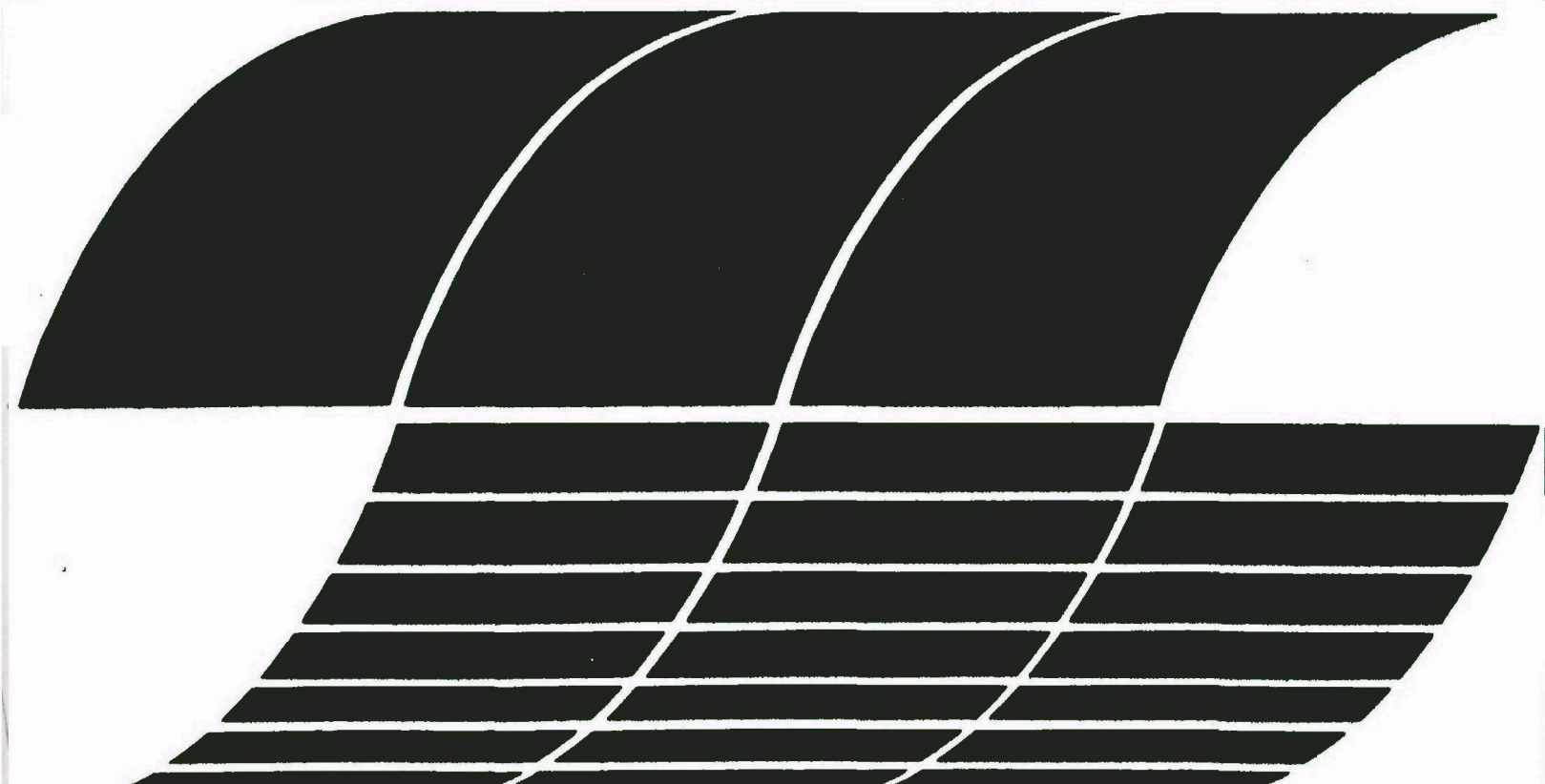




Investigation of Advanced Thermal - Chemical Concepts for Obtaining Improved MSW - Derived Products

Interagency
Energy/Environment
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Report



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INVESTIGATION OF ADVANCED THERMAL-CHEMICAL
CONCEPTS FOR OBTAINING IMPROVED MSW-DERIVED PRODUCTS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report presents information resulting from a study of chemical and thermal treatments to improve the quality of the products derived from the organic fraction of municipal solid waste. Processes for obtaining a carbon char and a powdered fuel are described in depth. It is hoped that the information provided in this report will be of assistance to researchers and developers concerned with resource recovery endeavors.

Francis T. Mayo, Director
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ABSTRACT

A number of resource recovery projects have been instituted to recover fuel, energy, and mineral components from refuse. Although a number of these programs have been effective, the quality of the products recovered could be enhanced to improve their marketability. The purpose of this study was to investigate the potential of known processes that could improve the quality of the fuels or other products derived from the organic fraction in refuse.

To effectively accomplish the stated objective for this study, a comprehensive review of processes for making refuse a better fuel was performed. Information was obtained from the open literature, and through personal contacts. Possible processes for improving the quality of products from the organic fraction derived from municipal solid waste (MSW) were determined, and descriptions were developed for each process. To better evaluate the different processes, an analytical framework for technical and economic assessment was developed to serve as a guide for analysis, as well as for the information acquisition phase of the study. The literature search identified major thermal and chemical processes used in the pulp and paper, wood, textile, and resource recovery industries.

This study concentrated on those processes designed to produce a carbon char, a powdered fuel, and liquid and gaseous fuels from the municipal solid waste. Of particular interest in the production of carbon char were those chemical treatments that promote char formation at lower pyrolysis temperatures. For the production of powdered fuels, the chemical and thermal treatments which cause cellulose embrittlement were of most interest. For the production of gaseous and liquid fuels two processes were evaluated: Worcester Polytechnic's hydrogenation-liquefaction process and Wright-Malta's steam injection pyrolysis process.

