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CATALYTIC CONVERSION OF BIOMASS TO FUELS

Final Report

By
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MASTER

Work Performed Under Contract No. AC03-78ET11013

Catalytica Associates, Inc.
Santa Clara, California

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Solar Energy

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SUMMARY

This report presents an assessment and perspective concerning the application of catalytic technologies to the thermochemical conversion of biomass resources to fuels. The major objectives of the study are:

- To provide a systematic assessment of the role of catalysis in the direct thermochemical conversion of biomass into gaseous and liquid fuels.
- To establish the relationship between potential biomass conversion processes and catalytic processes currently under development in other areas, with particular emphasis on coal conversion processes.
- To identify promising catalytic systems which could be utilized to reduce the overall costs of fuels production from biomass materials.

The report is divided into five major parts which address the above objectives. In Part III the physical and chemical properties of biomass and coal are compared, and the implications for catalytic conversion processes are discussed. With respect to chemical properties, biomass is shown to have significant advantages over coal in catalytic conversion processes because of its uniformly high H/C ratio and low concentrations of potential catalyst poisons. The physical properties of biomass can vary widely, however, and preprocessing by grinding is difficult and costly. Conversion technologies that require little preprocessing and accept a wide range of feed geometries, densities, and particle sizes appear desirable.

Part IV provides a comprehensive review of existing and emerging thermochemical conversion technologies for biomass and coal. The underlying science and technology for gasification and liquefaction processes are presented. For example, in gasification, the most significant catalytic effect for improving reaction rates involves the use of catalysts which decrease the activation

energy. All catalysts studied to date, however, improve rates modestly by increasing the concentration of gasification sites rather than decreasing the activation energy. This result indicates that high catalyst concentrations and efficient wetting of the char by catalyst are essential to maximize gasification rates with current catalysts. Relative to coals, biomass offers significant advantages in gasification because of its higher reactivity, lower char production, and the possibility of adiabatic steam pyrolysis processes which result in greater energy efficiency.

In biomass liquefaction the major objective is to break down the polymeric structures and remove oxygen in order to produce a liquid fuel of high calorific value. This contrasts with coal liquefaction, in which the addition of hydrogen or removal of carbon is required in order to increase the H/C ratio and produce a liquid product. To date, significant problems have been encountered with biomass liquefaction processes because of the production of low-quality fuels which are unstable in storage and highly corrosive. Upgrading of the products appears necessary to produce a usable fuel.

In Part V the potential applicability of coal conversion technologies to biomass for the production of gaseous and liquid fuels is assessed. A total of twelve gasification and eight liquefaction technologies are critically examined. The major problem areas in the thermochemical conversion of biomass are the diverse physical properties of biomass feedstocks requiring preprocessing or the use of a variety of technologies applied regionally and the low quality of liquid fuels produced from biomass.

In Parts VI and VII recent advances in catalysis and engineering that impact on the problems in biomass conversion are discussed, and recommendations for future R&D work are presented. Approaches which appear most promising for biomass gasification include molten-salt and adiabatic steam pyrolysis processes. Molten-salt processes can utilize a wide range of biomass materials without requiring preprocessing, and would accomplish rapid, effective gasification. Such processes appear to be suitable for biomass because of the small scale

dictated by collection constraints on the feedstock. Adiabatic steam pyrolysis appears attractive because the product is rich in methane and the efficiency is high.

In liquefaction, the production of high-quality stable fuels will probably require upgrading of the initial product. In this regard, recent developments with shape-selective catalysts capable of effectively removing oxygen from feeds and producing aromatics appear promising.

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PART I. INTRODUCTION

The dwindling supply of indigenous petroleum in the United States and the increasing dependence on foreign imports have provided incentive for the development of alternative sources of energy. In this regard, coal, shale oil, and tar sands have received considerable attention in recent years. Coal, which represents a vast indigenous fuel supply, continues to be the most intensively explored alternative to petroleum. Extensive science and technology are being applied by both government and industry to economically convert coal to clean-burning gas and liquid fuels. Many of the conversion technologies being explored or developed involve the use of catalysts to improve overall reaction rates and to modify the relative rates of the various reactions to favor high selectivity to the desired products. Significant problems have been encountered in the catalytic conversion of coal, however, because of the high level of sulfur and other impurities which are detrimental to catalysts and present significant environmental problems (Cusumano, 1979).

In view of such problems, a clean source of fuels becomes particularly attractive. In this respect, the utilization of biomass appears promising, and research on the conversion of this source to gas and liquid fuels has escalated in recent years. Included in the biomass resource are forest and agricultural products and residues, animal wastes, and municipal solid waste. Although the total biomass production represents only a portion of known coal reserves, as shown in Table I-1, biomass possesses the unique characteristics of being a renewable source of energy with a low concentration of impurities. This latter aspect is particularly favorable with regard to catalytic conversion processes. Another advantage of biomass is that, unlike fossil fuels, its utilization does not contribute to the increase in atmospheric CO₂ concentration, with the accompanying potential detrimental effects on the global climate.

Table I-1
WORLD ENERGY RESERVES
 (Unit: 1973 World Energy Production=1)

	<u>Total Reserves</u>	<u>Proven Recoverable Reserves</u>
Gas	46	8
Oil	73	17
Shale oil and tar sands	250	47
Coal	730	66
Biomass**	66	--

*Estimated from a world production of 146×10^9 tons with
 an energy content of 2.3×10^{18} Btu (Reed, 1975).

The general approaches for converting biomass into fuel products involve biological, enzymatic, and thermochemical processes. Although biological and enzymatic methods are currently being investigated, these approaches are usually limited by their low tolerance to temperature and environmental variations. Furthermore, such processes are generally characterized by low reaction rates and thus require significant capital investment in large or multiple reactors. These latter problems can be overcome through thermochemical conversion processes which utilize inorganic catalysts; however, the use of such catalysts to enhance the thermochemical conversion of biomass has been limited to date. Therefore, a systematic assessment of the role of catalysis in the thermochemical conversion of biomass to identify promising catalytic systems, and to establish the relationship to catalytic processes currently under development in areas such as coal conversion, appears timely. The utilization of inorganic catalysts in the thermochemical conversion of biomass to gas and liquid is the focus of this study.

PART II. SCOPE AND OBJECTIVES

The resurgence of interest in synthetic fuels production has focused attention on the use of catalysis to improve the economics and efficiency of conversion processes. The major advantages of catalytic approaches are the improvement of reaction rates and selective conversion to the desired products. The former advantage allows increased throughput or a reduction in reactor size, whereas the latter improves the overall efficiency of the process. Although catalysis has been extensively explored for the gasification and liquefaction of coal, little effort has been expended to utilize the advantages of catalytic conversion for biomass. With the increasing interest on the part of both government and private industry in the United States and abroad in the production of fuels from renewable resources, an assessment of the potential for catalysis in biomass conversion is particularly important.

The major objectives of this study are:

- To provide a systematic assessment of the role of catalysis in the direct thermochemical conversion of biomass into gaseous and liquid fuels.
- To establish the relationship between potential biomass conversion processes and catalytic processes currently under development in other areas, with particular emphasis on coal conversion processes.
- To identify promising catalytic systems which could be utilized to reduce the overall costs of fuels production from biomass materials.

The approach of the study involves a review of the technical and patent literature concerning pertinent information on:

- The relevant physical and chemical properties of biomass and coal to establish the major differences in these resources that will impact on the choice of conversion technologies.
- The existing and emerging concepts for the thermochemical conversion of biomass and coal to gaseous and liquid fuels.

This background provides the basis for identifying the major technical problem areas in thermochemical conversion technologies. It also allows an assessment of the potential applicability of the various coal conversion concepts to biomass which, because of the marked differences in physical and chemical properties, may significantly reduce or alleviate the problems encountered with coal.

Limitations and problems which are specific to biomass feedstock are also identified. Finally, the most promising technologies for the thermochemical conversion of biomass to gaseous and liquid fuels are identified, and the problems which must be solved to develop these technologies are discussed. Emphasis in this study is on the chemistry and reactor engineering aspects of thermochemical conversion processes rather than on total systems and detailed economic analysis. Thus, recommendations concerning technologies for future development are based on conclusions regarding the most promising catalytic and reactor engineering concepts and a judgment as to their potential economic validity.

PART III 1. INTRODUCTION

Understanding the physical and chemical properties of biomass relative to coal is essential for an assessment of their relative suitabilities for synthetic fuel production. The purpose of this section, therefore, will be to provide a perspective for the differences in physical and chemical properties to allow assessment of various biomass and coal conversion technologies in subsequent sections of this report.

A comparative analysis of the physical and chemical properties of biomass and coal demonstrates the progressive changes which occur during the coalification process in view of the fact that coal has its origin in biomass. The coalification process proceeds in a stepwise manner in which biomass is first converted, under favorable environmental conditions, to humic acid. Through the combined effects of heat, pressure, and time, humic acid is sequentially transformed into peat, lignite, subbituminous coal, bituminous coal, and ultimately, anthracite. As this coalification process proceeds, there is a progressive decrease in the oxygen content, with a concomitant increase in carbon content. This upward shift in the carbon/oxygen ratio results in increased energy content at the successive levels (higher ranks) of the coal.

In this section the properties of biomass are first discussed in detail to provide a perspective for the physical structure and chemical composition of this resource. This background is important for assessing the potential problems in the catalytic conversion of biomass to fuels and for identifying the most promising technologies. Next, the chemical and physical properties of coal are briefly reviewed and finally, the implications of the differences in the properties of coal and biomass are discussed.

2. BIOMASS

2.1 PHYSICAL PROPERTIES

The definition of the term biomass varies, depending on whether one includes residues of the living material within a given area in that definition. In the present discussion we will include such materials as agricultural and timber industry residues; along with unprocessed living material. The rationale for this inclusion is based on the demonstrated availability of those materials.

2.1.1 FUNDAMENTALS OF PLANT STRUCTURE

When biologists discuss the properties and characteristics of biomass, they usually consider materials derived from plants, animals, bacteria, and fungi. However, when biomass is being examined as a potential source of fuel for thermochemical processes, the focus of attention narrows to that of forest and agricultural products and residues. These resources have the unique capacity to capture the sun's photic energy, and store it in the form of reduced carbon compounds. The major portion of these compounds are long-chain carbohydrates--polysaccharides--such as starch, cellulose, and hemicellulose. Because of the recognized role of starch in human nutrition, it is unlikely that the value of starch as a convertible form of stored chemical energy will ever exceed its value as food. It is largely for this reason that we will not consider starch in this section, in spite of its abundance in plants.

Cellulose, hemicellulose, and lignin, the compounds of interest as potential fuel sources, are not directly involved in plant nutrition as is, for example, starch. Their primary function is to serve as mechanical support. These materials are found outside the living portion of the plant cell, in what is called the cell wall. The organization of plant cell walls is remarkably similar over a wide range of plants, and the following discussion of plant cell wall architecture is applicable to both herbaceous plants, such as agricultural residue, and woody forest products, such as pulp and timber residues.

Plant cell walls are composed of two relatively well-organized layers: an outer primary wall and an inner secondary wall. Cementing the cells together at the primary wall interface is a less well-organized layer of intercellular material called the middle lamella. The middle lamella is formed of galacturonic acid residues (a glucose derivative) which polymerize to form pectic compounds as shown in Fig. III-1. Calcium and magnesium salts of pectic acid and other pectic compounds make up the majority of the intracellular binding material in the middle lamella. The breaking down of this lamella is the first step in any process requiring separation of cells.

The primary wall is the first wall formed in a new plant cell. It is a thin ($2-3\mu$) and relatively flexible envelope composed of cellulose molecules deposited in a regular lattice. The long cellulose molecules are wound together to form microfibrils, each of which may contain some 2000 cellulose molecules. The microfibrils then wind together to form threads, which in turn coil together to form "cables". An individual cable may be up to 4 microns long, and may contain some 500,000 cellulose molecules. As a result of this structural organization, the cellulose within the primary wall has a tensile strength equivalent to that of an equal thickness of steel. As cellulosic fibrils are laid down within the the cell wall, capillary spaces are formed which fill with water and larger molecules, such as hemicellulose and lignin. The lignin substance appears to be deposited only by cells about to lay down secondary walls, and this deposition is rapidly followed by a cessation of internal life function. Lignin serves solely as a mechanical support in the plant structure.

Not all plant cells form a secondary wall. However, for those that do, it is laid down inside the primary wall. The secondary wall is deposited within cells which have ceased to grow, and provides a structural support for the plant body. Secondary walls are considerably thicker than primary walls, and the cellulosic fibrils they contain are arranged in three distinct layers of differing orientation. The extra thickness and the laminar, plywood-like structure of the cellulosic elements give secondary walls their greater strength. The major portion of woody plants is formed of cells having secondary walls.

Fig. III-1. Structural Formulas of Galacturonic Acid and Salts of Pectic Acid.

2.1.2 DENSITY AND SPECIFIC GRAVITY

The density of plant biomass can vary over a wide range, depending on the nature of the biomass. Density is a particularly important physical parameter for determining the suitability of a given type of material for synthetic fuel, especially with regard to reactor engineering aspects of biomass conversion, as discussed in subsequent sections of this report. A large part of the weight and volume of fresh plant biomass is water. Pulpwood, for example, loses between 10 and 20% of its volume on complete drying (Wenzl, 1970), and undried agricultural residues such as corn stover, bagasse, or rice straw may have even higher water contents. Because of the large and variable amounts of moisture in plant material, it is essential that any data on density or specific gravity take water content into account.

Table III-1 presents representative density values for a variety of woody plant species. Density and specific gravity are genetically determined from species to species. However, in many cases, environmental factors can affect density. In the case of timber products the density depends on the ratio of summer wood to spring wood, and this ratio can be modified through certain silvicultural techniques (Wenzl, 1970; Spurr, 1973). The range of variation in density values for various plant species gives some indication of the potential feedstock variability in synthetic fuel production. The frequency distribution of density for a number of pulpwood species is shown in Fig. III-2.

2.1.3 MOISTURE

As discussed in the previous section, water constitutes a significant fraction of the weight and volume of fresh plant biomass. In some cases the water content may be so great that the material will not ignite or burn without some pretreatment to reduce the water content. This problem can be serious with peat, which may have water contents in excess of 90% in certain instances (Bodle, 1978).

Table III-1

DENSITY VALUE FOR WOODY PLANT SPECIES

(Antal, 1978; Tillman, 1978)

Plant material	Specific gravity	Bulk density, lb/ft ³	
		Dry	Green
<u>Hardwood</u>			
White ash	0.60	37.4	47.0
Beech	0.64	39.9	54.0
White birch	0.55	34.3	51.0
Red oak	0.63	25.0	65.0
<u>Softwood</u>			
Balsam fir	0.36	22.5	52.0
Eastern hemlock	0.40	25.0	49.0
Pitch pine	0.46	28.7	54.0
Sitka spruce	0.37	23.7	--
(Bagasse, from sugarcane)	---	(5.0)	--

Fig. III-2. Frequency Distribution of Density of Various Species of Wood (Trendelenburg, 1936).

- A = *Pinus strobus*, 844 samples, av 0.359 g/cm³
- B = Spruce, 1962 samples, av 0.455 g/cm³
- C = Pine, 2918 samples, av 0.489 g/cm³
- D = Larch, 1910 samples, av 0.551 g/cm³
- E = Beech, 1773 samples, av 0.671 g/cm³
- F = Oak, 994 samples, av 0.647 g/cm³

For fuel utilization the upper limit of water content is approximately 67% (Tillman, 1978). Pretreatment for the purpose of drying the biomass may require a large expenditure of energy. For example, it has been estimated that the energy consumption per pound of water lost in drying biomass is of the order of 1060 Btu. For biomass of high water content a significant fraction of the available energy is consumed in the drying process. Biomass moisture content is found to vary both between species, and within an individual plant, depending on the part of the plant being examined. As a result, only approximate values can be determined for biomass feedstock moisture. Table III-2 summarizes some data on moisture content for representative types of plant materials.

2.2 CHEMICAL PROPERTIES

Plant biomass is composed of three basic polymers: cellulose, lignin, and hemicellulose. The proximate analysis of representative woody and nonwoody biomass materials with regard to these three components is shown in Table III-3. In addition to the aforementioned constituents, biomass contains smaller amounts of resins, terpenes, fats, and ash minerals which have potential effects on the conversion of biomass to synthetic fuel. The following discussion will briefly characterize the components in biomass.

2.2.1 CELLULOSE

Cellulose forms the primary component of the plant cell wall in all plant species, making it the major part of any biomass feedstock. Cellulose is composed of alternating alpha-D-glucose subunits in the chain configuration. These subunits are joined by beta-1,4-glycosidic bonds. Such a structure produces a long unbranched chain (1000 to 10,000 monomers per chain), and allows adjacent chains to lay side by side with their hydroxyl groups, forming interchain hydrogen bond linkages (Fig. III-3). The overlapping chains of cellulose form a combination of highly ordered crystalline regions, and less-ordered amorphous regions. Each individual molecular chain passes through both amorphous and crystalline regions.

Table III-2
MOISTURE CONTENT FOR VARIOUS PLANT SPECIES AS RECOVERED FROM NATURAL SETTING
 (SRI, 1974; Babcock and Wilcox, 1963)

<u>Plant Material</u>	<u>Moisture, %</u>
Bagasse (sugarcane)	
As harvested	52
Field dried	15
Buckwheat hulls	10
Bamboo canes	10
Coconut hulls	13
Beechwood	13
Birchwood	12
Oak	
Wood	13
Bark	7
Pinewood	12
Spruce bark	0
Redwood bark	0

Table III-3
CHEMICAL PROXIMATE ANALYSIS OF BIOMASS
(Wenzl, 1970; Tillman, 1978; Antal, 1978; Shuster, 1978)

Species	Cellulose, %	Hemicellulose, %	Lignin, %
<u>Woody Plants</u>			
Beech	45.2	32.7	22.1
White birch	44.5	36.6	18.9
Red maple	44.8	31.2	24.0
Eastern hemlock	45.2	22.3	32.5
Jack pine	45.0	26.4	28.6
White spruce	48.5	21.4	27.1
White birch	41.0	27.3	18.5
Aspen poplar	49.1	21.2	18.1
<u>Nonwoody</u>			
Alfalfa stems	42	13	17.9
Corn cobs	37	38	5.9
Cotton stalks	49	13	22.1
Peanut hulls	47	12	37.0
Rice hulls	40	21	22.7
Wheat straw	49	27	12.5
Grasses (mean range: 2)	25-40	25-50	0-15
Volatile matter for average biomass = 87.3%

Fig. III-3. Chemical Structure of Cellulose (Haworth, 1929).

The crystalline regions within the bulk cellulose are most resistant to acid hydrolysis. On the average, cellulose is 85% crystalline and 15% amorphous (Shuster, 1978). Because of the strength of the interchain hydrogen bonds, especially within the crystalline regions, cellulose is both high in tensile strength and extremely insoluble in water.

The technical term alpha-cellulose refers to the portion of pulp insoluble in 17.5% alkali. This property of cellulose can be used to separate it from the next major group of plant product to be considered: the hemicelluloses, which by definition, are soluble in 17.5% alkali (Noller, 1961).

2.2.2 HEMICELLULOSE

The hemicelluloses comprise a variety of hydrolyzable carbohydrates found in association with the plant cell wall. The hemicelluloses generally form short branched chains, with between 40 and 200 monomers per molecule. The three major groups of hemicelluloses are the xylans, mannans, and galactans-polymers of xylose, mannose, and galactose, respectively (see Fig. III-4). The xylans are present as arabinoxylans, glucuronoxylans, and arabinoglucuronoxylans, containing an arabinose unit or a glucuronic acid unit, or both. Mannans are present as glucomannans and galactomannans. The galactans, which are relatively rare, are found as arabinogalactans.

Hemicelluloses differ in solubility because of variations in average molecular weights, distribution of functional groups, and molecular structure. Hemicellulose solubility is also affected by the relationship of hemicellulose to other cell-wall components, especially the lignins, and this relationship varies somewhat from species to species. Xylans are most abundant in corn stalks and grain hulls, and are the predominant hemicellulose species in hardwoods (deciduous trees). Softwoods (conifers) contain both xylans and mannans (Wenzl, 1970).

Fig. III-4. Chemical Structure of Major Constituents of Hemicellulose (Wenzl, 1970).

2.2.3 LIGNINS

The term lignin refers to a fairly large and chemically complex group of noncarbohydrate plant products having similar chemical characteristics. Lignin is higher in carbon and hydrogen content, and lower in oxygen, than either cellulose or hemicellulose. There is some uncertainty concerning the structure of lignins, because their low solubility in most organic solvents makes them subject to molecular degradation during isolation. The lignins appear to be formed of polymerized phenylpropyl subunits, with side-group substitutions making up the various derivatives, as shown in Fig. III-5.

There are two common forms for the phenyl portion of the lignin molecule: guaiacyl and syringyl. Lignins from softwoods are formed exclusively of guaiacylphenylpropyl and syringylphenylpropyl moieties (Wenzl, 1970; Salsbury, 1969).

Polymerization of the lignin monomers involves both ether bonds and carbon-carbon bonds. The presence of carbon-carbon bonds in the lignin polymer is in large part responsible for the polymer's extremely low solubility. The potential ether and carbon-carbon bond structures in lignin are shown in Fig. III-6.

2.2.4 RESINS AND FATS

Although resins constitute a small portion of the bulk of woody plant biomass, they represent complex chemical structures which could affect the action of catalysts in certain types of biomass conversion processes, particularly liquefaction.

Plant resins have similar origins, and, to a lesser extent, similar properties. They are classified into four groups: free resin acids, fatty acids, fatty acid esters, and unsaponifiable material. The relative amounts of these compounds vary significantly between coniferous and deciduous woods. Conifers contain appreciably greater quantities of resin than deciduous woods (1 to 10% for con-

Fig. III-5. Chemical Structures Proposed for the Subunits of Lignin (Wenzl, 1970).

Fig. III-6. Possible Ether and Carbon-Carbon Bonded Structures in Lignin (Wenzl, 1970).

ifers vs <1% for deciduous). Coniferous wood resins are high in resin acids, while deciduous woods contain little or no resin acids (Wenzl, 1970). Resins can be more readily extracted from conifers than from deciduous woods. This is so because coniferous resins are present primarily outside the cells within cell-lined canals called resin ducts. Deciduous resins are primarily found within thin-walled storage cells (Salsbury, 1969).

The deciduous wood resins are mostly fatty acids and unsaponifiable material. Conifer resins, such as the "pitch" found on cut pine or fir wood, consist of a mixture of volatile oils and resin acids collectively called oleoresins. Oleoresins belong to the class of terpenoids which comprises cyclic and acyclic unsaturated hydrocarbons and their derivatives, built of isoprene (C_5H_8) subunits (Fig. III-7).

Fig. III-7. Isoprene Unit

Terpenoids are classified according to the number of isoprene monomers. Monoterpenes are $C_{10}H_{16}$, sesquiterpenes are $C_{15}H_{24}$, and diterpenes are $C_{20}H_{32}$ containing 2, 3, and 4 isoprene units respectively. Oleoresin volatiles are generally monoterpenes and sesquiterpenes, while resin acids are diterpenes. Figure III-8 shows representatives of the two major types of diterpenic acid found in coniferous wood resins.

2.2.5 ASH

Ash is the noncombustible inorganic residue formed during the combustion of biomass through a number of complex reactions, the analysis of which is beyond the scope of the present report. The ash content of various woody and nonwoody biomass materials ranges from 0.2 to 3.0%, as shown in Table III-4, together with the elemental analysis. Table III-5 shows the composition of ashes derived from various plant materials, while experimental data on the fusibility of typical biomass ashes are presented in Table III-6.

Fig. III-8. Representative Diterpenic Acids Found in Coniferous Wood Resins. (Wenzl, 1970).

Table III-4
ULTIMATE ANALYSIS OF BIOMASS
 (Tillman, 1978; Antal, 1978)

Species	C, %	H, %	O, %	N, %	S, %	Ash, %
<u>Hardwood</u>						
Beech	51.6	6.3	41.5	0.0	0.0	0.65
Maple	50.6	6.6	41.7	0.25	0.0	1.35
Hickory	49.7	6.5	43.1	0.0	0.0	0.73
Poplar	51.6	6.3	41.5	0.0	0.0	0.065
<u>Softwood</u>						
Pine bark	52.3	5.8	38.8	0.2	0.0	2.9
Douglas fir						
Wood	52.3	6.3	40.5	0.1	0.0	0.8
Bark	56.2	5.9	36.7	0.0	Trace	1.2
Western hemlock	50.4	5.8	41.4	0.1	0.1	2.2
Redwood	53.5	5.9	40.3	0.1	0.0	0.2
<u>Nonwoody</u>						
Rice hulls	38.5	5.7	39.8	0.5	0.0	15.5
Rice straw	39.2	5.1	35.8	0.6	0.1	19.2
Bagasse						
As harvested	32.4	2.8	---20.1---		Trace	1.7
Field dried	41.4	5.0	---35.6---		Trace	3.0

Table III-5
ASH ANALYSIS OF BIOMASS
 (Babcock and Wilcox, 1963; SRI, 1974)

Species	% oxide of ...						
	Si	Al	Fe	Ca	Mg	Na+K	CO ₃
Corn	53.9	4.7	5.4	6.0	6.4	23.8	--
White fir bark	1.7	3.2	3.2	60.8	3.0	10.4	11.5
Spruce bark	32.0	11.0	6.4	25.3	4.1	10.4	7.0
Pine bark	39.0	14.0	3.0	25.5	6.5	7.3	--
Oak bark	11.1	0.1	3.3	64.5	1.2	9.2	--
Redwood bark	14.3	4.0	3.5	6.0	6.6	28.6	--

Table III-6
FUSIBILITY OF BIOMASS ASH
 (Babcock and Wilcox, 1963)

Species	Reducing Atmosphere			Oxidizing Atmosphere		
	Initial			Initial		
	deformation	Softening	Fluid	deformation	Softening	Fluid
Pine bark	1193	1226	1265	1210	1249	1288
Oak bark	1477	1493	1504	1471	1499	1510

3. COAL

This section will briefly review pertinent physical and chemical properties of coal to provide a perspective for the significant differences relative to biomass. More detailed information on the various properties are contained in the literature referred to in this section.

3.1 PHYSICAL PROPERTIES

3.1.1 CLASSIFICATION OF COAL

Coal is formed from biomass through the combined action of heat and pressure over a long time period. The extent to which the coalification process has progressed determines its position in the coal classification scale. Over the years, many classification systems have been proposed for coal because of the variable nature of native coals. The generally accepted coal classification system in the United States is that developed by the American Society for Testing and Materials (ASTM). Method D-388-66 classifies higher-ranked coals by their fixed carbon content on a dry-weight basis, and lower-rank coals (below high-volatile bituminous) on a Btu/lb moist-weight basis. Within the ASTM system the coals are further characterized by their agglomeration tendencies. Table III-7 shows the current ASTM coal classification system.

3.1.2 DENSITY

Many properties of coal which affect its behavior during conversion into synthetic fuels are related to density. Particle density can be considered as one measure of intermolecular distances, which in turn are related to the accessibility of the coal molecules to the various process reagents. In addition, coal density directly affects process cost through its relationship to such factors as transportation cost and grindability. The density of coal increases with rank, from 1.2 g/cc for lignite, to 1.75 g/cc for anthracite (Table III-8).

TABLE 111-7

CLASSIFICATION OF COALS BY RANK^a

Class	Group	Fixed carbon, % ^b	Volatile matter, % ^b	Heating value, Btu/lb ^c	Agglomerating Character
I Anthracitic	1. Meta-anthracite	>98	<2	---	Nonagglomerating
	2. Anthracite	92 to 98	2 to 8	---	
	3. Semianthracite	86 to 92	8 to 14	---	
II Bituminous	1. Low-volatile Bituminous Coal	78 to 86	14 to 22	---	Commonly Agglomerating
	2. Medium-volatile Bituminous Coal	69 to 78	22 to 31	---	
	3. High-volatile A Bituminous Coal	<69	>31	>14,000	
	4. High-volatile B Bituminous Coal	---	---	13,000 to 14,000	
	5. High-volatile C Bituminous Coal	---	---	11,500 to 13,000	
III Subbituminous	1. Subbituminous A Coal	---	---	10,500 to 11,500	Nonagglomerating
	2. Subbituminous B Coal	---	---	9,500 to 10,500	
	3. Subbituminous C Coal	---	---	8,300 to 9,500	
IV Lignite	1. Lignite A	---	---	6,300 to 8,300	Nonagglomerating
	2. Lignite B	---	---	<6,300	

^aCoal ranks are listed according to the ASTM D388 system.^bDry, mineral-free basis.^cMoist, ash-free basis (MAF).

TABLE III-8
APPROXIMATE DENSITIES OF AMERICAN COALS
 (Cameron, 1975)

Rank	Particle density, g/cc	Bulk density, g/cc	Bulk density, ^a lb/ft ³
Anthracitic	1.7	0.85	53
Bituminous	1.4	0.70	44
Subbituminous	1.3	0.65	41
Lignitic	1.2	0.60	38

^aAssuming that void fraction is 0.5.

Bulk density is dependent on rank, moisture, particle size, and void space. Representative bulk-density values, as they vary with size and percent void space, are presented for a typical coal in Table III-9. The relation between particle density and carbon content of coal according to van Krevelen (van Krevelen, 1961) is shown in Fig. III-9. It is interesting to note that with increasing carbon content, density decreases to a minimum value at approximately 85% carbon, which corresponds to low-volatile bituminous coal. This relates to grindabilities, which tend to be highest in this range, as discussed in the next section.

3.1.3 GRINDABILITY

Grindability is a measure of the amount of work required to produce fines of a given size, as compared with standard coal samples. It is determined by Hardgrove machine method (ASTM Method D-409-71), which gives the highest Hardgrove grindability indices to coals that are easiest to grind.

Although medium- and low-volatile bituminous coals tend to have high Hardgrove grindability indices, there appears to be little relationship between coal rank and grindability. Table III-10 presents some Hardgrove grindability indices for a variety of U.S. coals.

3.1.4 POROSITY AND INTERNAL SURFACE AREA

According to van Krevelen (van Krevelen, 1961), there are two separate pore systems in coal. One of these, the Micropore system, comprises pores in the 5-8 Å range which are inaccessible to such molecules as CO₂ and N₂ at the low temperatures used in surface-area determinations by BET methods. This observation probably explains some of the conflicting literature concerning internal surface area for coals. Surface areas determined by argon and neon absorption at room temperature appear to give the most dependable values, especially for higher-ranked coals.

TABLE III-9
VARIATION IN BULK DENSITY OF A COAL FOR VARIOUS SIZE FRACTIONS
 (Cameron, 1975)

<u>Particle size of coal sample</u>	<u>Bulk density, lb/ft³</u>	<u>Percent voids</u>
Mine run	55	37
Lump (plus 6 in.)	50	43
6 x 3 in.	48	45
3 x 2 in.	46	47
2-in. screenings	49	44
2 x 1-1/2 in.	45	48
3/4 x 7/16 in.	42	52
7/16 x 0 in.	47	46
5/16 in. x No. 10	45	48
1/16 in. x 48 M	42	52
No. 48 x 0	35	60

Fig. III-9. Density of Coals vs Carbon Content (van Krevelen, 1961).

TABLE III-10
REPRESENTATIVE HARDGROVE GRINDABILITY VALUES FOR VARIOUS COALS
 (Cameron, 1975)

State	County	Bed	Mine	Hardgrove
				Grindability Index
Alabama	Walker	Black Creek	Drummond	46
Colorado	Mesa		Cameo	47
Illinois	Stark	No. 6	Allendale	61
Illinois	Williamson	No. 6	Utility	57
Indiana	Pike	No. V	Blackfoot	54
Iowa	Lucas	Cherokee	Big Ben	61
Kansas	Crawford	Bevier	Clemens	62
Kentucky	Bell	High Splint	Davisburg	44
Kentucky	Muhlenburg	No. 11	Crescent	55
Missouri	Boone	Bevier	Mark Twain	62
Montana	Richland		Savage	62
New Mexico	McKinley	Black Diamond	Sundance	51
North Dakota	Burke		Noonan	38
Ohio	Belmont	No. 9	Linda	50
Pennsylvania	Cambria	Lower Kittanning (Bituminous)	Bird No. 2	109
Pennsylvania	Indiana	Lower Freeport (Bituminous)	Acadia	83
Pennsylvania	Schuylkill	Various (Anthracite)		
Pennsylvania	Washington	Pittsburgh	Florence	55
Pennsylvania	Westmoreland	Upper Freeport	Jamison	65
Tennessee	Grundy	Sewanee	Ramsey	59
Utah	Carbon	Castle Gate	Carbon	47
Virginia	Buchanan	Splash Dam	Harman	68
Virginia	Dickerson	Upper Banner		84
Virginia	Wise	Morris	Roda	43
West Virginia	Fayette	Sewell	Summerlee	86
West Virginia	McDowell	Pocahontas No. 3	Jacobs Fork	96
West Virginia	Wyoming	Powellton	Coal Mtn.	58
West Virginia	Wyoming	No. 2 Gas	Kopperston	70
Wyoming	Campbell	Smith/Rowland	Wyodak	59

Table III-11 presents data on porosity, pore volume, and internal surface area, for a variety of coals containing 78-88% carbon.

