THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A TECHNICAL AND ECONOMIC EVALUATION OF SELECTED BIOMASS-TO-FUELS CONVERSION PROCESSES

A Thesis

Submitted to the Graduate Faculty

in Partial Fulfillment of the Requirement for the

Degree of

MASTER OF SCIENCE
(Petroleum Engineering)



by

CARL F. POMEROY

Norman, Oklahoma

April 1979

UNIVERSITY OF OKLAHOMA
LIBRARY

Downloaded from SHAREOK. Persistent Handle URL: https://hdl.handle.net/11244/335866

LD
4321
.8t
cop.2

A TECHNICAL AND ECONOMIC EVALUATION OF SELECTED BIOMASS-TO-FUELS CONVERSION PROCESSES

A THESIS

APPROVED FOR THE SCHOOL OF PETROLEUM

AND GEOLOGICAL ENGINEERING

By



ABSTRACT

The major objective of this study was to determine the economic and technical feasibility of existing methods for producing readily useable fuel from biomass. A thorough literature search was undertaken in an effort to evaluate the most promising and advanced biomass conversion processes about which published information was available. A ranking method was then developed to compare the selected processes.

A major problem that was encountered was the lack of completeness in the reported data. This incompleteness indicated that there was a major need for essential design information concerning changes of biomass during storage and detailed process design and scale-up information which simply were not available.

The most promising processes were found to be gasification and bioconversion types. The pyrolytic oil processes were less feasible by this ranking method.

ACKNOWLEDGEMENTS

The author expresses sincere gratitude to those who contributed the time, advice, services, encouragement, and support that made this investigation possible.

Special thanks are extended to Dr. J.M. Radovich and Dr. S.S. Sofer for providing invaluable guidance, assistance, and encouragement.

A debt of thanks is owed the Electric Power Research Institute for providing funding for the major portion of this project. Thanks is also owed Cities Service Company for providing the author support and assistance in attending night school as an employee.

The author's wife, Dorine, is thanked most sincerely for her understanding and support throughout this endeavor.

TABLE OF CONTENTS

Page

LIST OF TABLES vi

LIST OF ILLUSTRATIONS vii

Chapter

I. INTRODUCTION 1

II. CONVERSION METHODS 3
Pyrolysis 3
Gasification. 5
Anaerobic Digestion 7
Fermentation. 8

III. CONVERSION ROUTES. 9
Evaluation Methodology. 9
Details of Selected Pyrolysis Processes . . 15
Occidental Flash Pyrolysis. 15
Waste-to-Oil. 24
Tech-Air Pyrolysis. 27
Details of Selected Gasification Processes 29
Purox Process 29
Moore-Canada Gasifier 34
Syngas Process. 36
SNG Production by Anaerobic Digestion . . . 38
Ethanol Production by Fermentation. 41

IV. OVERALL COMPARISON OF CONVERSION PROCESSES . . 46

V. CONVERSION TECHNOLOGY CONCLUSIONS. 51

BIBLIOGRAPHY. 53

APPENDIX

I. Energy and Material Balance Calculations . . . 57

II. Economic Comparison Calculations 66

LIST OF TABLES

Table		Page
1.	Conversion Process Types.	4
2.	Selected Biomass Conversion Processes	12
3.	Net Material Balances	16
4.	Net Energy Balance.	18
5.	Energy Flow Streams and Energy Evaluations. . .	19
6.	Pyrolytic Oil Properties.	23
7.	Crude Product Gas Compositions.	33
8.	Ranking of Processes.	49
9.	Overall Ranking of Conversion Processes	50
10.	Conversion Processes in Order of Overall Ranking	50
11A.	Capital and Operating Cost for Biomass-to-Fuels Conversion Processes (from Mitre Corp.)	70
11B.	Capital and Operating Cost for Biomass-to-Fuels Conversion Processes (from Alich, et al.) . . .	71
11C.	Capital and Operating Cost for Biomass-to-Fuels Conversion Processes (from Schooley, et al.). .	72

LIST OF ILLUSTRATIONS

Figure		Page
1.	Biomass-to-Fuel Conversion Routes	10
2.	Conversion Process Evaluation Terms	14
3.	Flash Pyrolysis Flow Diagram.	21
4.	Waste-to-Oil Flow Diagram	26
5.	Georgia-Tech Air Pyrolysis Flow Diagram	28
6.	Purox Flow Diagram.	30
7.	Moore-Canada Flow Diagram	35
8.	Syngas Flow Diagram	37
9.	Biogas Flow Diagram	42
10.	Fermentation Flow Diagram	45

A TECHNICAL AND ECONOMIC EVALUATION OF SELECTED BIOMASS-TO-FUELS CONVERSION PROCESSES

CHAPTER I

INTRODUCTION

Biomass represents a renewable, alternative resource base that potentially can be converted to clean liquid fuels to reduce dependency on conventional sources of petroleum. Fuel from biomass also could be used for site specific applications such as steam or electric power generation. The purpose of this study is to make a preliminary evaluation of existing or developing technology for converting biomass to more readily useable fuels.

Biomass, for the purpose of this evaluation, is defined as organic matter such as trees, plants, agricultural crops, and grasses which can be grown specifically for the production of fuels. This definition includes forestry and agricultural wastes but excludes human and animal wastes--municipal solid waste (MSW), sewage sludge, manure. "Water" crops--aquaculture and mariculture--are also excluded. This biomass, as a feedstock, imposes a number of a priori constraints on the technology necessary to

convert it into fuels. Biomass, as received at the plant battery limits, has a very high moisture content. Most biomass contains about 50% water while some, such as kelp and water hyacinth, contain 80-95%. (Contrast this to MSW which has 25% water on the average.) Biomass is a difficult solid to handle because of the variety of sizes, shapes, and textures. The availability of some biomass is seasonal and stored biomass undergoes physical and chemical changes. Preprocessing steps must be designed to cope with these feedstock characteristics. Biomass feedstock availability, by its diffuse nature and seasonality, also dictates modest conversion plant sizes compared to that normally encountered in the chemical process industry. The objective of this study, then was to evaluate conversion processes designed for biomass feedstocks having high moisture content and difficult solids-handling characteristics and being available in modest amounts. This evaluation was based on available technical and economic data.

CHAPTER II

CONVERSION METHODS

All processes were screened initially for the following criteria:

1. Does the process produce a product which ultimately can be converted to a liquid fuel?
2. Is the process applicable to biomass as defined?

The initial screening was taken from Radovich, et al.(1). A brief discussion is presented here.

There are two fundamental methods of converting biomass to fuel which satisfy these criteria: thermochemical conversion and biochemical conversion. The process types considered in this evaluation are listed in Table 1.

Pyrolysis

Pyrolysis is the thermal decomposition of carbonaceous materials by indirect heat transfer in the absence of O_2, without addition of steam or carbon monoxide to the

TABLE 1

CONVERSION PROCESS TYPES

Thermochemical Conversion

1. Pyrolysis
2. Gasification (partial oxidation, hydrogasification)
3. Liquefaction (direct hydrogenation)

Biochemical Conversion

1. Anaerobic digestion
2. Fermentation

reactor. Pyrolysis is similar to the old wood distillation process. Operating conditions are 900-1700°F, and atmospheric pressure. Pyrolysis produces varying amounts of liquids, gases, and chars depending on the nature of the feedstock and on operating conditions. The liquid products contain highly oxygenated organics (organic acids) which are partially soluble in water and thus corrosive. Liquid product yields are maximized by rapid heating rates (short residence times) to moderate temperatures (1000°F) and immediate quenching of the gases and condensable vapors (2). This prevents cracking of the organic liquids. Product gases consist mainly of CO, H_2, CO_2 and CH_4. Approximately 45-60% of the feed mass (dry basis) shows up in the liquid and gaseous products (3). Non-condensable gas yields are maximized by holding the char and volatile components at

high temperatures for long residence times. The remaining carbon will be in the residual char, which also contains about 50% of the original heat content of the feed.

Gasification

There are a number of reactions which occur in processes for gasifying biomass. Depending on the other reactants added to the biomass feed, the relative amounts of CO, CO_2, H_2, CH_4 and light hydrocarbon gases in the product fuel gas can be varied. Partial oxidation is comparatively simple and can be represented by the following reactions:

$$C_6H_{10}O_5 + 1/2\ O_2 \rightarrow 6CO + 5H_2 + Heat \quad (1)$$

or

$$C_6H_{10}O_5 + Heat \rightarrow 6C(g) + 5H_2O(g) \quad (2)$$

$$C_{(s)} + 1/2\ O_2\ (air) \rightarrow CO + Heat \quad (3)$$

$$C_{(s)} + H_2O_{(g)} + Heat \rightarrow CO + H_2$$

steam gasification

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 + Heat \quad (4)$$

Steam is usually injected to maximize the amount of CO and H_2 produced. The BTU content of the gas can be increased if pure oxygen rather than air is used. Hydrogasification maximizes CH_4 yields in the product gas. The hydrogasification reactions can be represented by the following equations:

$$C_6H_{10}O_5 + \text{Heat} \rightarrow 6C_{(s)} + 5H_2O_{(g)} \quad (5)$$

$$C_{(s)} + 1/2\ O_2 \rightarrow CO + \text{Heat} \quad \text{partial oxidation} \quad (6)$$

$$C_{(s)} + H_2O_{(g)} + \text{Heat} \rightarrow H_2 + CO \quad (7)$$

$$CO + H_2O_{(g)} \rightarrow H_2 + CO_2 + \text{Heat} \quad \text{water-gas shift} \quad (8)$$

$$C_{(s)} + 2H_2 \rightarrow CH_4 + \text{Heat} \quad \text{hydrogenation} \quad (9)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O_{(g)} \quad \text{methanation} \quad (10)$$

or

$$C_5H_{10}O_5 + 1/2\ O_2 \rightarrow 6CO + 5H_2 + \text{Heat} \quad \text{partial oxidation} \quad (11)$$

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 + \text{Heat} \quad \text{water-gas shift} \quad (12)$$

$$C_6H_{10}O_5 + 1/2\ O_2 + H_2 \rightarrow 3CH_4 + 3CO_2 \quad \text{hydrogenation} \quad (13)$$

The overall yield of methane is enhanced by high pressure operation.

Liquefaction

If biomass is to be liquefied, hydrogen must be added at high temperatures and pressures. Appreciable amounts of hydrogenation can occur according to the following catalyst-promoted reaction:

$$\text{Biomass} + H_2 \xrightarrow[\text{catalyst}]{} \text{liquids} \quad (14)$$

or

$$H_2O_{(g)} + CO \rightleftharpoons H_2 + CO_2 \quad (15)$$

$$\text{Biomass} + H_2 \xrightarrow{\text{catalyst}} \text{liquids} \quad (16)$$

Liquid fuels also can be obtained by converting synthesis gas (a mixture of CO and H_2) to methanol or Fischer-Tropsch hydrocarbons. The basic synthesis reaction for methanol production is

$$CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3OH \quad (17)$$

Methanol can then be converted to gasoline by the Mobil process

$$n\ CH_3OH \xrightarrow{\text{catalyst}} (-CH_2-)_n + nH_2O \quad (18)$$

An alternative route to liquid fuels is Fischer-Tropsch Synthesis which is represented by the reaction

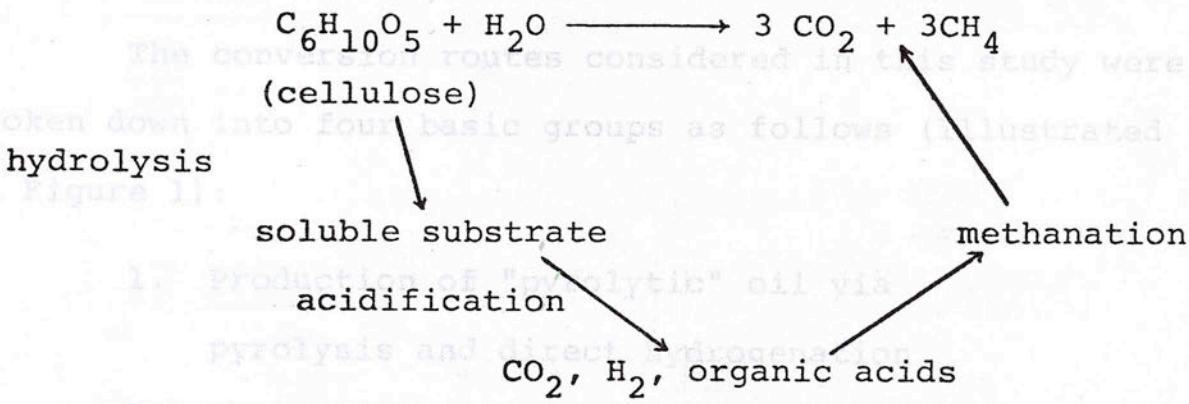
$$n\ CO + (2n+1)\ H_2 \xrightarrow{\text{catalyst}} C_n\ H_{2n+2} + nH_2O \quad (19)$$

$$n\ CO + 2n\ H_2 \xrightarrow{\text{catalyst}} C_n\ H_{2n} + n\ H_2O \quad (20)$$

Anaerobic Digestion

Methane generation by the bacterial decomposition of organic material is a naturally occurring process. Anaerobic digestion of sewage has long been used as a waste treatment process in the United States. Successful develop-

ment of anaerobic digestion processes for the conversion of biomass to methane has only been recently accomplished. The anaerobic digestion process consists of series and parallel reactions which are catalyzed by certain bacteria. The overall reaction is shown schematically below:



Anaerobic digestion is carried out under mesophilic (30-37°C) or thermophilic (55-60°C) conditions, in which different bacteria are responsible for the digestion reactions.