A major accomplishment of this project was the identification and laboratory verification of chemical treatments for cellulose embrittlement. As a result of preliminary laboratory studies the basic requirements were defined for producing a fine powdered fuel from the organic fraction of MSW. More quantitative measurements of the embrittlement process parameters are recommended. The problems which could be encountered during the chemical treatment of shredded MSW must also be determined. The

information obtained from these studies could provide the basis for a detailed engineering and economic analysis for a full scale facility to produce a fine powdered fuel.

CONTENTS

Foreword	iii
Abstract	iv-v
Figures	vii
Tables	viii
Acknowledgment	ix
1. Introduction	1
2. Conclusions and Recommendations	3
3. Background	4
4. Literature Search	14
5. Carbon Char Production	16
6. Powdered Solid Fuel	44
7. Liquid and Gaseous Fuels From the Organic Fraction of Municipal Solid Waste	59
References	66
Bibliography	68

FIGURES

<u>Number</u>		<u>Page</u>
1	Results of thermogravimetric analysis in a nitrogen atmosphere	20
2	Basic flow plan for Harendza-Harinxma process. .	22
3	Modified Black-Clawson wet process	25
4	Material and energy balance based on 1 ton MSW to the processing facility	26
5	Flow plan for a plant to convert MSW to a carbon char	37
6	Experimental arrangement used for embrittlement studies	46
7	Resource recovery plan to produce powdered fuel	52
8	Cellulose hydrogenation	61
9	Flow plan for the WPI process	62

TABLES

<u>Number</u>		<u>Page</u>
1	Refuse Composition	5
2	Chemical Analysis of Refuse	5
3	Paper Wastes in Municipal Refuse	6
4	Pyrolysis Reactions of Cellulose	11
5	Potential Char Promoters	18
6	Analysis of the Inert Fraction in the Carbon Char	23
7	Material and Energy Balance Calculation for One Ton of Municipal Solid Waste	27
8	Material Balance Calculations for a Carbon Char Production Process	38
9	Estimated Capital Costs (1977 Dollars)	42
10	Estimated Annual Operating and Maintenance Costs (1977 Dollars)	42
11	Potential Revenue Sources	43
12	Chemical Embrittlement of Paper Screening Study ..	47
13	Combustion Analyses of Paper Powders (Weight Percentage)	48
14	Material Balance for a Powdered Fuel Process	53
15	Estimated Capital Costs (1977 Dollars)	57
16	Estimated Annual Operating and Maintenance Costs (1977 Dollars)	57
17	Potential Revenue Sources	58

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SECTION 1

INTRODUCTION

Effective refuse disposal is a problem that has perpetually plagued mankind. Historically our solid waste has either been buried or burned with little regard for the environmental consequences. In recent years, greater emphasis has been directed toward recovering the valuable mineral components and energy contained in the waste. Utilization of the waste components can reduce the environmental impact of waste disposal and conserve natural resources. A number of resource recovery projects have been instituted to recover fuel, energy, and mineral components from refuse. Although a number of these programs have been effective, the quality of the products recovered could be enhanced to improve their marketability.

The purpose of this study was to investigate the potential of known processes that could improve the quality of the fuels or other products derived from the organic fraction in refuse. Since cellulose products are the major constituents of the organic fraction in refuse, it seemed likely that a number of the processes employed in the pulp, paper, and textile industries would have considerable potential for refuse processing.

To effectively accomplish the stated objective for this study, a comprehensive review of processes for making refuse a better fuel was performed. Information was obtained from the open literature, and through personal contacts. Possible processes for improving the quality of products from the organic fraction derived from municipal solid waste (MSW) were determined, and descriptions were developed for each process. These descriptions included: (a) the techniques and procedures required; (b) the type of industry or application in which the process is employed; (c) the current status of this technique (such as laboratory, pilot, or full-scale plant operation); and (d) economic information about the process. To better evaluate the different processes, an analytical framework for technical and economic assessment was developed to serve as a guide for analysis, as well as for the information acquisition phase of the study.

The literature search identified major thermal and chemical processes used in the pulp and paper, wood, textile,

and resource recovery industries. A brief summary of the information obtained from the literature search is presented in the background section of this report. This study concentrated on those processes designed to produce a carbon char, a powdered fuel, and liquid and gaseous fuels from the municipal solid waste. Of particular interest in the production of carbon char were those chemical treatments that promote char formation at lower pyrolysis temperatures. For the production of powdered fuels, the chemical and thermal treatments which cause cellulose embrittlement were of most interest. For the production of gaseous and liquid fuels two processes were evaluated: Worcester Polytechnic's hydrogenation-liquefaction process and Wright-Malta's steam injection pyrolysis process.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The technology of cellulose chemistry does provide opportunities for processing the organic fraction of Municipal Solid Waste (MSW) to obtain improved products. In this study laboratory processes for obtaining a carbon char and a fine powdered fuel have been identified. In addition laboratory processes for liquid and gaseous fuels described in the literature have been reviewed.

Several chemical treatments for promoting char formation at lower temperatures have been determined. The patented process developed by Dr. Harendza-Harinxma was assessed to be impractical as a means of char production on a large scale. A more feasible means to produce char might be by incorporation of a char promoter in the Black Clawson wet process. A market for the char has not been firmly established. Any market requiring rigid specifications for the carbon char would not be satisfied due to the fluctuations in the content of raw solid waste.

During the course of this project two processes for the production of liquid and gaseous fuels were reviewed. Both the Worcester Polytechnic Institute process and the Wright-Malta Corporation process were selected because of this unique potential. However, after review it was concluded that both processes were not practical for implementation on large scale at the present time.