3.2 CHEMICAL PROPERTIES

The chemical composition of coal is generally expressed by proximate and ultimate analyses. The proximate analysis gives the composition of coal in terms of volatile matter, fixed carbon, and ash content, while the ultimate analysis shows the percentage of carbon, hydrogen, oxygen, sulfur, nitrogen, and ash. Proximate and ultimate analyses for a number of coals are summarized in Table III-12.

3.2.1 COAL STRUCTURE

There are two schools of thought concerning the chemical structure of coal. One school suggests that coal is largely composed of condensed aromatic rings, while the other proposes that coal largely consists of quaternary aliphatic carbon atoms (and <50% aromatic carbon atoms). In both of these structural systems, the H/C ratio is low, in agreement with ultimate analysis data. A detailed discussion of the argument supporting each of these viewpoints is beyond the scope of this study. Recent work by Whitehurst et al. (Whitehurst, 1977) suggests that the degree of aromaticity of coal varies with rank, beginning at approximately 40% for subbituminous coals, and exceeding 90% for anthracitic coals (Fig. III-10). Whitehurst et al. further suggest that the aromaticity in coal is independent of the H/C ratio, in contradiction to the opinion of van Krevelen and others (van Krevelen, 1961).

Coal can be visualized as a highly cross-linked polymer with a combination of condensed aromatic and aliphatic regions. The aromatic regions have great internal cohesiveness compared with the aliphatic regions, which have connecting bonds. At high temperatures coal fragments into aromatic radicals (Whitehurst, 1977). In the presence of hydrogen-donor solvents, these free radicals are inactivated by transfer of hydrogen atoms, and converted to stable, solvent-refined coal with mean molecular weights ranging between 300 and 1000.

TABLE III-11
PORE STRUCTURES OF SOME COALS
(van Krevelen, 1961)

Coal		Moisture, % (air-dried coal)	Porosity	Pore volume, cm ³ /g			Internal surface, m ² /g
C, %	H, %			Total	Macro	Micro	
78.0	4.5	7.5	0.194	0.176	0.073	0.103	181
78.1	4.5	6.2	0.188	0.169	0.074	0.095	165
84.7	4.9	2.7	0.139	0.121	0.039	0.082	120
81.2	4.4	2.7	0.146	0.125	0.042	0.083	128
80.5	---	2.7	0.142	0.120	0.064	0.056	131
84.5	4.5	2.5	0.138	0.118	0.051	0.067	110
82.3	---	2.1	0.100	0.090	0.052	0.038	90
88.6	4.9	1.4	0.125	0.107	0.042	0.065	90
88.0	4.8	1.3	0.120	0.102	0.043	0.059	82
85.5	---	1.0	0.088	0.070	0.035	0.035	70
87.6	4.5	0.9	0.097	0.073	0.043	0.030	84
85.8	4.8	0.8	0.118	0.100	0.041	0.059	85
85.7	---	0.6	0.070	0.058	0.038	0.020	40

TABLE III-12
COMPOSITIONS OF TYPICAL COALS
(SERI, 1979)

Type of Coal	Lignitic (N. Dakota)	Subbituminous (Montana)	Bituminous (Illinois #6)	Bituminous (Pittsburgh)	Anthracitic (Pennsylvania)
<u>Proximate Analysis, wt%</u>					
Volatile matter	26.6	34.7	36.0	30.5	9.3
Fixed carbon	32.5	43.6	41.9	58.2	75.6
Moisture	33.7	10.5	13.2	2.0	3.4
Ash	7.2	11.2	8.9	9.3	11.7
<u>Ultimate Analysis, wt%</u>					
Carbon	62.9	66.8	70.8	75.8	80.6
Hydrogen	4.2	5.0	4.9	4.7	3.4
Nitrogen	1.0	1.5	1.3	1.5	1.0
Sulfur	0.9	1.2	3.4	2.2	0.8
Oxygen	20.1	13.0	9.3	6.3	2.1
Ash	10.9	12.5	10.3	9.5	12.1
Heating Value, Btu/lb (wet)	7,100	10,600	11,100	13,600	13,100

Fig. III-10. The Relationship of Aromaticity and Rank (Whitehurst, 1977).

The radical subunits which are not capped by hydrogen tend to recombine to form coke.

3.2.2 ASH

The major constituents of coal ash are SiO_2 , Al_2O_3 , and Fe_2O_3 , as shown in Table III-13. The ash composition of coal appears to be related to rank; there are progressively higher SiO_2 , Al_2O_3 , and Fe_2O_3 contents with increasing rank, and a concomitant decrease in the CaO and SO_3 contents.

ASTM has developed standard methods for testing the fusibility of coal ash (D-1857-68). These methods show that the initial deformation temperature for most U.S. coal ash is between 1100 and 1400°C (2012 and 2552°F) (Cameron, 1975).

3.2.3 FUNCTIONAL GROUPS

Oxygen, sulfur, and nitrogen occur in coal as components of various reactive functional groups. The major coal functional groups containing these elements are shown in Fig. III-11. Metals are usually present as salts or porphyrins. The nature of the functional groups changes as the coal is processed, especially under severe operating conditions (Whitehurst, 1977).

3.3 IMPLICATIONS OF THE CHEMICAL AND PHYSICAL PROPERTIES OF BIOMASS AND COAL FOR FUELS PRODUCTION

In this section a brief summary of the key differences in the chemical and physical properties of biomass and coal is presented as a basis for assessing the utility of coal conversion concepts for biomass and the suitability of biomass as a feedstock for synthetic fuels production. Table III-14 provides a general comparison of the physical and chemical properties of biomass and coal. Clearly there are marked differences which appear to favor biomass over coal as a feedstock for synthetic fuels. The H/C ratio of biomass is especially favorable, approaching values typical of petroleum-derived fuels. This is illustrated by the

TABLE III-13

ANALYSIS OF ASH FROM SELECTED U.S. COALS
(Cameron, 1975)

<u>State/County</u>	<u>Percent of Moisture-Free Coal</u>		<u>Analysis of Ash, Percent</u>									
	<u>Ash</u>	<u>S</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>TiO₂</u>	<u>P₂O₅</u>	<u>CaO</u>	<u>MgO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>SO₃</u>
Alabama, Jefferson	13.6	3.8	38.4	22.2	35.6	1.1	0.12	1.7	0.8	0.2	2.2	0.6
Colorado, Routt	8.5	0.8	48.4	30.6	4.7	1.2	1.50	4.6	1.5	0.2	0.6	4.8
Illinois, Schuyler	10.3	3.6	48.0	14.7	18.7	0.6	0.44	10.4	0.6	0.2	1.8	2.1
Kentucky, Bell	9.4	1.2	50.5	30.0	11.4	1.2	0.61	1.8	1.1	0.4	3.0	0.8
Montana, Big Horn	4.2	0.4	22.1	15.5	6.4	1.2	0.11	18.9	6.6	1.0	0.4	2.1
New Mexico, McKinley	16.3	1.1	61.9	22.9	7.8	0.8	0.011	3.2	1.5	0.7	1.1	2.1
North Dakota, Mercer	12.1	1.1	23.8	10.5	10.1	0.6	0.27	16.6	5.1	8.2	0.6	23.5
Ohio, Belmont	10.8	4.3	42.4	19.6	27.5	0.9	0.15	4.0	1.2	0.2	3.6	1.3
Pennsylvania, Allegheny	7.9	2.0	49.2	24.8	20.3	1.0	0.14	1.8	0.5	0.2	3.6	1.3
Utah, Carbon	8.1	0.4	50.5	10.3	4.9	0.9	0.62	17.2	7.6	0.4	0.4	6.6
West Virginia, Barbour	10.6	2.9	37.8	27.3	31.1	1.4	0.11	1.1	0.6	0.2	1.1	1.2
Wyoming, Carbon	6.4	0.6	24.5	4.2	9.0	0.9	0.21	30.8	4.7	0.1	0.5	14.4

Fig. III-11. Major Functional Groups in Coal.

Table III-14

GENERAL COMPARISON OF THE PHYSICAL AND CHEMICAL
PROPERTIES OF BIOMASS WITH COAL

	<u>Coal</u>	<u>Biomass</u>
H/C	0.2-0.8	1.6
O/C	0.007-0.25	0.68
Ash	7-12 wt%	0.2-3 wt%
S	0.8-3.4 wt%	Traces
N	1-5 wt%	Traces
H ₂ O	Bit., 2%	Bark, ~0%
	Subbitum., ~10%	Wood, ~10%
	Lignite, ~30%	Bagasse, ~50%
Density, g/cc	1-2(Lig.)-1.75 (Anthr.)	0.4(S-wood)-0.6 (H-wood)
Volatile matter, %	9(Anthr.)-36 (Bitum.)	~87

comparison in Fig. III-12, which shows that the H/C ratio of biomass is comparable with that of fuel oil. Figure III-12 also provides a comparison of typical O/C ratios of biomass with those of various coals. The oxygen content is, of course, maximum with biomass producing the lowest Btu content of the materials compared (Fig. III-13). The implications of the elemental compositions for upgrading are that conversion of coal to liquid fuels requires an increase in the H/C ratio either by the addition of hydrogen (hydroliquefaction) or the removal of carbon (pyrolysis). Conversion of biomass to liquids, on the other hand, may be achieved by removal of oxygen, an approach which forms the basis of the liquefaction project currently under way in Albany, Oregon.

In gasification, the elemental composition of biomass, coupled with this higher reactivity and larger fraction of volatile matter, also appears favorable in that the steam, oxygen, and feed requirements would be lower relative to coal.

Perhaps the most attractive aspect of the chemical properties of biomass is the low concentration of impurities, S, N, and ash. Figure III-14 provides a general comparison of S, N, and ash levels of biomass, coals, and petroleum-derived products. The low concentrations of impurities in biomass significantly reduce the heteroatom removal requirement relative to processing of coal-derived fuels. In addition, the low impurity concentration broadens the scope of potential catalytic systems which could be applied for synthetic fuels production. This is particularly true for poison-sensitive catalysts which are used in combination with gasification catalysts in single-step processes to generate particular products such as CH₄, H₂, CO or synthesis gas (Robertus, 1979).

Although the chemical properties of biomass, in general, are quite uniform and attractive for synthetic fuel production, the physical properties vary considerably, depending on the biomass resource, e.g., wood chips, hulls, straws, and stalks. Such materials are not easily preprocessed by grinding to the small particle sizes attainable with coal. Therefore, preprocessing and feeding are important considerations in choosing conversion technologies for biomass.

Fig. III-12. Comparison of the H/C and O/C Ratios of Biomass with Petroleum-Derived Products and Coal.

Fig. III-13. Energy Content of Biomass Relative to Petroleum-Derived Products and Coal.

Fig. III-14. Approximate Impurity Levels in Biomass Relative to Other Fuel Sources.

Conversion processes that require little preprocessing and accept a wide variety of feed geometries and particle sizes appear desirable. Alternatively, it is likely that several technologies applied on a regional basis and designed to handle feedstocks with a specified range of physical properties will evolve.

PART IV 1. GASIFICATION

1.1 GENERAL CHEMICAL AND ENGINEERING ASPECTS OF GASIFICATION

The discussion in this section will concern some relevant general aspects of gasification reactors with emphasis on the extensive knowledge and experience with coal as the feed. The nature of the chemical reactions which occur in coal gasification are presented first, followed by a brief description of gasification reactors. Next, the role of catalysts in gasification, particularly the steam-carbon reaction is discussed. Finally, some unique aspects of biomass gasification which indicate significant advantages over coal as a fuel source are discussed.

1.1.1 CHEMICAL REACTIONS IN GASIFICATION

Gasification processes are of three types:

- Steam gasification processes which depend on steam carbon reforming as the key gasification reaction.
- Hydrogasification processes which are based on the reaction of carbon with hydrogen to produce hydrocarbons.
- Pyrolysis processes which are thermal degradation processes carried out in the absence of added steam or hydrogen. Such processes usually produce liquid as well as gaseous products.

In addition to these processes which are common to biomass and coal, biomass undergoes a unique gasification process, namely exothermic pyrolytic decomposition in the presence of steam. This important aspect of biomass gasification is discussed in Sec. 1.1.4.

The important chemical reactions in gasification are summarized in Fig. IV-1 for a fixed-bed reactor.

Fig. IV-1. Schematic Showing the Important Reactions in Gasification of Coal.

In a given gasification system, the various reactions occur at rates and to extents which depend upon temperature, pressure, gas composition, the nature of the coal, and the nature and amount of added catalyst.

Devolatilization reactions occur during the initial heating of the feed coal or in the pyrolysis processes. Methanation and CO shift reactions are important because they affect the product gas composition. The rates at which these reactions reach equilibrium are strongly influenced by catalysts.

For steam gasification processes the steam-carbon reaction is the critical step since it is responsible for gasifying the bulk of the solid feed. Because of the importance of this reaction in gasification, the current understanding of the role of catalysts in the steam-carbon reaction is discussed in Sec. 1.1.3, Part IV. This reaction is endothermic and the heat required for the gasification to proceed is usually supplied by in situ combustion of part of the coal feed by air or oxygen. When air is used, the product gas is contaminated with nitrogen. For SNG or syngas production, therefore, gasification must be conducted using oxygen.

A more novel approach to the problem of supplying heat to the steam-carbon reaction involves the use of a solid which carries both sensible and chemical heat. This approach is exemplified by the CO₂ Acceptor process. In this process hot calcined dolomite (principally CaO) is contacted with the feed coal to supply sensible heat and chemical heat, which is released by the exothermic reaction between dolomite and product CO₂:

The spent dolomite is regenerated in a separate vessel using air combustion of the gasification by-products.

The hydrogasification reaction can occur as one of the many simultaneous reactions in the steam gasification system since hydrogen is generated by the shift and steam-carbon reactions and by the reverse of the methanation reaction. A few processes use hydrogasification as the primary gasification reaction. The HYDRANE process described in this section is one such process. Since the reaction of hydrogen with coal is exothermic, the heat supply is not a major process concern. On the other hand, hydrogen required by the process must be generated in a separate unit and represents a significant cost factor in the process.

1.1.2¹ GASIFICATION REACTOR TYPES

Based on the method of solid-gas contacting in the reactor, four types of gasification reactors are widely recognized:

- Fixed-bed
- Fluid-bed
- Entrained-flow
- Molten-bath

In this section the principal features of these reactors are briefly described to provide background for subsequent discussions of gasification technologies.

1.1.2.1 Fixed-Bed Reactor

Fixed-bed gasification reactors are used in the Lurgi, Wellman-Galusha, and Stoic Combustion processes. A bed of coal is gasified at the bottom of the reactor while fresh coal is fed at the top. Coal moves downward by gravity flow at a rate determined by the rate of gasification below. Some fixed-bed gasifiers are equipped with a mechanical agitator which improves the homogeneity of the coal bed and prevents the formation of clinkers.

The feed coal in the fixed-bed operation is usually sized between 1/8 and 1-1/2 in. Fines are not desirable because they cause channeling of the product gas through the coal bed. Coals with caking tendency present potential problems such as bed-plugging and attendant unreliable operation.

1.1.2.2 Fluid-Bed System

Fluid-bed coal gasification processes which use this system include Winkler, HYGAS, and CO₂ Acceptor. Such processes depend on the fluidization of the solid fuel by the gasifying media. From an engineering standpoint, operation of this type of reactor is much more complex than in the fixed-bed system. For example, to maintain good fluidization, it is necessary to simultaneously control a number of process parameters such as the solid particle size and density, the fluid velocity, temperature, etc. Furthermore, it is important to realize that the coal particles undergo changes within the fluidized system. Thus, the particle size of the solid is being reduced as gasification proceeds, and its physical characteristics may also change.

The major problems associated with the fluid-bed coal gasifiers are particle agglomeration and erosion. The former limits the use of caking coals unless a decaking step is incorporated ahead of gasification.

The particle size of the feed coal is usually less than 1/4 in., but there are significant differences among the individual processes with respect to the desired range of the feed coal sizes. Some fluid-bed reactors, such as U-Ga, handle the feed coal size up to 1/4 in., while others, such as Synthane, require the coal size to be reduced below 20 mesh (about 1/32 in.).

1.1.2.3 Entrained-Flow Gasifier

In the entrained-flow gasifier, of which the Koppers-Totzek gasifier is an example, fine coal particles pulverized to 200 mesh or smaller are swept into the gasifier by the gaseous reactants. In the reactor, gasification takes place very

quickly in the order of a second or less. This system of gasification is known for its ability to handle a variety of coals, including caking coals.

1.1.2.4 Molten-Bath System

In this system, coal is gasified within the mass of molten salt or molten iron. The molten-iron system was used by ATGAS, while the Kellogg process employed a bath of molten sodium carbonate. Although the molten-bath concept is quite simple, there are some critical problems which prevented commercial development of the ATGAS and Kellogg processes. These include:

- Reactor lining which resists corrosion as well as erosion
- Introduction of the reactants into the bath
- Handling of by-product ash, slag, sulfur compounds
- Contamination of product gas with salt vapor
- Regeneration of spent bath material.

Atomics International has reviewed the development of the molten-salt process for coal gasification and has made significant progress towards alleviating these problems. The Atomics International process is discussed in Sec. 1.3 1.4 of Part IV.

1.1.3 THE ROLE OF CATALYSTS IN STEAM GASIFICATION

1.1.3.1 General Remarks

The steam gasification of carbonaceous materials can be schematically represented by Fig. IV-2. As the temperature increases, the first processes to occur are pyrolysis and devolatilization, which produce ash-containing char and volatiles. With regard to pyrolysis, biomass is much more reactive than most coals, as is illustrated by Fig. IV-3. Pyrolysis of cellulose is initiated at relatively low temperatures (300-500°C), and a large portion of the feed (70-90 wt%) is converted to volatile matter (Antal, 1979). The higher the heating rate, the less char is produced. In fact, Lewellen et al. (Lewellen, 1976) have reported

Fig. IV-2. Steps in Steam Gasification

Fig. IV-3. Comparison of the Pyrolysis Reactivity of Cellulosic Materials and Coal(Antal, 1978).

complete volatilization of cellulose at the very rapid heating rates of $>10,000^{\circ}\text{C}/\text{sec}$. The pyrolysis of coal requires higher temperatures than that of biomass (Fig. IV-3), and the proportion of volatiles produced is much lower ($< 50 \text{ wt\%}$).

At temperatures above 600°C , secondary reactions of the devolatilization products occur. These processes may be influenced by the addition of catalysts to direct the reactions toward particular products (Robertus, 1979). In the absence of a catalyst, the secondary reactions of the volatilization products are similar to steam-cracking reactions (Antal, 1979).

At the highest temperatures, $>700^{\circ}\text{C}$, the pyrolytic char undergoes steam gasification to produce H_2 , CO , and CO_2 via the following reactions:

The high temperatures required to promote the carbon reactions (I and III) reflect the slow rates of these reactions and the desirability of using catalysts.

For steam-gasification processes in which methane is the desired product, the chemical dilemma is an inefficient thermal balance:

<u>Gasification</u>	$\Delta H_{298^\circ K},$ <u>kcal/mole</u>	<u>Reaction</u> <u>Temperature</u>
$2C + 2H_2O \rightleftharpoons 2CO + 2H_2$	+62.76	1000°C(1800°F)
<u>Shift</u>		
$CO + H_2O \rightleftharpoons CO_2 + H_2$	-9.83	300°C(600°F)
<u>Methanation</u>		
$3H_2 + CO \rightleftharpoons CH_4 + H_2O$	-49.27	400°C(700°F)
<hr/>	<hr/>	
$2C + 2H_2O \rightleftharpoons CH_4 + CO_2$	+3.66	

Thus, the sum of the reactions which give rise to the formation of CH_4 are nearly thermoneutral. However, the water-gas shift and methanation steps are carried out at much lower temperatures for thermodynamic reasons and catalyst maintenance. Therefore, the exothermic heat generated in these two steps cannot be efficiently utilized at the higher temperature for steam gasification. The potential solution to the problem is catalytic gasification at 800-900°F. Then the heat from the shift and methanation steps could supply that required for the gasification reactions. This possibility of a "single-step" gasification has been a primary motivation for catalytic steam gasification.

To use a "single-step" gasification reactor, the gasification, water-gas shift, and methanation reactions must be catalyzed simultaneously. This requires a bifunctional catalyst. For the steam-gasification reaction, alkali-metal oxides and carbonates are among the best catalysts. The water-gas shift and methanation reactions are usually catalyzed by metal catalysts such as Ni or Fe. Consequently, combinations of Ni and other transition metals with the alkali-metal oxides or carbonates have been explored as "single-step" gasification catalysts (Robertus, 1979; Willson, 1974; Haynes, 1974; Kalina, 1974). Massive amounts of catalyst are usually required for acceptable activity with coal that

contains significant quantities of catalyst poisons such as sulfur. With biomass, however, the concentrations of potential catalyst poisons, particularly sulfur, are significantly lower, which may provide incentive for the development of methanation catalysts that are unaffected at the low sulfur concentrations typical of biomass.

Because the carbon-steam reaction is the slowest process in gasification of chars derived from biomass, it is useful to focus on catalysis of this reaction. A number of recent studies have provided important insight regarding the role of the catalyst in steam gasification. These studies and their implications for biomass conversion are discussed in the following section.

1.1.3.2 Catalyzed Steam Gasification of Carbon

Much of the earlier work on the carbon-steam reaction was in conflict in that different authors reported that the same catalyst enhanced, had no effect on, or even suppressed the rate of gasification, (Otto, 1977). This circumstance undoubtedly resulted from improper attention to the influence of heat- and mass-transfer effects and from the ambiguities in the reporting of rate data. The results of the majority of the earlier work did not contribute much to the understanding of the role of the catalyst in steam gasification.

In a recent series of reports, Shelef and coworkers have carefully examined the effect of a variety of catalysts in the steam gasification of pure graphite and coal chars (Otto, 1977, 1977a, 1979, 1979a). These authors measured gasification rates in the presence and absence of catalysts under conditions which eliminated mass-and heat-transfer effects. Only under such conditions can the effect of catalysts be quantitatively established. In addition, Shelef et al, compared gasification rates on the basis of specific surface area (quantity of carbon gasified per unit time per unit area) rather than on the basis of unit weight. The importance of making comparisons on a unit-area basis is illustrated by the data in Table IV-1. When compared on a weight basis, the gasification rates at the extremes differ by a factor of 1750, whereas on a unit-area basis the

difference is only a factor of 15.7. Clearly the difference in reactivity of the materials is due primarily to the large variation in surface areas. The higher specific area reactivity of the Braunkohle was shown to be due to the catalytic effects of native ash. The data in Table IV-1 indicate that false conclusions concerning catalytic effects may be reached when data are compared on a weight basis, particularly if the addition of a catalytic agent produces a modification of the surface area of the material to be gasified.

TABLE IV-1
COMPARISON OF THE STEAM GASIFICATION OF COAL
CHARS AND GRAPHITE AT 850°C (Otto, 1977b)

<u>Coal</u>	BET area, <u>m²/g</u>	<u>μg/g/min</u>	Relative <u>rate</u>	<u>μg/min/m²</u>	Relative <u>rate</u>
Braunkohle	436	2100	1750	4.7	15.7
Pittsburgh					
Seam	407	280	233	0.7	2.3
Graphite	3.6	1.2	1	0.3	1.0

Other important aspects of the work by Shelef et al. concern the mode of catalytic action. These authors compared the activation energies and specific-area rates of the carbon-steam reaction in the presence and absence of catalysts. The results are summarized in Figs. IV-4 and IV-5. Figure IV-4 shows that the activation energy of the carbon-steam reaction is not significantly affected by the addition of alkaline-earth catalysts, Ca, Sr, and Ba. The rate of gasification on a specific-area basis, however, increases substantially in the presence of these catalysts, with Ba exhibiting the greatest enhancement.

Fig. IV-4. Comparison of Activation Energies (kcal/mole) and Rates ($\mu\text{g}/\text{m}^2/\text{min}$) for Catalyzed and Uncatalyzed Steam Gasification of Graphite. Data pertain to reaction at 850°C and 0.3 at% catalyst concentration (Otto, 1979a).

Figure IV-5. Comparison of activation energies (kcal/mole) and rates ($\mu\text{g}/\text{m}^2/\text{min}$) for catalyzed and uncatalyzed steam gasification of graphite. Data pertain to reaction at 850°C and 1 wt% catalyst concentration (Otto, 1977).

Similar results are obtained with catalysts from the Group VIII elements (Fig. IV-5). In this case activation energies appear to be decreased somewhat; however, Shelef et al. concluded that this was because of the onset of mass-transport effects, rather than a catalytic lowering of the activation energy. For the Group VIII metals, much greater enhancements in specific-area gasification rates were obtained (7600, relative to the uncatalyzed reaction), with rhodium exhibiting the highest activity. It is unlikely that expensive catalysts such as rhodium could even be seriously considered as a gasification catalyst. The implications of the results illustrated in Figs. IV-4 and IV-5 become apparent from the Arrhenius equation:

$$\text{Gasification rate} = A \exp(-E_a/RT),$$

where A is the pre-exponential factor related to the concentration of catalytic sites, and E_a is the activation energy. The most desirable effect of a catalyst is to decrease E_a , which leads to an exponential increase in rate. Rate is also enhanced by increasing the concentration of catalytic sites, but the effect in this case is linear. The data in Figs. IV-4 and IV-5 indicate that the activation energy of the steam gasification is unaffected by the catalysts examined to date, and that the enhancement in rate is primarily due to an increase in the pre-exponential factor, i.e., the concentration of catalytic sites. This implies that the catalyst does not affect the rate-determining step of the carbon-steam reaction but may increase the concentration of reactive species which participate in the rate-determining step. In a simplified scheme, the carbon-steam reaction can be envisioned as two steps, viz.,

- Activation of H_2O

- C-C Bond Rupture (rate-determining)

In this scheme the catalyst increases the concentration of the species $[O_{(a)}]$ but does not alter the energetics of the rate-determining step involving C-C bond

rupture. Thus, the rate of gasification is increased without altering the activation energy as observed experimentally.

The fundamental studies of Shelef and coworkers have significant implications concerning catalysis of the carbon-steam reaction. The results indicate that the largest catalytic enhancement of the reaction rate is achieved when contact between the catalyst and the carbon is maximized. Indeed, Shelef et al. found from careful characterization studies by physical techniques that the efficacy of Ba as a catalyst relative to Ca and Sr was due to more effective wetting of the carbon (Otto, 1979a). The Ba catalyst tended to spread uniformly over the surface of the carbon during the reaction, whereas the other catalysts were less effective in this regard. If the catalyst effectively wets the carbon during the gasification reaction, the amount of catalyst necessary to achieve the maximum effect will depend on the surface area of the carbon, as shown in Fig. IV-6. For high-surface-area carbons, very large catalyst concentrations are required; therefore, recovery of the catalyst is necessary. Clearly, the most desirable catalyst is one which would enhance the rate of the carbon-steam reaction by lowering the activation energy, rather than by increasing the pre-exponential factor. Catalysts which lower the activation energy, in the absence of mass-transport effects, could be used in exceedingly low concentrations and thus reduce or alleviate the recovery problem.

If catalysts that lower the activation energy cannot be found, gasification technologies that provide for maximum catalyst-carbon contact throughout the course of gasification, or that do not form char, may be attractive. Molten-salt reactor technology or the Wright-Malta process described in Secs. 1.2.1.3 and 1.3.1.3 of Part IV may fulfill this role, as discussed in Parts VI and VII.

1.1.4 EXOTHERMIC THERMAL DECOMPOSITION OF BIOMASS

In the gasification of biomass by partial combustion or pyrolysis, the reactions discussed for coal also occur for the char product. However, there is another important gasification process unique to biomass pyrolysis in the presence of steam, namely, exothermic thermal decomposition. The occurrence of an exothermic

Fig. IV-6. Relationship Between Catalyst Concentration Required to Achieve Monolayer Catalyst Coverage (Maximum Catalyst-Carbon Contact) and Carbon Surface Area. Example is presented for a barium catalyst, assuming area covered by one Ba atom is $7.6 \text{ \AA}^2$.

process in the steam pyrolysis of biomass has been reported in several studies (Coffman, 1979; Beck, 1979; Antal, 1979). The exothermic process is the key to the Wright-Malta technology discussed in Sec. 1.2.1.3, Part IV. Available data from Wright-Malta indicate that the exothermicity of the steam-pyrolysis of biomass is sufficient for self-sustained gasification. A recent thermodynamic analysis (SERI, 1979) provides a perspective for the adiabatic decomposition temperatures and the product distribution from the pyrolysis of wood in the presence and absence of steam at various pressures. Table IV-2 presents the calculated data for gasification of dry sulfur and ash-free wood having the composition:

The pertinent points illustrated by the table are as follows:

- In thermodynamic equilibrium, only free carbon, H_2 , H_2O , CO , CO_2 , CH_4 , and N_2 are present in significant amounts.
- Various other products, such as hydrocarbons and oxygenated or nitrogenous compounds, may form as intermediates, but they are not equilibrium products.
- In the absence of moisture or added steam, the equilibrium decomposition pyrolysis of dry wood at 640°C (1184°F) gives the following carbon products: 64% carbon, 17% CO , 13% CO_2 , and 6% CH_4 , in addition to H_2 and H_2O .
- Increasing the temperature lowers the C , CO_2 , and CH_4 yields; however, CO yields are increased. Increasing the pressure has the opposite effect.
- The presence of water in the form of moisture in the wood or as steam, has a dramatic effect on the equilibrium product distribution in the decomposition of wood. The formation of CO_2 and CH_4 is favored, and the formation of C and CO is suppressed.
- Because of the exothermicity of the decomposition reaction, an adiabatic decomposition temperature can be calculated for wood that ranges from 229 to over 800°C (444 to over 1472°F), depending on the amount of water added and the pressure used.

TABLE IV-2
ADIABATIC DECOMPOSITION OF WOOD ($\text{CH}_{1.4} \text{O}_{0.59}$)

Pressure, psig	H ₂ O, moles	Temp., °C	Decomposition products, moles				Notes
			C	CO	CO ₂	CH ₄	
0	0	640	0.64	0.17	0.13	0.06	Dry wood
0	1.02	229	0.37	0.0	0.29	0.34	
300	0	787	0.61	0.17	0.12	0.11	
0	0.51	459	0.49	0.01	0.28	0.22	Wood at 40% moisture, dry basis
400	0.51	549	0.43	0.01	0.27	0.28	
1000	0.51	569	0.42	0.01	0.27	0.29	
0	1.02 ^a	455	0.26	0.02	0.41	0.31	Wood at 40% moisture under steam at 727°C
0	1.52 ^b	452	0.03	0.03	0.54	0.40	
400	1.02	546	0.18	0.02	0.40	0.39	
400	1.52	546	0.0	0.03	0.50	0.47	
1000	1.02	567	0.17	0.02	0.40	0.41	
1000	1.52	568	0.0	0.02	0.50	0.48	

^aCorresponds to 80% moisture, dry basis.

^bCorresponds to 120% moisture, dry basis.

The results of the thermodynamic analysis indicate that at the proper conditions of temperature, steam concentration, and pressure, a self-sustained steam pyrolysis of biomass is feasible with little or no production of char. The primary reactions responsible for the exothermic process are most likely the water-gas shift and methanation reactions. Because the data in Table IV-2 pertain to equilibrium, catalysts would not affect the results other than to increase the rate at which equilibrium is attained. Any increase in rate would, of course, improve the process economics by reducing the reactor size requirements.

1.2 BIOMASS GASIFICATION TECHNOLOGIES

This section reviews the major biomass gasification processes. These processes, which are summarized in Table IV-3, are concerned with the production of gaseous fuels as the primary product. The principal gasification reactions in the processes discussed are steam gasification, pyrolysis, partial oxidation, and hydrogasification. Direct-combustion processes are not within the scope of this study.

Biomass gasification was investigated rather extensively in the early part of this century. One principal application considered was the manufacture of producer gas for internal combustion engines. This resulted in the development of several small gasifiers suitable for stationary or mobile engines (Horsfield, 1976). Today, biomass gasification is pursued with broader goals encompassing the production of low- and intermediate-Btu gas, SNG, synthesis gas, methanol, and ammonia.