Fermentation

Ethanol can be produced from cellulosic material by a combination of hydrolysis and fermentation. The hydrolysis and fermentation steps are

$$(C_6H_{10}O)_n + n\ H_2O \xrightarrow{\text{acid}} n\ C_6H_{12}O_6 \quad \text{hydrolysis} \qquad (21)$$

$$n\ C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\ C_2H_5OH + 2CO_2 \quad \text{fermentation} \qquad (22)$$

The hydrolysis step is accomplished by treatment with acid or the addition of hydrolytic enzymes.

CHAPTER III

CONVERSION ROUTES

The conversion routes considered in this study were broken down into four basic groups as follows (illustrated in Figure 1):

1. Production of "pyrolytic" oil via pyrolysis and direct hydrogenation.
2. Production of syngas for on-site use as a fuel or as feedstock to convert to methanol, gasoline, or Fisher-Tropsch liquids.
3. Production of SNG by anaerobic digestion. SNG can be used as fuel or as a feedstock for methanol or Fischer-Tropsch liquids synthesis.
4. Production of alcohol (primarily ethanol) by fermentation.

Evaluation Methodology

An extensive literature search uncovered a host of possible conversion schemes for the various routes discussed above (4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16,

BIOMASS TO FUEL CONVERSION ROUTES

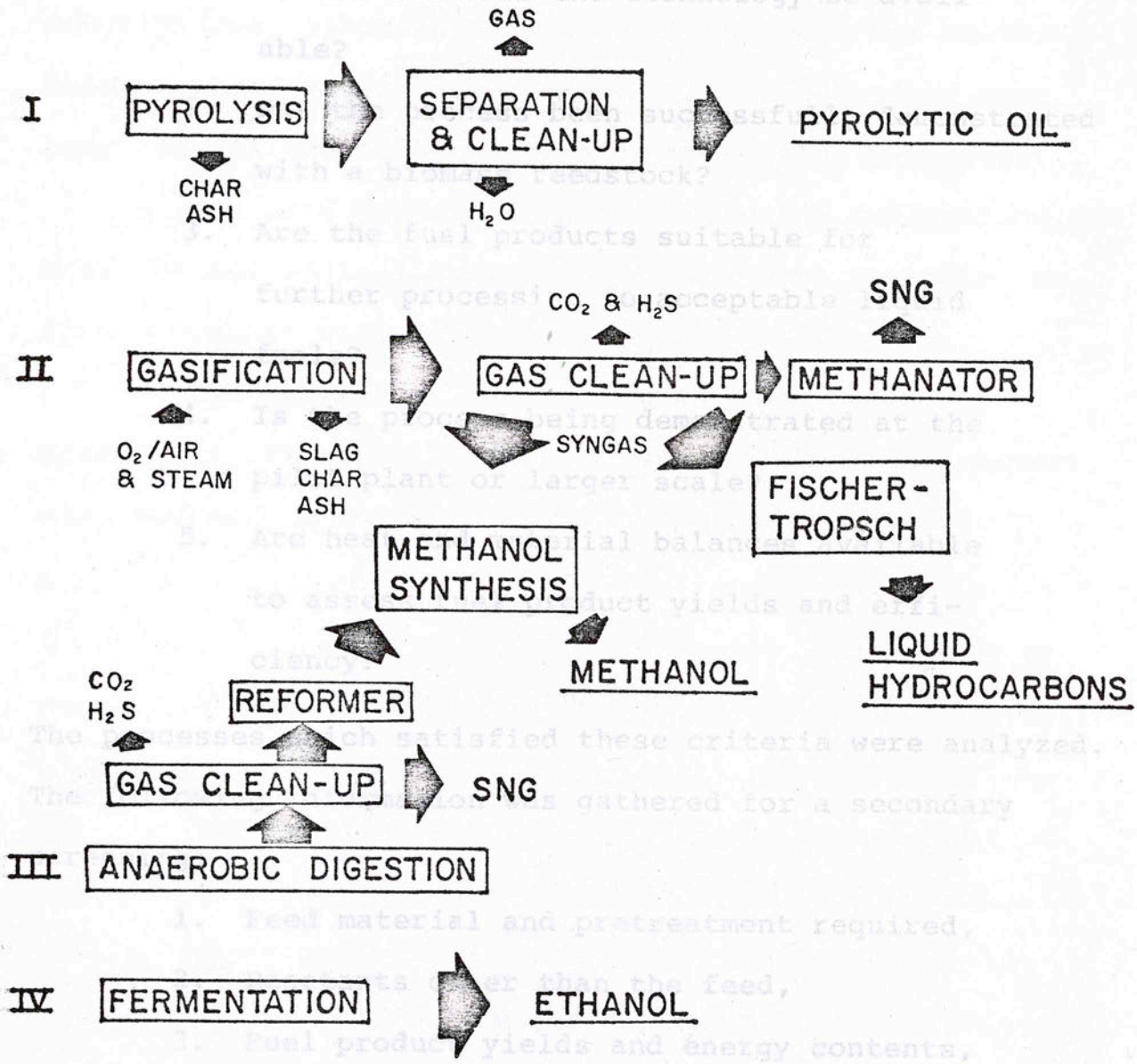


Figure 1. Biomass to Fuel Conversion Routes.

17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28). The criteria used for a preliminary screening were

1. Is process development currently being continued and will the technology be available?
2. Has the process been successfully demonstrated with a biomass feedstock?
3. Are the fuel products suitable for further processing to acceptable liquid fuels?
4. Is the process being demonstrated at the pilot plant or larger scale?
5. Are heat and material balances available to assess fuel product yields and efficiency?

The processes which satisfied these criteria were analyzed. The following information was gathered for a secondary screening:

1. Feed material and pretreatment required,
2. Reactants other than the feed,
3. Fuel product yields and energy contents,
4. Reactor type and operating conditions,
5. Development status,
6. Availability of additional process information.

Based on the results obtained from this screening, a final list of processes was prepared. In some cases, the final selection was influenced by the development status and the availability of detailed process information. Detailed descriptions, simplified flow diagrams, heat and material balances, and efficiency and economic calculations were compiled for the final ranking of conversion processes.

The data presented in the following evaluations are based on available literature and, whenever possible, on direct contact with developers.

The results of the preliminary and secondary screenings are shown in Table 2 for the different conversion routes. A discussion of these results follows.

TABLE 2

SELECTED BIOMASS CONVERSION PROCESSES

Conversion Route	Process
I	Occidental Flash Pyrolysis
	Georgia Tech Air Corp.
	Waste-to-Oil
II	Purox
	Moore-Canada
	Syngas
III	Biogas (IGT)
IV	Fermentation

In order to compare the efficiency of the selected processes, a number of terms have been defined which will

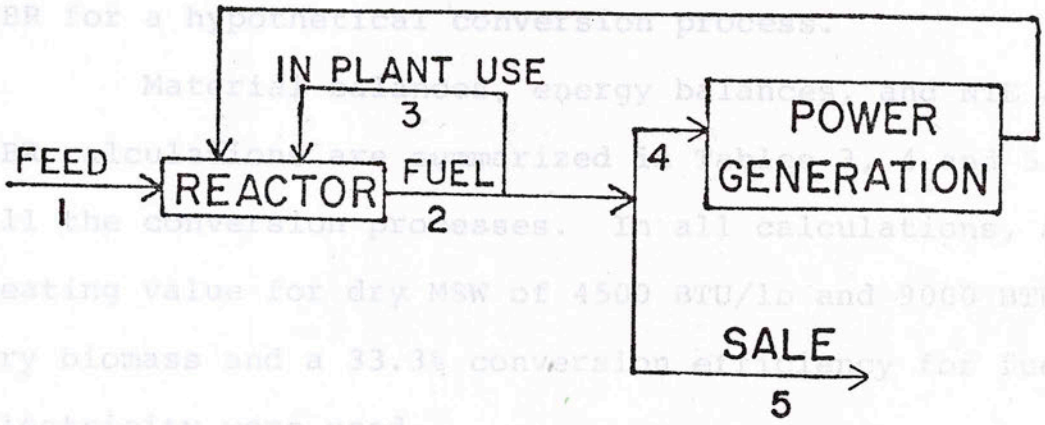
be used throughout the remainder of this report. The Net Thermal Efficiency (NTE) is defined as

$$NTE = \frac{\text{energy content of fuel product - energy consumed in process}}{\text{energy content of feed}}$$

NTE is a measure of the net energy conversion of feed into fuel product. The energy contents are given by the heats of combustion (HHV) of the product and feed streams. NTE is similar to the cold gas efficiency (ratio of product gas HHV to feed HHV) used to compare the efficiency of coal gasifiers. It differs in that the parasitic energy requirements are subtracted from the fuel product energy. However, like the cold gas efficiency, NTE neglects the sensible and latent heat in the fuel product which could be converted to power. Thus, NTE favors low temperature conversion processes (e.g. biochemical conversion) and penalizes high temperature processes (e.g. gasification and pyrolysis). NTE also ignores the "quality" of the energy, putting raw feed on the same BTU level as synthetic fuels. The realistically recoverable energy in the raw feed may be only 30-70% of the BTU content used in the NTE calculations. To account for the energy quality an energy benefit ratio is defined:

$$EBR = \frac{\text{energy content in fuel product}}{\text{energy consumed in conversion process}}$$

CONVERSION PROCESS EVALUATION TERMS



NET THERMAL EFFICIENCY

$$NTE = \frac{2 - (3 + 4)}{1}$$

ENERGY BENEFIT RATIO

$$EBR = \frac{2}{3+4}$$

Figure 2. Conversion Process Evaluation Terms.

Note that in many cases the energy consumed during conversion is of high quality (e.g. electric power, fuel gas). EBR indicates the gain in useable energy by the conversion process. Figure 2 illustrates the calculation of NTE and EBR for a hypothetical conversion process.

Material balances, energy balances, and NTE and EBR calculations are summarized in Tables 3, 4 and 5 for all the conversion processes. In all calculations, a heating value for dry MSW of 4500 BTU/lb and 9000 BTU/lb for dry biomass and a 33.3% conversion efficiency for fuel to electricity were used.

Details of Selected Pyrolysis Processes

Occidental Flash Pyrolysis

This process is well documented for use with wood and municipal solid wastes. Tests have been made with a bench scale reactor and a pilot plant. A 181.4 t per day (200 tons per day) demonstration plant is currently in operation in El Cajon, California.