A major accomplishment of this project was the identification and laboratory verification of chemical treatments for cellulose embrittlement. As a result of preliminary laboratory studies the basic requirements were defined for producing a fine powdered fuel from the organic fraction of MSW. More quantitative measurements of the embrittlement process parameters are recommended. The problems which could be encountered during the chemical treatment of shredded MSW must also be determined. The information obtained from these studies would provide the basis for a detailed engineering and economic analysis for a full scale facility to produce a fine powdered fuel.

SECTION 3

BACKGROUND

Due to the many problems associated with the conventional practices of landfilling and incineration, a number of new techniques are being developed to improve the management of municipal refuse. The majority of these new techniques are concerned with recovering and utilizing the valuable materials in solid waste. Resource recovery is the term applied to the numerous processes and systems being designed to recover components of waste and convert them to useful products. Systems have been developed for energy recovery; compost production; fiber, glass and metal recovery; and alcohol and protein production. The major emphasis has been on those processes designed to recover the thermal energy in waste. Although many of the systems developed have been relatively successful, the quality and consistency of the fuel produced or the energy generated has not been completely satisfactory. Higher quality and greater consistency in the waste-derived fuel or energy is necessary if it is to be marketable for large-scale usage.

The most commonly used process for recovering the thermal energy in municipal waste incinerates the raw refuse directly and uses the heat to generate steam. Steam-raising municipal incinerators are common in Europe and Asia, and during the past several years a number of units have been built in the United States. In addition to direct combustion of raw refuse, a number of processes have been developed for recovering fuel products from the refuse. Fuel recovery is based largely on the use of shredding, magnetic separation, and air classification to obtain the light weight or predominately organic solid fraction from the refuse. A few pilot and demonstration processes have also been developed which convert the organic fraction to a liquid or a gaseous fuel.

3.1 Municipal Refuse

Municipal refuse is a heterogeneous mixture of organic and inorganic wastes discarded from the residential and commercial sectors of the community. The composition of the refuse fluctuates from day to day and season to season. An average distribution of the components in refuse is shown in Table 1. The moisture content of the refuse can vary from 15

TABLE 1¹. REFUSE COMPOSITION

<u>Components</u>	<u>Weight (%)</u>	
Paper	28.9	} Organic Fraction
Plastics	3.4	
Rubber and Leather	2.5	
Textiles	1.6	
Wood	3.7	
Food Wastes	17.8	
Yard Wastes	20.3	
Glass and Ceramics	10.4	
Metal	9.7	
Ferrous - 8.7		
Aluminum - 0.7		
Other - 0.3		
Miscellaneous	1.7	
	100.0	

to 50% but averages about 27%. A typical chemical analysis for refuse is presented in Table 2. From 70 to 80% of the dry weight of refuse will be organic materials, and about 75% of this organic fraction is cellulose.

TABLE 2². CHEMICAL ANALYSIS OF REFUSE

<u>Components</u>	<u>Weight (%)</u>
Carbon	28.00
Hydrogen	3.50
Oxygen	22.35
Nitrogen	0.33
Sulfur	0.16
Moisture	20.73
Inert	24.93

As shown in Table 1, paper is the single largest component of municipal refuse. Food and yard wastes are the next largest components. These wastes plus the wood and textile wastes contribute significant quantities of cellulose to the waste stream. A breakdown of the paper wastes found in refuse is compiled in Table 3. The cellulose content of these products varies from 50 to 90%.

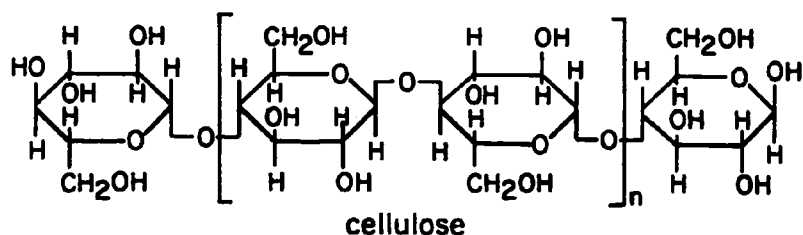
TABLE 3³. PAPER WASTES IN MUNICIPAL REFUSE

Type	Weight %
Newsprint	40
Container and Packaging Board	22
Coarse Paper	13
Book Paper	12
Sanitary and Tissue	8
Fine Paper	4
Ground Wood Paper	1
	100

3.2 Cellulose

Cellulose is a carbohydrate polymer composed of anhydro-glucose units with the empirical formula $C_6H_{10}O_5$. It is the chief structural element and major constituent of the cell walls of trees and of other higher plants. Cellulose is the most abundant and versatile of all naturally occurring organic compounds and plays an increasingly important part in the life of civilized man as a component in many products that he requires daily. It is relatively inexpensive and, unlike some other basic raw materials, it is replenishable.

Cellulose is a linear polymer of glucose containing up to 10,000 monomer units (molecular weight 1,500,000) linked together by β -1,4,D-glucosidic links. Cellulose has the same chemical structure, regardless of whether it occurs in softwoods, hardwoods, flax, cotton, etc. As a result of chemical action such as pulping or bleaching, the native cellulose may be somewhat modified, i.e., the polymer chain is shortened and the terminal group may be converted to a carboxyl group. Certain groupings, such as carbonyl groups which may be formed under certain conditions of bleaching (hypochlorite at pH of about 8.0), result in an instability in the polymer which can result in subsequent yellowing and degradation on aging.



Cellulose is used in its natural fibrous form in paper products and as chemical raw material for the manufacture of cellulose derivatives (cellulose nitrate, ethylcellulose, cellulose acetate, etc.) and regenerated cellulose products (tire cord, viscose rayon, cellophane, etc.).

Cellulose undergoes such reactions as: (1) oxidation; (2) depolymerization; (3) hydrolysis; (4) substitution of hydroxyl groups; (5) reduction of end groups, etc. This range of reactions suggests the possibility that a variety of chemical treatments could attack cellulose and break it down in such a manner that its value as a fuel could be enhanced.

