

A number of innovative approaches to gasification are being explored in which specific chemical reactions are induced to produce specific products. Examples include reaction of biomass with Br_2 to produce HBr and CO_2 . The HBr is then electrolyzed to produce H_2 (Darnell 1979). As a second example, one might envision an electrochemical scheme for H_2 from biomass analogous to the recent proposed method for coal (Coughlin and Farooque 1979).

8.4 FIGURES OF MERIT FOR GASIFICATION AND COMBUSTION PROCESSES

"Figures of merit" useful in comparing gasification and combustion processes are discussed in this section.



8.4.1 Volumetric Energy Content of Fuel Gases

The "volumetric energy content," typically quoted in Btu/SCF in the U.S., is a "figure of merit" for gases.

Caution must be used in reporting or reading energy contents of gases, as they can be misleading. The measurement of the volumetric energy content is straightforward for cold, clean gases. However, if gases are produced and used hot and containing combustible tars, the "equivalent volumetric energy content" released on combustion may be as much as 50% higher than that for cold, clean gas.

The energy contents of gases are seen in Table 8-2 to vary from less than 100 Btu/ft³ for blast furnace gas to 1000 Btu/ft³ for natural gas (methane). The volumetric energy content is indeed important in the distribution and storage of gases. Pipelines are expensive; at present, only natural gas can be distributed economically over long distances. Before the transcontinental pipelines were built during the 1940s, however, medium energy gas was regularly distributed city-wide and presumably this could be done again for industrial parks or city use. (The presence of carbon monoxide may rule out distribution to homes, although this was done prior to 1940.)

The volumetric energy content is not of prime importance in determining the suitability of gases for combustion applications, except for gases below about 200 Btu/ft³, where flame temperature and heat transfer may be affected (see Fig. 11-1). Low Btu gases may also require special burner designs.

8.4.2 Energy Conversion Rates in Various Processes

Two other figures of merit often used in combustion and conversion processes are the heat released or converted per unit area and the heat released or converted per unit volume. These figures in turn dictate the size and cost of equipment. Typical combustion processes for solid fuels release 400 Btu/ft²-h and 30 Btu/ft³-h. In contrast, combustion of gas or oil typically releases 100 Btu/ft³-h in process heat burners and up to 5000 Btu/ft³-h in automobile engines and turbines—hence the necessity of using gas or liquid fuels in these important applications.

Gasification processes typically convert 500-1000 Btu/ft²-h in updraft and downdraft air gasifiers (50-100 Btu/ft³-h) while fluidized beds convert 100-500 Btu/ft³-h. Operation on oxygen and/or at high pressure can increase these rates three- to tenfold. Thus, it is apparent that gasification processes have a high thruput relative to their combustion counterparts. This is due to the fact that most of the energy is not actually converted to heat in the gasifier, but only converted to another form.

Char conversion to gas is the most difficult stage of gasification and accounts for most of the dwell time of biomass in the gasifier. Pyrolysis systems, producing char, oil, and gas, therefore have even higher throughputs than gasifiers: typically 500 Btu/ft 3 -h. Again, this is due to the fact that pyrolysis makes a minimal change in the feedstock at quite low temperatures, and the char is not gasified.

8.4.3 Turndown Ratio

A figure of merit that is likely to become widely used in evaluation of gasifiers is the "turndown ratio":

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Table 8-2. ENERGY CONTENT OF FUEL GASES AND THEIR USES

Name	Source	Energy Range (Btu/SCF)	Use
Low Energy Gas (LEG) [Producer Gas, Low Btu Gas]	Blast Furnace, Water Gas Process	80-100 On-site industrial heat and pow process heat	
Low Energy Gas (LEG) [Generator Gas]	Air Gasification	150-200	Close-coupled to gas/oil boilers Operation of diesel and spark engines Crop drying
Medium Energy Gas (MEG) [Town Gas; Syngas]	Oxygen Gasification Pyrolysis Gasification	300-500	Regional industrial pipelines Synthesis of fuels and ammonia
Biogas	Anaerobic Digestion	600-700	Process heat, pipeline (with scrubbing)
High Energy Gas (HEG) [Natural Gas]	Oil/Gas Wells	1000	Long-distance pipelines for general heat, power, and city use
Synthetic Natural Gas (SNG)	Further Processing of MEG and Biogas	1000	Long-distance pipelines for general heat, power, and city use



R = maximum gasification rate/minimum gasification rate.

The turndown ratio is an inherent property of most common processes. As an illustration, a light bulb typically has a turndown ratio of 1; that is, it can only operate at full rated power. Recently, solid-state devices have been used in low-cost switch controls that give a turndown ratio of more than 10 for dimming the lights, and many homes now have several of these devices in selected rooms. An automobile has an infinite turndown ratio, since it will go all speeds including zero.

On the other hand, many devices have no turndown capability (a ratio of R=1), and in many cases such capability would be very desirable. An oil-fired furnace is either on or off, and though the heating rate is made variable by cycling, the efficiency suffers in comparison to that which could be achieved by a continuous lower-level operation.

The recent advent of airtight woodstoves is an attempt to get a high turndown ratio for wood heat, since it is difficult to operate wood heat on an on/off basis. However, operation at low air input involves the problem of creosote generation, air pollution, and chimney fires.

Fixed bed air gasifiers have a high turndown ratio, typically at least five. This property is very useful in situations where the gas is required on an intermittent or varying-load basis, such as operation of engines, drying, and heating.

On the other hand, fluidized bed gasifiers have a narrower range of operation (R=2) and must operate close to their design limit at all times or be started and stopped. Unfortunately, the field of gasification is so new that very little reliable data on established systems is available. We hope that the turndown ratio will be recognized as an important parameter of gasifiers and will be included in measurements and specifications of gasifiers.

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Directory of Current Gasifier Research and Manufacturers

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CHAPTER 9

DIRECTORY OF CURRENT GASIFIER RESEARCH AND MANUFACTURERS

9.1 INTRODUCTION

The first part of this chapter is a summary, in tabular form, of industrial and institutional facilities performing biomass and municipal waste gasifier research and development or manufacturing biomass gasifiers. Information presented includes gasifier type (air, oxygen, pyrolysis, etc.) contact mode (updraft, downdraft, or fluidized bed), primary fuel products, number of operating units, and size of units. For comparison, a summary of major coal gasification processes is included.

Questionnaires were sent to the manufacturers and researchers listed in Section 9-2; their detailed responses are given as a directory listing characteristics of existing gasifiers.

Although we have tried to make this list as complete as possible, the rate at which this field is developing makes it very difficult to maintain a completely current list. We apologize in advance to anyone we missed and urge those not represented to submit a directory sheet for future revisions of the list.

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9.2. SURVEY OF GASIFIER RESEARCH, DEVELOPMENT, AND MANUFACTURE *

NOTATION: (by columns)

Input: A = air gasifier; O = oxygen gasifier; P = pyrolysis process; PG = pyrolysis gasifier; S = steam; H = hydrogasification; C = char combustion.

Contact Mode: U = updraft; D = downdraft; O = other (sloping bed, moving grate); F1 = fluidized bed; S = suspended flow; MS = molten salt; MH = multiple hearth.

Fuel Products: LEG = low energy gas (about 150-200 Btu/SCF) produced in air gasification; MEG = medium energy gas produced in oxygen and pyrolysis gasification (350-500 Btu/SCF); PO = pyrolysis oil, typically 12,000 Btu/lb; C = char, typically 12,000 Btu/lb.

Operating Units: R = research; P = pilot; C = commercial size; CI = commercial installation; D = demonstration.

Size: Gasifiers are rated in a variety of units. Listed here are Btu/h derived from feedstock throughput on the basis of biomass containing 16 MBtu/ton or 8000 Btu/lb, SMW with 9 MBtu/ton. () indicates planned or under construction.

	Gasi	fier Type				
Organization	Input	Contact Mode	Fuel Products	Operating Units	Size (Btu/h)	Comments
9.2.1 Air Gasification of Bi	om ass					
Alberta Industrial Dev. Edmonton, Alb., Can.	A	Fl	LEG	1	30 M	
Applied Engineering Co. Orangeburg, SC 29115	A	U	LEG	11	5M	
Battelle-Northwest Richland, WA 99352	A	U	LEG	1-D	-	
B.C. Research Vancouver, B.C., Can. VC5 262	A	F1 ·	LEG	2	1-4M	

Biomass Corp. Yuba City, CA 95991	A	D	LEG	1	2M
Bio-Solar Research & Development Corp. Eugene, OR 97401	A	U	LEG	1	-
Century Research, Inc. Gardena, CA 90247	A	U	LEG	1	80 M
Davy Powergas, Inc. Houston, TX 77036	A	U	LEG-Syngas	20	-
Deere & Co. Moline, IL 61265	A	D	LEG	1	100 kW
Eco-Research Ltd. Willodale, Ont., Can. N2N 558	A	F1	LEG	1	16M
Environmental Energy Eng., Inc. Morgantown, WV 26505	Α	F1	?	1	3M
Environmental Energy Eng., Inc. Morgantown, WV 26505	A	D	LEG	1	0.1-0.5M
Environmental Energy Eng., Inc. Morgantown, WV 26505	A	Fl	MEG	1	-
Forest Fuels, Inc. Keene, NH 03431	A	U	LEG	4	1.5-30 M
Foster Wheeler Energy Corp. Livingston, NH 07309	A	U	LEG	1	-

^{*}Unless otherwise noted, the gasifiers listed here produce dry ash (T less than 1100 C) and operate at 1 atm pressure. (Coal gasifiers and future biomass gasifiers may operate at much higher pressures.)

	Gasifier Type		~				
Organization	Input	Contact Mode	Fuel Products	Operating Units	Size (Btu/h)	Comments	
Georgia Institute of Tech. Eng. Exp. Station Atlanta, GA 30332	A	U	LEG	1	0.5M		
Haleyon Assoc., Inc. East Andover, NH 03231	A	U	LEG	4	6-50 M		
Imbert Air Gasifier 5760 Arnsberg Z, Germany	A	D	LEG	500,000	34k-34M		
Industrial Development & Procurement, Inc. Carle Place, NY 11514	A	D	LEG	Many	100-750 kW		
Lamb-Cargate Industries, Ltd. New Westminster, B.C., Can.	Α	U/F1	LEG	?	4M		
Lamb-Cargate Industries, Ltd. New Westminster, B.C., Can.	A	U	LEG	2	25M		
Pioneer Hi-Bred Interna- tional, Inc. Johnston, IA	A	D	LEG		9M		
Pulp & Paper Research Inst.,* Pointe Claire, Quebec, Can. H9R 3J9	A	D	LEG	_	-		
Purdue Univ. Agricultural Eng. Dept. W. Lafayette, IN 47907	A	D	LEG	1	0.25M		
Saskatchewan Power Corp. Regina, Sask., Can. S4P-0S1	A	F1	LEG	1 or 2	25M		

Texas Tech Univ. Dept. of Chem. Eng. Lubbock, TX 79409	A	F1	LEG	1	0.4M
Texas Tech Univ. Dept. of Chem. Eng. Lubbock, TX 79409	A	U	LEG	1	-
Univ. of California Dept. of Agricultural Eng. Davis, CA 95616	Α	D	LEG	1	64,000
Univ. of California Dept. of Agricultural Eng. Davis, CA 95616	A	D	LEG	1	6M
Univ. of Missouri at Rolla Rolla, MO	A	=		1P	
Vermont Wood Energy Corp. Stowe, VT 05672	A	D	LEG	1	0.08M
Westwood Polygas Vancouver, B.C., Can. V6G 2Z4	Α	U	LEG	1	-
9.2.2 Oxygen Gasification of Biomass					
Battelle-Northwest Richland, WA 99352	O,A-S	U	=	1	-
Davy Powergas, Inc. Houston, TX 77036	-	-	-	-	-
Environmental Energy Eng., Inc. Morgantown, WV	0	D	MEG	1P	0.5

^{*}Operates at 1-3 atm pressure.

	Gasifier Type					
Organization	Input	Contact Mode	Fuel Products	Operating Units	Size (Btu/h)	Comments
IGT-Renugas Chicago, IL	o,s	Fl	MEG	_	1	
Rockwell Int. Canoga Park, CA 91304	O,A		-	_	· =	
9.2.3 Pyrolysis Gasification of Biomass						
A&P Coop (Angelo Industries) Jonesboro, AR	P	0	MEG (C)	1C	-	
Arizona State Univ. Tempe, AR	PG	F1	MEG	1	1	
Battelle-Northwest Richland, WA 99352	P	Fl	MEG	1		
ENERCO Langham, PA	P	_	MEG, PO, C	1P, 1C	-	
ERCO Cambridge, MA	P	Fl	PO, C	1P, (1C)	16, (20)	
Garrett Energy Research & Engineering Ojai, CA	MH		MEG	1P	-	
Gilbert Associates Reading, PA 19603	P	F1	-	1R	-	
Princeton Univ. Princeton, NJ 08544	PG	0	MEG,C	IR	-	

	M. Rensfelt Sweden	PG	0	MEG,C	IR	
	Tech Air Corp. Atlanta, GA 30341	P	U	MEG, PO, C	4P, 1C	33
	Texas Tech Univ. Lubbock, TX	PG	F1	MEG	1P	-
	Univ. of Arkansas Fayetteville, AR	P	0	MEG (C)	IR	-
	Wright-Malta Ballston Spa, NY*	PG	0	MEG (C)	1R, 1P	4
	9.2.4 Biomass Hydrogasification					
	Battelle-Columbus** Columbus, OH 43201	Н	F1,U,S	PG,PO,C	1-Res	
III-35	9.2.5 Air Gasification of Solid Municipal Waste (CSMW)					
	Andco-Torrax*** Buffalo, NY	Α	U	LEG	4C	100M
	Battelle-Northwest Richmond, VA 99352	-	-	_	-	-
	9.2.6 Oxygen Gasification of SMW					
	Calorican Murray Hill, NJ	0	U		-	9M

^{*}Operates at 1-3 atm pressure.

^{**}Operates at less than 70 atm pressure.

^{***}These gasifiers produce slagging (T greater than 1300 C) instead of dry ash.

	Gasifi	ier Type				
Organization	Input	Contact Mode	Fuel Products	Operating Units	Size (Btu/h)	Comments
Union Carbide Corp. (Linde) Tonowanda, NY***	0	U	MEG	1	100M	
9.2.7 Pyrolysis Gasification of SMW						
Envirotech Concord, CA	P	МН	LEG	1 P	_	
ERCO Cambridge, MA	P	Fl	MEG	IP	16	
Garrett Energy Research & Eng. Hanford, CA	P	МН	MEG	1 P	-	
Michigan Tech Houghton, MI	P	ML	MEG	- -	-	
Monsanto Enviro-chem. Systems Baltimore, MD	P, C	K	LEG, O, C	1 D	20 (375)	
Nichols Engineering Belle Mead, NJ	P	_	MEG, C	-	-	
Occidental Research Corp. El Cajon, CA	P	Fl	PO, C, MEG	1 C	_	
Princeton Univ. Princeton, NJ	P	0	MEG, C	2R	1 -	
Pyrox Japan	P, G, C	Fl	MEG	1C		Derived from Bailie process

	Rockwell International Canoga Park, CA 91304	P	MS	MEG, C	1P	16	
	Univ. of West Virginia at Wheelebrator Morgantown, WV	P, G, C	F1	MEG	1P	=	Bailie fluidized bed system
	9.2.8 Coal Gasification*						
	Babcock & Wilcox Co. Barberton, OH	A/O	S	LEG/MEG	1P (1-20 atm pressure)	400M	Semicommercial unit of 15 ft ID (400 tons/day) operated for one year in 1955. Slurry feed is pumped to raise pressure and then spray dried by recycle gas. Still in development.
Ш-37	Battelle-Columbus Battelle Mem. Inst. 505 King Ave. Columbus, OH	PG	Dual Fl	MEG	1P (7 atm pressure)	25M	Agglomerating ash is heated in an air-blown combustor and recirculated to a steam-blown pyrolyzer.
	BCR Bituminous Coal Research, Inc.	PG	3-F1	LEG	1P (16 atm pressure)	1.2M	Three-stage process: Devolatilization/ gasification/char com- bustion.
	Bi-Gas Bituminous Coal Research, Inc. 350 Hockberg Rd. Monroeville, PA 15146	O-S	S	MEG	1P (34-100 atm pressure)	120M	

^{*}There are dozens of systems being investigated for the gasification of various kinds of coal. We include here those that have long been commercialized or are presently being actively developed, for comparison with biomass gasifiers.

		Gasifi	er Type				
	Organization	Input	Contact Mode	Fuel Products	Operating Units	Size (Btu/h)	Comments
	CO ₂ Acceptor Conoco Coal Dev. Co. Research Div. Library, PA	PG	2-F1	MEG	1P (16 atm pressure)	30M	Char is burned to regenerate CaO/(CO ₂ acceptor), which is recirculated to gasifier.
	DOE-METC Morgantown Energy Technology Center Collins Ferry Rd. Box 880 Morgantown, WV	A-S	U(Stirred)	LEG	1P (20 atm pressure)	20 M	
7	FW Stoic Stoic Combustion Pty. Ltd. Johannesburg, South Africa	A-S Two-Stage	U	LEG	4	22-90M	Diameter available: 6.5, 8.5, 10, 12.5 ft
	Hydrane DOE-MERC Morgantown, WV	н ₂	S	HEG	1P (200 atm pressure)	0.2M	Laboratory scale
	Koppers-Totzek Koppers Co., Inc. Koppers Bldg. Pittsburgh, PA	0-S	S	MEG	39P (1-30 atm pressure)	450M- 860M	
	Lurgi American Lurgi Corp. 377 Rt. 17 Hasbrouck Heights, NJ	O-S	U	MEG	66P (30 atm pressure)	800M	
	McDowell-Wellman Eng. Co.	A/O-S Single-Stage	Ü	LEG/MEG	15	3-100M	Standard sizes available: 3.5, 6.5, 8, 10 ft diam.

	Riley-Stoker Corp. Riley Morgan Gasifer Riley Morgan Gasifier	A/O-S Single-Stage	Ü	LEG/MEG	10	100M	More than 9000 units sold through 1940s	
	SYNTHANE DOE-PETC 4800 Forbes Ave. Pittsburgh, PA	0-S	Fl	MEG	1P (70 atm pressure)	72M		
	Wellman-Incandescent Applied Technology Corp. Houston, TX	A-S Two-Stage	Ū	LEG	30	14-100M	Mostly in South Africa Diameter available: 4.5, 5.5, 6.5, 8.5, 10, 10.75, 12 ft	
	Wilputte Corporation	A-S Single-Stage	U	LEG		67M	More than 250 units operated from 1913 to 1945	
Ш-39	Winkler Davy Powergas, Inc. P.O. Drover 5000 Lakeland, FL	O/A-S	Fl	LEG/MEG	41P (1 atm pressure)	1100M	None in the United States	
	Woodall-Duckham	A/O-S Two-Stage	U	LEG/MEG	40	100M		



Organization

Address

704 Cambridge Building

Alberta Industrial Developments Ltd.

Edmonton, Alberta Canada T5J 1R9

Personnel

Phone

Richard P. Assaly

(403) 429-4094

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Thermex-Reactor- (Fluid Bed) 70 ton/day

30 million Btu/hr. Design and module size unlimited.

Status (research, pilot scale, commercial, etc.)

PROTOTYPE - Now ready for commercial use.

General Information (description, photo, sketch, etc.)

Gas Generator Process by Fluid Bed (Pyrolysis) includes flash drier/ feed bin/gasifier (Thermex-Reactor) operates on air, close couple gas connection for boilers, driers, etc.

Process can maximize gas or charcoal production. High efficiency process with low operating cost system can operate on very fine raw material higher heating values of gas than other systems.

Plans for Future

Short Term - 1979-80 Three to six reactor installations up to 10 tons/hr.

Long Term - High pressure (400-600 GPSI) system for SynGas.

Name Richard P. Assaly

Date January 16, 1979



Organization

Address

1525 Charleston Hwy.

Applied Engineering

Orangeburg, S. C. 29115

Personnel

Phone

J. F. Jackson

803-534-2424

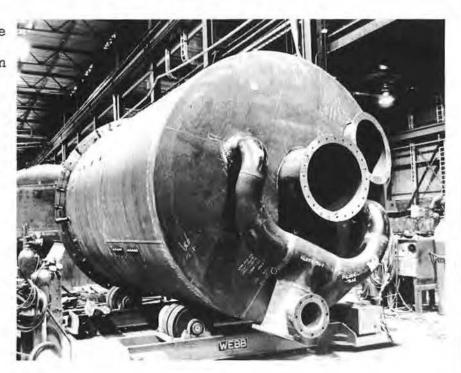
Type of Gasifier (up/down draft, size, fuel, application, etc.)
Boiler retrofit of a continuous updraft unit sized to provide
25mm BTU/Hr. via the gasification of whole tree chips.

Status (research, pilot scale, commercial etc.)

Commercial application.

General Information (description, photo, sketch, etc.)

Proprietary grate and burner design gives the unit the capability of producing 25 MMBtu/h on a continuous basis. Commercial application comprises a turn-key installation consisting of wood chip storage and handling, gasification, boiler retrofit package, and control system.



Plans for Future

Commercial/Industrial Application - design, manufacture, and installation of biomass gasification equipment and related hardware.

Name James Jackson

Date Navember 8 - 1978



Organization

BIOMASS AIR GASIFIER DIRECTORY

Address

Battelle-Northwest P.O. Box 999, Richland, WA 99352

Personnel Phone L.K. Mudge 946-2268 P.C. Walkup 946-2432 D.G. Ham 946-2083

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Updraft. Diameter: 1 ft; working bed height: 5 ft. Solids processed: corn stalks, grass straw, wood chips, wood pellets, industrial wastes, coke, charcoal, coal

(research, pilot scale, commercial, etc.) Status

Operational at a small pilot scale.

General Information (description, photo, sketch, etc.)

The gasifier is refractory lined and is equipped with an eccentric, rotating grate and a mechanical feed distributor. Solid feed is introduced at the top of the reactor through a lock hopper and auger. A schematic of the gasifier is shown in Figure 1, and a photo is attached.

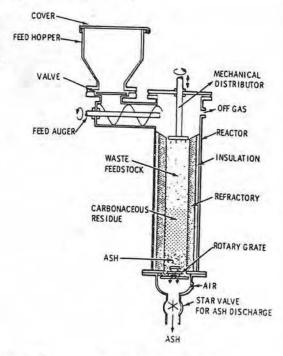


Figure 1 Schematic of small gasifier

Plans for Future

Continue operation of the gasifier to characterize gasification characteristics of different solids.

Name Lyle K. Mudge Date 9 January 1979



Organization

B.C. Research

Address

3650 Wesbrook Mall

Vancouver, B.C.

V6S 2L2

Personnel

Phone

Canada

Dr. Douglas W. Duncan

(604) 224-4331

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Fluidized bed wood waste gasifier using run-of-the-mill sawdust or hog fuel.

(research, pilot scale, commercial, etc.) Status

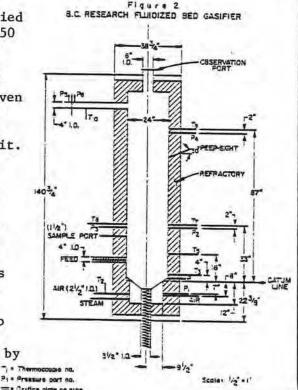
106 Btu/hr unit available at B.C. Research for research use. 4x106 Btu/hr unit at Saskatchewan Forest Products, Hudson Bay, Saskatchewan.

General Information (description, photo, sketch, etc.)

The B.C. Research unit has the dimensions shown in the attached sketch. Air is supplied below the pinhole grate by a 3 HP blower (150 CFM capacity). Run-of-mill hog fuel containing up to 50% moisture (total weight basis) is fed into the combustion zone just above the grate where the volatiles are driven off and consumed. The 5 ft bed consists of charcoal and ash. Surplus ash is withdrawn intermittently through the bottom of the unit. The raw gas (100-150 Btu/sdcf) exits via a port near the top of the reactor, passes through a dry cyclone to a furnace where it is burned.

The 4x106 Btu/hr unit in Saskatchewan is similar except that the reactor has an expanded freeboard above the ash bed to aid in particulate removal and the raw gas exits from the top of the reactor where it passes through a cyclone and then through a gas cleaning system. The raw gas is intended to fire a diesel generator set.

The Btu gasifier is being commercialized by Lamb Cargate Industries Ltd., 1135 Queens Ave., New Westminster, B.C., V5L 4Y2.



Plans for Future

Continue research studies on research reactor. Generate financing to build 20x106 Btu/hr prototype.

Name / Louistonia Date

January 24, 1979



Organization

Address

Biomass Corporation

951 Live Oak Blvd., Yuba City, Ca. 95991

Personnel |

Phone

Theodore H. Crane, President

(916) 674-7230 Robert O. Williams, Vice President Engineering

Type of Gasifier (up/down draft, size, fuel, application, etc.) Downdraft, fuel from prune pit size to 2x2x2 "hay-cubes" 5000 Btu per pound and up heating value, biomass or coal.

Status (research, pilot scale, commercial, etc.)

Commercial system. 1 to 15 million Btu per unit. Manifold units to 70 million Btu.

General Information (description, photo, sketch, etc.) The BIOMASS GASIFIER is a down draft, co-current flow, fixed bed reactor for conversion of solid carbonaceous fuel to low-Btu fuel gas. The fuel gas may be directly substituted for natural gas or fuel oil in existing or new boilers with only a change in the burner. Available standard low Btu gas burners are standard commercial products in sizes up to 100 million Btu.

The Biomass gasifier discharges no tar, oils or liquors which could require expensive or hazardous disposal by the operator. The char residue contains carbon and inorganic matter suitable for blending with conventionally produced charcoal for briquettes or as a low sulfur metallurgical carbon source. The residue is inert and may be land filled if there is no other use for it.

A large internal fuel hopper and a system of sealed external hoppers, augers and knife gate valves allow continuous operation with full automation of the fuel cycle and no possibility of gas leaks at any time.

The design analysis of the various sized Biomass gasifiers includes a detailed thermal stress study. The suspended design of the gasifier shall allow full expansion of the gasifier eliminating stress build-up, a subsequent shell cracking. Details of system designs, system sizing and economic analysis of the benefits of gasifier ownership available upon application.

Plans for Future

Detailed studies of the use of the biomass gasifier as a fuel source for internal combustion engines. These studies will include complete mass and energy balances and the wear factor upon the engines.

Name THEODORE H. CRANE Date January 16, 1979



rsonnel Phone		ASS AIR GAS				
rsonnel 35 (503) 6 pe of Gasifier (up/down draft, size, fuel, app draft, tank size 12' x 25', burns WOODEX® solid for any heat application. atus (research, pilot scale, commercial, etc.) mmercial and research neral Information (description, photo, sketch, 0-Solar Research & Development Corp, manufactures rning WOODEX® pelletized solid fuel, and producing lue from a non-fossil derivative. The gas is call seen applied for. The gas can be used to produce	•				ov Divers	
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neral Information (description, photo, sketch, o-Solar Research & Development Corp. manufactures rning WOODEX® pelletized solid fuel, and producing lue from a non-fossil derivative. The gas is calls been applied for. The gas can be used to produce	search, pilo	ot scale,	commercia	1, etc.)		
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	ined by prop	rietary me	thods, ca	n be use	in glass	smelting.
ans for Future Bio-Solar Research & Development WOODEX® plants with G-GAS producers providing he			-			

Date 31 January, 1979

Name <u>Ted Carpentier</u>



Organization

Address

Century Research, Inc.

16935 S. Vermont Avenue, Gardena, Calif. 90247

Personne1

Phone

Dr. Steve S. Hu

(213) 327-2405

Mr. Howard R. Amundsen

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Up-draft, Layer-zoned, Oxi-reduction Minimax Gas Producer, 10 ft diameter for standard model, Fuel: animal waste, agriculture waste, forest waste, paper waste, etc. Gas fuel for electricity, steam, cement/brick plant, chemical feedstock

Status (research, pilot scale, commercial, etc.) for ammonia/alcohol manufacturing.

Commercial

General Information (description, photo, sketch, etc.)

Overall dimension of standard 10 ft diameter unit: 35 ft tall represented by 15 ft of hopper and gravity feed system, 10 ft of combustion chamber, and 10 ft of residue cone and residue discharge system.

The unit can process approximately 100 tons of feed stock per day and produce 50 to 100 million btu equivalent of producer gas per hour.

The producer gas is composed of approx. 20-25% CO, 10-15% H2, 2%+ CH4, and 5-10% CO2 and 50-60% N2 (by volume). It contains 125-165 btu per cu ft under std temp and pressure condition. It can reach 2700 deg F flame temperature.

A typical Century Research/Bainien gasification plant is composed of 5 component systems: Frontend feed stock processing system, Gasification system, Test and automatic control system, Environmental cleanup system, and End product synthetization or utilization/application system.

Marketable product on the basis of 1978 calculations is priced at \$2. to \$2.50 per million btu.

Plans for Future

Development of semi-portable or portable version of the standard model, so that the gasifier can process lower daily tonnage with high efficiency and on site to site basis.

Name Steve Hu / Howard R. Amundsen Date January 16th, 1979



Organization

Address

Davy Powergas Inc.

P.O. Box 36444

bavy Towergas The.

Houston, Texas 77036

<u>Personnel</u> <u>Ph</u>

Phone

1500 in USA Worldwide (713) 782-3440

Type of Gasifier

(up/down draft, size, fuel, application, etc.)

Up draft fixed bed type, up to 13' 6" producing both gas engine fuel and ammonia synthesis gas.

Status (research, pilot scale, commercial, etc.)

Commercial - More than twenty gasifiers built & operated

General Information (description, photo, sketch, etc.)

This fixed bed 'Waste Refuse Producer' is an offshoot of the Powergas Corp. Ltd. fixed bed producer of which more than one thousand gasifiers were built and operated. This biomass unit has operated on wood, wood bark, cotton seeds, bagasse, etc. Most of these units have been shut down due to the availability of natural gas and oil. We believe that one or two are still operating in Southern Africa.

Plans for Future

Davy is still promoting biomass gasification with air and now with oxygen. We are presently proceeding with the design of a 2000 TPD methanol plant based on wood gasification.

Name

Edgar E. Bailey
Product Manager

Date

Jan 16 1979

Organization

Address

Technical Center

Deere & Company

3300 River Drive

Personnel

Phone

Moline, IL 61265

N. A. Sauter

309/757-5275

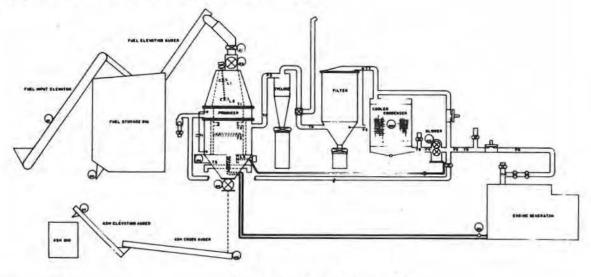
Type of Gasifier (up/down draft, size, fuel, application, etc.) Continuous, portable, downdraft unit for converting agricultural residues to gas and to electricity via 100 kW diesel generator set

(research, pilot scale, commercial, etc.) Status

Research Tool

(description, photo, sketch, etc.) General Information

Unit is generally described in Chapter 8, Solid Wastes and Residues -Conversion by Advanced Thermal Processes, American Chemical Society Symposium Series, Washington, D. C. 1978.



Schematic of portable 100 w farm power plant

Plans for Future

Not currently active

11 January 1979

Organization DEKALB AgResearch, Inc. Address DeKalb, Illinois

Personnel Stan Bozdech Harold Zink Phone 815 758-3461

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Up-draft with combustion system to dry seed Fuel-dry corn cobs

Status (research, pilot scale, commercial etc.)

Pilot scale at 1.6 million BTU's/hour proven in actual drying tests. Scale-up to 6 million BTU's on line in fall of 1980.

General Information (description, photo, sketch, etc.)

Gasifier System was designed to overcome slagging at the grates and, through a close-coupled arrangement, with primary air mixed in a Commercial Burner Head, to complete combustion in a torroidal chamber. Clean combustion gases are tempered to 110 F for drying as they exit combustion chamber. Complete system operates as a vacuum.

Plans for Future

Name

Date November 7, 1979



Organization

Address

Eco-Research Limited

P.O.Box 200, Station A

Personnel

Willowdale, Ontario. M2N 5S8

John W. Black

416-226-7351

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Fluidized Bed Gasifier Application - wood, municipal refuse

Status (research, pilot scale, commercial, etc.)

25 TPD pilot plant - ready for commercialization Sept. '79

General Information (description, photo, sketch, etc.)

The pilot plant started up in May '76 and has been used both as a combustion unit with in-bed steam generation and a gasification system for the production of a low BTU fuel gas. Materials gasified have included tires, wood, wood wastes, agricultural biomass and municipal refuse.

Plans for Future

Plans for the near term include a continuous demonstration test of about 3 months and oxygen gasification

Name John W. Black

Date January 16, 1979



Organization

Address

Energy Resources Company Inc.

185 Alewife Brook Parkway Cambridge, MA 02138

Personnel

(ERCO)

Herbert M. Kosstrin

(617) 661-3111

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Continuous fluidized bed pyrolysis unit for conversion of agricultural and industrial wastes to produce low Btu gas, char and

(research, pilot scale, commercial etc.) Status

Pilot scale unit available for client testing Commercial units now under construction

General Information (description, photo, sketch, etc.)

Pilot unit described in paper given at Institute of Gas Technology Symposium: "New Fuels and Advanced Combustion Technologies," March, 1979.

Plans for Future

Continued commercialization for waste to energy units

Name

Date November 1, 1979

Herbert M. Kosstrin

Ш-52



Organization

Address

Environmental Energy Engineering Inc. P.O. Box 4214, Morgantown, W.Va. 26505

Personnel

Phone

Dr. Richard C. Bailie

(304) 983-2196

Type of Gasifier (up/down draft, size, fuel, application, etc.)

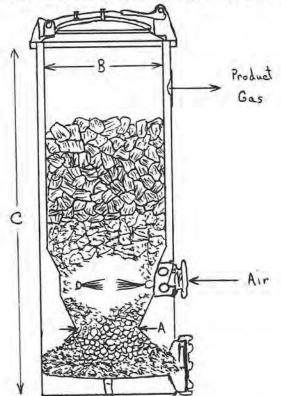
Downdraft gasifier operating on char, wood blocks or pelletized wood. Operates commercial burner that can be used for crop drying, furnace industrial heat and internal combustion engine. Cap. 100,000/hr to 500,000 Btu/hr.

Status (research, pilot scale, commercial, etc.)

Batch system ready for commercial application but no manufacturer exists. Continuous system requires additional development.

General Information

(description, photo, sketch, etc.)



Plans for Future

A = 5 in.

C = 50 in.

Test in small commercial operations replacing natural gas. Test oxygen enriched air systems. Modify for continuous operation.

Name R. C. Bailie

Date Jan 24, 1979



Organization

Address

Environmental Energy Engineering Inc. P.O. Box 4214, Morgantown, W.Va. 26505

Personnel

Phone

Dr. Richard C. Bailie

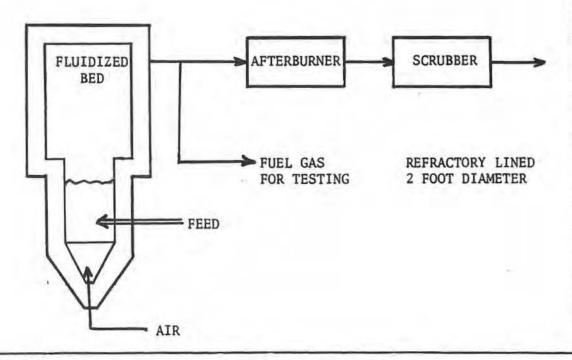
(304) 983-2196

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Fluidized bed operating on wood blocks, sawdust or pellets. Operates commercial burner which can be used for crop drying, furnace industrial heat and internal combustion engine. Air blown, Cap. 3 x 10⁶ Btu/hr.

Status (research, pilot scale, commercial, etc.)

Pilot plant test facility for different feed stocks.

General Information (description, photo, sketch, etc.)



Plans for Future

Available for commercial development.

Name P. C. Bailie

Date Jan. 24, 1979



Organization

Address

Environmental Energy Engineering, Inc. P.O. Box 4214, Morgantown, W.Va 26505

Personnel

Phone

Dr. Richard C. Bailie

(304) 983-2196

Type of Gasifier (up/down draft, size, fuel, application, etc.)

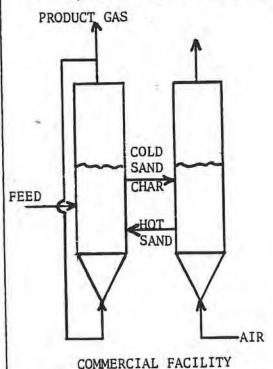
Two fluidized beds which can produce 300 Btu/ft3 gas not diluted with No without need for oxygen plant. Operates on most any cellulosic feed.

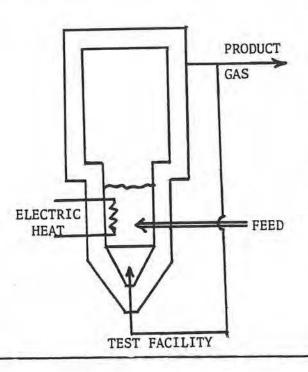
(research, pilot scale, commercial, etc.) Status

Research - Pilot facility

(description, photo, sketch, etc.) General Information

Sketch of commercial system is shown below. Test facility adds heat electrically instead of circulating sand as shown.





Plans for Future

Demonstrate with sand circulation.

R.C. Bailie

Date Jan. 24 1978



Organization

Address

Technical Center

Forest Fuels, Inc.

Antrim, N. H. 03440

Personnel

Phone

M. H. Stevens

603-588-2994

R. A. Caughey

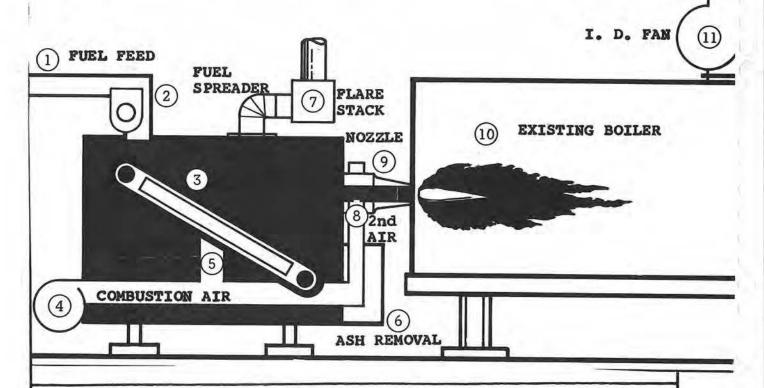
Type of Gasifier (up/down draft, size, fuel, application, etc.)
up draft, moving grate, close-coupled, using pulp chips, log saw
dust, planer shavings, sized debarking waste - dried to 10-20%
dry weight basis- to run package, sectional boilers, or direct fire

Status (research, pilot scale, commercial etc.)

to provide plant or process heat for kilns, factories, schools. 2mm BTU/hr. to 25mm BTU/hr.

Pilot and limited commercial

General Information (description, photo, sketch, etc.)



Plans for Future

Prove market readiness and increased sales in Northeast - and elsewhere on qualified basis.

Name john C. Callerin for

Date November 2, 1979



Organization Foster Wheeler Energy Corp.

Address

110 South Orange Avenue

Livingston, New Jersey

07039

Personnel

Phone

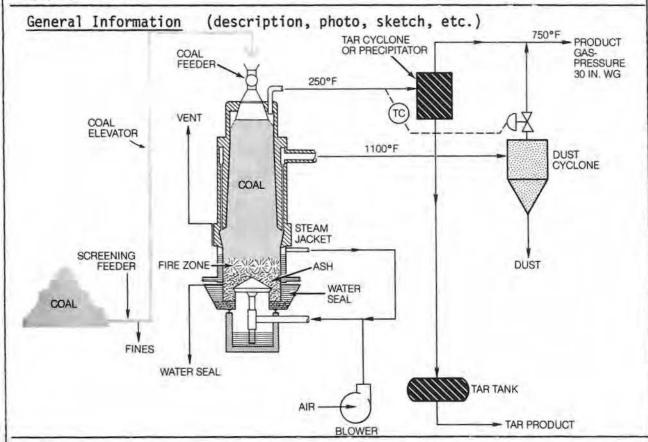
Roger J. Broeker

201-533-2667

Type of Gasifier (up/down draft, size, fuel, application, etc.)

updraft

Status (research, pilot scale, commercial, etc.)
Gasifier is commercial on coal. Have bench scale gasifier and 2-ft diameter test gasifier available for test work on wood.



Plans for Future

Name R. J. Broeker

Date

1/12/79



Organization

Address

Georgia Institute of Technology Personnel Experiment Station Room 1512-A C&S Building 33 N Avenue - Atlanta, Ga. 30332 Phone

Jerry L. Birchfield

(404) 894-3448

Tomas F. McGowan

Type of Gasifier

(up/down draft, size, fuel, application, etc.)

Up draft, 1/2 million Btu/hr, textile drying

Status (research, pilot scale, commercial, etc.)

Research, under design and construction

General Information (description, photo, sketch, etc.)

Up draft gasifier operating under forced draft. Product gas will be burned in a closecoupled arrangement. Hot combusted gases will be mixed with air for textile drying and curing tests.

Plans for Future

Experiments with pellets, dry and wet chip wood fuels.

Name Thomas F. McGowan

Date

2-22-79



Organization

Address

Halcyon Associates, Inc.

Maple Street, East Andover, N.H. 03231

Personnel

Phone

William G. Finnie, President

(603) - 735 - 5356

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Up draft - 6 MMBTUH through 50 MMBTUH - Green or dry wood waste or biomass fuel - For direct heating, boiler firing & direct power generation.

<u>Status</u> (research, pilot scale, commercial, etc.) Commercial - 4 units sold, others being negotiated.

General Information (description, photo, sketch, etc.)

The Halcyon Gasifier produces cool clean gas using green or dry hogged size fuel or biomass. Calorific value is around 150 BTU per cubic foot. When burned, particulates are less than .02 pounds per million BTU with low Nox, well within E.P.A. requirements, without any cleaning of flue gases.

The gasifier operates below ash fusion temperatures and the grates are automatically self-cleaning. Ash removal is automatic.

Series of controls on the gasifier allows for automatic operation

with little supervision.

A burner of up to 100 MMBTUH capacity, which can be adapted to fit most existing oil or natural gas fired boilers, can be supplied. The burner is capable of firing oil and/or natural gas as well as producer gas.

Output of the gasifier and burner(s) is controlled by regulating the gas flow actuated by boiler steam pressure or dryer/furnace temperature. Full modulation and flame failure safety features to meet insurance company requirements are included.

On power generation or direct drives, the gas is further cleaned to remove sub-micron size particles, and directly fuels internal combustion or compression ignition engines. This further cleaning may be used also when gas is burned where extremely low particulates are required.

Maintenance and power requirements are low.

Plans for Future

To engineer, manufacture, and apply units for commercial and industrial requirements.

Name William G. Finnie Date January 18, 1979

Organization IMBERT AIR GASIFIER Address Steinweg Nr. 11, 5760 Arnsberg 2, Germany

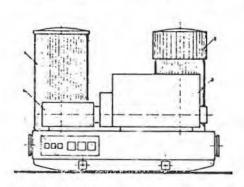
Personnel Walter Zerbin

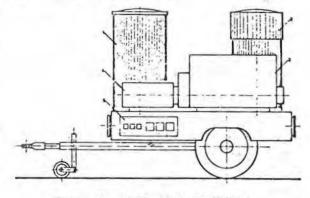
Phone (0 19 31) 35 49 Telex 84 222 ins d

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Downdraft air gasifier for diesel power generation

Status (research, pilot scale, commercial, etc.) 500,000 built and used over last 40 years

General Information (description, photo, sketch, etc.)
10 to 10,000 km gasifier power plants. complete.





Power plant TSG 10 to 60 KVA

000 000

Power plant FSG 10 to 60 KVA 1. 6

1. Gas producer
2. Gas-Cooling and cleaning plant
3. Motor
4. Elektric-Generator
5. Switch-Gear
6. Zyklon
7. Dost container
8. Chassis
9. Feeding installation
10. Fuel

Name (TBR)

Date 3/27/79

Power plant SSG 50 to 200 KVA



Organization

Address ONE OLD COUNTRY ROAD

CARLE PLACE, N.Y. 11514

INDUSTRIAL DEVELOPMENT AND PROCUREMENT INC.

AND PROCUREMENT INC.

Personnel Representing: Moteurs Duvant Phone

one 516-248-0880

Jules A. LUSSIER, Vice-President

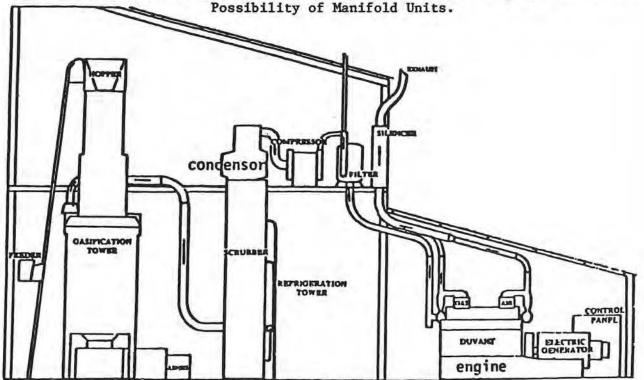
Type of Gasifier (up/down draft, size, fuel, application, etc.)

Down draft - 1 to 8 million BTU per unit. Fuel: Wood waste, chips, bark, corn cobs, rice husks, cotton gin residues, coffee shells, coconut shells and husks, sun flower seed residues, paper mill sludge, other miscellaneous organic waste.

<u>Status</u> (research, pilot scale, commercial, etc.) Commercial Several Duvant Dual Fuel Engine systems have been delivered and installed in Europe, Africa, South Pacific, Asia, Central America.

General Information (description, photo, sketch, etc.)

Complete energy systems consisting of a low BTU gas production unit, a filtering and cooling unit and a dual fuel engine - generator set. Range 100 to 750 KW.



Plans for Future

Promote and develop sales in North America.

Name Philippe Santini

Date March 27, 1979



Organization

Address

1135 Queens Avenue

Lamb-Cargate Industries Ltd.

Phone

NewWestminster, B.C.

Personnel

604/521-8821

F.H. Lamb, President

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Up-Draft, 4 x 10⁶ B.T.U./hour, clean hog fuel

Status (research, pilot scale, commercial, etc.)

Pilot Scale

General Information (description, photo, sketch, etc.)

Semi-fluid bed reactor, complete with fuel metering and continuous ash discharge. Fuel metering adjacent to the grate.

Equipped with gas cleaning station consisting of:

- a) cyclone
- b) wet centrifugal scrubber
- c) gas dryers.

Hudson Bay, Saskatchewan, installation includes gas engine generation.

Plans for Future

Package generation unit for small isolated communities, dry kilns, dryers, etc.