The combustion process takes place separately from the pyrolysis reactor. The char (solid organic residue) produced in the pyrolysis reaction is oxidized with air in the char burner. The hot gas is then recycled into the pyrolysis reactor where it provides the energy for the reaction. The pyrolysis reactor is an indirectly heated, cocurrent flow, entrained bed reactor. A simplified

TABLE 3

NET MATERIAL BALANCES (kg)

Process	In		Out	
Occidental Flash Pyrolysis (6)	Biomass	100(dry)	gas	30
			water	10
			oil	40
			char	20
Waste-To-Oil (29)	wood	100(dry)	flue gas	295
	air	230	oil	35
			ash	trace
Tech-Air (30)	bark	100(dry)		
	air	49	char	23
			oil	25
			gas	68
			H_2O	33
Purox	MSW: 100:			
	24 ash		gas	75
	57 dry organics		water	30
	19 H_2O		oil	--
	O_2	25	slag	20
Moore-Canada (10)	wood	100	gas	263
	air	164	ash	3
	steam	17	water	15

TABLE 3 (continued)

NET MATERIAL BALANCES (kg)

Process	In		Out	
Syngas (31)	dry organics	100	gas	130
	steam	34	ash	5
	O_2	19	water	18
Biogas (21)	dry organics	100	gas	61
	process water	29	nondigested solids	39
			water	29
Fermentation (10)	wood	100	ethanol	16.4
			residue	85.6

UNIVERSITY OF OKLAHOMA LIBRARY

TABLE 4

NET ENERGY BALANCE: BTU'S

(BASIS: 1 lb. DRY FEED)

Process	In		Out	
Occidental	Biomass	4500-9000	gas	internal use
Flash Pyrolysis (24,26,32)	Operating energy		char	internal use
	purchased	645-30	oil	2200-3930
	internal	6-450		
Waste-to-Oil (32)	Biomass	9000	gas	internal use
	Operating energy	NA	char	trace
			oil	5250
Tech-Air (30)	Biomass	8740	gas	3980
				(internal use
	Operating energy		char	3250
	purchased	NA	oil	1170
	internal	3980		
Purox (24)	Biomass (MSW)	4500	gas	3649
	Operating energy		char	internal use
	purchased	1323	oil	internal use
	internal	NA		
Moore-Canada (10)	Biomass	9000	gas	7070
	Operating energy		char	NA
	purchased	213	oil	internal use
	internal	25		
Syngas (31)	Biomass	9000	gas	6679
	Operating energy		char	internal use
	purchased	NA	oil	NA
	internal	549		
Biogas (21)	Biomass	9000	gas	5935
	Operating energy			
	purchased	212		
	internal	0		
Fermentation (10)	Biomass	9000	ethanol	2021
	Operating energy		furfural	102
	internal	6354	methanol	84
			residue	6354
				(internal use

TABLE 5

ENERGY FLOW STREAMS AND ENERGY EVALUATIONS (BTU)

Process	Stream (see Figure 2) 1	2	3	4	5	NTE	EBR
Flash Pyrolysis							
24 MSW	4500	2200	6	645	1549	34.4%	3.38
32 BARK	9000	3930	450	29	3450	38.3%	8.2
Waste-To-Oil 33	9000	5250	NA	NA	NA	58.3%*	NA
Tech-Air 30	8740	5150 (oil=1170)	3980	NA	NA	13.4%*	1.29*
Purox: MSW 24	4500	3649	274	1323	2052	45.6%	2.29
Moore-Canada 10	9000	7070	25	645	6400	71.1%	10.6
Syngas 31	9000	6679	549	NA	NA	68.1%	NA
Biogas 21	9000	5935	0	635	5300	58.9%	9.35
Fermentation 10	9000	8561	6354#	0	2207**	24.5%	1.35

NA - Not available

*limited information available on process energy requirements, thus value shown here is high.

**includes ethanol, methanol, furfural.

#assumes all the residue is available to generate the required process steam at 50-60% efficiency.

process flow diagram is given in Figure 3. The material and energy balances are in Tables 3 and 4.

The feed to the pyrolysis reactor must be finely shredded (<14 mesh) and dried to about 3 wt.% moisture. The feed material resembles vacuum cleaner fluff. It is introduced into the reactor by a screw feeder which enters the transfer line, where the feed is carried into the reactor by the circulating product gas from the char burner. The pyrolysis takes place at approximately 510°C (950°F) and 1 atm gauge pressure. This temperature maximizes the liquid yield; higher tempeatures promote further cracking and the production of gas. A short residence time also helps reduce the amount of gas produced. The pyrolysis product stream is rapidly quenched to insure that the products remain at reaction temperature for a short time period. This cooling is done with a shell and tube heat exchanger to prevent a high water concentration in the product stream.

Separation of the combustion and pyrolysis zones allows the pyrolysis to take place in the absence of air or oxygen. Also, no hydrogen or catalyst is used.

The yield in Flash Pyrolysis is approximately 40 kg oil per 100 kg of organics on a dry basis. This oil has a higher heating value of 23,320 BTU/kg (10,600 BTU/lb). A material balance for the process is given in Table 3. There are some special problems that must be dealt with when using the pyrolytic oil (Its properties are given in

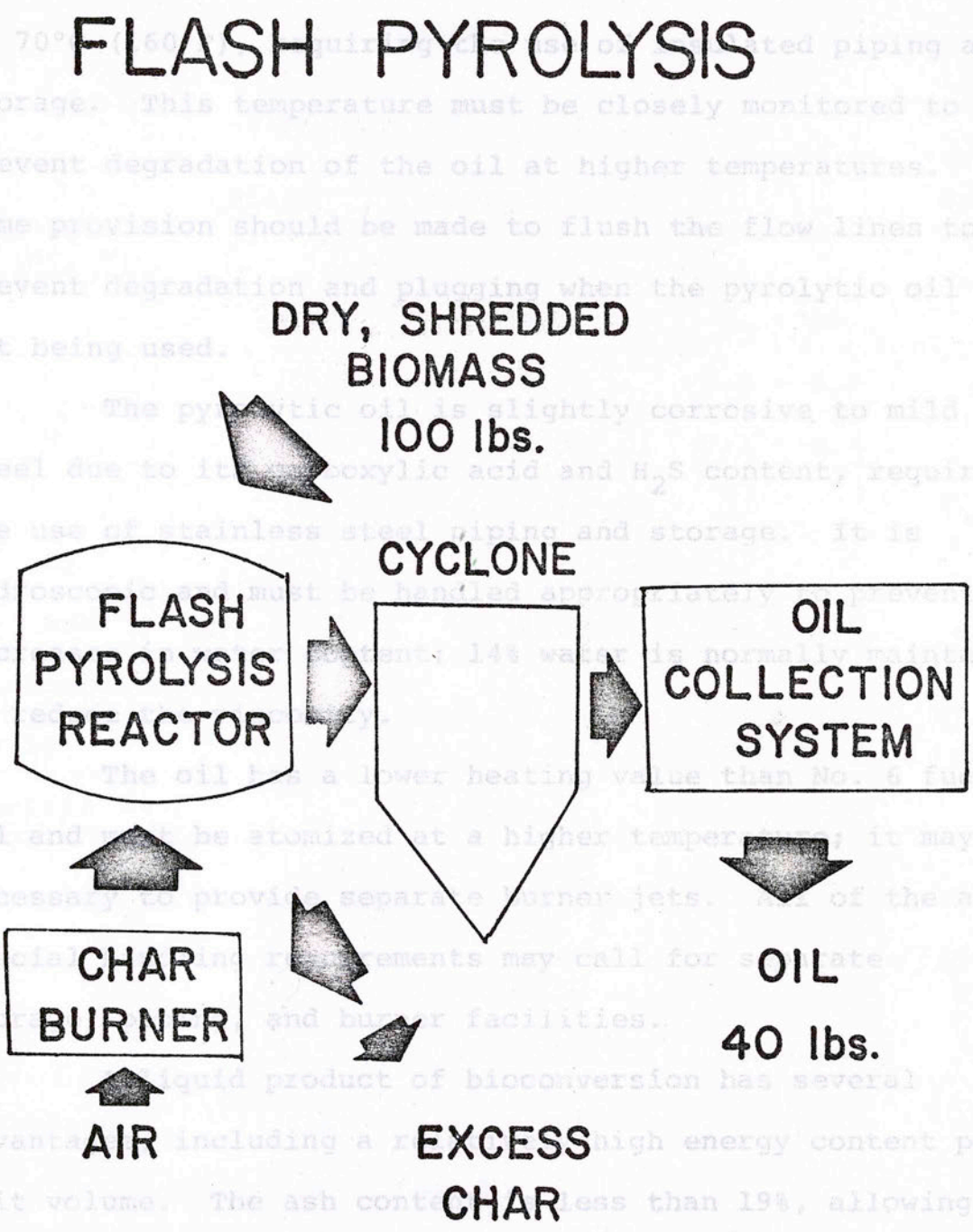


Figure 3. Flash Pyrolysis Flow Diagram.

Table 6.) It is very viscous and must be pumped and stored at 70°C (160°F), requiring the use of insulated piping and storage. This temperature must be closely monitored to prevent degradation of the oil at higher temperatures. Some provision should be made to flush the flow lines to prevent degradation and plugging when the pyrolytic oil is not being used.

The pyrolytic oil is slightly corrosive to mild steel due to its carboxylic acid and H_2S content, requiring the use of stainless steel piping and storage. It is hydroscopic and must be handled appropriately to prevent increases in water content; 14% water is normally maintained to reduce the viscosity.

The oil has a lower heating value than No. 6 fuel oil and must be atomized at a higher temperature; it may be necessary to provide separate burner jets. All of the above special handling requirements may call for separate storage, piping, and burner facilities.

A liquid product of bioconversion has several advantages, including a relatively high energy content per unit volume. The ash content is less than 19%, allowing use in facilities without ash handling equipment. The liquid fuel is easier to transport and store than solid fuel. Pyrolytic oil has a low sulfur content and may be blended with higher sulfur content No. 6 fuel oil to meet environmental requirements. It can be used in large industrial

TABLE 6

PYROLYTIC OIL PROPERTIES

Composition (Wt. %)	Flash Pyrolysis	Georgia-Tech Air	Waste-to-Oil	No. 6 Fuel Oil
C	57.0	59.5	86 - 88	85.7
H	7.7	7.0	6.4 - 6.7	10.5
N	1.1	0.9	0.1 - 0.4	*
S	0.2	0.01		0.5-3.5
Cl	0.3	--		--
Ash	0.5	0.08	4 - 6.4	2.0
Heating Value (BTU/lb)	(10,600)	(10,655)	(15,000)	(18,200)
BTU/kg	23,320	23,441	33,000	40,040
Specific Gravity	1.3			0.98
Viscosity	(14% H_2O)	(14% H_2O)		
Temperature	(190°F) 87.8°C	(167°F) 75°C	?	(190°F) 87.8°C
SSU	1150	170	1000-5000	340
Reference	(24)	(6)	(6)	(24)

* Nitrogen + Oxygen is 2.0 wt.%

applications that are using No. 6 fuel oil, such as electric utilities and steam-electric power plants.

All of the demonstration work has been done with an MSW feed. Considering only the dry-organic material in the MSW and extrapolating the energy balance for MSW (21) gives an NTE of 34.4% and EBR of 3.38. However, based on data for tree bark pyrolysis in a 3.6 t per day (4 dry tons/day) pilot plant (32), NTE is 38% and EBR is 8.2. The yield of pyrolytic oil increases by 4%, but the energy requirements for the biomass feed preparation have decreased dramatically.

Currently (July 1978), the demonstration plant is shut down while an engineering evaluation is completed. To date, only 300 barrels of pyrolytic oil have been produced at a rate of 0.6 BBL per ton of raw MSW. This compares to a predicted yield of 1.13 BBL/ton. During these production runs, the system never was operated under optimum conditions.

Waste-to-Oil

The Waste-to-Oil process converts biomass to liquid fuel by carboxylolysis. Carboxylolysis is the catalytic conversion of cellulose to oil in the presence of carbon monoxide and water. The biomass is hydrogenated at 315.6-371.1°C (600-700°F) and 1.38×10^7 - 2.8×10^7 Pa (2000-4000 psi) in the presence of the sodium carbonate catalyst.

This process has been tested on a bench scale and in a .9-.45 t per day (1-1/2 dry tons per day) pilot plant

in Albany, Oregon. A schematic of the conceptual design of a commercial Waste-to-Oil plant is shown in Figure 4. The pilot plant does not generate its own CO and the reactor (a stirred tank) has been bypassed because of mechanical problems with the agitator and reactor head seals. The biomass feed (wood chips) is first dried to 3% or 4% moisture, then ground in a hammer mill to about 50 mesh. This material, which has the consistency of flour, is blended with recycled product oil (oil recycle ratio is 5). This slurry is very viscous and presents some pumping problems. The wood/oil slurry, with up to 30% solids is pumped through a preheater and then into the reactor by a high pressure positive displacement pump (the reactor is bypassed in the pilot plant). Residence times are 20-60 minutes. Pilot plant capacity is 1000 kg/d yielding 400-500 kg/d of oil. The commercial plant yield would be 35% wt. because some of the biomass feed would be diverted to syngas production. Material balances are shown in Table 3.

The pyrolytic oil has a heating value of approximately 33,000 BTU/kg (15,000 BTU/lb). Its properties are shown in Table 6. It is a very viscous material and increases in product oil viscosity have been the cause of some pilot plant shutdown during test runs. This pyrolytic oil is also corrosive and presents the same problems as discussed in the flash pyrolysis section.