3.3 Fuel Recovery

3.3.1 Dry Processing

The most common method for fuel recovery is the one which was developed in an EPA demonstration program with the City of St. Louis and the Union Electric Company. In this process the refuse is shredded and air-classified to separate the light-weight materials (predominantly organic substances) from the heavier materials (glass, metal, and other noncombustibles). This shredded light fraction, termed RDF (refuse-derived fuel) fluff, has been successfully co-fired with coal in a Union Electric boiler. Several plants have been built and a number of others are planned to produce an RDF fluff. Although each plant may have a somewhat different processing procedure, the fuel fraction is primarily the shredded organic materials with a small percentage of noncombustible fines (glass, stone, metal, dirt, etc.). The quantity of noncombustible material in the refuse-derived fuel, as well as its moisture content and particle size will depend on the specifics of the particular process. Also, for some of the advanced systems the concept of pelletizing the RDF fluff is being studied. Fuel pellets are easier to handle and are more compatible with many boiler designs for fuel injection.

3.3.2 Wet Processing

In addition to the dry processes for recovering the fuel fraction, Black Clawson has developed a wet process based on papermaking technology. This hydropulping process was primarily designed for recovery of paper fibers but can recover over 90% of the organic fraction. The waste is suspended in water and mechanically broken down in size. The slurry from the hydropulper is mechanically dewatered to about 50% solid content. This product has been fired in bark and bagasse-type boilers and in a pilot study was pelletized and fired in a spreader-stoker type boiler.

3.3.3 Powder

A proprietary process for recovering a powdered fuel has been developed by Combustion Equipment Associates (CEA). The air classified, shredded light fraction is chemically treated during a hot ball milling process. It is believed that the chemical and heat treatment cause embrittlement of the cellulose. The ball mill material is screened to 20 mesh fraction. This fine powder contains about 15% inert material which can be reduced by a second air classification. The powdered fuel produced by CEA is marketed under the trade name Eco-Fuel II. This material has a heating value of 7500-8000 Btu/lb, and density of 30 lbs/ft³, a moisture content of approximately 2% and an ash content of approximately 10%.

3.4 Fuel Enhancement Processes

3.4.1 Physical and Chemical Processes

Converting the organic fraction of refuse into a finely powdered fuel offers a number of advantages. In powdered form the refuse is more compatible with the fuel used in suspension fired boilers; it is more easily slurried with oil for firing in liquid fuel units; and it is more easily pelletized for use in moving-grate units.

A number of thermal and chemical treatments have been identified that promote the conversion of the organic fraction in refuse to a fine powder. Since the major constituent of the organic fraction is cellulose (75%), the treatments are based primarily on the technology of cellulose processing. Most of these processes are chosen to embrittle or degrade the cellulose by reducing the degree of polymerization. If the acid or oxidizing treatment uses very strong chemical agents over a prolonged period of time, the cellulose can be transformed into a fine powder. In addition to degradation, certain acid treatments can also promote crosslinking of adjacent molecules, which makes the cellulose rigid and brittle. Heating cellulose in air up to temperatures of 400°F will also result in embrittlement. This is achieved by crosslinking reactions between adjacent molecules, which occur as part of the dehydration process during extended heating. Cellulose treated with formaldehyde also undergoes embrittlement as a result of the formation of oxygen bridges. The formation of ethers and esters of cellulose can also be used as a means for forming powdered fuels. Solidified cellulose ether and ester derivatives are easily ground into fine powders.

Another means for cellulose decomposition is acid hydrolysis. Cellulose is soluble in concentrated solutions of sulfuric, phosphoric, and hydrochloric acids. The end

product of cellulose hydrolysis is glucose. However, continued chemical action on the glucose results in the formation of hydroxymethylfurfural, which produces levulinic acid and formic acid. The glucose recovered from hydrolysis can also be fermented to ethyl alcohol. The feasibility of employing this process for large scale treatment of MSW is questionable.

Combinations of chemical and thermal treatments can also be employed for cellulose decomposition and conversion to liquid fuels. A number of these liquefaction processes have been developed. The conversion of wood products to liquid and gaseous products dates back to the early 1900's. Most commonly, cellulose products were hydrogenated at temperatures from 300-930°F at elevated pressures and in the presence of a catalyst.

Two recently reported processes for the liquefaction of municipal waste were developed by the Bureau of Mines and Worcester Polytechnic Institute. In the Bureau of Mines process, cellulose waste is treated with carbon monoxide and water to obtain a liquid fuel. The reaction is carried out in an autoclave at temperatures of 480-750°F and pressures of 1400-4200 psia. Sodium carbonate is frequently used as a catalyst for this reaction. However, the alkali salts present in municipal refuse also can serve as the catalyst. A small scale demonstration project is underway to evaluate the feasibility of this process in Albany, Oregon.

The Worcester Polytechnic Institute process converts municipal solid waste to a usable liquid fuel. In this process, shredded refuse is slurried in paraffin oil and mixed with a 0.2% nickel hydroxide catalyst. The slurry is pressurized with hydrogen to 1000 psig in an autoclave and heated to 800°F. This hydrogenation reaction in the presence of a nickel catalyst results in the production of oils (bitumens) from the cellulose products in refuse. It does not appear that this laboratory process is feasible for a full scale MSW treatment facility.

3.4.2 Thermal Processes

Thermal decomposition of refuse in the absence or partial absence of oxygen (pyrolysis) has been used for the production of useful fuels. Solid, liquid, or gaseous fuels can be obtained by a variety of pyrolysis processes. The quantity of char, bitumen-like liquid, and gas produced varies and is a function of the time-temperature sequence for each particular process. At the present time the commercial processes of four chemical companies have received considerable attention: (1) Carborundum Company; (2) Monsanto Enviro-Chem Systems; (3) Occidental Research Corporation; and (4) Union Carbide.