Name F.H. Lamb

Date

1979 February 21



<u>Organization</u>	Address 1135 Queens Avenue
Lamb-Cargate Industries Ltd.	New Westminster, B.C.
Personnel Personnel	Phone
F.H. Lamb, President	604/521-8821
Type of Gasifier (up/down draft, Up-draft, 25 x 10 ⁶ Net BTU,	
Status (research, pilot scale, co	
General Information (description,	, photo, sketch, etc.)
is fed in up through the bott chamber gasifies the green ho in the second chamber with a There are two 25 x 10 BTU/ho One in British Columbia direct	og fuel and the gases are burned
Plans for Future Going up to	150 x 10 ⁶ BTU/hour and firing lime



Organization

Address

Morbark Industries, Inc.

P.O. Box 1000, Winn, MI. 48896

Personnel

Phone

Ivor Bateman

517-866-2381

Type of Gasifier (up/down draft, size, fuel, application, etc.)

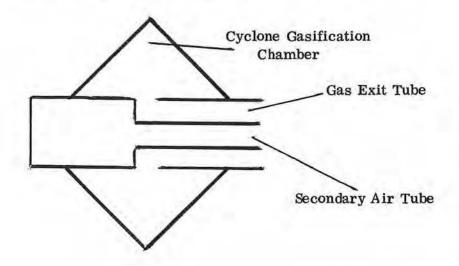
25 Million BTU/HR Cyclone Suspension gasifier, sawdust up to 25% moisture - 1/4' wood chips.

Status (research, pilot scale, commercial etc.)

Commercial Model Under Test

General Information (description, photo, sketch, etc.)

The gasifier produces low BTU gas at below ash fusion temperatures. It is ideally suited for direct coupling to a boiler, drier or any application where heat is required and also as a retro fit for gas or oil burners. Ash removal is continuous and automatic. Particulate emmision is in the order of 500 parts per million. Gasification is achieved with a partial burning process primary air required for gasification is 11/4 pounds air per pound fuel.

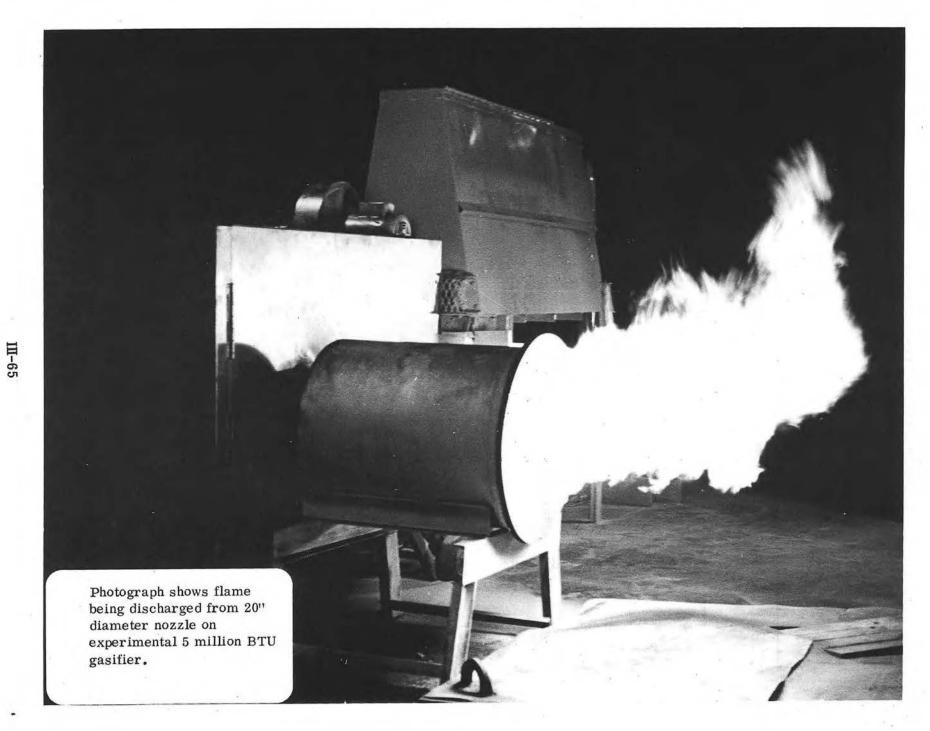


Plans for Future

To engineer and apply units for commercial and industrial requirements

Name Ivor Bateman

Date Nov. 5, 1979





Organization

Address

PIONEER HI-BRED INTERNATIONAL, INC. 5700 MERLE HAY ROAD, JOHNSTON, IA. 50131

Personnel .

Phone

Walter Stohlgren

1-515-245-3721

(up/down draft, size, fuel, application, etc.) Type of Gasifier

Down Draft 9×10^6 Btu/Hr. Corn Cobs. Seed Dryer.

(research, pilot scale, commercial, etc.) Status

Research, Commercial

General Information (description,

Testing close coupled burner.

Looks good for eliminating the tar problem.



Plans for Future

Redesign grate to eliminate the ash caking problem.

Date

February 6, 1979



Organization

Address

570 St. John's Blvd.,

Pulp and Paper Research Institute

Pointe Claire, Quebec, Canada H9R 3J9

of Canada Personnel

Phone

(514) 697-4110

S. Prahacs and M.K. Azarniouch

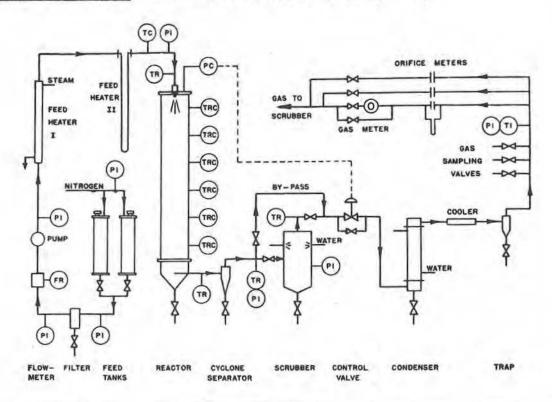
Type of Gasifier (up/down draft, size, fuel, application, etc.)

Down draft reactor, 316 SS, 12 in. diameter, 15 ft. high, suitable for spent pulping liquors and lignocellulosic material, pressure - 45 psig/atmospheric, temperature - 1450°F/1650°F.

Status (research, pilot scale, commercial, etc.)

Pilot scale (presently not operated).

General Information (description, photo, sketch, etc.)



Plans for Future

To carry out gasification tests on lignocellulosic material.

Name S. Prahacs

Date January 15, 1979



Organization

Address Agricultural Engineering Department

Purdue University

W. Lafayette, IN 47907 Phone

Personnel

Robert M. Peart, Michael Ladisch

(317) 749-2971

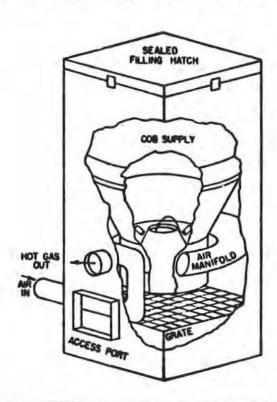
Type of Gasifier (up/down draft, size, fuel, application, etc.)

Downdraft, corn cobs, for direct firing of corn dryer.

(research, pilot scale, commercial, etc.) Status

Research, crude operational model only

General Information (description, photo, sketch, etc.)



This batch unit holds about 300 pounds of cobs, is about 8 feet tall, 31.5 inches square, mild steel except for stainless steel support cone. Air flow 25 scfm, heat output estimated approximately 250,000 Btu/hr (50 pounds of cobs/hr). We have gasified cobs of from 15-25% moisture, wet basis.

Plans for Future

Build continuous flow unit for more accurate measurement of input/output.

Test turn-down ratios, cob moisture, air flow, insulation.

Build bench test unit for more accurate tests on composition as affected by operating variables.

Name Robert M. Peart

January 16, 1979 Date



Organization

Address

Saskatchewan Power Corporation

2025 Victoria Avenue, Regina, Sask.

Personnel

Phone

S4P 0S1

G.A. Weisgerber

(306) 525-7611

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Updraft unit for converting wood waste to gas and to electricity via 150 kW diesel generator set.

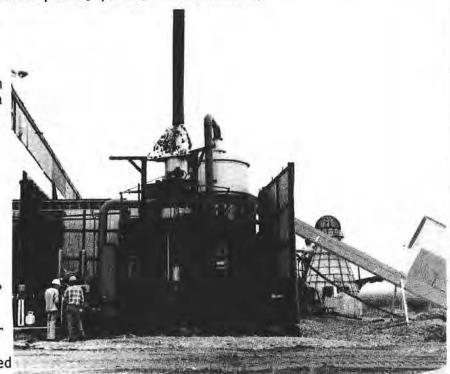
Status (research, pilot scale, commercial etc.)

The 1.2 MW unit has been operated with various wood feeds. An industrial burner and diesel generator set have been successfully run.

General Information (description, photo, sketch, etc.)

The wood gasification plant, located at the Saskatchewan Forest Products Corporation's plywood plant in Hudson Bay, Saskatchewan, is a joint venture of the Saskatchewan Power Corporation, Saskatchewan Forest Products Corporation, and the Federal Government of Canada.

The objectives of the current project are:
i) to investigate the feasibility, economics, environmental acceptability and practicability of power generation via wood gasification in isolated northern communities,



ii) to process wood waste from forest product industries to produce fuel gas, and iii) to develop a Canadian technology.

Plans for Future

Immediate plans are to operate on a continuous basis for an extended period to demonstrate commerciability.

Name & A Weingerten

Date

1979 December 10



Organization

Address

Dept. of Chemical Engineering

Texas Tech University

Lubbock, TX 79409

Personnel

Phone

Harry W. Parker

(806) 742-3553

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Prototype is up-draft batch, but subject to change. Objective is to utilize gin trash for fueling internal combustion engines on irrigation wells.

(research, pilot scale, commercial, etc.) Status

pilot scale

General Information (description, photo, sketch, etc.)

The present gasifier is a simple up-draft batch gasifier 20 inches in diameter. This gasifier will have to have significant modifications to succeed in gasifying gin trash for operation of irrigation wells. Another type of gasifier may be selected.

Plans for Future

Determine feasibility of gasifying un-cubed gin trash for powering irrigation wells. If it is feasible a cost estimate will be made.

Name Harry W. Parker

Date

January 15, 1979



Organization

Address

University of California at Davis

University of California

Department of Agricultural Engineering

Davis, CA 95616

Personnel

Phone

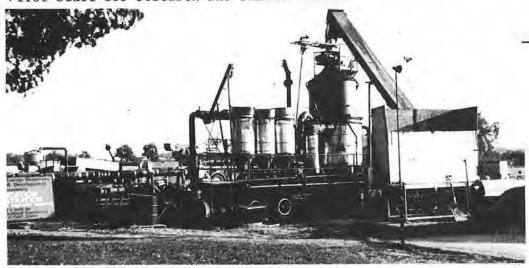
John R. Goss, Professor

(916) 752-1421/0102

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Downdraft, 4-foot firebox, 54 ft³ fuel capacity including active firebox volume 500 to 1100 lb/hr of hogged kiln dried lumber waste and other agricultural and forest residue.

Status (research, pilot scale, commercial, etc.)
Pilot scale for research and demonstration.



Pilot plant gas producer mounted on semi-trailer for transport to various test locations. Removal of upper cylinder and fuel feed assembly to meet 13 ft 6 inch transport height. Operation is monitored and fuel feed and ash removal automatically controlled from control and instrument panel mounted in cabin at front of trailer. Firebox volume - 38 ft³. Ash grate basket - 143/ft³. Ash pit - 69 ft³. Gas producer weighs 3.9 tons. Firebox and lower outer cylinder constructed from A515 steel flat stock. Lower cylinder insulated with 2" thick J-M Thermo 12. Normal output 4 to 6 million Btu/hr on dry wood chips. Maximum output about 8 million Btu/hr (NTP) of combustible gases. To left of gas producer are the hot gas cyclone and three hot gas fiberglass bag filters. Combustion air blower and gasoline engine drive on ground at rear of trailer.

Plans for Future

Property of California Energy Commission awaiting further program development. Inquire Commission at 1111 Howe Avenue, Sacramento, CA 95825. (916) 920-6033.

Mama	T-1 D C	D -1	T 1070
Name	John R. Goss	Date	January, 1979



Organization

University of California at Davis Department of Agricultural Engineering Personnel |

Address University of California Davis, CA 95616

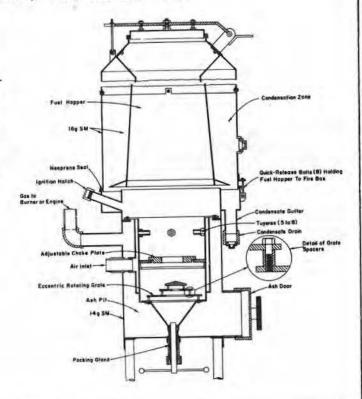
Phone

Type of Gasifier (up/down draft, size, fuel, application, etc.) Downdraft, 12-inch firebox, 1.8 ft3 fuel capacity, 30 to 80 pounds/hour fuel rate with agricultural and forest residues.

(research, pilot scale, commercial, etc.) Status Laboratory scale gas producer to investigate gasification characteristics of fuels and test variations in design parameters.

General Information (description, photo, sketch, etc.)

The gas producer fuel is batch fed by opening the gasketed cover at Fuel cylinders with difthe top. ferent configurations can be inserted for particular physical characteristics of fuel. A fuel column 32 inches high is accommodated above the firebox. Tuyere nozzle sizes and lengths and elevation of choke plate and choke diameter can all be changed. Ash grates of various configurations can be interchanged with the one shown. Hand turning of the grate has been replaced with a small fractional horsepower motor, gear reducing box and roller chain drive.



Plans for Future

Continue investigating gasification characteristics of agricultural and forest residues and low-Btu gas utilization before and after solid particulate filtration and then after cooling and condensing.

Name	John 1	R.	Goss	Date	January,	1979



Organization

Address

University of Missouri-Rolla

GROW Project: University of Mo. Rolla

207 Harris Hall

Personnel

Phone

Rolla, Mo. 65401

Y. Omurtag, Project Manager

SITE:

Office: 314-341-4560 314 341-4857

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Fluid bed using sand and air as fluidizing medium, 40 in ID x 14ft.

20001b/hr sawdust feed.

(research, pilot scale, commercial etc.) Status

Phase I: Low BTu gas pilot plant operation, data almost complete, Medium energy and other research is being planned.

General Information (description, photo, sketch, etc.)

The overall objective of the GROW program is to conduct a research and development program which will lead to the early commercialization of wood gasification technology to process wood residues typical of those found in the Missouri Ozark regions. Optimum commercialization parameters for low and medium BTU gas production as a substitute for natural gas will also be determined. The facility can be used in conducting research or providing training in the areas of fluidized bed reactor operations, feed stack handling, and marketing of various products resulting from operating such systems. First and foremost, however, it will allow for the determination of optimum design for energy conversion systems which use wood and other bio-energy sources. The equipment is suitable for gasification research of all types of biomass including, but not restricted to, wood chips, sawdust, animal manure, or corn cobs and other agricultural by-products. The project is expected to take from 18 months to two years after the start of testing and could prove to be invaluable in providing information about such energy conversion and its possible contribution to society.

The GROW project has the largest capacity reactor involved in the Bio-mass Thermochemical Conversion Program. As such, the GROW project has the potential to become the showcase project for the entire Thermochemical Program.

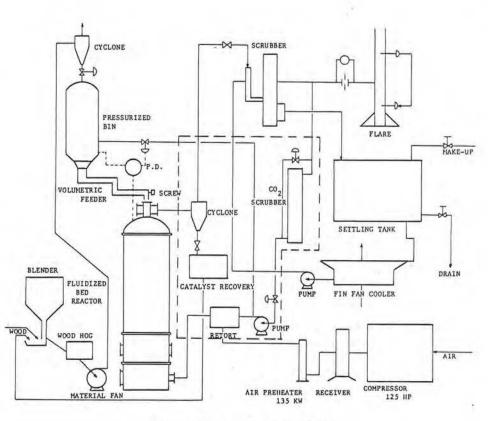
See Attached Experimental Facility Flow Diagram:

Plans for Future

Phase II: Medium Btu Gas with re-cycle to be completed by August, 1980.

Name





UMR-COORS EXPERIMENTAL FACILITY FLOW DIAGRAM



types of gasifiers

Name Peter H. Bauer

BIOMASS AIR GASIFIER DIRECTORY

Organization Address The Vermont Wood Energy Corporation P.O. Box 280 Stowe, VT 05672 Phone Personne1 802-253-7220 J. Phillip Rich, President Cadwallader E. Brooks, Treasurer Peter H. Bauer, Project Engineer Type of Gasifier (up/down draft, size, fuel, application, etc.) Close-coupled, down draft, semi-automatic (wood chips or pellets, manually loaded), thermostatic on/off operation, roughly 80,000 BTU/hr. output (research, pilot scale, commercial, etc.) Status One semi-automatic test model under development, about 2/3 of the way to successful operation. (description, photo, sketch, etc.) General Information The gasifier is intended for use with a home-size furnace, to convert a used or new furnace from oil flame to wood gas flame, or possibly as an adjunct installation with oil burner gun still in place. The gasifier, about the size of a small suitcase, is surrounded by an insulating enclosure and has a chip hopper above it. Combustible gases are led through about 3 feet of pipe to the combustion chamber of a former oil burning furnace. The gasifier has been operating successfully using forced draft, and an induced draft system is under development. When the thermostat signals for heat, the electrical/electronic control system begins a timed sequence of events, operating an electric fuel igniter, and then blowers, solenoid operated valves, tickler shaft motor, low fuel level detector motor, and the gas igniter electrodes. The controls shut off and turn on the system when signalled by the thermostat. Safe shutdown occurs upon electric supply failure or in case of various system failures or low fuel level. Plans for Future Completion of development of semi-automatic test model... Development of automatic test model by replacing chip hopper with a surge

Date January 12, 1979

bin, and adding a conveyor and storage bin for the fuel... Testing, prototype installations, modifications, marketing, production, and sales of one or both



BIOMASS 02 GASIFICATION DIRECTORY

Organization Address

Battelle-Northwest P.O. Box 999, Richland, WA 99352

 Personnel
 Phone

 L.K. Mudge
 946-2268

 P.C. Walkup
 946-2432

 D.G. Ham
 946-2083

D.G. Ham 946-2083

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Updraft. Diameter: 3 ft; working bed height 10 ft. Solids processed: wood municiple wastes, industrial wastes, coal, charcoal, coke.

Status (research, pilot scale, commercial, etc.)

Operational at pilot scale.

General Information (description, photo, sketch, etc.)

The gasifier is refractory lined. Solid feed is introduced at the top of the reactor through a lock hopper. A drag chain conveyor feeds the lock hopper arrangement. Steam and air, or oxygen, is introduced into the bottom of the reactor through a stationary grate. Continuous solids discharge is not provided with this gasifier. Ash is removed from the gasifier bottom after accumulation of an ash layer of about 3 ft. in depth.

Plans for Future

Continue operation of the gasifier to characterize gasification characteristics of different combustible solids.

Name D. G. Ham

Date 3/5/79



BIOMASS Og GASIFICATION DIRECTORY

Organization	Address
Energy Systems Group Rockwell Molten Salt	8900 De Soto Avenue
Personnel	Canoga Park, California 91304 Phone
C. Trilling, D. McKenzie	C. R. Faulders, Marketing Rep.
S. Yosim, J. Ashworth	(213) 341-1000, Extension 2045
Type of Gasifier (up/down draft, Molten salt gasifier, currently b operated air-blown or oxygen-blow	size, fuel, application, etc.) being applied to coal gasification; can be vn. The salt used is sodium carbonate.
other carbonaceous fuels. Proces	mmercial, etc.) is used to gasify ~500 lb/hr of coal or ss Development Unit (PDU) for coal in operation under contract to DOE.
General Information (description,	
lined with monofrax brick. T a few atmospheres pressure, a preparation and feed of both	3 ft ID, 4 ft OD, stainless steel vessel This unit can be operated air-blown, up to and includes facilities for continuous fuel fuel and carbonate. The melt can be sh an overflow nozzle, but there is no melt
including coal and carbonate	ation PDU is a completely integrated system feed, coal gasifier, melt overflow and ar removal, and regeneration of sodium bed in the attached paper.
Plans for Future The PDU will be operated on the c Follow-on effort to include oxyge	current contract the remainder of this year en gasification is expected.
Name - Collandor	Date
C. R. Faulders	March 6, 1979

March 6, 1979



Organization Angelo Industries

Address PD Box 212,

A & P Coop Co.

Jonesboro, Ark, 72401

Personnel

Phone

501 935 1234

J. F. Angelo Jr.

932 7733

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Rotary Pyrolyser for wet and dry biomass; produces char and process heat

Status (research, pilot scale, commercial, etc.)
Process operated since 1971 for commercial charcoal production, 40 tons/day.
Joint project with U. of Arkansas to increase energy yields and determine energy balance (see U. of Arkansas).

General Information (description, photo, sketch, etc.)



Plans for Future

Name (TBR)

Date 3/24/79

LA IN. TUBE BUNDLE FOR SAMPLING AND TEMPERATURE PROBES

PYROLYSIS SYSTEMS DIRECTORY

Organization

Address

Battelle-Northwest

P.O. Box 999, Richland, WA 99352

Personnel L.K. Mudge Phone 946-2268

P.C. Walkup D.H. Mitchell

R.J. Robertus Type of Gasifier

(up/down draft, size, fuel, application, etc.)

Diameter: 11 in; working bed height 4.5 ft. Agitated Fluid bed.

Wood chips are processed in this gasifier.

Status (research, pilot scale, commercial, etc.)

Operational as a process development unit.

General Information (description, photo, sketch, etc

The gasifier is refractory lined and is equipped with a mechanical agitator. The wood chips are fluidized in the reaction zone. The agitator is provided to "stir" catalysts used in the production of methane, ammonia synthesis gas, hydrocarbon synthesis gas, hydrogen, or carbon monoxide. Wood feed is introduced into the bottom of the reaction zone with an auger. A schematic of the reactor is shown in Figure 1.

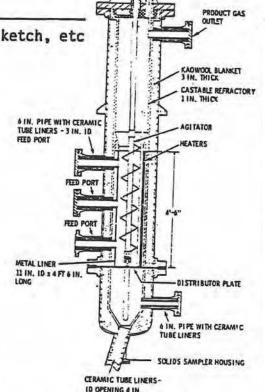


Figure 1. Biomass Gasification Reactor

Plans for Future

Unit will be used for the development of catalyzed biomass gasification processes.

Name

L.K. Mudge

Date

5 March 1979



Organization

Address 139 A. Old Oxford Valley Road

Langhorne, PA 19047

Enerco Incorporated

Personnel

Phone

215/493-6565

Miles J. Thomson Eugene W. White

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Continuous, portable, cross-current pyrolytic converter for converting biomass into charcoal, pyrolysis oil, and medium BTU gas.

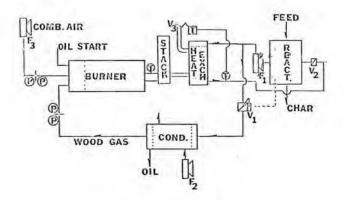
Status

(research, pilot scale, commercial etc.)

Commercial

General Information (description, photo, sketch, etc.)

The unit is unique in its means of recirculating hot gases to accomplish pyrolysis without using air or oxygen in the reactor. A general description is available from a paper given as part of a symposium on Thermal Conversion of Solid Waste and Biomass, American Chemical Society Annual Meeting September 9-14, 1979, Washington, D.C.



Schematic Diagram of Enerco Pyrolysis Unit

Plans for Future

Complete the demonstration of our commercial unit with the T.V.A. at Maryville College and install up to 45 commercial sites with the assistance of U.S.D.A. guaranteed loans.

Name Mily J. Thomas

Date November 5, 1979



Organization

Address 185 Alewife Brook Parkway

Cambridge, MA 02138

Energy Resources Company, Inc.

Personnel

Phone

(617) 661-3111

Dr. Herb Kosstrin - Manager of Research & Engineering

Daniel R. Traxler - Marketing Manager

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Fluidized Bed Gasification utilizing a wide variety of agricultural, forest products, industrial and municipal wastes.

Status (research, pilot scale, commercial, etc.) Pilot scale fluidized bed reactor in operation with 18 feedstocks utilized since 1976 (20" I.D. reactor, 16 MM Btu/hr). Second generation plant (20 MM Btu/hr) under construction and due for operation in second quarter of 1979.

General Information (description, photo, sketch, etc.)

In June of 1978 Energy Resources received a contract to design, build and operate a trailer mounted, transportable, fluidized bed gasification plant. The plant can convert agricultural wastes and forest residue into storable and transportable fuel products, pyrolytic oil and char. This competitive procurement was awarded jointly by EPA (Cincinatti) and the State of California's Solid Waste Management Board and Energy Commission. The plant is nominally rated at 90 tons per day of dry waste. The plant is scheduled for operation the third quarter of 1979 in California.

Commercial product offerings include Fluidized Bed Combustion Steam Boilers up to 100,000 pounds per hour and Fluidized Bed Gasification Systems. The FBG Systems are capable of handling a wide range of feedstocks including agricultural, wood, industry and municipal wastes with up to 60% moisture content. Modular, skid mounted systems are available in 50 and 100 MM Btu/hr output sizes. Custom applications are up to 250 MM Btu/hr. Complete materials handling equipment is available in addition to emission control equipment to meet all federal and state regulations.

<u>Plans for Future</u>: Further commercialization of Fluid Bed Gasification Systems to industries having a combustible waste product and an internal energy demand requiring oil and gas. In addition, various types of industrial and agricultural wastes are continually being tested and evaluated to become an economical feedstock for a Fluid Bed Gasification System.

Name Daniel R. Traxler

Date March 2, 1979



Organization

Address

Garrett Energy Research & Engineering, 911 Bryant Pl., Ojai, Ca.

Personnel

Phone

Donald E. Garrett, President 805-646 Ritchie D. Mikesell, Project Mgr. Dinh Co. Hoang, Pilot Plant Supervisor 805-646-0159

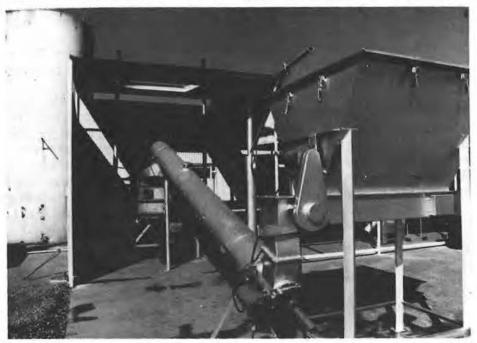
Type of Gasifier (up/down draft, size, fuel, application, etc.) Multiple hearth. This not an air gasifier, as all heating is indirect. Agricultural wastes are processed to produce a medium - BTU gas.

(research, pilot scale, commercial, etc.) Status

Pilot scale. Shake-down stage.

General Information (description, photo, sketch, etc.)

Predrying, direct contact drying, pyralysis, combustion, and water gas reaction are done sequentially in this device.



Plans for Future

Name Ritchie D. Mikesell

Date 2/27/79



Organization

Address

Prime Contractor - Gilbert Associates, Inc.

P.O. Box 1498

Major Subcontractors

Phone

Reading, PA 19603

West Virginia University and Environmental Energy Engineering, Inc.

(215) 775-2600

Type of Gasifier (up/down draft, size, fuel, application, etc.)

A two foot ID fluid bed gasifier operated with biomass and solid waste for research and development application.

Status (research, pilot scale, commercial, etc.)

Process development unit (PDU)

General Information (description, photo, sketch, etc.)

The 2'-0" ID fluidized bed gasifier can be operated with a biomass feed rate of up to 2 TPD biomass or solid waste. The hot gases leaving the top of the gasifier pass through a cyclone to remove particulates to a splitter where the stream is split into a product stream and a recycle stream. The gasifier can be modified so that it can operate as packed bed, entrained bed or freefall bed. The hot product gas is scrubbed and is analyzed for the gas composition.

Plans for Future

Tests will be performed using 4 to 5 biomass feedstocks in combustion, pyrolysis and gasification modes of operation.

Name

James T. Stewart

February 26, 1979 Date

Manager, Fuels Conversion Energy Research Division



Organization

Princeton University

Personnel

M. J. Antal F. E. Rogers W. E. Edwards Address

D-215 Engineering Quadrangle Princeton, New Jersey 08544

Phone

(609) 452-5136

Type of Gasifier (up/down draft, size, fuel, application, etc.)

batch, electrically heated, zoned, tubular plug flow reactor

<u>Status</u> (research, pilot scale, commercial, etc.)

research, bench scale system

General Information (description, photo, sketch, etc.)

The one inch diameter, tubular quartz reactor has 3 zones of uniform temperature and is operated in a batch mode using 0.25 g samples of selected biomass material. It was designed to provide kinetic data on the gas phase reactions of pyrolytic volatile matter in steam. Rates of production as a function of temperature for CO_2 , CO, H_2 , CH_4 , C_2H_4 , C_2H_6 , and C_3H_6 have been measured for cellulose and a selected wood species.

Plans for Future

Research on the effects of pressure on gasification rates and products. Research on the use of very high heating rates for biomass gasification.

Name Michael J. Antal, Jr.

Date March 7, 1979



Organization

Tennessee Valley Authority

Personnel

E. Lawrence Klein

Address

Division of Land and Forest Resources Forestry Bldg., Norris, Tennessee 37828

(615) 494-9800

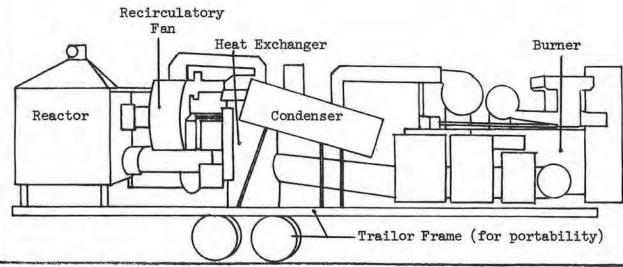
Type of Gasifier A continuous, portable, recirculating, pyrolysis unit capable of producing 1 ton of charcoal, 90 gallons of char oil and 8 million Btu's of medium Btu gas per hour from 3 tons of wood, designed to produce a fuel from wood to fire a natural gas/oil boiler.

Status

The unit is currently in the research/testing stage.

General Information

TVA purchased this unit from ENERCO, Inc., of Langhorne, Pennsylvania, original designer and manufacturer.



Plans for Future After extensive testing and any necessary modifications have been made, this unit will be taken to Maryville College to fuel the boiler.



Organization

Address

Texas Tech University

Lubbock, Texas 79409

Department of Chemical Engineering Personnel

Phone

Steven R. Beck

Uzi Mann

(806) 742-3553

Type of Gasifier (up/down draft, size, fuel, application, etc.)

Fluidized Bed, 50 1b/hr, any biomass for conversion to medium-GTU gas

Status (research, pilot scale, commercial, etc.)

Pilot scale testing has been in progress for 2 years.

General Information (description, photo, sketch, etc.)

A counter current pyrolysis reactor for cattle wastes has been invented which allows volatile organic compounds to escape from the heating zone very rapidly. This results in a different product mix than has been observed in other pyrolysis research, containing unusually high concentrations of ethylene. Fuel values of gases plus the sparing of petroleum needs by ethylene, if economically feasible, would supplement petroleum supplies. The work includes studies in an existing 1/2 ton/day test reactor to determine the influence of temperature, residence time, pressure, and feedstock materials on the yield and quality of the products of reaction. The scope of work includes economic assessments of the process, utilizing animal manures and other biomass materials as feedstocks. Studies include the effects of reactor geometry and solid/gas contact in cold models. Relationships for the design of a staged reactor will be developed. This work may benefit programs on coal hydrogasification and coal gasification.

Plans for Future

Evaluate other feedstocks. Develop kinetic model of reactor.

Name Steven R. Bock Date 1/5/19



1 Ton/Day Rotary Kil	down draft, size, fuel, application, etc.) n Pyrolysis Unit ot scale, commercial, etc.)
	ot scale, commercial, etc.)
mesearch being conde	acted on wood pyrolysis
1) Evaluation of com 2) Construction and (1 ton/day) to de	Mercial (A & P Coop) rotary kiln (Hicks) operation of pilot scale rotary kiln etermine scale factors (Turpin) asic studies and service to above (Mccalum) DE



BIOMASS HYDROGASIFICATION DIRECTORY

Organization

Battelle

Address 505 King Avenue

Columbus Laboratories

Columbus, OH 43201

Personnel H. F. Feldmann

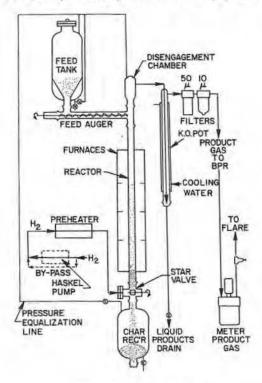
Phone (614) 424-4732

Type of Gasifier (up/down draft, size, fuel, application, etc.) 3-in. I.D. externally heated rated at 2000 F at 1000 psig with provision for continuous operation as fluid bed, free fall or moving bed. Can be fed H2, syngas, or steam to simulate various gasification atmospheres.

(research, pilot scale, commercial, etc.) Status

Research reactor

General Information (description, photo, sketch, etc.)



PRESSURIZED CONTINUOUS GASIFICATION SYSTEM

Plans for Future

Coal and biomass gasification

Name Henry Feldman Date February 22, 1979



SMW OXYGEN GASIFICATION DIRECTORY

Organization

Union Carbide Corporation

Linde Division

Personnel

G. F. Hagenbach

Product Manager - Purox

Address

Post Office Box 44

Tonawanda, New York 14150

Phone

716/877-1600

Type of Gasifier (up/down draft, size, fuel, application, etc.)
Oxygen-blown slagging pyrolysis in a moving-burden shaft furnace

Status (research, pilot scale, commercial, etc.)

Commercial (for municipal solid waste)

General Information (description, photo, sketch, etc.)

Materials are fed near the top of the furnace and descend as a moving burden, in countercurrent contact with generated gases, through subsequent drying, pyrolysis and partial oxidation-melting zones. Pyrolysis of organic materials yields reducing gases and char. The char is subsequently burned in the hearth area, where nearly-pure oxygen is introduced. Non-volatile inorganics are slagged within the hearth, and tapped continuously.

Heat recovered from the rising hearth gases drives the endothermic pyrolysis and drying steps. Gas withdrawn from the top of the furnace - consisting primarily of carbon monoxide, hydrogen, carbon dioxide, light hydrocarbons and moisture - is further processed according to its intended use as a fuel or synthesis gas.

Commercial scale experience to date has been limited to processing of municipal solid waste and codisposal of sewage sludge with refuse. Laboratory scale tests have been carried out on additional materials.

Plans for Future

Commercially market Purox Systems for processing municipal wastes. Expand the technology for processing wood wastes and other biomass materials when warranted by market conditions.

Name -

G. F. Hagenbac

Date

March 2, 1979



Chapter 10

Survey of Current Gasification Research

T. B. Reed, D. Jantzen, R. Desrosiers, T. Milne SERI



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CHAPTER 10

SURVEY OF CURRENT GASIFICATION RESEARCH

10.1 INTRODUCTION

The art of gasification is two centuries old, yet research in gasification has hardly begun. This paradoxical situation has arisen from the relative ease with which operating gasifiers can be built and run, so that research may at first appear to be redundant and unnecessary. The argument is fallacious, and both fundamental and process research are needed.

10.1.1 Fundamental Research

The most significant research in biomass gasification was done in Sweden during and after World War II (Generator Gas 1979). A small group at the Swedish Agricultural Machinery Institute has continued this work, but primary emphasis has been on air gasification and minor improvements in small air gasifiers.

Modern techniques of thermogravimetric analysis, calorimetry, and gas analysis make possible a better understanding of the pyrolysis process itself and of post-pyrolysis reactions. Modern understanding of the thermodynamics and kinetics of gasification reactions can enhance the degree of control and the yield of char reactions.

10.1.2 Process Research

Modern methods for achieving high-intensity heating will permit more rapid pyrolysis than could be attained earlier, resulting in very different products. Modern fluidized and suspended bed operation promises to greatly enhance unit yield and to decrease tars and char. Current catalytic techniques can give higher yields of valuable products at lower temperatures, and molten salt approaches can produce specific compounds in high yield.

New materials of insulation and fabrication will permit construction of more reliable gasification units with longer lifetimes. Modern gas separation techniques will make possible more efficient gas separation and reduced emissions. Microprocessors and new methods of measuring temperature and pressure will permit close control of gasification processes for higher efficiency and lower emissions. New methods of oxygen production will permit simple production of medium energy gas for pipeline or synthesis use. New biomass preprocessing technologies, such as densification, will permit gasification of previously unuseable materials. The development of the gas turbine will make possible generation of electric power in small units with high efficiency. New catalytic processes will permit the production of methanol, ammonia, gasoline, methane, glycol, and other chemicals from biomass.

10.2 CURRENT BIOMASS GASIFICATION RESEARCH PROCESSES

The following pages summarize the experimental approach and results for a number of current biomass gasification processes. Representative processes presently in an active research phase were chosen for each of the major types of biomass gasification presented



in the Ch. 9 survey (air gasification, oxygen gasification, etc.). The R&D survey presented in this chapter is not intended to be comprehensive, and the inclusion or exclusion of a process does not reflect the merit of that process in comparison to other processes. Process descriptions, product distributions, and product compositions were obtained from the open literature; references are given for those wishing to study these processes in greater detail.



10.2.1 Air Gasification

GASIFICATION CASE SUMMARY

PROCESS:

Molten Salt Air Gasification (Rockwell International Corp.).

FEEDSTOCK:

Sawdust, rubber, nitropropane, sucrose, coal, X-ray film.

HEAT SOURCE:

Air combustion of portion of feedstock.

GAS/FUEL CONTACT: (Figure 10-1) Feed and makeup Na2CO3 are transported pneumatically by air to molten salt combustion furnace, where the air and feed are injected into the molten salt bath. A portion of the feed is combusted with the transport air. Gas generated in the process leaves through the furnace head for downstream processing.

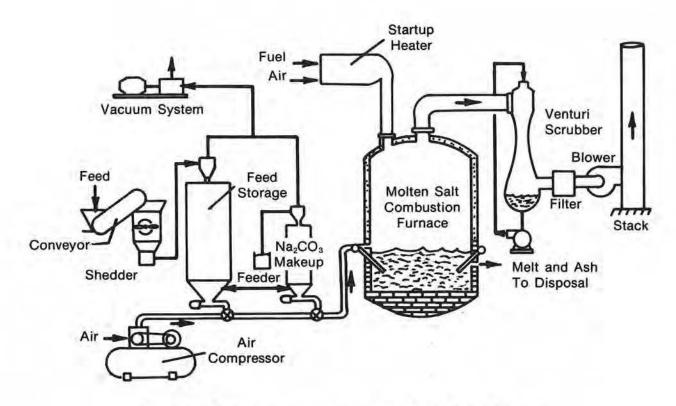


Figure 10-1. Schematic of Molten Salt Pilot Plant, Rockwell International Corporation.

Table 10-1. GASIFICATION OF WASTES, ROCKWELL INTERNATIONAL CORP., MOLTEN SALT PROCESS

Waste		Air feed rate (SCF/min)	Fuel feed rate (lb/h)	Percent theoretical air ^a	Composition of off-gas (vol. %)				Higher heating	
	Temperature °C				CO ₂	со	н ₂	сн4	C ₂	value ^D (Btu/SCF)
Rubber	920	1.63	1.81	33	4.0	18.4	16.0	2.4	1.1	155
Wood	951	1.00	2.08	30	14.5	20.3	21.1	3.0	0.9	181
Nitropropane	1000	2.50	2.58	75	11.0	8.0	9.0	NM^{C}	NM^{C}	55
Film	1015	4.50	5.34	51	16.5	12.0	11.7	2.6	0.2	107
Film	958	2.50	6.58	22	16.0	18.3	14.1	5.2	1.2	179

^aPercentage of air required to oxidize material completely to ${\rm CO_2}$ and ${\rm H_2O}$.

^bCalculated from composition of off-gas.

^cNot measured.



ASH/CHAR:

No char is produced, and the ash is removed with molten salt.

PRODUCTS:

Low-Energy Gas - Compositions of product gases for various

feedstocks and operating conditions are given below:

OPERATING CONDITIONS:

= 920-1015 C Temperature Pressure = atmospheric Salt $= Na_2CO_3$ = 0.5-2.0 fps Air, superficial velocity

Air, required for

= 18-75% complete combustion

SIZE:

= 2 ft I D Length = 10 ftSalt charge = 1 ton

FUNDING, LOCATION, PERSONNEL:

The process was developed by the Atomics International Division, Rockwell International Corporation at Canoga Park, Calif., under an Energy Research and Development Administration (ERDA) contract.

REFERENCE:

Yosim, S. J; Barklay, K. M. 1977. "Production of Low-Btu Gas from Wastes, Using Molten Salts." Ch. 3 in Fuels From Wastes. Anderson, L. L.; Tillman, D. A., eds. New York: Academic Press.

COMMENTS:

The process eliminates char disposal by consuming char in the combustion furnace. This is advantageous in gasifying feedstocks where any char produced would have high ash content with minimal or no market potential. The molten salt is reported to act as a sulfur or chlorine scavenger, which should help to alleviate pollution problems in gasifying a high sulfur feedstock such as coal or municipal solid waste containing high levels of plastics (e.g., PVC).

The gasification process has been shown to be technically feasible, but process economics have not been presented.



PROCESS:

SERI Air Gasification Test Facility.

FEEDSTOCK:

Wood pellets.

HEAT SOURCE:

Partial oxidation.

GAS/FUEL CONTACT: Cocurrent, Countercurrent, and Fluidized bed.

ASH/CHAR:

Dry ash.

PRODUCTS:

Low-energy gas.

OPERATING

CONDITIONS:

Atmospheric pressure.

SIZE:

0.5 MBtu/h

FUNDING, LOCATION,

PERSONNEL:

SERI Task No. 3356.20

1617 Cole Blvd. Golden, Colo. 80401

PERSONNEL:

R. Desrosiers, T. Reed, F. Posey (SERI)

M. Graboski (Colo. School of Mines - Consultant)

COMMENTS:

The product of the gasification reactor studies will be process information for several reactor types, all based on a common set of fuels. The reactor types being considered are updraft and downdraft fixed bed, entrained flow, and fluidized bed reactors. In addition to mass and energy balances, temperature and gas composition profiles will be obtained as well as residence time distribution data. The plan is to design a system with flexible peripheral components to accommodate the entire spectrum of reactor types. The emphasis in this phase of the program is not on optimized reactor design but on precise analytical and kinetic data. Each reactor will be simply constructed to provide the desired gas-solid contacting method, and after preliminary runs to define a set of stable operating conditions, a comprehensive set of physical, chemical, and rate data will be collected. As the data is gathered, reactor models will be continuously tested and updated.



PROCESS:

Texas Tech University - Syngas from Manure (SGFM)

FEEDSTOCK:

Feedlot cattle manure.

HEAT SOURCE:

Partial oxidation of feedstock.

GAS/FUEL CONTACT: Steam and air are fed to the bottom of the fluidized bed through a distribution plate, and the feed manure is fed from the top of the reactor. The reactor is termed a falling bed reactor; there is no circulating refractory material.

ASH/CHAR:

Dry char is removed from the bottom of the reactor and can be used to satisfy heat requirements for the process.

PRODUCTS:

Ammonia syngas to yield about 0.5 kg ammonia per kg of dry, ash-free manure; ethylene with a yield of 21-70 g per kg of dry, ash-free manure.

OPERATING CONDITIONS:

Atmospheric pressure and 600-700 C.

SIZE:

Reactor is 2.5-m long, with a main body 1.5-m long and 15 cm in diameter, and a top section 20 cm in diameter by 60-cm long for separation of the solids and gas. A schematic of the system is shown in Fig. 10-2.

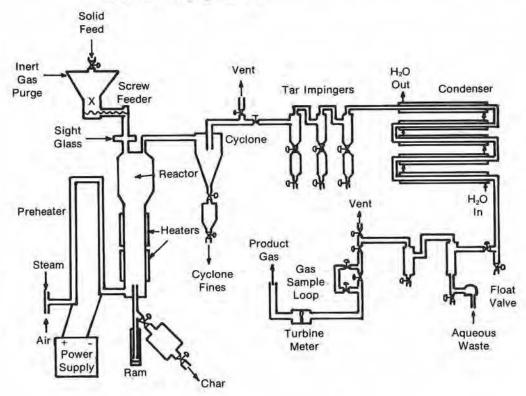


Figure 10-2. SGFM Pilot Plant, Texas Tech University III-101

I.K-73

Table 10-2. SUMMARY OF OPERATING CONDITIONS AND PRODUCT GAS DATA FOR SGFM PROCESS

Operating Conditions		Run Number							
	1	6a	6b	7	8	9	10		
Manure feed rate (kg dry, ash-free/h)	5.22	7.21	16.15	12.97	12.34	12.70	8.26		
Manure feed rate (kg as received/h)	7.76	10.60	23.61	18.95	18.05	18.01	11.75		
Air feed rate (kl/h)	1.149	1.700	1.487	1.904	1.402	4.249	0.76		
Steam feed rate (kg/h)	5.44	4.54	4.54	3.63	3.08	2.72	3.72		
Particle size (in)	>0.95	>0.95	>0.95	>0.95	>0.95	>0.32	>0.32		
Average temperature (°C)	711	695	641	617	629	668	628		
Product gas data ^a									
Total dry gas (1/g dry, ash-free)b	1.19	(0.667)	0.580	0.406	0.455	(0.718)	0.31		
Heat value (HHV) (cal/l)	2855	2918	3790	3380	3523	2624	3345		
Gas composition (vol %)									
H ₂	25.2	22.2	20.0	28.2	17.4	15.1	20.9		
N ₂	14.6	27.8	15.1	23.2	26.7	36.8	24.2		
CH ₄	12.8	7.7	12.6	9.2	14.1	8.9	11.7		
co	11.6	15.3	21.3	16.4	21.2	20.3	22.4		
co_2	30.8	20.7	22.1	15.4	14.1	14.2	14.8		
C_2H_4	4.7	6.4	8.5	4.9	5.8	4.2	5.5		
C ₂ H ₆	0.3	0.5	0.4	2.7	0.7	0.5	0.5		

^aAll data are average values from at least two samples. Individual gas samples were analyzed on the gas chromatograph using at least two injections.

^bValues in parentheses are back-calculated values using a nitrogen balance.



FUNDING, LOCATION, PERSONNEL:

The reactor construction and testing was done by Texas Tech University in Lubbock, Tex., from January 1974 to June 1977 under EPA grant No. S 802934. Additional data to better define heat and mass balances were obtained with support from ERDA contract E29-2-3779. Bechtel National, Inc. developed two conceptual plant designs, to produce ammonia syngas and ammonia syngas plus ethylene, from 1000 dry tons per day of manure, on subcontract from Texas Tech. Phase II of the ERDADOE contract is now in progress, seeking to develop data for partial oxidation and pyrolysis of wood, wood residues, and agricultural residues.