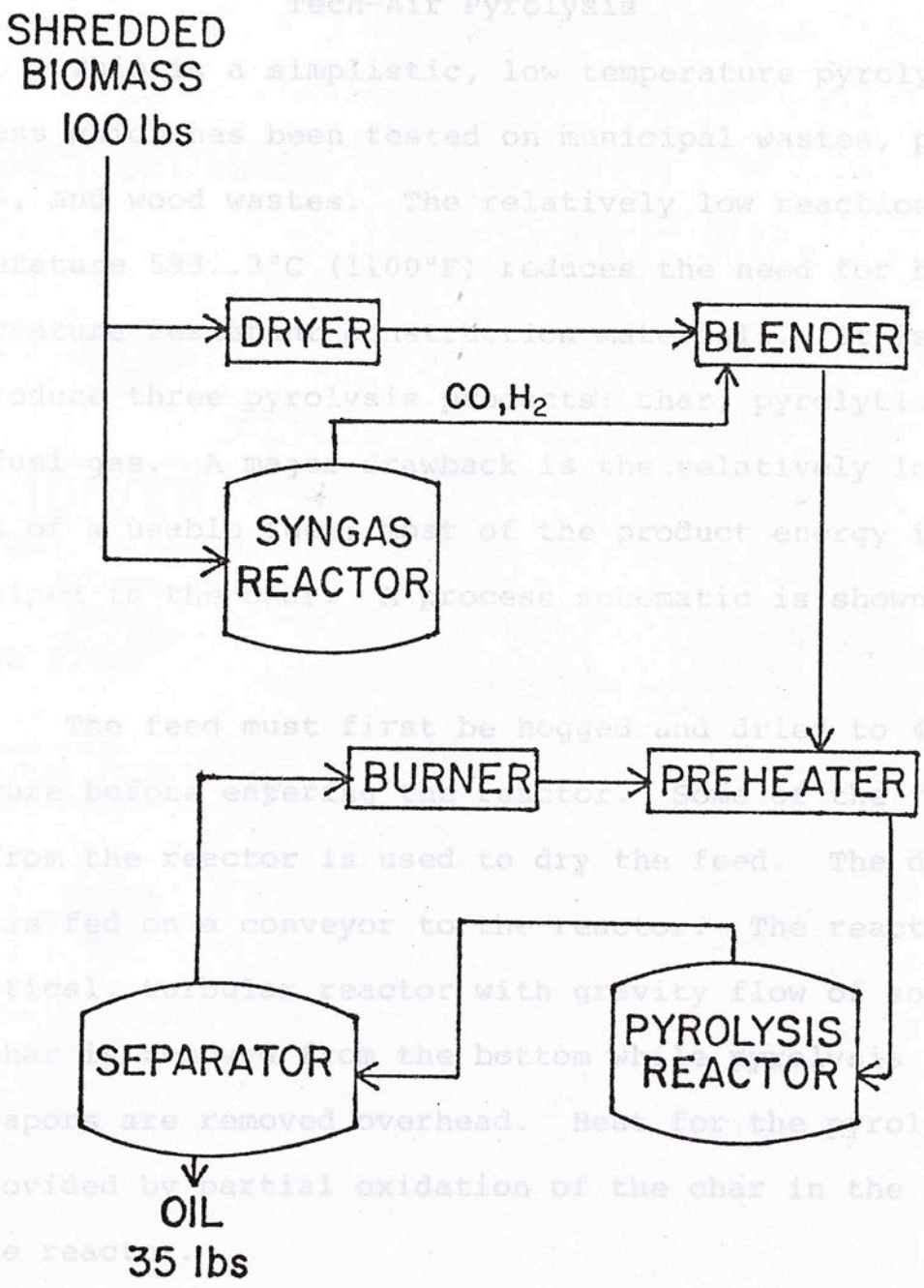


Figure 4. Waste-to-Oil Flow Diagram.

The energy balances are given in Table 4. There was no information supplied by the developer concerning the process energy requirements. These requirements would lower the NTE given in Table 5.

Tech-Air Pyrolysis

This is a simplistic, low temperature pyrolysis process which has been tested on municipal wastes, peanut hulls, and wood wastes. The relatively low reaction temperature 593..3°C (1100°F) reduces the need for high temperature resistant construction materials. It is designed to produce three pyrolysis products: char, pyrolytic oil, and fuel gas. A major drawback is the relatively low yiels of a usable fuel; most of the product energy is contained in the char. A process schematic is shown in Figure 5.

The feed must first be hogged and dried to 4 wt % moisture before entering the reactor. Some of the fuel gas from the reactor is used to dry the feed. The dry feed is fed on a conveyor to the reactor. The reactor is a vertical, turbular reactor with gravity flow of solids. The char is removed from the bottom while pyrolysis gas and vapors are removed overhead. Heat for the pyrolysis is provided by partial oxidation of the char in the bottom of the reactor.

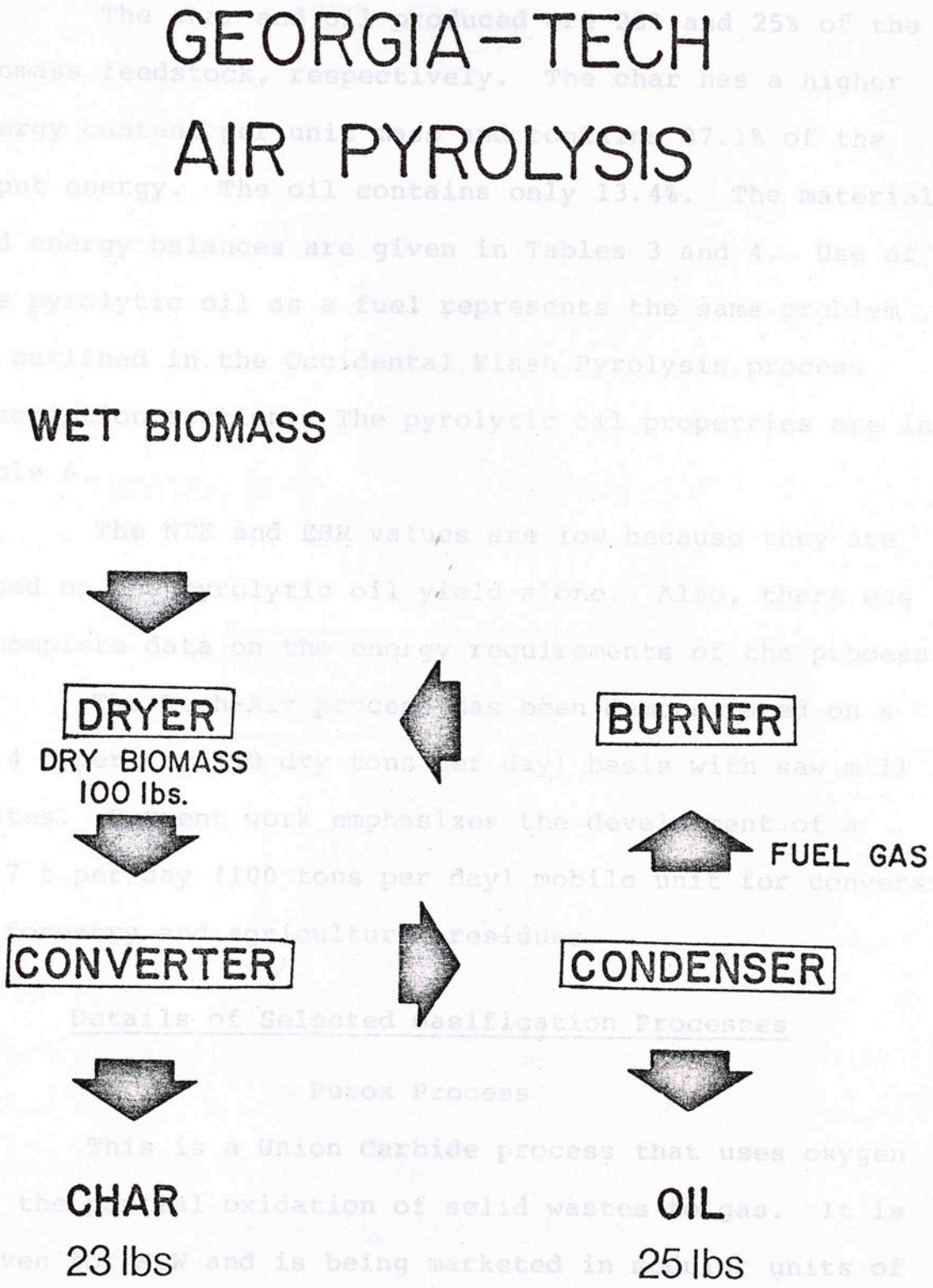


Figure 5. Georgia-Tech Air Pyrolysis Flow Diagram.

The char and oil produced are 23% and 25% of the dry biomass feedstock, respectively. The char has a higher energy content per unit mass and contains 37.1% of the input energy. The oil contains only 13.4%. The material and energy balances are given in Tables 3 and 4. Use of the pyrolytic oil as a fuel represents the same problem as outlined in the Occidental Flash Pyrolysis process description section. The pyrolytic oil properties are in Table 6.

The NTE and EBR values are low because they are based on the pyrolytic oil yield alone. Also, there was incomplete data on the energy requirements of the process.

The Tech-Air process has been demonstrated on a 45.4 t per day (50 dry tons per day) basis with saw mill wastes. Current work emphasizes the development of a 90.7 t per day (100 tons per day) mobile unit for conversion of forestry and agricultural residues.

Details of Selected Gasification Processes

Purox Process

This is a Union Carbide process that uses oxygen for the partial oxidation of solid wastes to gas. It is proven for MSW and is being marketed in modular units of 288.5 t per day (318 tons per day). These units have three vertical-shaft converters in parallel with one spare, allowing one to be serviced without reducing plant throughput. An overall process diagram is shown in Figure 6.

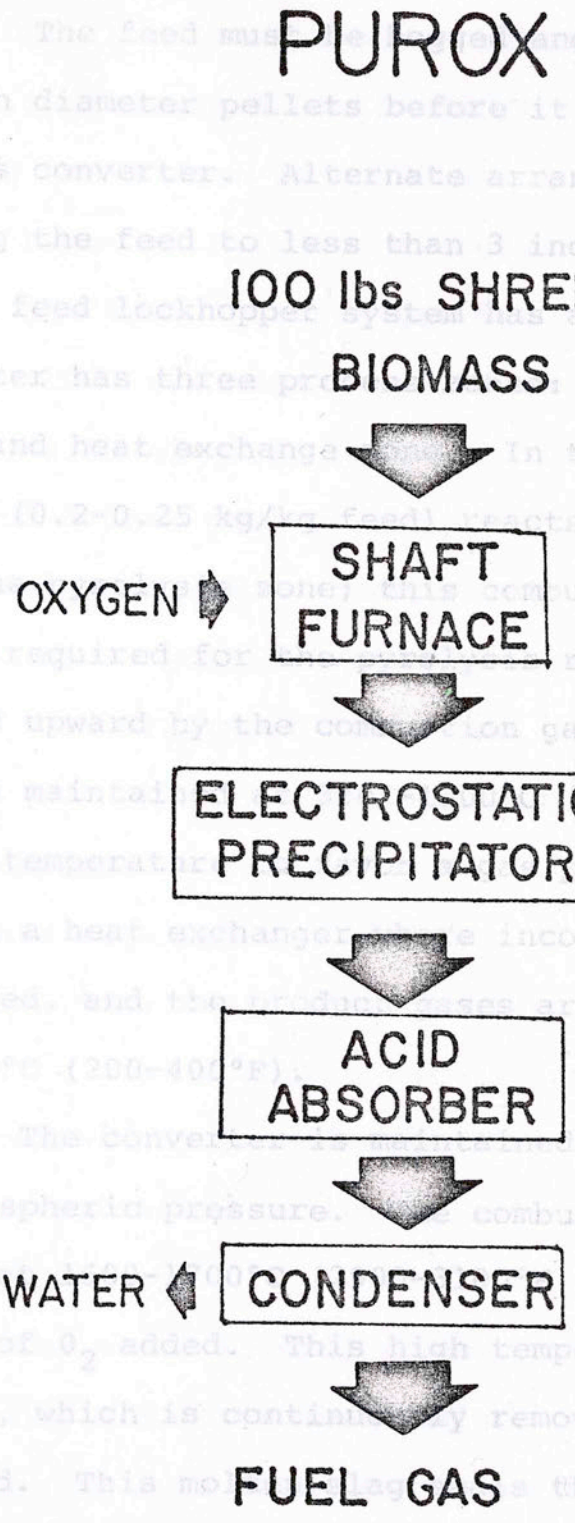


Figure 6. Purox Flow Diagram

The feed must be hogged and then compacted into 14-inch diameter pellets before it is ram injected into the biomass converter. Alternate arrangements call for hammer milling the feed to less than 3 inches and then injecting it. A feed lockhopper system has also been used. Each converter has three process zones: combustion zone, pyrolysis zone, and heat exchange zone. In the bottom zone, the oxygen (0.2-0.25 kg/kg feed) reacts with the char residue from the pyrolysis zone; this combustion provides the energy required for the pyrolysis reaction. This energy is carried upward by the combustion gases. The pyrolysis zone is maintained at 320°-1000°C (600°-1800°F), a high enough temperature to favor a gas product. The upper zone acts as a heat exchanger where incoming biomass is heated and dried, and the product gases are cooled to around 100-200°C (200-400°F).