Monsanto Enviro-Chem Systems developed a pilot process termed the Langard System which is being demonstrated in a 1000 ton per day (TPD) facility in Baltimore, Maryland. (This demonstration project has encountered a number of operational problems)⁴. Shredded refuse is partially burned with air in a large rotary kiln. The products of this process are a low Btu fuel gas (100 Btu/scf), a carbon char, and a glassy aggregate. The ferrous metal is removed prior to combustion. The fuel gas is burned in an afterburner to raise steam in a waste heat boiler. The solid residue, which contains about 50% char, is quenched and processed in a flotation separator. The char, which is floated off the top of the cell, is landfilled and the aggregate could be marketed as a roadfill material.

The Torrax process developed by the Carborundum Company is a high temperature, air-fed slagging pyrolysis process. This process converts refuse to a low heating value fuel gas, char, and a fused frit. High process temperatures permit fusion of the inert fraction of the refuse. Superheated air introduced into the furnace supplies the thermal energy for slagging of the noncombustibles. Natural gas or a fraction of the pyrolysis gas can be used to preheat the air. The low heating value of the pyrolysis gas (150 Btu/scf) requires that it be used for steam generation in an adjacent boiler unit. The carbon char recovered during the pyrolysis gas cleaning stage can be reinjected into the gas at the boiler as a means of increasing the heating value of the gas and improving the energy recovery efficiency of the Torrax process. This process is being evaluated in several European facilities.

Union Carbide's Purox system is another slagging pyrolysis process. However, in this system oxygen is used in place of air and the pyrolysis gas produced has a higher heating value (300-375 Btu/scf). Although raw refuse can be directly processed in the furnace, it is advantageous to coarsely shred the refuse and remove the ferrous metal prior to pyrolysis. Liquid and solid organics entrained in the pyrolysis gas are removed and recycled back to the furnace to be decomposed. The only products from the Purox system are the medium Btu fuel gas and a glassy slag. A 200 TPD pilot facility is being studied in South Charleston, West Virginia.

The Occidental Research Corporation has developed a short residence time, flash pyrolysis process which converts finely shredded, air-classified refuse into a combustible liquid, a medium Btu fuel gas and a char residue. The char and fuel gas are recycled for use in the pyrolysis system. The process is designed to maximize the liquid fuel yield. This liquid fuel is a highly oxygenated acidic tar, which is somewhat corrosive and viscous. A 200 TPD plant to demonstrate this process has just been completed in El Cajon (San Diego County), California.

In addition to the four major commercial pyrolysis processes described, there are other pilot and laboratory processes that utilize a variety of existing and furnace designs and produce a wide range of fuel products. Rotary kilns, vertical and horizontal shaft furnaces, fluidized bed furnaces, and a variety of batch type reactors have been employed for fuel production. A number of these systems may reach commercial status within the next several years.

3.5 Thermal Decomposition of Cellulose

An effective insight to the pyrolysis of municipal solid waste can be obtained by studying the thermal decomposition of cellulose and cellulose products. The pyrolysis of cellulose can be viewed as a two stage process: (1) dehydration; and (2) depolymerization, though there does not appear to be a sharp delineation between the two. Below 390°F the predominant reaction is dehydration. Water vapor and traces of carbon dioxide, formic and acetic acids, and glyoxal are evolved. Between 390°F and 535°F both dehydration and depolymerization reactions occur. Larger quantities of carbon dioxide, formic and acetic acids, and glyoxal are evolved at these temperatures. In addition, small amounts of carbon monoxide may be released. Above 535°F the primary pyrolysis reaction is depolymerization. This is achieved by scissions of the C-O bonds in the cellulose chain, either in the rings or between rings. Scissions of C-O in the rings result in the disintegration of the ring to yield CO₂, CO and H₂O. Scissions of the C-O bonds between rings results in the production of levoglucosan molecules. Depending on the reaction conditions levoglucosan may either volatilize or decompose thermally to yield gases and a carbonaceous material. The main volatile products from levoglucosan decomposition are CO, H₂, CH₄, CO₂, acetic acid, ethanol, acetaldehyde, acetone, biacetyl, methylethyl ketone, ethylacetate, and tars. Above 930°F secondary decomposition and gasification of the char occur. A summary of the pyrolysis reactions for cellulosic materials is presented in Table 4.

TABLE 4. PYROLYSIS REACTIONS OF CELLULOSE

<u>Temp. (°F)</u>	<u>Process</u>	<u>Major Volatile Products</u>
<390°F	dehydration	water vapor
390-535°F	endothermic dry pyrolysis	CO ₂ , water vapor and acetic acid
535-930°F	exothermic pyrolysis to char	CO, H ₂ , CH ₄ , CO ₂ , acetic acid, ethanol, acetalde- hyde, acetone, biacetyl, methylethyl ketone, and tars
>930°F	gasification of char	HCHO, H ₂ , and CO

As indicated, organic liquids, char, water, and a gas are produced from the pyrolysis of cellulose. The quantities generated are controlled by the heating rate, final temperature and length of exposure to final temperature. In general, the char will constitute between 20-40% of the final product mix, the organic liquids and gas phase can vary between 10-40%, and water constitutes the remaining fraction. The thermal process employed can be designed to maximize the end products desired from the cellulose wastes. Higher heating rates and higher temperatures produce larger quantities of gas and less char. Conversely, lower heating rates and lower temperature processes result in increased char production.

The quantity of char, the composition of the gases and liquids evolved, and the necessary reaction temperatures can be significantly affected by the presence of chemical agents in the cellulose materials. A number of chemical compositions have been identified which increase the quantity of char produced and decrease the amount of combustible gases and tars formed. Many of these compounds were developed for flameproofing cellulosic materials.