REFERENCES:

- 1. Huffman, W. J. et al. 1978. Conversion of Cattle Feedlot Manure to Ethylene and Ammonia Synthesis Gas. EPA-600/Z-78-026. Feb.
- 2. Hipkin, H. G.; Basuino, D. J. 1978. Syngas From Manure A Conceptual Plant Design. Prepared for Texas Tech University by Bechtel National, Inc.; Final Report; July.
- Huffman, W. J. et al. 1977. "Ammonia Synthesis Gas and Petrochemicals from Cattle Feedlot Manure." Presented at Symposium on Clean Fuels from Biomass. Orlando, FL: Jan. 27.
- 4. Huffman, W. J. et al. 1978. "A Review of Heat/Mass Balances and Product Data for Partial Oxidation of Cattle Feedlot Manure." Presented at AIChE National Meeting. Atlanta, GA; Feb. 26.
- Beck, S. R. 1979. "Application of SGFM Technology to Other Feedstocks." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO; June 1979. Golden, CO: Solar Energy Research Institute; p. 339.

COMMENTS:

The Bechtel study (a conceptual plant design) concluded that the process is not competitive with natural gas re-former plants at the present but will become economical as the price of natural gas increases. The process would be competitive with syngas from coal.

Removal of ethylene is not justified under present economic conditions, but as the cost of syngas decreases, recovery does become economical.

There are a number of changes in design which can reduce the cost substantially.



10.2.2 Oxygen Gasification

GASIFICATION CASE SUMMARY

PROCESS:

Battelle - Pacific Northwest Laboratory

Gasification of Biomass in the Presence of Catalyst

(lab-scale and pilot demonstration unit).

FEEDSTOCK:

Wood, bark.

HEAT SOURCE:

Electric radiation heaters, hot feed gas.

GAS/FUEL CONTACT: Lab-scale:

Lab-scale: Steam and feed cocurrent flow through reactor,

pilot demonstration unit-stirred fluidized bed.

ASH/CHAR:

Dry ash.

PRODUCTS:

Variable, depending on catalyst and operating conditions. Conditions for optimizing CH₄, H₂, CO, hydrocarbon synthesis gas,

and ammonia synthesis gas will be investigated.

OPERATING CONDITIONS:

Up to 800 C at 1 atm.

SIZE:

Pilot demonstration unit-20 kg/h dry wood.

FUNDING, LOCATION, PERSONNEL:

Pacific Northwest Laboratory (Richland, Wash.) laboratory studies—L. J. Sealock. Pilot demonstration unit design, procurement, installation—R. J. Robertus. Technical and economic feasibility studies—L. K. Mudge

Funded by DOE, Nov. 1977 to Sept. 1979. Contract EY-76-C-06-1830. Continuing.

REFERENCES

- Sealock, L. J., Jr., et al. 1978. "Catalyzed Gasification of Biomass." Presented at 1st World Conference on Future Sources of Organic Raw Materials. Toronto, Canada; June 16.
- Mudge, L. K. et al. 1979. "Catalytic Gasification of Biomass." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO; June 1979. Golden, CO: Solar Energy Research Institute; p. 351.



COMMENTS:

The work at PNL is aimed at determining the ability of selected catalysts to alter the kinetics of biomass gasification; to produce methane, hydrogen, carbon monoxide, or synthesis gas for generation of ammonia, methanol, or hydrocarbons; and at determining the technical and economic feasibility of catalyzed biomass gasification. The work will culminate with the operation of a pilot demonstration unit to demonstrate the selected reaction systems and an economic analysis of these systems.



PROCESS:

Downdraft Gasifier (Swedish Hessleman Model 50/13 generator) operated with air or oxygen-enriched air by Environmental En-

ergy Engineering.

FEEDSTOCK:

Charcoal, hardwood blocks, pine blocks, wood pellets.

HEAT SOURCE:

Combustion of char and tars.

GAS/FUEL CONTACT:

Air is injected into the middle of the gasifier where combustion occurs. A constriction in this zone results in higher temperatures and greater decomposition of tars. Pyrolysis occurs in the top zone of the gasifier, and chars and pyrolytic tars pass downward through the combustion and reduction zones. Product gases recirculate through the pyrolysis zone, providing heat for pyrolysis, and are removed for use in an industrial burner or internal combustion engine. A schematic of the gasifier is given in Fig. 10-3.

ASH/CHAR:

Ash goes through a grate at the bottom of the gasifier and is collected in an ash pit.

PRODUCTS:

Low-Btu Gas (heating value 110-295 Btu/SCF). The gas composition and heating value are functions of the oxygen concentration of the combustion gas used. Figure 10-4 shows the effect of oxygen concentration upon product gas composition, and Fig. 10-5 shows the effect upon gas heating value.

OPERATING CONDITIONS:

Combustion Zone Temperature = 2000-2300 F Combustion Gas Oxygen = 21-100 vol %

SIZE:

Hessleman Vedgasierk, Type T-500, NR 110964/10 with a throat diameter of 5 in.

FUNDING. LOCATION. PERSONNEL:

The gasifier was operated by personnel of Environmental Energy Engineering, Inc., Morgantown, W. Va., under the supervision of Dr. R. C. Bailie, under a grant from the Solar Energy Research Institute (Contract No. AH-8-1077-1).

REFERENCE:

Environmental Energy Engineering, Inc. 1979. "Hessleman Gas Generator Testing for Solar Energy Research Institute." P. O. No. AH-8-1077-1.

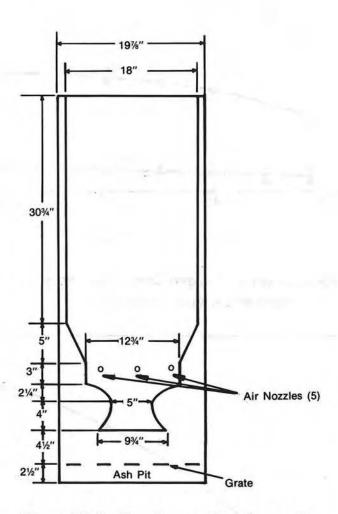


Figure 10-3. Hessleman Gas Generator, Environmental Energy Engineering



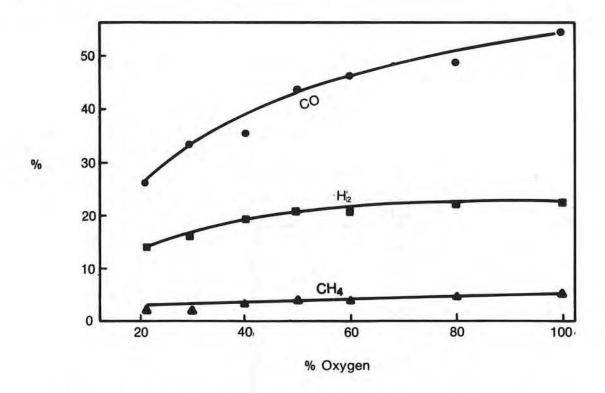


Figure 10-4. Effect of Oxygen Concentration on Gas Composition, Hessleman Gas Generator

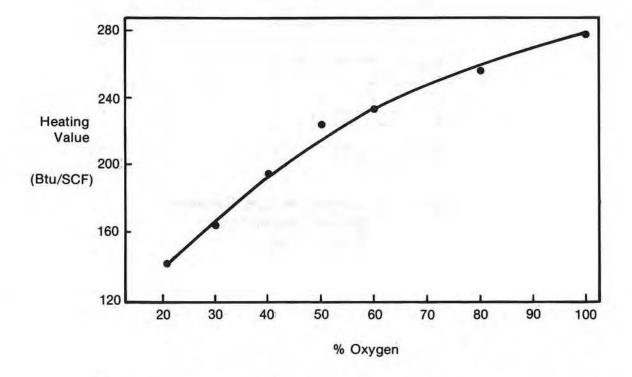


Figure 10-5. Effect of Oxygen Concentration on Gas Heating Value, Hessleman Gas Generator



PROCESS:

SERI Oxygen Biomass gasifier.

FEEDSTOCK:

Initially pellets, other coarse forms in final process.

HEAT SOURCE:

Oxygen (or air) combustion.

GAS/FUEL CONTACT: Downdraft gasifier, 10 atmosphere pressure.

ASH/CHAR:

Dry ash.

PRODUCTS:

Medium Btu, clean syngas (CO, H2) for oxygen operation, low-

Btu gas for air operation.

SIZE:

Prototype, 1-5 MBtu/h (100-500 lb biomass/h)

100-300 ton/day in final process.

FUNDING, LOCATION,

PERSONNEL:

SERI Task no. 3356.20

Solar Energy Research Institute,

1617 Cole Blvd. Golden, CO 80401

T. Reed and M. Graboski (consultant) Colo. School of Mines.

COMMENTS:

Oxygen pressurized gasification can provide a medium Btu gas from farm or forest residues for synthesis of methanol or ammonia to give fuel or fertilizer. Small gasification systems recover in mass production, and lower transport and handling the higher investment and labor required for smaller plants.



PROCESS:

Purox Process (Oxygen-fed Slagging Pyrolysis),

Union Carbide Corporation.

FEEDSTOCK:

Municipal solid waste.

HEAT SOURCE:

Combustion of pyrolytic char, tars, and liquids.

GAS/FUEL CONTACT:

In the Purox process, municipal solid waste (shredded and magnetically sorted) is fed into the top of a shaft furnace and oxygen is fed at the bottom. Pyrolytic char is combusted with the oxygen at the bottom of the gasification furnace, providing enough thermal energy to produce temperatures in the range from 2900 to 3100 F and to produce a molten slag from all non-combustible materials. This molten slag is romoved for quenching and disposal.

Combustion gases rise counter currently through the MSW producing gas, liquids, and char. The liquids and char are burned in the combustion zone. The pyrolytic gas rises through the furnace, drying and preheating the feed. A diagram of the process is given in Fig. 10-6. Gases leave the furnace for further processing to produce a medium energy fuel gas.

ASH/CHAR:

The char is consumed during the combustion step to provide process heat. The ash is removed in a molten form from the reactor and quenched to form a granular frit.

PRODUCTS:

Medium Energy Gas: A comparison of this product gas with methane is given in Table 10-3.

OPERATING CONDITIONS:

Temperature (maximum) = 3100 F

Pressure

= atmospheric.

SIZE:

200 ton/day Raw Refuse Conversion Facility.

FUNDING, LOCATION, PERSONNEL:

The process was developed by Union Carbide Corporation in Tarrytown, N.Y., at a 5-ton/day scale. A 200-ton/day facility is

located in South Charlestown, W. Va.

REFERENCES:

Shulz, H.M. (Principal Investigator) et al. 1976. Resource Recovery Technology for Urban Decisionmakers. New York: Urban Technology Center, Columbia University.

Tillman, D. A. 1976. "Mixing Urban Waste and Wood Waste for Gasification in a Purox Reactor." Thermal Uses and Properties of Carbohydrates and Lignius. Schafizadeh, F.; Sarkanen, K. V.; and Tillman, D. A., eds. New York: Academic Press.

Desrosiers, R. E. 1979. Process Designs and Cost Estimates for a Medium Btu Gasification Plant Using a Wood Feedstock. SERI/TR-33-151. Golden, CO: Solar Energy Research Institute.

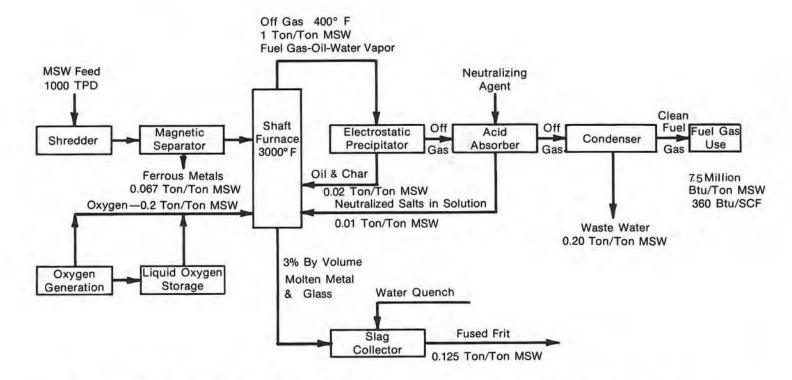


Figure 10-6. Union Carbide Corporation Purox System Oxygen-Fed Slagging Pyrolysis



Table 10-3. COMPARISON OF COMBUSTION CHARACTERISTICS OF PUROX GAS AND METHANE

Component	Volume %	Heat of Combustion (Btu/SCF)	Air Required for Combustion (SCF/SCF)	Volume of Flue Products (SCF/SCF)
Purox Gas				
CO	44	322	2.38	2.88
H_2	31	275	2.38	2.88
CO_2	13	0	0	1
CH ₄	4	913	9.53	10.53
C_2H_4	1	1,513	14.29	15.29
N_2	1	0	0	1
H ₂ O	6	0	0	1
	100	280	2.43	2.97

Methane

Heat of Combustion 913 Btu/SCF
Air Required for Combustion 9.53 SCF/SCF
Volume of Flue Products 10.53 SCF/SCF

	Purox Gas	Methane	
Feed (SCF/MBtu)	3,600	1,095	
Air Required for Combustion (SCF/MBtu) ^a	8,700	10,440	
Volume of Flue Products (SCF/MBtu)	10,500	11,530	
Heat Release (Btu/SCF)	95	87	
Compression Power (kWh/MBtu)b	5.7	1.8	

^aBased on a minimal amount of air needed to convert gas to ${\rm CO_2}$ and ${\rm H_2O_{\scriptsize \bullet}}$

^bGas compressed to 35 psig from 1 atm, 100 F, with 75% efficiency.



10.2.3 Pyrolysis Gasification

GASIFICATION CASE SUMMARY

PROCESS: Arizona State University: Dual Fluidized-Bed Flash Pyrolysis

System.

FEEDSTOCK: Organic fraction of MSW, kelp residue, synthetic polymers, ag-

ricultural biomass sources.

HEAT SOURCE: Recirculated inert and catalytic solids.

GAS/FUEL CONTACT: Fluidized bed.

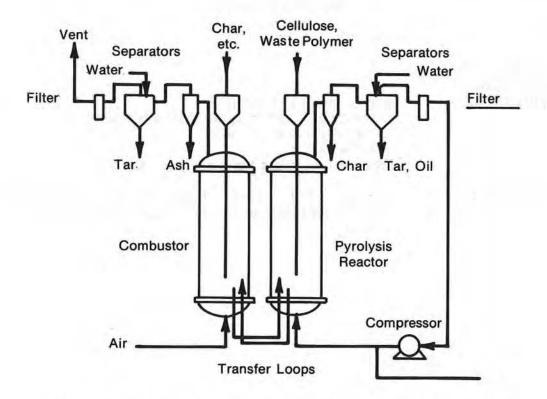


Figure 10-7. Thermal Gasification, Arizona State University



ASH/CHAR:

Char circulated to combustor for process heat. Dry ash sepa-

rated from combustor.

PRODUCTS:

Typical gas phase yields of 75-85%. Typical pyrolysis gas com-

position (cellulose source) is:

	mole %
C ₂ H ₄	5-15
Ćo⁴	35-45
H ₂	10-20
CH ₄	10-15
C_2H_6	1-5
CO ₂	15-30

OPERATING CONDITIONS:

Temperatures of 500-1000 C. Pressures 0-5 psig. Inert and

catalytic fluidizing solids.

SIZE:

25 lb/h.

FUNDING, LOCATION, PERSONNEL:

Prof. James L. Kuester

College of Engineering & Applied Sciences

Arizona State University

Tempe, AR

Supported for last three years by the EPA.

REFERENCE:

Kuester, J. L. 1979. "Liquid Hydrocarbon Fuels From Bio-

mass." Presented at Honolulu meeting of ACS, April 1-6.



PROCESS:

Battelle-Columbus, Multi-Solid Fluid Bed Reactor, Batch-Solids

Fluid-Bed Gasifier, Multiple Catalysts, Hydrogasification.

FEEDSTOCKS:

Forest residues, hard and soft woods.

HEAT SOURCE:

Circulatory bed material or external furnace.

GAS/FUEL CONTACT: Fluid bed.

ASH/CHAR:

Dry ash.

PRODUCTS:

Wood ash and CaO shown to be effective gasification and shift catalysts. Hydrogasification has given up to 18% CH4 (uncatalyzed.) Detailed studies in progress.

OPERATING CONDITIONS:

Temperatures of 625-825 C. Steam, H2, recycle gas environment. Variety of catalysts and incorporation methods. Fluid and entrained bed operation.

SIZE:

10 lb/h.

FUNDING, LOCATION, PERSONNEL:

H. F. Feldman. Battelle Columbus Laboratories. Fuels from Biomass Systems Branch Contractor.

REFERENCES:

- Feldman, H. F. 1978. "Conversion of Forest Residues to a Methane-Rich Gas." Presented at IGT Symposium, Washington, D.C., Aug. 14-18.
- Feldman, H. F.; Choi, P. S.; Liu, K. T. 1978. "Conversion of Forest Residue to a Methane-Rich Gas." Presented at Sixth Biomass Thermoconversion Contractors Meeting, Biomass Energy Systems. Univ. of Arizona, Jan. 16-17.
- Feldmann, H. F., et al. 1979. "Conversion of Forest Residue to a Methane-Rich Gas." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO; June 1979. Golden, CO: Solar Energy Research Institute; p. 439.



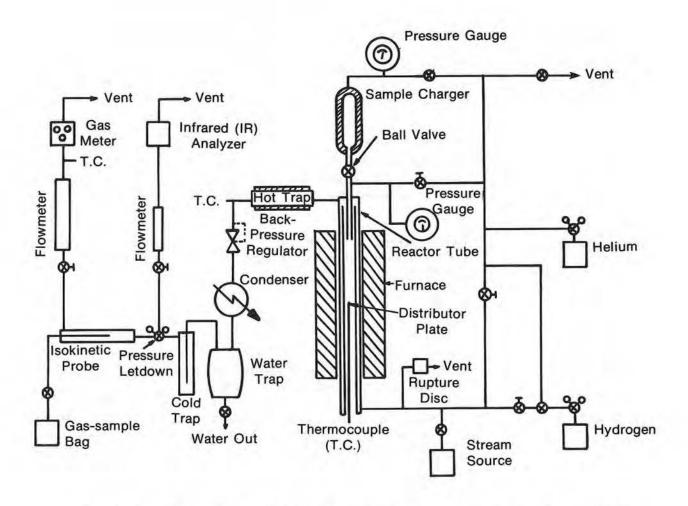


Figure 10-8. Bench-Scale Batch Reactor, Battelle-Columbus Laboratory



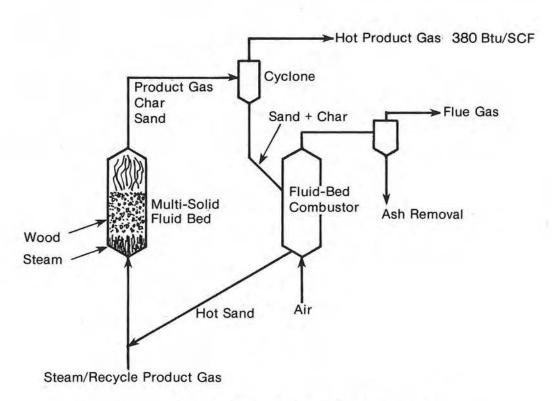


Figure 10-9. Schematic of MSFBG Process

PROCESS:

Garrett Multiple Hearth Biomass Gasifier.

FEEDSTOCK:

Any form of biomass that can be fed through a 14-in. diameter

screw, including materials of high moisture content.

HEAT SOURCE:

Recirculated hot char and heat transfer through metal wall.

GAS/FUEL CONTACT: Five hearths are used to accomplish drying, pyrolysis, two stages of char combustion, and ash cooling. Each chamber is isolated from the others. Drying is accomplished by countercurrent contact of feed with fuel gas from the combustion hearth. The dried feed is pyrolyzed by hot char delivered from the combustion chamber by a steam lift. Positive solids transport is achieved by internal hollow rakes. The char residue from the second hearth is dropped to the combustion hearths, which produce hot char and steam for pyrolysis. Ash from the combustion hearths drops to the ash cooler where combustion air is preheated.

ASH/CHAR:

Dry ash exits from the bottom hearth. All char is used in satis-

fying heat requirements for the process.

PRODUCTS:

Medium Btu Gas.

Feed Material	Ma	nure	Sawdust	
Solids temperature (°C) H ₂ O in feed (wt. fraction) H ₂ O in pyrolysis gas (vol. fraction)	635 0.4316 0.6480	657 0.052 0.3976	631 0.0995 0.1916	653 0.2995 0.4090
g/g dry, ash-free feed (mol. fraction)				
$^{\text{CO}_2}_{\text{CO}}_{\text{H}_2}_{\text{H}_2}_{\text{C}_2\text{H}_4}_{\text{C}_2\text{H}_6}$	0.509 0.118 0.035 0.054 0.016 0.006	0.323 0.118 0.017 0.048 0.014 0.011	0.341 0.312 0.016 0.086 0.016 0.012	0.379 0.307 0.017 0.089 0.020 0.011
Total (g/g dry, ash-free feed)	0.738	0.531	0.783	0.823
LHV (Btu/SCF)	294	343	387	385



OPERATING CONDITIONS:

Gas Temperature (°C)

 Drying hearth
 100-300

 Pyrolysis
 600-750

 Combustion
 1100-2000

Gas velocity 0.1 ft/s.

SIZE:

(Pilot Demonstration Unit) Each hearth is 4 ft in diameter, 1 ft in height.

(Projected) Capital investment for 100-ton/day plant would be \$1.9 million (1977).

FUNDING, LOCATION, PERSONNEL:

An exploratory, bench-scale, pilot unit and laboratory study was completed by the Garrett Energy Research and Engineering (GERE) Co. from May 25, 1976 to June 24, 1977 under ERDA Contract No. E (04-3) -1241. This work included an evaluation of each of the processing steps required in the multiple hearth equipment. First, the jacketed, vacuum, screw-flight conveyor was tested. Then, a single hearth was used to study the design variables involved in direct contact drying, steam-char pyrolysis, and combustion.

Testing of the entire process is currently being performed under DOE contract EY-76-C-03-1241. The pilot plant is located in Hanford, Calif.

REFERENCES:

- Garrett, D. E. 1977. Conversion of Biomass Materials into Gaseous Products, Final Technical Report. Work performed by Garrett Energy Research and Engineering for ERDA; Contract No. E(04-3) -1241, Oct.
- 2. Garrett, D. E. 1977. Thermochemical Conversion: Biomass Gasification. Presented at the Second Annual FFB Symposium, Troy, N.Y. June 20-22.
- Garrett, D. E. 1979. "Conversion of Biomass Materials to Gaseous Products." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO: June 1979. Golden, CO: Solar Energy Research Institute; p. 445.

COMMENTS:

The incorporation of two stages of drying which use waste heat from flue gas makes the GERE process suitable for very moist feeds. It appears that the process could be economical even at a plant size of 50 ton/day.

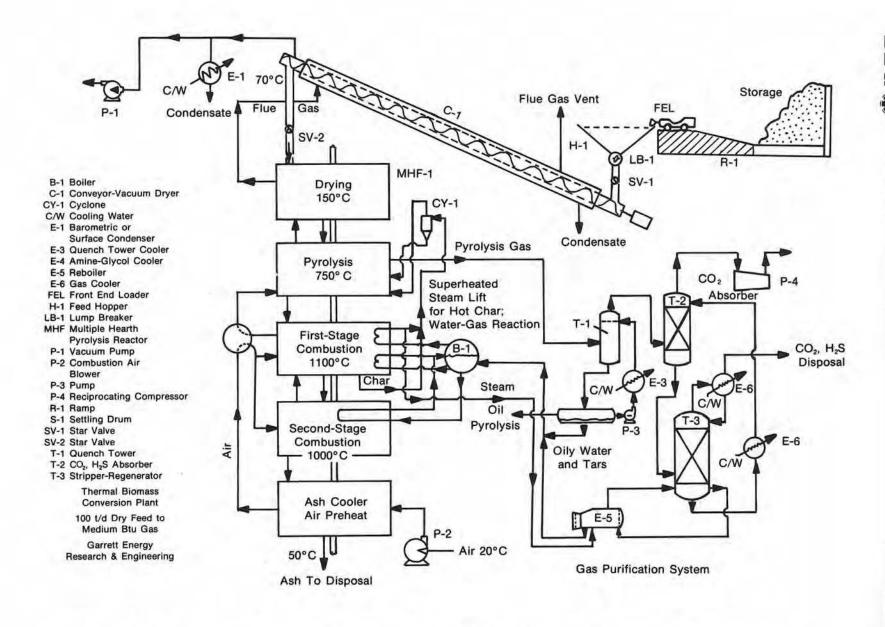


Figure 10-10. Thermal Biomass Conversion Plant, Garrett Energy Research and Engineering.

PROCESS:

Naval Weapons Center, China Lake - Flash Pyrolysis Process

FEEDSTOCK:

MSW (Ecofuel II, 200 μ m minimum dimension;-probably any

small-particle biomass form).

HEAT SOURCE:

Kiln, heated with char, byproducts, etc.

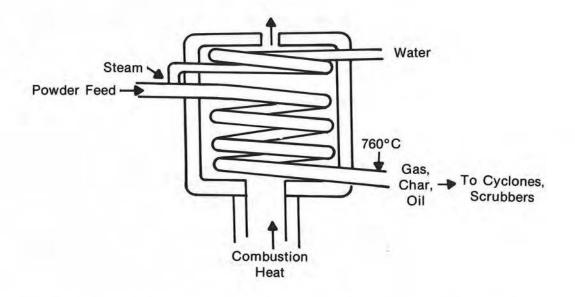


Figure 10-11. Flash Pyrolysis Process, Naval Weapons Center.

GAS/FUEL CONTACT: Suspended flow, typically 50 milliseconds.

ASH/CHAR:

Dry ash.



PRODUCTS:	(Dry)	Mass (%)	Energy (%)
	Gasoline precursors	24	53
	(C ₂ +)	36	16
	CH₄	4	11
	H ₂	1	6
	CŐ ₂	16	-
	Char	19	14

NOTES:

The MSW char energy content is 7000 Btu/lb (versus 14,000 Btu/lb for carbon) and is high in ash. The byproduct gases contain 415 Btu/SCF.

The process has been developed primarily for the production of gasoline. Pure ethylene was converted to a 90 motor octane number (MON) gasoline by thermal polymerization. The gasoline precursors were converted to a gasoline having virtually the same physical appearance and distillation characteristics.

SIZE:

Bench scale, 10 lb/h maximum.

PROJECTIONS:

From one ton (metric) of waste, the process would produce:

226 lb of gasoline (41 gal); 25 lb of light oil (5 gal); 228 lb of char and ash; 501 lb of by-product gases, some of which would be burned for process heat; 192 lb of CO₂; and 28 lb of tar.

The authors have used a preliminary evaluation made by Dow Chemical under contract to EPA and scaling techniques commonly used in the oil industry to produce economic projections of cost of gasoline from MSW. A few representative figures are:

Plant size (ton/day)	100	100	500	1000
Tipping fee (\$/ton)	8	8	8	8
Rate of return (%)	_	15	15	15
Municipal Amortization (%)	8	_	_	_
Gasoline cost (\$/gal)	0.80	1.35	0.55	0.38

Credits of \$4.85/ton are taken for inorganics in waste.

PROCESS ADVANTAGES:

Process can convert a wide variety of biomass feedstocks at 0-\$2/MBtu to gasoline worth \$5/MBtu with immediate product acceptance. Process steps are relatively simple and similar to present refinery practice. All medium Btu by-product gas, char, and tars would be consumed for process energy, so that only premium quality hydrocarbon fuels would be the final products.



PROCESS DISADVANTAGES:

Process has only been demonstrated with finely divided feedstock. It is capital intensive and will require technical personnel for operation.

FUNDING, LOCATION, PERSONNEL:

Process developed starting May 1975, under EPA contracts EPA-IAG-D5-0781 at the Naval Weapons Center, China Lake, Calif. 93555, under James P. Diebold, Charles Benham, and Garyl D. Smith. EPA Funding now withdrawn; process being discontinued at China Lake during 1979. Work is resuming at SERI under the direction of James Diebold and Tom Reed.

REFERENCES:

- 1. Diebold, J. P.; Benham, C. B.; Smith, G. D. Wastes to Unleaded, High-Octane Gasoline. EPA-IAG-D6-0781.
- 2. Diebold, J. P. 1980. Research into the Pyrolysis of Pure Cellulose, Lignin, and Birch Wood Flour in the China Lake Entrained Flow Pyrolysis Reactor. SERI/TR-332-586.

 Golden, CO: Solar Energy Research Institute.
- 3. Diebold, J. P.; Smith, G. D. 1979. "Noncatalytic Conversion of Biomass to Gasoline." ASME Solar Energy Conference. ASME 79-Sol-29. March.
- 4. Diebold, J. P. 1979. "Gasoline from Solid Wastes by a Noncatalytic Thermal Process." ACS Symposium on Thermal Conversion of Solid Wastes and Biomass. September.
- 5. Diebold, J. P.; Smith, G. D. 1979. "Thermochemical Conversion of Biomass to Gasoline." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO: June 1979. Golden, CO: Solar Energy Research Institute; p. 139.



PROCESS:

Steam Gasification of Biomass, Princeton University.

FEEDSTOCK:

Cellulose.

HEAT SOURCE:

Electrical Resistance Heaters.

GAS/FUEL CONTACT:

The pyrolysis unit (see Fig. 10-12) is operated in a semi-batch mode by passing steam over a small batch sample of biomass material at pyrolysis temperatures, then using gas-phase pyrolysis reactions to convert pyrolytic gases to synthesis gases.

ASH/CHAR:

Char is collected and weighed at the end of the experiment.

PRODUCTS:

Synthesis Gas - representative compositions are shown below for cellulose pyrolysis.

Table 10-4. STEAM PYROLYSIS OF CELLULOSE, PRINCETON (Experimental Conditions and Results)

Pyrolysis Temp. (°C)	500	500	500	500	500
Gas Reactor Temp. (°C)	600	500	600	700	600
Gas Reactor					
Res. Time (s)	10	9	6	6	2
Gas Analysis (Vol. %)					
СО	55	40	52	53	55
H_2	10	11	10	13	10
có,	16	42	20	13	20
CH ₄	8	2	8	12	6
C_2H_4	4	1	4	5	6
$C_3^2H_6^2$	1	1	2	1	1
C2H6	2	1	1	1	2
Other	4	2	3	2	2 3
Cal. Value (MBtu/ton)	6.2	0.98	5.4	9.7	3.6

SIZE:

Bench scale.

FUNDING, LOCATION, PERSONNEL:

Supported the last several years by the U.S. EPA. Michael J. Antal, Jr., Princeton University Department of Mechanical

Aerospace Engineering.

REFERENCE:

IGT Conference on Energy from Biomass and Waste. Aug.

1978. Wash., D.C.

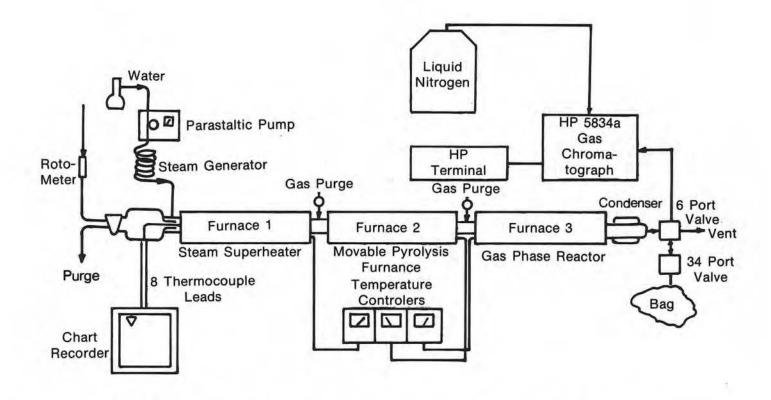


Figure 10-12. Schematic of the Tubular Quartz Reactor Experiment, Princeton University



GASIFICATION CASE SURVEY

PROCESS:

Flash Pyrolysis and TGA Studies

Royal Institute of Technology, Dept. of Chemical Technol-

ogy, Stockholm, Sweden.

FEEDSTOCK:

Wood, straw, municipal solid waste, peat, coal, graphite.

HEAT SOURCE:

TGA Studies

- electrical heating of biomass sample - superheating of steam and other gases Flash pyrolysis reactor - electrical heating.

GAS/FUEL CONTACT: Solids are fed to the pyrolysis reactor by means of a screw feeder and mixed with steam or other gas at the inlet of an electrically heated, down-flow pyrolysis reactor. Steam or inert gas can be added at any level in the reactor.

ASH/CHAR:

Char and ash are removed by a cyclone at the exit of the pyrolysis reactor.

PRODUCTS:

The major products are a medium energy gas and tar. Figure 10-13 (a) shows the amount of gas produced during flash pyrolysis of peat and solid waste. Figure 10-13 (b) shows the product distribution during pyrolysis of solid waste. Figure 10-13 (c) gives the composition of product gas during solid waste pyrolysis. Figure 10-13 (d) shows gas composition for various biomass materials.

Figures 10-14 (a, b) present TG-curves and DTG-curves for TGA pyrolysis of various biomass materials.

OPERATING CONDITIONS:

 to 1000 C Temperatures

 to 100 C/min in TGA **Heating Rate**

to 1000 C/s in flash pyrolysis reactor

Pressure

atmospheric

SIZE:

Pilot demonstration unit: 0.1 - 1.0 kg/h.

FUNDING, LOCATION, PERSONNEL:

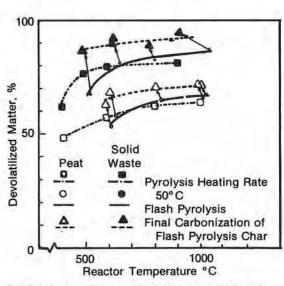
The pyrolysis studies are being performed by personnel at the Royal Institute of Technology, Department of Chemical Technology, Stockholm, Sweden, under the direction of E. Rensfelt.

Grant support is provided by the Swedish National Board for Energy Source Development and the Swedish Board for Technical Development.

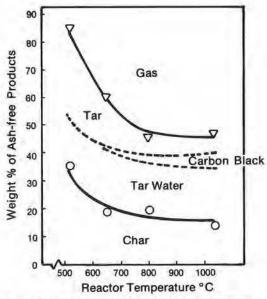


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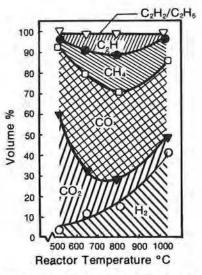
Rensfelt, E. et al. 1978. "Basic Gasification Studies for Development of Biomass Medium - Btu Gasification Process." Energy from Biomass Wastes. Chicago, IL: Institute of Gas Technology.



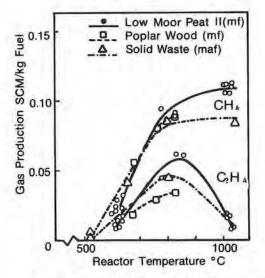
(a) Pyrolysis of Peat and Solid Waste at Different Heating Rates and Residence Times, Percentage Devolatilized of m.f. Peat (Low Moor Peat II) resp. m.a.f. Solid Waste Versus Pyrolysis Temperature



(b) Flash Pyrolysis of Solid Waste. Product Distribution at Different Reactor Temperatures



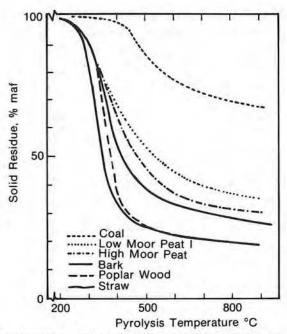
(c) Flash Pyrolysis of Solid Waste. Composition of Product Gas at Different Reactor Temperatures



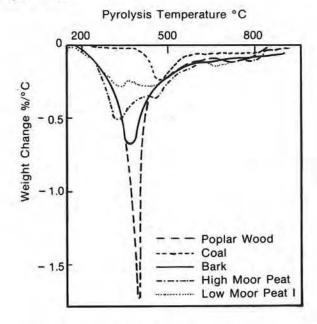
(d) Flash Pyrolysis of Peat, Poplar Wood, and Solid Waste. Production of Methane and Ethylene Versus Reactor Temperature

Figure 10-13. Flash Pyrolysis Yields, Royal Institute of Technology, Stockholm, Sweden





(a) Pyrolysis in Argon of Different Fuels, TG-Curves. Solid Residue (maf) as Percentage by Weight of Fresh Fuel (maf). Heating Rate 20° C/min for Bark, Straw, Coal, and Low Moor Peat and 50° C/min for High Moor Peat and Poplar Wood



(b) Pyrolysis in Argon of Different Fuels, DTG-Curves as Percentage by Weight (maf) per Centigrade Heating Rates, See (a)

Figure 10-14. TGA Results for Pyrolysis of Biomass, Royal Institute of Technology, Sweden



PROCESS: Solar Energy Research Institute, fundamental studies of flash

pyrolysis kinetics and mechanisms.

FEEDSTOCK: Finely divided (10-1000 μm) powders of wood, cellulose, lignin.

HEAT SOURCE: Variety of experimental approaches ranging from contact heat-

ing, through transport-line reactors to radiant heating.

GAS/FUEL CONTACT: Short residence time reactors (1 to 10⁻³ s).

ASH/CHAR: May reach fusion temperatures.

PRODUCTS: Olefins, other unsaturates.

OPERATING

CONDITIONS: 500-2000 C; 1 to 10⁻³ s; 1 atm; inert, steam, and H₂ environ-

ments; fast quenching and collection of gaseous, liquid, and

solid products.

SIZE: Laboratory scale.

FUNDING, LOCATION,

PERSONNEL: SERI Project 3356.10, Fundamental Studies in Thermal Conver-

sion. T. Milne, M. Soltys.

COMMENTS: Experimental work initiated in October 1979.



PROCESS:

SERI/Naval Weapons Center flash pyrolysis to olefins.

FEEDSTOCK:

Ligno-cellulose materials.

HEAT SOURCE:

Externally heated tube reactor.

GAS/FUEL CONTACT: Feed is entrained in a steam carrier and passed through a hot tube at such a rate as to achieve rapid heatup at millisecond residence times.

Dry ash, char.

PRODUCTS:

ASH/CHAR:

Char (1-20%) and olefin-rich gas (unsaturates about 25% wt).

SIZE:

20-30 lb/h.

FUNDING, LOCATION,

PERSONNEL:

SERI task no. 3356.30

1617 Cole Blvd. Golden, Colo. 80401

J. Diebold, T. Reed

COMMENTS:

In addition to optimizing the yield of olefins from the pyrolysis process, development work will be performed on olefin separation, thermal polymerization to gasoline, and hydration to mixed alcohols. Pyrolysis efforts will be directed toward the

use of scalable reactor designs.



PROCESS:

Batch, quasi-steady-state, and pneumatically stirred reactors.

University of California, Berkeley.

FEEDSTOCK:

Wood, kraft black liquor, MSW.

HEAT SOURCE:

External from laboratory furnaces.

GAS/FUEL CONTACT:

Entrained flow, fixed bed.

ASH/CHAR:

PRODUCTS:

The approximate weight percentage of organics is char 2.5%; tar 7%; and gases 90.5%: H_2 1%, CH_4 10%, C_2H_4 5%, CO 62%,

and CO₂ 13%.

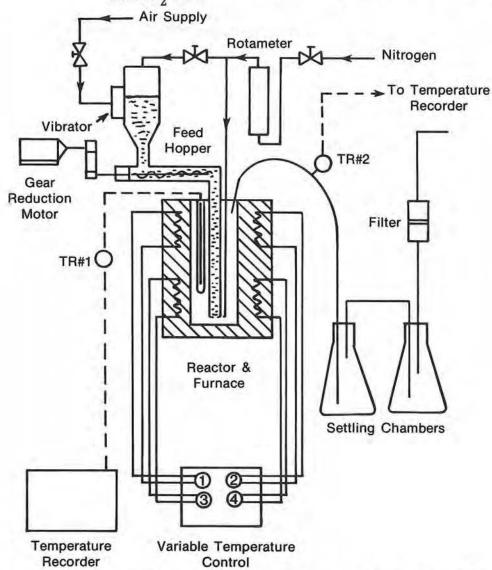


Figure 10-15. Bench-Scale Reactor, University of California, Berkeley



OPERATING CONDITIONS:

White fir particles, 20-40 mesh. Rate of heating, about 1000° C/s. Maximum temperature, 843 C. Residence time, 3 seconds.

SIZE:

Various.

FUNDING, LOCATION, PERSONNEL:

Prof. D. C. Brink

College of Natural Resources University of California

Berkeley, CA

REFERENCES:

- Brink, D. L.; Massoudi, M. S. 1978. J. Fire & Flammability. Vol. 9: p. 176.
- 2. Brink, D. L. 1976. Applied Polymer Symposium No. 28. New York: John Wiley & Sons; p. 1377.



GASIFICATION CASE SUMMARY

PROCESS:

West Virginia University Fluid Bed Pyrolysis Process

FEEDSTOCK:

MSW, sewage sludge, sawdust, manure, plastic, coal

(partial drying, separation of noncombustibles, and size reduc-

tion to less than 1 in. are required).

Table 10-5. SOLID WASTE FEED ANALYSIS FOR WEST VIRGINIA UNIVERSITY STUDIES

Waste Material	Carbon ^a (Wt. %)	Hydrogen ^a (Wt. %)	Ash ^a (Wt. %)	Moisture (Wt. %)	Heating Value (Btu/lb Dry)
msw ^b	30.25	4.03	40.17	5.49	5,500
Sawdust	47.20	6.49	0.97	2.62	8,114
Chicken manure	28.25	4.65	24.70	4.91	5,789
Cow manure	37.45	3.99	16.12	7.82	7,396
Animal fat	77.77	11.79	0.34	4.62	16,368
Tire rubber	76.11	7.15	4.40	1.91	15,401
PVC plastic	41.18	5.25	0.15	0.47	9,129
Nylon	84.18	10.07	0.08	1.48	13,481
Bituminous coal	73.36	5.34	7.57	3.42	13,097
Sewage sludge	18.43	2.21	62.95	42.16	3,900

^aDry basis; moisture is found by difference.

HEAT SOURCE:

Natural gas burner/sand bed (Pilot demonstration unit)

Char combustion in dual bed/recirculating sand (projected)

GAS/FUEL CONTACT: Fully fluidized, well-mixed sand bed.

ASH/CHAR:

Dry ash and char elutriated from bed and separated from off-

gas in a cyclone.

^bAverage of five tests.



PRODUCTS:

Table 10-6. WEST VIRGINIA UNIVERSITY: PYROLYSIS OPERATING CONDITIONS AND RESULTS

Waste Material	Temperature (°F)	Dry Feed Rate (lb/min)	Gas Production (SCF/lb) Dry)	Gas Phase Thermal Efficiency
MSW ^a	1,420	0.40	9.34	0.72
Sawdust ^b	1,520	0.35	18.29	0.90
Chicken manure	1,280	0.39	9.53	0.51
Cow manure ^C	1,400	0.39	9.86	0.44
Animal fat	1,400	0.36	16.53	0.67
Tire rubber	1,370	0.36	5.36	0.22
PVC plastic	1,485	0.41	6.39	0.29
Nylon	1,530	0.31	8.59	0.26
Bituminous coal	1,440	0.34	10.92	0.36
Sewage sludge	1,420	0.22	9.48	0.88

^aAverage of five tests.

OPERATING CONDITIONS:

T = 1400-1500 F, P = 0-10 psig Superficial gas velocity: 1.5 ft/s

Feed rate: 40-80 lb/h-ft2.

SIZE:

(Pilot demonstration unit)

Bed ID: 15 in., 15-16 lb/h (0.7 tons/day)

Capital Investment: \$150,000.

(Projected) Bed ID: 12 ft, 170 tons/day Capital investment for a plant to process

1,000 tons/day of dried refuse: \$19.6 million (1978).

FUNDING, LOCATION, PERSONNEL:

Principal Investigator: Dr. Richard C. Bailie

Department of Chemical Engineering, West Virginia University

Morgantown, W. Va.

bAverage of three tests.

^cAverage of two tests.

Table 10-7. WEST VIRGINIA UNIVERSITY PYROLYSIS GAS ANALYSIS

			Gas Ana	lysis (Dry	Basis, Vol.	%)			Low Heating
Waste Material	H_2	co_2	CH ₄	СО	C_2H_2	C_2H_4	С ₂ Н ₆	С3Н8	Value (Btu/SCF)
MSW ^a	44.47	15.78	6.96	24.76	4.97	1.49	0.66	0.91	421
Sawdust ^b	29.32	12.13	11.04	43.79	3.12	0.36	0.36	NM	398
Chicken manure	35.91	29.50	8.31	21.37	2.22	NM	0.61	NM	308
Cow manure ^c	31.07	20.60	7.70	38.06	1.86	NM	0.31	NM.	328
Animal fat	11.57	27.63	18.12	14.72	25.05	NM	2.91	NM	683
Tire rubber	33.81	15.33	29.09	5.67	12.94	NM	3.17	NM	661
PVC plastic	41.02	19.06	14.51	20.76	4.02	0.21	0.43	NM	412
Nylon	45.38	6.03	15.47	34.64	0.0	NM	0.0	NM	403
Bituminous coal	46.88	11.68	16.63	21.72	2.08	NM	1.01	NM	435
Sewage sludge	47.01	22.88	11.22	15.57	3.12	NM	0.21	NM	360

^aAverage of five tests.

NM = not measured.

^bAverage of three tests.

^cAverage of two tests.



Funding initiated with HEW grant for waste disposal studies in 1966. Work completed under EPA Contract No. R01 EC 00399-03 EUH. Final report submitted August 1, 1972. Nonexclusive license granted to Wheelabrator Incineration.

REFERENCES:

- 1. Bailie, R. C. U.S. Patent 3,853,498. "Production of High Energy Fuel Gas From Municipal Wastes."
- 2. Bailie, R. C., Burton, R. S. 1979. "Fluid Bed Pyrolysis of Solid Waste Materials." Combustion. p. 13; Feb.
- Alpert et al. 1972. "Pyrolysis of Solid Waste: A Technical and Economic Assessment." Prepared for WVU by SRI, Sept. NTIS PB 218-231.

COMMENTS:

The work at West Virginia University was aimed at characterizing the pyrolysis behavior of solid waste components. Mass balances based on carbon were seldom closed to better than 90%. Gas analyses were precise, but the char and oil were not characterized. Gas yields were strongly dependent on bed temperature, increasing rapidly to 1400 F (760 C) and then leveling off at higher temperatures.

The dual fluidized bed system envisioned for the commercial scale plant was described by Bailie in his patent. The projected economics were reported by SRI. No prototype was built in this country; however, a plant using the same concept is now operating in Japan.



GASIFICATION CASE SUMMARY

PROCESS:

Wright-Malta Steam Gasification Process

FEEDSTOCK:

Any form of biomass that can be screw-fed, including very wet

materials.

HEAT SOURCE:

Condensing high-pressure steam.

GAS/FUEL CONTACT:

Solids are transported by a slowly rotating screw and are maintained in close contact with a gas stream consisting mostly of steam (Fig. 10-16).

ASH/CHAR:

Residues are dropped from the end of the screw flight into a lock hopper.