The converter is maintained at a low pressure close to atmospheric pressure. The combustion zone is maintained at 1600-1700°C (2900-3100°F) by controlling the amount of 0_2 added. This high temperature gives a slag residue, which is continuously removed from the reactor and quenched. This molten slag seals the pyrolyzer and apparently helps protect the refractory from corrosion. A relatively high concentration of ash is needed in the feedstock for formation of this slag. The wastes are drawn off continuously and fed into a water quench tank. The waste is then collected in granular form and used for landfill.

The product gas has a heating value of 285-350 Btu/scf and represents 8.25×10^6 BTU/t MSW (7.5×10^6 BTU/ton). The fuel gas stream is 65-75 wt. % of the dry biomass input. Material balances are given in Table 3.

The Purox process gas has several disadvantages for use as a fuel gas when compared to methane. The composition of the gas is given in Table 7. The Purox gas has a high water and sulfur content, requiring additional processing to reduce the moisture content and remove the sulfur. It has a lower heating value per unit volume and is more expensive to transport and store. The H_2 content of the gas requires special consideration to prevent escape into the atmosphere, including annulus piping. The CO content of the gas required the addition of a special odorizer due to its toxic nature. These transportation problems indicate that a site specific use is desirable. The sulfur can be removed by an amine scrubbing step; this is necessary to reduce pollution and to prevent corrosion of copper piping.

There are several advantages for this process. The gas has a lower combustion air requirement and the flue gas volume is less than that of methane, giving slightly higher theoretical efficiency. The use of pure oxygen drastically reduces the amount of N_2 in the gas and lowers compression costs for further processing compared to air feed gasification processes. This is a source of syngas ($CO + H_2$) for methanation, methanol or Fischer-Tropsch synthesis.

TABLE 7

CRUDE PRODUCT GAS COMPOSITIONS (VOL. %)

	Purox	Moore-Canada	Syngas (estimated)	Biogas
Wet Basis				
CO	45.6	24.2	8.7	--
H_2	27.3	19.3	17.4	--
CO_2	12.8	9.0	21.3	40
H_2O	4.7	3.2	42.5	--
CH_4+	8.0	3.6	10.1	60
N_2	1.0	40.2	--	--
O_2	--	0.5	--	--
Ref.	6	10	31	21
Dry Basis			(estimated)	
CO	35.7	25.0	15.1	
H_2	28.9	20.0	30.3	
CO_2	23.4	9.3	37.3	
CH_4+	10.1	3.7	17.3	
N_2	1.7	41.5		
O_2		0.5		
Ref.	24	10	30	
BTU/SCF	350-390	180	329	600

Energy balances and efficiency calculations are summarized in Tables 4 and 5. The EBR is relatively low because of the high processing energy requirements.

The material and energy balance information presented here was developed from data based on a MSW feed conversion in a 181.44 t per day (200 tons per day) plant. No actual runs have been made with biomass, although a computer simulator model developer by Union Carbide predicts comparable yields. A 9.1 t per day (10 tons per day) pilot plant at Tonawanda, New York, is being readied for operation with homogeneous biomass feedstocks. No definite test plans for the facility have been formulated.

Moore-Canada Gasifier

The Moore-Canada gasifier is a relatively simple process that is suitable for biomass feedstocks. Commercial units in modules of 54.43 t per day (60 dry tons per day) capacity are being used to gasify forest residues. A mixture of air and steam is the gasifying medium. The addition of steam increases the amount of H_2 in the product gas from about 10% to 20% by partial completion of the water-gas-shift reaction and steam gasification of the char. A process flow diagram is shown in Figure 7.

The biomass feed in hogged form is introduced into the top of the reactor through the hoppers; back-leakage of gas is minimized by a rotary grate in the bottom of the

MOORE - CANADA

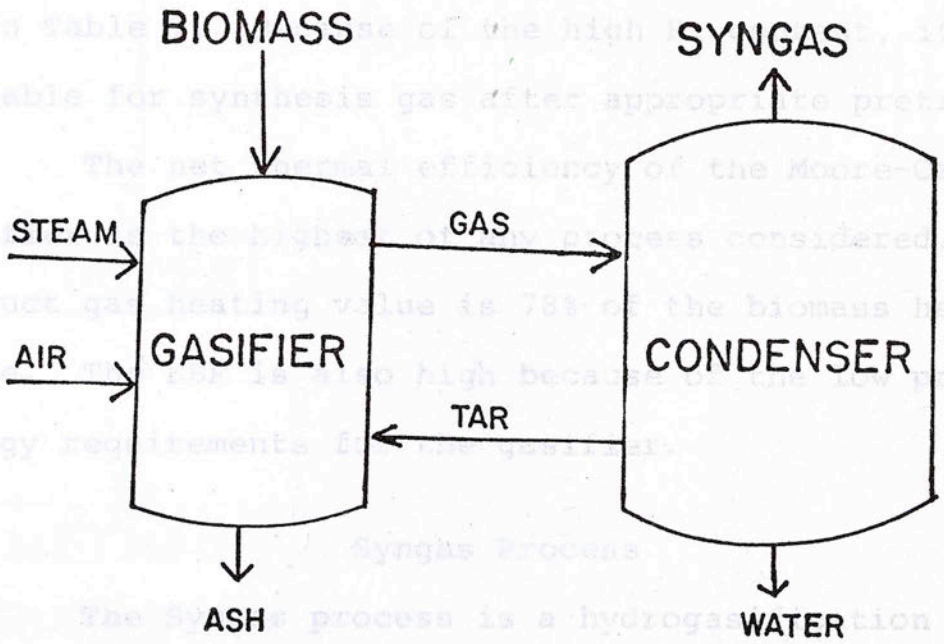


Figure 7. Moore-Canada Flow Diagram.

feed chute. The reactor is a vertical, moving packed bed. Steam, air, and decanted tar from the product gas scrubber are added at the bottom of the reactor. The maximum reactor temperature is about 1204.4°C (2200°F); reactor pressure varies from 7-3 psig (bottom-top). Unconverted material is discharged in solid, granular form. Material and energy balances are given in Tables 3 and 4.

This process gives a gas with a low heating value, 180 BTU/SCF due to the high N_2 content. The gas composition is in Table 7. Because of the high H_2 content, it appears suitable for synthesis gas after appropriate pretreatment.

The net thermal efficiency of the Moore-Canada gasifier is the highest of any process considered. The product gas heating value is 78% of the biomass heating value. The EBR is also high because of the low process energy requirements for the gasifier.

Syngas Process

The Syngas process is a hydrogasification process being developed [.09 dry t per day (0.1 dry tons per day)] for conversion of biomass to a methane-rich gas. Steam and oxygen are used to gasify residual char in one reactor, while the hydrogen-rich gases provide the heat for pyrolysis in a second reactor (see Figure 8).

The biomass is first shredded and then fed (via lockhoppers) to the first stage reactor where it is dried, devolatized, and hydrogasified to produce gas and char.

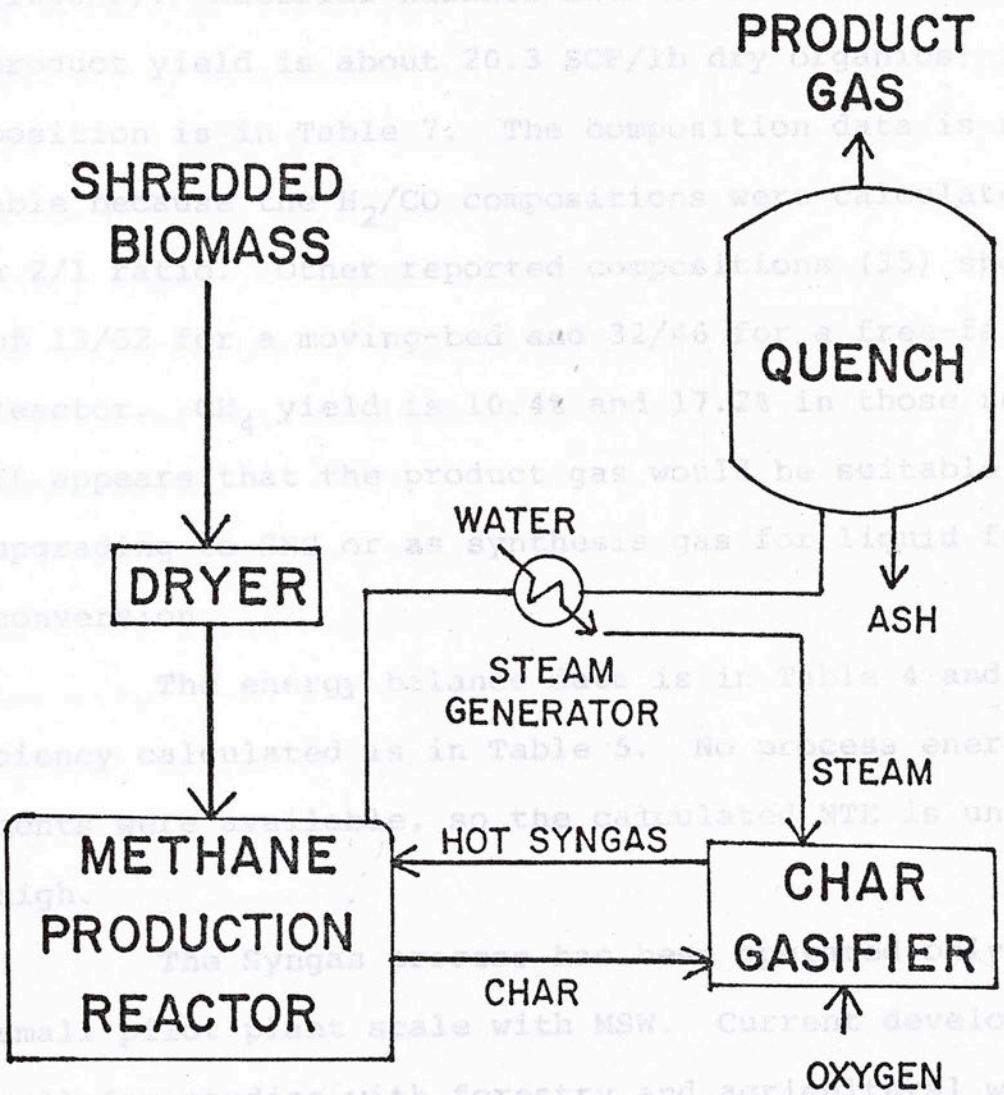


Figure 8. Syngas Flow Diagram.

This reactor is a vertical flow, moving-bed or free-fall reactor which operates at 648.9-871.1°C (1200-1600°F), 250 psig. The residual char goes to a second stage where it is gasified with steam and oxygen (0.13 kg/kg feed) at 648.9°C (1200°F). Material balance data is in Table 3. The gas product yield is about 20.3 SCF/lb dry organics; its composition is in Table 7. The composition data is not reliable because the H_2/CO compositions were calculated assuming a 2/1 ratio. Other reported compositions (35) show H_2/CO of 13/52 for a moving-bed and 32/46 for a free-fall reactor. CH_4 yield is 10.4% and 17.2% in those reactors. It appears that the product gas would be suitable for upgrading to SNG or as synthesis gas for liquid fuel conversion.

The energy balance data is in Table 4 and the efficiency calculated is in Table 5. No process energy requirements were available, so the calculated NTE is unrealistically high.

The Syngas process has been operated only on a small pilot plant scale with MSW. Current development plans call for studies with forestry and agricultural wastes in larger demonstration units.

SNG Production by Anaerobic Digestion

Thermochemical conversion processes become economically and thermodynamically prohibitive as the moisture content of the feed rises. These high moisture feeds are

suitable for microbiological processing, including fermentation (see next section) and anaerobic digestion. There are a large number of operations demonstrating the feasibility of converting high moisture waste to fuel gas by anaerobic digestion. Most of the present large-scale operations are concerned with the processing of feedlot and dairy manure to produce methane. A number of small scale studies have demonstrated the feasibility of digesting other types of biomass such as grass and kelp. However, the application of anaerobic digestion to other biomass feedstocks will require additional demonstration on a large scale.

The basic process involves the retention of a slurry in which anaerobic bacteria digest organic materials in two steps. In the first step, enzymic action from acid-forming bacteria breaks down the starches, proteins, and cellulose into simpler low molecular weight organic acids and carbon dioxide. Next, methane-producing microorganisms convert the organic acids to methane and carbon dioxide. A typical gaseous product stream contains 600 BTU/SCF. The energy content of the gas may be increased by the removal of carbon dioxide and trace amounts of hydrogen sulfide with a MEA scrubber. The gas may be further dried to a pipeline quality gas.

While numerous variations of the anaerobic digestion process have been proposed and tested by many groups, the

important process variables remain the same--temperature of operation, retention time, and reactor configuration. Temperatures may be either psychrophilic, mesophilic, or thermophilic; that is, low temperature (60°F or so), medium temperature (90°F or so), or high temperature (140°F or so). The reaction at psychrophilic conditions are very slow, while the reaction at the higher temperature is fastest and requires a shorter residence time. However, the parasitic power requirement is greater because of the energy required to keep the reaction at that higher temperature. Digestion may take place in one large reactor in a batch process or in a series of smaller reactors approaching a plug-flow process. Typical yields are four to five cubic feet of gas per pound of dry feed.