TABLE IV-3

BIOMASS GASIFICATION PROCESSES

Process	Status	Reactor Type	Feed	Gasifying Agent	Pressure	Temp.	Products	Comments
Purox (Union Carbide)	Commercial (200 tons/day)	Fixed-bed	Biomass, MSW	O ₂ /steam	Atm	3000°F at comb. zone, 400°F prod gas exit	MBG	
Andco-Torrax (Andco, Inc.)	Commercial (220 tons/day)	Fixed-bed	MSW, Biomass	Air/steam	Atm	220-2300°F to slag ash in second comb.		
Forest Fuels (Forest Fuels, Inc.)	PDU	Inclined-grid, partial oxidation	Wood chips	Air	Atm			No steam fed
Georgia Tech	Portable unit	Fixed-bed, partial oxidation, pyrolysis	Agricultural wastes	Air	Atm		LBG, tar, oil	No steam fed
Flash Pyrolysis (Occidental)	200-ton/day demo plant under construction	Pyrolysis		Heat; no air, O ₂ , H ₂ , or catalyst is used	Atm			
Envirotech	Demo plant	Multiple-hearth		Air	Atm			
Battelle-Pacific NW	A 20-kg/hr PDU under design	Fluid-bed	Sawdust	O ₂ or O ₂ /A ₂ O, catalyst	Atm	600°C	MBG	K ₂ CO ₃ or Na ₂ CO ₃ used as catalyst
Battelle-Columbus	Bench-scale	Dual-vessel fluid-bed (hot sand and feed)	Forest residue	Steam in gasifica- tion liquid air in combustor, catalyst	N.A.	750°C	MBG	CaO or wood ash used as catalyst
Wright-Malta	A 6-ton/day PDU under design	Inclined rotary kiln	Greenwood	Steam, catalyst	300 psig	700-1100°F	MBG	Wood ash used as catalyst
Garrett	PDU	Multiple hearth	Manure	Pyrolysis	Atm	600°C	MBG, tar, oil	
Texas Tech	1/2-ton/day PDU	Fluid-bed	Manure	Air or O ₂ /steam	Atm and higher	1000°C	LBG, MBG	
UC Davis	Bench scale	Partial oxide	Straw, rice, hulls, nut shells	Air	Atm	1200°C	LBG	Mobile unit
Moore-Canada	Commercial	Fixed-bed	As-received greenwood	Air/steam	Atm	1200°C	LBG	

Note: MBG = Medium-Btu gas

LBG = Low-Btu gas

1.2.1 CATALYTIC PROCESSES

1.2.1.1 Battelle-Columbus Laboratories Process (Battelle Laboratories, Columbus, Ohio).

This program covers the effect of catalysts on the gasification of forest residues to provide methane-rich gas, and the development of reactor concepts for commercial application and process flowsheets for technical and economic evaluation of the processes under consideration (Feldmann, 1978).

Calcium oxide and wood ash itself are the best catalysts found so far. Carbon conversions and gas selectivities for CaO-treated wood are shown in Fig. IV-7. In order to take advantage of the high reactivity of wood, the reactor must be able to operate at high gas velocities. Battelle expects its multisolid fluid-bed (MSFB) reactor to accomplish this, since it operates at velocities ten times as high as other fluid-bed reactors.

Wood chips are fed into a dense-phase fluid bed of inert particles. The heat for this bed and improved contact in it is provided by hot entrained char or ash particles from a fluidized combustion bed in which part of the entrained char particles formed in the MSFB are burned. The schematic flow in and out of the MSFB reactor system is shown on Fig. IV-8.

Fig. IV-7. Steam Gasification Of Calcium-Oxide-Treated Wood

Fig. IV-8. Schematic of Proposed MSFB Gasification Process

A planned commercial plant for handling 500 tons per day has the following design features:

Wood feed	40% moisture	
Carbon conversion	78%	
Gasifier temperature	750°C	(1382°F)
Combustion temperature	975°C	(1788°F)
Circulating burden	264 tons/hr	
Product gas composition	CH ₄	13.5%
	CO	33.2
	CO ₂	15.4
	H ₂	35.6
	C ₂	2.1
	N ₂	0.2

High heating value 350 Btu/scf

1.2.1.2 Battelle-Pacific Northwest Laboratories Process (Battelle Laboratories, Richland, Washington)

The current study concerns the gasification of wood waste (saw dust) with these specific objectives:

- Determine the kinetics of the gasification with various reagents with and without catalysts.
- Design, construct, and operate a process demonstration unit.
- Develop the appropriate methods for the production of pine gases (H₂, CO, CH₄).
- Develop method for the recovery of the catalyst.

Laboratory experiments carried out in a 2-in. stainless steel pipe established that the presence of Na₂CO₃ and K₂CO₃ is beneficial in the steam gasification of lodgepole pine at 650°C (1200°F); up to 80% of the carbon in the wood treated is gasified. A process development unit (PDU) is being designed for processing 20 kg of dry wood per hour. The reactor tube (see Fig. IV-9) is made of a castable refractory, but the actual reactor space, 11 in. i.d. X 54 in. long, is lined

Fig. IV-9. Biomass Gasification Reactor (Mudge, 1978)
Battelle-Pacific Northwest Laboratories

with stainless steel. The reactor is provided with an agitator, sampling tubes, an electrical heater, ceramic-lined feed parts, and a distributor through which steam and gases enter and fluidize the sawdust. The unit is to be operated around 600°C (1110°F) at 1 atm pressure, and about 10 minutes residence time. The PDU includes a lock hopper and screw conveyor for feeding the sawdust and cyclones, scrubbers, and receivers for separating and collecting the products (Mudge, 1978; Walkup, 1978).

In its present configuration the PDU is limited to handling fluidizable material. For large applications the electric heat supply will have to be replaced by combustion heating.

1.2.1.3 Wright-Malta Process (Wright-Malta Corporation, Ballston Spa, N.Y.)

The original steam gasifier developed by Wright-Malta for green wood chips consisted of a tube provided with an internal motor-operated auger and heater. The reactor was inclined about 15° from the horizontal and was supplied at its lower cooler end with wood chips from a reservoir and with water by a metering pump. The gaseous and liquid products formed were released, cooled, collected, measured, and analyzed (Wright-Malta, 1977).

The bench-scale experiments (10 lb/h) have shown that optimum conditions for green wood chips are 300 psi, a maximum temperature of 593°C (1100°F), a residence time of 30 to 60 min and an alkaline catalyst (Coffman, 1978). The use of an indirectly heated rotary kiln is preferred. The reaction is sufficiently exothermic to be self-sustaining without an external heat supply when recuperative heating is used. The overall efficiency of the conversion is expected to exceed 85%.

In December, 1978, the design of a process development unit (PDU) for handling 6 tons/day of green wood was started. It is planned to be 18 in. in diam and 40 ft long and will serve as a model for a 200-ton/day production unit, 5 ft in diam and 150 ft long.

The green wood chips and wood ash serving as the catalyst, will enter the PDU kiln (see Fig. IV-10) through a hopper, a weighing conveyor, a lock, and a conveying auger. The chips tumble as the slightly inclined kiln rotates and are warmed gradually on travelling downward. At about 177°C (350°F) decomposition by steam starts. Decomposition reaches a maximum at 260°C (500°F). The gasification takes about 1 h and consumes most of the wood. The gases and vapors flow concurrently with the solids and are steam-reformed into fuel gas at the 370-593°C (700-1100°F) temperature range. The solid residue is removed at the hot end of the kiln through ball valves. The hot gases and vapors are filtered through a sintered metal filter and then flow counter-currently to the flow of solids, through the jacket of the kiln. At the cool end of the kiln the condensed liquid, mostly water, is separated from the gases and is percolated through fresh wood chips to recover organic material. The gasification reaction produces enough heat to sustain itself, but for start-up a steam boiler is provided.

Laboratory studies are carried out in a rotating batch autoclave (called a "minikiln") with a capacity of 10 lb of wood chips. It is provided with a gas-sampling tube, a heating jacket, and thermocouples for differential thermal analysis. Also used is an externally heated continuous reactor 1.7 in. in diam and 10 ft long (called the "biogasser"), in which sawdust is carried forward by an auger.

In good runs there is a smooth temperature gradient up to 593-621°C (1100-1150°F). At the discharge end of the continuous reactor, essentially all of the organic material is vaporized, and the resulting gas has the following composition:

Methane	18%
Ethane and higher	8%
Hydrogen	28%
Carbon monoxide	1%
Carbon dioxide	45%

Fig. IV-10. Wright-Malta Biomass Gasifier Schematic (Coffmann, 1978)

At lower temperatures or at high feed rates, the gasification is incomplete and some tar forms.

The gasification of paper in the "minikiln" at various temperatures is shown in Fig. IV-11, while the effect of pressure on gasification is presented in Fig. IV-12. A maximum of gasification occurs around 300 psig, probably as the consequence of tar formation at higher pressures.

The process requires a unique kiln reactor which is relatively small in diameter but extremely long. For example, a 200-ton/day unit is estimated to be 5 ft in diam x 150 ft, and the entire vessel is to be pressurized to 300 psig and rotated. The reactor vessel consists of two concentric compartments. The annular space between them is used to supply heat to the gasification zone as hot product gas passes through countercurrently to the flow of solids within the inner space. These are rather demanding mechanical requirements, and the process must be demonstrated in such critical areas as:

- (1) Pressure seals between the rotating reactor and feed charge and ash discharge ports should have reasonable operating life.
- (2) Enough agitation should be provided throughout the gasifier length so as to prevent solids agglomeration.
- (3) Heat-transfer surface between the hot product gas and the gasification zone should be kept free of deposits.

1.2.2 NONCATALYTIC PROCESSES

1.2.2.1 Andco-Torrax Process (Andco, Inc.)

This is a high-temperature slagging pyrolysis process for unsorted municipal refuse in which the heat necessary is generated by partial combustion of the char formed by pyrolysis of the organic components of the refuse. The high temperature for melting all metallic and mineral components of the refuse is

Fig. IV-11. Gasification of Paper as a Function of Peak Temperature at 200 psi.

Fig. IV-12. Gasification of Wet Sawdust in the Minikiln and Biogasser. Effect of Pressure at 593°C. (1100°F).

reached by using in the combustion section of the pyrolytic gasifier air preheated to 980-1150°C (1800-2100°F) in regenerative towers. The gases formed in the gasifier are burned completely in a secondary combustion chamber to provide heat for the boiler of a steam turbine-generator. A minor portion of the combustion gases from the secondary combustion chamber is used periodically to reheat the regenerative towers filled with refractory (Jackson, 1974; Bechtel, 1977).

In this process all of the refuse is charged to the gasifier, after the large pieces have been cut up by shears. The refuse descends by gravity through the drying, pyrolysis, and combustion zones of the gasifier.

The combustible gas mixture, composed of CO, CO₂, H₂, H₂O, N₂, and hydrocarbons, leaves the gasifier at 426-538°C (800-1000°F). It has a heating value of 120-250 Btu/scf and produces, on combustion in the secondary combustion chamber, a temperature of 1204-1260°C (2200-2300°F).

The regenerative towers are periodically heated by a portion of the hot gases from the secondary combustion chamber and "blasted" by air being preheated for the combustion zone of the gasifier. The molten slag from the inorganic portion of the refuse is continually drawn off and quenched in water.

Work on the Andco-Torrax process was started in 1969 by Torrax Systems, Inc., a development company jointly owned by Andco, Inc. and the Carborundum Company. Since 1971 a 75-ton/day pilot plant, built under the sponsorship of EPA, New York State, Erie County, and the American Gas Association, has been in operation near Buffalo, N.Y., and serves for demonstration, engineering development, and studies on refuse of various compositions.

Bechtel (Bechtel, 1977) found the Andco-Torrax process to be one of the two most efficient refuse processing methods from a technical and economic standpoint and recommended it for consideration by the South Coast Basin Area of Southern California. The energy balance for this process is shown in Fig. IV-13.

Fig. IV-13. Andco-Torrax Energy Balance (Bechtel, 1977).

1.2.2.2 Envirotech Process (Envirotech Corp.)

This process uses a multiple-hearth furnace for the pyrolysis gasification of mixtures of sewage sludge and Refuse-Derived-Fuel (RDF). The resulting gas is suitable for heating a waste-heat boiler to produce 600 psig (825°F) steam for electric power generation.

This process has been used in a full-scale test to process various sludge-RDF mixtures for the Central Costa County Sanitary District of California. On the basis of this test, the Envirotech process has been incorporated in the expansion of the existing facilities of the Sanitary District (Bio-Energy Directory, p. 123).

1.2.2.3 Occidental Flash Pyrolysis Process (Occidental Research Corp.)

This short-residence-time pyrolysis process has been tested with coal, municipal solid waste, and biomass. A schematic process flow around the gasifier is shown in Fig. IV-14.

Finely shredded (-14 mesh) dry feed is carried into the reactor by recycle product gas, along with hot recycle char from the combustion. As the gas stream in the pyrolysis reactor is very turbulent, and ash and feed particles are small, there is good heat transfer to the feed particles. The pyrolytic reaction occurs within seconds at about 510°C (950°F) and about 1 atm gauge pressure.

The solids (char-ash) in the reactor affluent are separated from the product vapors in cyclones. Char is then burned in preheated air in a vessel in order to raise the temperature of the solids for recycle to the pyrolysis reactor.

The products of the process are oil, gas, and char. Most of the gas and char are consumed in the process. The main product is oil. For this reason, the process will also be discussed as a biomass liquefaction method in a later section.

Fig. IV-14. Occidental Flash-Pyrolysis Process (Bechtel, 1977).

Product compositions and yields obtained from various solid wastes at 500°C (950°F) are shown in Table IV-4. The yields are based on the organic portion. The gas yield is substantially higher at 788°C (1450°F), as shown by Table IV-5 (Preston, 1976).

1.2.2.4 Forest Fuel (Caughey) Process (Forest Fuels, Inc.)

Forest Fuels, Inc., Keene, N.H., is developing a marketable wood/gas burner to replace oil or gas used in industrial boilers. The project started in 1975. The unit under development consists of a wood/gas generator for converting dry wood into a hot combustible gas and a nozzle burner assembly for delivering the gas and air to the boiler or furnace firebox (Bio-Energy Directory, p. 172).

This type of apparatus is described in U.S. Patent 4,030,895, issued June 21, 1977 to R. A. Caughey of Forest Fuels. The main feature of this patent is the mechanical design of a grate on which the gasification occurs. A flow chart showing the progress of wood chips from the dryer through the generator and the combustion of the wood gas is presented in Fig. IV-15.

1.2.2.5 Garrett Process (Garrett Energy Research and Engineering, Inc.)

This process uses a multiple-hearth reactor (4-ft diam) for the production of medium-Btu gas from manure or other waste (see Fig. IV-16).

Manure partially dried in a flue gas-heated vacuum conveyor enters the top drying section of the reactor, where it is completely dried by contact with flue gas and is gradually moved by rabbles attached to a vertical rotating shaft to the pyrolysis hearth below. This hearth is entered through an air lock and is heated indirectly through a common wall by the heat of the combustion hearth below it. The pyrolyzed material is fed to the combustion hearths through an air lock and is moved by toothed rabbles gradually through two combustion zones. The ashes are cooled on the last bottom hearth while preheating the air for combustion.

TABLE IV-4

FLASH PYROLYSIS OF SOLID WASTE FEEDSTOCKS AT 454-565°C (850-1050°F)
(Longanbach and Bailey, 1976)

	<u>Animal waste</u>	<u>Rice hulls</u>	<u>Fir bark</u>	<u>Grass straw</u>	<u>Municipal solid waste</u>
Feed analysis, %					
C	39.3	39.4	48.3	45.0	44.2
H	4.7	5.5	5.3	6.0	5.7
N	2.3	0.5	0.2	0.5	0.7
S	0.6	0.2	0.0	0.5	0.2
O	28.1	36.1	34.3	42.0	42.3
Cl	1.7	0.2	0.2	0.4	0.2
Ash	23.3	18.2	11.7	5.7	6.7
Char analysis, %					
C	34.5	36.0	49.9	51.0	48.8
H	2.2	2.6	4.0	3.7	3.3
N	1.9	0.4	0.1	0.5	1.1
S	0.9	0.1	0.1	0.8	0.4
O	7.9	11.5	24.3	19.2	12.8
Cl	3.7	0.2	0.2	0.5	0.3
Ash	48.8	49.2	21.4	24.3	33.3
Btu/lb	(5,449.0)	(6,100.0)	(8,260.0)	(8,300.0)	(9,000.0)
Yield, %	48.1	35.9	41.6	23.2	20.0
Gas analysis, %					
H ₂	6.1	23.3	6.3	9.6	11.7
CO	21.9	28.5	14.7	53.9	34.9
CO ₂	55.9	40.8	64.7	26.9	35.4
CH ₄	6.1	3.5	10.5	3.8	5.7
C ₂ H ₄	0.5	0.8	1.0	0.8	4.0
C ₂ +	1.8	0.8	1.2	2.8	2.4
H ₂ S	7.8	2.4	1.7	2.2	0.4
Btu/scf	(226.0)	(215.0)	(222.0)	(349.0)	(350-500)
Yield, %	10.8	12.1	8.2	5.2	30.0
Oil analysis, %					
C	64.8	62.4	60.5	58.6	57.0
H	6.9	5.8	6.0	5.6	7.7
N	7.0	1.4	0.5	1.3	1.1
S	0.2	0.1	0.1	0.1	0.2
O	19.8	29.4	30.7	33.9	33.6
Cl	0.2	0.3	0.2	0.1	0.2
Ash	1.1	0.6	2.1	0.5	0.2
Btu/lb	(11,800.0)	(10,400.0)	(10,300.0)	(9,400.0)	(10,500.0)
Yield, %	20.0	44.2	28.7	35.7	40.0

TABLE IV-5

GASIFICATION OF MUNICIPAL REFUSE AT 788°C (1450°F) (Preston, 1976)

Gas analysis, mol %

H₂ 16.7

CO 17.9

CO₂ 23.1

CH₄ 15.4

C₂ 22.2

C₃+ 4.7

Btu/scf 770.0

Yield, % 80.0

Fig. IV-15. Block Flow Diagram of the Forest Fuels (Caughey) Process

Fig. IV-16. Multiple Hearth Reactor Of Garrett Energy Research And Engineering (Garrett, 1978)

The use of air locks in the pyrolyzing hearth prevents the mixing of flue gas and pyrolysis gas.

According to Mikesell (Mikesell, 1978), the first phase of the work was performed in a bench-scale, single-hearth reactor (Garrett, 1977), in which direct contact drying, pyrolysis, water-gas char gasification, and combustion were studied in turn. Pyrolysis runs carried out with moist manure and sawdust gave these results:

	<u>Rovine manure</u>		<u>Sawdust</u>		
Temperature, °C	635	657	631	640	653
°F	(1175)	(1215)	(1168)	(1184)	(1207)
Carbon gasified, %	42.9	37.3	17.2	32.2	30.3
Volatiles pyrolyzed, %	83.3	88.3			
Pyrolysis gas, low heat value, Btu/scf	272	319	360	358	357

1.2.2.6 Georgia Tech Process (Georgia Institute of Technology)

This process converts agricultural or forestry wastes by low-temperature, partial-oxidation pyrolysis in a fixed-bed generator into combustible gas, oil, and char (Georgia Institute of Technology, 1976). The process, sometimes referred to as the EES process, has been under development at the engineering experimental station since 1968 and is embodied in a mobile waste-conversion system. In operation with the mobile unit, oil and char are the desirable products. Thus they are maximized, while the product gas is used for the process heat and for power generation. According to the developer, a 200-ton/day unit, which can be mounted on two trailers, has the following unique features:

- (1) It is self-sufficient in energy.
- (2) It does not need an outside water supply.
- (3) It is provided with a gasoline engine operated on low-Btu product gas to supply process power.
- (4) The unit can handle feed containing up to 50% moisture.
- (5) Size and weight of the trailers would be such that the unit can be transported readily and without a special highway permit.

Figures IV-17 and IV-18 show the plan and elevation views of the two trailers and the unit arrangements. On the basis of a raw feed containing 50% moisture, this mobile unit is estimated to produce 0.456 ton of oil-char mixture from a ton of dry feed. The heating value of the oil-char mixture is about 11,500 Btu/lb.

The powdered oil-char fuel could be burned in either suspension-fired or in stoker-fired boilers with essentially no modification. It could be also blended with coal.

1.2.2.7 Moore-Canada Process (Moore-Canada Co., Richmond B.C.)

Low-Btu gas is produced from "as-received" wood waste containing 40-50% moisture in a plug-flow or moving-bed reactor (see Fig. IV-19) by using a mixture of air and steam as the oxidizing medium.

The biomass feed is introduced into the top of the reactor through hoppers. Steam and air, and by-product tar are added at the bottom of the reactor. The maximum reactor-temperature is about 1204°C (220°F). Typical data for product composition and material and energy balances of the Moore-Canada process are shown in Table IV-6.

1.2.2.8 Purox Process (Union Carbide Corp.)

This process uses oxygen to convert municipal solid waste to fuel gas and slag. It has been in commercial operation for over three years at South Charleston, W.Va., and has processed up to 200 tons of refuse per day. It requires 0.25 ton

Fig. IV-17. Plan and Elevation Views of Trailer I (Georgia Tech., 1976)

Fig. IV-18. Plan and Elevation Views of Trailer II (Georgia Tech., 1976)

Fig. IV-19. Moore-Canada Biogasifier (Radovich, 1979)

TABLE IV-6
Moore-Canada Biogasifier Data (Radovich, 1979)

Typical product gas composition:

	<u>%</u>
CO	24.2
H ₂	19.3
CO ₂	9.0
H ₂ O	3.2
CH ₄ +	3.6
N ₂	40.2
O ₂	0.5

Material Balance:

<u>Feed (lb)</u>		<u>Product (lb)</u>	
Wood	100	Gas	263
Air	164	Ash	3
Steam	<u>17</u>	Water	<u>15</u>
	281		281

Energy Balance:

Input Btu/lb dry feed		Output Btu/lb dry feed	
Biomass	9000	Gas	7070
Operating Energy		Char	na
Purchased	213	Oil	Internal use
Internal	25		

of O_2 per ton of refuse and produces 0.75 ton of medium-Btu fuel gas, 0.2 ton of residue, and 0.3 ton of waste water.

Shredded refuse freed from valuable metals is charged to a vertical shaft furnace and descends gradually. Oxygen is introduced into the bottom of the shaft and reacts with char produced from organic material in the upper section of the furnace by pyrolysis under the influence of hot combustion gases. The glass and metal present in the refuse melt and form a slag.

The hot combustion gases gradually cool as they ascend through the refuse. In the middle section of the furnace, the gases cause pyrolysis at $315-982^{\circ}C$ ($600-1800^{\circ}F$), and dry the incoming refuse in the top section. The gases leaving the reactor at $93^{\circ}C$ ($200^{\circ}F$) are freed from entrained char, tar mist, oil, and water vapor by a recirculating water scrubber and an electrostatic precipitator. Liquids and solids are returned to the furnace. Condensate water produced by the combustion and pyrolysis is treated and discharged to the sewer (Tillman, 1976; Bechtel, 1977; Jackson, 1974).

Raw solid waste stored in a deep pit is transferred by grapple cranes into hoppers and is then transported to shredders. Ferrous metals are removed from shredded refuse by magnetic separation. Then the refuse is air-classified and screened to remove those materials which contain low levels of aluminum. The aluminum is recovered from the rest by the conventional electrical method. The residue from this operation and the screened aluminum-poor fraction are combined and used as the feed for the pyrolysis.

The Purox process needs an air-separation plant to supply the oxygen, and optionally a waste-water treatment unit.

The main Purox product is fuel gas having the typical composition shown in Table IV-7 (Bechtel, 1977). It is compressed to 50-225 psig for use in power generation. The by-product, molten slag, is quenched with water and is used for fill.

TABLE IV-7

PUROX GAS COMPOSITION (Bechtel, 1977)

<u>Component</u>	<u>Vol% (dry)</u>
Hydrogen	28.94
Carbon monoxide	35.72
Carbon dioxide	23.42
Methane	5.51
C ₂ -hydrocarbons	2.71
C ₃ -hydrocarbons	0.37
C ₄ -hydrocarbons	0.33
C ₅ ⁺ -hydrocarbons	0.96
Miscellaneous organics	0.04
Hydrogen sulfide	0.06
Oxygen	0.10
Nitrogen and argon	1.69
Water-soluble organics	0.15
Oils	Trace
Total	100.00

Bechtel (Bechtel, 1977) found the Purox process to be one of the two best refuse processing methods from technical and economic standpoints and recommended it for consideration by in the South Coast Basin Area of Southern California.

The energy balance for the Purox system is shown in Figs. IV-20 and IV-21 for producing either fuel gas or electricity.

1.2.2.9 Texas Tech Process (Texas Tech University)

This process, also known as the SGFM (Synthesis Gas from Manure) process, produces medium-Btu gas by the pyrolysis of manure or other solid wastes at up to 1000°C (1832°F). High temperatures are achieved by burning part of the feed and contacting the waste with the combustion gases and steam (Beck, 1978, 1978a).

Manure gasifications carried out at 517 to 636°C (962-1177°F) gave 0.39 to 1.23 liters of dry gas per gram of dry ash-free feed. The gas had a heating value of 250-330 Btu/scf.

Pyrolysis runs were also carried out with mesquite after the feed system had been modified to prevent clogging. Texas Tech has operated a 0.5-ton/day SGFM pilot since 1975. The work has been funded by DOE's predecessor, ERDA, since September 1976. Bechtel was retained to review the Texas Tech work, to develop conceptual designs for two plants for utilizing 1000 tons of manure per day to produce ammonia, synthesis gas, and ethylene, and to provide estimates for capital and operating costs.

In the conceptual design the reactor uses a pressurized, fluid bed (Fig. IV-22). The cold feed enters at the top of the reactor and falls the length of the vapor disengaging section. Fluidization is supported by injection of steam and air at the bottom of the bed through a distributor ring. Some distance above this air ring, tar and hydrocarbon recycles are injected. Char is discharged from the bottom at a controlled rate. The reactor shown was sized for a capacity of 1569

Fig. IV-20. Purox Energy Balance--Process Product, Fuel Gas (Bechtel, 1977)

Fig. IV-21. Purox Energy Balance--Process Product, Electricity (Bechtel, 1977)

Notes

1. Operating overhead pressure is 45 psia, at 1230°F
2. Four cyclones required, each with 20-ft dip leg.
3. Materials: Vessel; refractory-lined carbon steel; internals, stainless steel.

Nozzles

- ① Manure feed-in with 10-ft distributor pipe
- ② Steam/air in with distributor ring
- ③ Tar recycle in
- ④ Light hydrocarbons recycle in
- ⑤ Char out
- ⑥ Effluent gas out

Fig. IV-22. Texas Tech Reactor (Hipkin, 1978)

tons/day of manure containing 25% moisture, and uses a 10-ft-deep fluidized bed, operating at a 1.6 ft/s superficial velocity.

The gases from the top of the fluid bed pass through cyclones in the vessel. The hot crude gas stream leaving the reactor contains pines, tar, and water.

The Bechtel report (Hipkin, 1978) concludes that the SGFM process is not competitive with natural-gas reformer plants at current gas prices, and that the recovery of ethylene from syngas is not justified. Increasing prices and decreasing availability of natural gas could make the SGFM process competitive. The report also recommends further experimental work to improve material and heat balances, to collect data on kinetics, and feed and product composition and characteristics. Additional engineering studies are also needed on the separation of particulates and dissolved organics, on the use of char as a source of heat for the reactor, and on other process steps.

1.2.2.10 Other Relevant Processes

In connection with a feasibility study of energy recovery from solid waste in the South Coast Basin Area of Southern California, Bechtel (1977) considered 17 different processes, the characteristics of which are summarized in Table IV-8. The previous sections discussed only the Andco-Torrax, Purox, Flash Pyrolysis, and the two Battelle processes. The Tech-Air process (last column) is based on technology developed by the Georgia Institute of Technology.

Rasch (Rasch, 1978) reviews the waste-gasification methods and briefly describes the following additional processes:

- The Destrugas process uses an externally heated vertical furnace for pyrolyzing refuse and has provisions for handling liquid wastes (Willerup, 1973).
- The Kobe Steel process (Takamura, 1975) pyrolyzes rubber and plastics waste in an externally heated rotating inclined drum.

TABLE IV-B
PROCESSES FOR THE RECOVERY OF ENERGY FROM SOLID WASTE (Bechtel, 1977)

	<u>Andco Inc.</u>	<u>Union Carbide Corp. Linde Division</u>	<u>Occidental Research Corp.</u>	<u>Barber-Coleman Co.</u>	<u>Battelle-Northwest Research Laboratories</u>
Process name	Andco-Torrax	Purox	Flash Pyrolysis	Puretec	None
Type of reactor	Vertical fixed-bed	Vertical fixed-bed	Vertical-transport flash pyrolysis	Moving hearth with molten lead	Fixed-bed
Reactor pressure, temperature	Atmospheric, 3000°F	Atmospheric, 3000°F	Slight pressure, 900°F	Atmospheric, 1200°F to 1500°F	n.a., 1830°F
Reactor feed pretreatment requirements	Unsorted	Shredding	Shredding to -20 mesh, metals and glass removed, drying to 3% H ₂ O	Shredding 1- to 2-in. particle size	Shredding
Higher heating value (dry basis) of product gas or oil	120 to 250 Btu/scf	300 to 370 Btu/scf	10,500 Btu/lb	500 Btu/scf	172 Btu/scf, including oils and tars
Estimated commercial reactor module capacity	200 to 300 tons/day	200 tons/day	n.a.	200 TPD	N.A.
Process reactants (other than MSW)	None	Oxygen	None	None	Air and steam
Primary product yield	Fuel gas, or 2.5 to 3.0 lb steam/lb MSW	Fuel gas, 20,000 scf/ton MSW	1 bbl oil/ton MSW	Fuel gas - 10,000 scf/ton MSW	n.a.
Other products (excluding metals and glass)	None	None	Fuel gas - 500 Btu/scf (6,700 scf/ton MSW, used internally)	Fuel gas can be processed to recover benzene, toluene, xylene	None
Process effluent streams to disposal	Inert solids, quench water	Inert solids, condensate quench water	Char/ash, condensate, and combustion flue gases	Flue gas from MSW drying, quench water, inert solids	Inert solids
Status of process	Commercial Plant	Demonstration Plant	Demonstration Plant	Pilot Plant	Pilot Plant
Largest unit built	220-ton/day commercial plant in Luxembourg. Two more commercial plants under construction in Europe.	200-ton/day demonstration unit in S. Charleston, W.Va.	200-ton/day demonstration plant under construction in San Diego, Ca.	1 ton/day	1 ton/day
Development history	65-ton/day demonstration plant in Orchard Park, N.Y.	5-ton/day pilot plant in 1970-1973. Demonstration unit in operation since 1974.	4-ton/day pyrolysis, pilot plant built by Garrett R & D Co. about 1971.	Pilot unit dismantled.	Process is an outgrowth of 1969 effort to pyrolyze photographic lab wastes. Longest sustained test run only a few hours. Awaiting further development funds.
Development funding source	Andco, EPA, American Gas Assn.	Union Carbide Corp.	EPA, Occidental, San Diego County Gas & Elec. Co.	Barber-Coleman	Battelle-Pacific Northwest Research Laboratories
Is processing being actively marketed?	Yes	Yes	No, waiting for operating experience on demonstration plant	No, company is going out of business	No

TABLE IV-8 (Continued)
PROCESSES FOR THE RECOVERY OF ENERGY FROM SOLID WASTE (Bechtel, 1977)

	<u>Chevron Research and Development Co.</u>	<u>Devco Management Co.</u>	<u>Ecology Recycling Unlimited, Inc.</u>	<u>Energy Research and Development Administration</u>	<u>Enterprise Co.</u>
Process name	Chevron White Gas	Devco	Agajanian	Waste-to-oil	Deco
Type of reactor	Vertical fixed-bed	Rotary kiln	Rotary kiln (en- closed in refrac- tory structure)	Continuous stirred tank	Jacketed, horizontal cylinder with auger.
Reactor pressure, temperature	200 psig, 1500°F	Atmospheric, 1800°F	Atmospheric, 800°F	4100 psig, 700°F	Slight vacuum, 1000°F to 1100°F
Reactor feed pretreatment requirements	Shredding	None	Shredding to minus 3 in.	Shredding to minus 40 mesh, air classifica- tion drying to 4% moisture	Under development
Higher heating value (dry basis) of product gas or oil	300 Btu/scf, including oils and tars	Approx 150 Btu/scf product gas or oil	360 Btu/scf	13,700 Btu/lb	Approx 18,000 Btu/lb
Estimated commercial reactor module capacity	240 tons/day	n.a.	n.a.	n.a.	50 tons/day
Process Reactants (other than MSW)	Air and steam	Steam	Air	None	Carbon monoxide, hydrogen, sodium carbonate
Primary product yield	21,000 scf/ton MSW	n.a.	n.a.	2 bbl of oil/ton MSW	1 bbl oil/ton MSW
Other products (excluding metals and glass)	None	Building bricks have been made out of solid residue	None	None	Fuel gas: 400/Btu/scf (4,000 to 5,000 scf/ton MSW, used internally
Process effluent streams to disposal	Inert solids, condensates, quench water	n.a.	Char, inert solids	Wastewater, unreacted solids, dryer exhaust gases	Char/ash, condensate quench water, combus- tion gases.
Status of process	Pilot-plant (batch) bench-scale (continuous)	Demonstration plant	Pilot plant	Pilot plant	Demonstration plant
Largest unit built	n.a.	120 tons/day	10 tons/day	3-ton/day plant in Albany Oregon, just completed construction phase	A module rated at 50 tons/day is being tested at a Los Angeles, Sanitation District facility.
Development history	Development effort discontinued	Discontinued	n.a.	Original bench- scale work done at Pittsburgh Energy Research Center (by Bureau of Mines). Several-year test program planned on pilot plant.	Process developed by Duke Engineering Co. Santa Ana, Ca.
Development funding source	Chevron Research and Development Co.	Devco Management	Ecology Recycling Unlimited, Inc.	ERDA	Enterprise Co.
Is processing being actively marketed?	No	No	n.a.	No--not applicable	Yes--a 150-ton/day plant has reportedly been sold to a New York firm.