PRODUCTS:

Medium Btu gas consisting chiefly of $\rm H_2$ and $\rm CO_2$. In Fig. 10-17, the dependence of composition on temperature and pressure is illustrated (solid lines) and compared with calculated equilibrium compositions (dashed lines).

OPERATING CONDITIONS:

T = 400-1500 F P = 0-3000 psigCatalyst: Na₂CO₃.

SIZE:

ID = 2.5 in. Length = 10 ft

FUNDING, LOCATION, PERSONNEL:

The Wright-Malta Corp. is located in Ballston Spa, N.Y. Preliminary investigation of design variables, performed on a batch-fed minikiln gasifier (Fig. 10-18), was funded by the Empire State Electric Energy Research Corp. Product studies with MSW were funded by the U.S. EPA. Work on coal was sponsored by the N.Y. State Energy Research and Development Authority. DOE is currently funding further development work.

REFERENCES:

- Hooverman, R. H.; Coffman, J. A. 1977. "Rotary Kiln Gasification of Biomass and Municipal Wastes." <u>IGT Sym-</u> posium on Clean Fuels from Biomass and Wastes. Orlando, FL; Jan. 25-28.
- Wright-Malta Corp. 1979. Steam Gasification of Biomass. Progress Report No. C00/4124-4, for Fuels from Biomass Program. U.S. Dept. of Energy. Nov. 1.
- 3. Coffman, John A. 1979. "Steam Gasification of Biomass." 3rd Annual Biomass Energy Systems Conference Proceedings: The National Biomass Program. Colorado School of Mines, Golden, CO: June 1979. Golden, CO: Solar Energy Research Institute; p. 349.



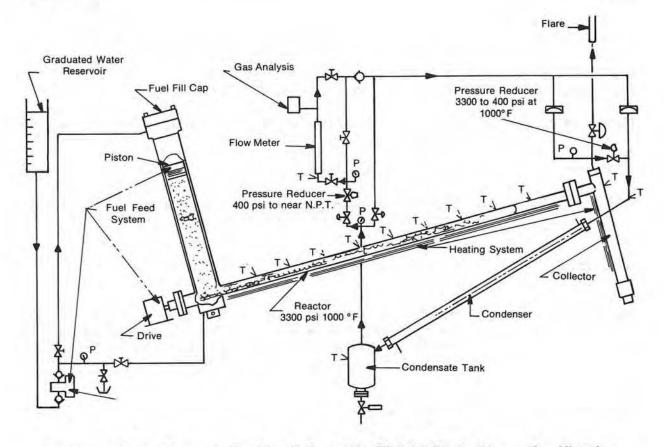


Figure 10-16. Biomass Gasifier Schematic, Wright-Malta Steam Gasification

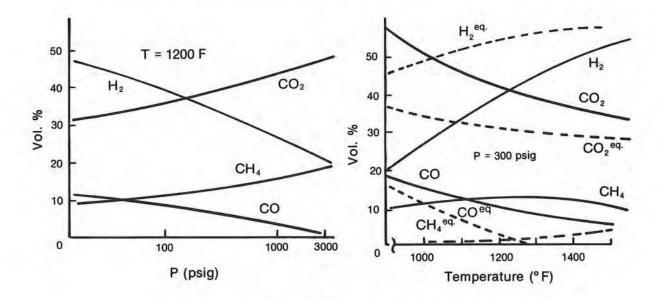


Figure 10-17. Medium-Btu Gas

Figure 10-18. Wright-Malta Batch-fed Minikiln Scale Drawing



COMMENTS:

The behavior of the steam gasification system has been explored over a wide range of operating conditions both with and without an added catalyst.

Pressure - Solid to gas conversion was greatest in the pressure range from 400-500 psig. More residue was obtained at lower and higher pressures. The catalyst was effective in reducing char production below 600 psig; it was ineffective above this pressure. Also, the form of the residue changed from loose and granular below 600 psig to compact, 1-2 cm lumps at higher pressures.

Temperature - Above 1400 F (760 C) the gas composition is very near the equilibrium composition. Below this temperature, the steam re-forming reactions are not fast enough to convert CO and CH₄ to H₂. (Note: WM reports only metal wall temperatures and exit gas temperatures). The time-temperature history of the feed as it passes through the continuous reactor is a slow heating in the presence of steam. An interesting feature of the minikiln batch procedure is that the isolated events of pyrolysis and steam gasification can be followed, as illustrated in the plot of gas evolution and temperature vs. time in Fig. 10-19. Pyrolysis begins at 150 C and is complete at 400 C. Steam gasification of char begins at about 500 C. Note that the steam shifts all the CO to CO₂; in fact, one of the chief characteristics of the WM gas product is an extremely high H₂/CO ratio.

Particle Size - Tests in the minikiln indicated that the process was insensitive to the form of the biomass charge. However, only finely divided materials have been used in the continuous reactor for mechanical reasons. Related to this feeding problem is the ratio of water to solid: most of the data have been obtained by feeding a sawdust slurry. Work is under way to alter the feed system to permit lower water/charge ratios.

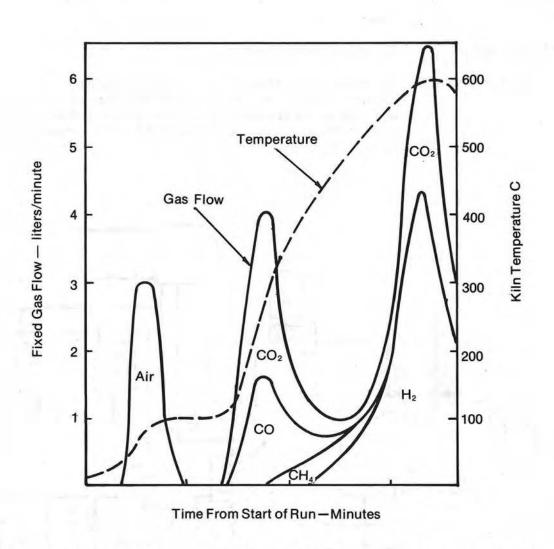


Figure 10-19. Fixed Gases Evolved, Typical Minikiln Run, Wright Malta



10.2.4 Hydrogengasification and Bromine Conversion

GASIFICATION CASE SUMMARY

PROCESS:

Institute of Gas Technology Hydrogasification Process.

FEEDSTOCK:

Peat, various coals.

HEAT SOURCE:

Electrical resistance heaters.

GAS/FUEL CONTACT: Hydrogen (and steam if desired) is preheated and mixed with feed at the entrance of a helical coil reactor. The reactor is operated as an entrained flow reactor in an isothermal or a constant heat-up mode. A diagram of the PDU reactor system is given in Fig. 10-20.

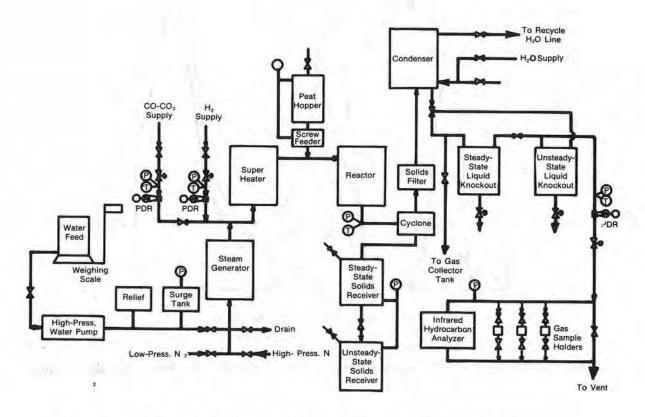


Figure 10-20. IGT Hydrogasification Process, Block Flow Diagram for the Process Development Unit (PDU)



ASH/CHAR:

Char is removed by a cyclone and solids filter.

PRODUCTS:

Products are hydrocarbon gases, heavy hydrocarbons and carbon oxides. Figures 10-21(a) and 10-21(b) show typical yields during peat hydrogasification in the bench-scale reactor.

OPERATING CONDITIONS:

Laboratory-Scale Reactor	Process Development Unit
0.022-0.048	5-12.5
H ₂ , He	H ₂ , H ₂ -H ₂ O, Synthesis Gas 4.3-36
4-71	4.3-36
855-1500	1000-1500
24-48	400-1030
4-7.7	8-14
0.005	0.011
	Reactor 0.022-0.048 H ₂ , He 4-71 855-1500 24-48 4-7.7

SIZE:

Laboratory scale (0.05 lb/h)

Process development unit (12.5 lb/h).

FUNDING, LOCATION, PERSONNEL:

The IGT hydrogasification process has been developed by personnel at the Institute of Gas Technology, Chicago, Ill., under

joint sponsorship of DOE and IGT.

REFERENCES:

Punwani, D. V.; Nandi, S. P; Gavin, L. W.; Johnson, J. L. 1978. "Peat Gasification - An Experimental Study." Presented at 85th

National Meeting of the AIChE, Philadelphia, PA.

Weil, S. A.; Nandi, S. P.; Punwani, D. V.; Kopstein, M. J. 1978.
"Peat Hydrogasification." Presented at 176th National Meeting

of ACS, Miami, Fl.

COMMENTS:

The IGT hydrogasification has been shown to be technically feasible for gasification of peat and coal. Experimental data on biomass and process economics are needed before the usefulness of this process can be compared to the other major types of

biomass gasification processes.



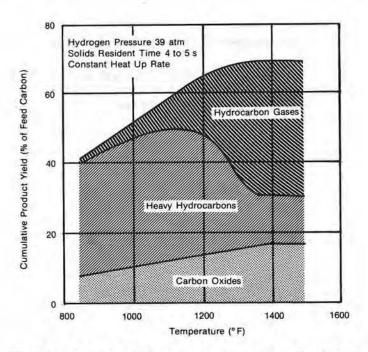


Figure 10-21a. Effect of Temperature on Product Yields Obtained During Peat Gasification, IGT Hydrogasification

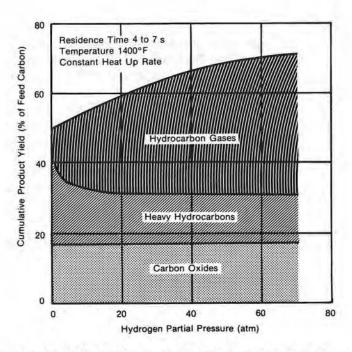


Figure 10-21b. Effect of Hydrogen Partial Pressure on Product Yield Obtained During Peat Gasification, IGT Hydrogasification



GASIFICATION CASE SUMMARY

PROCESS:

Bromine Conversion of Biomass to HBr Followed by Electrolysis

to H2. Rockwell Energy Systems Group.

FEEDSTOCK:

Wood, sugarcane, water hyacinth, kelp, lignin, Eco Fuel II.

HEAT SOURCE:

Small glass ampules in electric furnace.

GAS/FUEL CONTACT:

Aqueous bromination under pressure.

ASH/CHAR:

Filtered from product solution.

PRODUCTS:

Almost entirely CO2 and HBr in bromination step.

OPERATING

CONDITIONS:

At 250 C and 30 min. there is 95-96% conversion to HBr.

SIZE:

Laboratory tests on gram samples.

FUNDING,

LOCATION, PERSONNEL:

SERI H2 - Production Program. Canoga Park, CA. A. J.

Darnell, principal investigator.

REFERENCES:

Paper to be presented at 1979 World H2 Energy Conference.



10.2.5 Solar-Thermal Gasification

GASIFICATION CASE SUMMARY

PROCESS: Gasification of biomass using an integral pyrolysis entrained

flow reactor/solar receiver.

FEEDSTOCKS: Agricultural wastes and products-straw, cornstalks, Sudan

grass, sunflowers, etc.

HEAT SOURCE: Lab studies: Electric tube furnace

Field tests: 6-meter diameter parabolic dish solar con-

centrator.

GAS/FUEL CONTACT: The biomass is entrained and transported through the stainless

steel heat transport coil by either steam or pyrolysis gas.

ASH/CHAR: The ash and char are collected from the quench water.

PRODUCTS: Hydrogen, propylene, acetylene, methane, carbon monoxide,

carbon dioxide, and ethylene; traces of butenes and saturated

hydrocarbons.

OPERATING

CONDITIONS: 700° C to 1500° C at 1 atm pressure.

SIZE: 10-20 lb/h

FUNDING, LOCATION,

PERSONNEL: SERI Task No. 3457.13

1617 Cole Blvd. Golden, Colo. 80401

C. Benham, G. Bessler, P. Bergeron, M. Bohn, R. Kemna, and

R. Passamaneck.

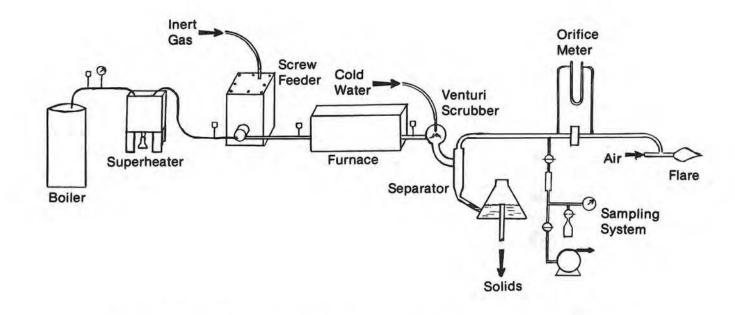


Figure 10-22. Laboratory Apparatus for Biomass Pyrolysis (SERI)



Chapter 11

Economics of Air Gasification for Retrofitting Oil/Gas Boilers

T. B. Reed, D. Jantzen, W. P. Corcoran, R. Witholder SERI



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CHAPTER 11

ECONOMICS OF AIR GASIFICATION FOR RETROFITTING OIL/GAS BOILERS

11.1 INTRODUCTION

Many industrial concerns converted from coal to natural gas or oil during the last decade to meet more stringent emission requirements. Now they are faced with much higher fuel prices and the possible curtailment or total interruption of supply. Their most obvious course is to convert those boilers that originally used coal back to coal or to wood or to replace new oil/gas package boilers with new coal/wood installations. Both options are relatively expensive and also will require less stringent emission controls.

A less obvious option is the use of a biomass (or coal) gasifier to retrofit the existing gas/oil boiler to an intermediate-energy gas generated in situ, using the "close-coupled gasifier" (described in Chapter 8). In this chapter we examine the technology and economics of biomass gasifiers and compare the economics of retrofit to the economics of complete combustion installations for biomass.

11.2 GASIFIER OPERATION

A partial list of manufacturers of gasifiers suitable for converting gas/oil boilers is given in Table 11-1, including the type of gasifier, the size, and status of development. A more complete list is given in Section 9.2.

Table 11-1. PARTIAL LIST OF BIOMASS GASIFIER MANUFACTURERS IN THE UNITED STATES

Name	Туре	Status ^a	Size (MBtu/h)
Applied Engineering, Orangeburg, SC	Updraft	D	8
Biomass Fuel Conversion, Yuba City, CA	Downdraft	D	14
Century Research, Gardena, CA	Updraft	C	85
Davis Gasifier, U. of Calif., CA	Downdraft	D	14
DeKalb Agricultural Research, DeKalb, IL	Updraft	D	1.7
Forest Fuels, Keene, NH	Updraft	C	1-12
Foster-Wheeler, Livingston, NJ	Updraft	D	50
Halcyon, E. Andover, NH	Updraft	C	8
Pioneer Hi-Bred Inst., Johnston, IA	Updraft	D	7
Woodex Corp., Eugene, OR	Updraft	C	10

^aStatus of project: C-Commercial (at least one unit in field); D-Demonstration and testing.



The gases produced by these gasifiers contain CO, H_2 , and hydrocarbon gases as their principal fuel ingredients and N_2 , CO_2 , and H_2O as diluents. If the gases are cooled and conditioned for use in engines or a pipeline, they have a typical energy content of 90 Btu/SCF and are called low energy gas (LEG), producer gas, and gen-gas or generator gas. A typical analysis shows: CO = 20.5%; $H_2 = 15.3\%$; $CO_2 = 7.4\%$; $O_2 = 1.4\%$; hydrocarbons = 8.1%; $N_2 = 47.4\%$ (Williams and Gross 1977).

If these gases are to be used for heating, it is not desirable to remove the pyrolysis oil vapors and the sensible heat; these same gases then have an effective heat content of 140 to 200 Btu/SCF, depending on temperature, feedstock, type of gasifier, etc.

11.2.1 Efficiency of Combustion of Medium Energy Gas (MEG)

The energy content of a gas is very important if the gas is to be shipped by pipeline. However, the flame temperature and flue gas mass produced varies with energy content by only a small amount because large quantities of air must be added for combustion. The relative efficiency of boilers using gases of various energy contents are shown in Fig. 11-1 as a function of energy content of the gas (Bechtel Corporation 1975). Here it can be seen that efficiency is actually higher for the medium energy gases (MEG) (with energy content around 350 Btu/SCF) than it is for high energy gas (HEG) with energy content about 1,000 Btu/SCF. The efficiency falls rapidly below about 200 Btu/SCF. It can be seen that there is little loss for MEG, but considerably more for low energy gas (LEG).

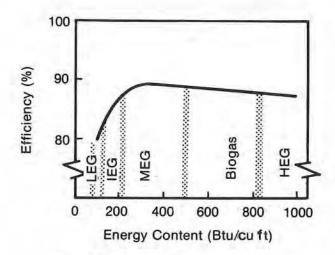


Figure 11-1. Boiler Efficiency Vs. Gas Energy Content



11.2.2 Scale of Close-Coupled Gasifiers

Table 11-1 shows that there are a number of close-coupled gasifiers being developed in the capacity range from 1 to 100 MBtu/h. There also may be some need for even smaller gasifiers, for example, for heating apartments and shopping centers. At present, there are no proven biomass gasifiers with operating capacities greater than 100 Btu/h, and there would seem to be a need for this size for large process steam installations, especially in the paper industry. However, coal gasifiers have been built at this larger scale and there seems to be no technical barrier to scaling gasifiers to larger or smaller sizes.

11.2.3 Efficiency of Close-Coupled Gasifiers

Since all the gas generated is burned and the sensible heat of the gas stream is also conserved in close-coupled gasifiers, these units can have very high efficiencies. Essentially complete combustion of the resulting gas is easily achieved as a result of the two-stage combustion in the gasifier and boiler. The only losses in the gasifier are the heat losses from the outer surfaces and heat to the ash, which is negligible. The Century gasifier is reported to have a thermal efficiency of 90% (Amundsen 1976), while the Davis gasifier operates at a typical efficiency of 85% (Gross 1978). The early gasifiers used for transportation in Europe had thermal efficiencies of 80% even after the tars had been cooled and scrubbed (Reed and Jantzen 1979).

11.2.4 Retrofitting Close-Coupled Gasifiers to Existing Boilers

The gases produced in the gasifiers listed in Table 11-1 can be burned in existing oil/gas installations, and a number of commercial installations have been made. The gas is somewhat more difficult to burn than natural gas and requires insulated piping to prevent condensation of pyrolysis oils and tars. A gas pilot flame or a flame holder is used to ensure combustion. However, the conversion problems are minimal.

In general, the modifications needed for retrofitting existing boilers are not documented, but a recent feasibility study at the California State Central Heating and Cooling Plant in Sacramento has used the Davis gasifier to power one of their boilers (Fuels Office 1978) for 158 h. The gasifier is 8 ft in diameter and 15 ft tall and produced 16 MBtu/h. Tests were run using two fuels: kiln dried wood chips purchased for \$9/ton or \$12.50/ton delivered; and pelleted white fir sawdust purchased for \$25.50/ton or \$35/ton delivered. The heating value of the gas varied from 182 to 206 Btu/SCF. Emissions were: 0% SO₂ observed (0.2% allowable); 130 ppm NO_x (200 ppm federal standard); and 0.703 lb/h particulates (4.09 lb/h allowable). Some condensate, tar, and charcoal were collected; however, the California Division of Water Quality concluded that they would not present a serious disposal problem.

Minor problems encountered during the test runs included burning out of an auger motor and some tar buildup in the delivery line. Most of the problems were associated with the temporary nature of the hookup for testing and should be no obstacle to commercialization. There was no noticeable deterioration of the metal parts. (Gasifiers that were built 60 years ago are still in operation.) During the tests, the gasifier production rate was controlled manually by controlling the intake air. Moreover, since gasifiers have been used to operate trucks, cars, and tractors, it has been proven that they can respond quickly to changes in load.



11.3 ECONOMICS OF RETROFITTING GASIFIERS TO EXISTING BOILERS

Two manufacturers with commercial experience have projected costs for commercial-sized gasifiers and their assumptions and costs are given in Table 11-2 (Gross 1978; Amundsen 1976). The gas costs derived (\$0.73 and \$1.06 per MBtu) are attractive relative to natural gas costs. However, the two biomass-derived gas costs cannot be compared to each other directly because of different assumptions used and the different sizes of the units.

Table 11-2. OPERATING COSTS OF GASIFICATION

	Gasifier A ^a	Gasifier Bb
Fuel	Walnut hulls	Chaparral
Rated gas production (MBtu/h)	14.1	85
Rated feed rate (ton/h)	1.19	7.87
Capital cost (\$)	125,000	350,000
Efficiency (%)	85	90
Annual Operating Costs (\$)		
Depreciation (10%)	12,580	35,000
Repairs and maintenance (3%)	3,774	10,500
Utilities (water, power)		38,795
Operating labor	6,000 (250 days)	14,600 (365 days
Taxes and insurance (2%)	2,516	
Interest (7%)	8,806	
Profit		494
Gasification cost (\$)	33,676	98,895
Fuel cost (\$)	28,571 (\$4/ton)	689,450(\$10/ton)
Total operating cost (\$)	62,247	788,345
Annual gas production (MBtu)	85,000	744,600
Gasification cost (\$/MBtu)	0.40	0.13
Gas cost (\$/MBtu)	0.73	1.06

^aData from Gross (1978).

In order to make these costs more directly comparable with each other and with other energy costs, we have used the cost analysis method developed at the Electric Power Research Institute (EPRI) for the Energy Research and Development Administration (ERDA) (Jet Propulsion Laboratory 1976). This method, developed initially to compare steam and power costs of fossil and nuclear fuels, has been used recently at SERI to develop a computer program for comparing various solar energy costs as well (Witholder 1978). The program uses certain assumptions (see Table 11-3) to determine anticipated capital flows and operating costs over the lifetime of the facility. These costs are then

bData from Amundsen (1976).



Table 11-3. FIRST-YEAR GAS COST AS A FUNCTION OF INPUT FUEL COST

	Biomass Cost				
	\$10/ton	\$20/ton	\$30/tor		
Gasifier A	1978 Cost \$1.41	\$2.58	\$3.74		
(14 MBtu/h)	Levelized Cost (2.08)	(3.78)	(5.49)		
Gasifier B	1978 Cost \$1.44	\$2.72	\$3.99		
(85 MBtu/h)	Levelized Cost (2.12)	(3.99)	(5.86)		

Assumptions:

Effective federal in Other taxes	come tax rates	0.48 0.82	(fraction of
other taxes		0.02	present value of capital investment)
Insurance premiums		0.0025	(fraction of present value of capital investment)
Capitalization Ratios:		Rate	of Return
Debt	0.50		0.08
Common stock	0.40		0.12
Preferred stock	0.10		0.08
Rates of Inflation (%)			
General economy	5 5		
Capital costs	5		
Operating costs	6		
Maintenance	6 7		
Fuel costs	7		



used to derive a fuel cost for the first year of the application and also a levelized cost over the assumed lifetime of the facility.*

We have used the EPRI/ERDA/SERI program to determine the cost of gas produced in the gasifiers described in Table 11-2 as a function of input fuel cost. These first-year fuel costs are shown in Table 11-3, derived from the assumptions listed. The levelized fuel costs are given in parentheses. In order to show the sensitivity of gas cost to the fuel, operating, and capital costs, these factors are listed separately in Table 11-4 for a fuel cost of \$20/ton. Since the gas cost depends linearly on fuel costs, the gas cost can be computed for any other input fuel cost by multiplying the fuel contributions from Table 11-4 by the fuel cost and dividing by 20; gas costs for other capital or operating costs can be determined in the same manner.

Tables 11-3 and 11-4 demonstrate that the principal factor determining gas cost is the cost of the biomass fuel used, with operating costs and capital costs affecting gas cost to a much lesser extent; thus gasification of low-cost forest and agricultural wastes (costing \$0 to \$15/ton) is very attractive in these days of rising fuel costs. Other biomass feed-stocks, such as cull trees and straw (costing \$15 to \$40/ton), are less attractive in comparison with today's natural gas costs but may soon be competitive. Other advantages for the use of gasifiers are that they can be operated intermittently when gas or oil is unavailable or too costly (depending on spot prices for both gas/oil and biomass), and that they dispose of unwanted biomass (which of itself would have a negative fuel value).

11.4 COMPARISON OF ALTERNATE FUEL CONVERSION OPTIONS

If it is difficult to establish cost guidelines for retrofitting gas/oil boilers with close-coupled gasifiers, it is even more difficult to compare these costs with those of other conversion options in a time of rapidly changing costs and varying availability of fossil fuels. In a recent study on wood combustion economics made by the Forest Products Laboratory (FPL), the authors explained that "the procurement cost of combustion equipment options is a dominant factor in their selection. In a combustion equipment survey, cost data were found to be very difficult to obtain without establishing point designs. Repetitive contact with manufacturers and review of published data ultimately resulted in a set of cost curves" (FPL 1976). We have used similar methods here to evaluate the use of gasifiers to retrofit existing gas/oil installations and to compare these costs to those of other options.

The options available today for converting from gas/oil are:

- Reconversion to solid fuel of an originally solid-fueled installation (which had been converted from gas/oil). Where possible, this is probably the most economical conversion, yet often the solid fuel handling equipment will have been scrapped, new emission control equipment will have to be added, and the existing boiler is likely to be old and inefficient.
- Replacement of the existing gas/oil boiler (often relatively new) and installation of a new solid fuel system burning coal or wood or other biomass. This will cost

^{*}The levelized cost is the constant price at which the gas must be sold over the life of the project to produce the required rated return.



Table 11-4. DETAILED COST BREAKDOWN FOR \$20/TON FUEL

	Gasi	fier A	Gas	ifier B
	(15 MBtu/h)		(85 MBtu/h)	
	1978 Cost	Levelized Cost	1978 Cost	Levelized Cost
Operating costs	\$0.11	\$0.15	\$0.13	\$0.19
Capital costs	0.06	0.09	0.13	0.19
Fuel costs	2.55	3.75	2.32	3.40
Total costs	\$2.72	\$3.99	\$2.58	\$3.78

Assumptions:

Capital and operating co Plant capacity factor = Tax and insurance rates	0.92	able 11-2	
Effective federal inc	0.48		
Other taxes		0.82	(fraction of
			present value of capital investment)
Insurance premiums		0.0025	
			present value of capital investment)
Capitalization Ratios:		Rate	of Return
Debt	0.50		0.08
Common stock	0.40		0.12
Preferred stock	0.10		0.08
Rates of Inflation (%)			
General economy	5		
Capital costs	5		
Operating costs	6		
Maintenance	6		
Fuel costs	7		



on the order of \$8 to \$30/lb steam/h and will require installation of new emission control equipment.

3. Installation of a close-coupled gasifier to operate the existing gas/oil equipment. This will cost on the order of \$4 to \$9/lb steam/h (see Tables 11-3 and 11-4) and will make use of much of the existing installation. It also permits using gas/oil where and when they are available and economical and permits use of biomass wastes that otherwise would not have value as fuels.

Figure 11-2 compares the costs of these options. It appears that the cost of adding a gasifier to an existing package boiler (Option 3) is about two-thirds the cost of installing a new wood-fired boiler (Option 2).

In general, the cost of package wood-fired boilers (\$8 to \$18/lb steam/h) is considerably less than that for field-erected boilers (\$15 to \$25/lb steam/h), which are required for generating steam in excess of about 10⁵/lb steam/h as shown by the FPL (1976) results in Fig. 11-2. An early study for several paper industries in Maine indicated the advantages of close-coupled gasifiers for retrofitting very large existing boilers (typically 2-10 X 10⁵/lb steam/h) with gasifiers (Reed and Stevenson 1975). At present, this attractive option for larger boilers is not available because there are no gasifiers with capacities greater than 10⁵/lb steam/h. Development of such a gasifier would allow the paper industry to convert from gas/oil at a minimum cost.

11.5 COMPARISON OF NEW CONSTRUCTION ECONOMICS

If gasifiers are more economical for retrofit, it may be asked whether their combination with an inexpensive gas/oil boiler (two-stage combustion) may also be preferable to conventional package wood-fired boilers for new installations. Adding the lower two curves of Fig. 11-2 gives prices for a complete new gasifier-boiler system of \$6.90-\$19.00/lb steam/h as compared to \$6.20-\$18.00/lb steam/h for conventional package wood-fired boilers. The closeness of these numbers is probably fortuitous, and it would be premature to conclude that the two-stage combustion option using a gasifier is superior to the conventional package wood-fired boiler, yet this possibility cannot be ruled out and should be investigated further. The economics which could favor the gasifier-boiler combination are the very low price of conventional gas/oil boilers as compared to wood boilers and the relative simplicity and low cost of gasifiers as compared to wood furnaces. In addition, the emissions from gasifiers may be lower than for conventional wood firing, and the turndown ratio of gasifiers may be superior to that for wood firing. Use of gasifiers would permit return to fossil fuel (dual fuel capability) should that be desirable.

A recent study on a fluidized-bed, medium energy gasifier now under development suggests that the combination of this more expensive technology with package boilers is at least comparable in cost to installation of solid fuel combustion equipment (Bailie and Richmond 1978).

11.6 CONCLUSIONS

- Gasifiers are now being developed for retrofitting existing boilers in the 10^4 - 10^5 /lb steam/h (10-100 MBtu/h) range to use wood and biomass residues.
- The cost of gas from these gasifiers is estimated to be \$1.40-\$2.70/MBtu for biomass feedstock costing \$10 to \$20/ton.



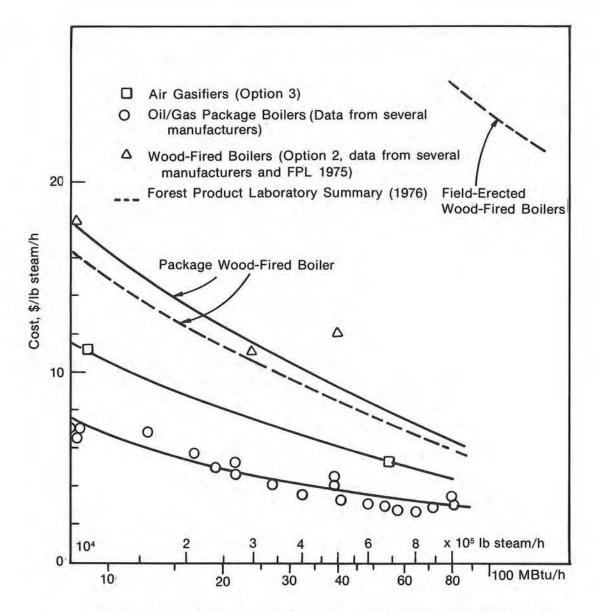


Figure 11-2. Cost Comparisons Between Retrofitting Existing Equipment and New Installations



- The addition of a close-coupled gasifier to an existing gas/oil boiler will cost on the order of two-thirds the cost of installing a new package wood-fired boiler.
- Although gasifiers larger than 100 MBtu/h (10⁵/lb steam/h) are not presently available, they could probably be used to convert existing field-erected gas/oil boilers to biomass more economically than construction of new wood-fired boilers.
- The use of a gasifier plus a low cost gas/oil boiler for new construction is comparable in cost to wood package boilers and should be investigated for future installations, particularly where dual fuel operation is desired.

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Chapter 12

Gas Conditioning

R. Bennett Mittlehouser Corp.



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CHAPTER 12

GAS CONDITIONING

12.1 INTRODUCTION

Biomass gasifiers of current design produce a raw gas consisting chiefly of carbon monoxide and hydrogen, with minor amounts of methane, higher molecular weight hydrocarbons, sulfur compounds, tars, and oil. When burned as a boiler fuel, the raw gas requires little or no cleanup. If the product gas is intended for use as a synthesis gas (for example, in the production of methanol) it will require substantial cleanup. Further improvements in gasifier design may reduce and even eliminate the tar and oil problems associated with gas cleanup. These improvements may also greatly reduce the formation of undesirable hydrocarbons. However, system studies for near-term commercial production of synthetic fuels from biomass must be based on current technology.

Many options are available for cleaning raw gas from currently available biomass gasifiers. However, before detailed designs of commercial facilities can be made, some preliminary review of available technology is needed to evaluate methods for the separation of tars, oil mists, and undesirable hydrocarbons from the raw gas and to examine the costs and requirements of each technology.

A study on gas conditioning was performed by the Mittelhauser Corporation under contract to SERI. Specific objectives of the study were to:

- Survey the technology available for eliminating oil mists from a hot gas stream.
- Estimate tolerances of commercial methanol synthesis catalysts for CH₄, C₂H₂, C₂H₄, C₂H₆, H₂S, and Cl.
- Survey the technology available for separating CH₄ and higher hydrocarbons from a CO-H₂ mixture.
- Estimate incremental costs of upgrading a 500 ton/day raw pyrolysis-gas stream to a synthesis gas for a methanol plant; specifically, a Purox gasifier, ICI methanol process.

The study was based on the following general assumptions:

- The ambient atmospheric pressure was assumed to be 14.7 psia.
- The overall methanol synthesis facility was assumed to be a grass-roots plant in the northeastern United States. The gas cleanup facilities to be studied were assumed to be part of the larger complex; thus, electric power, cooling water, and steam would be available as needed by the cleanup facilities. It was also assumed that concentrated waste hydrocarbon gases could be used as fuel in the plant's auxiliary steam generation system. Wastewater from the gas cooling step was assumed to require treatment as part of the gas cleanup system.
- · All costs were taken on a first quarter 1979 basis.
- Synthesis gas compression facilities were specifically excluded from the scope of the study. A qualitative assessment was made of the effect of different gas separation schemes and synthesis gas compression requirements.



- The methanol synthesis loop was assumed to be an Imperial Chemical Industries 50-atm process for manufacturing crude methanol.
- Generally, all plant units processing the main synthesis gas stream were designed to operate on a 90% stream factor. Spare parts were included to ensure this and to allow for on-line maintenance that could not be accomplished in a normal, once-per-year "turnaround."

Attention was focused on review and definition of the available technologies for oil mist elimination, gas separation, and gas cleanup. The designs developed here are felt to be reasonable, workable, and generally representative of the capital and operating requirements associated with the function each system performs. However, these designs are not optimized and should not be regarded as such. It is not possible to optimize a given section of a plant without considering fully all of the physical and economic interactions between that section and the remainder of the plant. Such considerations were outside the scope and time frame of the study, and were not made.

The study was based on 500 short tons per day of raw gas from a Union Carbide Corporation Purox gasifier fed with wood waste. The composition of the wood waste was based on that used in a study by Raphael Katzen Associates (1975). Yield data were based on published studies on the Purox process by Ralph M. Parsons Company (1978) and the City of Seattle (Mathematical Sciences 1974). These data were augmented by telephone conversations with Union Carbide technical personnel responsible for the Purox process.

Based on the sources cited above, the following assumptions were made:

- Oil yield on wood waste was assumed to be twice as high as on municipal refuse.
 The composition was assumed to be 94.6% carbon by weight; the balance hydrogen (Mathematical Sciences 1974).
 - Based on conversations with Union Carbide personnel, it was assumed that the oil was entrained in the raw gas as droplets from 1 to 10 microns in diameter. No specific size was available; it was assumed that 99.99% of the droplets were equal to or less than 10 microns diameter. The gas was assumed to be available at 400 F, 3 psig, as this was consistent with pressures and temperatures found in the literature (Ralph M. Parsons 1978).
- The wood waste was arbitrarily assumed to contain 0.1 wt % sulfur. This results
 in a quenched gas sulfur content comparable to that from municipal refuse. According to information from Union Carbide personnel, this is a conservatively
 high estimate.
- The yield of water-soluble organics was assumed to be the same as for municipal refuse. The composition was taken from the Ralph M. Parsons (1978) study.
- The moisture content of the feed was assumed to be 25 wt %, the same as in the Raphael Katzen (1975) study.
- Oil recovered in the gas cooling section was assumed to be recycled to extinction in the gasifier.
- Apart from water-soluble organics, sulfur, and oil, the raw gas yield was assumed to be the same as in Parsons (1978).



Tables 12-1 and 12-2 show the assumed rate and composition of the biomass feed and the effluent raw gas, respectively. This raw gas was used as the basis for all work done in this study.

Table 12-1. GASIFIER FEED (WOOD WASTE) COMPOSITION

Component	Feed Rate (lb/h)	Weight Fraction
Carbon	11,509.17	0.38049
Hydrogen	1,427.42	0.04719
Oxygen	9,017.00	0.29810
Nitrogen	22.69	0.00075
Sulfur	30.25	0.00100
Moisture	7,562.07	0.25000
Ash	679.68	0.02247
	30,248.28	1.00000

12.2 OIL MIST ELIMINATION

A brief review was made of the available technologies for removing oil droplets from a hot gas stream. For each technology a short description was prepared and currently commercial applications, expected efficiencies, advantages and disadvantages, rough utility requirements, and appropriate costs were reviewed and tabulated. The major effort was expended on the review of the applicable devices for oil mist removal currently on the market.

There are five basic mechanisms for collection of oil droplets from a flowing gas stream:

- Gravitational sedimentation. This will be of little consequence for droplets in the 1-10 micron size range.
- Inertial impaction and interception. This is a very effective method for mist removal that relies on multiple changes of direction of gas flow to cause collisions between droplets and a solid barrier.
- Centrifugal deposition. This mechanism relies on imparting a circular vortex motion to the gas stream, causing oil droplets to be hurled outward against a wall by centrifugal force. This is not particularly effective for droplets smaller than 5 microns in diameter.
- Electrostatic precipitation. If an electrostatic charge is induced on the droplets, they can be removed from the gas stream by a potential gradient. This mechanism is effective on all droplet diameters and can achieve a high collection efficiency.
- Droplet growth. The enlargement of a droplet by condensation on it of additional liquid, or by collision with other droplets, allows the droplet to be more easily collected by centrifugal force or inertial impaction.



Table 12-2. TYPICAL GASIFIER YIELD, INCLUDING EFFECT OF OIL RECYCLE

(Basis for Gas Conditioning Discussions)

Component	Mol Wt	Yield lb/h	Weight Fraction	lb/mol/h	Dry, Oil-Free Mole Fraction
H ₂	2.016	526.62	0.012639	261.22	0.236668
co	28.01	12,197.01	0.292726	435.45	0.394522
CO ₂	44.01	11,498.28	0.275957	261.27	0.236713
CH ₄	16.043	978.23	0.023477	60.98	0.055249
C_2H_2	26.04	198.43	0.004762	7.62	0.006904
C_2H_4	28.05	641.26	0.015390	22.86	0.020711
C ₂ H ₆	30.07	98.61	0.002367	3.28	0.002972
C ₃ H ₆	42.08	91.65	0.002200	2.18	0.001975
C ₃ H ₈	44.09	18.75	0.000450	0.43	0.000390
C ₄ H ₈	56.10	203.27	0.004878	3.62	0.003280
C ₄ H ₁₀	58.12	105.26	0.002526	1.81	0.001640
C ₅ H ₁₂	72.15	835.15	0.020043	11.58	0.010492
N ₂ +Ar	28.02	385.67	0.009256	13.76	0.012467
NH ₃	17.03	25.11	0.000603	1.47	0.001332
H ₂ S	34.08	25.71	0.000617	0.75	0.000680
Acetic acid	60.05	174.84	0.004196	2.91	0.002636
Methanol	32.04	216.28	0.005191	6.75	0.006116
Ethanol	46.07	84.09	0.002018	1.83	0.001658
Acetone	58.08	84.09	0.002018	1.45	0.001314
MEK	72.10	16.94	0.000407	0.23	0.000208
Propionic acid	74.08	67.15	0.001612	0.91	0.000824
Butyric acid	88.10	16.94	0.000407	0.19	0.000172
Furfural	96.08	84.09	0.002018	0.88	0.000797
Phenol	94.11	16.94	0.000407	0.18	0.000163
Benzene	78.12	9.98	0.000240	0.13	0.000118
Total dry oil-free		28,600.35	0.686403	1,103.74	1.000000
Oil		3,364.82	0.080755		
Total dry		31,965.17	0.767158		
Water vapor	18.016	9,701.83	0.232842	538.51	0.487896
Total		41,667.00	1.000000		1.487896



The following paragraphs examine the ways in which different scrubbing media and equipment might utilize these five mechanisms to remove oil mists from biomass pyrolysis gas.

12.2.1 Scrubbing Media

For removing oil droplets from the raw gas stream either oil or water or a combination of the two can be used as scrubbing media. Wet scrubbers use a liquid stream, either water or oil, to remove small liquid hydrocarbon droplets from a gas stream. The liquid droplets are captured by the liquid or by the scrubber mechanical structure and then washed off by the liquid. Table 12-3 outlines the salient features of oil and water scrubbing.

Table 12-3. FEATURES OF OIL AND WATER SCRUBBING

	Oil Scrubbing	Water Scrubbing
Disposal of purge liquid	Thermal oxidation with heat recovery or re- cycle after fractiona- tion	Water treatment before discharge
Oil droplet removal con- siderations	Entrainment and satura- tion of gas stream with oil	Oil entrainment from $\mathrm{H}_2\mathrm{O}$
Makeup quality	Oil might require fractionation to achieve proper boiling range material	Condensate quality water
Metallurgy	Carbon steel equipment is probably adequate if no water condensation occurs	Water will be acidic due to contaminants in gas: stainless steel scrubber required
Source of scrubbing medium	Available if oil produced by process can be used; otherwise must be imported	Readily available

12.2.1.1 Oil Scrubbing

If a multicomponent oil is used as the scrubbing medium, the lower-boiling components of the oil tend to saturate the gas stream at the operating temperature and pressure of the scrubbing device. A small amount of oil is unavoidably entrained in the gas stream. These two characteristics of oil as a scrubbing medium significantly reduce its capability to remove oil droplets from a raw gas stream. A purge stream equal to the quantity of oil removal from the gas stream must be taken out of the scrubbing system to maintain a



constant oil inventory. This purge stream can be fractionated to remove contaminants and recycled as scrubbing oil makeup or burned as a source of heat energy.

The scrubbing oil has the composition and physical properties of the oil removed from the Purox gas stream. To decide whether this oil is suitable for scrubbing, more physical property data on this oil are required. Ideally, the oil should have low viscosity at the system pumping temperature and a high boiling point to minimize vaporization losses. If the oil collected from the gas is not suitable as a scrubbing medium and cannot be upgraded by fractionation, scrubbing oil must be imported.

The oil scrubbing system can be made of carbon steel as long as there is no water condensation during removal of the oil droplets. If water condenses, it will collect the acidic components of the gas stream and corrode the carbon steel.

12.2.1.2 Water Scrubbing

If water is used as the scrubbing medium, the gas is saturated with water at the outlet temperature and pressure of the scrubbing system. Generally, water condenses from the gas stream and must be purged from the scrubbing system. Oil droplets removed from the gas stream by the water must be separated from the water phase. Furthermore, all the water-soluble components in the raw gas stream are present in the water. Consequently, the purge water would require treatment before discharge to make it environmentally acceptable.

Oil captured by the water in the scrubbing system may be reentrained in the gas stream. For example, in a plate column the raw gas may pick up the oil floating on the surface of the water.

The scrubbing water probably is corrosive to carbon steel due to the presence of organic and inorganic water-soluble acids. Consequently, the water scrubbing system might have to be stainless steel unless the surface were protected by passivation with $\rm H_2S$ or were coated with a corrosion-resistant material.

12.2.2 Oil Mist Elimination Devices

12.2.2.1 Plate Scrubbers

A plate scrubber is a vertical tower with one or more horizontal trays mounted on its inside surface. Gas enters at the bottom of the tower and must pass through perforations, valves, slots, or other openings in each plate before leaving the top of the scrubber. The scrubbing medium is introduced at the top plate and flows over each plate as it moves downward. In some designs, the gas passes through holes covered with caps. The caps act as impingement plates and are set below the liquid level on the plates. At low gas velocities, lightweight caps on alternate rows rise first while the heavyweight caps in the other rows remain in the closed position. All the caps are finally opened when the gas flow reaches the design condition.

The liquid flows across each tray and is kept in a froth by the gas, which exits each cap at high velocity. Fine droplets of liquid are generated that will absorb impurities from the gas stream. Also, adiabatic cooling and condensation or humidification of the gas



stream occurs. Before the gas stream leaves the scrubber it passes through a mist eliminator to remove liquid droplets.

In oil mist separation devices that use wet scrubbing, collection efficiency increases with pressure drop. For plate scrubbers, gas pressure drops of as much as 6 to 15 in. of water can be achieved. Approximately 80% of droplets of 5-micron and larger diameters can be removed with a pressure drop of 10 in. of water. The oil droplet collection efficiency is set by the performance of the mist eliminators. If the water is used as the scrubbing medium, some of the oil removed from the gas is reentrained as the gas passes through the oil-water mixture. If oil is used as the scrubbing medium, product oil is removed, but scrubber oil is entrained and vaporized in the gas stream.

12.2.2.2 Packed Bed Scrubbers

Scrubbers contain packing such as rings or saddles. The gas-liquid contact may be cocurrent, countercurrent, or cross flow. The primary collection mechanisms in packed beds are inertial impaction and centrifugal deposition with subsequent drainage.

Collection efficiency for droplets larger than 0.3 micron rises as packing size decreases. Approximately 50% of 1.5-micron droplets can be removed by a column packed with 1-in. Berl saddles or Raschig rings. A 1/2-in. packing can achieve 50% removal of 0.7-micron droplets at a gas velocity of 30 fps.

Packed scrubbers are subject to plugging but can be shut down periodically to change the packing. Temperature limitations are of special importance when plastic packing is used, and corrosion can result when metallic packing is used. Packed columns have the same reentrainment problems as those described for plate columns.

12.2.2.3 Spray Scrubbers

A spray scrubber collects oil droplets or liquid droplets that have been atomized by spray nozzles. The properties of the droplets are determined by the configuration of the nozzle, the liquid to be atomized, and the pressure at the nozzle. Sprays leaving the nozzle are directed into a chamber shaped so that the gas passes through the atomized droplets. Horizontal and vertical gas flow paths have been used, as well as spray trajectories either cocurrent, countercurrent, or crossflow to the gas. If the tower is vertical, the gas flow must be slower than the terminal settling velocity of the droplets to prevent massive droplet entrainment.

Droplet collection in these units results from inertial impaction on the droplets generated by the spray. Droplet removal efficiency is a complex function of droplet size, gas velocity, liquid-to-gas ratio, and droplet trajectories. The optimal droplet diameter varies with fluid flow parameters.

Spray scrubbers utilizing gravitational settling can remove about 50% of 2-micron particles at moderate liquid-to-gas ratios. Gas phase pressure drop is usually very low. Spray scrubbers are almost immune to plugging on the gas flow side but are subject to severe problems on the liquid side. The circulating scrubber medium can erode and corrode nozzles, pumps, and piping. Nozzles are subject to plugging with circulating solids. The liquid-to-gas ratio depends on the removal efficiency required but can run as high as 30 to



100 gal per 1000 ft³ of gas treated: thus, sprays generate a heavy loading of liquid, which must be collected.