The effluent stream has a high BOD content and must usually be treated in a conventional sewage plant. Similarly the undigested sludge must be incinerated or landfilled. It is for these reasons that the major applications for anaerobic digestion have been in areas where waste disposal is a problem in the first place--sewage sludge, manure, and MSW.

The potential extension of the anaerobic digestion process to the concept of an "energy farm" depends mainly on the required effluent treatment and by-product recovery. In one case, it may be possible to recycle most of the effluent to the farm for use as a fertilizer. In this case, the high volume of effluent involved would preclude

transportation for long distances. Even so, a pilot-scale demonstration of such a process would be required.

Figure 9 is a simplified diagram of a biogas process. In this case, 45.4 kg (100 pounds) of shredded, ash-free, dry biomass are mixed and digested to yield over twenty pounds of pure methane gas. For processes containing no sulfur in the feed, H_2S removal is not a problem. In either case, CO_2 scrubbing and drying is required for the production of pipeline quality gas. The sludge must undergo sewage treatment and contains all the refuse inorganics which were initially introduced with the feed. Material and energy balances are in Tables 3, 4, and 5.

Ethanol Production by Fermentation

Microbiological processes can lead to the formation of literally thousands of chemical compounds. By 1975, 453,600 t per year (500,000 tons per year) of fermentable sugars were being used annually by the chemical industry to produce materials ranging from antibiotics to vitamin C. While butanol and other industrial chemicals may be produced this way, consideration will be given only to the production of ethanol for use as a liquid fuel.

Ethanol has major uses both as a fuel and as a chemical feedstock. It is a clean fuel and contains approximately 30% more energy per unit mass than methanol. The direct conversion of simple sugars into ethanol by fermentation leads to a concentration of approximately 80% of

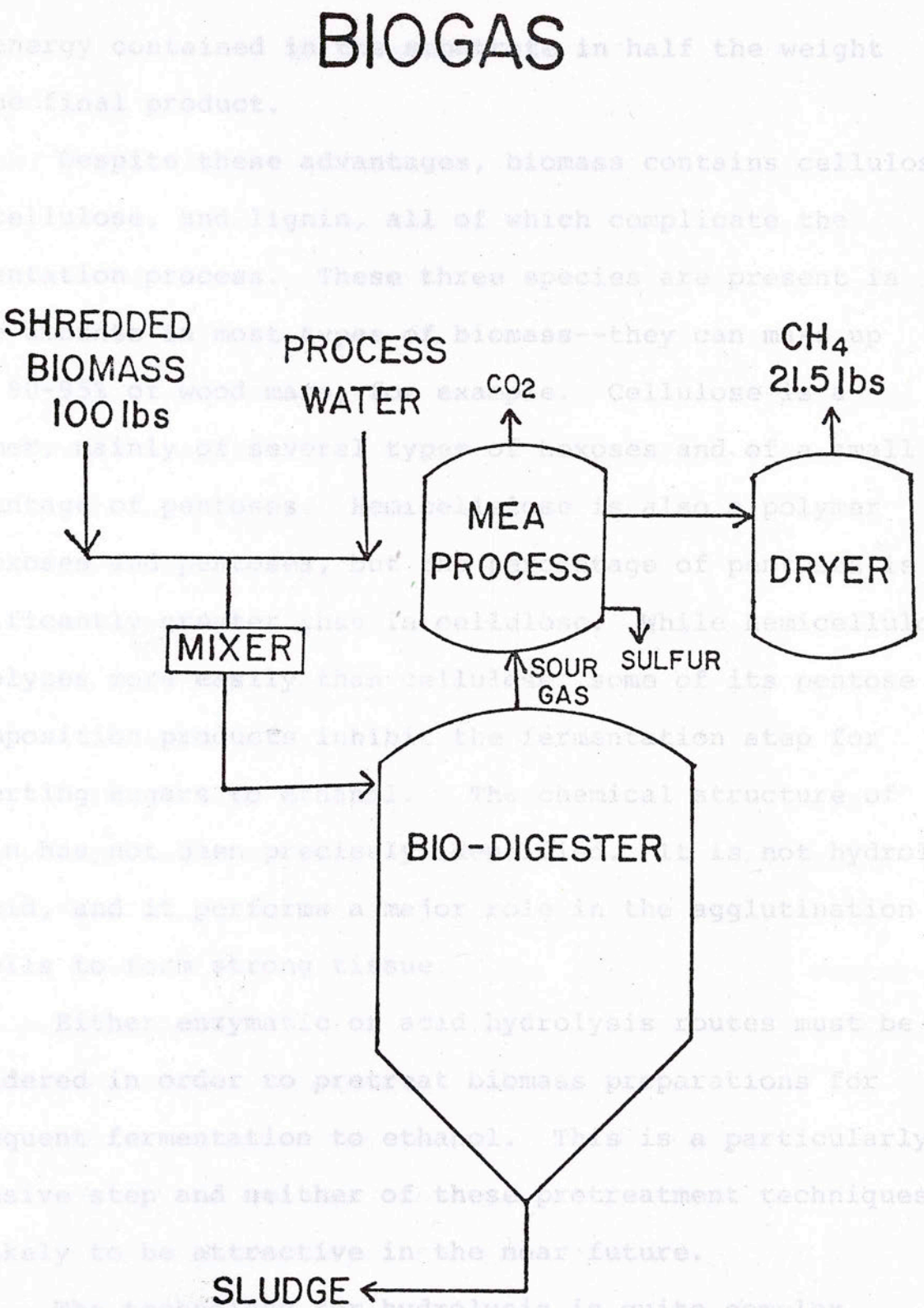


Figure 9. Biogas Flow Diagram.

the energy contained in the substrate in half the weight of the final product.

Despite these advantages, biomass contains cellulose, hemicellulose, and lignin, all of which complicate the fermentation process. These three species are present in large amounts in most types of biomass--they can make up from 90-95% of wood mass, for example. Cellulose is a polymer, mainly of several types of hexoses and of a small percentage of pentoses. Hemicellulose is also a polymer of hexoses and pentoses, but the percentage of pentoses is significantly greater than in cellulose. While hemicellulose hydrolyzes more easily than cellulose, some of its pentose decomposition products inhibit the fermentation step for converting sugars to ethanol. The chemical structure of lignin has not been precisely identified. It is not hydrolyzed by acid, and it performs a major role in the agglutination of cells to form strong tissue.

Either enzymatic or acid hydrolysis routes must be considered in order to pretreat biomass preparations for subsequent fermentation to ethanol. This is a particularly expensive step and neither of these pretreatment techniques is likely to be attractive in the near future.

The technology for hydrolysis is quite complex, but many processing approaches are in a relatively advanced stage of development (see 6). They generally involve use of acids such as sulfuric acid or hydrochloric acid, or

the use of enzymes. Rate operations such as the diffusion of acid into the cellulosic particle render process control particularly difficult. For example, too much hydrolysis may lead to the decomposition and/or repolymerization of the sugars. The sugars forming on the outside of a particle may saccharify the surface, rendering the permeation of acid into the interior of the wood particle. For enzyme hydrolysis, it is also possible that a pretreatment involving delignification (as is done in wood pulping) may be necessary.

Once the sugars are obtained by hydrolysis, however, conversion to ethanol is quite straightforward and widely practiced in industry.

Fermentation to ethanol is very expensive, both from the capital investment standpoint and the production cost standpoint. The steps include sterilization, microorganism preparation, pasteurization, fermentation, centrifugation, and distillation. In addition, the stillage must be concentrated by evaporation (see Figure 10).

The major advantage of fermentation is that it can handle very dilute and wet feedstocks. On this basis, the long range opportunities for this technology are distinctly desirable.

FERMENTATION

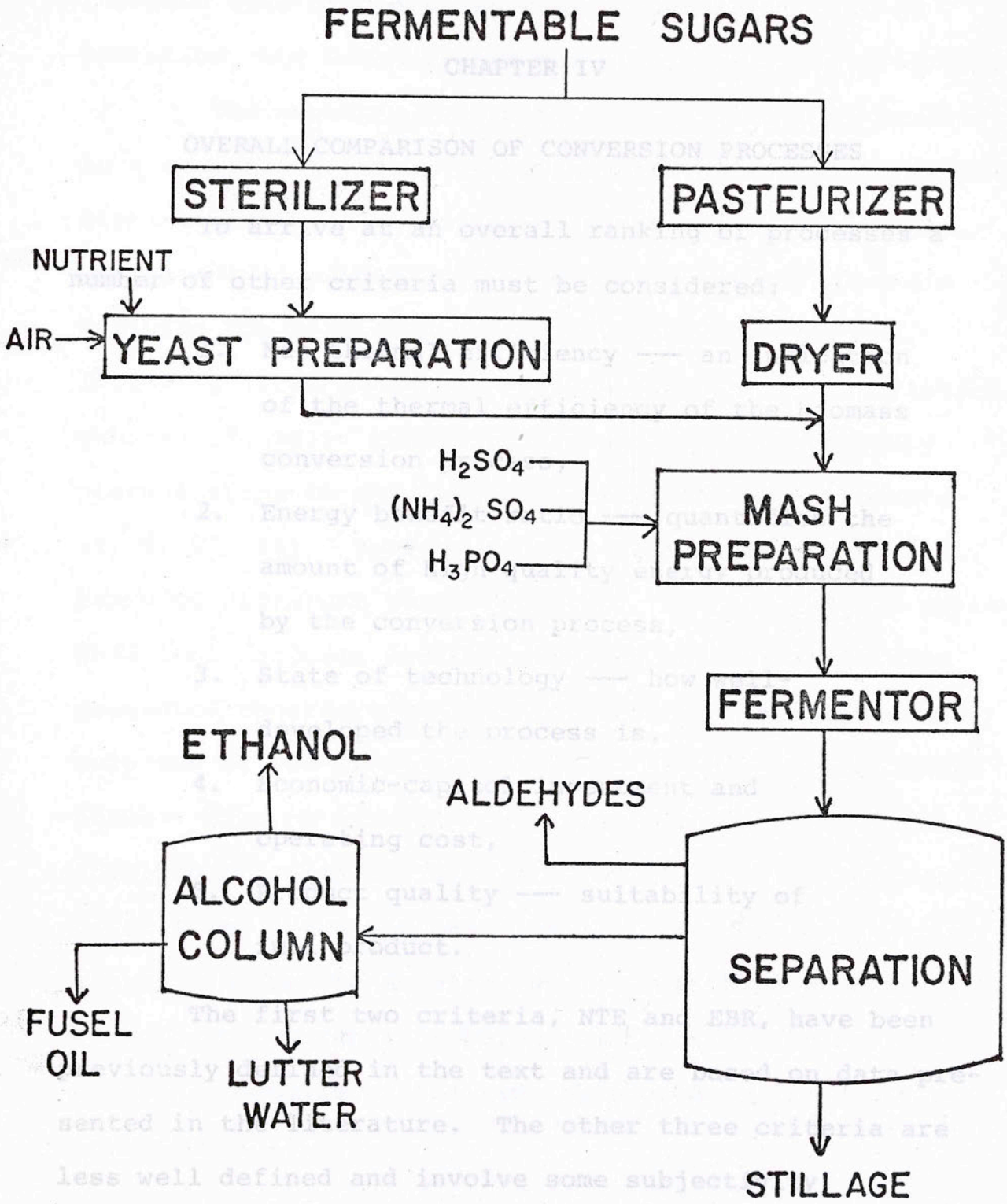


Figure 10. Fermentation Flow Diagram.

CHAPTER IV

OVERALL COMPARISON OF CONVERSION PROCESSES

To arrive at an overall ranking of processes a number of other criteria must be considered:

1. Net thermal efficiency —— an indication of the thermal efficiency of the biomass conversion process,
2. Energy benefit ratio —— quantifies the amount of high quality energy produced by the conversion process,
3. State of technology —— how well-developed the process is,
4. Economic-capitol investment and operating cost,
5. Product quality —— suitability of fuel product.

The first two criteria, NTE and EBR, have been previously defined in the text and are based on data presented in the literature. The other three criteria are less well defined and involve some subjectivity.

The ranking in the category of state of technology is based on development and operating experience. This includes size of operating plants, length of time in operation, and demonstrated use of biomass as a feedstock.