In general, the flameproofing agents are selected to direct the pyrolysis process toward maximum production of char, minimum production of tars, and the highest possible proportions of water and carbon dioxide. Over 400 chemicals have been evaluated for use in flameproofing treatments of cellulosic materials. The highly effective compositions are all soluble in water, and most are salts of either strong acids or bases. Strong acids encourage pyrolysis to carbon and water by their reactivity with hydroxyl groups in the cellulose chain. Elimination of water by removal of hydroxyl and hydrogen atoms allows the carbon atoms joined by a double bond to remain as a charcoal residue. In addition, many oxidizing agents attack cellulose and have been found to be effective fire retardants. Oxidized cellulose pyrolyzes rapidly at lower temperatures giving high charcoal residues.

A number of laboratory and pilot processes have been developed to produce charcoal from cellulose wastes by pyrolysis. Except for the work of Dr. A. Harendza-Harinxma,⁵ there is no reported use of chemical additives to promote the quantity of char produced. In most of the processes reported in the literature pyrolysis was carried out between 930-1650°F and the char residue was about one-third to one-fourth of the product mix. From 20-50% of the char residue was inert material, and the char usually contained about 15% volatile materials.

3.6 Biological Processes for Product Recovery

A number of anaerobic digestion processes have also been developed for generating methane gas from solid organic wastes. In many of these processes, municipal refuse and sewage sludge can be combined in the digester. Maximum energy recovery is less than 50% since over half the organics are not digestible. This residue must be disposed of or used in some other type of fuel recovery process.

A variety of chemical processes have also been developed for converting the organic portion of the refuse into other useful products. Wet oxidation, hydrolysis, and photodegradation processes have been developed in the laboratory for producing protein, glucose, alcohol, yeasts, and acids from solid wastes. None of these processes has progressed to the full-scale demonstration phase.

3.7 Some Current Problems

Although many of the laboratory, pilot, and full scale projects have demonstrated the basic technical feasibility of the various energy recovery systems, there are still a number of problems in trying to utilize these processes for full scale MSW processing. This has been particularly true for those processes producing fuels derived from refuse. Problems in materials handling, storage, and combustion have been encountered. Incomplete combustion, increased particulates in the effluent, corrosion, and large fluctuations in heat content have been reported in a number of the full scale demonstration projects. The translation of laboratory and pilot technologies to full size scale-up has also presented a number of difficulties. Improved quality and greater consistency of product are necessary if the waste-derived fuel is to be a marketable product for large-scale usage.

SECTION 4

LITERATURE SEARCH

A literature search was conducted to identify processes for improving the quality of the products from the organic fraction of municipal solid waste. In addition to seeking more information about the conventional resource recovery processes, processes for treating cellulose were also researched. Mechanical, thermal, and chemical treatments used in cellulose processing were of particular interest since cellulose is the major constituent in the organic fraction. References concerned with solid waste management and the wood, textile, pulp, and paper industries were sought. An on-line literature search of the following data bases were conducted:

1. CHEMICAL ABSTRACTS. Chemical Abstracts Condensates covers the chemical literature from 1970 to the present and includes chemical engineering and chemical processes. Solid waste treatment was reviewed as well as chemical processes for cellulosic materials. Subject searching is available through general subject section codes, title words, and assigned descriptors.

2. COMPENDEX (Engineering Index). This data base describes the engineering literature from 1970 to the present. Engineering aspects of solid waste processing and engineering processes concerned with cellulosic materials were covered.

3. NATIONAL TECHNICAL INFORMATION SERVICE (NTIS). This data base covers Federal Government research and development reports from 1964 to the present. All scientific and technical disciplines are represented. Subject search capabilities are provided by the Committee on Scientific and Technical Information or COSATI Code, title words, and assigned descriptors and identifiers.

4. SMITHSONIAN SCIENCE INFORMATION EXCHANGE (SSIE). This data base contains information about recent and on-going research. Approximately 2-year coverage is provided. Project descriptions are maintained of Federal Government projects covered by grants and contracts, many state and local government projects, and university and foundation projects. All scientific and technical disciplines are covered. Subject

retrieval can be performed by title, abstract words, and assigned subject terms.

5. SOLID WASTE INFORMATION RETRIEVAL SYSTEM. In addition, the EPA Solid Waste Information Retrieval System was searched for pertinent items from its data base.

As a result of these searches, over 1,000 citations were obtained and screened to identify the pertinent references. Those so identified were ordered for review. Several hundred documents and patents were ordered. The documents received were logged in and filed, according to subject area. The bibliography of compiled references is presented in Appendix I.

SECTION 5

CARBON CHAR PRODUCTION

Thermal decomposition of organic materials in the absence or partial absence of oxygen (pyrolysis) is used to produce solid, liquid, and gaseous fuels. The quantity and composition of the carbon char, bitumen-like liquid, and gas obtained varies with the nature of the organic starting material and the time-temperature treatment. The chemistry of cellulose pyrolysis provides a reasonable model for the pyrolysis of refuse, since cellulose is the major organic constituent (75%) of the organic fraction.

Although a number of pyrolysis processes have been developed to produce carbon char, our literature research only found one process using chemical treatment to promote char formation. In the patented process developed by Dr. A. Harendza-Harinxma, sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) is used to promote carbon formation at temperatures below 660°F, whereas in most of the conventional pyrolysis processes reported in the literature, pyrolysis is achieved with thermal treatments from 930°F to 1650°F. In addition, the char yield is reportedly increased for the sodium aluminate process. The char residue comprises 20-40% of the final product mix, and contains from 30-50% inert material originating from the paper and plastic fillers and the fine glass, metal, and stone retained in the raw solid waste. The char also contains about 15% volatiles.