TABLE IV-3 (Continued)
PROCESSES FOR THE RECOVERY OF ENERGY FROM SOLID WASTE (Bechtel, 1977)

	<u>Kemp Reduction Co.</u>	<u>Monsanto Enviro-Chem Systems, Inc.</u>	<u>Pan American Resources Inc.</u>	<u>Pyrolysis Systems Inc.</u>	<u>Rocketdyne</u>	<u>Tech Air Corporation</u>
Process name	Kemp	Monsanto Landgard	Lantz Converter	X-50 Pyrolyzer	Rocketdyne Waste Processing	Tech-air
Type of reactor	Double coaxial horizontal cylinders	Rotary kiln	Rotary kiln (enclosed in refractory structure)	Horizontal bed	Vertical fluidized bed	Two vertical fixed beds
Reactor pressure, temperature		Atmospheric, 2000°F	Atmospheric, 1400°F	Slight vacuum, 1700°F	185 psig, 1600°F	Atmospheric, 1100°F
Reactor feed pretreatment requirements		Shredding	Shredding	Shredding and metals removal	n.a.	Shredding, air classification, drying
Higher heating value (dry basis) of product gas or oil		120 Btu/scf	n.a.	400 Btu/scf	250 to 500 Btu/scf	Approx 150 Btu/scf
Estimated commercial reactor module capacity		1000 tons/day	n.a.	240 tons/day	150 tons/day	240 tons/day
Process reactants (other than MSW)		No. 2 fuel oil	None	None	None	Air
Primary product yield		21,000 scf/ton MSW or 2.4 lb steam/lb MSW	n.a.	10,400 scf/ton MSW	15,000 to 18,000 scf/ton MSW	9,100 scf/ton MSW
Other products (excluding metals and glass)		None	n.a.	None	None	Fuel oil: 6 gal/ton MSW (16,800 Btu/lb)
Process effluent streams to disposal		Quench water, char	n.a.	Quench water, char, tars, inert solids, condensate	n.a.	Inert solids, condensate, quench water
Remarks	Solids move through inner cylinder by wire conveyor. Heat for pyrolysis is supplied by burning natural gas in outer cylinder.		Heat for pyrolysis is supplied by burning product gases in refractory outside kiln.	Heat for pyrolysis is supplied by burning product in radiant tube heaters in reactor		Light and heavy fractions are pyrolyzed separately.
Status of process	Pilot plant	Commercial-Sized Demonstration Plant	Pilot plant	Pilot plant	Pilot plant proposed	Pilot plant
Largest unit built	0.5 tons/day	1000 tons/day	4 tons/day	24 tons/day. A demonstration plant is being designed for the City of Riverside, Ca.	15 tons/day	20 to 30 tons/day
Development history	MSW R&D program completed. Ongoing work on sewage and agricultural wastes. Currently negotiating to build a 100-ton/day plant in Washington.	35 TPD pilot plant operated for 2 years. Demonstration plant in debugging stage; improvements are contemplated.	System without energy recovery built at Ford Motor Co., Milpitas, Ca. in 1968.	About 5 years development by Resource Sciences, Inc. The former Pyrotele Process is very similar; it was tested in a 2 ton/day plant. Pyrotele is out of business.	Discontinued	Company has been purchased by American Can Co. Pilot plant has been operated on wood wastes.
Development funding source	Kemp Reduction Co.	Monsanto, EPA, City of Baltimore	Pan American Resources, Inc.	Resources Sciences, Inc.	Rocketdyne	Tech-Air Corp.
Is processing being actively marketed?	Yes - Proposal to Santa Barbara County was rejected	No	n.a.	Yes - proposal submitted to Riverside, Ca.	n.a.	Yes - several proposals have been submitted.

The Bio-Energy directory also lists the following gasification processes and projects currently in progress:

- Corn cob gasification: DeKalb Ag Research, Dekalb, Illinois, and Pioneer Hi-Bred International, Johnston, Iowa.
- Flash pyrolysis: University of Minnesota.
- Steam pyrolysis: Princeton University.
- Pyrolysis of automobile wastes: Pyro Sol, Inc., Redwood City, Ca.
- University of California at Davis.

For additional processes, see Jackson (Jackson, 1974).

1.3 COAL-GASIFICATION TECHNOLOGIES

An overview of coal-gasification processes is presented in Table IV-9, showing their development status, operating characteristics, and main products. The processes are grouped according to reactor types into fixed-bed, fluid-bed, entrained-flow, and molten-bath processes. This section will discuss in detail the catalytic and noncatalytic coal-gasification technologies.

1.3.1 CATALYTIC PROCESSES

1.3.1.1 The ATGAS Process (Applied Technology Corporation)

The ATGAS process (Oil and Gas Journal, 1973) carries out the gasification in the presence of molten iron in which the fixed carbon and sulfur of the coal are retained, and the volatiles are converted to gaseous products. The carbon dissolved in the iron is then gasified with oxygen and steam to yield additional CO-H₂ mixture. This is potentially suitable for gasifying various carbonaceous materials, ranging from petroleum coke to subbituminous coal.

**TABLE IV-9
COAL GASIFICATION PROCESSES**

<u>Fixed-Bed</u>	<u>Status</u>	<u>Gasifying Agents</u>	<u>Feed-Coal Type</u>	<u>Gasifier</u>		<u>Product</u>
				<u>Pressure, psig</u>	<u>Temperature, °F</u>	
1. Large	Commercial	Steam - O ₂ (air)	Noncaking, mildly caking	300-400	1800	LBG, MBG, naphtha
2. Wellman- Golusha	Commercial	Steam - air	Noncaking, mildly caking	0	1200	LBG, oils, tars
3. Stoic Combustion	Commercial	Steam - air	Noncaking, mildly caking	0	Top prod gas: 250 Bottom gas: 1100	LBG, oils, tars
<u>Fluid-Bed</u>						
1. Winkler	Commercial	Steam - air (O ₂)	Noncaking	0	<1800	LBG
2. CO ₂ Acceptor	PDU	Steam	Lignite	150	1500	MBG
3. Westinghouse	PDU	Steam - air	Noncaking, mildly caking	230	Devolat: 1300-1500 Gasif: <2000	LBG
4. Hygas	PDU	1/2-CO	Noncaking, mildly caking			MBG, LBG
5. U-gas	Pilot plant	Steam - air (O ₂)	Noncaking, mildly caking	300-350	1900	LBG, MBG,
6. Synthane	PDU-inactive	Steam - O ₂ (air)		1000	Dense phase 1800 Dilute phase 1400	LBG, MBG, SNG
7. Hydrane	PDU	H ₂	All coals			SNG
8. Battelle- Union Carbide	Pilot plant	Steam - O ₂	All coals	100	Gasif zone 1700 Ash-agglom. zone 2000	MBG
9. Exxon Catalytic	Pilot plant	Steam	All coals	500	1300	SNG
<u>Entrained-Flow</u>						
1. Koppers- Totzek	Commercial	Steam - O ₂	All coals, peat	0	2700	MBG (Syngas)
2. Texaco	Semi- Commercial	Steam - O ₂	All coals, peat asphalt, SRC	<800	2700	MBG (Syngas)
3. BiGas	PDU	Steam - O ₂	All coals	1000	1000	MBG
<u>Molten-Bath</u>						
1. Atgas	Lab scale inactive	Steam - O ₂ (air)	All coals	0	2500-2700	LBG, MBG
2. Kellogg	Lab scale inactive	Steam - O ₂ (air)	All coals	Up to 1200	1700	MBG
3. Atomics International	PDU (air blown)	Steam - air (O ₂)	All coals	300	1850	LBG, MBG

Abbreviations: PDU = Process development unit
 LBG = Low-Btu gas
 MBG = Medium-Btu gas
 SNG = Synthetic natural gas

Figure IV-23 shows the ATGAS coal-gasification scheme. The gasifier is a refractory-lined vessel containing the molten iron at 1370-1482°C (2500-2700°F). It is operated at near atmospheric pressure. Pulverized coal (-1/8 in.) and limestone are injected through lances, with steam as the carrier. Oxygen is charged through separate lances. Since coal contains volatile matter, it literally explodes when it contacts the molten iron. Because of the resulting high surface area of the coal, a relatively short residence time is sufficient for solubilization of carbon and sulfur.

The limestone reacts with the dissolved sulfur to form calcium sulfide, and it also fluxes the ash. Slag is continuously withdrawn from the surface of the molten iron and is desulfurized with steam to yield a desulfurized lime-bearing slag (part of which is recycled) and a gaseous stream consisting of S, SO₂, and H₂S, which is processed to recover sulfur.

The offgas from the gasifier is cooled in a waste-heat boiler and is scrubbed to remove particulates. The resulting clean gases are converted to SNG by the usual CO-shift and methanation steps.

Table IV-10 shows the process streams for an ATGAS unit producing 250 million scf/d SNG with a heating value of 940 Btu/ft³ (La Rosa, 1973).

The technical feasibility of the ATGAS process is reported to have been established only on a laboratory-scale unit (a 2-ft diam batch reactor), and for short operating periods (Verma, 1978). Development efforts have been focused on the following:

- (1) Control of particulates in the gasifier offgas
- (2) Control of slag viscosity
- (3) Desulfurization of slag
- (4) Selection of gasifier refractory bricks
- (5) Means for injecting reactants into molten bath
- (6) An oil-cooled metal lance.

Fig. IV-23. ATGAS Process (LaRosa, 1973).

Table IV-10

Process Streams for a 250-Million-scf/d ATGAS Unit

<u>Stream No.</u>	<u>Description</u>	<u>Rate, tons/hr</u>
1	Coal, 4% sulfur 13,100 Btu/lb	641
2	Oxygen (50 psig)	379
3	Limestone	43
4	Steam for coal- limestone injection (50 psig)	71
5	Gasifier offgas (2500°F, 65% CO, 35% H ₂)	43 million scf/h
6	Iron	20
7	Sulfur	25
8	Desulfurized slag (1% S)	64
9	ATGAS (100°F 1000 psig, 93% CH ₄ , 4% H ₂ , 3% inerts)	10.5 million scf/h

The process requires extensive handling systems for limestone and slag, and facilities for production of iron and purification of sulfur.

The solution of the problems connected with these and other items must be demonstrated on a large-scale operation.

1.3.1.2 Exxon Catalytic Coal Gasification (Exxon Research and Engineering Co.)

This process (Vadovic, 1978; Koh, 1978) uses an alkali metal carbonate or hydroxide as the catalyst in a fluidized-bed gasification of coal. Its relatively low gasification temperature (704°C, 1300°F) and high pressure (500 psig) favor the formation of methane.

The catalyst, in the form of an aqueous solution of alkali carbonate or hydroxide, is sprayed onto the coal before it is charged. Potassium carbonate or a mixture of potassium and sodium carbonates is generally preferred over the more active cesium compounds because these materials are readily available, and they cost less than cesium compounds. The weight percent of the catalyst in the feed coal is said to be between 10 and 30% on a dry basis (Koh, 1978).

A simplified flow diagram for the process is shown in Fig. IV-24. Coal is ground and screened to minus 8 mesh. An aqueous solution of alkali is then sprayed on the coal. Then the feed is dried and pressurized and injected into the reactor. Hydrogen and carbon monoxide from the methane recovery step and steam are preheated to approximately 85°C (150°F) and then injected into the bottom of the reactor to fluidize and react with the coal. Because of the substantial concentration of hydrogen in the recycle stream, one of the principal reactions is hydrogasification of the coal to methane. This exothermic reaction supplies the heat required by the endothermic steam-carbon reaction occurring simultaneously. Thus, the overall gasification reaction can be represented as follows:

Fig. IV-24. Overall Flow Plan of the Exxon Catalytic Coal-Gasification Process (Vadovic, 1978)

Since this reaction is essentially thermoneutral, major heat input to the gasifier is not required.

The product stream is cooled to condense water. Following an acid gas removal step, the net gas, now containing H_2 , CO , and CH_4 , is cryogenically treated to separate CH_4 as SNG. Ash and char residues from the gasification step are sent to a catalyst recovery unit in which the catalyst is washed out by countercurrent water washing. There is some tendency for trace metals to build up in the recycle catalyst; this problem is being investigated.

Under DOE contract, Exxon will operate the 1-ton/d demonstration unit at the just completed Baytown, Texas facilities, to obtain data for a later scale-up (Chemical Engineering, 1978).

1.3.1.3 Molten-Salt Process (M. W. Kellogg Company)

This process uses a bath of molten sodium carbonate to provide gasification heat and also to catalyze the reaction of coal with steam:

Pulverized coal, steam, and oxygen are charged into the molten salt contained in a refractory-lined vessel. The coal is gasified at 1200 psig and $926^\circ C$ ($1700^\circ F$). The process can handle caking as well as noncaking coals (Cover, 1973).

In earlier stages of development, Kellogg had worked on a two-vessel system in which the molten salt circulated between the gasification reactor to supply the reaction heat and the combustion vessel to pick up the sensible heat (Kellogg, 1966). In the latter, heat was generated by combustion of coal with air. Thus, in principle, this reaction scheme would have produced product gases free of nitrogen contamination. However, Kellogg has since adopted a one-vessel concept that uses oxygen for combustion. Kellogg claims that the new system is simpler in design and yet as effective as the two-vessel forerunner (Cover, 1973). The

Kellogg molten-salt process was under active development in 1960's and early 1970's in a bench-scale unit. However, in 1974, Kellogg discontinued work on this process.

Figure IV-25 shows the single-vessel gasifier system. Coal crushed to minus 12 mesh is stored and pressurized in lock hoppers, and then carried into the gasifier pneumatically by a stream of preheated oxygen-steam.

Sodium carbonate recycle from the salt recovery step is also carried into the gasifier by the same carrier gas. The main portion of the preheated oxygen and steam is admitted into the bottom of the gasifier. Table IV-11 shows a typical composition for the gaseous peroduct from gasification of a western subbituminous coal.

The sulfur in coal reacts with the salt to form sodium sulfide (Na_2S). This species is present in the melt at a level determined by an equilibrium reaction:

Ash accumulates in the melt, but its concentration is kept at about 8% by the removal of excess ash in an auxiliary system. The salt purge is first settled at the bottom of the gasifier and at this point contains 16% ash. The melt is quenched and then dissolved. After filtration of the solids, the dilute sodium carbonate solution is carbonated for the precipitation and recovery of sodium bicarbonate. The recovered salt is calcined, and the resulting sodium carbonate is recycled to the gasifier.

The major developmental concern has been the selection of refractory lining for the gasifier. Extensive testing of a wide variety of material has shown that Monofrax A®, a fused, cast, high-purity alumina withstands the corrosion attack of the molten salt (Cover, 1974).

Fig. IV-25. Kellogg Single-Vessel Gasifier System (Cover, 1973).

TABLE IV-11

KELLOGG MOLTEN-SALT GASIFICATION PROCESS:
TYPICAL RAW GAS COMPOSITION FROM WESTERN SUBBITUMINOUS COAL

<u>Gas</u>	Composition,
	<u>vol %</u>
H ₂	34.8
CO	26.0
CO ₂	10.3
H ₂ O	22.6
CH ₄	5.8
N ₂	0.3
H ₂ S	0.2

1.3.1.4 Atomics International Molten Bath Process (Atomics International Division, Rockwell International)

This is a pressurized (20-30 atm), air-blown, molten-salt gasification process. The process uses sodium carbonate at temperatures of about 1700-1800°F. Atomics International is currently funded by DOE to conduct a demonstration of the process using a 1-ton/h process development unit (PDU) at the company's field laboratory in Santa Susana, California.

Figure IV-26 is a schematic flow diagram of the PDU. A detailed drawing of the gasifier quench assembly is shown in Fig. IV-27. Coal is crushed, mixed with makeup sodium carbonate, and transported by compressed air into the bottom of the melt bed. No steam is added; therefore, the predominant reactions are partial oxidation and pyrolysis. The salt-bath temperature ranges between 1700 and 1850°F. The lower temperature is preferred from the standpoint of vaporization loss of the salt and corrosion control, while the higher temperatures ensure complete gasification and lower melt viscosity.

The molten bath contains dissolved sulfur compounds (principally sodium sulfide and some sulfate) and suspended particulates (unburned coal or carbon, and ash). To control the concentration of these materials, an overflow port is provided for continuous melt withdrawal. As shown in Fig. IV-27, the spent salt is treated for ash removal, sulfur removal, and finally recovery of the salt. The salt is centrifuged from the recovery system as sodium bicarbonate, which is dried and calcined to the carbonate form for recycle to the gasifier.

The main problem areas which have been addressed by Atomics International in developing the molten-salt process are similar to those experienced by Kellogg and others:

- Short life of refractory linings because of corrosion, thermal stress, erosion, etc.
- Vaporization of salt into product gas

Fig. IV-26. Process Flow Diagram of the PDU (Kohl, 1978)

Fig. IV-27. Gasifier/Quench Assembly (Kohl, 1978).

- Viscosity increase with the level of particulate loading in the melt
- Means of introducing the reactant into the melt
- Auxiliary facilities, including the salt regeneration system
- Buildup of impurities in recycle streams
- Salt freezeups in various lines.

According to recent information obtained from the developers (Atomics International, 1979), progress toward alleviating these problems has been made. In particular AI has demonstrated that:

- Monofrax A® lining will withstand the reaction environment in the PDU for more than a year without appreciable degradation.
- The ash removal, salt regeneration, and green liquor circulation have been continuously demonstrated for more than 200 h.

The viability of the AI molten-salt process has been demonstrated for chemical waste destruction--a process which recently received the IR-100 award (Industrial Research/Development, 1979).

1.3.2 NONCATALYTIC PROCESSES

1.3.2.1 Bi-Gas Process (Bituminous Coal Research Company, Monroeville, PA)

This process (Linden, 1976) was developed under the sponsorship of the Office of Coal Research and the American Gas Association. Its gasifier consists of a two-stage unit (see Fig. IV-28) that processes pulverized coal in an entrained-flow reactor at 70 to 100 atm. Fresh coal and steam are fed to the upper section (stage 2), where the coal comes in contact with the hot synthesis gas at 1482°C (2700°F) produced in the lower section of the gasifier. Coal is quickly devolatilized, and the oils and tars are thermally cracked while the entrained mass flows upward. The synthesis gas and char leave stage 2 at about 927°C (1700°F). The char is separated and recycled to stage 1, where it is gasified with a steam-oxygen mixture at about 1482°C (2700°F). Widely differing

Fig. IV-28. Schematic Diagram of the Bi-Gas Process..

ranks of coal can be handled in this process. Those examined include North Dakota lignite, Wyoming subbituminous C coal, and Pennsylvania high-volatile A bituminous coal.

With regard to the current status of the Bi-Gas process, a 120-ton/d pilot plant for the production of high-Btu gas started operation in 1976 at Homer City, Pennsylvania. A fluidized-bed methanator with a capacity of 6,000 scf/h has also been constructed.

1.3.2.2 CO₂ Acceptor Process (Conoco Coal Development Co.)

This process is one of several second-generation coal-gasification processes. A 40-ton/d pilot plant in Rapid City, South Dakota, has been in operation since 1972. The process is applicable to lignite or subbituminous coals.

Subbituminous coal must be pretreated before it is gasified. Bituminous coals are difficult to gasify by this process since they require higher gasification temperatures, which would interfere with the thermodynamics of the CO₂ acceptor system.

The technical feasibility of the process has been established; however, further development is needed in a few critical areas, one of which is in the CO₂ Acceptor system.

The CO₂ Acceptor process is based on the so-called acceptor reaction between carbon dioxide and lime:

This is a highly exothermic reaction and thus can provide heat for the coal gasification reaction.

The use of the acceptor offers three major advantages:

- The product gas is free of nitrogen contamination.
- The required solids circulation rate is lower than in other heat carrier processes depending solely on sensible heat as the heat source. Typically, one pound of dolomite circulating in the CO₂ Acceptor process provides about 101 Btu as sensible heat and 316 Btu as exothermic heat of the acceptor reaction (Fink, 1973).
- The product gas contains a lower concentration of CO₂ and of H₂S, as they are chemically combined with the acceptor.

A schematic diagram of the process is shown in Fig. IV-29. The heart of the process is the system of two fluidized-bed reactors: a gasifier and a regenerator. Moisture-free, pretreated lignite is gasified with steam in the gasifier operating at 150 psig and 815°C (1500°F).

The hot acceptor returned from the regenerator at 1010°C (1850°F) showers through the char bed, supplying both sensible and chemical heat as it combines with CO₂. The amount of the acceptor circulated to gasify 1 ton of pretreated dry lignite is about 5.1 tons (Jahnig, 1974).

The spent acceptor collected at the bottom of the gasifier is then pneumatically conveyed to the regenerator, where it is calcined in a fluidized bed, utilizing heat of combustion of residual char with air.

The typical product gas composition given in Table IV-12 for a lignite gasification shows that pressurized operation at a relatively low gasification temperature results in the generation of substantial amounts of methane. The low nitrogen content of the product gas is also noteworthy--a consequence of not using air combustion in the gasifier.

Fig. IV-29. Carbon Dioxide Acceptor Process Schematic (DOE, 1975)

TABLE IV-12

AN EXAMPLE OF PRODUCT COMPOSITION FROM
CO₂ ACCEPTOR PROCESS (Fink, 1975)

Feed: North Dakota lignite (Velva)

System pressure: 150 psig

<u>Product Composition, dry basis</u>	<u>Mol%</u>
H ₂	55.98
CO	15.45
CO ₂	10.88
CH ₄	14.14
N ₂	3.00
H ₂ S	0.132
NH ₃	0.427

<u>Lignite analysis</u>	<u>Wt%</u>
C	66.2
H	4.5
O	21.6
N	0.8
S	0.7
Ash	6.2

In operation of the pilot plant, the following problem areas have been recognized:

- Erosion of solids transfer lines
- Plugging of transfer lines
- Fines buildup in gasifier and regeneration
- Maintaining delicate pressure differentials between gasifier and regenerator.

1.3.2.3 Flash Pyrolysis (Garrett R & D Co., formerly a subsidiary of Occidental Petroleum Corp.)

This process shown schematically in Fig. IV-30, is the precursor of the related biomass flash-pyrolysis process described in Sec. 1.2.2.3. It operates at 50 psi and 593-906°C (1100-1650°F) in an entrained-flow reactor in which pulverized coal is heated by circulating hot ash transferred from a second reactor in which part of the char is burned. The process produces gas, tar, and char. So far, only laboratory and pilot-plant work have been carried out, and the feasibility of the process on a larger scale has yet to be demonstrated (Verma, 1978).

1.3.2.4 Hydrane Process (DOE Pittsburgh Energy Research Center)

The Hydrane process (Feldman, 1973; Gray, 1975; Linden, 1976; Verma, 1978) is based on the direct reaction of coal with nearly pure hydrogen to form methane in a two-stage hydrogasifier. As shown in the process diagram (Fig. IV-31), pulverized raw coal is fed to the first stage, operated at 70 atm and 750 to 900°C (1382 to 1652°F), where it falls freely through the hydrogen-methane mixture produced in the second stage. While passing through this dilute zone, the coal particles have little tendency to agglomerate because of their low concentration and are rendered nonagglomerating by the hydrogasification reactions. The residual coal in the second stage is fluidized in the hydrogen feed gas at 70 atm and 900-980°C (1652-1796°F). About 20% of the carbon in the coal is converted to methane in the first stage, and another 25% is converted in

Fig. IV-30. Garrett Process

Fig. IV-31. Schematic Diagram for the Hydrane Process (Gray, 1975)

the second stage. Process is prepared from the residual char by a three-step procedure consisting of fluidized reaction of the char with steam and oxygen, shift reaction of the resulting CO, and removal of CO₂.

The Hydrane process is based on initial studies (Feldman and Yavorsky, 1973) carried out in separate bench-scale units that simulated the first and second stages in the proposed hydrogasifier (Fig. IV-31). Coals examined in the first stage unit included Pittsburgh seam coal, Illinois No. 6 coal, and North Dakota lignite. With regard to recent status, it is reported (Linden et al., 1976) that a 10-lb/h integrated pilot plant is in operation, and scale-up to a 24-ton/d pilot plant in Morgantown, West Virginia is planned.

1.3.2.5 Hygas Process (Institute of Gas Technology)

The Hygas process (Linden, 1976; Anastasia, 1975; Bair, 1977; Lee, 1977) is a coal-hydrogasification process. The heart of this process consists of a four-stage fluidized reactor in which coal hydrogasification and steam-oxygen gasification take place (see Figs. IV-32 and 33). Coal is fed to the top fluidized stage, where it is flashed at 68 atm (1000 psi) and 315°C (600°F). The dried coal then enters the first stage of the hydrogasifier, where hydrogen-containing gases convert about 20% of the coal to methane at 649°C (1200°F). The partially converted coal drops to the second stage of the hydrogasifier where an additional 25% of the coal is converted into hydrogen-rich gas at about 927°C (1700°F). Temperature control in this stage is maintained by the balance between the exothermic coal-hydrogen reaction and the endothermic coal-steam reaction. The resulting char then descends into the bottom stage of the reactor, where steam and oxygen react with the remaining carbon to form H₂, CO, and CO₂ at 1010°C (1850°F). Oxygen is added to burn part of the char in order to supply heat for the endothermic steam-carbon reaction. Steam-oxygen gasification was chosen as the most desirable mode of hydrogen production after comparison of this process with alternative types of char conversion (steam-electrothermal and steam-iron).

Fig. IV-32. Hydrogasifier for the Hygas Process
(Anastasia, 1975)

Fig. IV-33. Schematic Diagram for the Hygas Process
(Anastasia, 1975)

The technical feasibility of the Hygas process has been demonstrated by an integrated pilot plant (75 tons/d) operated in Chicago under sponsorship of DOE and AGA. Long-term hydrogasification tests have been made with Montana lignite, noncaking Montana subbituminous coal (Bair, 1977) and Illinois No. 6 caking bituminous coal (Lee, 1977).

1.3.2.6 Koppers-Totzek (Heinrich Koppers GmbH)

This process (Farnsworth, 1973) represents commercially proven technology. A number of the K-T reactors are currently in operation, mainly in Asia and Europe, for generating synthesis gas for ammonia production. Gasification is done at near-atmospheric pressure in the entrained reactor, which is equally suited for caking and noncaking coals, and can also handle such noncoal feeds as peat and petroleum residues. A joint effort between Koppers and Shell International has been under way to develop a pressurized K-T gasifier. According to a recent announcement, a 150-ton/day prototype unit capable of operating at 30 atm is due to startup soon at Dutch Shell's Harburg Refinery near Hamburg (Chemical Engineering, 1978). The new version will have a significant economic advantage over the existing K-T process because of its compact size and saving on syngas compression costs.

Figure IV-34 shows a schematic drawing of the currently available K-T gasifier. A mixture of steam and O_2 carries the dry pulverized coal (minus 200 mesh) into the gasifier, which is essentially an open vessel operating at near-atmospheric pressure and around $1480^\circ C$ ($2700^\circ F$).

Because of the entrained-flow scheme, the residence time is short, on the order of a few seconds. Low pressure, combined with high gasification temperature, suppresses methane formation; therefore, the offgas contains essentially H_2 , CO , CO_2 , and relatively small quantities of CH_4 , N_2 , and H_2S . Typical K-T gasifier data for operation on various U.S. coals are given in Table IV-13.

Fig. IV-34. K-T Gasification and Heat Recovery (Farnsworth, 1973).

TABLE IV-13

K-T GASIFIER DATA FOR U.S. COALS (Farnsworth, 1973)

	<u>Western Coal</u>	<u>Illinois Coal</u>	<u>Eastern Coal</u>
GASIFIER FEED			
Dried coal to gasifier			
Analysis, vol%			
C	56.76	61.94	69.88
H ₂	4.24	4.36	4.90
N ₂	1.01	0.97	1.37
S	0.67	4.88	1.08
O ₂	13.18	6.73	7.05
Ash	22.14	19.12	13.72
Moisture	2.00	2.00	2.00
Gross heating value, Btu/lb	9,888.00	11,388.00	12,696.00
Oxygen lb/net ton dried coal	0.649	0.704	0.817
Oxygen purity, %	98.0	98.0	98.0
Process steam, lb/net ton dried coal	272.9	541.3	587.4
GASIFIER PRODUCTS			
Jacket steam, lb/net ton dried coal	347.8	404.9	464.9
High-press. steam, lb/net ton dried coal	2,147.1	2,292.2	3,023.6

TABLE IV-13

K-T GASIFIER DATA FOR U.S. COALS (Farnsworth, 1973) (Continued)

	<u>Western Coal</u>	<u>Illinois Coal</u>	<u>Eastern Coal</u>
GASIFIER PRODUCTS			
Raw gas			
Analysis, dry basis, vol%			
CO	58.68	55.38	55.90
CO ₂	7.04	7.04	7.18
H ₂	32.86	34.62	35.39
N ₂	1.12	1.01	1.14
H ₂ S	0.28	1.83	0.35
COS	<u>0.02</u>	<u>0.12</u>	<u>0.04</u>
Total	100.00	100.00	100.00
Gross heating value, Btu/scf	295.1	290.2	294.4
Gas make (scf/net ton dried coal)	51,783.0	59,489.0	66,376.0
Slag make (net ton/net ton dried coal)	0.222	0.190	0.138
Process efficiency, %	88.2	85.0	90.3
Coal-to-gas efficiency, %	77.3	75.8	77.0

The ash formed from the coal melts at the operating temperature. For most coals, more than 50% of ash flows down the gasifier wall as molten slag and drains into a slag quench tank. The remainder leaves as finely divided fly ash entrained in the offgas. The hot gas stream is directly water-quenched to solidify slag droplets, and is then passed through a waste-heat boiler to generate steam at pressures as high as 1500 psig. The gas is further cleaned in a high-energy scrubber to reduce the entrained solids to 0.002-0.005 grain/scf; the temperature decreases from 176 to 35°C (350 to 95°F).

1.3.2.7 Lurgi Process (Lurgi Mineralstechnik GmbH)

This process uses the most widely commercialized fixed-bed coal gasifier in the world. It is an intermediate-pressure process and can operate on air or oxygen. The existing Lurgi gasifiers have difficulties in handling caking coals typically found in the U.S. because of bed-plugging problems.

Figure IV-35 shows the reactor and a schematic of the reaction zones. Coal crushed to 1/4 to 1-3/4 in. is fed through the lock hopper at the top of the reactor. Devolatilization takes place at temperatures between 649 and 871°C (1200 and 1600°F) as fresh coal comes into contact with hot gases rising from the combustion zone. Gasification occurs as the coal moves downward. Heat for the endothermic reactions is furnished by combustion of carbon at the lower part of the coal bed. A residence time of 45-60 min is required for complete gasification. The maximum reactor temperature is normally maintained at about 982°C (1800°F) to prevent ash fusion and formation of clinkers. The gasifier operates at pressures between 300 and 400 psig. Because of low gasifier temperature and pressurized operation, methane content in the product gas is high and runs about 10% on a dry, nitrogen-free basis. The gasification products also include a significant amount of tar. Table IV-14 shows data for the gasification of a New Mexico coal by the Lurgi process.

Fig. IV-35. Lurgi Coal Gasifier (Moe, 1973)

TABLE IV-14

GASIFICATION OF NEW MEXICO COAL BY THE LURGI PROCESS (Moe, 1973)Material requirements

Coal (New Mexico, dry)	1.00 ton/d
Oxygen	0.27 ton/d
Steam	1.02 ton/d

Coal analysis dry, ash-free

Fixed carbon	52.9 wt%
Volatile matter	47.1 wt%
C/H wt ratio	(13.41)
S	0.91 wt%
N	1.37 wt%

Product, dryMol%

H ₂	38.81
CO	19.55
CO ₂	28.90
CH ₄	11.09
C ₂ H ₄	0.40
C ₂ H ₆	0.61
H ₂ S	0.32
N ₂ + Ar	0.32

Note that the Lurgi gasifier consumes a large quantity of steam--6.7 moles of steam per mole of oxygen, for the example given. Steam is mainly used to cool the combustion zone to below the ash adhesion point (Pollaert, 1978).

The slagging version of the Lurgi gasifier currently being developed by a consortium of international companies at Westfield, Scotland, is reported to use much less steam. The combustion takes place with 1.0-1.5 moles steam per mole of O_2 (Savage, 1977). This has been achieved by modifying the gasifier so that the temperature at the combustion zone can be allowed to reach the slagging range without forming clinkers.

1.3.2.8 Stoic Process (Foster Wheeler Energy Corporation, Livingston, N.J.)

This process uses an atmospheric pressure, two-stage, fixed-bed coal gasifier (Lewis, 1978). This gasifier, designed by Stoic Combustion Pty., Ltd. of South Africa, has been used in some 30 installations outside of the United States. In the United States, this technology is available from the Foster Wheeler Energy Corporation, and the first FW-Stoic gasifier has recently been constructed at the University of Minnesota under a cost-share contract with DOE. The 3-ton/h unit is a full-scale unit aimed at supplying the existing boilers which previously had operated on natural gas (Lewis, 1978).

Figure IV-36 shows a simplified diagram of the FW-Stoic gasifier. Gasification is accomplished in two zones: the distillation and gasification zones. The feed is sized 1/2 to 1-1/2 in. or 1-1/2 to 3 in. The main body of the gasifier is a steel shell with a refractory lining in its upper section and a water jacket in the lower section.

The refractory-lined section consists of four equally sized segments in which separate streams of coal flow downward. Process steam, generated from the water jacket, is mixed with air and charged through a rotating grate.