12.2.2.4 Venturi Scrubbers

A venturi scrubber uses high gas velocities (200 to 400 fps) to atomize liquid into droplets and then accelerate the droplets to promote droplet collection. Liquid may be introduced in several ways without affecting collection efficiency. Usually the liquid is introduced at the entrance to the throat through several straight pipe nozzles directed radially inward.

Oil mist removal from the gas is achieved by coalescence with the generated droplets. Removal efficiency increases with throat velocity and liquid-to-gas ratios.

Venturi scrubbers are the smallest and simplest of all scrubbers. They do not plug easily but are subject to corrosion due to the high throat velocity. They can be built with adjustable throat openings to permit variation in pressure drop and collection efficiency. Liquid-to-gas ratios ranging from 5 to 20 gal per 1000 ft³ have been used. It is important to note that all of the scrubbing liquid is entrained in the gas and must be removed by subsequent separation.

Ejector venturis are spray devices in which a high-pressure spray is used both to collect the droplets and to move the gas. High relative velocity between the liquid and the gas helps droplet separation.

12.2.2.5 Wet Scrubber Combinations

Combinations of wet scrubbers can be used for oil droplet removal. For example, a venturi scrubber can be used to remove the bulk of the oil droplets, followed by a plate scrubber to separate the entrained liquid from the gas.

12.2.2.6 Mist Eliminators

Beds of fibers called mist eliminators can be used in various configurations for collecting oil droplets. The fibers can be made from plastic, spun glass, fiberglass, or steel. Fibrous packings usually have a very high void fraction ranging from 97% to 99%. The fibers should be small in diameter for efficient operation but strong enough to support collected droplets without matting. A cocurrent, countercurrent, or cross flow arrangement can be used to flush any collected material from the fiber.

Collection in a mist eliminator is by inertial impaction as the gas flows through the fibers. Efficiency increases as fiber diameter decreases and as the gas velocity increases. Approximately 50% of 5- to 10-micron droplets can be removed by a knitted wire mesh made of 0.11-in. diameter wire.

Mist eliminators are susceptible to plugging, and they can be impractical where scaling persists. They also are especially sensitive to chemical, mechanical, and thermal attack.



12.2.2.7 Wet Electrostatic Precipitation (ESP)

Wet electrostatic precipitators operate by electrostatically charging the oil droplets as they pass through a corona developed by a negatively charged electrode. Each droplet in the gas stream is attracted to a grounded collection plate or to the inside walls of the pipes through which the gas flows. After collection, the liquid is washed down by additional liquid flowing countercurrently to the gas. The wet ESP is very efficient for collecting very small, submicron-sized droplets; electric power usage is negligible, and pressure drop across the ESP is very low, usually less than 1 in. of water.

Droplet collection is extremely efficient; essentially all droplets larger than 1-micron diameter can be collected. Disadvantages of wet ESP are high capital cost, poor performance when flow variations are encountered, and high maintenance requirements. For a wet ESP to operate satisfactorily, the gas must be cooled from 400 F to about 150 F. This often requires a wet scrubber ahead of the ESP to saturate the gas, with the ESP then used as a final cleanup device.

12.2.3 Similar Applications

The use of scrubbers to control various air pollution sources was studied in a survey carried out as part of the work reported in the <u>Scrubber Handbook</u> (APT, Inc. 1972). The only wet scrubbers reported to be used for oil mist removal are packed bed, mist eliminators, and spray towers. Wet ESP is used to remove entrained coal tar and coal tar mist from coke oven gas (COG) in COG processing plants. Table 12-4 summarizes the application of the various scrubbers.

12.2.4 Summary of Findings

Table 12-5 summarizes the findings of this survey. The major operating costs of wet scrubbers are power requirements for circulation of the scrubbing medium. For mist eliminators and ESP, power requirements are minimal. Capital costs of wet scrubbers can vary widely depending on design and operating conditions of the devices surveyed; mist eliminators are generally least expensive and ESP the most expensive.

12.3 METHANOL CATALYST TOLERANCE

Available information was reviewed and suppliers of commercial methanol synthesis catalysis were contacted by telephone to determine the catalyst tolerances to impurities found in the raw pyrolysis gas. A table was prepared containing the catalyst supplier, synthesis process, catalyst type, specific poison, and maximum recommended concentration. In addition to hydrocarbons, H₂S, COS, chlorides, nitrogen compounds, and HCN were investigated.

The study of methanol catalyst tolerances produced surprisingly sparse results. This is due at least partly to the fact that most manufacturers have little or no operating experience with synthesis gases derived from feedstocks such as coal, municipal solid waste, or biomass. Most present commercial methanol processes are based on a synthesis gas produced by steam re-forming natural gas, LPG, or naphtha. Therefore, the only hydrocarbon present to an appreciable extent is methane. Nitrogen is present primarily as N₂.



Table 12-4. SURVEY OF SCRUBBER APPLICATIONS IN A VARIETY OF INSTALLATIONS

			Scrubber Type		
	Plate	Packed	Mist Eliminators	Spray	Venturi
Calcining	6 (1)b	2 (1)	(0)	13 (5)	21 (23)
Combustion	17 (3)	(0)	(0)	5 (2)	2 (2)
Crushing	6 (1)	(0)	(0)	(0)	(0)
Drying	39 (7)	(0)	(0)	10 (4)	18 (19)
Gas Removal	17 (3)	72 (33)	40 (2)	45 (18)	9 (10)
Liquid Mist Recovery	0 (0)	24 (11)	60 (3)	7 (3)	(0)
Smelting	17 (3)	2 (1)	(0)	20 (3)	50 (54)

^aThe table should be read vertically. For example, 39% of plate-type scrubbers are used to control discharges from drying processes.

Little information is available about the potential catalyst poisoning capabilities of olefins, acetylene, HCN, $\rm NH_3$, and $\rm NO_x$. Available information is usually expressed in qualitative terms. The three catalyst suppliers contacted indicated that little is known about synthesis catalyst poisons in synthesis gases produced by the gasification of municipal solid waste, biomass, or coal.

The catalyst suppliers were concerned primarily with sulfur and chlorine. When the sulfur and chlorine levels are lower than 50 ppm each, zinc oxide provides a satisfactory means of desulfurization and dechlorination. The literature commonly refers to complete sulfur removal by means of zinc oxide guard beds. Most methanol synthesis plants use zinc oxide as the final desulfurization step, just prior to steam re-forming. However, activated carbon must be used when acetylene is present, because the high temperatures (500-700 F) required for proper use of zinc oxide cause polymerization of the acetylene and plugging of the beds.

^bThe numbers in parentheses refer to the number of separators reporting information to the survey.

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Table 12-5. SUMMARY OF MIST ELIMINATION SURVEY RESULTS

Device	Plate Scrubber	Packed Scrubber	Spray Scrubber	Venturi	Mist Eliminator	Wet ESP
Pressure drop (in. H ₂ O)	10	0.24-0.5 ^d	1 - 3	10 - 30	1 - 3	1
Droplet size (microns) at percentage removal	5 at 80	1.5 at 50	2 at 50	5	5 - 10 at 50	1 at 100
Circulation (gpm/1000 acfm)	2-50	2-50	30-100	5-20	₃₋₅ e	Variable
Capital cost	(a)					(b)
Operating cost	Power	Power	Power	Power	Minimal	Minimal
Maintenance cost	Nominal	Nominal	Nominal	Nominal	Nominal	High

^aPlate scrubber is the most expensive wet scrubber; venturi is the least expensive wet scrubber.

^bWet ESP is the most expensive of all devices considered.

^cThree to five gpm/ft² of mist eliminator cross-sectional area.

dPressure drop per foot of packed height.



Methane and heavier paraffin hydrocarbons, together with nitrogen and water vapor, are inert. However, their presence in significant quantities reduces the conversion of CO and H₂ to methanol by lowering the partial pressures of these reactants.

Table 12-6 summarizes the information obtained from the study.

12.4 GAS SEPARATION TECHNOLOGY

Using as a basis the Purox raw gas shown in Table 12-2, a rough estimate was made of the rate and composition of the gas, leaving out the oil mist elimination step. The primary objective of the gas separation study was to review various methods of removing unsaturated hydrocarbons from the synthesis gas. Our early review of available data indicated that paraffin hydrocarbons are not poisons to the catalyst. However, technology was incorporated in each design that would remove most of these paraffins from the synthesis gas to reduce the purge gas requirements in the methanol synthesis process.

Removal of sulfur compounds and chlorine from the synthesis gas is accomplished in facilities separate from the gas separation units. The design of these facilities is discussed in Section 12.5.2.2.

The three separation technologies reviewed were hydrogenation, re-forming, and cryogenic separation. Process alternatives to these technologies were examined qualitatively and are discussed in Section 12.5.2.9.

12.4.1 Hydrogenation

12.4.1.1 Design Basis

A block flow diagram of hydrogenation technology is shown in Fig. 12-1. The hydrogenation scheme consists of two principal sections: the first provides for the hydrogenation of olefins by the hydrogen in the clean raw gas, and the second is designed to remove CH_4 and heavier paraffins from the gas by oil absorption.

Katalco Corporation is a leading supplier of methanol synthesis catalyst for the ICI 50-atm process. Their technical representatives recommended catalysts and process conditions for the hydrogenation section. A two-stage hydrogenation unit was selected, due to its reliability and ease of operation. The unit is designed to reduce the olefin content of the exit gas to 100 ppmv. Katalco supplied catalyst bed volumes, estimated reactor inlet temperature and temperature rises across each stage of hydrogenation, and gave catalyst prices and estimated catalyst lives. For the oil absorption section, a rough design was prepared based on published literature (Sherwood and Pigford 1952).

12.4.1.2 Process Description

In the following discussion, reference is made to Fig. 12-2, Process Flow Diagram for Gas Separation—Hydrogenation, and the associated material balance shown in Table 12-7. The battery limit of the hydrogenation technology is the outlet of the chlorine guard beds. At this point the sulfur and chlorine have essentially been completely removed from the gas, which is at 150 F and 121 psig.



Table 12-6. METHANOL SYNTHESIS CATALYST POISON TOLERANCE

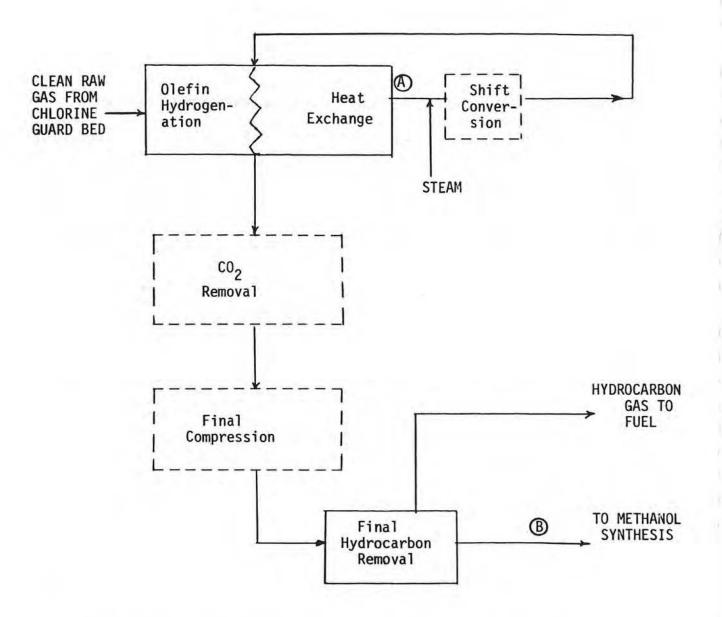
		In	formation Source			
Information	Supplier: United Catalysts Louisville, KY	Supplier: Haldor-Topsoe Houston, TX	Supplier: Katalco, Inc. Oak Brook, IL	Literat	ure ^a	Literature ^b
Process	ICI (50 atm)	Haldor-Topsoe (50-150 atm)	ICI (50 atm)	Not sp	ecified	300-400 atm
Catalyst Type	C79-4 Cu-Zn Base	Cu-Zn-Cr Oxides		Cu- Based	Zn- Based	ZnO 570-750 F
Component:						
C ₂ H ₂	Possibly poisonous	Unknown	Apparently not a problem		not poison-	Poison at more than
C ₂ H ₄ , higher olefins	Possibly poisonous	Unknown	Apparently not a problem		ous in "small quantities"	3 ppm
CH ₄ , C ₂ H ₆ , higher paraffins	Inert	Inert	Inert			
Sulfur (as H ₂ S, COS, CS ₂)	0.1 lb sylfur per ft ³ of catalyst ^c	Poison at more than 0.03 ppm	Poison at more than 0.5 ppm	Poison at 0.7 ppm	Rever- sible Poison	Poison at more than 3 ppm
Chlorides	0.035 lb per ft ³ catalyst ^c	Poison at more than 0.03 ppm	Poison at more than 0.2 ppm			
NH ₃	Possible poison with liquid H ₂ O present	Unknown				
NO _X	Unknown	Possible poison			May cause amine for- mation	
HCN	Unknown	Possible poison	Possible poison			
Fe, Ni						Form car- bonyls with CO, causing CH ₄ for- mation over the catalyst

a_{Natta} 1955.

bManufacturing Chemist 1978.

^cCatalyst is spent when this level is reached in the upper half of the bed.





Notes:

Units in dotted outline are not part of the separation scheme; gas at point A contains no more than 100 ppmv olefins, wet basis; and gas at point B contains no more than 3.8 mole percent hydrocarbons, wet basis.

Figure 12-1. Hydrogenation Block Flow Diagram

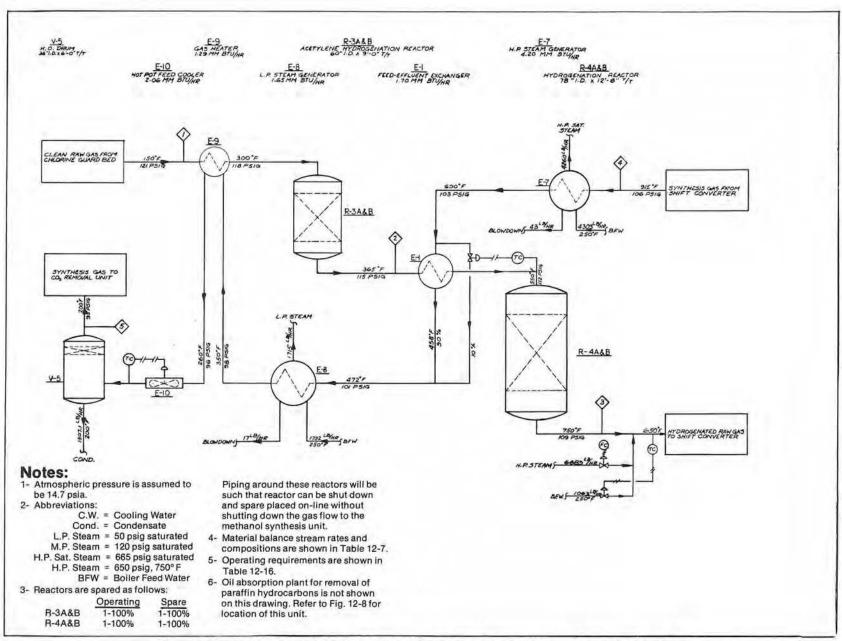


Figure 12-2. Process Flow Diagram for Gas Separation—Hydrogenation

Table 12-7. MATERIAL BALANCE FOR GAS SEPARATION—HYDROGENATION (Refer to Fig. 12-2)

				Stream Number			
	1	2	3	4	5	6	7
Component (lb-mol/h)	Clean Gas from Chlorine Guard Bed	Acetylene Hydrogena- tion; Reactor Effluent	Hydro- genation Reactor Effluent	Shift Converter Effluent	Synthesis Gas to CO ₂ Re- moval Unit	Synthesis Gas to Methanol Synthesis	Hydrocarbon Gas to Fuel
Н2	261.22	253.60	217.32	440.83	440.83	440.83	
co	435.45	435.45	435.45	211.94	211.94	211.94	
CO ₂	261.27	261.27	261.27	484.78	484.78	34.36	
CH ₄	60.98	60.98	60.98	60.98	60.98	27.56	33.42
C_2H_2	7.62						
C_2H_2 C_2H_4	22.86	30.48					
С ₂ Н ₆	3.28	3.28	33.76	33.76	33.76	0.44	33.32
C_3H_6	2.18	2.18					
C3H8	0.43	0.43	2.61	2.61	2.61		2.61
C4H8	3.62	3.62					
C_4H_{10}	1.81	1.81	5.43	5.43	5.43		5.43
C_5H_{12}	11.58	11.58	11.58	11.58	11.58		11.58
$N_2 + Ar$	13.76	13.76	13.76	13.76	13.76	13.76	
H ₂ S	>0.5 ppm ^a						
H ₂ O	14.66	14.66	14.66	221.13	148.58	1.03	-
TOTAL	1,100.72	1,093.10	1,056.82	1,486.80	1,414.25	729.92	86.36

^aMaximum value; less than 0.1 ppm expected.



The poison-free gas, containing about 3 vol % unsaturated hydrocarbons, is heated and hydrogenated in two steps. In the first step, the raw gas is heated to 300 F against the partially cooled shift converter effluent gas in exchanger E-9 and passed over a bed of palladium-on-allumina catalyst contained in reactors. The palladium catalyst selectively hydrogenates acetylene to ethylene. This prevents polymerization of the acetylene at the higher temperatures used for general olefin hydrogenation. The exit temperature of this bed, about 365 F, is higher than normally employed. However, the CO concentration in the gas tends to moderate the reaction. The hydrogen partial pressure in this reactor is about 31 psia, which is sufficient to carry the hydrogenation essentially to completion.

In the second step, the acetylene hydrogenation reactor effluent is heated from about 365 F to 550 F against higher temperature shift effluent in exchanger E-1. The gas is then passed over a bed of nickel-molybdenum catalyst in reactor R-4A&B. In this bed, hydrogenation of the remaining olefins takes place. The palladium catalyst used in the first hydrogenation step is poisoned by sulfur; therefore, sulfur has been removed from the gas prior to that step. However, in the absence of sulfur, cobalt-molybdenum catalyst, which ordinarily would be used in hydrogenating olefins, promotes the methanation reaction:

$$CO + 3H_2 - CH_4 + H_2O$$

To prevent this loss of synthesis gas, the nickel-molybdenum catalyst has been used for second-stage hydrogenation.

Hydrogenated synthesis gas exits reactor R-4A&B at a temperature of approximately 750 F. Attemperated steam is then added as required for shift conversion, and the gas passes to the shift converter, which is not considered part of the gas separation scheme.

Both R-3 and R-4 are provided with full-capacity spares. In case excessive olefin breakthrough occurs, plugging of the catalyst by polymerized acetylene or poisoning of R-3 by sulfur breakthrough will result and each bed can be taken off line and the spare bed put in service.

Shift converter effluent is cooled in exchangers E-7, E-1, and E-9 by generating 665 psig saturated steam and preheating the hydrogenation reactor feed streams. Between E-1 and E-9 the shift effluent is cooled in exchanger E-8 by generating 50 psig saturated steam. This is done to keep the tube wall temperatures in E-9 sufficiently low to prevent polymerization of the olefins in the feed to R-3A&B. Final cooling is done in air cooled exchanger E-10, with condensate separation in vessel V-5. The cooled gas at 200 F then passes into the CO₂ removal unit, which is not considered part of the gas separation scheme.

The final part of the hydrogenation-gas separation process is an oil absorption unit. This unit follows final compression of the synthesis gas to about 750 psig. After being cooled to 100 F, the gas passes through the absorber, in which it flows countercurrently to a stream of absorption oil of approximately 161 molecular weight. The oil removes paraffinic hydrocarbons from the gas. Rich oil from the base of the absorber is pumped to a steam stripper where the absorbed gases are distilled overhead and sent to the fuel gas system. Regenerated lean oil is pumped back to the absorber. The treated gas from the oil absorption unit contains approximately 4 mole % $\mathrm{CH_4}$ and heavier hydrocarbons. It goes directly into methanol synthesis. The theoretical methanol make from this synthesis gas is 162,970 lb/day.



An overall rough energy balance for the hydrogenation technology is presented in Table 12-8. This balance excludes the oil absorption unit, as no energy balance was made for that unit.

Table 12-8. ENERGY BALANCE FOR HYDROGENATION (10⁶ Btu/h)^a

Inputs	
Raw gas	156.37
BFW import	1.15
Steam import ^b	9.22
Electric power	0.06
Outputs	
Shifted gas to CO ₂ removal	157.35
Steam export	6.97
Cooling losses	2.06
Blowdown	0.02
Condensate export	0.18
	166.58

^aEnergy quantities include sensible enthalpies and higher heating values relative to 60 F, 1 atm pressure with water in the liquid state. Oil absorption is not included in the energy balance.

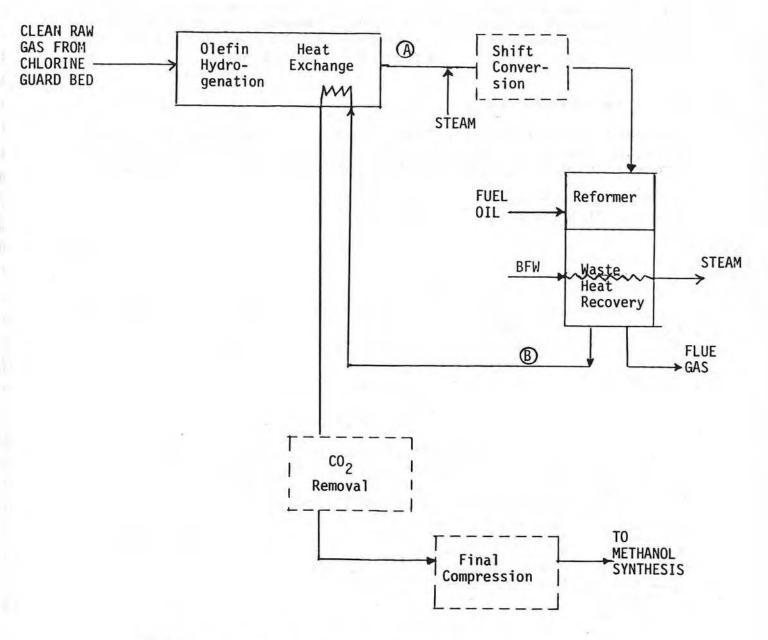
12.4.2 Re-forming

12.4.2.1 Design Basis

The re-forming technology for hydrocarbon separation is shown schematically in Fig. 12-3. KTI, Inc., a leading supplier of steam-hydrocarbon re-forming furnaces, prepared a process design package for the re-forming step shown in the figure. To prevent cracking of olefins in the re-forming furnace, with subsequent carbon laydown, KTI recommended the hydrogenation of all olefinic compounds upstream of the re-former. Therefore, the hydrogenation unit described in Section 12.4.1 was also incorporated in this gas separation scheme. The re-former converts only paraffin hydrocarbons to CO and H₂. Furthermore, KTI recommended that the shift converter be placed between the olefin hydrogenation section and the re-former. This was done to reduce the concentrations of CO entering the re-former and to prevent cracking of CO with subsequent carbon laydown.

bSteam includes attemperation water.





Notes:

Units in dotted outline are not part of the separation scheme, gas at point A contains no more than 100 ppmv olefins, wet basis; and gas at point B contains no more than 0.05 mole percent hydrocarbons, wet basis.

Figure 12-3. Re-forming Block Flow Diagram



KTI provided heat and material balance data for the re-former, shift converter, and waste heat recovery sections. Although the shift converter is not included in the "re-forming" scheme, knowledge of process conditions around it is required to specify steam requirements and to design the heat exchange trains for the scheme.

12.4.2.2 Process Description

Reference is made in the following discussion to Fig. 12-4, Gas Separation—Re-forming, and to the associated material balance shown in Table 12-9. The battery limits of reforming technology are the same as for the hydrogenation technology just described.

Re-forming uses high temperatures and catalytic activity to crack higher paraffin hydrocarbons to CH_4 and to re-form the methane to CO and H_2 :

$$C_2H_6 + H_2 \rightarrow 2CH_4$$
, (12-2)

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
. (12-3)

Because of these high temperatures, all of the unsaturated hydrocarbons should be eliminated from the gas to prevent carbon laydown on the catalyst. In addition, high inlet concentrations of carbon monoxide can cause carbon laydown due to the Boudouard reaction:

$$2CO \rightarrow C + CO_2. \tag{12-4}$$

Therefore, the gas must undergo shift conversion before it enters the re-forming furnace.

Clean raw gas from the chlorine guard beds is heated and hydrogenated exactly as in the hydrogenation technology discussed in Section 12.4.1. Effluent from reactor R-4A&B is quenched from 750 F to 662 F with attemperated steam and is fed to the shift converter. The shift converter is not considered part of the gas separation technology.

Shift converter effluent at 904 F passes to the re-forming furnace, H-2. The shift converter effluent, lean in CO, contains sufficient steam such that no additional steam injection is required before the furnace. The re-former feed gas is heated to 1004 F in the convection section of the furnace and fed to the catalyst beds, where the hydrocarbons are re-formed to CO and H₂. The re-former is fired with imported No. 2 fuel oil at a rate of 3,582 lb/h.

Waste heat is recovered from the re-forming furnace flue gases by generating high-pressure superheated steam at 650 psig, 750 F. The saturated steam produced by the high-pressure steam generator, E-20, is also superheated.

The re-former effluent, containing no hydrocarbons heavier than methane and containing hydrogen and carbon monoxide in the proper ratio for methanol synthesis, is cooled first by generating high-pressure saturated steam in exchanger E-20; it is cooled further against the hydrogenation reactor feed streams in exchangers E-19 and E-18, with an intermittent stage of low-pressure saturated steam generation in exchanger E-21.

The synthesis gas is finally cooled to 200 F in air-cooled exchanger E-22 before being fed to the ${\rm CO}_2$ removal unit. This unit and downstream units are not considered to be part

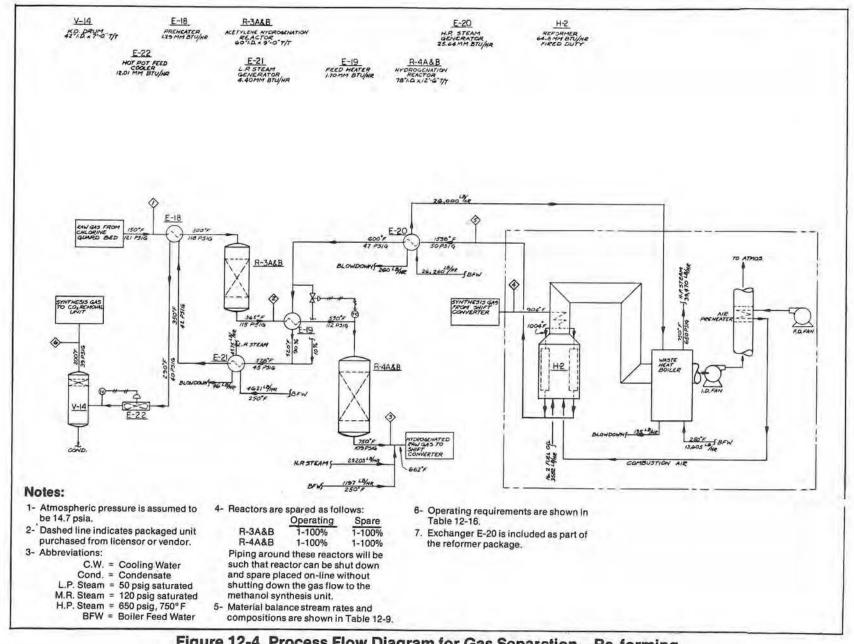


Figure 12-4. Process Flow Diagram for Gas Separation—Re-forming

Table 12-9. MATERIAL BALANCE FOR GAS SEPARATION - RE-FORMING (Refer to Fig. 12-4)

				Stream Number			
	1	2	3	4	5	6	7
Component (lb-mol/h)	Clean Gas from Chlorine Guard Bed	Acetylene Hydrogena- tion; Reactor Effluent	Hydro- genation Reactor Effluent	Shift Converter Effluent	Reformer Effluent	Synthesis Gas to CO ₂ Re- moval Unit	Synthesis Gas to Methanol Synthesis
H ₂	261.22	253.60	217.32	579.33	952.59	952.59	952.59
CO	435.45	435.45	435.45	73.44	457.37	457.37	457.37
CO_2	261.27	261.27	261.27	623.28	454.05	454.05	74.21
CH ₄	60.98	60.98	60.98	60.98	1.26	1.26	1.26
C_2H_2	7.62						
C_2H_4	22.86	30.48					
C_2H_6	3.28	3.28	33.76	33.76			
C_3H_6	2.18	2.18					
C_3H_8	0.43	0.43	2.61	2.61			
C4H8	3.62	3.62					
C_4H_{10}	1.81	1.81	5.43	5.43			
C_5H_{12}	11.58	11.58	11.58	11.58			
$N_2 + Ar$	13.76	13.76	13.76	13.76	13.76	13.76	
H_2S	$< 0.5 \text{ ppm}^{a}$						
H ₂ O	14.66	14.66	14.66	1,117.99	1,072.53	513.48	26.97
TOTAL	1,100.72	1,093.10	1,056.82	2,522.16	2,951.56	2,392.51	1,526.16

^aMaximum value, less than 0.1 ppm expected.



of the gas separation technology. An energy balance for re-forming technology is presented in Table 12-10.

Table 12-10. ENERGY BALANCE FOR RE-FORMING (10⁶ Btu/h)^a

nputs	
Raw gas	156.37
BFW import	8.47
Steam import ^b	34.22
Fuel oil import	64.83
Electric power	0.55
	264.44
	185.63
Outputs Shifted gas to CO ₂ removal	185.63
Steam export	58.51
Cooling losses	12.01
	0.19
Blowdown	
Blowdown Condensate export	1.41
	1.41 5.75

^aEnergy quantities include sensible enthalpies and higher heating values relative to 60 F, 1 atm pressure, with water in the liquid state.

The gas to the methanol synthesis reactor section will contain approximately 1 vol % inert gases, mainly nitrogen, on a dry basis. The theoretical methanol make as a result of employing this technology is 351,700 lb/day, more than twice the theoretical methanol make attributable to gas separation by hydrogenation.

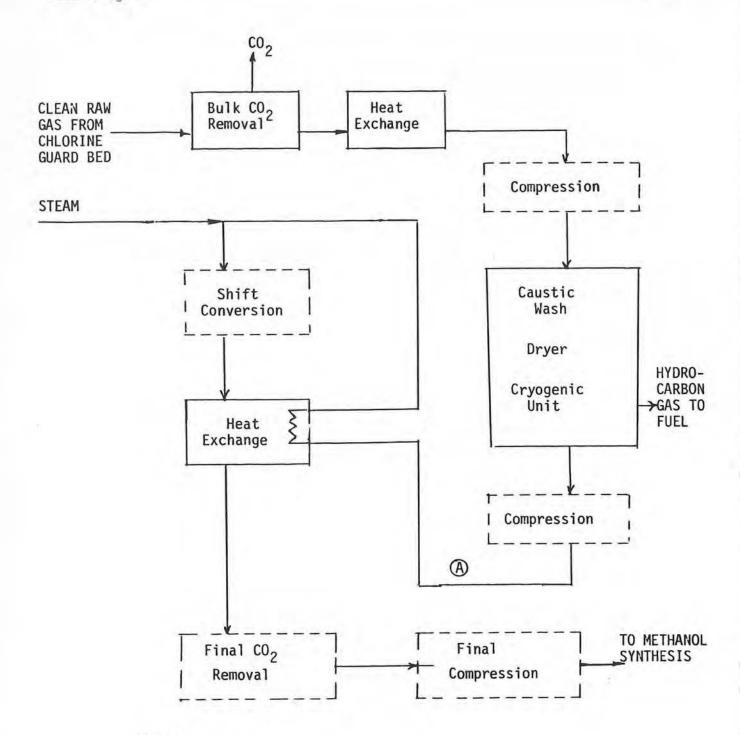
12.4.3 Cryogenic Separation

12.4.3.1 Design Basis

Cryogenic technology for hydrocarbon separation is shown schematically in Fig. 12-5. The central technology is expansion-refrigeration, for which a package unit was supplied

bSteam includes attemperation water.





Notes:

Units in dotted outline are not part of the separation scheme; and gas at point A contains no more than 1.5 mole percent hydrocarbons, wet basis.

Figure 12-5. Cryogenic Separation Block Flow Diagram



by Linde Division of Union Carbide Corp. However, this technology requires the following additional units ahead of the packaged unit to prepare the feed gas:

- bulk CO₂ removal,
- final CO₂ removal, and
- · dehydration.

In addition, compressors are required before and after the cryogenic unit. The compressor ahead of the unit raises the gas pressure to 400 psig prior to expansion, while the second compressor restores the original pressure of approximately 103 psig. Neither compressor was included in the design, operating requirements, or costs of this scheme; however, the qualitative effects of differences in compression requirements among the gas separation schemes are discussed in Section 12.5.2.4.

A hot potassium carbonate unit for bulk $\rm CO_2$ removal was designed by Mittelhauser from published methods (Kohl and Riesenfeld 1974; Maddox and Burns 1967). For final $\rm CO_2$ removal, caustic scrubbing was selected. Performance requirements and costs for a molecular-sieve dehydration unit were supplied by Linde.

12.4.3.2 Process Description

Reference is here made to Fig. 12-6, Gas Separation—Cryogenics, and to its material balance presented in Table 12-11.

Cryogenic separation technology requires that compounds which solidify or form hydrates at the low temperatures in the separation unit be removed from the gas before it enters the unit. Such compounds include $\rm H_2S$, $\rm CO_2$, $\rm HCl$, and water. As in the previously described technologies, chlorine guard bed effluent is taken as the battery limits of the gas separation technology. Therefore, only $\rm CO_2$ and water must be removed ahead of the cryogenic unit.

Clean raw synthesis gas is first heated to 200 F against CO₂ absorber overhead in exchanger E-12. It then enters the absorber, V-10, where about 96% of the CO₂ is absorbed by countercurrent stagewise contact with a hot aqueous potassium carbonate solution. Rich solution from the absorber flows to the stripper V-11, in which the CO₂ is liberated from the solution by reboiling with steam in exchanger E-11. The lean carbonate solution is pumped by P-8A&B back to the top of the absorber. The overhead from the top tray of the stripper is cooled against cooling water in a vertical tube bundle mounted in the top of the stripper. This process recovers water and potassium carbonate from the overhead; the cooled, CO₂-rich gas is vented to the atmosphere. Two atmospheric storage tanks, TK-1 and TK-2, have been included for fresh solution storage and to hold the liquid inventory of the system during planned maintenance shutdowns.

Gas from the CO₂ absorber, containing about 11,600 ppmv CO₂, is cooled to 100 F by heat exchange in E-12 and E-14. Condensate is separated in the knockout drum V-12. The cooled gas, at 110 psig, enters the cryogenic package.

The cryogenic unit relies on autorefrigeration of the gas by Joule-Thomson expansion to develop the low temperatures required for condensation of the hydrocarbons. First, the gas is compressed to 400 psig. Remaining carbon dioxide is removed from the gas by caustic scrubbing, and the gas is dehydrated by adsorption in a molecular sieve unit.

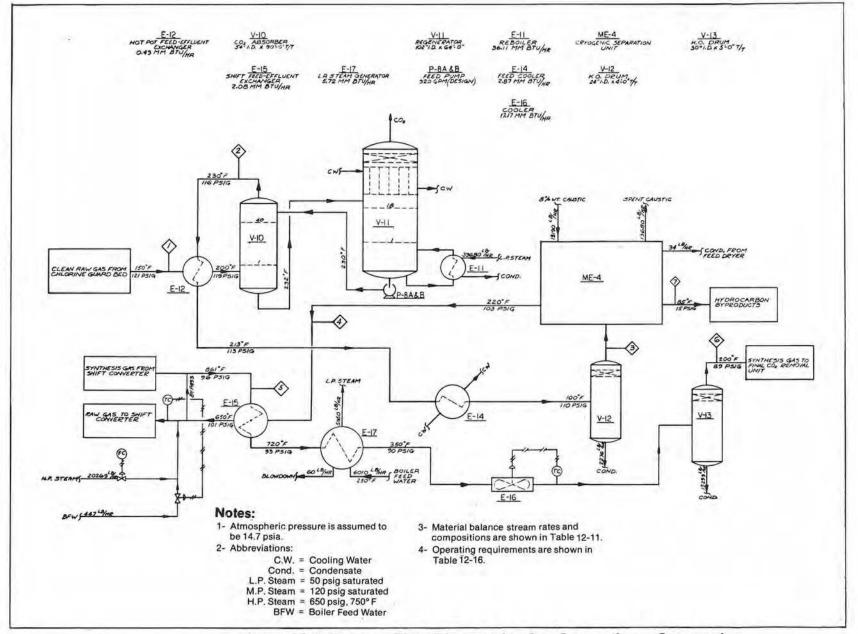


Figure 12-6. Process Flow Diagram for Gas Separation—Cryogenics

Table 12-11. MATERIAL BALANCE FOR GAS SEPARATION - CRYOGENIC SEPARATION (Refer to Figure 12-6)

				Stream	Number			
	1	2	3	4	5	6	7	8
Component (1b-mol/h)	Chlorine Guard Bed Effluent	CO ₂ Absorber Effluent	Cryogenic Unit Feed	Cryogenic Unit Effluent	Shift Converter Effluent	CO ₂ Removal Unit Feed	Synthesis Gas to Methanol Synthesis	Hydro- Carbon Gas to Fue
Н2	261.22	261.22	261.22	256.00	452.25	452.25	452.25	5.22
CO	435.45	435.45	435.45	413.68	217.43	217.43	217.43	21.77
CO2	261.27	11.21	11.21		196.25	196.25	33.83	
CH ₄	60.98	60.98	60.98	10.38	10.38	10.38	10.38	50.60
C_2H_2	7.62	7.62	7.62					7.62
C2H4	22.86	22.86	22.86					22.86
C2H6	3.28	3.28	3.28					3.28
С ₃ н ₆	2.18	2.18	2.18					2.18
C3H8	0.43	0.43	0.43					0.43
C4H8	3.62	3.62	3.62					3.62
C4H10	1.81	1.81	1.81					1.81
C5H12	11.58	11.58	11.58					11.58
$N_2 + Ar$	13.76	13.76	13.76	12.00	12.00	12.00	12.00	1.76
H ₂ S	<0.5 ppm ⁸							
H ₂ O	14.66	132.95	6.62		955.29	106.11	6.85	
TOTAL	1,100.72	968.95	842.62	692.06	1,843.60	994.42	705.74	132.73

^aMaximum value; less than 0.1 ppm expected.



Then the gas is passed through a cold-box exchanger package and expanded to produce the desired separation. The separated hydrocarbon by-product leaves the unit at 15 psig and 85 F and is sent to the plant fuel system. A second compressor is required to compress the cleaned synthesis gas from 40 psig to 103 psig. In order to be consistent with other hydrocarbon separation technologies, neither the inlet nor the outlet gas compressor is considered part of the gas separation technology. Their costs were not included in the cost of the cryogenic package.

The synthesis gas leaving the cryogenic separation unit contains about 1.5 mole % CH_4 . It is heated from about 220 F, the estimated compressor discharge temperature, to the shift converter feed temperature of 650 F in exchanger E-15 against the shift effluent gas. The shift converter effluent is further cooled to 200 F in exchangers E-17 and E-16, and condensate is separated in knockout drum V-13.

As in the other separation technologies, the final $\rm CO_2$ removal unit is not considered to be part of the cryogenic gas separation technology. The synthesis gas delivered to the methanol synthesis loop contains from 1 to 2 vol % $\rm N_2$. The theoretical methanol make is 167,190 lb/day, which is comparable to that from the hydrogenation technology. An energy balance for the cryogenic separation technology is presented in Table 12-12.

12.5 PYROLYSIS GAS CLEANUP

12.5.1 Design Basis

The gas cleanup facilities were designed to estimate the capital costs and operating requirements attributable to the upgrading of raw gas from a Purox gasifier to a quality suitable for feed to a methanol synthesis reactor. Design emphasis was placed on selecting units proven commercially in the same or similar service and on providing a conservative design wherever possible. Figure 12-7 shows schematically the various sections of the gas cleanup facilities.

The configuration of the gas cooling and oil mist elimination equipment was selected to match that used by Union Carbide Corp. at their Purox demonstration facility in South Charleston, W. Va. Union Carbide personnel reported satisfactory operation of these facilities during test runs. Design information provided by Union Carbide was used to size the raw gas spray cooler. The electrostatic precipitator performance data and costs were supplied by Koppers-Industrial Products, a leading manufacturer of tar-oil precipitation equipment.

Gravity settlers were designed for separating the raw gas scrubbing water from oil condensed in the scrubbers. No precise data were available on the ratio of oil removed in the scrubbing step to that removed by the precipitators; therefore, both the gravity settlers and the precipitators were designed to handle the entire plant net make of oil on a continuous basis.

Lastly, the final condenser, knockout drum, and all required pumps were designed and sized in-house based on a material and energy balance between the precipitation equipment and the battery limits of the section. The NH₃, CO₂, and H₂S contents of the gas leaving the knockout drum were estimated by using a computer program that predicts vapor-liquid equilibria in aqueous solutions of weak electrolytes.



Table 12-12. ENERGY BALANCE FOR CRYOGENIC SEPARATION (10⁶ Btu/h)^a

nputs	
Raw gas	156.37
BFW	1.14
Steam ^b	63.53
Fuel	1.00
Net compression ^c	1.76
Electric power	0.87
	224.67
Shifted gas to CO ₂ removal	89.13
Outputs Shifted roots GO	00.10
Steam	6.85
Cooling (loss)	55.78
Blowdown	0.01
Condensate	2.23
Flue gas	0.52
	69.48
Fuel gas	09.40
Fuel gas Acid gas	1.35

^aEnergy quantities include sensible enthalpies and higher heating values relative to 60 F, 1 atm pressure, with water in the liquid state.

^bSteam includes attemperation water.

 $^{^{\}mathbf{c}}$ Compression horsepower less interstage and aftercooler duty, for units in the cryogenic separation package.



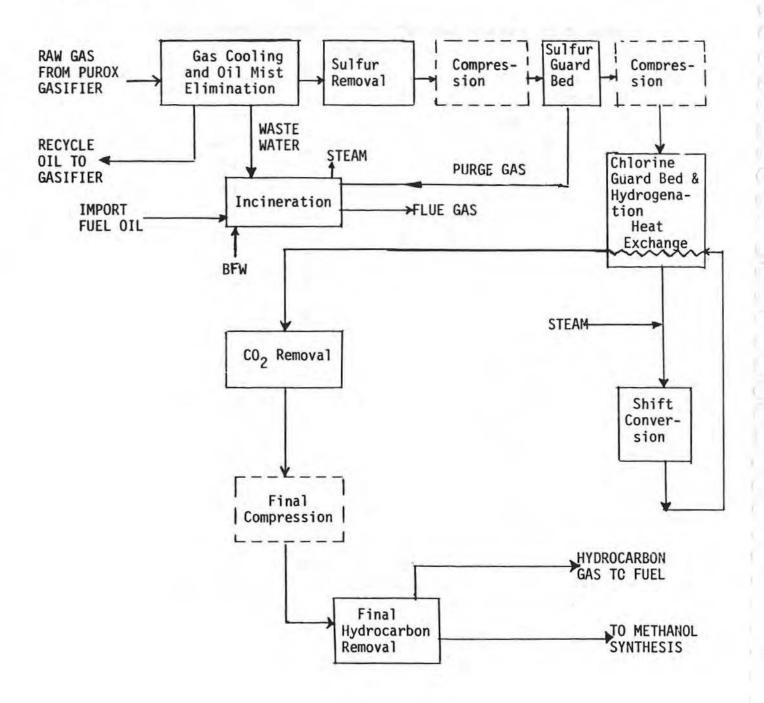


Figure 12-7. Pyrolysis Gas Cleanup Block Flow Diagram



With the selected hydrogenation scheme, sulfur removal to 0.5 ppm or less is required ahead of the first hydrogenation reactor. A Stretford unit appeared to be the best available technology for removing most of the sulfur from the raw gas. The Stretford process operates well at low pressures and especially at low ${\rm CO_2}$ partial pressure. The process produces a salable elemental sulfur product. Therefore, costs and utility requirements were estimated for a Stretford unit based on reducing the ${\rm H_2S}$ content of the gas from about 600 ppmv to 10 ppmv or less.

To protect the methanol synthesis and hydrogenation catalysts used in downstream processing, sulfur and chlorine guard beds of impregnated activated carbon were used. The unit was designed to reduce the $\rm H_2S$ content of the raw gas from 10 ppmv to less than 0.5 ppmv. The unit was located after the first stage of compression to take advantage of the somewhat elevated pressure and interstage cooling.

Although the amount of chlorine present in the raw gas was not quantified for this study, it was assumed that traces could be present due to the use of raw water in the plant. Katalco supplied data on the chlorine holding capacity of promoted alumina.

The hydrogenation and oil absorption designs developed for the review of gas separation technology were incorporated in the pyrolysis gas cleanup design without modification. The design work has previously been described in Section 12.2.

The shift conversion unit was designed to produce a $\rm H_2$ to CO ratio in the effluent of 2.08, as required for methanol synthesis. A maximum outlet temperature of about 950 F was used as a design basis. A 50 F temperature approach to equilibrium was assumed at the outlet of the reactor. The minimum inlet temperature was held at 650 F to provide optimum catalyst activity. A steam-to-dry-gas ratio of about 0.5 was used in the design.

Based on the above design data it was found that no shift bypass was required. Proper control of the unit can be maintained by attemperating the high-pressure superheated steam added to the feed.

Removal of carbon dioxide was done with a hot potassium carbonate unit because of the design data available in the open literature. The design specification for the product gas carbon dioxide content was 5% of the reactive components (H₂, CO, and CO₂) based on a previous study of methanol production from coal (McGeorge 1976).

The wastewater produced during raw gas cooling contains extremely high concentrations of water-soluble organic compounds. Conversations with Union Carbide technical personnel indicated that the water was extremely difficult to handle in a biological treatment system, although Union Carbide believed that their licensed Unox process might be able to treat this waste. The limited time-frame of the study prohibited obtaining performance data and cost estimates for a Unox system. Therefore, a rough design was prepared for an incinerator to burn the combustibles and evaporate the wastewater.

A waste gas stream is generated by the gas cleanup train; this is the regeneration gas stream from the activated carbon sulfur guard beds. This intermittent stream consists of either steam or nitrogen containing small amounts of sulfur and other gases. For this study, it was assumed that the regeneration gas would be incinerated in the same unit as the wastewater.

For waste heat recovery, a 50-psig steam generator was assumed to be included at the outlet of the incinerator.



Factored estimates of installed costs were prepared for each of the three gas separation technologies and for the gas cleanup train. First, equipment costs were estimated for each equipment item or vendor-supplied package.