5.1 Chemical Treatments for Char Production

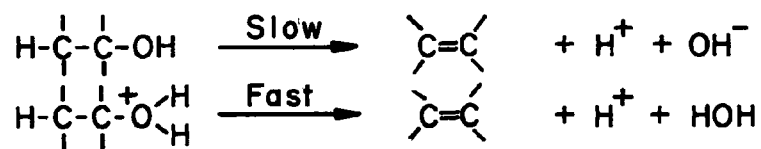
For conventional pyrolysis, carbon char production is maximized by using lower heating rates and lower temperatures of pyrolysis. As reported by Stevenson, et al,⁶ pyrolysis at 950°F produced 32% char while at 1670°F only 25% char was produced.

It has been observed that certain chemical treatments prior to pyrolysis can promote char formation at lower pyrolysis temperatures. Many of the chemical salts used to inhibit combustion in cellulose products (flame-retardants) serve to promote char production during pyrolysis. The effective fire retardants act chiefly by directing the decomposition of cellulosic materials toward the formation of few tars and more water and charcoal, and by initiating decomposition at lower temperatures.

A study of flame retardants by McGeehan and Maddock ⁷ provides a description of the semidurable and durable treatments for imparting flame retardance. In addition to the more elaborate permanent treatments, the authors describe nondurable treatments which involve water-soluble materials and are generally among the least expensive in terms of chemical and application cost.

To promote low temperature charring of municipal solid waste, research should clearly be directed to the nondurable chemical treatments because of their lower costs. A compilation of potential chemical compounds for promoting char formation and estimated quantities for treatment has been abstracted from the McGeehan and Maddock paper, and is presented in Table 5. The salts are usually combined and a synergism is often noted. For example, boric acid alone is ineffective as a flame retardant, but a mixture of 7 parts borax and 3 parts boric acid is effective at a ratio of 6.5 wt. per 100 wt. of fabric. This is better than pure borax, which requires 60% by weight to be effective.

As stated, salts that form acids or bases upon heating are usually effective char promoters. Salts of strong acids (chloride, bromide, iodide, sulfate, phosphate, etc.) and weak bases such as ammonia are the most effective. One mode of action for fire retardation is to increase the carbon residue and decrease the loss of flammable gases and liquids. One possible mechanism for this effect involves the well known catalytic ability of strong acids in bringing about dehydration of alcohols. Although dehydration formally involves loss of hydroxide ion (OH^-) from one carbon atom, and loss of hydrogen ion (H^+) from an adjacent carbon atom, such a reaction is quite difficult due to the powerful basicity of the hydroxide ion. Protonation of the hydroxyl group by an acid weakens the C-O bond, and permits the departure of water, a much weaker base than hydroxide ion.



Owing to the large number of hydroxyl groups in cellulose, repeated dehydrations are required to produce a highly carbonaceous material (char). This would suggest, for example, that acids of low volatility would be preferable to HCl, HBr and HI. However, a few calculations based on data provided by McGeehan and Maddock, reveal that on a molar basis ammonium bromide and iodide are better retardants than ammonium sulfate

TABLE 5. POTENTIAL CHAR PROMOTERS

<u>Chemical</u>	wt. of chemical	moles
	100 wt. of cellulose	100 wt. of cellulose
<u>Ammonium Salts</u>		
Bromide	7	0.071
Molybdate $[(\text{NH}_4)_2\text{MoO}_4]$	7	0.036
Phosphate $[(\text{NH}_4)_2\text{HPO}_4]$	12	0.091
Iodide	14	0.097
Sulfate	18	0.14
Chloride	22	0.41
Borate (NH_4BO_3)	24	0.31
<u>Sodium Salts</u>		
Tungstate $(\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O})$	9	0.027
Stannate $(\text{Na}_2\text{SnO}_3)$	18	0.085
Aluminate $(\text{Na}_2\text{Al}_2\text{O}_4)$	19	0.23
Silicate $(\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O})$	20	-----
Bisulfate (NaHSO_4)	30	0.25
Arsenate $(\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O})$	33	-----
Borate $(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O})$	60	0.16
<u>Miscellaneous</u>		
Phosphoric Acid	12	0.12
Zinc Chloride	12	-----
Calcium Chloride $(\text{CaCl}_2 \cdot 6\text{H}_2\text{O})$	14	0.064
Magnesium Chloride	16	-----

(high b.p.) or phosphoric acid, and ammonium phosphate (high b.p.) is between the bromide and the chloride in effectiveness. Obviously other factors such as acid strength, thermal stability of the salt, and flame retardation effects not related to dehydration (e.g., foaming and radical scavenging) must be considered to provide a quantitative explanation of effectiveness.

Calcium chloride is an effective retardant at the 14 wt. percent level. While this may seem excessive compared to several other salts, economics could make it a desirable reagent for enhancing char formation. The Solvay process for making soda ash (Na_2CO_3) produces calcium chloride as a by-product. Soda ash producers are permitted to dispose of CaCl_2 in the ocean, but not in fresh water. As a result, soda ash producers lacking access to the sea have a disposal problem. If CaCl_2 does serve effectively to increase charring at lower pyrolysis temperatures, it could be the most feasible chemical salt for use in treating refuse prior to pyrolysis treatment.

5.2 Laboratory Studies

During this project three char-promoting materials (NH_4Cl , CaCl_2 , and $\text{Na}_2\text{Al}_2\text{O}_4$) were coated on filter paper and evaluated in a nitrogen atmosphere (to eliminate any effects due to the presence of oxygen). Thermogravimetric analysis (TG), was used to study the pyrolysis of these papers as a function of the chemical treatment.

All of the chemical treatments initiate weight loss at lower temperatures than with untreated paper. The NH_4Cl treatment appears to induce decomposition between 390°F and 570°F, and does not leave a residue as does the $\text{Na}_2\text{Al}_2\text{O}_4$, and CaCl_2 . Interpretation of the resultant TG data was not by itself conclusive. Visual inspections of larger samples heated in a nitrogen atmosphere were also conducted to better assess the chemical treatment. The data from the TG for the three chemical treatments are presented in Figure 1.