Fig. IV-36. The FW-Stoic Gasifier (Lewis and Bress, 1978)

Hot gas rising from the gasification zone comes in direct contact with the descending coal, thus extracting moisture and volatiles. The net gas stream leaving the gasifier is called "top gas". Its temperature is about 120°C (250°F), which is below the dewpoint of many distillation products of the coal. After the removal of the coal-tar mist by an electrostatic precipitator, the top gas is mixed with the hot "bottom gas". The temperature of the resulting combined gas stream is higher than 260°C (500°F) and above the dewpoints of the hydrocarbon mists in the stream. This superheat eliminates problems with tar deposition in the gas transfer line or burners.

The "bottom gas" is generated from the gasification zone by the action of steam or coke which has been formed through the distillation zone. A portion of this gas leaves the gasifier at 593°C (1100°F) through passages in the refractory section, giving up some of its sensible heat to the distillation zone. This gas is essentially free of coal tars. The other portion of the bottom gas is allowed to rise through the coal bed in the distillation zone.

Table IV-15 shows the composition of the product gas obtained by combining the top and bottom gases with the tar-oil recovered from the top gas. The oil is in some respects similar to a No. 6 fuel oil, although it is somewhat heavier.

1.3.2.9 Synthane Process (U.S. Bureau of Mines)

This is a second-generation, high-pressure, fluidized-bed, coal-gasification process. A 72-ton/d pilot plant in Bruceton, Pennsylvania, was completed in 1975, and operation was started in July 1976. Since then, the plant has been undergoing a series of test runs focused on demonstrating the feasibility of the coal pretreatment and gasification steps. However, in late 1978, the plant was shut down and mothballed (Lewis, 1979).

In the Synthane process, the gasification is accomplished at 980°C (1800°F) in a fluidized bed at pressures up to 1000 psig. Figure IV-37 is a schematic of the Synthane process. Coal crushed to minus 20 mesh and pressurized to 1000 psig in

TABLE IV-15

PRODUCT COMPOSITION FOR FW-STOIC GASIFIER (Foster Wheeler, 1979)

Approximate Analysis

Hot Raw Gas*

<u>Component</u>	<u>Volume %</u>
H ₂	14.0-16.0
CH ₄	2.6-30.0
CO	29.0-30.0
CO ₂	3.0- 4.0
N ₂	47.6-51.4

* Excludes light oil and tar-oil content.

Analysis of Typical Tar-Oil

Physical properties

Specific gravity	1.0855
Viscosity, centistokes, 122°F	55.4
Viscosity, centistokes, 210°F	21.35
Pour point, °F	80
Flash point, C.O.C., °F	315
Higher heating value, Btu/gal	148

Chemical composition

<u>Component</u>	<u>%</u>
Carbon	85.92
Hydrogen	7.92
Oxygen	4.10
Nitrogen	1.05
Sulfur	0.22
Ash	0.11
Moisture	0.60
Total	100.00

SYNTHANE PROCESS
U. S. Bureau of Mines

Fig. IV-37. Schematic of Synthane Process

lockhoppers is fed to the pretreater, a fluidized-bed reactor, where the caking tendency of the coal is destroyed by partial devolatilization and mild superficial oxidation with an oxygen-steam mixture at 426°C (800°F). Pretreated coal is then fed to the top of the gasifier. The free-falling coal particles contact the raw synthesis gas rising from the fluidized bed below. The major portions of steam and oxygen consumed by the process are charged at the bottom of the reactor to gasify the coal at about 980°C (1800°F) and to maintain the solid particle in the fluidized state. Unreacted char containing about 30% of the carbon in the feed coal is withdrawn from the bottom of the gasifier via lockhoppers at atmospheric pressure. This char, along with tar and carbon dust recovered from the raw synthesis gas, is burned to generate the steam and power needed in the plant.

The raw synthesis gas combined with the pretreater offgas is passed through cyclones within the gasifier to separate the majority of entrained particles. Residual dust, tar, and excess water are removed by a water scrubbing. The waste water from this step contains ammonia, phenols, and other chemical impurities characteristic of coal gases (Loran, 1978). The scrubbed gas is ready for CO-shift conversion.

Table IV-16 lists the results of a pilot-plant Synthane gasification operating at 600 psig. This pressure is somewhat lower than that of the commercial Synthane process.

1.3.2.10 Texaco Coal-Gasification Process (Texaco Inc.)

In the Texaco process, a coal-water slurry is gasified with oxygen in a reactor similar to that used in Texaco's long-established commercial oil-gasification process. In addition to the 15-ton/d pilot-plant unit at Texaco's Montebello research center, a 150-ton/d unit is currently in the start-up phase in West Germany. The Tennessee Valley Authority is designing a 150-ton/d unit for installation at Muscle Shoals, Alabama. Also in March 1977, Texaco and Southern California Edison jointly announced their intention to obtain funds for the construction of a 1000-ton/day, coal-gasification, combined-cycle demonstration plant near Barstow, California.

TABLE IV-16

TYPICAL PRODUCT GAS COMPOSITION AND YIELDS FROM SYNTHANE
GASIFICATION OF VARIOUS COALS AT 600 psig (Haynes, 1973)

	<u>Pittsburgh</u>	<u>Illinois No. 6</u>	<u>Montana Rosebud</u>	<u>North Dakota Lignite</u>
Average maximum				
temperature, °F	1814	1760	1629	1587
Coal ash, %	7.9	14.2	11.6	7.2
Coal moisture, %	1.5	2.7	10.2	23.0
Average coal feed rate				
lb/h	17.5	23.7	27.8	37.0
lb/h-ft ³	30.7	50.4	59.2	78.2
Product gas composition, %				
H ₂	30.3	35.4	37.3	36.2
CO	27.0	12.3	11.4	17.2
CO ₂	23.2	35.3	38.0	32.6
CH ₄	18.2	13.9	11.3	12.9
C ₂ H ₆	0.9	1.6	1.5	0.8
H ₂ S	0.4	1.6	0.5	0.3
Product gas yield				
Scf/lb coal, maf	18.0	22.3	21.0	19.3
Percent carbon gasifier	64.9	66.5	72.0	59.0
Steam rate, lb/lb coal	1.0	1.5	1.3	0.6
Oxygen rate, lb/lb coal	0.29	0.26	0.24	0.14

A schematic process flow diagram of the Texaco pilot plant is shown in Fig. IV-38. The coal-water slurry (about 50/50 weight ratio) is heated in a fired heater to a temperature below 100°C (212°F), then mixed with oxygen, and sprayed at the top of the gasifier. Gasification takes place at temperatures between 1093 and 1538°C (2000 and 2800°F) above 200 psig. The reactor is a cylindrical pressure vessel with a refractory lining. It consists of two vertically connected zones: an upper (gasification) zone and a lower zone where molten slag and soot are quenched in a pool of water. The hot gaseous products, still containing entrained solid particles, leave the reactor and enter a venturi-type contactor-mixer, where additional water is injected to cool and wash the gas stream. The gases are then again scrubbed with water in a separator and freed from fines in a packed tower.

The process can handle all types of carbonaceous materials, including caking and noncaking coals and coke. No liquid product is formed, which greatly simplifies the process. The product gas has a very low methane content (less than 1%) because of the high reactor effluent temperature of over 1093°C (2000°F).

In recent pilot-plant runs, Texaco successfully gasified the SRC filter cake containing 53 wt% ash. Table IV-17 shows the pilot-plant data for this run and for the gasification of a high-ash SRC. In both cases, almost all carbon in the feed was gasified. The oxygen consumption was 0.64 pound per pound of filter cake and 0.88 pound per pound of SRC. Since one half of the filter cake was ash, the amount of oxygen consumed per unit weight of carbon in feed is actually greater for the filter cake than for the SRC.

The Texaco pilot plant and the one used in the above tests is designed to operate at pressures up to 28 atm (Robin, 1976).

Fig. IV-38. Texaco Pilot-Plant Process Flow Diagram (Robin, 1978).

TABLE IV-17

GASIFICATION OF SRC FILTER CAKE AND SRC BY TEXACO PROCESS (Robin, 1978)

<u>Feed analysis, wt%</u>	<u>SRC Filter Cake</u>	<u>High-Ash SRC</u>
C	38.4	77.6
H	2.5	5.3
N	0.5	1.3
S	5.2	2.0
Ash	52.2	10.7
O	1.2	3.1
 <u>Gasification</u>		
Reactor pressure, psig	350	350
Slurry concentration, wt% solids	70	100
Steam rate, lb/lb solid	-	0.42
O ₂ rate, lb/lb solid	0.64	0.88
Carbon gasified, %	99.8	99
Dry product gas, scf/lb solid	18	39
Product gas analysis, wt%		
H ₂	30.58	37.96
CO	40.51	55.07
CO ₂	25.77	6.22
N ₂	0.37	0.54
H ₂ S	2.51	0.03
COS	0.14	0.05
CH ₄	0.00	0.04
Ar	0.12	0.09

1.3.2.11 Union Carbide-Battelle Agglomerating Ash Burner Process (Battelle Columbus Laboratories)

This process uses a two-stage fluidized-bed coal gasifier operating at 100 psig. In the agglomerating burner vessel coal is combusted in air at 1038-1260°C (1900-2300°F) to produce hot agglomerated ash. This is circulated to the steam gasifier, where the sensible heat of the agglomerates is used to gasify coal. Thus, the product syngas is free of nitrogen contamination.

The design of a 25-ton/d process development unit (PDU) began in 1972. The plant was completed in 1976 at Battelle's Engineering Station in West Jefferson, Ohio. Battelle operated the PDU from September 1976 through January 1978. Most of the runs used a noncaking western coal (Montana Rosebud seam subbituminous coal). Through the experiences obtained during PDU runs, the plant modifications necessary for achieving a steady-state operation were identified, but in January 1978, the PDU plant was mothballed.

A schematic diagram of the Battelle agglomerating ash coal gasifier process is shown in Fig. IV-39. In the burner vessel, coal is burned in air in a fluidized bed at 1065-1149°C (1950-2100°F). The hot, agglomerated ash particles leave the combustor at 1093°C (2000°F) and are charged to the gasifier by a steam lift. In the fluidized gasifier there is a net downward flow of agglomerated ash. In passing through the gasifier, the hot particles transfer a portion of their sensible heat to support the gasification reaction. Ash agglomerates are continuously stripped of carbon by the upward flow of steam. Typically the fluid bed in the gasifier maintains a temperature of about 927°C (1700°F). The temperature of the ash agglomerates drops from about 1093°C (2000°F) to 815-871°C (1500-1600°F) in passing through the gasifier. Most of the ash agglomerates are continuously returned to the burner vessel by an air lift.

A conceptual plant for gasifying an eastern coal to produce 250 billion Btu/d of high-Btu gas was prepared by Battelle. A material balance of this plant for the gasifier and combustor section is shown in Figure IV-40. Since the net

Fig. IV-39. Burner-Gasifier Feed and Circulation System of the Union Carbide-Battelle Process (Mink, 1978)

	①	②	③
	Lb Mole/Hr	Lb Mole/Hr	Lb Mole/Hr
CH ₄	-	9,937	-
CO	-	24,988	-
CO ₂	-	10,531	27,054
H ₂	-	44,127	-
N ₂	130,969	395	131,110
H ₂ S	-	779	-
O ₂	34,396	-	3,127
SO ₂	-	-	896
H ₂ O	-	28,149	9,077
Total, wet	165,365	116,906	171,284
Total, dry	165,365	90,757	162,187
Temperature, °F	80	1,700	2,100
Pressure, psig	0	100	100
Dew Point, °F	-	240	170
Flow, SCFM	1,048,500	739,800	1,083,800
Flow, ACFM	1,086,700	393,900	683,800

Fig. IV-40. Material Balance for the Union Carbide-Battelle Process
(Battelle, 1978)

amount of coal charged to the gasifier is 477.8 tons/h, while the agglomerated ash recycle to the combustor is 9785.6 tons/h, about 20.5 tons of ash must be circulated for each ton of coal gasified.

1.3.2.12 U-Gas Process (Institute of Gas Technology)

The U-Gas process uses a single-stage, fluidized-bed coal gasifier operating at 300-350 psig pressure with either air or oxygen (Loeding, 1973; Patel, 1975, 1977). Coal of any rank is acceptable. Fluid-bed temperatures ranges between 982 and 1093°C (1800 and 2000°F), depending on the type of coal. A higher temperature is maintained in the lower section of the gasifier, where the ash particles are agglomerated and separated. The process does not produce liquid products.

The pretreatment of caking coals and steam-air (or oxygen) gasification are being studied under IGT'S Hygas process-development program. The technical feasibility of these aspects of the U-Gas process have been established. The ash-agglomeration phenomenon has been under investigation in a 4-ft diam x 25-ft high gasifier operating at pressures up to 2 atm (Patel, 1975). As of May 1977, 67 runs had been made on this unit. More than 650 tons of coal-derived char have been processed. Gasifying agents included air-steam, oxygen-steam, and air-oxygen steam mixtures. Recently, the pilot plant was modified so that it can process coal instead of being limited to char as originally designed.

Figure IV-41 shows the schematic of the U-Gas process. Caking coal, crushed to minus 1/4 in., is fed to the pretreater and contacted there with air at 371-427°C (700-800°F) in a fluidized bed at system pressure to eliminate its caking tendency. The pretreatment is omitted for noncaking coal.

The coal is gasified by steam and air (or oxygen) in a single-stage, fluidized bed at about 1038°C (1900°F) and at 300-350 psig. Residence time is about 45 min. Fluidizing gas velocity is 1.0-2.5 ft/s.

Fig. IV-41. U-Gas Process (Patel, 1977)

Ash is agglomerated into large particles and discharged from the bottom of the gasifier. This is achieved by a carefully controlled flow of steam-air mixture at the base of the fluid bed. The temperature at this point is higher than that of the bulk of the fluid bed and is near the ash-softening point. This causes the ash particles to agglomerate into larger and heavier particles until they lose bouyancy and fall into the collecting bin below. Fines in raw syngas are separated by external cyclones and returned to the agglomerating point in the gasifier.

Table IV-18 shows the results of the pilot-plant gasification of a metallurgical coke.

1.3.2.13 Wellman-Galusha Process (McDowell-Wellman Engineering Co.)

This process (Culbertson, 1978; Davis, 1977; Verma, 1978) uses a fixed-bed coal gasifier which operates at atmospheric pressure on air or oxygen. The commercial experience has been predominantly with the air-blown designs. The Wellman-Galusha gasifiers were in widespread industrial use in the United States and throughout the world in the early part of this century. Today, around seven gasifiers are operating in the United States.

There are two types of Wellman-Galusha gasifiers. The standard nonagitated type and the agitated type, the rated capacity of the latter is about 25% higher than that of the former. Unlike the standard gasifier, the agitated type can handle volatile caking bituminous coals. Using a 20-ton/d pilot plant equipped with an agitator, DOE has been working on the development of a pressurized version of the Wellman-Galusha gasifier since 1968 at Morgantown Energy Research Center, West Virginia.

Figure IV-42 shows a schematic of the agitated gasifier. Crushed and sized coal is fed to the gasifier from the top. As the coal is gasified, particles move downward and are finally discharged as ash through the rotating grate. The

TABLE IV-18

U-GAS PILOT-PLANT GASIFICATION OF
METALLURGICAL COKE - NEAR-ATMOSPHERIC PRESSURE (Patel, 1977)

Gasifier Feed (Bethlehem coke breeze)

Proximate analysis, wt%

Moisture	2-4
Volatile matter	3
Ash	11.0
Fixed carbon	83.0

Ultimate analysis, dry, wt%

Ash	11.0
Carbon	86.5
Hydrogen	0.4
Sulfur	0.3
Nitrogen	0.6
Oxygen	0.7

Bulk density, lb/ft³ 52

Particle density, lb/ft³ 93

Initial deformation temperature
under oxidizing conditions, °F 2340

TABLE IV-18 (CONTINUED)

Pilot-Plant Data	Air-stream feed, no fines recycle				O ₂ enriched air- steam feed with feed recycle	O ₂ steam feed, no fines recycle			O ₂ steam feed with fine recycles	
	Run 10	Run 31	Run 36	Run 48	Run 31	Run 39	Run 47	Run 48	Run 51	Run 53
Number of cyclones										
Internal	1	0	0	1	0	0	1	1	1	1
External	1	2	2	2	2	2	2	2	2	2
Average bed temperature, °F	1872	1884	1900	1895	1920	1940	1910	1928	1940	1960
Coke breeze feed rate, lb/hr	387	489	567	345	628	443	439	365	492	528
Average solid feed mesh size	14	14	16	16	14	16	16	16	16	16
Venturi throat diameter (in.)	3	3	2	2	3	2	2	2	2	2
Venturi throat velocity (ft/sec)	89	99	151	146	79	246	172	167	108	112
Total bed superficial velocity (ft/sec)	2.2	2.01	2.05	2.1	2.23	1.83	2.16	2.07	2.0	2.0
Product gas heating value* (Btu/scf)	94	87	92	75	122	208	205	191	202	218
Carbon gasification efficiency† (%)		96.5	93		97.8	96.5		94	94	96.1
Fines elutriation rate †† (lb/hr)		285	238	66	127	166	99	62	51	38.5
Agglomerate production rate (lb/hr)	39	43	34	31	50	20	26	42	64	57
Analysis§										
Carbon(%)	46.7	21.0	35.0	43.3	15.4	21.2	38.1	30.5	30.1	19.7
Ash(%)	53.9	79.0	65.0	56.7	83.6	73.8	61.9	69.5	69.9	80.3
Average agglomerate mesh size	No agglom- erate	7	12	No agglom- erate	1/4"	5	No agglom- erate	14	14	8
Product gas composition, dry¶ (%)										
CO ₂	10.3	14.3	13.9	14.7	12.6	33.6	39.0	42.7	39.2	34.5
CO	12.2	15.5	16.6	12.0	21.8	24.6	24.9	21.3	23.3	29.8
H ₂	15.5	8.8	11.7	10.3	14.2	35.1	35.0	35.4	36.9	34.9
CH ₄	0.3	0.5	0	0.2	0.4	0.7	1.1	0.6	0.6	0.8
N ₂	61.7	59.9	57.3	62.7	50.9	0	0	0	0	0

*Calculated higher heating value based on gas analysis.

†Based on carbon input compared to carbon lost in agglomerates.

††Based on elutriated fines collected in first and second-stage external cyclones, whether fines recycle was used or not.

§Agglomerate carbon analysis includes any entrained fines collected with agglomerates.

¶Nitrogen purge-free basis.

Fig. IV-42. Wellman-Galusha Agitator-Type Gas Producer.

gasifier walls are unlined steel, cooled by a water jacket. For gasification, air and steam generated in the gasifier shell are injected under the revolving grate.

The agitator has a revolving horizontal arm which also spirals vertically below the surface of the coal bed to maintain the uniformity of the fuel bed. The agitator arm and its vertical drive shaft are made of heavy steel tubing and are water-cooled. The arm is revolved by a variable-speed drive.

Raw gas containing particulates, tar, and oils leaves the gasifier in a temperature range of 426-538°C (800-1000°F) for anthracite and at 593-649°C (1100-1200°F) for bituminous coal. Typical compositions of raw gases leaving the gasifier are shown in Table IV-19.

1.3.2.14 Westinghouse Coal-Gasification Process (Westinghouse Electric Corp.)

This process (Salvador, 1978; Andermann, 1978; Archer et al., 1975) features two fluidized-bed reactors operated at 230 psig. The first reactor, the devolatilizer, is used to devolatilize and decake coals as required. Devolatilized char circulates to the second reactor, the gasifier, where air or oxygen and steam are used to gasify the char at 1093°C (2000°F), the ash agglomerating temperature. The devolatilizer is designed to decake the fresh coal by creating an intimate mixture of coal and char particles, which is noncaking.

A 15-ton/d process development unit was completed in 1974 and started up in 1975. The feasibility of the devolatilizer was demonstrated in 1976 with a variety of coals, including highly caking eastern bituminous coals. During 1977 and 1978, the gasifier was successfully operated in a series of runs for a cumulative time of 1500 h.

Figure IV-43 shows the flow of materials between the devolatilizer and the gasifier. Dry crushed coal is fed into a central draft tube of the devolatilizer. In this tube, the coal feed and large quantities of recycle

TABLE IV-19

COMPOSITION (DRY BASIS) OF RAW GASES FROM A WELLMAN-GALUSHA GASIFIER
(Dravo, 1976)

Steam-Air-Blown Operation

Feed coal	Bituminous	Anthracite
HHV of coal, Btu/lb, dry	14,000	13,500
Mole %, CO	28.6	27.1
CO ₂	3.4	5.0
H ₂	15.0	16.6
CH ₄	2.7	0.5
N ₂	50.3	50.8
Tar, lb/ft ³	0.001	-
HHV, Btu/scf, dry	168	146

Fig. IV-43. Westinghouse Fluidized-Bed Gasification Process
(Salvador and Holmgren, 1978)

solids, char and/or lime sorbent, are mixed and carried upward by the gasifier effluent at 927-982°C (1700-1800°F), flowing at velocities in excess of 15 ft/s. Thus, the coal feed quickly reaches the fluid bed, where it is devolatilized and partially hydrogasified. A lime-bearing material is added to the devolatilizer to receive sulfur. Char is withdrawn from the fluid bed in the devolatilizer and pneumatically transported into the combustion/agglomeration reactor. In this reactor, char is combusted with air to produce the heat necessary for the agglomeration of ash-rich particles and for the steam gasification of the char.

As the temperature in the combustion zone reaches 1038-1093°C (1900-2000°F), ash becomes sticky and forms spherical agglomerates which defluidize and are removed continuously from the bottom of the reactor. On the basis of the results obtained with the devolatilizer and the gasifier, Westinghouse has estimated a material balance for the integrated system shown in Fig. IV-44.

1.3.2.15 Winkler Coal-Gasification Process (Davy Powergas, Inc.)

This process uses a single-stage, fluid-bed coal gasifier operating on air or oxygen at atmospheric pressure. The first commercial Winkler gasifier was put into operation in 1926. Since then, 64 gasifiers in 22 plants have been commissioned. Of these gasifiers, 38 are currently in operation. Davy Powergas now offers a Winkler-type gasifier designed to operate at pressures up to 42 psig (Goodman, 1977). Because the process does not have a decaking step, it would have difficulties in handling caking coals.

Figure IV-45 shows the Winkler gasifier. Coal is introduced to the gasifier through a screw conveyor at a lower section of the fluid bed. The fluidizing gas consisting of air or oxygen and steam enters the vessel at several points, including one below the coal feed. In the fluidized bed, the coal particles react with oxygen and steam to yield a product gas containing hydrogen, carbon monoxide, carbon dioxide, and methane. Typical gas compositions for air-blown and oxygen-blown operations are shown in Table IV-20. The gasification temperature varies with the type of coal. For lignite, it is about 800°C (1475°F).

Fig. IV-45. The Winkler Coal Gasifier (Banchik, 1977)

TABLE IV-20

TYPICAL WINKLER GAS COMPOSITIONS (Banchik, 1975)

	Composition, vol%, dry					HHV, dry Btu/scf
	<u>CO₂</u>	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>	<u>N₂</u>	
Air-blown	10	22	12	0.7	55.3	116.6
O ₂ -blown	20	38	39	1.5	0.5	263.5

The gasifier temperature is maintained below the softening point of ash to avoid agglomeration. To ensure this, the gasifier is equipped with a radiant waste-heat boiler situated immediately above the fluid bed. The boiler serves to cool the gas to 177-204°C (350-400°F) before it leaves the gasifier, which is sufficient to prevent sintering of the fly ash on the refractory walls of the exit duct.

As a result of fluidization, the ash particles are segregated according to size and weight. About 70% of the ash in the feed coal is entrained in the raw product gas, while the remainder falls down through the fluid bed into the ash collector at the bottom of the gasifier (Banchik, 1975). The bulk of the fly ash is removed in the waste-heat train and in the cyclones. The reduction of the gas velocity by about 60% by cooling in the boiler section and the change in direction of flow cause the fly ash to settle. At the bottom of the waste-heat boiler, about 30-40% of the ash is removed, and the cyclones collect another 45-50%. The remainder of the ash is removed in turn by water scrubbing and by an electrostatic precipitator.

Table IV-21 shows the operating data of a commercial Winkler unit for oxygen-blown operation. To gasify a lignite containing 8.6% moisture, the oxygen consumption was 0.52 lb/lb coal. The unit achieved a carbon gasification efficiency of 90.6% and generated a product gas whose total heating value was 73.9% of the heating value of the feed coal.

1.3.2.16 Miscellaneous Processes

Some of the other coal gasification processes are briefly described here.

GEGAS Process (General Electric): The gasifier for this process is a fully stirred, pressurized, fixed-bed reactor equipped with a special coal feeder. So far, the process has been tested only in a laboratory-scale unit. For feeding coal, GE envisions the use of an extruder. The feed coal, crushed to minus 1/6

TABLE IV-21

LIGNITE GASIFICATION BY WINKLER UNIT (Banchik, 1975)Lignite

Size: 0-1 mm = 60%

1-8 mm = 40%

Lower heating value = 5210 kcal/kg (9375 Btu/lb)

Moisture = 8.6 wt%

Ash = 4-5 wt%, sintering point = 900°C, mp = 1280°C

C = 68.2%, H=5.2%, O=25.2%, N=1%, S=0.5%

Product GasTypical composition: CO₂ = 13.8%, CO = 48.2%, H₂ = 35.3%CH₄ = 1.8%, N₂ = 0.9%

Higher heating value: 287.3 Btu/scf

Operating Data

		Per million Btu of HHV of dry product gas
Lignite		133 lb
O ₂ (100% pure)		69 lb
LP steam		21 lb
Condensate		23 lb
Electricity		7 kWh
HP steam, exported		100 lb
Carbon gasification	$= \frac{C \text{ in gas}}{C \text{ in coal}} \times 100$	90.6%
Gasification efficiency	$= \frac{\text{Heating value of gas}}{\text{Heating value of coal}} \times 100$	74.9%

in. will be mixed with the by-product tar, and preheated to 930°C (200°F). By the use of the extruder, GE hopes to utilize all the coal fines and the tar, produce an optimum feed size, and inject it into the gasifier in one operation (Kydd, 1975).

Riley-Morgan (Riley Stoker Corp.): This process (Verma, 1978) uses an agitated fixed-bed coal gasifier (Fig. IV-46). A distinct feature of this gasifier is the rotation of the reactor shell and ash pan as a single unit. The gasifier operates at atmospheric pressure with air or oxygen. Sized noncaking coal is used as feed. The fuel bed is supported on an ash bed which, in turn, is supported on the rotating ash pan. Coal is fed from the top through a lock hopper into the gasifier, which operates at a pressure of 40 in. of water (maximum). A pilot plant is located in Worcester, Massachusetts.

Wilputte Process (Wilputte Corporation): This process uses a commercial fixed-bed atmospheric gasifier (Fig. IV-47) operating on air or oxygen, and is equipped with an agitator to maintain uniform distribution of the coal bed (Verma, 1978). The coal feed is crushed to minus 4 in. and has a residence time of about 2 h.

Combustion Engineering Process (Combustion Engineering, Inc.): This process uses (Fig. IV-48) a slagging entrained-flow gasifier operating at atmospheric pressure, which is provided with two gasification zones in a vertical cylinder. In the combustor section a portion of the feed coal and recycle char is gasified with air or oxygen under slagging condition 1650°C (3000°F). Steam and the balance of the coal feed are fed to the zone immediately above the combustor, such that they are entrained in the very hot gases rising from below. In the reductor section, coal is devolatilized and gasified by the sensible heat given off by the combustor gases. Gases leave the reductor zone at about 870°C (1600°F) and are directed downward into a waste-heat boiler. The cooled gas then flows through a spray drier, a cyclone, and a scrubber. The spray drier serves to recover char from the aqueous slurry obtained in the scrubber. Char and ash thus collected are recycled to the pulverizer for the combustor. The process will accept all types of coal that is pulverized to minus 200 mesh.

Fig. IV-46. Riley-Morgan Coal Gasifier

Fig. IV-47. Wilputte Low-Btu Gas Producer (Verma, 1978)

Fig. IV-48. Combustion Engineering Coal Gasifier (Patterson, 1978).

Rockwell International Hydrogasification Process (Rockwell International, Energy Systems Group): This process uses the Rockwell rocket-injection system a carryover from aerospace technology (Chem. Engineering, 1978). It is based on the entrained-flow concept and uses a feed-injection system consisting of a central tube that feeds pulverized coal into two or more streams of hot, 1093°C (2000°F) hydrogen. Thorough mixing takes place in 2 to 3 ms at the entrance to the reactor, which is pressurized to 500-2000 psig.

Under a DOE contract, Rockwell has tested a 1-ton/hr reactor. The company has now obtained an \$18 million DOE contract to build and operate a 100-ton/day gasification reactor. The primary gasification reaction is hydrogasification, resulting in the formation of methane. Some tar and the expected amount of ash also form.

1.4 PERSPECTIVE FOR THE TECHNICAL LIMITATION IN GASIFICATION TECHNOLOGIES

The established and emerging coal-gasification technologies utilize an amazing variety of fixed reactors, the operation conditions of which range from atmospheric pressure to 1000 psi, and from 700°C (1292°F) to 1500°C (2732°F). Some of the processes use solids or melts circulating between the gasifier and another reactor to provide heat, reaction medium, catalyst, or reagent for the gasification. In others, the gasifier is equipped with mechanical agitation to ensure the uniform passage of the coal or ash.

Each of these reactor designs has certain limitations, and each new design aims at improving some shortcoming. The reason for the existence of this multitude of gasifiers stems essentially from the following factors:

- The nature of the available coal, particularly its reactivity, caking tendency, and ash contents.
- The type of gas desired, whether low- or medium-Btu gas, SNG, or syngas.

The reactivity of coal varies with its rank. Lower-ranking coals are more reactive and can be gasified at lower temperature, as shown by the following minimum temperatures of gasification (Verma, 1978):

Lignite	615°C (1130°F)
Subbituminous	715°C (1320°F)
Semianthracite	765°C (1410°F)
Coke	815°C (1500°F)

The production of methane-rich gas depends on the hydrogasification reaction which is favored by elevated pressures and the temperature range, 670-950°C (1400-1742°F), while syngas (H₂/CO) can be produced at lower pressures and higher temperatures.

A temperature limitation is also set, in the case of the CO₂-Acceptor process, by the equilibrium in the reaction

used for supplying heat for the gasification reaction. Because of the reversibility of this reaction, the gasification in this process must be operated below 815°C (1500°F).

Another important coal property that determines the selection of the appropriate gasifier is the tendency to cake. Caking coals require pretreatment before they can be processed in most gasifiers, but they can be handled directly in entrained-flow and molten-bath reactors.

Fixed-bed (and moving-bed) gasifiers operate at lower temperatures than do other types, have good thermal efficiency, and produce a gas low in particulates. They generally require high residence times and noncaking or pretreated coal of uniform size, generally between 1/8 and 1-1/2 in. Fines are not desirable, as they cause channeling in the bed. Coals that cake tend to cause bed plugging and generate substantial amounts of heavy oils and tar--a disadvantage if syngas or high-Btu gas is the desired product.

Fluid-bed gasifiers also need pretreatment for caking coals, but can handle varied feeds in the crushed or pulverized form. Fluid-bed operation ensures good solid-gas contact and mixing and uniform bed temperature, but allows only limited variations in gas flow for maintaining fluidization and avoiding excessive entrainment. Even in normal operation, the gases produced have a high dust level.

Entrained-flow gasifiers operate with pulverized coal, oxygen, and steam fed concurrently from the bottom. Since the gasification occurs very rapidly (in a second or less) at the prevailing high reaction temperatures (1200-1500°C or 2192-2732°F) and in the dilute phase, agglomeration of the coal particles cannot take place. This type of gasifier can process caking coals without pretreatment. Because of the high reaction temperature, the product gas contains no methane or tars. It has a high level of ash particles, however.

Molten-bath gasifiers use the fused medium to accelerate gasification and to desulfurize the coal fed. The use of molten iron is applicable to various types of coals from subbituminous to coke, but entails problems connected with providing a durable refractory lining for temperatures around 1400°C (2552°F), the injection of the reactants, slag viscosity, and the high ash content of the product gas. Molten alkali carbonate, operating at much lower temperatures (700-930°C or 1290-1700°F), can be used at elevated pressures (500 psig) to catalyze the formation of methane. This is a promising aspect, but the mechanical and chemical difficulties connected with this type of reactor have to be overcome. These problems are corrosion of the refractory lining, loss of salt by vaporization, clogging of transfer lines, and complexity of salt regeneration and purification.

The unconventional heating method of circulating hot or reactive solids (agglomerated ash in the Union Carbide-Battelle process, or calcined dolomite in the CO₂-Acceptor process) in the gasifier leads to syngas free of nitrogen, but is inflicted with problems connected with erosion and plugging of transfer lines for solids.

Among the gasification processes discussed, only the molten-bath processes use an added reagent or reaction medium that has a catalytic effect on the gasification reactions. Still, these processes are not catalytic processes in the usual sense in view of the large proportion of the additive used and its involvement in other reactions.

By and large, biomass gasification uses techniques similar to those used in coal gasification, but there are some important differences, limitations, and also certain advantages connected with biomass.

Of the various types of biomass materials, only woody plants and collected municipal solid wastes are available in sufficient quantity to serve as feedstock for commercial-scale gasifiers. Agricultural crop residues and animal manure are of secondary importance because of fluctuating availability and problems of centralized collection.