The equipment costs were next factored into module costs, using factors developed inhouse for installation labor and for materials such as piping, concrete, steel, instrumentation, electrical equipment, insulation, and paint. To the sum of direct materials and labor were added indirect charges such as payroll fringes, field expenses, tools, and equipment. Each of these factors was based on published data but was escalated separately to first quarter 1979 dollars using individual cost indices.

The modular costs were then combined to form factored cost estimates. To the sum of the modular costs were added allowances for process contingencies and offsites and for contractors' expenses and fees. Individual process cost contingencies were applied to each section of a given design rather than applying an overall contingency which might be high for some sections and low for others. In this way, the differences among technologies and their degrees of process risk were quantified individually.

Operating requirements for each section of each design were estimated from vendor-supplied information or from experience with the design or commercial operation of similar units. These operating requirements included utilities, operating and maintenance labor, and catalyst and chemical makeup requirements.

Utilities costs were estimated from the design requirements. In the gas separation technology review, steam requirements for shift conversion were included as a utility, even though the shift conversion unit itself was not considered part of the separation technology. This was done because it was found that the shift conversion section differed significantly for each of the three separation technologies studied.

The shift conversion section was not redesigned for each case, and a qualitative assessment of the effect of each separation technology on the costs of shift conversion is presented in Section 12.6.3. Based on the same sources, labor, chemical, and catalyst makeup requirements were also estimated for each section.

No costs were assigned to the operating requirements developed for this study. In-plant "transfer prices" of utilities can be estimated only by full consideration of the entire processing complex and its many interfaces with the subsystem under study; such a consideration was beyond the scope of this chapter. Also, labor rates are a strong function of the individual plant's location; only a generic location was used for this study. However, it is possible to make qualitative judgments among technologies based solely on the physical operating requirements themselves; such a discussion is presented in Section 12.6.

12.5.2 Process Description

This section describes a conceptual gas cleanup train designed to upgrade raw pyrolysis gas from a Purox biomass gasifier to methanol synthesis gas. Reference is made to Fig. 12-8 and to the material balance presented in Table 12-13.

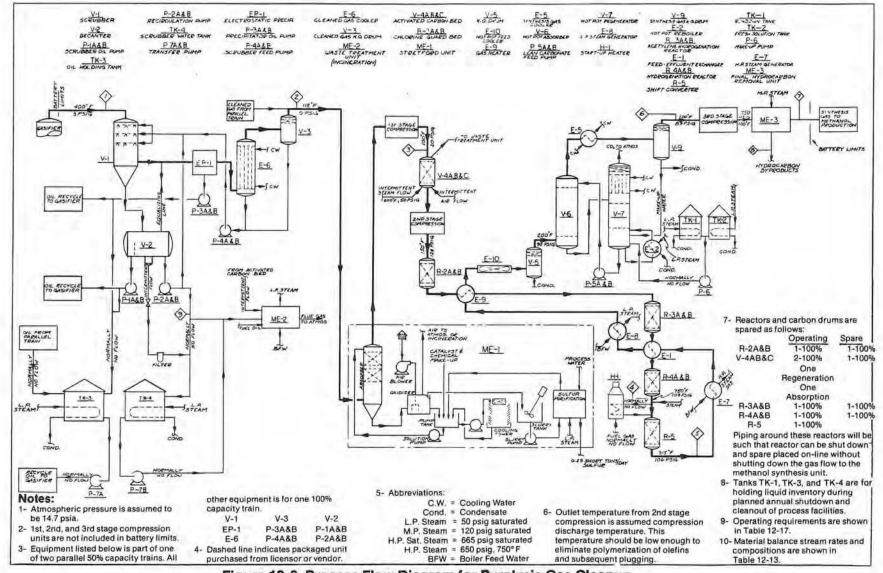


Figure 12-8. Process Flow Diagram for Pyrolysis Gas Cleanup

MATERIAL BALANCE FOR PYROLYSIS GAS CLEANUP (Refer to Figure 12-8) Table 12-13.

	Stream No.									
	ī	2	3	4	5	6	7	8		9
Component (1b mol/h)	Gasifier Effluent ^a	Stret- ford Feedb	Stret- ford Effluent	Hydro- gen- ation Effluent	Shift Converter Effluent	Synthesis Gas to Compression	Synthesis Gas to Methanol Synthesis	Hydro- carbon Gas to Fuel	Component (lb/h)	Purge Water
H ₂	261.22	261.22	261.22	217.32	440.83	440.83	440.83		NII3+-free	1.252
H ₂ CO	435.45	435.45	435.45	435.45	211.94	211.94	211.94		NHA	20.097
CO ₂	261.27	261.27	261,27	261.27	484.78	34.36	34.36		CO2-free	1.401
CH4	60.98	60.98	60.98	60.98	60.98	60.98	27.56	33.42	HCO3	65.84
C2H2	7.62	7.62	7.62						CO ₃ H ₂ S HS	0.51
CoHA	22.86	22.86	22.86						H2S	0.009
C ₂ ² H ₆ C ₃ H ₆ C ₃ H ₈ C ₄ H ₈	3.28	3.28	3.28	33.76	33.76	33.76	0.44	33.32	115	0.093
Calle	2.18	2.18	2.18						NH2COO	0.90
CaHo	0.43	0.43	0.43	2.61	2,61	2.61		2.61	Methanol	216.280
CAHO	3.62	3.62	3.62						Ethanol	84.090
C4H10	1.81	1.81	1.81	5.43	5.43	5.43		5.43	Acetic acid	174.840
C5H12	11.58	11.58	11.58	11.58	11.58	11.58		11.58	Acetone	84.090
N2+Ar	13.76	13.76	13.76	13.76	13.76	13.76	13.76		MEK	16.940
NHa	1.47	0.10							Propionic acid	67.15
ńн₃ н₂S	0.75	0.75	10 ppm	<0.5 pp	m ^e				Butyric acid	16.940
Acetic acid	2.91								Furfural	84.09
Methanol	6.75								Phenol	16.940
Ethanol	1.83								Benzene	10.160
Acetone	1.45								Oil	63.82
MEK	0.23								Water	7,521.86
Propianie acid	0.91									agent of the
Butyric acid	0.19									
Furfural	0.88									
Phenol	0.18									
Benzene Oil ^d	0.13									
H ₂ O	538.51	121.00	30.53	14.66	221.13	7.32	1.03			
Total	1,642.25	1,207.91	1,116.59	1,056.82	1,486.80	882.57	729.92	86.36		8,447.30

^aTotal for both trains, ^bFlow used for design. ^cMaximum value; less than 0.1 ppm expected. ^dOil flow at 3364.82 lb/h.



12.5.2.1 Gas Cooling and Mist Elimination

Raw pyrolysis gas leaving the Purox gasifier enters the gas cooling and mist elimination section at 400 F, 3 psig. At Union Carbide's recommendation, two parallel sets of gasifiers and gas cooling/mist elimination units, each producing 50% of total capacity, were assumed to be required to produce 500 ton/day of raw gas.

The raw gas is first scrubbed with water in a cocurrent spray tower, V-1, to remove entrained particulates and some of the oil produced in the gasifier. The gas is cooled to 150-180 F by adiabatic saturation. The water, with particulates and condensed oil, flows by gravity to the decanter V-2, where oil and water are separated by gravity settling, although the specific gravities of the oil and water are so close that settling is quite difficult. A boot is provided in the water section of the decanter into which solids can settle. This boot is blown down intermittently to the waste treating section of the plant through a cartridge filter.

The aqueous condensate is pumped by P-2A&B back to the scrubber V-1. Net condensate is withdrawn and pumped to the waste treatment section. As shown in Table 12-13, this condensate contains approximately 11% by weight of water-soluble organic compounds.

Oil recovered from the decanter is pumped by P-1A&B to the gasifier, in which it is assumed to be recycled to extinction.

It is anticipated that frequent maintenance may be required in the gas cooling and mist elimination section, particularly in the scrubbing and decanting equipment. Therefore, holding tanks TK-3 and TK-4 were provided to contain the liquid inventory of the system during shutdown and cleanout operations. Tank TK-3 has a capacity of one day's net oil make, while Tank TK-4 can hold one week's make of aqueous condensate to allow for shutdowns in the waste treatment section of the plant.

Gas leaving the scrubber V-1 is saturated with water at 150-180 F and 2.5 psig. Next it flows through a wet electrostatic precipitator EP-1 in which oil mist is recovered from the gas. The precipitator is designed to remove 99% of the oil mist and is sized to handle the entire gasifier net oil make. In addition, spare units are provided so that one unit may be cleaned without shutting down the entire gas cleanup train. This extremely conservative arrangement should provide maximum reliability in removing oil mists from the raw gas.

Oil collected in the precipitator is pumped by P-3A&B back to the gasifier, in which it is recycled to extinction.

The gas leaving the precipitator is next cooled to 115 F against cooling water in exchanger E-6, and condensate is separated from the gas in knockout drum V-3. Downstream of this point, the two parallel, 50% capacity trains are manifolded into a single 100% capacity train.

12.5.2.2 Sulfur Recovery

The cooled gas next flows through a Stretford unit ME-1, in which H₂S is scrubbed from the gas. Data from the Purox process operating on municipal solid waste have levels of organic sulfur in cooled, scrubbed gas of less than 1 ppmv, showing that the Stretford process is effective in high-efficiency sulfur removal.



The Stretford process is a licensed proprietary process of the Northwest Gas Board, United Kingdom. It operates by absorption of H₂S in a solution of sodium carbonate, sodium meta-vanadate, and anthraquinone disulfonic acid. Through a series of oxidation-reduction reactions, the H₂S is first converted to HS ion, then oxidized to elemental sulfur. The sulfur is released as a froth by air blowing through the solution. The froth is skimmed from the oxidation tank and processed in a melter to recover solution, producing about 0.29 ton/day of marketable elemental sulfur. The scrubbed gas leaving the Stretford unit contains no more than 10 ppmv of H₂S.

12.5.2.3 Guard Beds

The sweetened gas is next compressed to about 20 psig and passed over a bed of impregnated activated carbons for final sweetening. Three beds are used, V-4 A,B,C. At any time, one bed is on adsorption service, one is being regenerated by steam or nitrogen from the air separation plant associated with the Purox process, and the third is a spare. Placing the carbon unit between compression stages takes advantage of low interstage gas temperatures to greatly enhance adsorptive capacity. The gas leaving the carbon beds contains less than 0.5 ppmv of sulfur.

Regeneration gas from the carbon beds, an intermittent stream, is incinerated in the waste treatment unit of the plant.

The sweetened gas is compressed to about 124 psig and passed through a chlorine guard bed, V-2A&B, of promoted alumina, which will reduce the chlorine content of the outlet gas to less than 0.2 ppmv. A full-capacity spare is provided for the chlorine guard bed, allowing for shutdown of a bed and removal of the spent guard material without shutting down the gas cleanup train.

12.5.2.4 Compression

Compression has been excluded from consideration in this study; however, in designing the gas cleanup facilities, consideration was given to the placement of process units relative to compression and to the compression requirements.

In the processing scheme selected for design, most of the gas cleanup is done at pressures below 150 psig to minimize the requirements for compressing CO₂ to elevated pressures. Only oil absorption is done at methanol synthesis pressure. It has been found that the first- and second-stage compressors must be designed very carefully to minimize discharge temperatures. Excessive temperatures can cause polymerization olefins in the gas, and the larger polymers can plug valves. We have assumed that the discharge temperature from second-stage compression is held to 150 F.

12.5.2.5 Gas Separation

In the gas cleanup described here, hydrogenation and oil absorption technology were used. The processes and equipment involved are described in Section 12.4 and are not repeated here.



12.5.2.6 Shift Conversion

Hydrogenated pyrolysis gas must be shifted to provide the correct H_2 to CO ratio for methanol synthesis. This reaction,

$$CO + H_2O \rightarrow CO_2 + H_2$$
,

is performed in the shift converter R-5. An iron-chrome high-temperature shift catalyst is used to shift approximately 50% of the CO in the feed gas to CO_2 . In the current design, no bypass of gas around the shift reactor is required to obtain the desired ratio of H_2 to CO (2.08). Instead, the reaction is controlled by the addition of attemperated steam upstream of the reactor.

No spare is required for the shift converter because the spare guard beds and hydrogenation facilities upstream of the shift converter ensure that shift catalyst poisons never reach the shift reactor. The shift catalyst is a rugged catalyst that should be extremely long-lived and require very little maintenance. Catalyst changeouts can be done during planned maintenance shutdowns.

Shift effluent gas is cooled against hydrogenation reactor feeds and by raising steam, and it is then sent to CO₂ removal.

A startup heater, H-1, heats the shift and hydrogenation reactors during startups. Its duty has been set at 2.0×10^6 Btu/h, which is approximately 35% of the shift preheat duty required in normal service. The shift section can be "boot-strapped" to full throughput once a 20% gas flow has been established and the shift reaction is initiated.

12.5.2.7 CO2 Removal

CO₂ produced in the shift conversion step is removed from the gas in a CO₂ removal unit similar to that detailed in Section 5.3.3. Hot potassium carbonate solution is used to absorb CO₂ from the synthesis gas in absorber V-6. The solution is regenerated in the stripper V-7. Two atmospheric storage tanks, TK-1 and TK-2, have been included for fresh solution storage and to hold the liquid inventory of the system during maintenance shutdowns.

12.5.2.8 Waste Treatment

Wastewater produced by the condensation of water in the gas cooling and mist elimination section is evaporated, and the combustible organics are incinerated in the waste treatment unit, ME-2. This unit is a thermal oxidizer with waste heat recovery capability. The wastewater is oxidized with supplemental fuel oil firing to raise the combustion chamber temperature to 1800 F. Thirty-percent excess air is used based on fuel oil heating value; the total heat release in the combustion chamber is 26.2 x 10^6 Btu/h. About 45% of the oxidizer heat release is recovered in a packaged water-tube steam generator. Fifty-psig saturated steam is generated in this equipment. The flue gas exits to the atmosphere at approximately 400 F.



12.5.2.9 Process Alternatives

There are a number of process alternatives for each section of the gas cleanup facilities. Although scope and time limitations did not permit a detailed examination of these alternatives, some qualitative assessments were made.

Process and equipment for gas cooling and oil mist elimination were discussed in Section 12.5.2.1. Although an electrostatic precipitator is more costly than other devices, it has been proved in performance at South Charleston. Union Carbide reported that a venturi scrubber had been tested for oil mist elimination at South Charleston but had not performed effectively.

A number of sulfur removal technologies other than the Stretford method were considered for the gas cleanup service. Two of them were MEA and solid iron oxide.

MEA (monoethanolamine) absorption removes hydrogen sulfide from the cooled raw gas by chemical absorption. After regeneration of the solvent by heating, the $\rm H_2S$ is released from solution and flows overhead from the regenerator. It is then converted to elemental sulfur in a Claus sulfur recovery unit. Based on in-house experience with such processes, we concluded that in the small size under consideration, the separate MEA-Claus installations would be more costly than a single Stretford unit.

Solid iron oxide has been used for many years to purify both natural and synthetic gases containing trace amounts of $\rm H_2S$. Perry Gas Processors, Inc., a supplier of commercial iron oxide units, estimated that 15 vessels, each 90 in. by 20 ft high, would be required. The estimated life of the total inventory of the beds was 150 days. Because of its high anticipated capital and operating costs, such an installation was not considered for this application.

Zinc oxide is a widely used alternative for trace sulfur removal. Katalco, a leading supplier of zinc oxide, was contacted to ascertain the usefulness of zinc oxide in the gas cleanup train. The applicability of zinc oxide is affected by the choice of olefin hydrogenation scheme. For the selected scheme, sulfur had to be removed ahead of the acetylene hydrogenation reactor to prevent poisoning of the palladium catalyst. However, Katalco indicated that acetylene would polymerize in the zinc oxide beds. This makes the use of zinc oxide incompatible with two-stage hydrogenation.

Three alternatives for separation of hydrocarbon gases from the synthesis gas were considered, in addition to those studied in detail. The alternatives are single-stage hydrogenation, molecular sieve adsorption, and low-pressure refrigerated oil absorption. These alternatives were not examined in detail, but some observations are presented below.

Olefins and acetylene can be hydrogenated over a single-stage cobalt-molybdenum catalyst, rather than the two-stage scheme adopted in the study. In a single-stage hydrogenation, however, acetylene may crack and lay down carbon on the catalyst. The catalyst can be regenerated periodically by burning off the carbon with air. Use of the single-stage scheme would permit the use of high-temperature zinc oxide for trace sulfur removal, as the cobalt-molybdenum catalyst is not poisoned by sulfur. Therefore, the zinc oxide single-stage hydrogenation scheme may be attractive for this service. The two-stage hydrogenation scheme was selected for its anticipated operating simplicity; i.e., lack of a periodic burnoff of the catalyst beds.



An alternative to the removal of paraffin hydrocarbons by high-pressure oil absorption is their adsorption in a molecular sieve pressure-swing-adsorption (PSA) unit. This type of unit was briefly discussed with the supplier, Union Carbide Corp. A rough estimate of capital cost indicated that a PSA unit would be more costly than the oil absorption system. Furthermore, losses of $\rm H_2$ and CO predicted by Union Carbide for the PSA unit were significantly higher than those predicted for an oil absorption unit. Therefore, this alternative was not considered further.

Another alternative in gas separation would be to use a single refrigerated oil-absorption step to remove both olefins and paraffin hydrocarbons ahead of shift conversion. Mittelhauser performed preliminary process simulations on such a system, using the SSI/100 computer program. With a lean oil temperature of -40 F, approximately 25% of the CH₄ and essentially all of the acetylene, olefins, and heavier paraffins can be removed in a reasonable-sized absorber. Unfortunately, scope and time constraints prevented completion of the process design work. The alternative, however, should be investigated further when conceptual commercial designs are undertaken.

Several process alternatives exist for removing CO_2 from synthesis gases. Hot potassium carbonate is often used as a chemical solvent for CO_2 . Other commercial CO_2 removal processes use either physical solvents or mixtures of physical and chemical solvents. Descriptions of these processes are available in the literature.

One physical solvent process that may be attractive in synthesis gas cleanup is Allied Chemical Corporation's proprietary SELEXOL process. This method is effective at higher pressures; in the absence of sulfur compounds the solvent is regenerated by pressure letdown or air stripping, without the use of steam for reboiling. This can result in a considerable savings in operating cost when compared with the hot carbonate process.

In further research work, alternative CO₂ removal processes for synthesis gas cleanup should be compared.

Mittlehauser investigated the possibility of using Union Carbide's UNOX process for treating the highly concentrated wastewater from the gas cooling and mist elimination sections. Design data and cost estimates could not be obtained in time for inclusion of such a design in the study. However, since this approach has been used in at least one conceptual study, it should be investigated further.

12.5.2.10 Technology Assessment

The investigations of methanol synthesis catalyst tolerance presented here reveal that little is known about potential poisons other than sulfur and chlorine. Synthesis gas from the biomass scheme may contain many more chemical species than commercial methanol processes that produce a synthesis gas by steam re-forming of natural gas, LPG, or naphtha.

Katalco, United Catalysts, and Haldor Topsoe were uncertain about the effects of many of the trace compounds for which more exact tolerance levels are required. In addition, the concentrations of these compounds in the raw synthesis gas produced from biomass should be better defined. Nevertheless, the gas cleanup system as designed represents a conservative approach to removing known and suspected methanol catalyst poisons.



All of the units and equipment designed for the gas separation technologies and gas cleanup designs presented here have been employed commercially or in demonstration facilities in the petroleum or coal and gas processing industries. The gas cooling and mist elimination designs were identical to those proven in performance at Union Carbide's Purox demonstration facility at South Charleston, W. Va.

The Stretford process, a joint development effort by the Clayton Aniline Company, Ltd. and the North Western Gas Board, was designed initially for the desulfurization of coke oven gas. The process has been used for treating refinery gases, synthesis gas and natural gas, and has been commercially used in Europe and the United States.

The impregnated activated carbon and promoted alumina material used as sulfur and chlorine guards have been used commercially for treating natural gas and light hydrocarbon feed stocks. The two-stage hydrogenation catalysts have been used extensively in refinery service. The simpler, single-stage hydrogenation over a cobalt-molybdate catalyst discussed in Section 12.4.1 has been used in acetylene service. However, the catalyst would require some laboratory test runs under expected conditions to determine the rate of catalyst coking. Catalyst suppliers are equipped to perform such tests.

Shift and re-forming systems have been widely used in the refining and methanol synthesis industries for years. Shift catalysts have been specifically developed for the coal-to-SNG industry. Cryogenic separation systems have generally been used for the purification of hydrogen but have been commercially modified for the separation of hydrocarbons from synthesis gas streams.

Many systems are available for removing carbon dioxide from synthesis gas streams. A proprietary system licensed by Benfield is a catalyzed, hot potassium carbonate system similar to the one used in this study. It has been employed at the British Gas Corporation, Westfield, test facility to remove acid gases from town gas.

12.5.2.11 Overall Review

For removing hydrocarbon contaminants from methanol synthesis gas, it appears that cryogenic separation is less favored economically as compared with hydrogenation. No such conclusions should be drawn between re-forming and hydrogenation, however. These two technologies have too many differences that should be studied in detail in the context of an overall, commercial-scale methanol plant design.

12.6 COST ESTIMATES

12.6.1 Capital Costs

The cost estimates for three gas separation technologies are summarized in Table 12-14. The hydrogenation technology is least costly in capital. The cryogenic separation technology is by far the most costly because of the high cost of the cryogenic package relative to the re-former and the oil absorption plant in the other technologies, and also because of the added CO₂ removal step ahead of the cryogenic package.

A qualitative assessment of the effects of the three gas separation technologies on capital requirements for other gas cleanup units is presented in Table 12-15. This table



Table 12-14. CAPITAL REQUIRED FOR GAS SEPARATION

	Costs in 7	Thousands of 1	979 Dollars
	Hydro- genation	Re-forming	Cryogenic
Equipment	384.7	1204.1	2150.8
Other materials ^a	259.1	195.9	444.1
Installation	192.1	159.7	342.3
Installed facilities,			
Field costs	835.9	1560.2	2937.2
Indirect charges ^b Initial charge of catalyst	303.8	303.0	709.1
and chemicals	70.8	106.8	45.7
Installed module	1210.5	1970.0	3692.0
Allowance for process			
contingencies ^C	174.5	180.1	399.3
Allowance for offsites ^d	114.0	189.9	364.6
Contractor's expenses and fee ^e	249.0	478.0	860.0
Total Capital Required	1748.0	2818.0	5315.9
Capital required per lb mol/h of synthesis gas	2.39	1.85	7.53
or synthesis gus	2.00	2.00	
Capital required per potential	01.45	10.00	00.50
daily ton of methanol	21.45	16.03	63.59
Estimated annual maintenance expense	36.3	59.1	110.7

^aIncludes piping, concrete, structural steel, instrumentation, electrical, insulation, and painting.

^bIncludes payroll fringes, field expenses, tools, and equipment.

^cCalculated as a percentage of module cost net of catalyst and chemicals. The percentage varies depending on the type of service.

^dAllowance for offsites, at 10% of net module costs, to enable connections, site preparation, retrofit adjustments, and required ductwork and controls.

^eCovers home office construction services, design engineering, drafting, procurement, project management, and general indirect and overhead expenses. The fee is based on a fixed percentage of the module plus the allowance for contingencies and for offsites.



Table 12-15. POSSIBLE EXTERNAL CAPITAL EFFECTS OF GAS SEPARATION TECHNOLOGIES

	Hydrogenation	Re-forming	Cryogenic
Shift Conversion			
Total mol/h		¥.	
to reactor (% bypass)	0	0	49.5
Dry	1042.16	1042.16	342.57
STM	444.64	1480.01	1151.54
Total	1486.80	2522.17	1494.11
Relative size	1.00	1.70	1.00
Projected cost	Base	Higher	Same
Final CO ₂ Removal			
Feed mols			
Inerts	780.89	1424.98	692.06 ^b
H ₂ O	148.58	513.48	106.11
có ₂	484.78	454.05	196.25
Total	1414.25	2392.51	994.42
Gas flow factor	1.00	1.69	0.70
mol CO2 in effluent	34.36	74.21	33.83
mol/h CO2 removed	450.42	379.84	162.42
SCF/min ČO, removed	2849.0	2402.5	1027.3
SCF/min ČO ₂ removed Prorated gpm solution ^c	1140.0	961.0	410.9
Approximate reboiler duty	33.1 10 ⁶	27.9 106	11.9 10
Projected cost	Base	Same	Lower
Compression			
Intermediate			
mol/h	-	4	842.62/692.06
Pin to Pout (psig)	-	100 to	400/40 to 103
Final			
mol/h (Dry)	815.25	1499.19	725.89
Pin to Pout (psig) Projected cost	89 to 750	37 to 750	84 to 750
Projected cost	Base	Much Higher	Much Higher
Methanol Synthesis			
% Inerts in feed			
(dry mol%)	10.4	6.0	8.0
Potential methanol			
(ton/day)d	81.5	175.9	83.6

a1.5 vol % CH4

bIncludes CH₄ at 10.38 mol/h

 $^{^{\}rm C}{\rm Based}$ on lean loading of 2.5 and rich loading of 5.0 SCF ${\rm CO_2/gal}$

^dMol/h CO 24 32.04/2000



shows that external costs are likely to be somewhat higher for re-forming and cryogenic separation than for hydrogenation. However, the table also illustrates the tremendous increase in potential methanol yield afforded by re-forming, a result of the conversion of the paraffin hydrocarbons to additional synthesis gas. For gas separation capital cost only, the total capital required per potential daily ton of methanol is \$21,450 for hydrogenation but only \$16,030 for re-forming.

12.6.2 Operating Costs

A summary of operating requirements for the three gas separation technologies is presented in Table 12-16. As discussed previously, the steam requirements for shift conversion have been included as part of the operating requirements to afford a more realistic view. The cryogenic separation technology is a heavy importer of steam, hydrogenation a moderate importer, and re-forming a net exporter of steam to the overall methanol-from-biomass plant. However, the re-forming technology requires a significant import of fuel oil with which to fire the re-forming furnace. The cost of this requirement at least partly offsets the value of the exported steam.

It should also be pointed out that the hydrogenation and cryogenic separation technologies supply a significant quantity of hydrocarbon fuel gas to the methanol-from-biomass plant, while the re-forming technology does not, having converted the hydrocarbons to synthesis gas instead.

Operation labor and maintenance expenses are lowest for hydrogenation and highest for cryogenic separation.

12.6.3 Incremental Costs of Gas Cleanup

Installed costs for gas cleanup are shown in Table 12-17.

The capital requirements of gas cleanup amount to about \$127,000 per potential daily ton of methanol.

The major capital cost items in pyrolysis gas cleanup are the electrostatic precipitators, at about \$2.2 million, installed cost, and the CO₂ removal unit at about \$1.8 million, installed cost. We believe that these costs may be lessened somewhat by selecting different processing facilities. However, selection of alternatives must be made by thorough comparisons on consistent bases that fully account for the differing effect of each alternative on the overall methanol plant.

Operating requirements for gas cleanup are summarized in Table 12-18. The most significant requirements in terms of potential cost are the steam imports and the fuel requirements for the Waste Treatment Unit, ME-2.

12.7 CONCLUSIONS AND RECOMMENDATIONS

The major conclusions that can be drawn from the study are as follows:

 Raw pyrolysis gas from the gasification of wood waste in a Purox gasifier can be upgraded to a synthesis gas which (so far as is now known to methanol catalyst



Table 12-16. OPERATING REQUIREMENTS FOR GAS SEPARATION

	Hydrog	genation	Re-forming		Cryogenic	
Cooling water (gpm)	ME-3	455			V-11 E-14 ME-4	2030 164 57
		455				2251
Steam export (lb/h) 50 psig, sat.	E-8	1715	E-21	4575	E-11 E-17 TK-1& TK-2	(39680 5950 (40
		1715		4575	111-2	(33770
120 psig, sat.	ME-3	(20240)				
650 psig, 750 F ^a	Shift E-7	(5683) 4260	Shift Re-former	(25203) 39470	Shift	(20269
		(2423)		14267		(20269
BFW import (gpm, 250 F)	Shift E-7	2.3 9.1	Shift Re-former	2.5	Shift	1.0
	E-8	3.7	E-21	84.6 9.8	E-17	12.7
		15.1		96.9		13.
Electric power (kWh/h)	E-10 ME-3	18.6 343.0	E-22 Re-former		E-16	119.
		361.6		161.8	P-8A&B	251.7
Fuel oil (lb/h)			Re-former	3582		
Fuel gas (SCFM)b					ME-4	20
Catalyst [ft ³ (life, yr)]	R-3 R-4	80(1) 211(3)	R-3 R-4	80(1) 211(3)	Dryer	59(3
Chemicals (lb/day)					K ₂ CO ₃ NaOH Conden-	
					sate	265,875
Operating labor (man-hour/day)	(5	12		2	4

^aDoes not include desuperheating water. ^bFuel gas at 1000 Btu/SCF (HHV). ^cMolecular Sieve.



Table 12-17. CAPITAL REQUIRED FOR PYROLYSIS GAS CLEANUP

	Costs in Thousands of Dollars
Equipment	3,144.1
Other materials ^a	1,300.2
Installation	1,052.1
Installed facilities, field costs	5,496.4
Indirect charges ^b	1,831.3
Initial charges of catalyst and chemicals	218.8
Installed module	7,546.5
Allowance for process contingencies ^c	511.9
Allowance for offsites ^d	736.9
Contractor's expenses and fee ^e	1,526.0
Total Capital Required	10,321.3
Estimated annual maintenance expense	331.1

^aIncludes piping, concrete, structural steel, instrumentation, electrical, insulation, and painting.

bIncludes payroll fringes, field expenses, tools, and equipment.

^cCalculated as a percentage of module cost net of catalyst and chemicals. The percentage varies depending on the type of service.

^dAllowance for offsites, at 10% of net module costs, to enable connections, site preparation, retrofit adjustments, and required ductwork and controls.

^eCovers home office construction services, design engineering, drafting, procurement, project management, and general indirect and overhead expenses. The fee is based on a fixed percentage of the module plus the allowance for contingencies and for offsites.



Table 12-18. OPERATING REQUIREMENTS FOR GAS CLEANUP

Cooling water (gpm)			Fuel oil (lb/h)		411
1,120,000	V-7	1960		ME-2	920
	E-5	259	Eurl man (SCEM)	100	920
	E-6 M-3	507 455	Fuel gas (SCFM)	H-1	40
	141-3	433			40
Steam export (lb/h)			(agnit)	V 44.DG	07.5
125 November 1	mvr. 1	(00)	Utility air (SCFM)	V-4ABC	37.5 37.5
50 psig, sat.	TK-1 TK-2	(20) (20)			31.3
	TK-3	(40)			
	TK-4	(350)			
	ME-1	(50)	Catalyst [ft3 (life,		
	E-2	(36400)	yrs)/vessell	V-4ABC	375(4)
	E-8	1715		R-2A&B	123(2)
	ME-2	12180		R-3A&B	80(1)
		(22985)		R-4A&B R-5	211(3) 564(4)
70 400 P	V-4ABC	(3750)			
50 psig, 400 F	V-4ABC	(3750)			
		(0.00)	Chemicals (lb/day)		
120 psig, sat.	ME-3	(20240)	O. 10. 10. 10. 10. 10. 10. 10. 10. 10. 10	K2CO3	8.6
120 paig, out.		(20240)		ADA	0.8
				V2O5	0.8
665 psig, sat.	E-7	4260		Na ₂ CO ₃	25
		4260			
650 psig, 750 F	R-5	6683	Operating labor		
2-0/		6683	(Man-hours/day)		
BFW import (gpm, 250 F)			Gas cooling and mist		
11 map 10p 1	R-5	2.3	elimination	1	2
	E-7	9.1			
	E-8	3.7	Sulfur removal	ŧ	3
	ME-2	26.1			
		41.2	Guard beds	3	3
Condensate import (gpm)	ME-1	.12	Gas separation		
		.12	Hydrogenation		3
			Oil wash	;	3
Electric power (kW)	52600000				
	EP-1	21.3	Chiffin		3
	E-10	18.6	Shift conversion	3	3
	P-1A&B P-2A&B	.3 8.9	Final CO2 removal		6
	P-3A&B	.3	r mar cog removar		
	P-4A&B	3.4	Waste treatment		3
	P-5A&B	161.2			
	P-6	1.9		4	2
	P-7A&B	.8			
	ME-1	14.9			
	ME-2	5.2			
	ME-3	343.0			
		579.8			



- suppliers) is of acceptable quality for commercial methanol synthesis. This upgrading is technically feasible with commercially available equipment.
- Several alternatives can be defined for a number of gas cleanup unit operations.
 At least some of these alternatives should be studied in more detail with a view to reducing the overall cost of gas cleanup.
- Among alternatives for separation of hydrocarbons from methanol synthesis gas, hydrogenation of olefins followed by oil absorption of paraffins and catalytic reforming appear to be more attractive than cryogenic separation.

Problems and uncertainties in the current literature include:

- Detailed characterizations of raw gas from gasification of wood waste in a Purox gasifier are not yet available. Such characterizations from commercial scale equipment are required to properly design downstream processing facilities, especially those in which performance is controlled by minor components such as HCN, COS, CS₂, NH₃, tars, oils, and water-soluble organic compounds.
- Detailed studies are needed of the long-term effects of compounds known or suspected to be present in biomass pyrolysis gas, on commercially available methanol synthesis catalysts.
- The biological treatability of Purox wastewaters from biomass gasification needs definition. Basic parameters for the design of biological treatment systems can be developed only from such treatability studies.
- The problem of scaleup to commercial methanol plant sizes must be addressed.
 At the 80-175 ton/day size addressed in this study, methanol production from
 biomass may or may not be economical. The relationship of product methanol
 cost to plant size must be quantified, together with problems associated with
 scaleup of plant facilities.

Based on the conclusions developed in this study, and the problems and uncertainties identified thereby, some aspects of a comprehensive research program may be defined. These research needs may be broadly classified as system level, subsystem level, and component studies.

On the system level, the following research programs should be undertaken:

- A conceptual commercial design should be made of a complete grass-roots plant to convert biomass to methanol. The suggested scale of the plant is 1500 tons per day, which is a reasonable scale for a large, single-train, methanol synthesis process. This design would identify and address system level problems associated with siting, construction, and operation of such a facility and would help to quantify the expected cost of methanol from such a plant.
- Comparative commercial scale designs of methanol plants using different biomass gasifiers should be performed to identify the most promising gasification processes for further commercial development. Particularly interesting would be comparison of air versus oxygen-blown gasifiers and atmospheric versus pressurized gasifiers.
- Sensitivity studies should be performed on commercial-scale designs to examine the effect of variations in design and of economic parameters on the cost of



methanol from biomass. These parameters include feedstock and fuel costs and overall plant size.

On the subsystem level, the following research activities are recommended:

- Studies of alternative wastewater treatment method.
- Study of optimal location of compression facilities.
- Study of process alternatives for CO₂ and sulfur removal for commercial-scale facilities.

Component studies that should be performed are as follows:

- An experimental program to characterize thoroughly the types and quantities of trace components, such as nitrogenated compounds, water soluble organics, and sulfur compounds, produced by developing biomass gasifiers. Included in this program are a correlation of these component production rates with gasifier conditions and development of a method for predicting the production of such components.
- Scaleup and operational studies of the biomass gasifiers themselves, with an objective of determining the optimal size of a commercial gasifier.
- Biological treatability studies on wastewaters produced from biomass gasification.
- Laboratory studies of long-term tolerances of commercially available methanol synthesis catalysts to various compounds produced in biomass gasification.

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Production of Fuels and Chemicals from Synthesis Gas

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CHAPTER 13

PRODUCTION OF FUELS AND CHEMICALS FROM SYNTHESIS GAS

13.1 INTRODUCTION

This chapter reviews the chemistry of synthesis gas (CO and H₂ mixtures) reactions and the state-of-the-art process technologies suitable for converting biomass-derived synthesis gas to various fuels and chemicals. The review includes three major product areas:

- alcohols,
- hydrocarbon fuels and gasoline, and
- ammonia.

The section on alcohols discusses the synthesis of methanol and higher alcohols. An indepth process evaluation and economic comparison of methanol technology is presented. The section on hydrocarbon fuels and gasoline evaluates conventional Fischer-Tropsch synthesis in terms of the various hydrocarbon fuels expected from a chain-growth process. A recent advancement in gasoline production from methanol is also presented. The final section discusses the technology of producing ammonia from synthesis gas.

13.2 FUNDAMENTAL ASPECTS OF SYNGAS CHEMISTRY

13.2.1 Thermodynamics

Reactions between hydrogen and carbon monoxide to form hydrocarbons, alcohol, and other chemicals are favored thermodynamically at lower temperatures, less than 700 C. These reactions were discovered over 75 years ago by Sabatier and Senderens. Some selected reactions are listed in Table 13-1, which also shows the approximate temperatures at which the Gibbs free energy for each reaction becomes zero and, hence, below which the reactions are favored (Stull et al. 1969). Figure 13-1 shows the temperature dependence of the equilibrium constants for most of the reactions in Table 13-1.

Several features in Fig. 13-1 are worth noting. Methane is favored at the highest temperatures, above 600 C. At lower temperatures, generally below 350 C, the formation of higher alkanes is favored at the expense of methane. Indeed, the insertion of a methylene group into a general straight chain hydrocarbon (see the reaction labeled "alkane + CH₂") is favored at temperatures below 380 C. Although not listed, branched chain hydrocarbons are favored thermodynamically at the expense of straight chains. Also, the formation of alkanes from hydrogen and carbon monoxide is favored as compared with olefins and alcohols. Within any one homologous series of alcohols and olefins, the longer chains (higher homologues) are favored.

Thus it is clear from thermodynamics alone that in nonspecific catalytic synthesis, such as the Fischer-Tropsch synthesis, a substantial amount of the products are heavy hydrocarbons. Conversions of methanol into gasoline (Mobil process) or higher alcohols (Union Carbide process) are strongly favored thermodynamically.

Table 13-1. SELECTED SYNTHESIS GAS CONVERSIONS

Reaction	Approximate T ($^{\circ}$ C) at Which $\Delta F = 0^{8}$	ΔH ^a (kcal/mol syngas)	Percent of Heating Value of Syngas Lost ^e
Methane:			
$CO + 3H_2 = CH_4 + H_2O$	690	-12.3	18.2
Ethane:			
$2CO + 5H_2 = C_2H_6 + 2H_2O$	510	-11.9	17.5
Propane:			
$^{3}\text{CO} + ^{4}\text{H}_{2} = \text{C}_{3}\text{H}_{8} + ^{3}\text{H}_{2}\text{O}$	470	-11.9	17.5
Nonane:			
$9CO + 19H_2 = C_9H_{20} + 9H_2O$	410	-12.0	17.8
Decane:			
$10CO + 19H_2 = C_{10}H_{22} + 10H_2O$	410	-12.0	17.8
Alkane + CH ₂			
$R-R' + CO' + 2H_2 = RCH_2R' + H_2O$	380	-12.0	17.8
Ethylene:			
$2CO + 5H_2 = C_2H_4 + 2H_2$	380	-8.4	12.4
Methanol:			
$CO + 2H_2 = CH_3OH$	140	-10.3 ^b	15.2 ^b
Ethanol:			
$2CO + 4H_2 = C_2H_5OH + H_2O$	300	-11.8 ^b	17.4 ^b

 $^{^{8}}$ In standard gas states unless otherwise noted.

^bAlcohols in liquid state.

^cSyngas heating value is approximately 67.8 kcal/mol.

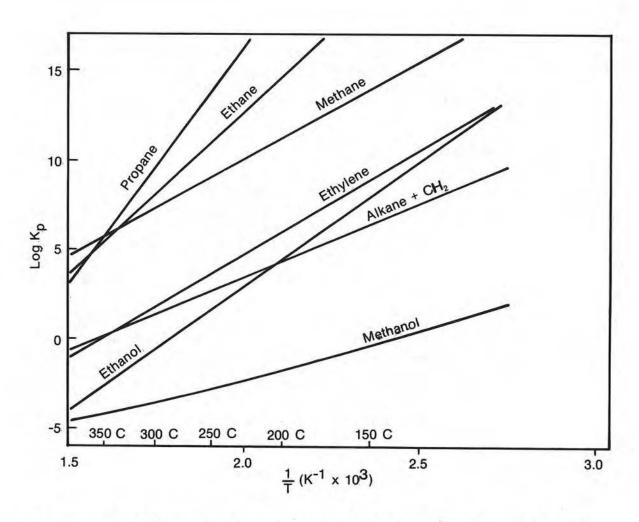


Figure 13-1. Temperature Dependence of the Equilibrium Constants for Reactions for the Synthesis of Hydrocarbons and Alcohols from Carbon Monoxide and Hydrogen



Table 13-1 (columns 3 and 4) also indicates another thermodynamic result that is important to energy efficiency in the synthesis of fuels: the heating value of the synthesis gas is degraded by conversion to other fuels, especially condensable fuels. Column 3 lists the enthalpy change for the reaction divided by the sum of the moles of the reactants. The last column is the ratio of this value to the heat of combustion of CO or H₂ (which are nearly the same on a molar basis) and represents the heat of combustion of the synthesis gas.

Syngas heating value is degraded least by its conversion to ethylene or methanol. For any hydrocarbon fuel the loss in chemical energy is less than 20% of the synthesis gas heating value. However, when the entire conversion process is considered, the net energy yield is still lower since energy is needed to operate the conversion process (e.g., energy is required for compression, gas cleaning, purification of product, etc.).

13.2.2 Kinetics and Mechanisms

Although the conversion of synthesis gas to hydrocarbons and alcohols is favored thermodynamically at temperatures below 350 C, such conversions do not proceed at a practical rate without the use of catalysts. Because of this rate limitation, an equilibrium distribution of products is never achieved in a practical reactor. Indeed, one of the most successful and widely used conversions is the synthesis of methanol which, according to Fig. 13-1, is the conversion least favored thermodynamically. To some extent the unfavorable thermodynamics are overcome by using high pressures, 50 to 200 atm in the case of methanol.

Some catalysts used for synthesis gas conversions are highly specific, favoring almost exclusively the formation of a single product. An example is the ZnO or ZnO-CuO catalysts used for methanol synthesis. Other catalysts may be less specific, especially Fischer-Tropsch catalysts and mixed oxides of Cr, Mo, Cu, Zn, alkaline earth, or alkali metals used to form higher alcohols. The Fischer-Tropsch catalysts include Group VIII metals, especially iron, cobalt, nickel, and ruthenium. Nickel catalysts, especially Raney nickel, are fairly specific for the synthesis of methane. Catalysts with other forms of nickel, and certain iron and cobalt catalysts favor polymerization of carbon atoms to form higher hydrocarbons. The catalysts containing iron and cobalt have been used in commercial Fischer-Tropsch processes to convert coal to liquid fuels.

The mechanisms of the catalytic conversions are not fully understood. For example, at least three possible mechanisms have been proposed for Fischer-Tropsch synthesis. Each mechanism has supporting but not conclusive evidence. Instead, evidence suggests that each catalyst type has a unique reaction mechanism. For these reasons, further consideration of kinetics and mechanism is deferred to discussions of the individual synthesis gas conversion processes.

Certain common features may be noted, however. First, all the conversion reactions are exothermic (column 3 of Table 13-1). Hence, reactors must be designed with provisions for removing the heat of reaction. Too high a temperature reduces the extent of equilibrium conversion and can destroy catalytic activity (e.g., by sintering).

Another common feature is that all the presently known, commercial, conversion catalysts can be poisoned by $\rm H_2S$ and other sulfur-containing compounds. This is especially troublesome for coal conversion but may not be too serious a problem for biomass conversion. Extensive research is underway to find catalysts less sensitive to sulfur.



13.3 ALCOHOLS

The significant alcohol synthesis technologies from ${\rm CO/H_2}$ can be divided into two major categories: methanol synthesis and higher alcohol synthesis. A summary discussion of each alcohol synthesis technology is presented in the following sections. Detailed process technology and economic data on methanol production via biomass gasification are described.

13.3.1 Methanol Synthesis

The synthesis of methanol dates from the 1920s, when methanol was produced together with other hydrocarbon liquids by Fischer-Tropsch synthesis (Nelleo 1951). Later studies at Badische Anilin und Soda Fabrik (BASF), W. Germany led to the development of methanol catalysts and were the foundation for modern methanol synthesis technologies. This area significantly advanced in 1966 when Imperial Chemical Industries (ICI) commercialized the first low-pressure catalyst (Strelzoff 1971).

The major reactions in the synthesis of methanol are:

$$CO + 2H_2 \longrightarrow CH_3OH,$$
 (13-1)

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O.$$
 (13-2)

Table 13-2 shows that the equilibrium conversion of CO and H_2 to methanol from synthesis gas is favored by high pressure and low temperature.

Table 13-2. EFFECT OF PRESSURE AND TEMPERATURE UPON THE EQUILIBRIUM CONCENTRATION OF METHANOL FORMED FROM A SYNTHESIS GAS WITH A HYDROGEN-CARBON MONOXIDE MOLE RATIO OF 4:1^a

	N	lole Percen	t in Product	Gas at Tem	perature (° C)
Pressure (atm)	240	280	300	340	380	400
50	26.0	13.9	8.7	2.88	0.94	0.57
100	31.7	25.7	20.4	9.95	3.95	2.43
150	32.8	30.1	27.0	17.3	8.47	5.56
200	35.1	31.8	30.1	23.0	13.3	9.44
300	33.3	32.8	32.1	28.6	21.4	17.0

^aFrom Strelzoff (1971).

Although the thermochemistry of methanol synthesis is well understood and is supported by ample data, the kinetics of the heterogeneously catalyzed reaction are still the objective of substantial research. The catalyzed reaction has been modeled in various ways, with the rate-determining step ranging from absorption of the reactants to desorption of the products.



Natta and his coworkers made detailed rate measurements on powdered catalysts, one consisting of ZnO and Cr₂O₃ and the other oxides of Zn, Cu, and Cr in the ratio of 2:1:1 (Natta 1955). An overall rate expression was developed for reaction:

where

r₁ is g-moles methanol/g catalyst/h,

k₁ is the equilibrium constant for reaction 13-1,

 γ_i^i is the activity coefficient of component i, and ρ_i^i is the partial pressure of component i.

The constants A, B, C, and D are characteristic of the catalyst and vary with temperature in the form:

$$\ln A = \alpha + \beta/RT.$$

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 (Catalytica Assoc. 1978). This may not be too important for the biomass synthesis of methanol, since most biomass materials contain little sulfur. Small amounts of sulfur can be removed by a zinc oxide guard bed or by activated carbon placed ahead of the catalyst beds.

13.3.1.1 Current Methanol Synthesis Processes

The current methanol synthesis technology is divided into three categories: the older, high-pressure technology; the newer, lower pressure technology; and a liquid-phase methanol synthesis process, presently under development.

High-pressure process. This process, representing a large fraction of the methanol production capacity at the present time, was used exclusively through 1966, when Imperial Chemical Industries introduced its low-pressure process (Strelzoff 1971). The highpressure process operates at 300-350 atm (4400-5100 psig) and 300-400 C (570-750 F). The catalyst used is a mixed oxide of zinc and chromium 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. Because the activity of the Zn/Cr catalyst is low at lower temperatures, a high temperature is required to achieve reasonable reaction rates. The high temperature results in equilibrium limitations on the synthesis reaction, requiring high pressures to drive the equilibrium.