The economic information is difficult to present in a consistent format since the data presented in various studies are based on different plant sizes, feedstocks, and extent of processing. The most developed economic analyses considered complete, site specific designs, including local feedstock availability and transportation charges (7, 24). Other studies include the necessary process steps to manufacture certain chemical products (6, 8, 10, 36). Various studies also present data in terms of different years' dollars. No one study is available that includes economic data on all eight specific processes considered in this evaluation; some include only one or two processes (10, 24, 32, 36), while others present data on general conversion methods rather than specific processes. Three studies (6, 7, 37) that contain capital and operating costs on at least four of the processes are used to develop rankings of those processes, with the three rankings being combined into an overall ranking. Details of the ranking procedure are contained in Appendix II.

Product quality is based on the suitability of the fuel for transportation, storage, and use in existing facilities. Ethanol is a clean liquid and of very high quality in all considerations. The other liquid products (pyrolytic oils) are very corrosive and viscous and are rated last. This reasoning leaves gasification products which fall in the middle.

Each of the conversion processes is ranked from 1 to 8 in each of these categories. Ten quality points are given for a ranking of 1; 9 for a ranking 2, etc. Twenty quality points are given for the NTE and EBR ranking of 1 and then the quality points are reduced by 2 for each ranking. The sum of the quality points then gives the final ranking. These results and calculations are summarized in the following Tables 11, 12, and 13.

Based on these technological criteria, the gasification processes rank the highest, the pyrolytic oil processes the lowest. Anaerobic digestion also is ranked high. Although fermentation is ranked first in two categories--state of technology and product quality, its poor energy conversion efficiency and high economic cost adversely affects its final, overall ranking.

TABLE 8

RANKING OF PROCESSES

Process	NTE	EBR	Technology	Economics	Product Quality
Moore-Canada	1	1	2	3	3.5
Syngas	2	5	8	4	3.5
Biogas	3	2	6	1	3.5
Waste-to-Oil	4	6	7	2	7
Purox	5	4	3	5	3.5
Flash Pyrolysis	6	3	5	6	7
Fermentation	7	7	1	7	1
Tech-Air	8	8	4	8	7

TABLE 9

OVERALL RANKING OF CONVERSION PROCESSES

						Pts*	Overall Ranking
Moore-Canada	20	+ 20	+ 9	+ 6	+ 7.5 =	62.5	1
Syngas	18	12	3	5	7.5	45.5	3
Biogas	16	18	5	8	7.5	54.5	2
Waste-to-Oil	14	10	4	7	4	39	5
Purox	12	14	8	4	7.5	45.5	3
Flash Pyrolysis	10	16	6	3	4	39	5
Fermentation	8	8	10	2	10	38	7
Tech-Air	6	6	7	1	4	24	8

*70 pts. maximum

TABLE 10

CONVERSION PROCESSES IN ORDER OF OVERALL RANKING

Moore-Canada
Biogas
Syngas & Purox
Waste-to-Oil & Flash Pyrolysis
Fermentation
Tech-Air

CHAPTER V

CONCLUSIONS

The many processes which yield fuels from biomass are in quite diverse stages of technical development. A number of the most promising technologies have been described and evaluated, but there are a large number of problems yet to be resolved.

One fundamental problem has been the uncertainty of basic design information. While there exist many publications containing limited experimental or design information, it is doubted that engineers from the oil or coal industry would rely on these data for the construction of a major biomass conversion unit. There is no single entity known as "biomass" and for that reason most data for conversion processes must be extrapolated to the case at hand. Processes have been tested for a number of different types of biomass, but little is known about the operating constraints placed on those processes by nature of the variation in feedstock properties.

Possibly because of this problem, the difficulties of scale-up with the more advanced technologies also have been evident. This may be observed by the recent problems

experienced in the area of flash pyrolysis, gasification, and carboxylolysis.

Indeed, some important problems scarcely have been investigated. Because of the seasonal variations in the availability of biomass, the problem of storage needs to be addressed in great detail. The very nature of biomass makes it susceptible to changes during storage, and the economic and technical implications of these changes need to be better defined. Further, the fate of the inorganic residues needs to be determined, along with the productivity of the biomass field as a function of the ash/inorganics recycle. The fate of bound nitrogen in the thermochemical reactions needs to be determined, particularly since the presence of bound nitrogen in liquid fuels has important environmental consequences. The other, more specific, problems involved with the individual technologies have been outlined in the body of this report.

Based on the limited data available, the processes most advanced technically are not necessarily the most favored from an energy or economic standpoint. All of these considerations have been used to evaluate the eight selected conversion processes, demonstrating that processes leading to the direct production of liquid fuels, such as fermentation, pyrolysis, and catalytic liquefaction, are at an economic and/or technical disadvantage when compared to either combustion or gasification schemes such as anaerobic digestion or thermochemical gasification.

BIBLIOGRAPHY

1. J.M. Radovich, et al. "Evaluation of the Potential for Producing Liquid Fuels from Biomaterials," University of Oklahoma, January 1979, EPRI AF-974.

2. J. Jones, "Converting Solid Wastes and Residues to Fuel." Chem. Eng., 1978, 85(1), 87.

3. D.E. Garrett, "Thermochemical Processing of Biomass Materials," Proceedings: Fuels From Biomass Symposium, University of Illinois, 1977.

4. "Clean Fuels from Biomass, Sewage, Urban Refuse, Agricultural Wastes," Symposium Papers, IGT Conference, Orlando, Florida, January 25-28, 1977.

5. "Clean Fuels from Biomass and Wastes," Symposium Papers, IGT Conference, Orlando, Florida, January 25-28, 1977.

6. "Silvicultural Biomass Farms," The MITRE Corporation/ METREK Division, May 1977, (5 vols).

7. J. Alich, et al., "Program Definition for Fuels from Biomass," Stanford Research Institute, Report to California Energy Resources, Conservation and Development Commission, October 1976, Project #5527.

8. Fuels from Sugar Crops: Report on System Study of Fuels from Sugarcane, Sweet Sorghum, and Sugar Beets, Vols. 1-5, (BMI-1957).

9. D.J. DeRenzo, Energy from Bioconversion of Waste Materials. Park Ridge, New Jersey: Noyes Data Corp., 1977.

10. R. Katzen & Associates, Chemicals from Wood Waste. Washington, D.C.: USDA, U.S. Forest Products Laboratory, December 1975, Pub. AN 4441.

11. P.N. Cheremisinoff and A.G. Morrisi, Energy from Solid Wastes. New York: Marcel Dekker, Inc., 1976.

12. Biomass Literature Search, Energy Production from Biomass Materials by Thermal Processing. Claremont, California: Conversion of Biomass into Gaseous Products, Garrett Energy Res. and Eng. Inc., August 25, 1976, No. E(04-3)-1241.

13. R.C. Bailie and M. Ishida, "Gasification of Solid Waste Materials in Fluidized Beds." AIChE Symp. Ser. 68 (122) 73, 1972.

14. Malcolm D. Fraser, "The Photosynthesis Energy Factory." Intertechnology Corporation, April 1977, ERDA Contract No. (48-18) - 2548.

15. "Feasibility Study: Conversion of Solid Waste to Methanol or Ammonia," Mathematical Sciences Northwest, Inc., for City of Seattle, September 1974.

16. W.E. Franklin, et al., "Resource Recovery: The State of Technology," Midwest Research Institute for Council on Environmental Quality, February 1973.

17. W.E. Franklin, et al., "Resource Recovery: Catalogue of Processes," Midwest Research Institute for Council on Environmental Quality, February 1973.

18. N.J. Weinstein, "Municipal - Scale Thermal Processing of Solid Wastes," RECON Systems, Inc., for U.S.E.P.A., 1977.

19. C.J. Huang and C. Dalton, "Energy Recovery from Solid Waste, Vol. 2, Technical Report," University of Houston for NASA, April 1973.

20. J.L. Keuster and L. Lutes, "Fuel and Feedstock from Refuse," Environ. Sci. and Tech. 10 (4), 1976, p. 339.

21. D.L. Klauss and S. Ghosh, "Fuel Gas from Organic Wastes," Chem. Tech. 3 (11), 1973, p. 689.

22. D.L. Klauss, "Make SNG from Waste and Biomass," Hydrocarbon Processing, 55 (4), 1976, p. 76.

23. N.W. Snyder, "Energy Recovery and Resource Recycling," Chem. Engr. 81 (22), 1974, p. 65.

24. Edison Coordinated Joint Regional Solid Waste Energy Recovery Project: Feasibility Investigation, Bechtel (77-RD-1), April 1977.

25. T. Jackson, Energy from Solid Waste. Park Ridge, N.J.: Noyes Data Corp., 1974.

26. "Fuels from Municipal Refuse for Utilities: Technology Assessment," Bechtel Corporation, March 1975, EPRI 261-1.

27. "Synthetic Fuels from Municipal, Industrial and Agricultural Wastes," NTIS Search, November 1975-1976 (NTIS/PS-77/0113).

28. Jerry L. Jones, et al., "Pyrolysis, Thermal Gasification, and Liquefaction of Solid Wastes and Residues," Presented at ASME 8th Nat'l. Waste Proc. Conference, Chicago, Ill., Mary 1978.

29. S.H. Chiang, J.T. Cobb, and G.E. Klinzing, "A Critical Analysis of the Technology and Economics for the Production of Liquid and Gaseous Fuels from Waste," Presented at 84th Nat'l. AIChE Meeting, Atlanta, February 1978.

30. J.A. Knight, et al., "Pyrolytic Conversion of Agricultural Wastes to Fuels," Presented at ASAE Meeting, Stillwater, Oklahoma, June 23-26, 1974.

31. H.F. Feldmann and J.K. Adlerstein, "The Syngas Process," Presented at ACS Anaheim Meeting, March 12-17, 1978.

32. F.B. Boucher, et al., "Pyrolysis of Industrial Wastes for Oil and Activated Carbon Recovery," May 1977, EPA-600/2-77-091.

33. Biomass Liquefaction at Albany, Oregon. Technical Report, Bechtel, March 1978.

34. T.K. Chow, D.W. Steinbridge, G.A. White, Screening Evaluation: Synthetic Liquid Fuels Manufacture. Ralph M. Parsons Co., August 1977, EPRI AF-523 (Research Project 715).

35. H.F. Feldmann, et al., "Pipeline Gas from Solid Wastes by the SYNGAS Recycling Process," Presented at ACS Meeting, Fuel Division Symposium, April 1976.

36. R.C. Bailie, "Technical and Economic Assessment of Methods for Direct Conversion of Agricultural Residue to Useable Energy," Plant Physiology Inst., West Virginia University, October 1976, No. 12-14-1001-598.

37. F.A. Schooley, et al., "Fuels from Biomass Commercialization Study (DOD) Mission Analysis," Stanford Research Institute, Report to the U.S. Department of Energy, Fuels from Biomass Systems Branch, October 1978.

APPENDIX I

ENERGY AND MATERIAL BALANCE CALCULATIONS

The information available on the eight selected processes was used to present energy and material balances on a consistent basis. The material balance data was presented on a 100 kg biomass feed when practical; Purox data was given with a 100 kg MSW feed basis. The energy balances were based on one pound of feed which was assumed to have a heating value of 9000 BTU/lb unless otherwise stated. Any available data on electric power consumption was converted to BTU/lb-feed and then multiplied by three to allow for the electric generation efficiency; this result was then used for energy flow "4" as illustrated in Figure 2. Energy flow "5" was then calculated as "2" - ("3" + "4").

The data presented on the Purox process and the Flash Pyrolysis processes, using MSW as a feedstock, were based on straightforward calculations using 441 and 215 BTU/lb-feed, respectively, for electricity requirements. The mass balance data was taken from the references.

Data was also available using bark as a feedstock for the Flash Pyrolysis process; the energy balance is included in Table 5 since bark is considered "biomass" in this paper. The raw data was for a 1200 ODT/D plant design with a 445 ton/day barkoil output. Electrical power requirements for the pyrolysis section were given as 200 kw, or 4800 kw-hr/day. It was assumed that 5% of the product oil was used internally to provide heat for the reactor.

The mass balance data for the Moore-Canada process was given for a reactor with 125,000 lb/day dry wood feed. This information was converted to a 100-lb feed basis and included in Table 3. The energy balance data was given for the entire plant with chemical products, so an attempt was made to isolate the pyrolysis reactor. The internal energy requirement (Stream 2, Figure 2) was calculated from the steam feed requirement of 20,000 lb/hr at 30 psig. An energy requirement of 25 BTU/lb feed was calculated using an enthalpy of 1172 BTU/lb for steam and a 75% steam generation efficiency. Turbine horsepower requirements were given for the reactor-gasifier blower (2,300) and for electric generation (9,300). A conservative estimate of the electricity needed was taken to be 90% of the 9300 horsepower required for electric generation plus the 2300 horsepower for the reactor-gasifier blower or the electric equivalent of 10670 horsepower. This converted to 645 BTU/lb feed using the factor of 3 for electric generation efficiency discussed above.