Since the main components of municipal solid waste are wood-derived products, in the following discussion wood will be used as a model for a biomass feedstock in gasification.

Neglecting its low N and ash content, moisture-free wood can be represented by the formula:

Such typical formulas for wood as

show the close relationship of wood to:

This excess hydrogen in wood makes the potential methane yield and carbon efficiency somewhat higher for wood than for lignite, peat, cellulose, or pure carbon, according to the equations:

				C Efficiency,
				<u>%</u>
Wood	$\text{CH}_{1.46}\text{O}_{0.58} + 0.34\text{H}_2\text{O}$	$\rightarrow 0.54\text{CH}_4 + 0.46\text{CO}_2$		54
Peat	$\text{CH}_{1.18}\text{O}_{0.46} + 0.48\text{H}_2\text{O}$	$\rightarrow 0.53\text{CH}_4 + 0.47\text{CO}_2$		53
Lignite	$\text{CH}_{0.62}\text{O}_{0.24} + 0.72\text{H}_2\text{O}$	$\rightarrow 0.52\text{CH}_4 + 0.48\text{CO}_2$		52
Cellulose	$\text{CH}_{1.67}\text{O}_{0.83} + 0.17\text{H}_2\text{O}$	$\rightarrow 0.50\text{CH}_4 + 0.50\text{CO}_2$		50
Carbon	$\text{C} + \text{H}_2\text{O}$	$\rightarrow 0.50\text{CH}_4 + 0.50\text{CO}_2$		50

As discussed in Sec. 1.1.4, the thermal decomposition of wood in the presence of steam is an exothermic reaction. The gasification of wood is a relatively fast reaction and starts at a lower temperature than coal gasification. It is catalyzed by small amounts of alkali metal carbonates, which are present in wood ash. The moisture naturally present in wood is another useful constituent since the minimum amount of water needed for conversion of wood into $\text{CH}_4 + \text{CO}_2$, according to the above equation, represents 27% moisture, based on dry wood.

Vertical moving-bed reactors are used in the gasification of municipal solid waste on a commercial scale by the Purox and Andco-Torrox processes, employing oxygen and air, respectively, as the gasifying reagent. Other emerging processes using moving-bed gasifiers for wood and other agricultural wastes are the Forest, Georgia Tech, and Moore-Canada processes. The Wright-Malta gasifier is an inclined, indirectly heated, pressurized rotary kiln utilizing the moving-bed principle, the catalytic action of wood ash, and the exothermicity of the reaction. This technique may encounter some problems connected with sealing, mechanical operation, feed agglomeration, and heating when scaled up to plant size.

Although there is some difficulty in comminuting wood to the proper size for fluidization because of its fibrous nature, sawdust and wood chips have been

successfully gasified in fluid beds by Battelle-Pacific Northwest and Battelle-Columbus. The former used an auger-agitated, electrically heated laboratory reactor and $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ as the catalyst, while the latter operated a "multi"-solid fluid bed heated by circulating hot char and ash; the feed is activated by catalytic amounts of CaO and wood ash.

The syngas-from-manure process of Texas Tech also uses a fluid-bed gasifier, but the results are yet inconclusive.

The entrained-flow concept was used for flash pyrolysis-gasification of the finely comminuted organic portion of municipal solid waste by the Occidental Research Corporation in a now-defunct, commercial-scale plant in Southern California. The failure of the plant was partly due to the low quality of the coproduced liquid fuel. It was claimed that the process is also applicable to the processing of rice hulls, fir bark, straw, and animal waste.

The Garrett process developed for the pyrolysis gasification of animal waste in an indirectly heated, mechanically raked multihearth reactor appears to have limited applicability in view of its complex mechanical design and inherent problems of scale-up.

2. LIQUEFACTION

2.1 GENERAL CHEMICAL AND ENGINEERING ASPECTS OF LIQUEFACTION

2.1.1 GAS-LIQUID-SOLID INTERACTIONS RELEVANT TO LIQUEFACTION

The gas-liquid-solid interactions in the liquefaction of a solid suspended in a liquid and undergoing a solid-catalyzed reaction with a gas represent a rather complicated system, in view of the involvement of two solids. These interactions are simpler in the slurry reactor. There, a gas reacts with a reactant dissolved in a liquid, in the presence of a suspended solid catalyst. This case is found, for example, in the H-coal process (see Sec. 2.3.1.3), and in regeneration of the hydrogen-donor solvent by catalytic hydrogenation. The gas-liquid-solid interactions for this and similar cases have been analyzed (Sherwood and Farkas, 1966; Carberry, 1976; Shah, 1979).

The concentration distribution for the gaseous and liquid (dissolved) reactants in such a system is shown in Fig. IV-49. The concentration breaks and discontinuities at the gas-liquid and liquid-solid interfaces occur because of the existence of stationary films.

Assuming first-order kinetics for the gaseous reactant, the overall reaction rate is influenced by various mass-transfer effects across the phase boundaries in the following manner:

$$\text{Rate} \propto \frac{\text{Partial pressure of A}}{\frac{1}{k_g a_b M} + \frac{1}{k_l a_b} + \frac{1}{k_c a_p} + \frac{1}{k a_p n}}$$

where k_g , k_l , and k_c are mass-transfer coefficients for the gas film within the gas bubbles and for the liquid films surrounding the bubbles and the catalyst particles, respectively; k is the first-order rate constant; n is the

Fig. IV-49. Concentration Distributions of Gaseous Reactant A and Liquid Reactant C (Shah, 1979)

intraparticle effectiveness factor; a_b and a_p are the area of the bubbles and the external area of the catalyst particles, respectively; and M is the Henry's law constant (Carberry, 1976).

Thus, the first three terms in the denominator represent, respectively, the film resistances for the gas and the liquid at the two interfaces. Of these, the first, the gas film resistance is usually small and can be neglected. The second, the gas-liquid film resistance, is inversely proportional to the area of bubbles, and decreases with increasing number and decreasing size of the bubbles--attainable by good mechanical agitation. The third term, the liquid-film resistance, is proportional to the reciprocal of the external area of catalyst. It can be reduced by using small catalyst particles and by increasing the catalyst loading, i.e., the amount of catalyst charged per unit reactor volume, while maintaining uniform catalyst distribution by adequate agitation.

The fourth term in the denominator, the kinetic resistance, is the reciprocal of the chemical reaction rate, which in turn is the product of three factors: the rate constant, the external area of the catalyst particles, and the intraparticle effectiveness factor, a measure of the utilization of the internal surface area of catalyst. The effect of catalyst particle size and loading is the same on the kinetic resistance as on the liquid-film resistance; use of smaller particles and higher loading reduce it. The effectiveness factor has a complex relation with the rate constant, the diffusion coefficient of the reactant, the catalyst particle size, and the porosity of the catalyst particle.

As increasing the diffusion into the pores of the catalyst raises the effectiveness factor, other things being equal, the use of catalyst particles that are smaller and have wider pores raises this factor and the overall rate.

Because of the involvement of relatively large molecules and of liquid reaction media in both coal and biomass liquefaction, the particle- and pore-size effects should be especially pronounced on the diffusivities, effectiveness factor, and overall reaction rate.

In applying the above conclusions to other coal- and biomass-liquefaction processes, the following points need consideration:

- The dissolution of coal in hydrogen-donor solvents is not a simple physical process, but represents a chemical degradation reaction, usually entailing hydrogen transfer from the solvent.
- The gas-liquid-solid interactions in the liquefaction of wood by carbon monoxide in the presence of sodium carbonate and recycle oil are not analogous to those occurring in coal liquefaction via the hydrogen-donor concept for these reasons. In the case of wood liquefaction, the direct formation of sodium formate according to

and the subsequent reduction of ketonic intermediates, formed from wood hydrolysis products by dehydration and isomerization, by the formate ion are important steps (Appell, 1977).

2.1.2 BIOMASS LIQUEFACTION

The major objective of biomass liquefaction is the production of liquid fuels of high calorific value. This can be accomplished by reduction in molecular weight (depolymerization) and removal of oxygen, since the H/C ratio of biomass resources is generally in the same range as that of liquid hydrocarbon fuels. There are two approaches to the removal of the oxygen with concomitant depolymerization. These are reduction of biomass with carbon monoxide or synthesis gas, and pyrolysis. From the economic point of view, processes which utilize carbon monoxide or synthesis gas for oxygen removal from biomass by carbon dioxide formation are more advantageous than processes that use hydrogen because this expensive reagent primarily ends up as water in biomass liquefaction. This contrasts with coal liquefaction, in which hydrogen is

incorporated into the liquid product. In pyrolysis of biomass, the principal reactions are depolymerization by cracking; oxygen removal is accomplished by dehydration, decarbonylation, and decarboxylation reactions.

This section includes a brief discussion of the relevant system parameters for the liquefaction of biomass by these approaches, and a description of processes under development. Processes for biomass liquefaction with carbon monoxide or synthesis gas originated from early studies at the Pittsburgh Energy Research Center (PERC), and are currently being developed at the PDU stage in Albany, Oregon.

The PERC studies were carried out on a variety of biomass materials in batch autoclave studies, and provided the following information on the influence of process conditions, solvents, and catalysts (Appell, 1977; El-Saied, 1977; Oelert and Siekman, 1976).

- Reaction system. Plant biomass consists of cellulose, hemicellulose, and lignin, the relative proportions of which vary with the nature of the biomass material. Cellulose is usually the most abundant component. Most liquefaction experiments at PERC were conducted at high pressure, and the reactor charge consisted of biomass feedstock (or pure cellulose), water, and an alkaline catalyst. The unit was pressurized with carbon monoxide, and the temperature raised to around 350°C, where it was maintained for a specific time with respect to the heating and cooling times. It is probable that reactions occur during the heating period which introduce ambiguities in the experimental conclusions. Autoclave designs for minimizing the effects of heat-up and cool-down periods on the results of liquefaction studies have been developed by Battelle-Pacific Northwest Laboratories. The product oil is commonly retrieved from the total product material by Soxhlet extraction, using acetone as the solvent for runs conducted below 300°C (572°F), and benzene for runs above this temperature.

- Reaction temperature. At a liquefaction temperature of 250-400°C (482-752°F) a variety of feeds may be converted to oils, but materials of high lignin content such as tree bark are more difficult to convert. The oil formed at 380°C (716°F) is a free-flowing liquid, with a viscosity of 650 centistokes at 50°C (122°F). Operation at 250°C (482°F) produces a solid or semisolid product (a bitumen) (Appell, 1977). Product carbonization occurs at temperatures above 400°C (752°F). Because the pressure developed at 250°C (482°F) is about 1500 psig, and 5000 psig at 400°C (752°F), operation in the lower temperature range has practical advantages.
- The influence of water. Water is a necessary component in biomass liquefaction. It apparently forms hydrogen by the shift reaction, aids in the hydrolysis of high-molecular-weight carbohydrates, acts as a solvent for the reaction, and decreases the extent of polymerization of water-soluble intermediates. The necessity for water in biomass liquefaction has several important practical implications. The operating pressure is substantially increased because of the high vapor pressure of water at the reaction temperatures. Also, there is a large thermal requirement to heat and vaporize the water.
- The influence of carbon monoxide. Carbon monoxide is commonly used as the reducing gas, as such, or in the form of synthesis gas. Synthesis gas costs less, but its use requires slightly higher pressures for obtaining the same results as with pure CO. Synthesis gas gives the same product oil quality as CO does. Carbon monoxide can react directly with oxygen in the biomass to form CO₂, or with water via the shift reaction to produce H₂, which in turn reacts with biomass.
- The influence of a catalyst. Sodium carbonate is an effective catalyst for the liquefaction of biomass, giving over 90% conversion, and an oil product yield of 45-50%. Other water-soluble compounds, such as hydroxides, bicarbonates, and formates of alkaline metals and alkaline

earths may also be used (Appell, 1977). The role of these catalysts in the liquefaction of biomass is not clear. However, it is postulated (Appell, 1977; Molton, 1978) that alkaline salts are converted by CO to formates, which then act as reducing agents by transferring hydrogen to unsaturated and oxygenated compounds. The hydrogen transfer step regenerates the alkaline in situ. Friedman et al. (Friedman, 1972) propose the following reaction sequence:

Initial reaction:

The alkali carbonates act also as catalysts for the water-gas shift reaction:

The resulting H₂ can react directly with the biomass feed to remove oxygen:

The above reactions may be written in terms of CO only (Friedman, 1972):

It has also been proposed that alkaline salts may have a beneficial effect by neutralizing the organic acids produced, which otherwise could promote char formation (Appell, 1977).

The other approach to the liquefaction of biomass is pyrolysis, or thermal decomposition in the absence of O_2 , H_2 , CO, or catalyst. This method has been investigated by Occidental Research Corporation, Oil Shale Corporation, and Tech-Air. In pyrolysis, the heat is supplied to the feedstock directly or indirectly, for example by mixing it with recycled hot ceramic balls, char, or ash. The pyrolysis reaction time is usually short. The products contain liquids, gases, and char, the proportion of which depends on the nature of the biomass, the reaction temperature, and the reaction time. Rapid heating to reaction temperature and rapid quenching of product vapors maximize liquid yields (Jones, 1978). Long reaction times favor the production of higher gas yields. In general, up to 60% of feedstock mass (dry basis) is converted to liquids and gases, and the remainder to char (Garrett, 1977).

2.1.3 COAL LIQUEFACTION

Coal is solid because of its low hydrogen content, characterized by H/C ratios in the range of 0.2-0.8. To liquefy coal, this ratio must be increased, either by the removal of carbon or by the addition of hydrogen.

When coal is heated to 450°C (842°F), its highly complex molecules are broken up into fragments that can either polymerize to char or form oil by reacting with hydrogen according to:

Char formation (1) can occur thermally or by acid catalysis, while oil formation (2) requires activation of molecular hydrogen by an appropriate hydrogenation catalyst or hydrogen transfer from a hydrogen-rich hydrocarbon, the so-called hydrogen-donor solvent. In some cases, mineral constituents of coal, and also AlCl_3 , SnCl_2 , or ZnCl_2 can serve as hydrogenation catalysts. The oil yield depends on the relative rates of reactions (1) and (2) and will be affected, therefore, by the nature of the catalysts present, the temperature, and the hydrogen pressure.

Coal-liquefaction processes can be divided into three groups:

- Hydroliquefaction processes. The Project Lignite Process, under development by North Dakota University, is an example of this approach, in which coal slurried in water is reacted with a H_2 -CO mixture, or H_2 at 1500-2500 psi and 400°C (752°F), with the natural minerals present in the lignite acting as the catalyst.
- H_2 -donor-solvent processes. In this type of process, a solvent having a relatively high H/C ratio is used as the hydrogen source to supply activated hydrogen for the thermally generated coal fragments. The following processes belong in this category: Consol Synthetic Fuel (CSF) H-Coal, Solvent-Refined Coal (SRC), and Exxon Donor Solvent (EDS).

In the hydrogen-donor solvent process, the solvent is exposed to elevated temperatures and pressure. Unconverted coal and ash are separated from

the liquid products, which are fractionated. A certain fraction is then hydrogenated to produce the hydrogen-donor solvent for recycle.

Typically, this hydrogenation is conducted in a trickle-bed reactor in the presence of a cobalt-molybdenum-based catalyst.

- Pyrolysis-hydropyrolysis processes. In these processes, the coal is heated to produce gas, liquids, tars, and chars. The reaction time is an important variable and is determined by the temperature and the reactor employed. The product liquids and tars are separated and in some cases, are further hydrotreated to produce low-sulfur liquids. The gases produced are used as process fuel. The char can be gasified to produce syngas ($\text{CO} + \text{H}_2$), which is scrubbed to remove H_2S and then may be used to produce SNG, electrical power, or more liquids via Fischer-Tropsch technology.

Examples of this type of process are the FMC-COED, Oil Shale Corporation-Toscoal, Occidental Flash Pyrolysis, and Rockwell Fast Hydropyrolysis processes.

In the last two processes, the total residence time of the coal in the heat-up, reaction, and quenching zones of the reactor is extremely short, of the order of milliseconds. Under these conditions, the coal disintegrates to highly reactive fragments which can form, on quenching, stable products of various molecular weights in the presence of H_2 .

2.2 BIOMASS-LIQUEFACTION TECHNOLOGIES

Because only three processes will be discussed in this section, a subdivision into catalytic and noncatalytic processes will not be made. It is noted, however, that the PERC/Albany depends on the use of sodium carbonate as the catalyst, while the Flash and Wood Pyrolysis processes are noncatalytic.

2.2.1 PERC/ALBANY PROCESS (Bureau of Mines Pittsburgh Energy Center)

This process is based on early studies of the Bureau of Mines Pittsburgh Energy Research Center (PERC), which showed that various biomass materials could be converted into an oily material by treatment with CO in the presence of alkaline catalyst at elevated temperature and pressures (Appell, 1977).

The construction of a process development unit in Albany, Oregon, for the liquefaction of wood chips was started in 1974. The original process is shown schematically in Fig. IV-50. Wood chips are dried, ground, blended with recycle oil, preheated, and reacted with CO in the presence of Na_2CO_3 at 350°C (662°F) and 100-250 atm in an electrically heated, stirred autoclave. The product leaving the reactor is cooled, freed from unreacted material and catalyst by centrifugation. It has the characteristics of a fuel, and part of it is used as recycle oil for slurring the wood chips. The CO needed is derived from wood chips by partial combustion.

The plant has been plagued with difficulties from the beginning. First it was operated by Bechtel, who had to bypass the autoclave and the centrifuge because of mechanical troubles. The preheater was subsequently utilized as the reactor. The oil yield, 35% (based on the wood consumed) represented 54% of its energy. The oil has low N, S, and ash contents, but it is unstable, as it tends to polymerize in storage.

More recently, the operation of the Albany facility was taken over by the Wheelabrator Cleanfuel Corporation, and its process was analyzed (SRI, 1979).

2.2.2 FLASH PYROLYSIS (Occidental Research Corporation)

The Flash Pyrolysis process, originally designed for coal pyrolysis (see Sec. 2.3.2.2) is applicable to a variety of organic materials such as animal waste, rice hulls, fir bark, grass straw, forest residues, sewage sludge, and municipal solid waste (Preston, 1976; Longanbach, 1976; Poher, 1977). The process has been developed in a 4-ton/d pilot plant in LaVerne, California. Recently a 200-ton/d

Fig. IV-50. Albany PDU Schematic (as built).

demonstration plant has been built near San Diego for the processing of municipal solid waste to produce 200 bbl/d of fuel oil, but technical problems have necessitated shutdown.

In this pyrolysis process, finely shredded organic material entrained by recycled product gas is exposed to high temperature for a short time in the absence of oxygen or catalysts. The feed is converted into char, gases, and oil. The heating is provided by hot char or ash, which is admixed to organic material in a highly turbulent gas stream to ensure good heat transfer. The hot char and ash result from the combustion of part or all of the char in a separate unit in which the circulation of the solids is arranged so that combustion gases and product gases are not mixed. The pyrolysis occurs at 510°C (950°F) at atmospheric pressure and takes only seconds. On leaving the reactor, the char and product vapors are separated in a cyclone, the char is burned in a separate unit, and the hot ash and remaining char are recycled to the pyrolyzer to supply the heat for the pyrolysis.

The vapors are quickly quenched to prevent further cracking, and the resulting products are separated into pyrolytic oil, gas, and water. The product gas is burned to provide heat for the driers, and some of the water formed is incorporated into the oil to control its viscosity. The approximate yield of oil is 0.2 lb/lb of dried refuse.

Typical properties of flash-pyrolysis (FP) oil and of No. 6 fuel oil are summarized in Table IV-22. The following differences are evident:

- FP oil contains significantly less sulfur.
- FP oil has substantially lower heating value.
- FP oil has higher viscosity and requires higher pumping and atomization temperatures.

TABLE IV-22

TYPICAL PROPERTIES OF NO. 6 FUEL OIL AND FLASH-PYROLYSIS OIL
(POBER AND BAUER, 1977)

<u>Characteristic</u>	<u>No. 6 Fuel Oil^b</u>	<u>Flash Pyrolysis Oil</u>
Composition, wt%		
Carbon	85.7	57.0a
Hydrogen	10.5	7.7a
Sulfur	0.7-3.5	0.2a
Chlorine	---	0.3a
Ash	0.05	0.5a
Nitrogen	2.0	1.1a
Oxygen	---	33.2a
Specific gravity	0.98	1.30a
HHV, Btu/lb	18,200	10,600a
Btu/gal	148,800	114,900a
Pour point, °F	65-85	90 ^b
Flash point, °F	150	130 ^b
Viscosity,		
SSU at 190°F	340	1,150 ^b
Pumping		
temperature, °F	115	160 ^b
Atomization		
temperature, °F	220	240 ^b

^aDry basis.

^bFlash-pyrolysis oil containing 14% water, as marketed.

Because of its slightly acidic properties, FP oil causes corrosion when stored in mild steel tanks. It undergoes degradation during storage at temperatures above 71°C (160°F).

2.2.3 WOOD PYROLYSIS PROCESS (Tech-Air)

This process has been under development for a number of years and is about to be used in a 50-ton/d commercial type (Knight et al., 1977).

According to a recent process analysis, this process operates as follows (SRI, 1979): Dried wood chips mixed with recycle oil and recovered solids are pyrolyzed by exposure to rising hot combustion gases, generated by air combustion of part of the char formed, and leave the pyrolyzer reactor at the bottom at 425-537°C (800-1000°F), while gases, oil, and entrained solids exit at 175-260°C (350-500°F). The reactor pressure is slightly above atmospheric. The pyrolysis gases are quenched by recycle oil in a venturi mixer, freed from entrained oil, used for wood drying, and eventually burned for power generation. The solids are removed from the oil by rotary vacuum filtration and are recycled in the form of filter cake to the pyrolyzer. The oil produced, representing 25% of the weight and 32% of the heating value of the dried wood charged, is low in sulfur, nitrogen, and ash, and has good burning characteristics. However, it is acidic and heat-sensitive, requiring special measures to prevent corrosion and gelling (Knight et al., 1977). Because the oil contains some carcinogenic compounds, it must be handled with caution. The char yield is 28%, representing 42% of the heating value of the wood.

2.3 COAL-LIQUEFACTION TECHNOLOGIES

2.3.1 CATALYTIC PROCESSES

The first four processes described in the following pages are based on the hydrogen-donor solvent principle and differ from each other in the way that the donor solvent is regenerated by hydrogenation. Three of these processes use

added catalysts, while the fourth (SRC) depends on the catalytic activity of mineral constituents naturally present in coal. The fifth process, the liquefaction of lignite by treatment with syngas in an aqueous medium, also utilizes catalysis by such ingredients.

2.3.1.1 Consol Synthetic Fuel (CSF) Process (Consolidated Coal Company)

Crushed and dried coal is slurried with a hydrogen-donor solvent in the proportion 1:2, pumped to 400-500 psia, and heated to 400°C (750°F). After a 40-min reaction time, the gases formed are separated, and ash and unreacted carbon are filtered off. The gases are desulfurized and are used for fuel. Solvent and dissolved coal are then catalytically hydrogenated in an ebullient catalytic reactor at 450°C (840°F) and 4200 psia with approximately 16,000 scf per ton of coal. The hydrogen-donor solvent is separated from the resulting synthetic crude oil by distillation and recycled (EPRI, 1976; Considine, 1977).

The flowsheet for the process is shown in Fig. IV-51.

2.3.1.2 Exxon Donor-Solvent (EDS) Process (Exxon Research and Engineering Company)

In this process crushed coal is liquefied in a tubular reactor at 427-471°C (800-880°F) and 1500-2000 psi in the presence of gaseous H₂ and a hydrogen-donor solvent, but in the absence of a catalyst. The hydrogen-donor solvent is a catalytically hydrogenated, 204-454°C (400-850°F) boiling fraction recovered from the liquid coal product by fractional distillation. The hydrogenation catalyst does not come into contact with coal and is thus ensured longer life and higher activity. The hydrogenated donor solvent is mixed with the reactor through a preheater (Exxon, 1978).

As shown by the flow diagram in Fig. IV-52, the slurry leaving the reactor is separated by distillation into gas, solvent, distillates, and a vacuum bottom slurry, which is coked to gas and additional liquids. The solvent fraction is hydrogenated and recycled. The gases formed in the liquefaction and in the coking are used for H₂ production and process fuel.

Fig. IV-52. Exxon Donor-Solvent Process (Exxon, 1978).

The EDS process is thus distinguished from similar coal-liquefaction processes by the catalytic hydrogenation of the solvent before its admixture to coal and by not using mechanical separation of solid and liquid products.

In terms of initial activity, Ni-Mo oxide on alumina is the preferred catalyst for solvent hydrogenation. Using Illinois bituminous coal, the EDS process yields 47 lb of C₃+ coal liquids per 100 lb of coal.

A 250-ton/d pilot plant was constructed in Baytown, Texas, and became operational in June, 1980. The \$240 million cost of the project has been underwritten by DOE and an industrial consortium consisting of an Exxon subsidiary, Phillips, Atlantic Richfield, EPRI, and Japan Coal Liquefaction Development Company (Chem. Week, 1978).

2.3.1.3 H-Coal Process Hydrocarbon Research

This process is a variant of the H-Oil process developed by Hydrocarbon Research earlier for the hydrogenation of heavy-oil residues (EPRI, 1976) and entails the use of a slurrying solvent and catalytic hydrogenation in a fluidized bed just as does the CSF process (Sec. 2.3.1.1). The processes differ in the sequence of hydrogenation and solids separation. In the H-Coal process hydrogenation precedes separation, while the CSF process separates the solids first.

The 1:2 finely crushed coal-solvent slurry is recirculated through a mixing tank and is then pumped at 2750 psia through a fired preheater into a specially designed fluidized ("ebullated")-bed catalytic reactor (see Fig. IV-53), which ensures good contact between gaseous, liquid, and solid reactants and the cobalt molybdate catalyst, and allows catalyst circulation, withdrawal of used catalyst, and addition of fresh catalyst during continuous operation with this multiphase system. The particle size of the catalyst is sufficiently large to prevent catalyst losses by entrainment with the slurry or vapor streams leaving the reactor.

Fig. IV-53. Ebullated-Bed Reactor, H-Coal Process (EPRI, 1976).

The hydrogenation is carried out at 454°C (850°F) and 2700 psia in 30 to 60 min and required 12,600 scf of hydrogen per ton of coal.

The gases are separated from the slurry leaving the reactor, then desulfurized and partly recycled to the reactor. The liquid products are freed of ash and unreacted carbon by filtration or other methods. Then the solvent is recovered by vacuum distillation and recycled.

The H-Coal process flowsheet is shown in Fig. IV-54.

2.3.1.4 Solvent-Refined Coal (SRC) Process (Pittsburgh & Midway Coal Mining Company)

There are two versions of this process (EPRI, 1976). In the 6-ton/d Wilsonville, Alabama, pilot plant the feed is bituminous coal (crushed to pass 200 mesh), slurried with solvent in the proportion 1:1.5-3. It is recirculated through a mixing tank and then pumped, together with hydrogen and recycle gas, through an oil-fired preheater into the hydrogenation reactor-dissolver at 458-471°C (800-890°F) and 1800 psia. This reactor is a vertical cylinder without any internal mixer. The reaction is noncatalytic, and takes about 30 min and consumes approximately 9000 scf of H₂ per ton of coal. On leaving the reactor, the product is cooled, and the gases are separated, desulfurized, and partly recycled with the coal slurry. After the pressure is reduced, the product is freed of ash and unreacted carbon by filtration, and from the solvent by vacuum distillation. The solvent is recycled. The remaining material, SRC, which is liquid above 149-204°C (300-400°F), is solidified on water-cooled plates.

The SRC II process operated in a 30-ton/d pilot plant in Fort Lewis, Washington, uses more severe conditions [2000 psig, 449-465°C (840-870°F), and 20,000 scf H₂ per ton of coal] to convert coal into an ashless liquid fuel containing less than 0.5% sulfur.

Fig. IV-54. Process Flow in the H-Coal Process (EPRI, 1976).

In this process the products from the dissolve-reactor are separated into gases and liquids. The gases are desulfurized and worked up to LPG, methane, and H₂, the last-mentioned for recycle into the reactor. Part of the liquid product containing suspended mineral constituents is returned to the mixing tank; the minerals serve as the catalysts in the liquefaction. The rest of the liquids, together with light liquid condensate from the gaseous products, is fractionated into naphtha and fuel oil, some of the latter is taken over in a vacuum tower. The residue containing the mineral constituents is treated with O₂ and steam at 1370°C (2500°F) to produce CO and H₂, which is converted to pure H₂ via the water-gas shift reaction, and removal of CO₂ and H₂S. The H₂ is recycled to the reactor, while the mineral ash is recovered in the form of slag for fill.

Typical data on the Wilsonville SRC operation are given in Table IV-23. The process flowsheet is shown in Fig. IV-55.

2.3.1.5 Project Lignite (University of North Dakota)

This process, also known as solvent-refined lignite (SRL) process, consists in treating lignite with a CO-H₂-water mixture at 1500-2500 psi at approximately 400°C (750°F). It gives a product, SRL, with these characteristics:

Molecular weight	~450
Analysis, %	
C	89
H	6
O	3
N	1
S	1
Inorganic	nil

According to NMR, SRL is highly aromatic and has one acid group and 0.1 base group per average molecule. Ninety percent of the SRL can be converted by catalytic hydrogenation into gases and 20% light liquids, 15% light oil, and 20% heavy oil. The best catalyst for this hydrogenation is Ni-Mo/Al₂O₃, and the optimum conditions are 450°C (842°F) and 3500 psi.

Table IV-23
WILSONVILLE SRC OPERATIONS (Wolk, 1976)

Coal Source

State	Kentucky	Pennsylvania	Illinois	Illinois	Wyoming
Mine	Colonial	Loveridge	Burning Star	Monterey	Belle Ayr
Seam	9 and 14	Pittsburgh 8	6	6	Roland Smith

Feed Coal

Sulfur Content (%)	3.1	2.6	3.1	4.4	0.7
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Process Parameters

Temperature (°F)	800-850	855	820	855	855
Pressure (psig)	1500-2400	1700	1800	2400	2400
Coal Conversion (%)	91-95	91	90	95	85
SRC Output					
Yield (%)	55-65	69	63	54	47
Sulfur content (%)	0.8	0.9	0.9	0.95	0.1

Fig. IV-55. Process Flow in the SRC Process, Wilsonville (EPRI, 1976).

This process depends on the catalytic action of naturally present alkaline mineral constituents (Oelert and Siekman, 1976). A related process accomplishes coal liquefaction and desulfurization by treatment with syngas in the presence of cobalt molybdate and sodium carbonate catalysts, steam, and recycle oil (Fu and Illig, 1976).

2.3.2 NONCATALYTIC PROCESSES

Of the following pyrolysis processes, one uses direct heating by hot combustion gases, two use indirect heating by hot char and ash or ceramic balls, and one employs high-temperature hydrogen as a reactant and heating medium.

2.3.2.1 FMC-COED Process (FMC Corporation)

In this process coal is converted into gas, oil, and char in several stages in three fluidized-bed reactors. Part of the char produced is heated with oxygen and steam in the fourth (last) stage at 871°C (1600°F), and the resulting hot gases are used to heat and to completely devolatilize the char in the second and third stages, occurring in a two-stage reactor operating at 454 and 538°C (850 and 1000°F), respectively. The gases leaving the second stage are scrubbed with water to separate the oil and are used as synthesis gas (EPRI, 1974). The coal entering the process is first dried at 190°C (375°F) in a fluidized drier by combustion gases obtained by burning a portion of the char, then it passes to the first-stage fluidized reactor, where it is partially devolatilized at 315°C (600°F) by contact with hot air. The gas streams from this reactor and drier are freed from suspended oil by water scrubbing and are used to cool the hot char leaving the last stage. The char passes from the first-stage reactor successively through the other three stages in the subsequent two reactors. The process-flow scheme is shown in Fig. IV-56.

The product gas has a sufficiently high Btu content for conversion into pipeline gas. The pyrolysis oil yields synthetic crude on being hydrotreated.

Fig. IV-56. Process Flow Diagram for FMC-COED (EPRI, 1974).

2.3.2.2 Flash Pyrolysis (Occidental Research Corporation)

This process was originated by Garrett Research and Development Co., Inc., which was subsequently acquired by Occidental. Its objective is rapid pyrolysis of coal particles to produce gases and liquids; the heat is provided by hot char or ash particles entrained by pyrolysis gas. The hot char or ash is generated by combustion of part or all of the char in a separate unit, in such a way that mixing of combustion and pyrolysis gases is avoided (EPRI, 1974; Longanbach and Bauer, 1976).

The conceptual flow scheme of the flash-pyrolysis process is shown on Fig. IV-57. Pulverized coal is fed at 50 psig into the center vessel, where it comes into contact via turbulent pyrolysis gas with hot char and ash particles descending from the cyclone at the top. The coal particles reach 870°C (1600°F) in less than two seconds. The pyrolysis gas is separated from the char in cyclones, from which part of the char is fed to the combustion chamber (lower left). The combustion gases lift the hot ashes and its residual char in the upper cyclone, from which the hot particles enter the pyrolysis loop. The tar oil is recovered by condensing the vapor in the pyrolysis gas.

The rapid heating maximizes the production of gas and tar oil. The product distribution from a Big Horn, Wyoming, subbituminous coal is shown in Fig. IV-58.