Low-pressure process. The low-pressure process, originally introduced by ICI in 1966, is now available in a number of variations. All of these processes use a copper-based catalyst and require the feed to be free of sulfur and chlorine to maintain catalyst activity.



The original ICI process operated at temperatures below 300 C (570 F) and at a pressure of 50 atm (750 psig) (Strelzoff 1971). The use of the more active Cu/Zn/Cr catalyst requires very pure synthesis gas.

The growing use of methane steam re-forming produces an extremely pure feed gas, giving the sensitive copper-based catalyst a long life. In other respects, the low-pressure process is similar to the high-pressure process, requiring methanol condensation and synthesis gas recycle. Table 13-3 lists several low-pressure processes currently available with operating conditions and reactor designs. A high-pressure process is included for comparison. This table also identifies one of the major problems in methanol synthesis, the high heat of reaction. This results in a temperature increase in the reactor catalyst bed, magnifying the equilibrium limitations on the conversion. ICI uses cold-gas injection similar to the system used in the high-pressure process. Lurgi has introduced a tube-in-shell reactor design to closely control catalyst temperature, while Topsøe employs a radial-flow converter with a copper-based catalyst capable of operation to 350 C.

Table 13-3. TYPICAL METHANOL SYNTHESIS PROCESSES IN CURRENT USE

Vendor	Catalyst	Pressure (atm)	Temperature (°C)	Reactor Type	Cooling
ICI	Cu/Zn/Al	50-100	220-290	Single fixed-bed	Multiple gas quench
Lurgi	Supported Cu	30-50	235-280	Tube in shell	Steam generation
Topsøe	Cu/Zn/Cr	50-100	220-350	Radial flow	-
Vulcan- Cincinnati	Zn/Cr	300-350	300-400	Multiple bed	Cold-shot quench, plus external gas cooling

Liquid-phase methanol synthesis process. This process is in the developmental stage, but deserves some comment since published economic analyses forecast reduced costs for the product methanol (Shewin and Blum 1976). This process addresses one of the major problems in methanol synthesis: efficient removal of the reaction heat. A minimal temperature rise is achieved by fluidizing the catalyst in an inert liquid phase which is circulated outside of the reactor where the heat is removed. This close temperature control results in increased conversion to methanol. Problem areas can be the breakdown of the catalyst particles into easily lost, fine particles; inhibition of the catalyst by the fluid; and insufficient solubility of the synthesis gas in the fluid. Comparison of the economics of this process with the ICI process project a cost advantage of approximately 15% in the methanol produced (Shewin and Blum 1976).

The efficiency of methanol production generally has been based on the thermodynamic first law: the combustion enthalpy of the products divided by the energy of the



feedstocks plus energy losses. The reported efficiency values are summarized here (SAI 1978):

Process Description	Efficiency (%)
Large-scale natural gas methanol plant using ICI low-pressure process	50-60
Vulcan-Cincinnati high-pressure process	63-69
Large coal gasification plant using ICI low-pressure process	41-75
Wood biomass gasification and ICI low- pressure process	30-47

13.3.1.2 Alternative Biomass to Methanol Processes

The basic process for producing fuel grade methanol from biomass feedstocks employs a thermal gasification step as shown in Fig. 13-2. The major processing steps are described here.

Gas purification. The partially purified syngas from the biomass gasifier(s) is compressed to about 100 psig and treated in a two-stage system to remove carbon dioxide. In the first stage, a hot potassium carbonate system is used to reduce the carbon dioxide content to about 300 ppm; in the second stage, this is reduced to about 50 ppm, with methylethanolamine as the scrubbing agent. The net product is a gas that is essentially a mixture of carbon monoxide and hydrogen.

Shift reaction. After purification, the gas is compressed to 400 psig for shift conversion. Here, a portion of the carbon monoxide reacts with water vapor to form additional hydrogen, to the extent that the final gas contains the required 2:1 hydrogen to carbon monoxide molar ratio. The shift reaction also produces carbon dioxide, which must be removed from the gas prior to the methanol reaction. This is done in a second hot potassium carbonate absorption system, which removes about 97% of the carbon dioxide formed during shift.

Methanol synthesis and purification. The synthesis gas, containing a 2:1 hydrogen to carbon monoxide ratio, is compressed to 1,500 psig and fed into the methanol synthesis reactor. Approximately 95% of the gas is converted to methanol, the balance being lost in a purge stream fed to the boiler. The product then passes to a distillation train for separation of the light ends and higher alcohols. A fuel grade methanol product is produced. The mixture of light ends and higher alcohols is used as a fuel in the boiler.

13.3.1.3 Methanol Production Economics

Capital cost of methanol plants. Table 13-4 lists capital costs for methanol plants utilizing different processes and both conventional and unconventional feedstocks. Similar information for methanol plants utilizing biomass feedstocks is listed in Table 13-5. The capital cost data are summarized graphically in Figs. 13-3 and 13-4, including the data from Stull (1969). Costs of plants have been brought to a common basis for comparison.

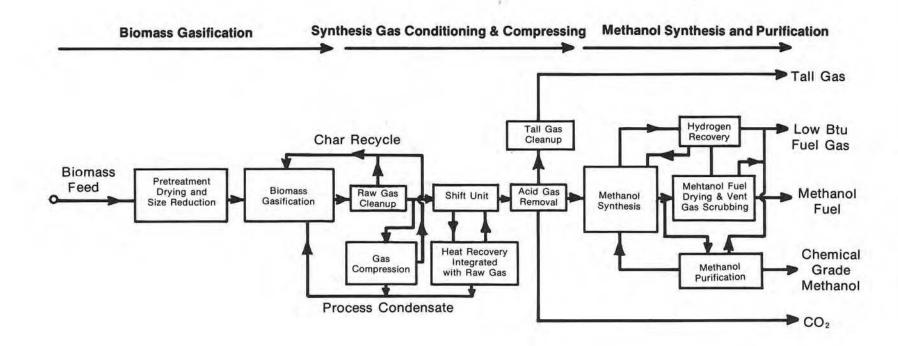


Figure 13-2. Simplified Biomass to Methanol Process Flow Diagram

SUMMARY COMPARISON OF CURRENT METHANOL PRODUCTION COSTS—CONVENTIONAL PRODUCTION TECHNOLOGIES AND FEEDSTOCKS (1980)² Table 13-4.

Plant Size		F	eedstock	Re-forming Oxidation or	Methanol	Capital	Annual Operation & Maintenance			Unit Production Cost ^D	
Source	(ton MeOH /day)	Туре	Throughput per/day	Gasification Process	Synthesis Process	Cost ^a (million \$)	Cost (million \$)	Feedstock Cost	(\$/gal MeOH)	(\$/ton MeOH)	(\$/ MBtu)
Exxon Res. & Eng. Co. (1977)	2000	Natural gas	70,900 MBtu	Steam methane re-forming	Low pressure	149	13.5	\$3.15/ MBtu	0.64	191.7	9.9
Exxon Res. & Eng. Co.	2000	Residual oil	79,100 MBtu	Partial oxidation	Low pressure	242	15.9	\$2.35/ MBtu \$15.0/barrel	0.74	221.6	11.4
Exxon Res. & Eng. Co.	2000	Illinois coal	3436 ton	Koppers Totzek	Low pressure	355	20.4	\$21.8/ton \$0.96/MBtu	0.74	225	11.4
Exxon Res. & Eng. Co.	2000	Illinois coal	3212 ton	Improved process (Texaco or Koppers-Shell)	Low pressure	315	17.8	\$21.8/ton \$0.96/MBtu	0,65	196	10
Badger Plants, Inc. 1978)	58,300	Coal	63,000 ton	Slagging gasifier	Lurgi low pressure	3800	593	\$31/ton	0.23	69	3.7
Ralph M. Parsons (1977)	16,392	Illinois coal	24,566 ton	Foster Wheeler gasification	Chem Systems low pressure	2100	114	\$31/ton \$1.26/MBtu	0.41	123	6.4
Ralph M. Parsons	16,392	Illinois coal	22,918 ton	British Gas Council/ Lurgi gasification	Chem Systems low pressure	1900	110	\$31/ton \$1.26/MBtu	0.39	117	6.1
Ralph M. Parsons	16,392	Illinois coal	24,574 ton	Koppers- Totzek	Chem Systems low pressure	2900	163	\$31/ton \$1.26/MBtu	0.53	159	8.3
Ralph M. Parsons	16,392	Illinois Coal	22,100 ton	Texaco gasification	Chem Systems low pressure	2400	134	\$31/ton \$1.26/MBtu	0.44	134	7.0
Wilson et al. 1977)	245	Refuse 25.8% moisture	1500 ton	Purox (Union Carbide)	Low pressure	126	16	\$-14/ton ^b	0.72	217	10
Mathematical Sciences Northwest (1974)	275	Refuse 25% moisture	1500 ton	Purox (Union Carbide)	ICI low pressure	31	3.1	\$-6.4/ton ^b	0.42	127	6.5

^aCosts have been extrapolated to 1980 dollars by using the Chemical Engineering Cost Index with appropriate extrapolation.

^bNegative numbers mean that the methanol producer receives money by taking the feedstock (which is refuse in this case). This money comes from the refuse and drop charges.

SUMMARY COMPARISON OF PROJECTED METHANOL PRODUCTION COSTS BIOMASS FEEDSTOCKS (\$1980)⁸ Table 13-5.

Plant Size (ton MeOH Source /day)	Size		lstock		Methanol	fass Conversion Efficiency dry ton	Capital	Annual Operation & Maintenance	Feedstock Cost	P	Unit roduction Cost ^a	
		Throughput y ton per/day)	Gasification Process	Synthesis Process	(feedstock/ ton MeOH)	Cost ^a (million \$)	Cost (million \$)	(\$/dry ton)	(\$/gal) MeOH)	(\$/ton MeOH)	(\$/ MBtu)	
Reed, T. (1976)	300	Wood (dried)	900	Purox	Available commercial process	3.0	45	5.0	30.3	0.58	173	8.9
Intergroup (1978)	1000	Wood 35% moisture	2380	Purox	Available commercial process	2.3	223	16	37	0.76	229	11.8
Mackay and Sutherland (Canada) (1976)	1000	Wood (dried)	3160	Purox	ICI medium pressure	3.2	223	13.8	46	0.96	290	15
Mitre (Blake and Salo 1977)	1340	Wood 50% moisture	3400	Purox	ICI low pressure	2.5	130	21	45	0.66	199	10
Mitre (Blake and Salo 1977)	335	Wood 50% moisture	850	Purox	ICI low pressure	2.5	46	8.9	45	0.84	253	13
Raphael Katzen Associates (1975	500	Wood waste 50% moisture	1500	Moore- Canada	Vulcan Cincinnati intermediate pressure	3.0	90	7	48	1.35	404	20.7
Raphael Katzen Associates	2000	Wood waste 50% moisture	6000	Moore- Canada	Vulcan Cin. I.P.	3.0	237	N/A	48	1.02	304.0	15.6
SRI (1978)	666	Wood 50% moisture	1000	Oxygen blow gasification	not specified	3.0	100.8	9.0	19.1	0.51	154	7.96
SRI	1990	Wood 50% moisture	3000	Oxygen blow gasification	not specified	3,0	268.7	29,4	19.1, 38.2	0.50, 0.62	150, 185	7.77, 9.53

⁸Costs have been extrapolated to 1980 dollars by using the Chemical Engineering Cost Index with appropriate extrapolation.

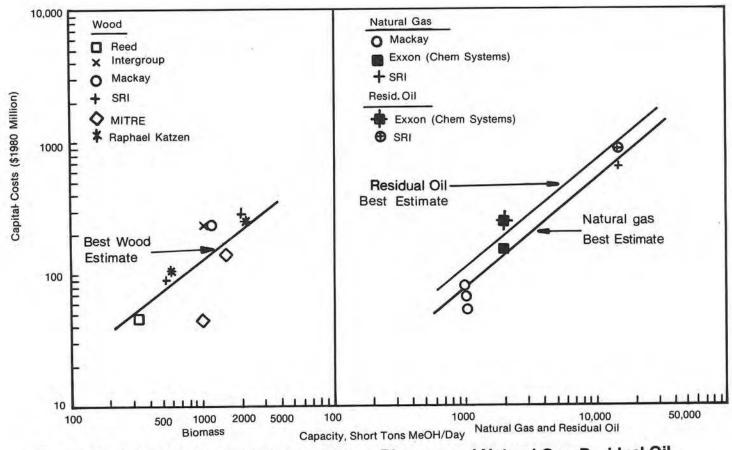


Figure 13-3. Capital Costs of Methanol Plant: Biomass and Natural Gas, Residual Oil

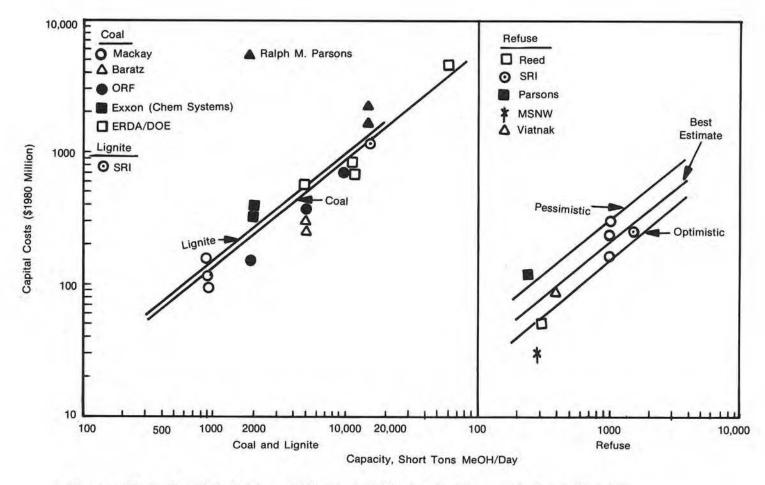


Figure 13-4. Capital Costs of Methanol Plants: Refuse and Coal, Lignite



Figures 13-3 and 13-4 show that the capital costs increase with the 0.8 power of plant capacity. For the same plant size, the capital costs of a residual oil-based plant average about 75% more than the costs of a natural gas-based plant. The capital costs of plants utilizing coal or lignite are even higher, about 150% more than the natural gas-based plant. The estimates for the capital costs of plants utilizing biomass or refuse fall into a range that overlaps the costs for coal-based plants.

Table 13-6 summarized capital costs at various scales based on "best estimate" cost lines. Where there is no entry, a plant of that size is not regarded as feasible at the present time because of raw material supply considerations (wood and refuse); or because the small size would preclude profit (natural gas, residual oil, lignite, and coal).

Table 13-6. CAPITAL COSTS OF METHANOL PLANTS

(Millions of 1980 Dollars)

		Methar	ol Plant Ca	pacity (ton/	'day)					
Feedstock	200	500	1000	2000	5000	60,000				
Wood	40	80	120	220	_	_				
Natural gas		_	78	136	283	Ξ				
Oil residue	1 -	_	112	190	397	-				
Coal	_		137	238	495	3800				
Lignite	_	_	146	255	531	_				
Refuse	54	112	195	_	-					

Operation and maintenance costs (O&M). O&M costs include the costs of utilities, chemicals and catalysts, labor, and maintenance and are listed in Tables 13-4 and 13-5. The O&M costs for coal plants are lower than for the SRI wood to methanol plant in the same size range. O&M costs for residual oil and natural gas plants are the lowest of all of the energy sources.

Methanol production costs. As shown in Table 13-5, typical estimated production costs of methanol from biomass range from \$0.58/gal to \$1.35/gal; the range for the non-biomass technologies is from \$0.42/gal to \$0.72/gal.

13.3.1.4 Alternative Methanol Process from Biomass-Methane Hybrid Feedstocks

Analysis of the current technology for large-scale methanol production from biomass by thermochemical gasification indicates that methanol production costs are significantly affected by plant size, feedstock cost, hybrid feedstock potential, 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 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 concepts could alleviate the resource constraint and reduce the methanol production costs. Of particular interest is production of methanol by mixing the synthesis gases obtained from biomass



gasification and from the re-forming of methane. A recent study estimated that methanol production from wood biomass could become economically competitive if it were based on the use of a biomass-methane hybrid feedstock (Intergroup 1978). The following sections discuss some of the technical and economic issues of such a system.

Technical advantages of biomass-methane hybrid methanol system. The current proposed technology for large-scale methanol production from renewable biomass feedstocks employs a thermal gasification process with no additional feedstocks after the gasification step (see Fig. 13-2). The synthesis gas thus produced is cleaned, compressed, and shifted to obtain the required stoichiometric ratio of hydrogen to carbon monoxide. Adjustment of the hydrogen-carbon monoxide ratio through use of the water-gas reaction lowers the mass conversion efficiency of the overall process.

Re-forming 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 biomass feedstock to about two to five times the level achievable by biomass gasification alone. In addition, the methane-hybrid methanol system, through elimination of the shift conversion, would reduce the CO₂ scrubbing requirements. Figure 13-5 is a simplified flow diagram of alternative biomass-methane hybrid methanol processes. Table 13-7 compares mass conversion efficiencies of a biomass and a methane-hybrid methanol system.

Table 13-7. COMPARISON OF THE RELATIVE MASS CONVERSION EFFICIENCY OF A SIMPLE BIOMASS AND A BIOMASS-METHANE HYBRID TO METHANOL SYSTEM

(Tons of methanol per ton of dry wood feed)^a

Gasification Process	Simple Gasification ^b	Methane Hybrid ^C
Purox	0.464	2.09
Moore-Canada	0.505	1.86
Koppers-Totzek	0.497	1.80
Wellman-Galusha	0.462	1.91

^aEstimated yields do not include fuels used for process energy or removed from the methanol reactor purge stream.

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 five years) without a significant capital cost penalty:

- Stage One would provide (within three years) a natural gas methanol plant with a
 deliberately under-capacity steam re-forming process.
- Stage Two would add the biomass gasifiers within one to three years from the start of initial methanol production.

^bGasification plus shift conversion to $H_2/CO = 2$.

^cGasification plus appropriate steam re-formed methane addition to adjust $H_2/CO = 2$.

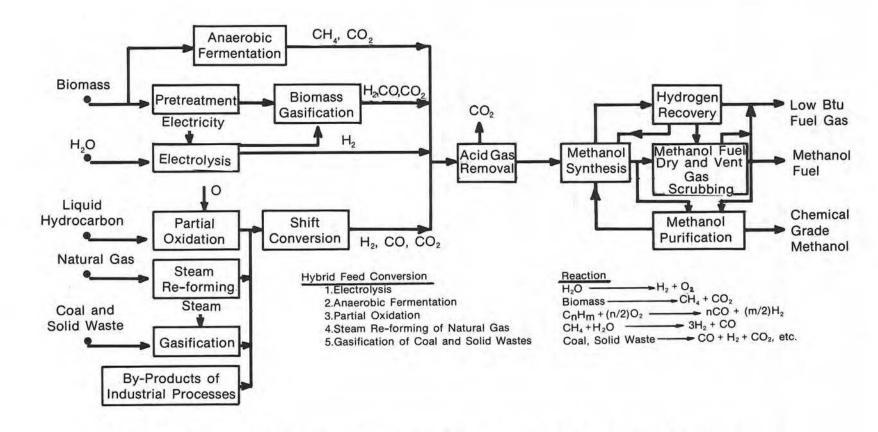


Figure 13-5. Biomass to Methanol Process Flow Diagram Using Hybrid Feedstock



The biomass-methane hybrid system also can be viewed as a mechanism for retrofitting existing methanol from natural gas plants. In this capacity, biomass gasifiers could replace as much as 30% of the natural gas feedstock. Therefore, the only capital cost requirement would 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 would also reduce the methanol production cost.

For longer term development (1990 and after), methanol production from biomass can benefit economically from consideration of several methane gas production alternatives including (1) anaerobic digestion of biomass, MSW, sewage sludge, or peat; (2) synthetic natural gas (SNG) production from fossil fuels; and (3) SNG from petroleum sources. Other possible biomass hybrid feedstocks also are being investigated. One is to augment the biomass gas stream with hydrogen only, although this hydrogen hybrid is estimated to be less cost effective than the methane-hybrid systems. In the long term, the hydrogen source could be generated from electrolysis of water, closed-cycle thermochemical decomposition, and hydrogen from fossil fuels.

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

13.3.2 Higher Alcohol Synthesis

The use of fuel-grade alcohols is not severely restricted by a requirement for high product purity. In this case, the less selective catalytic processes described below may be considered for liquid fuel production from syngas.

13.3.2.1 Mixed Alcohols Using Alkali Metal Oxide Catalysts

In the intensive efforts to find a suitable methanol catalyst during the past several decades it was discovered that several metal-containing catalysts could be used to produce mixtures of alcohols 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 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 13-8. It is noted that as the alkali ion concentration increases, the yield of methanol decreases and the yield of higher alcohols increases. For example, with a catalyst of 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% methanol, 38% higher alcohol (mostly ethanol), and 15% aldehydes and acetals.

The prospect of using a unique catalyst for the simultaneous production of methanol and ethanol appears to be attractive at this time. Further research and development work in these areas is highly desirable.

13.3.2.2 The "Oxo" Process

The production of aldehydes via the hydroformylation of olefins had been accomplished on the laboratory scale in the early portion of this century. Reviews of the application



Table 13-8.	METHANOL SYNTHESIS OVER ALKALI METAL OXIDE
	CATALYSTS AT 400 C AND 200 atm

Catalyst	Product Ratio (wt %)	% Yield (g/h)	% Methanol in Product	Other Liquid Compounds in Product
Cr ₂ O ₃ /MnO/Li ₂ O Cr ₂ O ₃ /MnO/Na ₂ O	1:0.93:0.10	47	76.9	21.7
Cr ₂ O ₂ /MnO/Na ₂ O	1:0.93:0.08	43	63.9	32.9
Cr ₂ O ₂ /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
2 3	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

of this reaction (Wender et al. 1957; Gates et al. 1979) attribute to Otto Roelen of Ruhrchemie AG in Germany the discovery of catalyst composition and reaction conditions at which the reaction of the following type could occur. The reactions are members of a general class and so they are referred to as "oxo" synthesis reactions:

$$\begin{array}{c} \text{CHO} \\ \text{RCH=CH}_2 + \text{CO} + \text{H}_2 \\ \hline \end{array} \rightarrow \begin{array}{c} \text{RCHCH}_3 \\ \text{RCH}_2 \text{CH}_2 \text{CHO} \end{array}$$

Reactants in the stoichiometric ratio were mixed with a cobalt catalyst at a pressure of 100 atmospheres and at temperatures between 50 and 150 C. Carbonyls [e.g., Co₂ (CO)₀] of cobalt, iron, nickel, and rhodium have been found to be active catalysts for this reaction. If the oxo reaction is followed by hydrogenation of the aldehyde, the overall result is production of an alcohol containing one carbon atom in excess of that of the original olefin.

Wender et al. (1957) report that in the hydroformylation of ethylene the free energy change of reaction varies from -13,900 cal/mole at 200 C to -14,460 cal/mole at 25 C. Since the reaction takes place in the liquid phase, the effect of total pressure on the equilibrium yield may be expected to be small. These considerations indicate that formation of aldehydes via the oxo synthesis is thermodynamically favored at temperatures below 200 C. The reaction is highly exothermic (-28 to -35 kcal/mole) and efficient heat removal is required for control of temperature. Gates, Katzer, and Schuit (1979) report that the following rate form may be representative of the kinetics of the oxo reaction:

$$\mathbf{r} = \frac{{^{k}} {^{C}C^{C}}_{RCH=CH_{2}} {^{P}H_{2}}}{{^{P}CO} {^{+}} {^{K}} {^{P}H_{2}}}$$



where C_C is the catalyst concentration and the pressure independent rate for 1:1 H_2/CO ratios is notable.

In the oxo reaction, olefins are reacted in the liquid phase with hydrogen and carbon monoxide in the presence of a dissolved catalyst. In addition to favorable thermodynamic effects, increased gas partial pressures of carbon monoxide and hydrogen increase the reaction rate through a proportional increase in liquid phase concentrations, and prevents decomposition of the cobalt carbonyl catalyst complex.

Presently, BASF Aktiengesellshaft in Germany and the Union Carbide Corporation in the United States operate large-scale oxo processes. In the BASF process, linear or branched chain olefins in the Cg-Cl7 range are converted to aldehydes which are hydrogenated to the corresponding alcohol. A dissolved cobalt catalyst is employed and is recycled without significant material loss. The oxo synthesis is conducted at temperatures in the 150-190 C range and at pressures in the 100-200 atmosphere range. The product alcohols are employed in the production of sulfated washing and wetting agents. In the Union Carbide process, n- and iso-butraldehyde are produced through hydroformylation of propylene at pressures of 7-20 atmospheres and at at a temperature of approximately 100 C. An organo-metallic complex of rhodium is employed to obtain a product containing an excess of the normal isomer. Separation columns are employed to provide product streams of high purity in each of the two isomers.

13.4 HYDROCARBON FUELS AND GASOLINE

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

The most highly developed technology for producing liquid hydrocarbons 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. High selectivity to specific fuels of the type described in Section 13.3 for alcohols is not achieved. The presence of large amounts of olefins and only a small fraction of aromatics makes the SASOL product undesirable for either gasoline or jet fuel without considerable upgrading. This problem is typical of all synthesis efforts based on the conventional Fischer-Tropsch type of catalysis.

The only novel approach to the synthesis of hydrocarbon fuels from CO and $\rm H_2$ has been pioneered by Mobil Oil Company over the last five years. Instead of relying on direct synthesis of fuels, the Mobil approach first synthesizes methanol and then proceeds through dimethyl ether as an intermediate to 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.

The Fischer-Tropsch and Mobil gasoline technologies are discussed in the following sections.



13.4.1 Fischer-Tropsch Synthesis

13.4.1.1 Catalysts, Product Distribution, and Kinetics

The Fischer-Tropsch reaction is the nonspecific catalytic conversion of hydrogen and carbon monoxide to a mixture of hydrocarbons, alcohols, and other oxygenated hydrocarbons. Since its discovery over 75 years ago, a great deal of research has focused on the activities of a variety of catalysts, catalyst preparation, tailoring catalysts for specific products, and the reaction mechanism and kinetics. The early work was done by Fischer and Tropsch in the 1920s. They demonstrated synthesis at atmospheric pressure and showed that the Group VIII metals have the highest catalytic activities. Later research in Germany emphasized cobalt at low pressures and led to the production of Fischer-Tropsch fuels in Germany during World War II. Further research led to iron catalysts and synthesis at medium pressures (10 to 20 atm). This technology was utilized in the SASOL plant in South Africa, built in 1955. The SASOL plant is the only commercial Fischer-Tropsch plant in the world today.

Some of the main characteristics of Fischer-Tropsch synthesis using the major catalyst types are listed in Table 13-9. Ruthenium is the most active catalyst but is expensive and produces mostly high molecular weight products unsuitable for use as liquid fuels. Nickel, although a very active catalyst, produces primarily gaseous hydrocarbons. Cobalt, although it is active and produces a good mix of liquid products, is expensive. Iron has slightly less activity than cobalt but is much less expensive.

Table 13-9. SYNTHESIS CHARACTERISTICS OF FISCHER-TROPSCH CATALYSTS⁸

Catalyst	Temperature (°C)	Pressure (atm)	Products
Ruthenium	20	200	Hydrocarbons, high melting waxes
Cobalt	200	1 to 10	Paraffins, olefins
Nickel	200	1 to 10	Mainly methane but some paraffins and olefins
Iron	250	20	Paraffins, some olefins, and oxygenated hydrocarbons
Zinc Oxide	250-300	100-300	Methanol

^aFrom Stull (1969) and Strelzoff (1971).

Most research in the United States since World War II has dealt with iron catalysts, and most of the research has been conducted at the Bureau of Mines. Typical, commercially available iron catalysts include fused iron oxide (magnetite) with 0.4 to 0.6% $\rm K_2O$, 2 to 3% $\rm Al_2O_3$, and 0.2 to 0.4% $\rm SiO_2$ as promoters. The catalyst may be activated by reduction with $\rm H_2$ at 450 C. A typical precipitated iron catalyst contains 55.4% Fe, 12.1% Cu, and 0.6% K as $\rm K_2CO_3$. This catalyst is activated by treatment with $\rm H_2$ at 250 C. Another catalyst is prepared by precipitating $\rm Fe_2O_3$ on $\rm Al_2O_3$ followed by reduction with $\rm H_2$ at 450 C. Still another may be formed from lathe turnings of carbon steel (Univ. of Connecticut 1978).



Recent research at the Bureau of Mines and the University of Connecticut (1978) has shown that nitrided and carburized-nitrided fused iron catalysts improved yields of middle distillates and reduced yields of waxes and olefins. As shown in Fig. 13-6, this is achieved only at the expense of a modest increase in the yield of methane. Approximately 50 to 60% of the synthesis gas is converted to liquid products (Shultz et al. 1957).

For iron catalysts the best synthesis conditions appear to be approximately 250 C and 20 atm pressure. The H_2 :CO ratio should be in the range from 1:1 to 2:1. Lower ratios suppress the formation of methane but may tend to coke the catalyst. A 1:1 ratio corresponds to the actual usage ratio of H_2 and CO in the reaction (Univ. of Connecticut 1978). Although the actual reaction is

$$2H_2 + CO = [-CH_2 -] + H_2O$$
, (13-4)

part of the water produced is reconverted to hydrogen by the water-gas shift reaction at these conditions,

$$H_2O + CO = H_2 + CO_2$$
. (13-5)

Hence, the overall net reaction is approximately:

$$1.5H_2 + 1.5CO = [-CH_2-] + 0.5CO_2 + 0.5H_2O$$
. (13-6)

It is well known that water inhibits the formation of hydrocarbons, and ${\rm CO}_2$ has been reported to be a mild inhibiter. However, experience at SASOL has shown that the presence of ${\rm CO}_2$ reduces the selectivity of iron catalysts for ${\rm CH}_4$ production (Dry 1976). Basic constituents in the catalyst have a similar effect.

Sulfur also is known to have an inhibiting effect. However, recent research by Exxon Research and Engineering has indicated that iron catalysts, as well as cobalt catalysts, can be made sulfur-resistant to some extent by alkali metals (Madon et al. 1977). In the same work, it was reported that sulfided (and therefore sulfur-resistant) Co-Mo/Al $_2$ O $_3$, Ni-W/Al $_2$ O $_3$, and KOH-promoted MoS $_2$ were found to be active Fischer-Tropsch catalysts.

The rate of hydrocarbon production over iron catalysts is described by the expression:

$$r = \frac{k_0 e^{-E/RT}}{(P_{CO}) + a (P_{H_2O})}, \qquad (13-7)$$

where the inhibiting effect of water vapor is exhibited. Work at the U.S. Bureau of Mines and the University of Connecticut indicates that the activation energy is in the range of 19 to 20 kcal/mol (Univ. of Connecticut 1978). Lower values, 15 kcal at low temperatures and 6 kcal at high temperatures, were reported for the SASOL process by Dry (1976).

13.4.1.2 SASOL Process

A block diagram of the SASOL plant is shown in Fig. 13-7. Coal is gasified and the product is rigorously cleaned to contain only CO, H_2 , and CH_4 . The gas is divided into two



Temperati Activi		252 72	279 28	257 62	242 95	245 93	238 128	238 115
Pretreat		Reduced	Reduced Oxidized	Reduced Carburized Heated	Reduced Carburized	Reduced Carburized Nitrided	Reduced Nitrided Carburized	Reduced Nitrided
Phase	es	ų α-Fe	α-Fe, Fe₃O₄	Fe₃C, α-Fe	Fe₂C (Hägg), α-Fe	ε-Carbo- Nitride,	ε-Carbo- Nitride Fe ₃ O ₄	ε-Nitride
	100-	C ₁	C ₁	C ₁	·C ₁	C ₁	C ₁	C ₁
	90	$C_2 = 64$ $C_3 + C_4$ $= 80$, C ₂ =70/ C ₃ +C ₄	$C_2 = 60$ $C_3 + C_4$ $= 82$	$C_2 = 51$ $C_3 + C_4$	C ₂ =19		C ₂ =23
	80 ——	<185° C.	= 82 <185°C.	<185°C.	= 81	C ₃ + C ₄ = 72	C ₂ = 19	/// C ₃ +C ₄
stion	70 —	Br 85 OH 3.3 CO COOH 2.3	Br 77 OH 2.5		< 185°C Br 62 OH 2.4		C ₃ + C ₄ = 67	= 68
al Produc	60	11/1/	COOH \$ 2.5	185°-352° C	CO 1.1			<185°
Percent of Total Production	50-	185°-352°C Br 37 OH .51	185°-352°C	Br 43 OH .76		OH 7.9 CO COOH .97	< 185°C.	Br OH 12 CO
Perce	40 —	352°-464°C	CO COOH 85	352°-464°	185°-352°C Br 35 OH .8	Y/////	CO 1.8	COOH)
	30	> 464°C.	352°-464°C	////	352°-464°C	Br 27 OH 1.6	V/////	<i>\\\\\</i>
	20	-	> 464°C	> 464°C.	> 464°C	CO COOH) .55 352°-464° C		185°-352
	10	-				> 464°C.	CO COOH 1.1 352°-464° C	он со соон
	0-						>464°C.	352°-46

Figure 13-6. Product Distribution for Selected Fused Iron Catalysts Synthesis with 1H₂ + 1CO₂ Gas at 300 psig. (From Encyclopedia of Chem. Tech. 1964)

Notations in blocks: Br, Bromine number of fraction; OH, CO, and COOH, weight-percentages of these groups.



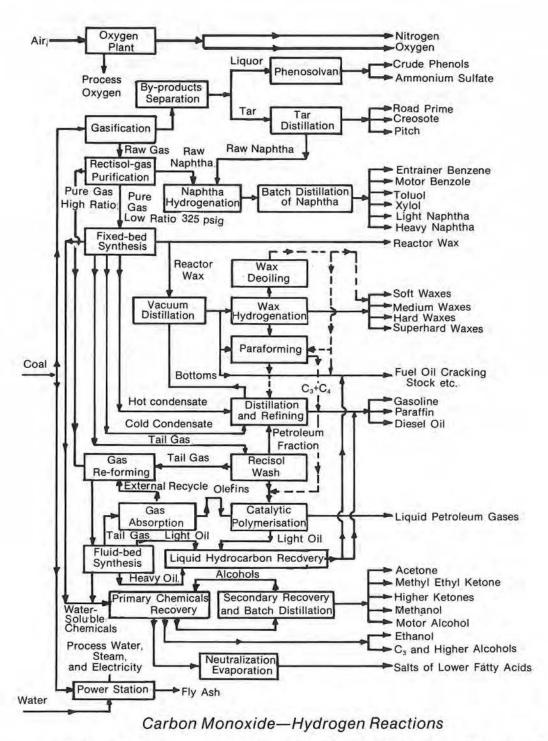


Figure 13-7. Block Diagram of the SASOL Plant (From Encyclopedia of Chem. Tech. 1964)



streams, the larger being fed to a fixed bed reactor (Fe-Cu catalyst) operating at 230 C and 360 psig. The tail gas, which is stripped of low-boiling hydrocarbons and $\rm CO_2$ by a Rectisol unit, is then combined with the remainder of the feed gas. This gas is re-formed over a nickel catalyst with steam and $\rm O_2$ to produce additional synthesis gas. A fluidized bed reactor (fused iron catalyst), operating at 325 C and 330 psig, converts this gas. Both reactor units contain internal recycle streams. Typical compositions of the fresh feed to the reactors are given below.

Volume Percent

	H ₂	CO	CO ₂	CH ₄	N ₂
Fixed bed	54	32	1	13	0
Fluid bed	62	22	7	5	4

As mentioned above, the only current commercial Fischer-Tropsch plant is that at Sasolbury, South Africa. The starting material is coal and the products include a high Btu gas, gasoline, diesel oil, waxes, and chemicals. Of the coal converted, approximately 40% is gasoline and 20% is diesel fuel. As of the early 1960s, only about 18% of the coal fed to the plant was converted to liquid products. Approximately 42% is used to provide power and process steam. The plant is commercially successful only because of a very unusual economic situation in South Africa. In a recent study by Air Products, fuels from Fischer-Tropsch were determined not to be competitive in the United States with methanol fuel synthesized from CO and $\rm H_2$ (Drissel 1977).

Numerous other Fischer-Tropsch processes have been proposed but none have become commercial. Most of them have unique ways of removing the heat of reaction and controlling the reactor temperature. The U.S. Bureau of Mines has developed two processes: the hot gas recycle, in which all the heat is removed in the gas; and a recycled catalyst-oil slurry, in which the heat is removed by the oil. This latter process is similar to the Chem Systems three-phase process for methanol synthesis.

Fischer-Tropsch synthesis appears to be well adapted for biomass conversion. Especially intriguing is the possibility of performing the conversion with little or no chemical cleaning of the gas from the gasifier. Gasified biomass typically has an H₂:CO ratio of approximately unity, which is correct for iron catalysts. The gas contains appreciable CO₂, which is beneficial for the production of liquid products. Finally, the gases from most biomass materials contain little sulfur, which is important if presently available catalysts are to be used. In spite of this adaptability, Fischer-Tropsch conversion may not be able to compete economically with conversion to methanol.

13.4.1.3 Fischer-Tropsch Liquid Fuels Costs

The literature cost data (Table 13-10) are from R. M. Parsons' study (1977) performed for the Electric Power Research Institute.

Table 13-10. FISCHER-TROPSCH COSTS⁸

(1980 Dollars)

Plant size: 5573 tons or 223,545 MBtu per day
Feedstock: 22,918 tons Illinois coal/day at
\$31/ton or \$1.26/MBtu

Gasifier: British Gas Council/Lurgi Slagger
Capital Cost: \$2,200M

Annual Operation and Maintenance: \$122M

Production Cost: \$6.7/MBtu or \$269/ton

R. M. Parsons' researchers judged that their cost estimates for the Fischer-Tropsch process are less accurate than their cost estimates for methanol production with the British Gas Council/Lurgi Slagging, Koppers-Totzek, and Texaco gasifiers. This is due to technological uncertainties. However, the capital, operating, and production costs per MBtu are within the same range as those from coal-to-methanol plants. The difference in capital costs between the British Gas Council/Lurgi Slagging methanol plant and the Fischer-Tropsch liquids plant arises from the higher capital cost of the Fischer-Tropsch synthesis unit (about twice the cost of the methanol synthesis unit).

13.4.2 Mobil Gasoline Technology

A class of crystalline zeolite catalysts recently 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 (Voltz et al. 1976). In this process, industrial-grade methanol is converted to hydrocarbons consisting mainly (greater than 75%) of a gasoline grade material with small amounts of LPG (C_3 and C_4) and fuel gas (C_1 and C_2). The overall gasoline yield can be increased to over 90% by alkylating the C_3 and C_4 olefins with the isobutane produced by the process. Figure 13-8 depicts the Mobil methanol-to-gasoline process flow scheme using a fixed bed reactor system.

The Mobil methanol-to-gasoline process offers a new route for the conversion of biomass to high-octane gasoline and other desirable products. The raw gasoline product is 30 to 50% aromatics, 45 to 55% 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 it could be blended with petroleum-derived gasoline.

13.4.2.1 Reaction Path and Potential Product Characteristics

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

^aFrom Ralph M. Parsons (1977).

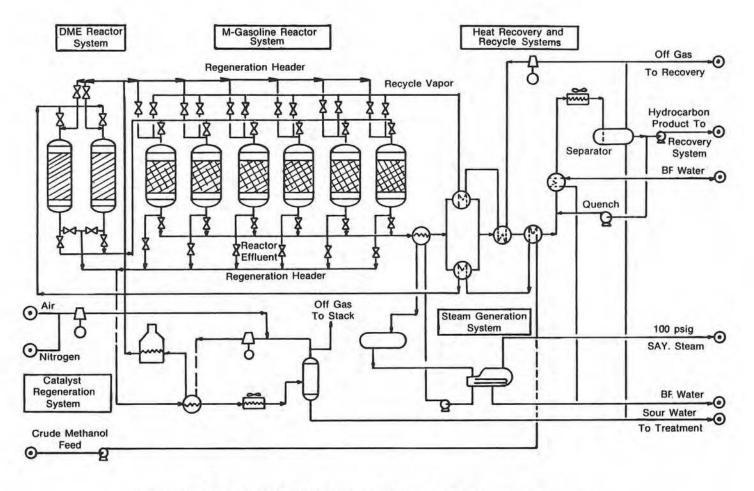


Figure 13-8. Mobil Methanol to Gasoline Process Flow Scheme — Fixed Bed Option (From Intergroup Consulting Economists 1978)



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 is used in a fluidized bed reactor.

Figure 13-9 shows the effect of space velocity on product distribution in methanol conversion to gasoline products.

Since the reaction path in the Mobil process 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 (Wise et al. 1977) has shown that, with catalyst and process modifications, it is possible to increase the level of the more desirable ethylene to about 30% at approximately 48% oxygenate conversion.

13.4.2.2 Alternative Gasoline Conversion Processes

Figure 13-10 shows an integrated process for converting biomass to high-octane gasoline via the fluidized bed reactor version of the Mobil methanol-to-gasoline process. Figure 13-10 shows that biomass, oxygen, and steam are suitably reacted to produce a synthesis gas that 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 processed further without separation. In either case, a methane stream is steam re-formed 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 re-forming, or both, and a hydrocarbon product comprised of C_5 + aromatic gasoline and C_4 - hydrocarbons.

In addition to the Mobil methanol-to-gasoline process, there are several other process alternatives for converting biomass-derived synthesis gas to gasoline products. They are described here.

A two-stage conversion of synthesis gas to dimethyl ether followed by conversion to gasoline products (U.S. patent 4,011,275). 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.

Conversion of synthesis gas having a smaller hydrogen to carbon monoxide ratio than that required for methanol stoichiometry is achieved by passing it over a zinc-chromium acid or copper-zinc-alumina-acid modified methanol synthesis catalyst. The product is a mixture of methanol and dimethyl ether. The mixture is then converted to hydrocarbons in a second stage, using zeolite catalysts operating at 700 F and a space velocity of 1 LHSV (liquid hourly space velocity) to produce a stream consisting primarily of ${\rm C}_5$ aromatic hydrocarbons.

Conversion of synthesis gas to methanol followed by carbonylation (U.S. patent 4,039,600). This process involves reacting carbon monoxide and hydrogen at about 450 to

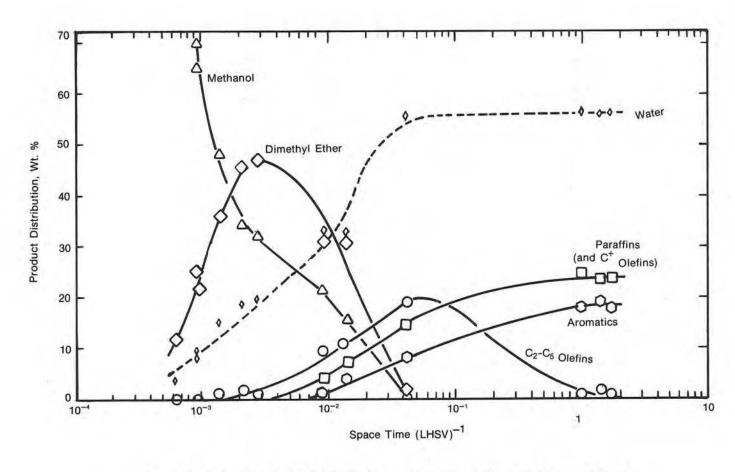


Figure 13-9. Product Distributions as a Function of Space-Time

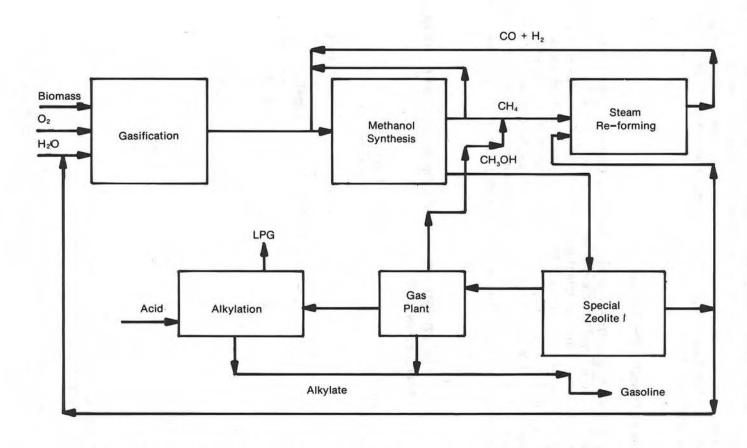


Figure 13-10. Integrated Simplified Flow Diagram of a Biomass-to-Gasoline Process



750 F, in contact with a methanol synthesis catalyst, to yield a gas stream of methanol and carbon monoxide. This mixture then is reacted at about 300 to 800 F in contact with a carbonylation catalyst, to form methanol and acetic acid. With a zeolite catalyst at about 500 to 1200 F, this mixture is converted to aromatic hydrocarbons in the gasoline-boiling-range. The particular admixture produced by the combination of methanol synthesis followed by carbonylation is convertible to a product unexpectedly higher in aromatic hydrocarbons than that predicted from a consideration of the conversion obtainable from individual reactants.

13.4.2.3 Economics of Gasoline Production

Costs of Mobil's methanol to gasoline process. Mobil Oil's process requires approximately 2.4 gal of methanol per gal of synthetic gasoline. The conversion cost from methanol escalated to 1980 is \$0.063 per gallon of gasoline (Voltz et al. 1976). This cost does not include the cost of producing the methanol feed. The total cost of each gallon of gasoline is thus the cost of manufacturing 2.4 gal of methanol plus \$0.063. Assuming 0.13 MBtu per gallon of synthetic gasoline, the production cost can be determined for this product. The calculations are shown in Table 13-11 for various sources and costs of methanol. On a Btu basis it is apparent that synthetic gasoline is about 23% more expensive than synthetic methanol.

Table 13-11. TYPICAL PRODUCTION COSTS OF MOBIL'S SYNTHETIC GASOLINE IN 1980

(Methanol costs from Tables 13-4 and 13-5)

		Cost of Methanol		st of soline
Source	Feedstock	(\$/MBtu)	(\$/gal)	(\$/MBtu)
Exxon	Coal	11.5	1.84	14.10
Badger	Coal	3.7	0.62	4.80
Ralph M. Parsons	Coal	8.3	1.34	10.30
Ralph M. Parsons	Refuse	10.0	1.79	13.80
Intergroup Consulting Economists	Wood	11.8	1.89	14.50
Raphael Katzen Associates	Wood	15.6	2.51	19.30

Table 13-12 shows the projected cost of producing gasoline via the Mobil process and is compared with estimates of production costs of obtaining gasoline from a synthetic crude oil produced from both coal and shale raw materials.

The alternative conversion process schemes differ from the basic Mobil methanol to gasoline process in that, while the synthesis gas produced from biomass is basically deficient in hydrogen for methanol synthesis, such synthesis gas may be ideally suited for conversion to gasoline or other products without the expense of going through an intermediate conventional methanol production stage. These process schemes could not only increase the carbon utilization efficiency from biomass resources but could also eliminate costly unit processes such as water-gas shift conversion and methanol purification.