The reference on fermentation gave an energy balance in units of BTU/hr. The wood feed energy rate was given as 1108.8 BTU/hr. This rate was used in converting the other energy flow streams to a 9000 BTU feed basis (since the heating value of wood is 9000 BTU/lb). The data used and the resultant energy balance are as follows:

	Given (BTU/hr)	9000 BTU Basis (BTU)
Feed:		
Wood	1108.8	9000
Products:		
Ethanol	249	2021
Furfural	12.6	102
Methanol	10.3	84
Total		2207
Residue:		
Pentoses	32.8	226
Residue	775	6128
Total		6354
Unknown		439

The unknown energy flow was assumed to be lost from the system in a manner such as heat loss. It should be noted that no purchased electricity is needed because the residue is burned to generate the required heat and electricity. The mass balance was also given as a flow rate in units of lb/hr. Using a feed rate of 123,000 lb/hr for wood, a product rate of 20,200 lb/hr of ethanol, and a basis of 100 lb feed gave 16.4 lb ethanol. The rest (85.6 lb.) was assumed to be residue.

The only information available to calculate an energy balance for the Waste-to-Oil process was a mass balance with the heating values of the feed and product. As a result, no allowance for process energy requirements was possible, resulting in a high value for the NTE. This

lack of data also prevented the calculation of the EBR. Mass balance data was given with a 100-lb wood feed, so no calculations were necessary to convert to the standard basis. Heating values for wood and oil were given as 9000 and 15,000 BTU/lb, respectively.

The mass balance for Tech-Air process was given with a basis of 100-lb bark feed as listed in Table 3. As in the case for Waste-to-Oil, there was limited information on process energy requirements, specifically the amount of electricity needed. The energy flows available were given as rates for a reactor having a 5% NCW Pine Bark feed of 4,000 lb/hr. These rates were then divided by 4000 to give an energy balance based on one-lb wood feed, which had a heating value of 8740 BTU. The raw and resultant energy data are given below:

Process Stream	Energy Rate (MMBTU/hr)	Basis (BTU)
Feed	35	8740
Oil	4.68	1170
Post Condensed Vapor	15.92	3980
Char	13	3250

The material balance in the Syngas reference was given for a feed of 70 lbs "organics" with 30 lbs moisture. This input data was divided by 70/100 to convert to a 100-lb dry "organics" basis. The output streams from the process were given as metal/glass, ash, and product

gas. This output data was incomplete since no amounts were provided with the metal/glass or ash streams. The product gas was given in lb-moles, allowing the calculating of the mass by multiplying by the molecular weight. These calculations are summarized below:

INPUT

Input Stream	Amount (lbs)	Basis: 100 lbs. organics (lbs)
Organics	70	100
Moisture	30	42.9
Steam	23.8	34
Oxygen	13.24	18.9
Total	137.04	195.8

PRODUCT GAS

Constituent	Amount (lb-moles)	Molecular Weight (lbs/lb-mole)	Amount (lbs)
H_2	1.134	2	2.27
CH_4	0.612	16	9.79
CO	0.567	28	15.88
CO_2	1.394	44	61.34
C_2H_6	0.034	30	1.02
C_6H_6	0.11	78	0.86
H_2O	2.771	18	49.88
Total	6.523		141.04

It was apparent that the above balance was in error since it showed more material leaving the process than coming in. One possible explanation was that the metal/glass and ash in the feed contains water that was neglected in the feed data and showed up as water vapor in the output gas. It was assumed that the error was in the water balance, and an attempt was made to present the data on a dry feed basis. Similar data on the part of the process where ash is removed was used to estimate the ash production. Therefore, this material balance should be taken as an approximation due to the above considerations.

The Syngas energy balance was based on 329 BTU/SCF heating value of produced gas and a given production/feed ratio of 20.3 SCF/lb organics. Multiplying these values gave a production ratio of 6679 BTU/lb organics. A process energy/feed ratio was based on material balance data indicating that .34 lb steam/lb organics was required. Assuming that the steam was saturated at 300 psi, the enthalpy change was 1210 BTU/lb allowing the calculation of process energy requirements. With an assumed steam generation efficiency of 75%, the process energy/feed ratio was 549 BTU/lb organics. This ratio was low since no information was available for process electricity requirements. Finally, the NTE calculation was made assuming a 9000 BTU/lb heating value for the organics.

The data used for the material balance for the Biogas process were taken from a projected mass balance for a demonstration plant. Feed for this plant consisted of refuse and sludge. Dry organics and dry sludge feed were used as a basis for the data presented here, since it approximates biomass feed. A material balance for biomass feed was calculated on available information that used a feed containing 39.3 dry refuse organics, 2 dry sludge, and 12 non-process water to produce 25.2 digester gas; a 100 lb dry biomass feed would then give 61 lbs product gas. It should be noted that the projected mass balance for the demonstration plant accounts for processes other than the anaerobic digester, so the resultant data presented here represents an approximation for the digester only. It was assumed that the 12 given as non-process water was needed to allow pumping through the digester and was included in the material balance here as process water.

The Biogas energy balance was given on a rate basis (BTU/day). This energy balance data was converted to a 9000 BTU feed basis instead of a one lb feed basis, since the feed was a mixture of MSW and sewage. The feed was given a 13.86×10^9 BTU/day heating value and the electrical energy usage was given as 9.54×10^4 kw-hr/day. The electricity requirement was converted to BTU/day, multiplied by 3, and put on a 9000 BTU feed basis by dividing by the feed rate as shown below:

$(9.54 \times 10^4$ kw-hr/day)(3410 BTU/kw-hr)(3) = 9.75×10^8 BTU/day

$(9.75 \times 10^8$ BTU/day)(9000 BTU)/$(13.86 \times 10^9$ BTU/day) = 635 BTU

Similarly, the given gas heating value rate of 9.14×10^9 BTU/day was converted to 5935 BTU. The only process energy requirement was that needed as electricity.

APPENDIX II

ECONOMIC COMPARISON CALCULATIONS

The goal of the rankings in the economics category was to compare the capital cost and operating expenses of the various processes based on information available. This information was difficult to compare since each study uses its own set of criteria. Some studies contained information on general conversion methods rather than the specific processes considered in this text. The most developed economic analyses include site specific design, MSW feedstock availability, transportation charges, and disposal costs or credits. Some economics comparisons include all steps necessary to manufacture certain chemical products. Other studies consider only one or two of the processes considered in this evaluation. There are also problems in trying to compare studies that use different plant sizes, different feedstocks, and costs based on different years' dollars.

An approach was decided upon to avoid the problems involved in comparing the various studies. Three studies that contain information on at least four of the processes were used to develop rankings of those processes. The three rankings were then combined into an overall ranking. The data used in the three rankings were standardized by using the NTE calculated in Section 3; the heating value of the feed as given in the three studies was multiplied by the NTE to determine the heating value of the product. The NTE was used to allow data on general conversion methods

to be compared with the specific processes considered here. The capital costs and operating expenses given in the studies were then divided by the calculated product heating value to present results on a consistent basis.

The economic data on fermentation and Biogas were given for a general conversion method in all cases. Data on Purox and Flash Pyrolysis were given specifically in two of the sources used. Information on an air-blown gasifier was used for Moore-Canada, but the cost included steam generation resulting in too high costs. Purox was also approximated by data on an oxygen-blown SNG conversion method. This approximation included conversion from medium BTU gas to SNG, resulting in higher costs. Data on the Purox process was used with the Syngas NTE since no specific economic data on Syngas was available. Cost information for catalytic liquification and pyrolysis was used for Waste-to-Oil and Flash Pyrolysis, respectively. No information was available on Tech-Air so it was rated last.

The rankings based on each economic comparison for both capital costs and operating cost were then used to determine the overall ranking. In cases where there was no clear indication as to what relative order two processes should be ranked, a subjective evaluation of the relative accuracy of the economic data was used.

The information taken from the three studies selected for economic comparisons were summarized in Tables 11A, 11B, and 11C. Information contained in each study were used to compare processes presented in that study only, with the results being combined as stated above. Each study used different criteria for evaluation. The economic data presented from Mitre (6) were in terms of 1976 dollars and were based on a 850 ton/day plant with wood feedstock. The data presented from Alich (7) were also in terms of 1976 dollars, but were based on MSW feed for a 1000 ton/day plant. Data from Schooley (37) were in terms of 1977 dollars and were for various plant sizes and feedstocks. Therefore, the data presented in the three tables should be compared within each table and not among tables.

TABLE 11A

CAPITAL AND OPERATING COST FOR BIOMASS-TO-FUELS CONVERSION PROCESSES

(FROM MITRE CORPORATION (6))

Process	Flash Pyrolysis	Purox	Fermentation	Syngas
Capital Cost (10^6)	16.53	18.14	127.46	18.14
Operation and Maintenance Cost (10^6/yr)	3.53	3.79	22.75	3.79
Feedstock Type	Wood	Wood	Wood	Wood
Feedstock Energy Content (BTU/lb)	8,500	8,500	8,500	8,500
Feed Rate (Ton/day)	850	850	850	850
Feed Energy Content Rate (10^{12} BTU/yr)	5.27	5.27	5.27	5.27
NTE	.383	.492	.245	.681
Output Energy Rate (10^{12} BTU/yr)	2.02	2.59	1.29	3.59
Capital Cost/Output Energy Rate ($/$10^6$ BTU/yr)	8.18	6.99	98.64	5.05
Operation and Maintenance Cost/Output Energy ($/$10^6$ BTU)	1.75	1.46	17.61	1.06
Ranking	3	2	4	1

TABLE 11B

CAPITAL AND OPERATING COST FOR BIOMASS-TO-FUELS CONVERSION PROCESSES

(FROM ALICH, ET AL. (7))

Process	Flash Pyrolysis	Purox	Moore-Canada	Syngas
Capital Cost ($\$10^6$)	25.2	25.4	23.0	25.4
Operation and Maintenance Cost ($\$10^6$/yr)	4.19	3.58	4.23	3.58
Feedstock Type	MSW	MSW	MSW	MSW
Feedstock Energy Content (BTU/lb)	4800	4800	4800	4800
Feed Rate (Ton/day)	1000	1000	1000	1000
Feed Energy Content Rate (10^{12} BTU/yr)	3.5	3.5	3.5	3.5
NTE	.383	.492	.712	.681
Output Energy Rate (10^{12} BTU/yr)	1.34	1.72	2.50	2.39
Capital Cost/Output Energy Rate ($\$/10^6$ BTU/yr)	18.78	14.73	9.22	10.65
Operation and Maintenance Cost/Output Energy ($\$/10^6$ BTU)	3.12	2.08	1.70	1.50
Ranking	4	3	1	2

TABLE 11C

CAPITAL AND OPERATING COST FOR BIOMASS-TO-FUELS CONVERSION PROCESSES

(FROM SCHOOLEY, ET AL. (37))

Process	Waste-To-Oil	Purox	Biogas	Fermentation	Syngas
Capital Cost ($\$10^6$)	144.9	238.5	23.91	27.9	283.5
Operation and Maintenance Cost ($\$10^6$/yr)	15.5	25.2	3.45	12.6	25.2
Feedstock Type	Wood	Wood	Manure	Algae	Wood
Feedstock Energy Content (BTU/lb)	9600	9600	7502	7993	9600
Feed Rate (Ton/day)	3000	3000	1125	1126	3000
Feed Energy Content Rate (10^{12} BTU/yr)	21.0	21.0	6.16	6.57	21.0
NTE	.583	.492	.589	.245	.681
Output Energy Rate (10^{12} BTU/yr)	12.26	10.31	3.63	1.61	14.27
Capital Cost/Output Energy Rate ($/$10^6$ BTU/yr)	11.82	23.14	6.59	17.33	16.71
Operation and Maintenance Cost/Output Energy ($/$10^6$ BTU)	1.27	2.45	.95	7.83	1.77
Ranking	2	4	1	5	3

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A TECHNICAL AND ECONOMIC EVALUATION OF SELECTED BIOMASS-TO-FUELS CONVERSION PROCESSES

A Thesis

Submitted to the Graduate Faculty

in Partial Fulfillment of the Requirement for the

Degree of

MASTER OF SCIENCE

(Petroleum Engineering)

by

CARL F. POMEROY

Norman, Oklahoma

April 1979

UNIVERSITY OF OKLAHOMA
LIBRARY

This volume is the property of the University of Oklahoma, but the literary rights of the author are a separate property and must be respected. Passages must not be copied or closely paraphrased without the previous written consent of the author. If the reader obtains any assistance from this volume, he must give proper credit in his own work.

I grant the University of Oklahoma Libraries permission to make a copy of my thesis upon the request of individuals or libraries. This permission is granted with the understanding that a copy will be provided for research purposes only, and that requestors will be informed of these restrictions.

NAME [redacted]

DATE [redacted]

A library which borrows this thesis for use by its patrons is expected to secure the signature of each user.

This thesis by Carl F. Pomeroy has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

NAME AND ADDRESS	DATE

OU-136