The advantages of this process are the good-quality pipeline gas and relatively simple operation. Its disadvantages are connected with the presence of sulfur in all four products: pyrolysis gas, combustion gas, oil, and char; the unsuitability of the process for handling eastern bituminous coals; and disposal of excess char.

Applications of this process in treating biomass are discussed in Sec. 2.2.2.

Fig. IV-57. Conceptual Schematic of the Garrett Flash-Pyrolysis Process (EPRI, 1974).

Fig. IV-58. Product Distribution in Garrett Coal-Pyrolysis Process (EPRI, 1974).

2.2.2.3 Toscoal Process (Oil Shale Corporation)

This process, originally developed for oil shale treatment, provides the heat needed for pyrolysis by circulating hot ceramic balls about 1/2-in. in diam heated by air combustion (see Fig. IV-59). The hot flue gases are used to preheat incoming coal but are not allowed to admix with the pyrolysis products which form on contacting the coal with the hot balls and steam at 482-521°C (900-970°F) in a pyrolysis drum. The char formed is separated from the balls in a trommel and passed on to a cooler. The balls are raised by an elevator and then fed by gravity to a heater and recycled. The pyrolysis gases, vapors, and entrained tar are fractionated, and part or all of gases is used in the ball heater (EPRI, 1974).

2.3.2.4 The Rockwell Flash-Hydropyrolysis Process (FHP) (Rockwell International)

This process is based on a very rapid reaction between coal and hydrogen heated to high temperature. High liquid yields are obtained at short reaction times on rapid quenching. The concept was experimentally investigated in 1/4- and 1-ton/h coal processing units. Figure IV-60 is a schematic of the 1/4-ton/h reactor, and Fig. IV-61 is the flow diagram for the 1/4-ton/h pilot plant.

Pulverized coal is fed in dense phase directly into the reaction chamber, where it is rapidly mixed with hydrogen that is preheated to approximately 1090°C (2000°F). Reactor wall temperature is usually maintained at around 815°C (1500°F) to eliminate plugging due to wall adhesion when caking coals are processed. The flash hydropyrolysis is conducted at 500 to 1500 psi. The mixing and reaction times are controllable variables, and coal residence times in the reactor range from 30 to 650 ms.

The reaction products pass from the reactor chamber into the quench zone cooled by a water spray. A proprietary heat exchanger serves to separate gas-liquid products from the char and provides efficient heat recovery. Rockwell claims that no filtration is required in this scheme because the liquid products are recovered from the vapor phase. The dry char produced is suitable for

Fig. IV-59. Oil Shale Corporation's Pyrolysis-Type Process for Producing Fuel Gas from Coal (EPRI, 1974).

Fig. IV-60. Schematic Diagram of ¼-ton/h Rockwell Reactor Assembly (Rockwell, 1977).

Fig. IV-61. Flow Diagram of 1/4-ton/h Rockwell Reactor Test System (Rockwell, 1977).

gasification to H_2 . Temperature, pressure, and residence time influence the product distribution of gaseous, liquid, and solid products and their composition.

Figure IV-62 shows the effect of reactor temperature on carbon conversion. Conversions around 60% are reported. According to Rockwell, this is consistent with the requirements for a commercial plant and with a thermal efficiency of 80%. Figure IV-63 shows the effect of residence time on carbon conversion. Approximately 50% of the liquid products boil below $343^\circ C$ ($650^\circ F$). Sulfur and nitrogen levels are 0.3 and 0.9%, respectively, in the $+93^\circ C$ ($+200^\circ F$) fraction. The yield of benzene, toluene, and xylene is up to 11% of the carbon feed. The gaseous product consists of ~85 vol% CH_4 , 10% CO , and 2% C_2 , and has an approximate heating value of ~900+ Btu/scf.

In the experimental unit, the hydrogen is fed through electrical heaters and partially combusted with oxygen. The high preheat temperature of $1090^\circ C$ ($2000^\circ F$) will present technical problems for a commercial process based on this technology. Also, efficient heat recovery will be of crucial importance for accomplishing satisfactory energy economy.

2.4 PERSPECTIVE FOR THE TECHNICAL LIMITATIONS IN LIQUEFACTION

The first four of the catalytic coal-liquefaction processes discussed depend on the solubility of coal in liquids derived from coal by hydrogenation. They involve the partial hydrogenation of the coal, either directly or via hydrogen transfer from the catalytically hydrogenated donor solvent, and the use of a hydrogenation-desulfurization catalyst, which is either added or is provided by some of the naturally-present mineral ingredients of coal.

These processes differ from each other mainly in using one or two steps for the coal liquefaction and for the hydrogenation of the solvent, and in recovering the liquid products by solid separation or by other methods.

Fig. IV-62. Effect of Reactor Temperature on Carbon Conversion (Rockwell, 1977).

Fig. IV-63. Effect of Reactor Residence Time on Carbon Conversion (Rockwell, 1977).

Among them, the H-Coal process is the simplest and involves the reaction of a preheated solvent-coal slurry with hydrogen in the presence of a catalyst, the particles of which are sufficiently large to be separable from the finer mineral and the unreacted coal and char particles. The limitations of the process are the exposure of the catalyst to the deactivating ingredients present in coal; the use of the catalyst in large particle sizes, which precludes optimum utilization of its activity; and the difficulties connected with the solid/liquid separation used.

The SRC process is essentially analogous to H-Coal process, but utilizes the natural minerals in the coal as catalysts.

In the Consolidated process, the hydrogenated donor solvent reacts first with coal in the absence of a catalyst. After the separation of solids and gases, the liquid is catalytically hydrogenated at 4200 psi. The solvent is recovered by fractional distillation.

The Exxon process avoids the problems of mechanical solid-liquid separation by recovering the liquid products from the reactor effluent by distillation. This procedure allows the hydrogenation of the solvent fraction without bringing the catalyst into contact with the higher-boiling product fractions and exposing it to their deactivating effect. However, the process requires an additional coking step for recovering liquid products from the distillation residues. The start-up of a 250-ton/d pilot plant based on this process seems to be an indication of the overall usefulness of the Exxon route.

The Project Lignite process uses syngas for coal liquefaction, and takes advantage of the catalytic activity of alkaline mineral constituents present in coal. In this process and in a related one employing cobalt molybdate-sodium carbonate as the catalyst, the carbon monoxide in syngas is utilized as a source of hydrogen for hydrogenation and desulfurization via the water-gas shift reaction catalyzed by alkali.

Of the noncatalytic coal-liquefaction processes, three depend essentially on pyrolysis, while the fourth uses high-temperature hydrogen as a reactant.

In the FMC-COED process, combustion gases heat the coal directly in a system of four fluidized reactors to successively higher temperatures, producing liquids, gases, and char. The complex reactor staging prevents agglomeration of coking coals and allows the char formed to pass through all reactors for eventual partial combustion in the last stage. The complicated reactor system and the relatively low liquid yield are shortcomings of this process.

The Flash Pyrolysis and Toscoal processes use hot char and hot ceramic balls, respectively, as indirect heating media in order to prevent the mixing of the combustion gases with product gases. Since the processes produce mainly gases and char, and only minor quantities of liquids, they show little promise as routes to coal liquefaction.

In the Rockwell process, hydrogen heated to 1093°C (2000°) reacts with coal for very short contact times to yield liquid products. The high reaction temperature, heat economy, and hydrogen consumption are expected to present problems in the commercial scale-up of this process.

While there is no biomass-liquefaction process analogous to coal liquefaction via the hydrogen-donor solvent method, the PERC/Albany and Flash Pyrolysis processes for biomass liquefaction (Secs. 2.2.1 and 2.2.2) have evident similarities to the Project Lignite and Flash Pyrolysis processes for coal liquefaction (Secs. 2.2.1.5 and 2.3.2.2).

According to a process study by SRI International, the overall reaction in the PERC/Albany process for the liquefaction of the wood used can be represented as

and gives 0.37 lb of oil per lb of dry wood. The oil contains 23.2% O and has a heating value of 14,000 BTU/lb (SRI, 1979). In addition to materials-handling

problems revealed in the operation of the 2-ton/d pilot plant, the major shortcoming of the PERC/Albany process is the instability of the product oil, resulting in polymerization on storage. Another potential problem of the oil is the corrosiveness reported for a similar product, for oil derived from cellulose by alkaline digestion; this oil caused pipeline corrosion and plugging (Morton, 1979).

The Flash Pyrolysis process as practiced in the California pilot and demonstration plant on municipal solid waste yielded approximately 0.2 lb of oil per lb of dried refuse. This oil has a substantially lower heating value than No. 6 fuel oil (10,600 vs 18,200 Btu/lb) and very high viscosity, necessitating the admixture of 14% H₂O to ensure pumpability. Because of its slightly acidic properties, the oil causes corrosion in mild steel tanks. It also undergoes decomposition on storage above 71°C (160°F).

The oil yield of 25% obtained in the Tech-Air pyrolysis process is somewhat better, but it is still below the 35-37% yield of the PERC/Albany process. The limitation of the pyrolysis technique is the relatively high yield (30%) of char, which is an undesirable fuel.

PART V. ASSESSMENT OF THE UTILITY OF COAL-CONVERSION
CONCEPTS FOR BIOMASS

1. GASIFICATION

There are many similarities between the gasification of coal and the gasification of biomass, and yet the past developmental efforts in these two fields cannot be said to have benefited from each other. Typically, the developers of coal technologies have not been involved in biogasifier development, or vice versa. However, with the increased emphasis on biomass as an important national energy source, this past trend is beginning to change.

So far, the developmental effort in coal gasification has been far more extensive than in biomass gasification. Consequently, a variety of coal-gasification processes have undergone semicommercial tryouts. Some of these technologies are specifically geared to meet the difficult engineering problems of coal gasification and may not apply to biomass, but many others are potentially applicable to biogasification.

Biomass has the following general characteristics that make it a more desirable raw material for gasification than coal.

- Lower sulfur and ash content
- Higher reactivity
- Less erosive
- No caking tendency

Thus, it is reasonable to suggest that the majority of coal-gasification processes are potentially applicable to biomass, with appropriate modifications to allow for differences in the physicochemical properties of coal and biomass.

According to a survey conducted by Gorham International, many developers of coal gasifiers confirmed this assessment (Gorham International, 1979).

However, care must be exercised when discussing the feasibility and suitability of coal technologies to biomass. Many coal gasifiers have features that are likely to be of little use in biomass conversion. For example, the decaking feature of the advanced gasifiers such as Synthane, Hygas, U-Gas, Lurgi-BCG, and GEGAS is not critical in biomass gasification. Similarly, process features designed to deal with the problem of the high sulfur and ash contents of coal may not be entirely required for biomass.

1.1 DENSITY DIFFERENCES

Coal and biomass have some similarity in chemical composition, but differ considerably in density. As shown in Table V-1, the particle densities of typical biomass are about half of those of coal. In fact, in comparing coal with dried biomass, this density differential becomes even more pronounced.

Because of low density, biomass is more easily fluidized or entrained than coal. This, in general, is an advantage, especially in connection with solid transport in feed and circulation systems. Conversely, care must be exercised in the design of fixed-bed and fluid-bed gasifiers so as not to allow excessive solid carryovers which would lead to conversion loss.

Most biomass materials are fibrous and have a tendency to form sticky masses when they are subjected to grinding. If wood flour of ultrafine particle size is needed, feedstock preparation would become very expensive due to high energy consumption (Siegel, 1975).

TABLE V-1

PARTICLE DENSITIES OF BIOMASS AND COAL
(Tillmann, 1978)

	Density, <u>g/cc</u>	<u>Moisture, %</u>	Density, <u>g/cc, 5% moisture</u>
White ash	0.75	21.3	0.63
White birch	0.82	35.2	0.57
Pitch pine	0.87	40.7	0.56
Hemlock	0.78	55.1	0.39
White cedar	0.45	35.7	0.31
Fir	0.83	53.8	0.43
Cypress	0.75	46.8	0.44
Anthracite	1.7		
Bituminous	1.4		
Subbituminous	1.3		
Lignite	1.2		

1.2 ASH HANDLING

Ash handling is a matter of great importance to both coal and biomass gasification. Ash from biomass is reported to be lighter (6-15 lb/ft³), extremely friable, and highly conductive, while coal ash is heavier (30-50 lb/ft³), less friable, and less conductive (Tillman, 1978).

Depending on the gasification temperature, ash is discharged as dry ash, agglomerated particles, or quenched slag. Table V-2 lists the softening point, melting point, and fluid point of coal ashes and of some wood bark ashes. When subjected to temperatures between the softening point and melting point, ash particles tend to agglomerate. In the U-Gas and Battelle-Union Carbide gasifiers, these agglomerated ash particles serve as heat carriers and also as a fluidizing medium. In the slagging gasifier, ash is subjected to temperature at or above its fluid point. Examples of coal gasifiers operating in this manner are the Koppers-Totzek, Texaco, and BGC-Lurgi gasifiers. For biomass, the Purox process uses the slagging mode.

Substantial quantities of ash are entrained in the product gas stream. For example, in the Winkler gasifier, about 70% of ash in feed coal is carried out of the reactor by the product gas, while the remainder descends through the fluidized bed. Wood emits relatively few particulates, but a greater proportion of wood ash may be carried overhead because of its lower density compared to that of coal ash.

For the separation of entrained ash from product gas, cyclones, scrubbers, and electrostatic precipitators are commonly used.

1.3 GASIFICATION PRESSURE

Pressurized gasification is commonly used in coal gasifiers, particularly in the second-generation advanced gasifiers, but is rather rare in biogasifiers.

TABLE V-2

TEMPERATURE BEHAVIOR OF ASH FROM COAL AND BIOMASS

	<u>Reducing Atmosphere</u>			<u>Oxidizing Atmosphere</u>		
	Softening temp., °F	Melting temp., °F	Fluid temp., °F	Softening temp., °F	Melting temp., °F	Fluid temp., °F
Coal						
Lignite ash (North Dakota)	2190	2208	2210	2260	2260	2272
Bituminous coal ash (Illinois)	1940	1960	2067	2390	2570	2585
Biomass						
Pine bark ash	2179	2239	2309	2210	2280	2350
Oak bark ash	2691	2719	2739	2680	2730	2750

A high gasification pressure is favored in SNG, synthesis-gas generation, and combined-cycle applications since subsequent compression cost of the gasifier product for downstream processing would not be as much as in the gasifier operation at atmospheric pressure. An EPRI study for methanol synthesis can be used to illustrate this point. The study includes a case involving a Koppers-Totzek atmospheric gasifier and another with a Texaco gasifier operating at 650 psig, both of which are integrated with the ChemSystems methanol synthesis process for the production of 17,288 tons/d of methyl fuel. According to the study, the synthesis-gas compression power required in two cases was: 440,000 hp for the Koppers-Totzek case and a mere 14,000 hp for the Texaco case. It is, however, important to point out that the compression requirement for the oxygen supply to the gasifier was greater for the latter case by 140,000 hp because of the higher gasification pressure. Therefore, a net difference between the two cases becomes the difference between the sum of the synthesis-gas and oxygen-plant compression requirements, and this can be calculated as 286,000 hp. In other words, the K-T case required 62% more compression power to prepare synthesis gas than the Texaco case.

In coal gasification, pressurized-reactor designs are being developed for all types of solid-gas contact systems. The following tabulation provides the reactor type and the representative pressures.

<u>Pressurized Coal Gasifiers</u>	
Fixed-bed	Lurgi (350 psig)
Fluid-bed	U-Gas (350 psig)
	Hygas (1000 psig)
	CO ₂ Acceptor (350 psig)
Entrained-Flow	BiGas (1000 psig)
	Texaco (up to 1200 psig)
Molten-Bath	Atomics International (300 psig)

One of the principal applications of the coal gasifier is integration with a gas turbine. Here, the product gas from a coal gasifier is fed into a gas turbine, which in turn generates electricity. It is anticipated that large power-plant gas turbines will use an expansion ratio of about 16:1 by 1990. Such turbines will then require a feed-gas pressure of about 20 atm to allow for control and other pressure drops (Kohl et al., 1978).

The gasification pressure is less important when product gas is intended for process heating or steam generation. Moreover, process design and operation of a gasifier is much simpler at atmospheric pressures than at elevated pressures.

1.4 CAKING TENDENCY

Caking tendency of coal in gasification is widely recognized as one of the critical design concerns, and a great deal of effort has been spent on overcoming the problem of coal agglomeration in the feeding system and in the gasification zone. On the other hand, biomass materials such as wood appear to have no significant caking tendency unless admixed to char at conditions under which clinkers can form. Biomass starts devolatilization at temperatures in the range of 300-500°C (572-932°F).

1.5 CATALYTIC GASIFICATION

Of the catalytic coal-gasification processes under development, those that use sodium carbonate and other alkali-metal compounds are of particular interest for biomass, in the gasification of which these and related compounds have demonstrated catalytic effects. On the other hand, the ATGAS process, which uses molten iron as a catalyst, a reactant, and a reaction medium, is of less interest for biomass because its extremely high reaction temperature and its operating complexity are not justified in view of the high reactivity of biomass.

The Exxon process (Sec. IV.1.3.1.2) uses an alkali-metal carbonate as a catalyst, and accomplishes gasification in a fluidized reactor at a relatively low temperature, 700°C (1300°F), at 500 psig, under which conditions methane formation is favored sufficiently to allow its direct recovery by cryogenic distillation after the removal of H₂S and CO₂. This process, currently in the 1-ton/d demonstration-plant stage, should be readily applicable to biomass.

Two other processes use sodium carbonate in the form of a molten bath which serves as a catalyst, and a desulfurizing reactant. One of these has been under study by Kellogg for many years, but is now abandoned. The other is being developed by Atomics International.

In the Atomics International process, coal, pulverized to -8 mesh, is mixed with the salt and carried into the molten bath by pressurized air. The gasifier can be operated at about 980°C (1800°F) and up to 30 atm pressure. The pressurized operation is required in order to minimize the formation of sodium carbonate fumes, which causes corrosion problems in downstream equipment.

The advantage of the molten carbonate gasifier is its capacity to:

- Completely gasify solid fuel
- Retain ash in the melt
- Retain sulfur in the melt.

Because of the retention of ash and sulfur by the melt, it is necessary to remove these impurities as they accumulate. This is accomplished by continuously withdrawing a slip stream of the melt and processing it. Some portion of the salt is discarded as spent material, but the remainder is recycled to the gasifier. While the operation of the gasifier is relatively simple, the salt regeneration entails many complex process steps.

In considering the application of the molten-salt gasifier to biomass, the low ash and sulfur contents are the attractive aspects of biomass. Because of the low concentrations of these critical impurities, the size and cost of the salt-regeneration portion of the plant will be significantly reduced. The molten-salt gasifier can handle all coals with only minimal crushing and without requiring sizing since the process accepts fines. In essence, all carbonaceous materials are potential feedstocks to this type of gasifier. The capability to handle all types of material without extensive size reduction is an attractive feature of the molten-salt process in connection with the gasification of biomass.

A few tests have been made in the area of molten-bath gasification of biomass by the following laboratories:

- Anti Pollution Systems, Inc., Pleasantville, N.J.
Molten salt - refuse and sludge
- Battelle-Northwest
Molten salt - refuse
- Michigan Tech. Univ., Houghton, Mich.
(Puretic Pyrolysis System)
Lead bath - forest and agricultural residues

The feedstocks tested in these runs were mostly municipal refuse and sludge. It is not yet known how the molten-salt gasifier will perform on such biomass materials as wood chips, sawdust, and agricultural residues.

For coal gasification, the melt temperatures range between 926 and 1010°C (1700-1850°F). The lower temperature is preferable from the standpoint of fume and corrosion control, while the higher temperatures ensure more complete reaction and lower melt viscosity. With biomass feed, it is quite possible that the required conversion can be achieved at temperatures lower than 926°C (1700°F) in view of the high reactivity of biomass. If so, this will have

significant impact in reducing the corrosiveness and the vapor pressure of the melt; however, the viscosity of sodium carbonate melt will increase as the temperature approaches its melting point of 859°C (1564°F). The viscosity problem can be overcome by using eutectic salt mixtures with lower melting points. Table V-3 lists some of the eutectic mixtures which can be prepared by combinations of Na, K, and Li carbonates.

TABLE V-3

PROPERTIES OF MOLTEN SALT

<u>Salt (weight ratio)</u>	<u>Melting Point</u>	
	<u>°F</u>	<u>°C</u>
Li ₂ CO ₃ (100)	1355	735
Na ₂ CO ₃ (100)	1564	854
K ₂ CO ₃ (100)	1645	896
CaCO ₃ (100)	2444	1340
K ₂ CO ₃ -Li ₂ CO ₃ (38/62)	910	488
K ₂ CO ₃ -Li ₂ CO ₃ (57.3/42.7)	928	498
Li ₂ CO ₃ -Na ₂ CO ₃ (50/50)	941	505
Na ₂ CO ₃ -K ₂ CO ₃ (56/44)	1310	710
Li ₂ CO ₃ -Na ₂ CO ₃ -K ₂ CO ₃ (43.5/31.5/25.0)	747	397

One drawback of these eutectic systems is that potassium carbonate and lithium carbonate, especially, are much more expensive than sodium carbonate:

Bulk Chemical Prices^a,

¢/lb

Sodium carbonate	3
Potassium carbonate	19
Lithium carbonate	93

^aChem. Mark. Rep., 1979.

The high cost of lithium carbonate may virtually eliminate this salt from consideration as a component of the eutectic mixture.

1.6 AIR VERSUS OXYGEN

In situ, partial combustion of the feed is widely used in gasification processes as the means of providing the needed heat. Either air or pure oxygen can be used as the source of oxygen. Air is the choice for most biomass gasifiers, whereas oxygen is frequently used in coal gasifiers, especially in advanced second-generation gasifiers, which operate at high pressures. The question of using air or oxygen in either biomass or coal gasification is a complex issue. Its resolution involves the following:

- (1) Oxygen is required for SNG or synthesis-gas generation except when the gasification is accomplished by the use of a solid heat-carrier such as in the CO₂-Acceptor or the Battelle Multi-Solid Fluidized-Bed processes.
- (2) The heating value of the product gas from an air-blown operation is 160 Btu/ft³, compared with 300 Btu/ft³ for the gas from an oxygen-blown gasification.
- (3) In air-blown operation, each volume of oxygen required is accompanied by 3.8 volumes of nitrogen. This nitrogen dilutes the gasification products and accompanies them through all downstream operations including

ash separation, liquids separation, acid-gas removal, and even into the gas-distribution system. Some of the significant economic penalties of air-blown operation relative to oxygen-blown operation are:

- Larger equipment is required through the gas-handling train.
 - Because of the N₂ dilution, efficiencies in impurity separation steps are lower.
 - In pressurized gasification, a major portion of the oxidant compression energy is spent on nitrogen.
- (4) Oxygen-blown operation requires a very energy-intensive air separation plant.
- (5) Capital investment for an air-separation unit is a significant portion of the cost of an oxygen-blown gasification plant. For example, a 8620-ton/d gasifier using 0.541 ton of oxygen per ton of product gas would require 4663 tons/d of oxygen. The capital investment for an air-separation plant with the rated O₂ capacity is about \$70 million, including the steam plant. In terms of daily oxygen capacity, the capital cost is about \$15,000/short ton of O₂. Note: Plant investment is based on Fluor's EPRI Rept. AF-244, July 1976; cost in mid-75 dollars.

According to the biomass collection schemes currently envisioned, a conversion plant will have an upper-limit capacity of about 2000 tons/d of raw biomass. If a 50% moisture content is assumed, this will lead to 1000 tons/d, based on dry biomass. The O₂ use per ton of dry biomass is typically about 0.5 ton; therefore, about 500 tons/d of O₂ is required in this biogasifier. With respect to commercial practice, the 500-ton/d capacity ranks at the top of the single-train capacity of modern air-separation plants.

1.7 GASIFICATION BY HEAT CARRIER

Several gasification schemes use circulating heat carriers for the gasification of the feed by means of the sensible heat or chemical heat of the carrier. The spent carrier is then regenerated in a separate vessel with air. An attractive feature of this concept is its capability to generate product gas, free of nitrogen contamination. The major processes based on this gasification concept are:

- CO₂ Acceptor (lignite)
- Battelle-Union Carbide Agglomerating-Ash (coal)
- Battelle-Columbus Multi-Solids Fluid-Bed (MSW or biomass)

The CO₂ Acceptor process is currently considered applicable only to lignite or pretreated subbituminous coal, because, among coals, they are the only ones reactive enough to be gasified at the relatively low gasification temperature [815°C (1500°F)] characteristic of the gasifier used in this process. Since biomass is considerably more reactive than lignite, it is very likely that the CO₂ Acceptor concept is applicable to biomass gasification. In this process, the gasification heat is mostly provided by an exothermic reaction of calcined dolomite with CO₂, which occurs in a steam-fluidized reactor charged with intimately mixed coal and hot dolomite. For biomass, the fluidization with dolomite may present some problems because of rather large density difference between the acceptor solid and biomass. In the gasification of

biomass by the CO₂ Acceptor reaction, the low ash and sulfur content of the feed is advantageous since it extends the life of the acceptor solids. Because of the high reactivity of biomass, the gasification may be accomplished at temperatures lower than those required for lignite. If so, this will lower the needed acceptor circulation rate and further extend the service life of the solids.

In the Battelle-Union Carbide process, the gasification heat is supplied in the form of sensible heat in hot, agglomerated ash. The ash agglomerate is produced in a separate vessel, where fresh coal and the circulating ash particles are brought to the ash softening point, 1038-1260°C (1900-2300°F), by air combustion. For biomass application, the feasibility of ash agglomeration must be demonstrated. There is also a question whether such a severe operation is needed for biomass gasification.

In this regard, the Battelle-Columbus Multi-Solids Fluid-Bed (MSFB) process appears more attractive for biomass than does the agglomerated-ash process. In the MSFB process, inert particles are used as the heat carrier; they circulate between the combustor and the gasifier. According to a conceptual design reported by Battelle (Feldman, 1978), gasification of wood is accomplished at 975°C (1787°F) in the combustor and at 750°C (1382°F) in the gasifier, with a solids circulation rate of 12.7 tons/ton of dry wood. This solids circulation rate is considerably higher than that required in the CO₂ Acceptor process, but it is lower than that in the Battelle-Union Carbide process, as can be seen in the following tabulation.

Feed	<u>CO₂ Acceptor</u> Lignite (dry)	<u>Battelle-Union Carbide</u> Eastern coal (15% moisture)	<u>Battelle Columbus</u> N ₂ coal (dry)
Carrier temp., °F			
Combustor	1850	2000	1787
Gasifier	<u>1500</u>	<u>1600</u>	<u>1382</u>
Δt	350	400	405
Carrier rate, tons/ton feed	5.1	20.5	12.7

The low carrier rate for the CO₂ Acceptor process is due to the utilization of the chemical heat. The difference between data for coal and wood gasification in the other two processes is attributable to the following:

- Wood contains less carbon and thus requires less heat for gasification via the endothermic steam-C reaction.
- The exothermicity of biomass during certain phases of gasification lowers the heat requirement.
- The moisture in coal in the case of Battelle-Union Carbide process requires additional heat for vaporization.

The effect of moisture in the feed can be significant because the heat required to vaporize and superheat water to the gasification temperature is about 1700 Btu/lb. Since the available sensible heat of the solid heat carrier is about 110 Btu/lb, a pound of solid fuel containing, e.g., 20 wt% moisture, would require about 3 lbs of heat carrier just for drying.

It has been well recognized in the development of the described gasifiers that solid circulation presents serious design and operating problems, and that minimizing circulation would greatly enhance process feasibility. In this

regard, the observations made above suggest that an attractive biomass gasifier could be based on the CO₂ Acceptor concept if predried feed is used. In such a process, the acceptor circulation could be held well below 5 tons/ton of feed.

1.8 PERSPECTIVE FOR THE APPLICATION OF MAJOR COAL-GASIFICATION PROCESSES TO BIOMASS

Table V-4 presents an overview of twelve major coal-gasification processes. Their significant features, process development status, and prospects for application to biomass are indicated.

2. LIQUEFACTION

Although coal and biomass (as exemplified by wood) are genetically related, their chemical and physical properties differ strikingly.

Coal has lower hydrogen and oxygen contents, but higher sulfur and nitrogen contents than wood. It is more oil-soluble, more hydrophobic, and less reactive than wood. The desired reactions in coal liquefaction are hydrogenation and desulfurization. On the other hand, wood liquefaction requires reduction as the main reaction, but little or no desulfurization.

Therefore, one would expect that wood liquefaction would require methods different from those used for coal liquefaction. Still, there are a number of common features of coal and biomass-liquefaction processes which are due to the following remarkable similarities in certain properties and reactions of these two types of raw materials:

- Pyrolytic decomposition of either type material gives, in addition to gas and char, liquid products.

TABLE V-4

MAJOR COAL-GASIFICATION PROCESSES AND PERSPECTIVE FOR THEIR APPLICATION TO BIOMASS

Process	Major Features	Process-Development Status	Prospects for Biomass Application
Battelle-Union Carbide	Fluid-bed, agglomerating-ash, two-vessel system. In gasifier, sensible heat in hot ash particles from combustor is utilized to steam-reform coal. In combustor, coal and residual carbon on circulating ash particles are burned with air to heat the solids. Pressurized operation (100 psig).	25-ton/d PDU in West Jefferson, Ohio has been operated since Sept. 1976. Major problems in maintaining the ash circulation. The PDU is being mothballed.	Ash agglomeration is essential. The PDU had plugging problems in ash-circulating systems. The concept is novel, but the operability has never been demonstrated. Because of the complexity of the system, it may be costly. Not recommended for biomass.
Westinghouse	Fluid-bed agglomerating-ash, two-vessel system. Pressurized operation (230 psig). Air- or O ₂ -blown. In devolatilizer, fresh coal is carbonized by hot gases from gasifier. Char from devolatilizer drops to gasifier, where air or O ₂ and steam are used to gasify at ash-agglomerating temperature.	15-ton/d PDU in Waltz Mill, Pa. has been operated since 1975. Devolatilizer and gasifier have been separately demonstrated. The two systems are to be combined in future testing.	The major function of devolatilizer is to decake the feed coal, which is unnecessary for biomass. In general the process may be too sophisticated for biomass.
Winkler (Davy Powergas Co.)	Fluid-bed, nonslagging, single-stage, atmospheric or pressurized (42 psig). Air- or O ₂ -blown. About 70% of ash is carried out in the product gas. Waste-heat boiler immediately above the fluidized bed prevents the flue gas temperature reaching ash-softening point.	Commercial. 62 gasifiers in 22 plants have been commissioned. Of these, 38 gasifiers are currently operational. All commercial units operate at atmospheric pressure.	Potentially applicable. However, fluidization of biomass must be carefully evaluated in relation to coal.
Koppers-Totzek (Koppers Co.)	Entrained, slagging, single-stage, atmospheric. O ₂ -blown. Coal pulverized to 200 mesh is gasified with O ₂ and steam at ash-slagging temperature (2700°F). Residence time a few milliseconds.	Commercial. Extensive applications in synthesis-gas generation for ammonia production. Combined capacity of the K-T coal gasifier built to date amounts to about 480 million scf/d of synthesis gas. Pressurized version is under development.	Commercial units have operated on biomass such as peat. Whether or not to adapt the K-T process for biomass is now a matter of economics. Costs involved in pulverizing biomass to 200 mesh and in drying should be carefully evaluated.
Texaco (Texaco, Inc.)	Entrained, slagging, single-stage, up to 800 psig. O ₂ -blown. Coal pulverized to 20 mesh is mixed as 50/50 water slurry and gasified with O ₂ at ash-slagging temperature (2700°F).	150-ton/d semicommercial plant near start-up in W. Germany. One of the most advanced second-generation coal gasifiers.	Practically any carbonaceous material can be gasified in this system. The moisture content of feed is not as critical as in the K-T process. Technology is available today; should be considered if the economics allow.

TABLE V-4 (CONTINUED)

Process	Major Features	Process-Development Status	Prospects for Biomass Application
Lurgi (Lurgi Mineraltechnik)	Fixed-bed, single-stage, nonslagging. O ₂ - or air-blown. Relatively large amount of steam is required to prevent gasification temperature from reaching the ash-softening point. Long residence time: 45-60 min. Pressurized operation at 300-400 psig. Coal size: 1/4 to 1-3/4 in. Fines not tolerated. Tars are by-product.	Commercial, with extensive operating experience. Slagging version of Lurgi gasifier, which uses less steam, is under development.	Potentially feasible. Feed size and its moisture content need careful attention. The user of the product gas must be able to utilize its pressure energy.
Wellman-Galusha (Wellman Engineering Co.)	Fixed-bed, single-stage, stirred, non slagging. Air or O ₂ , although air is predominantly used. Atmospheric operation. Fines not tolerated. Tars as by-product.	Commercial. Widely used in U.S. and Europe in early 1900's. It is making a comeback in U.S. A pressurized version is under development by DOE at Morgantown, W. Va.	Potentially feasible. Because of the simplicity of the gasifier design, this process may offer a new process specifically suited for biomass conversion. The stirring mechanism is another attractive feature of this process.
CO ₂ Acceptor (CONOCO Development Co.)	Fluid-bed, two-vessel system in the gasifier, coal is steam-reformed with heat supplied by hot CaO and by the reaction: $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ in the regenerator, CaCO ₃ is calcined to CaO by air combustion of chars from gasifier. Dried lignite or sub-bituminous coals only.	40-ton/d PDU at Rapid City, S. Dak. has been operated since 1972. However, further development is needed in areas like the acceptor (CaO) reaction systems and the acceptor circulation systems.	Conceptually feasible. However, because of uncertainties surrounding the acceptor systems, the application of this process to biomass may not be warranted at this time.
Synthane (Bureau of Mines)	Fluid-bed, single-vessel, O ₂ -blown. Nonslagging. High pressure (1000 psig). Pretreated coal of 20 x 0 mesh is carbonized during the free fall through long vertical space in gasifier. In the dense fluidized bed, coal is then gasified by O ₂ and steam. Char (ash) is removed.	72-ton/d PDU at Bruceton, Pa. has been operated since July 1976. Many operating problems, particularly in char handling. Plugging is the major problem. The PDU is being mothballed.	Conceptually feasible. But it is questionable whether such a sophisticated design is necessary for biomass. Not recommended for biomass application.
U-Gas (Institute of Gas Technology)	Fluid-bed, single-vessel, air/O ₂ -blown, 300 psig ash-agglomerating. Equipped with pretreater, so any coal can be used. Ash agglomeration is caused by running the gasification system at 2000°F. No liquid by-products. Coal size: 1/4 in. or less.	Ash-agglomerating phenomena have been under development, using a 4-ft diam 25-ft-high gasifier. Char has been the only feed tested in this unit. Under modification to test coal.	Ash agglomeration in biomass system must be demonstrated, since ash particles are important fluidizing medium. The PDU has rather impressive operating records. Potentially attractive candidate for biomass.