1K-23

Table 13-12. SYNTHETIC GASOLINE COSTS IN 1980 DOLLARS

Sources	Feedstock	Process	Production Cost (\$/MBtu)	Percent of Methanol Cost (from Coal)
Lawrence Livermore Laboratory (Intergroup Consulting Economists 1978)	Coal	Refining syncrude	5.1	75 (MeOH from Koppers- Totzek gasifier)
Amax Inc. (Intergroup Consulting Economists 1978)	Coal	Refining syncrude	8.0	115
Exxon Research & Engineering Co. (1977)	Shale	Refining syncrude	2.6	89 (MeOH from Lurgi gasifier)
(1011)	Coal	Refining syncrude	3.8	123 (MeOH from Lurgi gasifier)
Mobil (Voltz et al. 1976)	Coal	Conversion of methanol	Varies with methanol costs 8-13	123



13.5 AMMONIA

13.5.1 Thermodynamic and Kinetic Considerations

Ammonia is produced in large scale by passing hydrogen and nitrogen over an iron-based catalyst at elevated pressure and moderate temperature. The overall chemical reaction is expressed as:

$$N_2 + 3H_2 \xrightarrow{\text{catalyst}} 2NH_3$$

The equilibrium among N_2 , H_2 , and NH_3 is shown in Table 13-13 for the percentage of ammonia at equilibrium to 200 atm pressure. These data show the very beneficial effect of pressure on ammonia conversion at equilibrium and the opposite effect of increase in temperature.

Table 13-13. PERCENTAGES OF AMMONIA AT EQUILIBRIUM²

Tomponeture	$\frac{P_{\text{NH}_3}}{P^{1/2} - X P^{3/2} - Y}$	Ammonia in gas mixture (%) at pressures (atm)				
Temperature, (°C)	N ₂ AP H ₂	1	30	100	200	
200	0.660	15.3	67.6	80.6	85.8	
300	0.070	2.18	31.8	52.1	62.8	
400	0.0138	0.44	10.7	25.1	36.3	
500	0.0040	0.129	3.62	10.4	17.6	
600	0.00151	0.049	1.43	4.47	8.25	
700	0.00069	0.0223	0.66	2.14	4.11	
800	0.00036	0.0117	0.35	1.15	2.24	
900	0.000212	0.0069	0.21	0.68	1.34	
1000	0.000136	0.0044	0.13	0.44	0.87	

^aFrom Slack and James (1977)

The chemical processes involved in ammonia synthesis are fairly complicated, as are many heterogeneous catalytic reactions. At the conditions used in industrial ammonia synthesis, it appears that this step is the chemisorption of nitrogen onto a surface evered mainly by nitrogen atoms. The equation most widely used over the years to correlate ammonia synthesis rate data is the Tempkin-Pyzhev equation (Slack and James 1977) as shown in Table 13-14. In these equations, ω is the net reaction rate; k_1 and k_{-1} are the rate constants for synthesis and decomposition, respectively; and α is a constant.

The heart of any ammonia plant is the synthesis catalyst. The main constituents of the ammonia catalyst are FeO and Fe_2O_3 . Modern catalysts differ from the early ones mainly in the amount of metallic oxides added as promoters. These metallic oxides may include the oxide of aluminum, calcium, potassium, silicon, and magnesium.



Table 13-14. KINETIC EXPRESSIONS FOR AMMONIA SYNTHESIS⁸

$$\omega = k_{1} P_{N_{2}} \left[\frac{P_{H_{2}}^{3}}{P_{NH_{3}}^{2}} \right] - k_{-1} \left[\frac{P_{NH_{3}}^{2}}{P_{NL_{2}}^{3}} \right]^{1-\alpha}$$

$$\omega = \frac{k_{-1} \left(a_{N_{2}} K^{2} - a_{NH_{3}}^{2} / a_{H_{2}}^{3} \right)}{NN}$$

$$NN = \left[1 + K_{3} a_{NH_{3}} / a_{H_{2}}^{\omega} \right]^{2\alpha}$$

$$k_{-1} = k_{-1}^{o} \exp \left(-E_{-1} / RT \right)$$

$$k_{3} = k_{3}^{o} \exp \left(-E_{3} / RT \right)$$

$$= \frac{k P_{N_{2}}^{1-\alpha} \left[1 - \frac{1}{K} \frac{P_{NH_{3}}^{3}}{P_{N_{2}} P_{H_{2}}^{3}} \right]}{\left[\frac{1}{P_{H_{2}}} + \frac{1}{K} \frac{P_{NH_{3}}^{3}}{P_{N_{2}} P_{H_{2}}^{3}} \right]^{\alpha} \left[\frac{1}{P_{H_{2}}} + 1 \right]^{1-\alpha}}$$

$$\omega_{+} = k' P_{H_{2}}^{\alpha} P_{N_{2}}^{1-\alpha}$$

$$\omega_{+} = k' P_{H_{2}}^{\alpha} P_{N_{2}}^{1-\alpha}$$

13.5.2 Ammonia Synthesis Processes

At the present time, ammonia synthesis processes may be classified according to synthesis loop pressures as high pressure (500-800 atm), medium pressure (240-350 atm), and low pressure (100-190 atm). A flowsheet for the production of ammonia by a typical process, but starting with clean synthesis gas from a wood biomass gasifier, is shown in Fig. 13-11. The major processing steps are described here.

^aFrom Slack and James (1977)

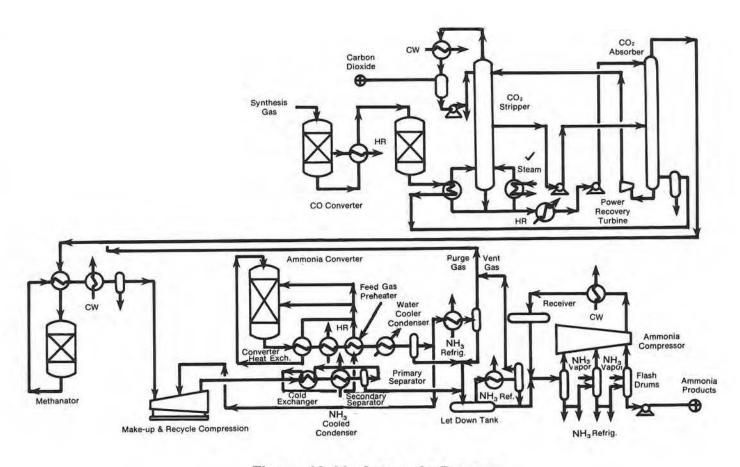


Figure 13-11. Ammonia Process



13.5.2.1 CO Shift

The synthesis gas is preheated to 550 F prior to entering the first-stage shift reactor. The gas is quenched with condensate to 400 F before it enters the second-stage shift.

13.5.2.2 Carbon Dioxide Absorption

The synthesis gas is then passed through the regenerator reboiler of a Benfield type CO₂ scrubbing system. The condensate from the reboiler passes to a degasser, where the process condensate is returned to the waste heat boiler as makeup. The synthesis gas then passes through the absorber where the CO₂ is absorbed at high pressure with the Benfield solution. The Benfield process is basically a promoted hot carbonate process.

The CO₂-enriched Benfield solution from the bottom of the absorber passes to a turbine, where its pressure is reduced, and then to the regenerator. The rich solution at low pressure is stripped free of CO₂ in the regenerator, and the Benfield solution then is recycled to the absorber.

13.5.2.3 Methanation

The synthesis gas from the Benfield system is methanated to remove the remaining carbon monoxide and carbon dioxide. The gas is preheated to 500 F by heat exchange with the gasifier exit stream. The effluent from the methanator is cooled in a water-cooled condenser to remove most of the water from the synthesis gas. The balance of the water is removed by means of a refrigerated condenser. Final traces of CO₂ and water are removed by means of a molecular sieve.

13.5.2.4 Ammonia Synthesis Loop

The makeup synthesis gas is compressed in a multiple-stage reciprocating compressor and pumped into the synthesis loop. The ammonia converter consists of a multiple-bed cold gas quench reactor, where the product of gas-ammonia mixtures is separated through a series of heat exchangers and condensers. The unconverted synthesis gas is recycled to the ammonia converter via a recycle compressor.

13.5.3 Economics of Ammonia Production

13.5.3.1 Capital Costs for Ammonia Plants

The capital costs from Tables 13-15 and 13-16 are summarized in Fig. 13-12. Wood-fed ammonia plants show a cost versus plant size exponent of 0.8, based on SRI data (Schooley et al. 1978), and 0.6 based on Mitre data (Blake and Salo 1972). Therefore, an average "best" estimate of 0.7 was assumed for this type of ammonia plant. This cost line is placed between the SRI cost line (high) and Mitre cost line (low) in Fig. 13-12.

Coal plants cost twice as much as methane-steam re-forming plants, while residual plants cost 50% more than re-forming plants, based on Exxon (1977) data. Mathematical Sciences Northwest's (1974) estimated cost for a refuse plant appears low, while Ralph Parsons' (1977) cost appears to be in the high range. To be conservative, Ralph M.

Table 13-15. SUMMARY COMPARISON OF CURRENT AMMONIA PRODUCTION COSTS (\$ 1980) FROM NON-BIOMASS FEEDSTOCKS⁸

	Plant Size	Fee	dstock	Re-forming, Oxidation or	Capital	Annual Operation & Maintenance		Unit Production
Source	(ton NH ₃ /day)	Туре	Throughput per/day	Gasification Process	Cost (million \$)	Cost (million \$)	Feedstock Cost	Cost (\$/ton)
Exxon Research and Engineering Co. (1977)	2000	Natural gas	70,000 MBtu	Steam methane re-forming	193.2	10.7	\$3.15/MBtu	210
Exxon Research and Engineering Co. (1977)	2000	Residual oil	12,424 gal	Partial oxidation	292.2	19.2	\$15/barrel \$2.35/MBtu	248
Exxon Research and Engineering Co. (1977)	2000	Illinois coal	3545 ton	Koppers Totzek	400.5	22.98	\$21.8/ton \$0.96/MBtu	248
Exxon Research and Engineering Co. (1977)	2000	Illinois coal	3315 ton	Improved process (Texaco or Koppers-Shell)	367.2	20.72	\$21.8/ton \$0.96/MBtu	227
Ralph M. Parsons (Wilson et al. 1977)	350	Refuse 25.8% moisture	1500	Purox (Union Carbide)	140	17.9	\$-14/ton ^b	134
Mathematical Sciences Northwest (1974)	335	Refuse 25% moisture	1500	Purox (Union Carbide)	39.7	3.9	\$-6.4/ton ^b	134

⁸Costs have been extrapolated to 1980 dollars by using the Chemical Engineering Cost Index with appropriate extrapolation.

bNegative numbers mean that the plant makes money by disposing of the refuse and collecting a fee.

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Table 13-16. SUMMARY COMPARISON OF AMMONIA PRODUCTION COSTS (\$ 1980) FROM BIOMASS FEEDSTOCKS⁸

Source	Plant Size (ton MeOH /day)	Fee Type	edstock Throughput (dry ton per/day)	Gasification Process	Mass Conversion Efficiency dry ton (feedstock/ ton MeOH)	Capital Cost (million \$)	Annual Operation & Maintenance Cost (million \$)	Feedstock Cost (\$/dry ton)	Unit Production (\$/ton MeOH)
Mitre (Blake and Salo 1977)	492	Wood 50% moisture	850	Purox gasification	1.7	53.8	9.4	45	154
Mitre (Blake and Salo 1977)	1970	Wood 35% moisture	3400	Purox gasification	1.7	132.9	21.4	45	120
McKee Corp. (1978)	400	Brava (Bamboo)	1270	Thermex gasification	3.2	64 (in Nicaragua)	33.2	19.6	213 (in Nicaragua)
SRI (Schooley et al. 1978)	500	Wood 50% moisture	1000	Oxygen blown gasification	2.0	110.1	9.6	19.1	300
SRI (Schooley et al. 1978)	1542	Wood 50% moisture	3000	Oxygen blown gasification	2.0	267.3	20.6	19.1 38.2	249 287

^aCosts have been extrapolated to 1980 dollars by using the Chemical Engineering Cost Index with appropriate extrapolation.



- O Natural Gas (Exxon 1977)

 Coal (Exxon 1977)

 Residual Oil (Exxon 1977)

 Refuse (Ralph M. Parsons 1977)

 Bamboo (McKee Corp. 1978)

 Wood (MITRE) [Blake and Salo 1977]

 Wood (SRI) [Schooley et al. 1978]
- Refuse (Mathematical Sciences Northwest 1974)

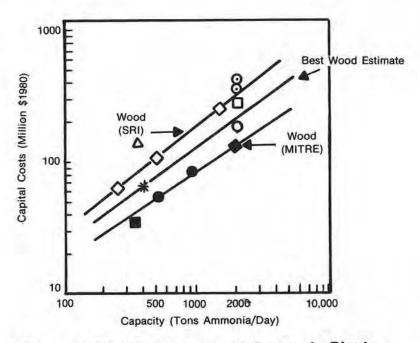


Figure 13-12. Capital costs of Ammonia Plants

Parsons' data are assumed to be more representative in light of the required equipment for shredding refuse and reclaiming metals. In addition, the Parsons data are more recent than those from Mathematical Sciences Northwest, and the costs of prototype equipment such as the gasifiers may be more current than those used by Mathematical Sciences Northwest.

The capital requirements for biomass-to-ammonia plants are slightly lower than those for coal, residual oil, and refuse plants. Table 13-17 summarizes capital costs at various scales based on "best estimate" cost lines. The cost lines for new biomass plants were assumed to have an exponent of 0.7.



Table 13-17. CAPITAL COSTS OF AMMONIA PLANTS

(Millions of 1980 dollars)

		Ammonia I	Plant Capacit	ty (ton/day)	
Feedstock	200	500	1000	2000	5000
Wood	40	80	130	220	
Natural gas	_	_	120	193	366
Oil residual	_	-	180	292	554
Coal	-	_	246	400	760
Refuse	95	180	-	_	

13.5.3.2 Operation and maintenance costs

Tables 13-15 and 13-16 also show the annual estimated plant operating and maintenance (O&M) costs. These include utilities (power and water), chemicals, labor, overhead, and maintenance. No capital depreciation charges or base feedstock costs are included. The costs show no definite pattern, although it is apparent that for plants in the 1500-2000 tons of ammonia per day range, annual O&M costs are quoted around \$20 million for the residual oil, coal, and wood plants. Steam re-forming of methane results in the lowest O&M cost.

13.5.3.3 Ammonia production costs

Tables 13-15 and 13-16 show that the estimated production costs of biomass-based ammonia range from \$120 to \$300/ton, while ammonia costs from other feedstocks range from \$134 to \$248/ton. The differential range is narrower than for methanol, indicating that ammonia may be able to penetrate the market more rapidly than methanol.

13.6 PROSPECTS FOR FUTURE RESEARCH AND DEVELOPMENT

A profitable potential exists for converting biomass-derived synthesis gases to fuels and chemicals through any of several thermochemical processes. The prospects for each type of process are summarized here.

13.6.1 Specialty Chemical Production

Ammonia production from biomass by current technology is both technically and economically attractive. The margin of this attractiveness should be enhanced by future technological improvements in biomass gasification for the production of hydrogen. The synthesis of other nitrogen-containing compounds from synthesis gas and simple organic molecules also should be explored. Such compounds might include aromatic isocyanates and simple amines.



13.6.2 Alcohol Fuels

In the near term, methanol is one of the most promising liquid fuels to be produced from biomass feedstocks. This can be realized by using a methanol hybrid production system with biomass and either methane or hydrogen feedstocks. The technical and economic advantages of such systems appear to allow biomass to compete with large-scale methanol production from coal and natural gas.

In the long term, 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. The new technologies include improved methanol synthesis processes, direct higher alcohol synthesis, conversion of methanol to gasoline (Mobil processes), and improvements in biomass gasification technology to produce a more easily used synthesis gas.

13.6.3 Fischer-Tropsch Products

Several aspects of the current, commercial Fischer-Tropsch process limit the potential application of this technology to biomass feedstocks. This process results in higher costs of liquid fuels than would be true for the Mobil gasoline process or methanol synthesis. However, opportunities exist for integrating an alcohol fuel, chemicals, and hydrocarbon fuel production by a Fischer-Tropsch synthesis. The economic attractiveness of an integrated production system depends upon the market potential of various products and byproducts. Also, carefully integrating process design and optimizing products for biomass feedstocks may be beneficial.

13.6.4 Gasoline Products

The new technology developed by Mobil for synthesizing gasoline from methanol and for direct synthesis of gasoline from synthesis gas may be economically attractive. Conceptual processes should be evaluated, especially those that include new biomass gasification techniques tailoring the synthesis gas composition to specific process requirements.



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Chapter 14

Governmental Aids to Commercialization of Air Gasification

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Another barrier that everyone faces in developing new energy sources is lack of capital. Not only was fossil fuel once cheap, but the equipment to burn it was also much cheaper than that required to burn wood or coal. Capital is in desperately short supply due to the 5-10 fold increase in oil costs (which then correspondingly increases the cost of coal, gas, and all manufactured goods that depend on energy); yet, capital must be found to finance new alternate-energy installations. A major factor favoring gasification is that it supplies a "retrofit fuel" for existing installations, thus reducing capital expenses.

We list these few barriers as examples of the many barriers to change because frequently they are not obvious, and we become frustrated by our lack of success without recognizing the hidden causes. Clearly, the continuing decrease in fossil fuel and the concomitant cost increases will force changes to alternatives no matter what the cost. Let us proceed to discuss positive actions that can be taken.

14.3 GOVERNMENTAL AIDS TO GASIFICATION COMMERCIALIZATION

Commercialization, by its very name, is not an activity primarily assigned to government. Nevertheless, government has often had a role in aiding certain developments considered to be in the national interest; for example, the U.S. Government has been very active in developing nuclear energy in cooperation with U.S. industries, and the present close cooperation of government and industry in Japan has rapidly developed new technologies and increased foreign trade.

Because of the energy shortages that developed as a result of the OPEC oil embargo of 1973-74, the U.S. government has announced its intention to help "commercialize" various alternate energy technologies, including solar energy and biomass. With the best of intentions, however, very little has been accomplished by the government towards commercialization of biomass since the establishment of the Energy Research and Development Administration (ERDA) in 1974 and the reorganization of ERDA to form the Department of Energy (DOE) in 1977. Meanwhile, the recent rapid development of wood stoves, forest industry wood use, and gasohol was led by private groups and industries, not government.

Abstracted here are suggestions received in answer to the letters of inquiry (see Section 14.4) and others that have been gleaned from discussions with those in the field.

- Several sizes of gasifiers should be demonstrated in order to raise the public awareness of gasification as one of the most attractive alternatives to the straight combustion of biomass.
- Gasifiers should be installed at government facilities where appropriate, particularly DOE and military installations.
- Large gasifier systems, involving fuel collection, drying, and distribution as well as gasification, should be demonstrated.
- Money should be passed through to the states to support regional energy programs in whatever way the states see fit.



- There should be fuel and equipment subsidies, generally in the form of tax rebates or writeoffs, market guarantees, government purchase, etc., which aid equally all manufacturers in the field or which give potential customers the incentive to use new energy forms.
- Technical and "state-of-the-art" information, such as this survey, should be made available to all interested parties.
- Documentation should be made of the availability of feedstocks in each season to permit the manufacturer and user to assess the degree to which gasification can be implemented.
- A "strike force" of technical, business, and legal experts should be created that can visit various installations or test sites and give advice on possible development options not obvious to the individual.
- An official liaison should be established with the \$150-million Canadian biomass program FIRE, instituted in 1978 to promote combustion and gasification of biomass, to learn from their successes and failures.
- Cooperation with foreign governments, which have had extensive experience in the field of gasification, should be instigated.

14.3.1 Attachment 1

From the "Bio Energy Commercialization Incentives" luncheon address by Paul F. Bente, Jr., Executive Director, BioEnergy Council, at the IGT-sponsored Conference on Energy Production from Biomass and Wastes, Orlando, Florida, January 23, 1979:

Keeping national goals and principles in mind, let us move on to several types of incentives that may be considered.

- One type is to mandate achieving goals without specifying the means. This happened, for example, when the government told the auto industry that its cars had to reach increasingly higher mileage performance over given periods of time, without telling them what had to be done to achieve this end result. An analogy would be to mandate over a period of time the addition to gasoline of increasing amounts of alcohol fuel, regardless of origin, or perhaps even restricted to biomass origin.
- Another approach is that of building a market by establishing economic subsidies
 that lower the price of a product to establish its use, much as our country now
 underwrites the cost of importing oil.
- Yet another way involves offering incentives to overcome institutional barriers that are chiefly financial in nature. There are many such possibilities to consider, foremost of which are loan guarantees where bank or investor financing cannot otherwise be secured.



- 4. Loan guarantees have the effect of lowering the interest rate on borrowed money by about 2%. However, loan guarantees, though authorized, are not presently operative in the DOE budget. An amendment is needed to create a line-item in the budget for a loan guarantee program.
- 5. USDA, through its Farmers Home Adminstration, has an effective loan guarantee program. In addition, the Food and Agriculture Act of 1977 set up a \$60 million loan guarantee program to guarantee loans of up to \$15 million for four industrial production projects to be selected from competitive proposals.
- 6. About 30 requests for such assistance were received. On January 12 the Commodities Credit Corporation Board ruled on the first three firms to qualify for such assistance. A guarantee was awarded to ENERCO, Inc., of Langhorn, Pennsylvania, which has a mobile wood pyrolysis unit that can also produce hydrocarbons. The guarantee will cover about \$5 million in loans for 45 mobile plants. A second guarantee was made to U.S. Sugars and Savannah Foods for a \$15 million loan for facilities at Cleviston, Florida to conduct acid hydrolysis of bagasse to sugars that will be fermented to make alcohol. This will be located adjacent to a sugar mill. A third guarantee is being made to Guaranty Fuels, Inc. in Independence, Kansas for \$5.8 million in loans covering 2 plants to pelletize forest wastes. Sometime next month the Board will select the fourth firm to be given a loan guarantee under this program. Let us hope that the interest rates which have soared dramatically will not be so high as to stop these projects from materializing.
- 7. Making direct government loans may even be necessary if a loan guarantee is not a sufficient incentive for lenders, or if interest rates from conventional sources of finance are too high, even with the lower rates made possible by guarantees.
- 8. Utilities are vitally concerned about being able to get financing for installation of biomass facilities. Offering investor-owned utilities government loans at reduced rates may be necessary to provide a significant incentive for their using biomass as fuel.
- 9. Another possibility is making an outright grant of funds, possibly on the condition that it must be matched by funds from other sources. This might be necessary to expand the resource of wood via cultivation, transportation, and energy conversion. Such a program should be applicable to public or private organizations as well as to individuals.
- 10. Another type of incentive is tax exemption. Under the IRS code, Economic Development Revenue Bonds of up to \$1,000,000 are tax exempt if they are issued to finance the cost of some portions of "municipal solid waste facilities." It is considered legally possible to use this vehicle to finance woodfueled electric generating plants. One such case has occurred, but it is questionable if others will. When and if tested, the IRS ruling will have to classify wood residues or wastes as "municipal solid wastes." Quite possibly this may not be the case. This situation could be clarified by amending the IRS act so that it clearly qualifies wood residues or wastes for such commercialization.
- 11. There are other taxes, such as the inventory tax and the capital gains tax, which can discourage production, harvesting, and use of biomass for energy. Amendments to exempt biomass from these taxes could help to spur commercialization.



- 12. There are still other possibilities to consider, including amendment to the IRS code for allowing rapid amortization to be applied against the cost of retrofitting or converting an existing energy production unit to use of biomass as a source of energy.
- 13. Another example might be amending the National Energy Act to allow a 20-40% investment tax credit on the basis of capital costs incurred for converting biomass as a source of energy.
- 14. We have heard of the solar tax credit that just went into effect for those who install solar devices to heat water, to heat or air condition buildings, or to insulate them. Heating homes with wood, which is stored up solar energy, seems just as deserving and could have a far greater impact, for it is more readily put to use by Mr. Public. Hence, there is a possibility of increasing self-sufficiency of homeowners and reducing their use of gas and oil by amending the law to allow wood heating stoves to qualify under the solar tax credit. [However, it is necessary that wood stoves meet emission standards in high population-density areas.]
- 15. Another incentive that would be both controversial and complicated to administer is redirecting funds used to pay farmers to set land aside in order to reduce production. Indeed, the funds could be used to pay farmers to produce biomass for fuel. This might be a bio-energy crop to trees, corn, or other crops for conversion to fuels and possibly other valuable coproducts such as feed supplements and fertilizers.
- 16. Another approach to incentives might be linked to environmental regulations involving the issuing of permits, including grandfathering arrangements. Combustion of biomass materials on a large scale will no doubt require emission control devices, which are expensive. Commercialization incentives might be offered by allowing quick amortization of capital expenditures for such equipment or by providing federal subsidies via procedures such as tax exempt industrial development bonds. Another possibility is to allow an investment tax credit, or to provide Small Business Administration loans of the economic injury type. These are designed to assist small industries that cannot benefit from the other procedures because they don't yet have enough cash flow to take a tax write-off or because they aren't yet making a profit.

Our government might emulate the commercialization effort being put forth by Canada. Canadians already use wood to the extent of 3-1/2 percent of total energy consumption. Their government desires to increase this several fold and last July launched a strong commercialization program earmarking funds to get industry to use more wood. Canada launched 5 programs that commit over \$300 million toward commercialization over the next 5 years.

The Forest Industry Renewable Energy (FIRE) program sets up \$140 million to be used over a 5-year period to contribute up to 20% of approved capital costs of systems using wood as an energy form. A companion program, Energy from the Forest (ENFOR), provides \$30 million over 5 years for a new contracted-out research program to implement large-scale use of forests to provide greater amounts of transportable fuels that will substitute for hydrocarbon fossil fuels in the late 1980s.



To spur these two programs, a series of cost-shared Federal-Provincial agreements will be set up involving a Federal contribution of \$114 million allocated over the next 5 years to bring current expensive prototypes to full-scale application. The Provincial contribution will be additional; but if this has been announced, I'm not aware of it.

In addition, a loan guarantee program is being set up to encourage generation of electricity from wood and municipal waste. The first project of its kind in any province is eligible for a guarantee of 50% of loan capital for a direct generating station and 66-2/3% for a cogenerating station.

With the aid of these programs, a 10% contribution of Canada's energy supply is considered possible by the year 2000.

14.3.2 Attachment 2

Specific suggestions of Richard C. Wright:

- Improve accuracy of media releases. There has been too much controversial and misleading publicity.
- Differentiate between air-blown coal gas producers and biomass gasifiers. These are entirely different devices.
- Promote recognition of forest products as equally important for renewable energy sources as for pulp and timber production.
- Encourage refining raw biomass into a uniform high-grade fuel. This is essential for optimum fuel utilization efficiency.
- 5. Sponsor voluntary grade or type specifications for refined biomass products. For example, identifying specifications such as ASTM D-396 for fuel oil, or the now obsolete "Commercial Standards" such as CS-95, anthracite coal size standards, etc.
- 6. Avoid massive financial grants for hardware development. Too much hardware is now being reinvented at public expense.
- 7. U.S. Federal support for a gasifier industry should be limited. Biomass gasification is now off to a good start. If left to serious competition in private industry, it will develop on a sound basis. Scientific help from a few well-qualified institutions, i.e., Georgia Tech., U. of C. Davis, etc., will be an advantage. Government grants to more, presently unqualified, agencies are not desirable.

14.3.3 Attachment 3

Summary of provision under Energy Tax Act of 1978 (part of NEA)-from DOE Summary:

Business Energy Tax Credits

A variety of tax credits for investment by business is provided. An additional 10% investment tax credit (nonrefundable except for solar equipment) is provided for investment in:



a. Alternative Energy Property: This applies to boilers and other combustors which use coal or an alternative fuel, equipment to produce alternative fuels, pollution control equipment, equipment for handling and storage of alternate fuels, and geothermal equipment. This credit compliments and provides a major economic underpinning for the coal conversion regulatory program. The credit is not available to utilities.

14.4 RETROFIT '79 FOLLOW-UP

"Appropriate Near-Term Role of Federal Government and Other Actions to Support a U.S. Air Gasifier Industry"

ORGANIZ	ATION			RECOMMENDATIONS	
Name	Туре	Primary Interest	Federal Action	State/Local Action	General Comments
Arkansas Power & Light Co. Little Rock, Arkansas	User/Utility	Development of: solid fuel gasifier for cogeneration; close-coupled biomass gasification system capable of switching from coal to wood. Concern: clean fuel availability.	Improve flexibility of combining technologies.		
Bio-Energy Consultant Council	Consultant	1. Fixed plant development.	1. '77 Farm Bill, Sec. 1420 pilot project loan guarantee program - possible approach.	 Market guarantees & major gasifier invest- ment tax credit (e.g., EPA-California program). 	Bob Kennel/Ultrasystems has concept for "strike- force," i.e., forester, economist, plant engi- neer on demand who
	2. Mobile-plant category. 2. Direct grants for several small-scale demos (e.g., bus/truck, auto, boat). Perhaps SERI could initiate. Note: Attachment 1 is a list of general bioenergy commercialization incentive suggestions by Dr. Paul Bente.		make immediate recom- mendation on practical conversion of wood through direct burning or gasification.		
Biomass Energy Institute, Inc. Winnipeg, Manitoba,	Canadian Government	General			1. Need to identify lo- cation and economic statistics of any com- mercially viable biomass gasifiers, not just those
Canada					in development stage. 2. Need closer look at shortcomings of stationary-type gasification (automation, ease of control, long-term consistency of operation).
					 Need active experimentation with rotary gasifiers, one of the most constructive activities toward technology commercialization.

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Century Research, Inc. Gardena, California	Hardware developer/ manufacturer	1. Feedstock supply.	 Government documentation of availability of feedstocks, i,e., ag/animal/wood industry wastes, low-grade lignitic deposits, etc. 		
Camonia		Importation of foreign technology.	Encourage importation of foreign technology and related research, development, and en- gineering experience.		
		 Financing for air gas- ifier installation. 	 Legislation authorizing government guarantee of special type of mortgage loan. 		
Richard Wright	Manufacturer	Economic growth of indus- try—general.		State funding/local sponsorship preferable	Favor "normal evolu- tion," i.e., "hands off"
Energy Research Associates				—less cost and better able to meet local needs.	by federal government. See Attachment 2 for specific recommenda-
Monroe, Wisconsin					tions.
Environmental Energy Engineering, Inc. Morgantown, West Virginia	Manufacturer	Biomass gasification dev- elopment—general.	U.S. support of Sweden's already developed facility/staff. This, plus cooperation, will help move U.S. to earliest possible commercialization.		1. Get units operating on modest scale to provide visual exposure—may require subsidy for extra labor needed. Concurrently with above develop less labor-intensive continuous units, larger units, and more effective units.
					 Establish environ- mental consequences as- sociated with biogas utilization in small and large units.

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ORGANIZ. Name	ATION Type	Primary Interest	Federal Action	RECOMMENDATIONS State/Local Action	General Comments
Environmental Energy Engineering, Inc. (continued)					3. Update Hessleman gasifier to a continu- ous operating and com- pact unit to serve as demo and operating unit
					for small-scale uses— demo of engine operation and firing existing gas burners of right size.
Gorham International, Inc. Portland, Maine	Paper Mill/ (Consultant)	Wood harvesting and distribution.	Specific: interest in DOE funding of joint demo project, with an industrial partner, involving use of downdraft gasifier chipper and dryer at or near harvesting site. (Industry partner to use chips itself or establish fuel distribution system for dry/graded chips.)		Attributes slow growth of industry to dependence of small-scale inplace gasifiers on secondary wastes (sometime negative value)—more rapid growth will require use of primary forest wastes as fuel. Need new/more economical harvesting methods, such as downdraft gasifier chipper/dryer described at left.
Haleyon Associates, Inc. E. Andover, New Hampshire	Hardware developer/ manufacturer	Economic growth of biomass gasifier industry—general.			Technology advancing slowly largely due to lack of DOE aid to smaller companies doing actual inventing/design/development. Small companies have no "in" at DOE to obtain funding for efforts to prove feasibility/practicality/economy in commercial applications.

E. Andover, New Hampshire

(continued)

Lamb/Cargate Industries, Ltd.

New Westminster British Columbia Supplier (British Columbia) Gasifiers in energysaving-related equipment. Federal role should be to reduce risks undertaken by supplier & purchaser of new technology. Canada has several such programs:

- 1. EDP govt, matches funds with supplier; income from sale divided equally between govt. & supplier.
- 2. Dept. Energy, Mines, and Resources (DEMR) - offer buyer 25% grant on cost of total energy saving system.
- 3. DEMR one-time 66% loan guarantee for financing cogeneration from wood (1 per province).

Technology design promotion—get number of units installed and operating, requires liaison with users. Small companies also hampered by terms, conditions, and guarantees required by purchasing agents and bureaucrats.

In view of 'inevitable' lack of DOE or other federal support, as public attention turns to alternate fuels, small companies: (a) may form alliances with larger ones—which have "in" with DOE—to obtain funds; (b) go public to get venture capital.

DOE should reduce excessive time for processing applications.

ORGANIZ. Name	ATION Type	Primary Interest	Federal Action	RECOMMENDATIONS State/Local Action	General Comments
National Center for Appropriate Technology	Consultant	Air gasifiers—general.	Should install units in govern- ment facilities. DOD—largest energy user—should be prime target. (Would aid self-suf-		Most private users tak- ing "show me" attitude toward use of air gasi- fiers.
Butte, Montana			ficiency of military instal- lations and be good PR.)		NO.
Pioneer Hi-Bred International, Inc.	User/Developer (large seed and grain company)	General	In general, government should stay out and let profit- oriented private industry handle.		Feel their work (use of corn cobs as fuel) dif- ferent from other alter- nate fuel projects & not
Des Moines, Iowa			However, tax credit for pri-		practical to "wait" for government sponsorship.
owa	vate industry's investment in technology development might be helpful, although documentation to satisfy tax authorities may be difficult.		Time required to get govt support too long.		
Ripley & Sun	?		Funding for development of portable/mobile equipment,		Vertical energy integra- tion needed in agricul-
Richland, Washington			and personnel training.		tural, forestry, and municipal wastes (areas where sources & potential uses physically close).
					Ag—demo in larger agri- business sector using available biomass re- sources, transport, and storage for use in air gas- ifiers to power farm ma- chinery.
					Forestry—collect, transport, process, and transport processed fuel form to sites for use in stokers, gasifiers. Possibly use gen-gas fueled trucks for transport.

Minicipal wastes—similar to above.

Stanford Research Institute

Menlo Park, California

Consultant

Proper design rather than just building gasifiers, which is currently the case.

Federal funding of R&D required to make air-blown gasification a commercially acceptable success. Suggestions: (1) technical and environmental evaluation of operating gasifier; (2) test varied feedstocks in commercial gasifier; (3) thermochemical modeling of data from (2) by computer; (4) cost analysis of biomass pretreatment and handling; (5) cost-effective analysis of preprocessed vs. "as-received" materials for gasification; (6) comparative cost benefit analysis of biomass gasifier vs. combustion unit for refitting gas/oil-fired industrial boilers; (7) study factors around biomass gasifier installation in terms of availability/ quality/cost of feedstock, local air pollution and residue disposal regulations, tax incentives for producing syngas, and socioeconomic impact of facility.

ORGANIZ Name	ATION Type	Primary Interest	Federal Action	RECOMMENDATIONS State/Local Action	General Comments
Texas Tech University Lubbock, Texas	Research	Effective Utilization of gasifiers—general.	Federal funding of information programs and demonstrations re: small gasifiers (for transportation and agriculture)—justifiable because small users can't make required technical/economic decisions themselves. Adapt World War II gasifier data to today's technology.		See rather limited utilization of air-blown biomass gasifiers. Direct combustion most effective, for new construction, for using biomass to produce steam, space heating, and electricity. See little need for govt. financial support & research in development and testing. Due to problems of high cost and fuel supply, govt. should not intervene but let market-place determine outcome
U.S. Forest Service, Forest Products Laboratory Madison, Wisconsin	Federal Government	General	Federal govt. could be helpful in moving gasification technology from pilot stage to commercialization. Specific suggestions: 1. Sec. 1420, '77 Farm Bill pilot project loan guarantees. 2. 1978 NEA—get clarification for manufacturers of how additional 10% tax credit for combustion units not using fossil fuels might apply to gasification units. (See Attachment 3 for summary of provision.) 3. Funding additional research to solve problems re: slag prevention & handling, tar cleanup pressurization, fuel bridging in unit, fuel handling outside unit.		

Vermont Wood Energy Corporation Stowe, Vermont	Hardware developer/ manufacturer	Home heating size gas- ification units.	I. Development of small residential gasifiers (particularly where socioeconomically beneficial, as in New England). 2. Development of retail fuel distribution system, via aid to interested individuals/groups.
Washington State Energy Office Olympia, Washington	State Government	General	1. Conduct gasification workshops every 6-8 months to introduce & educate new prospective private industry users to gasification products. Should also include how to handle dangers of gas use, potentially a significant barrier to commercialization. 2. Tax incentives, i.e., rapid write-off of capital investment in gasification equipment.
Wood Energy Consultants, Charlottetown, Prince Edward Is., Canada	Consultant (Canadian)	General	Sees major problem as lack of capital. Suggests Federal and/or state assistance by: 1. Purchase, by prepayment, a number of gasifiers up to \$250,000 per company. These gasifiers would be for future delivery at the stabilized production cost of the future. In the meantime, the manufacturer would have this money to finish development work and be capable of manufacturing units.

ORGANIZA	TION			RECOMMENDATIONS	
Name	Туре	Primary Interest	Federal Action	State/Local Action	General Comments
Wood Energy Consultants, Ltd. Charlottetown, Prince Edward Is., Canada (continued)			2. Loan guarantees to purchas the financial risk of nonper With the massive importati is spending much more mon by the failure of a few "pro gasifiers would help replace be available within 30 years be only to the extent of the 3. The first installations shoul tions near sawmills, where available and the economic these successes, the govern chased units (prepaid as in applicable government build 4. At this point, with working applications of the technolo could order a large enough ufacturer establish his asse under the government guara normal purchasers or the ex buildings.	formance is on the govt. on of oil, the Federal govt. ley than it would lose botype" gasifiers. These e oil that may not even s. These guarantees would e cost of the gasifier. Id be in rural applicate would is readily s make most sense. After ument can take its pur- #1) and retrofit the dings. models and successful logy, the government number to help the man- mbly line. The units antee program could go to	





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Chapter 15

Recommendations for Future Gasification Research and Development

T. B. Reed SERI



CHAPTER 15

RECOMMENDATIONS FOR FUTURE GASIFICATION RESEARCH AND DEVELOPMENT

15.1 INTRODUCTION

We believe that the development of biomass gasification should be at the maximum rate possible, consistent with sustainable supplies of feedstock, because biomass can supplement fuel supplies as oil and gas become increasingly costly or unavailable. Gasification can provide the gas needed for clean heat and power in our cities, and it is the basis for the synthesis of liquid fuels, SNG, and ammonia.

This survey outlines the value of gasification, the technical base for future work, and the activities now under way. The various people reading it will draw different conclusions. The conclusions on which work will be based at SERI and towards which we recommend guiding the national program are given here. These are not immutable, and we invite comment as to their validity and completeness.

This chapter is divided into recommendations on processes and recommendations on systems using those processes.

15.2 BIOMASS AND THERMAL CONVERSION PROCESSES

15.2.1 Pyrolysis Processes

Pyrolysis processes are complementary to gasification processes, since they produce some gas, but also char and oil. Thus, they can produce gaseous fuel for continuous use, while at the same time producing storable liquid and solid fuels that can be used for peak loads or sold on the market.

Charcoal can be produced very simply in existing pyrolysis processes. We recommend an evaluation of the degree to which char and charcoal may be used in the evolving renewable energy society. Presently, charcoal has many uses and commands prices of \$80-\$200/ton, depending on its quality. It is used for cooking, water purification, manufacture, chemical sysnthesis, etc. To what extent could the United States consume more charcoal?

Pyrolysis oils are also produced very simply and cheaply in pyrolysis processes. As produced today, they are smelly, high in oxygen, corrosive, and of uncertain value. However, crude oil was viewed similarly when it was first discovered. We recommend an integrated program to evaluate improved methods for oil production and collection, as well as laboratory work on chemical and thermal treatment to make higher-value products from the oil.

Pyrolytic gasifiers are not as well developed as oxygen gasifiers, but the majority of the research supported by the EPA and DOE has been in this area. We recommend continuing research and pilot work on many of these systems, because they promise higher efficiencies and lower costs than oxygen gasification in production of medium- or high-energy gas. However, it is not now clear the degree to which medium-energy gas will be distributed in the United States, and so full-scale development of pyrolytic gasifiers must wait



on decisions still to be made on the gas infrastructure in the United States. These decisions hinge on the future costs and availability of natural gas versus the costs of conversion of gas to methane for distribution. One possible development would be the use of medium-energy gas from biomass in captive installations and industrial parks, combined with conversion of coal to methane for domestic distribution.

We recommend top-priority development of flash pyrolysis processes that give a high yield of olefins and little oil or char. The olefins, in turn, can be converted directly to gasoline or alcohols. This seems to be the one truly new development in gasification since World War II. We recommend evaluation of time-temperature and of various feed-stocks and particle size options on yields at the bench level, combined with bench and engineering studies of process designs giving the very high heat transfer necessary to produce these nonequilibrium products. We also recommend evaluation of processes for reducing particle size at reasonable costs, since this may be a necessary adjunct to flash pyrolysis. Fast pyrolysis is a major part of the biomass thermal conversion program at SERI.

Finally, we recommend a continuing effort to sort out the molecular details of pyrolysis under carefully controlled, but realistic, laboratory conditions to provide a firm foundation for understanding and improving all gasification processes. For this purpose, a molecular beam sampling apparatus is being assembled at SERI to examine the molecular details of the pyrolysis reactions. In addition, thermogravimetric techniques are being used to study the mechanisms of thermal pyrolysis.

15.2.2 Air Gasification

Air gasifiers may find a place in domestic and commercial heating; such gasifiers will certainly be used in process heating and power for the biomass industries. Although research may improve air gasification, we recommend immediate commercialization at the present level of development. A gasification reactor has been constructed at SERI to make accurate measurements of the temperatures and compositions associated with each stage of air, oxygen, and steam gasification.

We recommend an expanded support for commercialization of air gasification at the national level. Many states are already buying gasifiers in the 1-100 MBtu/h range, appropriate for process heat in small- to medium-sized industries. Evaluative technical assistance and tax incentives would accelerate this effort.

There are no air gasifiers presently available that are larger than 100 MBtu/h—yet larger sizes are needed, for instance, to retrofit the very large boilers of the paper industry, which collectively burn 1-2 quad of oil. We recommend a joint government/industry effort to develop very large air gasifiers suitable for retrofitting large boilers.

15.2.3 Oxygen Gasification

We recommend development of a high-pressure oxygen gasifier capable of producing clean gas directly rather than by downstream treatment. This gas would be useful for synthesis of liquid fuels and ammonia, for limited pipeline distribution, or for operation of turbines for combined cycle co-generation. The present SERI program includes operation of a 100-lb/h proof-of-concept gasifier of this type. We recommend development of oxygen gasifiers for municipal waste, since the use of waste provides energy for urban areas, recycles metals, and eliminates landfills.



We recommend support for research on energy-efficient and smaller-scale methods for separation of oxygen from air.

15.2.4 New Gasification Methods

There should be continuing studies of the scientific feasibility of novel thermochemical schemes to gasify biomass to a variety of desired products (e.g., C_2H_2).

15.3 BIOMASS THERMAL CONVERSION SYSTEMS

In the past, economies of large scale have favored the use of coal as a gasification feedstock, while ease and cleanliness of gasification have favored using biomass. Now, biomass is produced in much larger quantities than previously (up to 3000 tons/day in modern paper plants and 10,000 tons/day of SMW in larger cities). Other factors that may favor the use of biomass as a gasifier feedstock will be improved methods and materials of construction, particularly new high-temperature, low-U-factor insulations; new methods of automatic sensing and control using microprocessors; and mass production of smaller units rather than individual engineering of large units.

There are a number of system studies that should also be performed as adjuncts to the biomass gasification program. We recommend that the relevance of scale to gasification plants should be studied immediately and, where appropriate, programs be initiated to overcome scale limitations. In particular, coal is likely to supply gas heat for our cities, where large plants can clean the gas sufficiently and make methane for distribution. Because biomass is much cleaner, it can be used on a smaller scale—and this is compatible with its wider distribution. If biomass residues must be processed at the 1000 ton/day level or greater to be economically viable, very little biomass will be used in this country. If it can be processed economically at the 100 ton/day level, it can be used widely.

We recommend a system study of biomass energy refineries to be used in conjunction with farming and forestry operations, taking in residues and converting them to the ammonia and fuel required to operate the farm and forest, while shipping any surplus of energy to the cities in the form of gaseous or liquid fuels.

15.4 BIOMASS BENEFICIATION

There are a number of processes that are being developed in the laboratory or commercially that alter the form of the biomass to make it more susceptible to thermal or biological processing. While not a direct part of biomass gasification, such processing can increase the ease and efficiency of conversion and would aid the integrated gasification program. They include:

- Densification—pelletizing of miscellaneous biomass forms to uniform pellets, briquettes, or logs that are easier to store and process than the natural forms
- Comminution—The pyrolysis rate depends on heat transfer to the biomass surface, followed by heat transfer through the biomass. The latter step is limiting in many cases, and use of small-particle biomass can affect both the process efficiency and the product distribution. A number of new, interesting processes for comminution are now being developed.



- Drying—Most gasification processes operate best on dry biomass, and a number of ingenious systems can be used for moisture reduction.
- Thermolysis—There are indications that some of the above processes also cause fundamental chemical changes that alter the energy content and structure of the biomass, making further thermal or biological processing more effective.

15.5 BIOMASS PRODUCTION/CONVERSION SYSTEMS

For the longer term, and for biomass conversion plants of large and small scale, economic analyses should be performed to identify suitable hybrid schemes. These include: production of methanol using a combination of biomass (low H/C ratio) and natural gas (high H/C ratio); joint electrolysis/gasification systems in which $\rm H_2$ and $\rm O_2$ are generated electrolytically, the oxygen is consumed in gasification, and the hydrogen increases the H/C ratio; and solar flash pyrolysis in which the high rate of heat transfer is supplied by solar collectors.

In the larger analysis, production of biomass should be an integral part of conversion processes. Therefore we recommend systems studies that include integral "energy farms," or "energy plantations," in which the central processing plant may produce fuels, chemicals, and fertilizers needed for increased production of biomass.

Finally, the production of biomass must be regarded as a steady-state activity for any continuing society. The fall of many past civilizations can be traced to an abuse of the land engendered by the pursuit of ever-increasing biomass yields. Therefore, we recommend that the long-range ecological effects of various land-use patterns be evaluated as soon as possible. We recommend that these studies consider biomass production for energy as an opportunity for land improvement, as well as considering its possible role in land degradation.

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