TABLE V-4 (CONTINUED)

Process	Major Features	Process-Development Status	Prospects for Biomass Application
ATGAS (Applied Technology Corp.)	Molten-iron bath, atmospheric. Pulverized coal (1/8 in.) and lime- stone are injected through lances into molten iron, with steam as carrier. Oxygen is charged separately. Ash be- comes slag. Sulfur reacts with lime.	Laboratory-scale demonstra- tion. Major unknowns are the life of reactor lining, means of injecting reactants into molten bath, and slag handling.	In very early stage of development. Has good feedstock flexibility. Appears to be a simple system, but the by-products handling and the melt regeneration may turn out to be rather cumbersome and complex. The technology is not of practical interest.
Kellogg Molten Salt (M.W. Kellogg)	Molten sodium car- bonate, 1200 psig, pulverized coal (12 mesh). O ₂ -steam as carrier of coal into molten salt. For reactor lining, fused-cast, high- purity alumina called Monofrax A® shows best corrosion resistance. Sulfur in coal becomes sodium sulfide. Ash is removed from the melt by water solu- tion-filtration- recrystallization.	Laboratory-scale demonstra- tion during 1960's and early 1970's. In 1974, the development efforts were terminated. Major unknowns are the life of reactor lin- ing, vaporization loss of salt, ash removal, and salt recovery system.	Because of rapid and complete gasi- fication, applicability to varied feedstocks, and the susceptibility of biomass gasification to catalysis by alkali, this process is of in- terest.

- Both materials are soluble in such solvents as anthracene oil, phenols, and high-boiling, heterocyclic nitrogen bases.
- Hydrogen or carbon monoxide can serve as a liquefying reagent for either material in the presence of appropriate catalysts.

In the following sections the utility of coal-liquefaction concepts for biomass will be discussed under two headings, covering catalytic and pyrolytic processes in turn.

2.1 CATALYTIC PROCESSES

This category includes hydrogen-donor solvent and hydroliquefaction processes.

In the donor-solvent process, a hydrogen-rich solvent is the source of hydrogen that is transferred in a thermal reaction to the coal dissolved in the solvent. The catalytic step in this process is the regeneration of the hydrogen-rich solvent by hydrogenation. The Consol, Exxon, and H-Coal processes belong to this category and differ from each other in separation steps and in the way the hydrogenation is carried out. The SRC process, although not using an added catalyst, can be considered a donor-solvent process since its operation is very similar to that of the H-Coal process but depends on the catalytic activity of mineral ingredients naturally present in coal.

Each of these processes consumes hydrogen in quantities ranging from 9000 to 20,000 scf/ton of coal.

While in coal liquefaction some of the hydrogen combines with the coal and thus adds to the heating value of the resulting liquid fuel, in the case of biomass liquefaction, hydrogen only serves as a reducing agent for removing oxygen.

It is noted that donor-solvent process for coal is based on (a) the solubility of coal in the hydrogen-rich form of the solvent, (b) the hydrogen transfer from solvent to coal, and (c) the availability of the solvent, preferably from coal. The feasibility of these requirements in the case of biomass liquefaction has not yet been demonstrated.

The problem of high hydrogen cost also prevails in hydroliquefaction processes, which use hydrogen directly for coal hydrogenation, as in the early Bergius studies. According to Kattel (Kattel, 1975), 30% of the overall cost of coal hydroliquefaction is accounted for by the production of hydrogen.

In coal liquefaction, the Project Lignite process (Part IV, Sec. 2.3.1.5) in which hydrogen is replaced by carbon monoxide or syngas depends on the formation of hydrogen via the water-gas shift reaction occurring in the presence of steam. This reaction, and the hydrogenation and hydrodesulfurization of coal are catalyzed either by natural mineral coal components containing alkali- and transition-metal compounds or by such added dual-function catalysts as cobalt molybdate-sodium carbonate (Fu and Illig, 1976).

The reactions in the liquefaction of cellulose, wood, and similar products by carbon monoxide are complicated, and differ from those occurring with coal. They entail various alkali-catalyzed reactions (including a sequence of hydrolysis, dehydration, isomerization, reduction, and decomposition) affecting the organic substrate. The reducing agent is the formate ion (Appell, 1977), which reacts and is regenerated according to:

This type of liquefaction is the basis of the PERC/Albany process, which has been under study for a number of years. According to an analysis by SRI International (1979), this process would operate at 2000 psi and 304°C (580°F) with a feed of ground wood dried to 10% moisture and then slurried with recycle oil, unconverted wood, and an alkaline catalyst recovered from the ash generated by the syngas plant gasifier. Problems encountered relate to solids separation, reactor design, and corrosivity and instability of the product oil.

One would expect that the oil quality could be improved by the use of the dual-function catalyst suggested for the liquefaction of coal by syngas in order to utilize the hydrogen present for hydrogenation and/or reduction. However, such a catalyst would have to be provided in a form that would allow its easy separation from the reaction mixture.

2.2 PYROLYTIC PROCESSES

Coal liquefaction by pyrolysis achieves the required increase in the H/C ratio by eliminating free carbon, and thus yielding substantial amounts of char. This method requires no added catalyst.

Of the coal-pyrolysis processes discussed (Part IV, Sec. 2.3.2), the FMC-COED and the Toscoal processes are too complex to be attractive for biomass application, especially in operation on a scale smaller than is usual for coal.

The Flash Pyrolysis process, originally developed for coal, has also been tested and adapted for biomass pyrolysis. A 200-ton/d plant based on this process and using shredded cellulosic material derived from municipal solid waste produced approximately 0.2 lb of oil per lb dried refuse, but the oil was too viscous for pumping without added water and was unstable and corrosive. The plant was eventually shut down because of technical problems.

Wood pyrolysis according to the Tech-Air process (Part IV, Sec. 2.2.3) is accomplished by direct heating with combustion gases in a fixed-bed reactor at atmospheric pressure. It yields 0.25 lb of oil and 0.28 lb of char per lb of dry wood. The oil has a satisfactory heating value and burning characteristics, but is corrosive and unstable and contains some carcinogenic compounds (SRI, 1979).

The Rockwell Flash Hydropyrolysis process depends on a rapid reaction of extremely hot hydrogen with coal, followed by quick quenching. It is in too early a stage of development for evaluation, but the use of hydrogen and the required high temperature appear to make it unattractive for biomass application.

2.3 PERSPECTIVE FOR THE APPLICATION OF MAJOR COAL-LIQUEFACTION PROCESSES TO BIOMASS

Table V-5 shows an overview of major coal-liquefaction processes. Their significant features, process-development status, and prospects for biomass application are indicated.

3. MAJOR PROBLEM AREAS IN THERMOCHEMICAL CONVERSION OF BIOMASS TO FUELS

Emerging processes for the conversion of biomass to fuel have many problems. Some of these arise from efforts to adapt established coal technology for biomass, while others are encountered in the development of novel methods.

TABLE V-5. OVERVIEW OF MAJOR COAL-LIQUEFACTION PROCESSES

Process	Major Features	Process-Development Status	Prospects for Biomass Application
CSF-Consol (Consolidated Coal Company)	Crushed coal and H ₂ -donor solvent slurried and reacted at 400-500 psig and 400°C for 40 min. Gases and solids separated, liquids catalytically hydrogenated in ebullient reactor at 4200 psia and 450°C with 16,000 scf/ton of coal. Donor solvent separated by fractional distillation and recycled.	Pilot-plant operation in Cresap, W. Va., capacity 70 tons/d.	High consumption of costly hydrogen would be too expensive for biomass application.
Exxon (Exxon Research and Engineering)	Slurry of crushed coal and donor solvent reacted in the presence of H ₂ but absence of catalyst at 1500-2000 psi and 450°C. Donor solvent catalytically hydrogenated and recycled.	A 250-ton/d pilot plant costing \$240 million is expected to be in operation early in 1980.	High consumption of costly hydrogen would be too expensive for biomass application.
H-Coal (Hydrocarbon Research)	Slurry of coal and donor solvent reacted with H ₂ in a fluidized catalytic reactor at 2700 psia and 454°C for 30-60 min. H ₂ consumption 12,600 scf/ton of coal. Liquid product separated from gases and solids, solvent recovered by fractional distillation, and recycled.	Pilot-plant operation. Capacity, 3 tons/d.	High consumption of costly hydrogen would be too expensive for biomass application.
Solvent- Refined Coal (SRC) (Pittsburgh & Midway Coal Mining Company)	Coal crushed to pass 200 mesh slurried with solvent reacted with hydrogen at 1800-2000 psia and 427-477°C in the absence of added catalyst, but depending on the catalytic activity of naturally present mineral constituents of the coal. After 30 minutes reaction, gases and solids are separated from the liquid, which is fractionally distilled to recover solvent and other products. Some of gases are recycled to the reactor, as is part of the liquid containing suspended mineral matter.	Six-ton/d pilot plant at Wilsonville, Ala., operating under less severe conditions and consuming 9000 scf of H ₂ /ton of coal produces solvent-refined coal (SRC) melting above 149-204°C and containing 0.1-0.9% S, depending on coal feed. The 30-ton/d pilot plant at Fort Lewis, Wash., operates under more severe conditions. It consumes 20,000 scf of H ₂ /ton of coal, and produces CH ₄ , LPG, and naphtha, in addition to fuel oil.	High consumption of costly hydrogen would be too expensive for biomass application.

TABLE V-5 (CONTINUED)

<u>Process</u>	<u>Major Features</u>	<u>Process-Development Status</u>	<u>Prospects for Biomass Application</u>
Project Lignite (Univ. N. Dak.)	Lignite is treated with CO-H ₂ in the presence of water without added catalyst at 1500-2000 psi and 400°C. The product, which contains 6% H, 3% O, 1% S, and 1% N, can be converted to gaseous and liquid hydrocarbons by catalytic hydrogenation. The syngas is activated by alkaline mineral constituents of lignite.	Pilot plant. A variation of this process is the liquefaction of coal by syngas in the presence of a cobalt-molybdate catalyst.	The PERC/Albany process for the liquefaction of wood is related to Project Lignite H ₂ it reacts wood chips with CO-H ₂ . In this case, the catalytic activity derives from the alkaline constituents in the wood.
FMC-COED (FMC Corporation)	Coal is gradually devolatilized and converted into char in three fluidized reactors operated at successively increasing temperatures ranging from 190 to 538°C. The reactors are heated by gases generated by the combustion of the char in a fourth reactor. The products constitute an oil suitable for conversion into synthetic crude by hydrotreating, or into a high-Btu gas.	Pilot plant in Princeton, N.J.	While this reactor system is too complicated for biomass application, a simpler version of pyrolytic treatment of wood in a fixed-bed reactor is the basis of the Tech-Air Wood Pyrolysis process (see Part IV, Sec. 2.2.3).
Flash Pyrolysis (Occidental Research)	Fine coal particles are rapidly pyrolyzed by heat from hot char and ash entrained by pyrolysis gas, and generated by the combustion of part of the char in another reactor. Products are pyrolytic oil, high-Btu gas, and char.	Pilot plant in La Verne, Ca., capacity 50 lb/h	This process has been applied to the pyrolysis of municipal solid waste which yields low-quality oil in pilot and demonstration plants.
Toscoal (Oil Shale Corp.)	Pyrolysis of coal accomplished by heat supplied via circulating hot ceramic balls.	Pilot plant adapted from unit developed for oil-shale treating at Golden, Colo. Capacity, 25 tons/d.	Heating method too complicated for biomass.
Rockwell Flash Hydropyrolysis (Rockwell International)	Fine coal particles reacted with H ₂ heated to 1090°C.	Test reactor (400-lb/h capacity) operation in experimental stage.	Process even when developed would be too expensive for biomass because of H ₂ consumption.

There are difficulties connected with transferring, reacting, and separating complex multiphase mixtures composed of biomass, oily and aqueous liquids, solid catalysts, and gases. The reactions occurring in such a complex process as wood liquefaction are not fully understood, nor are the desired steps under control.

While the beneficial catalytic effects of alkaline-metal carbonates in wood gasification and liquefaction have been recognized and are being used, there are problems in utilizing other catalysts connected with their recovery or separation.

However, the main shortcomings of the biomass-conversion technology under development are in two areas. First, because of the diverse nature and the variable composition of the different biomass materials, apparently a multitude of methods would be required for the efficient gasification of sawdust, wood chips, agricultural residues, municipal solid waste, and animal manure. The other problem area is the low quality of liquid fuel products obtained from biomass and especially of the PERC/Albany product. In the following sections these two areas will be discussed.

3.1 GASIFICATION OF VARIOUS BIOMASS MATERIALS

Biomass includes several types of materials, each type comprising numerous species with different compositions subject to regional and seasonal variations. From the processing point of view, the differences in moisture and ash content are significant, as are physical nature, texture, and shape.

For gasification in an entrained or fluidized bed, wood, because of its fibrous nature, requires expensive size reduction, unless available in the form of sawdust.

In fixed-bed gasification, wood gives liquid products similar to those obtained in its destructive distillation.

The pressure gasification of wood under development by Wright-Malta takes advantage of the catalytic effect of wood ash, and the exothermicity of the reaction. The process yields a gas rich in methane, but may encounter mechanical problems in scale-up.

For the gasification of agricultural by-products available only in limited quantities, Georgia Tech has developed a mobile unit.

There are two proven processes for the gasification of unsorted municipal solid waste in vertical-shaft furnaces, one of which, Purox, uses oxygen and the other, Andco-Torrax, uses air in combination with regenerative heating. A third process, Flash Pyrolysis, based on the pyrolytic gasification of finely shredded, sorted organic refuse in the entrained mode, failed after extensive tests.

For the gasification of manure, fluid-bed and multiple-hearth operations have been proposed. The latter method has also been used for gasifying sewage sludge.

Table IV-3 summarizes the catalytic and noncatalytic biomass gasification processes described in Part IV, Sec. 1.2. There are twenty or more other processes under study or in operation concerned with the gasification of solid waste.

While admittedly there is a need for special processes for the recovery of value from municipal waste, and for the gasification of agricultural by-products in mobile units, it would be desirable to have a single versatile method for gasifying wood, the most abundant biomass material. Such a process should be able to handle different types of wood in various forms, accomplish rapid and essentially complete gasification, and allow the convenient removal of ash and sulfur. The gasification should proceed preferably at temperatures and pressures favoring the formation of methane.

The molten-salt coal-gasification process studies by Kellogg and under development by Atomics International (Rockwell International) shows great promise of being able to serve as such a versatile process for the gasification of wood and related products.

As discussed in Part IV, Sec. 1.1.2.3 and Part V, Sec. 1.5, the molten salt process uses sodium carbonate as the catalyst, reaction medium, and reactant for coal gasification at 925-1000°C (1700-1850°F) and 1-80 atm (15 to 1200 psig), and accomplishes the following:

- Handles caking or noncaking coals without pretreatment or sizing.
- Completely gasifies the coal fed.
- Collects sulfur and ash in the melt.
- Provides for the regeneration of the spent melt.
- Produces no char or tar.

Since wood is more reactive than coal and contains less sulfur and ash than does coal, its gasification by the molten-salt process would have these additional advantages over coal gasification:

- Lower reaction temperature, resulting in higher methane yield and less corrosion of the refractory lining of the reactor.
- Molten-salt regeneration equipment and operation costs would be reduced.
- The problem in coal gasification associated with throughput limitation to prevent excessive agitation of the melt would be reduced because of the substantially smaller size of the envisioned biomass plant, compared with coal plants.

Also, wood and related feeds would require only moderate drying but no costly comminution.

In a limited number of tests on municipal refuse and sludge, the molten-salt process has already been applied to biomass (see Part V, Sec. 1.5).

3.2 QUALITY OF LIQUID FUELS FROM BIOMASS

The key problem in the liquefaction of wood is the poor control of desired reactions. In such pyrolytic liquefaction processes as Flash Pyrolysis and Tech-Air, the reactions are nonselective, involving scission and free-radical reactions. In the PERC/Albany process, which uses carbon monoxide, alkali, and water as reagents and catalysts, there is a complex sequence of reactions which probably starts out with the hydrolytic breakdown of cellulose and the generation of formate, and continues through the rearrangement of the breakdown products of cellulose and the reduction of the resulting intermediates by formate, to a host of reactive oxygenated compounds. These compounds can go on reacting during the liquefaction process or during the ensuing physical processing at elevated temperature and lead to the polymerized, polymerizable, and acidic compounds responsible for the poor quality of the oil derived from wood.

Table V-6 shown the properties of oils obtained by PERC/Albany and two pyrolytic processes. All three oils have satisfactory combustion characteristics and heating values, although the latter are substantially lower than the values for No. 6 heating oil (18,200 Btu/lb). The serious problems of all three oils are their acidity, which causes corrosion in storage and transport, and their polymerizing tendency.

According to Appell (1977), a CO group in a carbonyl compound formed via

TABLE V-6
PROPERTIES OF OILS DERIVED FROM BIOMASS

Source Composition, <u>wt%</u>	<u>PERC/Albany</u> Wood	<u>Flash Pyrolysis Oil</u> Refuse (cellulose)	<u>Wood Pyrolysis Oil</u> ^b Wood
C	69 ^a	57	58.8 (66.8)
H	7		5.6 (6.3)
O	23	33.2	23.4 (26.6)
S	Small	0.2	<0.1
N	Small	1.1	0.2
Cl	0	0.3	
Ash	Small	0.5	0.04
GO	--	--	12.0
Heating value, Btu/lb	14,000	10,600	12,200 (13,800)
Density, lb/bbl	425	455	400
Combustion properties	Satisfactory	Satisfactory	Good
Shortcomings	Unstable, polymerizes in storage, corrosive	Acidic, causes corrosion. Very viscous, needs 14% water ad- dition for pumpability. Undergoes de- gradation >71°C (160°F).	Acidic, heat-sen- sitive. Contains potentially carcinogenic com- pounds.

^a Approximate composition.

^b Water-free basis.

can react with active hydrogens in another molecule with water elimination leading to condensation. Under alkaline conditions, carbonyl groups can also migrate along the carbon chain. When two carbonyl groups reach vicinal positions the resulting diketone can undergo a benzylic acid-type rearrangement:

These and similar reactions may be responsible for the instability and acidity of the oil produced by wood liquefaction, although the hydroxy acids of the above-indicated type tend to decarboxylate readily.

According to Morton et al. (1979), liquid fuels derived from cellulose by alkaline digestion can cause corrosion and plugging in pipelines because of their acidity, which is caused by the presence of phenols.

One would expect that an accelerated reduction of the keto groups by increasing the rate of formation or the concentration of formate would decrease the tendency of the oil to polymerize. In this connection it would be important to ascertain whether the formation and the reaction of formate take place in the same or different phases.

If two phases are involved, one would expect that the presence of a common solvent for both formate and substrate would accelerate the reaction. The beneficial effect of certain solvents (cresol, acetophenone, isoquinoline, etc.) on the rate of cellulose liquefaction (Appell, 1977) may be such an effect.

Another approach to minimizing polymerization tendency and acidity of wood-derived oils would be catalytic upgrading by reducing the concentration of residual CO, COOH, and phenolic groups. Weisz et al. (1979) report that various oxygenated oils derived from biomass have been successfully converted into

hydrocarbons on ZSM-type catalysts. Therefore, there is reason to believe that such catalysts would be also useful in upgrading the PERC/Albany oil and similar products (see Part VI, Sec. 2).

PART VI. ADVANCES IN CATALYSIS
AND ENGINEERING IMPACTING
ON KEY PROBLEM AREAS

The following sections cover recent advances in reactor engineering and catalysis that offer promising routes to solving major problems or suggest fruitful research in biomass conversion.

1. MOLTEN-SALT GASIFIER

The successful coal-gasification tests accomplished in the molten-salt process-development unit and the significant programs made by Atomics International on the engineering aspects of this technology (see Sec. 1.3.1.4, Part IV) strongly suggest applicability in biomass conversion.

The attractive features of the molten-salt gasification of biomass include operation at lower temperatures because of the higher reactivity of the feed. Lowering the reaction temperature would not only reduce corrosion and salt vaporization problems but would also increase the methane yield. This aspect will be further discussed in Sec. 3.

2. CATALYTIC UPGRADING OF BIOMASS OILS

The recently reported (Weisz et al., 1979) catalytic production of high-grade fuel from biomass compounds by shape-selective catalysts promises to have applicability for oxygen-containing liquids obtained by biomass liquefaction.

The remarkable observation is that on Mobil's ZSM-5 catalyst high-molecular oily triglycerides and waxy esters containing up to 57 C atoms per molecule are smoothly converted at 400-500°C (752-932°F) into C₁-C₁₄ hydrocarbons, among which the C₆-C₉ aromatics predominate. The coke formation is very low, and the product distribution is not unlike that obtained on the same type of catalyst from methanol. It is of particular interest that a C₅₇ triglyceride in the conventionally represented form (a) would be too bulky to enter the cavity

structure of the ZSM-5 zeolite, and that therefore it has to assume the configuration (b) while diffusing into the catalyst pores.

(a)

(b)

The plant-derived materials used, corn oil, castor oil, and jojoba oil, have the common feature of containing only linear carbon chains in the high-molecular moiety as shown below:

Corn oil	$n\text{-C}_{17}\text{H}_{33}\text{COO}-\text{CH}_2$
	$n\text{-C}_{17}\text{H}_{33}\text{COO}-\text{CH}$
	$n\text{-C}_{17}\text{H}_{33}\text{COO}-\text{CH}_2$
Castor oil	$n\text{-C}_{17}\text{H}_{32}(\text{OH})\text{COO}-\text{CH}_2$
	$n\text{-C}_{17}\text{H}_{32}(\text{OH})\text{COO}-\text{CH}$
	$n\text{-C}_{17}\text{H}_{32}(\text{OH})\text{COO}-\text{CH}_2$
Jojoba oil	$n\text{-C}_{19}\text{H}_{37}\text{COO}-n\text{-C}_{22}\text{H}_{43}$
	and
	$n\text{-C}_{21}\text{H}_{41}\text{COO}-n\text{-C}_{20}\text{H}_{39}$

Once the large molecules are in the cavities of the catalyst, they break down, and the fragments are catalytically rearranged into aromatic and other hydrocarbon molecules; their size and shape are compatible with the dimensions of the zeolite cavities.

If the size of the molecules in the biomass-derived oils is such that the molecules can enter the structure of the ZSM-5 or related zeolite catalysts, mild treatment over such catalysts might remove part or most of the oxygen from the ether, hydroxyl, and carboxyl groups in the oils.

Another possibility for upgrading biomass oils would be conventional hydrotreating under mild conditions in an H-coal type reactor (see Sec. 2.2.1, Part IV). In this connection, the use of syngas for coal liquefaction in the presence of a dual-function cobalt molybdate-sodium carbonate catalyst (Batchelder and Fu, 1976; Fu and Illig, 1976) is of interest, since the same approach could be used under milder conditions for improving the quality of biomass oil. In the presence of this type of catalyst, the sodium carbonate catalyzes the water-gas shift reaction, and the cobalt molybdate provide the hydrogenation function. The reaction of course needs water, which could be added or generated from the oxygenated groups in the oil.

3. METHANE-RICH GAS FROM BIOMASS

According to thermodynamic calculations (SERI, 1979), the adiabatic decomposition of wood having the composition $\text{CH}_{1.400.59}$ in the presence of 1.52 moles of water (corresponding to 120% moisture, based on dry wood) gives the equilibrium products shown in Table VI-1 (of Table IV-1, Part IV) indicating these noteworthy points:

- At about 550 and 570°C (1020 and 1060°F) and 400 and 1000 psig, the gasification is complete. Methanol and carbon dioxide are the main products in almost equivalent amounts. Some hydrogen and a little carbon monoxide also form.
- At 400 and 1000 psig, the water and carbon dioxide-free gas contains 67 and 72% methane.

The temperatures given in Table VI-1 are the calculated temperatures reached on adiabatic exothermic decomposition of wood.

The Wright-Malta process (see Part IV, Sec. 1.2.1.3) approximates the above conditions and gasifies green wood in the presence of Na_2CO_3 at 300 psi and around 590°C (1100°F), taking advantage of the exothermic decomposition of wood under these conditions. The reported gas composition with the CO_2 -free composition in parentheses is given below:

CH_4 , %	18	(32.7)
C_2H_6 & higher, %	8	(14.5)
H_2 , %	28	(50.9)
CO , %	1	(1.8)
CO_2 , %	45	---

The relatively high methane yield and the very low CO yield are in qualitative agreement with the equilibrium data for lower temperatures.

In this connection, it is noteworthy that the Exxon process operating at 500 psig and 700°C (1300°F) gasifies coal, with sodium carbonate being used as a catalyst in the presence of steam and recycled H_2 and CO (Part IV, Sec. 1.3.1.2). The methane is present in the product gas stream at a sufficiently high level to allow its cryogenic recovery after the removal of the acid gases and water.

These data indicate that pressure gasification of biomass using alkaline catalyst can produce a methane-rich gas if the reaction temperature does not exceed 700°C (1300°F).

The molten-salt process appears to be a suitable method for the efficient gasification of biomass. It is expected to yield a methane-rich gas if the reactor temperature is below 700°C (1300°F).

In the conventional coal-gasification process the reaction temperature is about 980°C (1800°F), and sodium carbonate is used as the molten salt. While this salt cannot be used below 851°C (1564°F), its melting point, it forms lower-melting eutectic mixtures with potassium and lithium carbonates (see Table V-3 and Part V). There is a good chance that molten alkali salts of weak acids other than carbonic acid would also act catalytically in the gasification of biomass. Some of the salts of boric and silicic acids have melting points lower than that of sodium carbonate, as indicated below:

	Melting point,	
	°C	°F
Potassium pentaborate, $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$	7880	1436
Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$	741	1366
Potassium hydrodisilicate, KHSi_2O_5	515	959

Mixtures of these salts with each other or with alkali carbonates might give still lower-melting catalytically active melts.

Of course, any change in the currently used sodium carbonate melt, either by addition of, or by substitution with, another salt would necessitate a modification of the salt regeneration method developed for the sodium carbonate melt.

TABLE VI-1

EQUILIBRIUM PRODUCTS IN THE ADIABATIC DECOMPOSITION
OF WOOD ($\text{CH}_{1.40}\text{O}_{0.59}$) IN THE PRESENCE OF
1.52 MOLES OF H_2O (120% moisture)

Values in parentheses are percentages in water- and carbon dioxide-free gas.

<u>Decomposition Products, mole %</u>							
Temp, °C	Pressure, psig	C	CO	CO ₂	CH ₄	H ₂	H ₂ O
452	0	0.03	0.03	0.54	0.40	0.42	1.0
546	400	0.0	0.03 (4.3)	0.50	0.47 (67.1)	0.2 (28.6)	1.08
568	1000	0.0	0.02 (3.0)	0.50	0.48 (71.6)	0.17 (25.4)	1.09

PART VII. RECOMMENDATIONS FOR
FUTURE R&D WORK IN THERMOCHEMICAL CONVERSION OF BIOMASS TO FUELS

There are numerous problems in the thermochemical conversion of biomass to fuel. Some of the problems are in the application of coal-conversion technology to biomass processing, while others became apparent in the development of novel conversion methods designed especially for biomass.

The following recommendations are made for future research and development in gasification and liquefaction.

1. GASIFICATION

Biomass gasification is clearly more facile than coal gasification in that reaction rates are substantially greater, and the extent of char formation is usually quite low. It appears that a number of gasification processes under study could be utilized for biomass gasification, although some questions remain concerning the demonstration of the long-term reliability of these processes. A potential drawback of these approaches is their limited applicability with respect to variations in the physical and chemical properties of the biomass feedstock. In most cases, only one or two feedstocks which are of regional interest are being investigated. The requirement for certain feedstock characteristics with currently emerging processes means that a number of different processes will have to be developed or the biomass feed will have to be pretreated by grinding, drying, or other means to product uniform material with characteristics suitable for the particular process to be used. For biomass, such pretreatment is a major cost factor in the overall process.

For these reasons, it would appear suitable to direct attention to the development of a versatile gasification process that would be able to handle a variety of biomass materials without requiring pretreatment, and would accomplish rapid, effective gasification. In this regard, the molten-salt process, currently under intensive study by Atomics International for coal gasification,

seems to be a very promising candidate for biomass gasification. In the last four years Atomics International has made significant progress in the engineering aspects of molten-salt processing technology, particularly with regard to handling and regeneration of the melt, and has designed, built, and operated a 1-ton/h process-demonstration unit for coal conversion.

For biomass, the molten-salt route appears very interesting and advantageous because:

- A wide variety of materials could be used, without requiring costly grinding or extensive drying.
- Because of the low sulfur, nitrogen, and ash contents of biomass, molten-salt regeneration equipment and operating costs would be reduced compared with the cost for coal.
- The high reactivity of biomass would allow operation at lower temperatures than used for coal gasification, thus reducing corrosion of the reactor lining.
- Pressurized gasification by the molten-salt method at 600-700°C (1100-1290°F) is expected to produce a methane-rich gas.
- No char or tars are produced; hence disposal or removal of these materials is not required.

More specifically, the following aspects of biomass gasification by molten-salt technology are recommended for study.

- Demonstrate the gasification of various biomass materials under conditions currently used for coal gasification, including tests at the lowest temperature feasible with sodium carbonate (mp 851°C or 1564°F).

- Study the effect of the temperatures of gasification on the methane content of the product gas at 20 atm in the range of 500-750°C (932-1382°F) with salt mixtures composed of sodium, potassium, and/or lithium carbonates.
- Check the feasibility of using molten alkali-metal salts other than carbonates for biomass gasification. Examples of such salts are certain borates of sodium and potassium, and potassium hydrosilicate.
- Develop the needed regeneration and purification process for the most promising salt or salt combination.

The Wright-Malta process for self-sustained gasification should also be considered seriously for further development for the reasons discussed in Part IV, Sec. 1.1.4 and Part VI, Sec. 3.

2. LIQUEFACTION

In biomass liquefaction the key problem is to break down the cellulose and lignin polymers to fragments that can be converted to liquids by partial deoxygenation via reduction, hydrogenation, dehydration, rearrangement, decarboxylation, and other reactions. Noncatalytic, pyrolytic liquefaction processes involve non-selective radical reactions and give low-quality liquids in poor yields, 20-25% by weight on the dry feed.

Appreciably better oil yields in the 32-37% range are obtained in the catalytic PERC/Albany process in which wood is reacted with CO or a CO-H₂ mixture in the presence of aqueous sodium carbonate. However, even in this case, the oil has poor quality since it tends to polymerize in storage and, being acidic, causes corrosion.

Two approaches to the elimination or alleviation of the problems connected with poor oil quality appear to deserve attention: catalytic upgrading of the oil, and detailed study of the nature of the oil components causing instability and acidity and of the mechanism of their formation.

In catalytic upgrading two routes offer some promise. One is based on the observation (Weisz et al., 1979) that certain plant-derived natural oils (corn, castor, and jojoba oils) of high molecular weight and composed of triglycerides and long-chain esters are smoothly deoxygenated on ZSM-5 zeolite catalyst at 400-500°C (752-932°F), yielding C₁-C₁₄ hydrocarbons, among which the C₆-C₉ aromatics predominate. If the molecules of the oil derived from wood by the PERC/Albany process are not too bulky to enter the structural cavities of the ZSM-5 or related catalysts, catalytic treatment over these zeolites may remove from the oil some or all of the OH, >CO, and -COOH groups responsible for poor quality.

The other route would involve upgrading of the oil, either by mild conventional hydrotreating or by syngas treatment in the presence of a dual-function cobalt molybdate-sodium carbonate catalyst.

The fundamental study of the natural acidic and polymerizable components in the biomass-derived oil and of the mechanism by which they form would be of great assistance in designing better processing methods and in obtaining improved products. Continuation and intensification of work along the lines of the studies of Appell and coworkers at PERC, Morton and coworkers at Battelle-Pacific Northwest, and others are recommended.

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