Untreated filter paper undergoes slight darkening at 383°F, and becomes brown at 430°F. Similarly, NH_4Cl -treated paper begins to darken at 300°F and is nearly black at 383°F. The TG data are consistent with these observations.

In contrast, filter paper treated with CaCl_2 failed to show any darkening at 383°F, and is only slightly darkened by 428°F (the sample which had been heated to 383°F was brittle). The TG data for CaCl_2 -treated paper did not readily relate to the visual observations.

Other studies with CaCl_2 -treated newspaper were conducted concomitantly with the foregoing experiments. Some slight

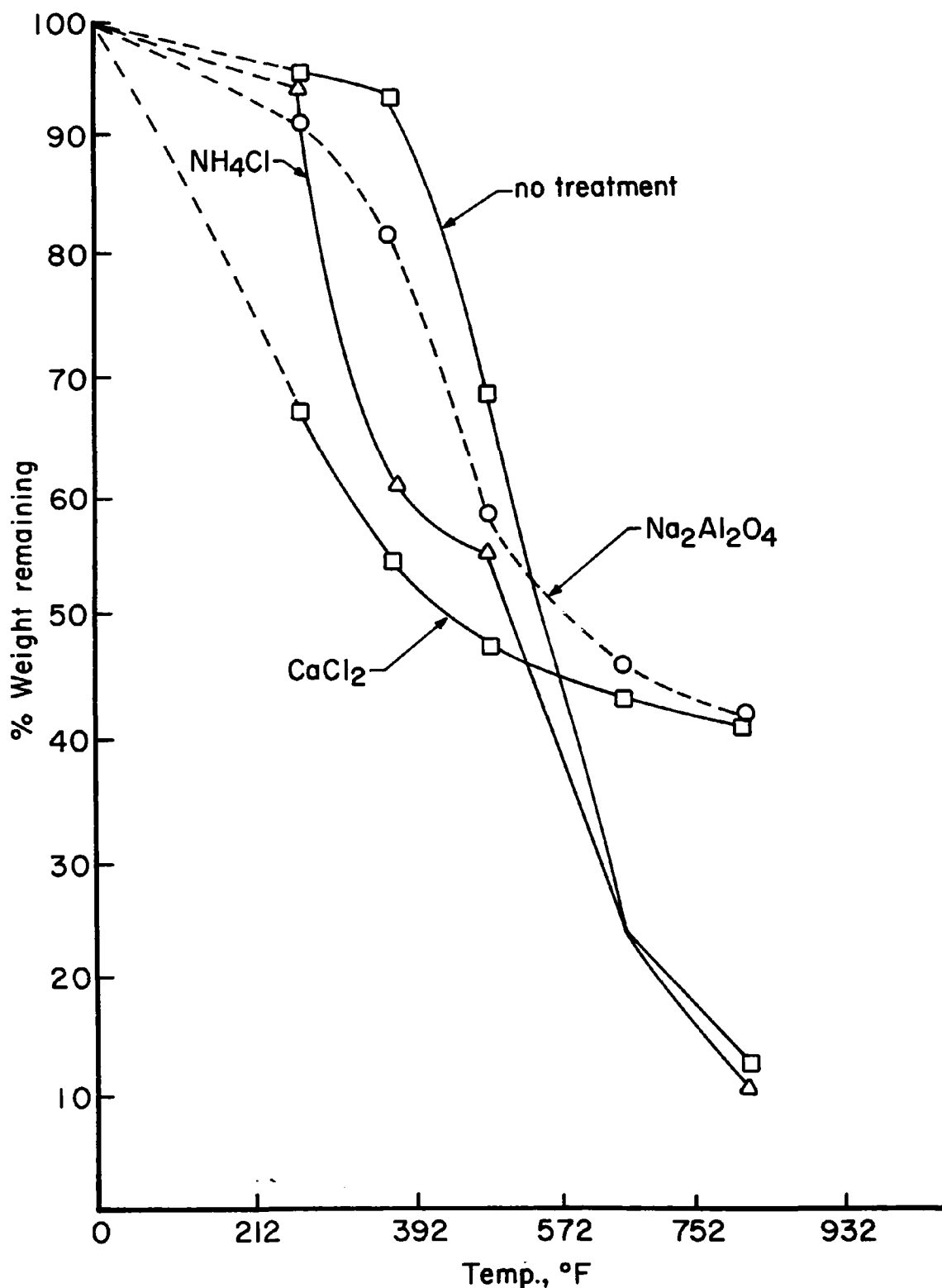


Figure 1. Results of Thermogravimetric Analysis in a Nitrogen Atmosphere.

char promotion was suggested by these results, but the effect was deemed too slight to be of significance.

The results from these preliminary studies showed that NH_4Cl was a more desirable char promoter than CaCl_2 and $\text{Na}_2\text{Al}_2\text{O}_4$. The NH_4Cl initiates the decomposition at lower temperatures and does not remain as a salt residue at the completion of the process. It also may be possible to recover the NH_4Cl vapors for reuse.

5.3 Evaluation of the Process Developed by Dr. A. Harendza-Harinxma

Dr. Harendza-Harinxma has developed a process to pyrolyze municipal refuse and sewage sludge to a char and fuel gas. The essence of this concept is the use of sodium aluminate to promote carbonization at low processing temperatures (480-570°F) with an increased production of char. The general flow plan proposed by Dr. Harendza-Harinxma is presented in Figure 2.

In this proposed process, sewage sludge is used as the solvent for a 2-4% solution of sodium aluminate. This solution is mixed with municipal refuse (two parts sludge to one part refuse). According to the flow plan the refuse is to be coarsely shredded, however, the metal and glass fraction need not be removed prior to carbonization. (Nevertheless, it would be desirable to remove the metal and glass prior to mixing the refuse with the sludge to prevent excessive wear on the processing equipment.) The slurry mixture is then mechanically dewatered, resulting in a thickened sludge of 40-60% solids. This sludge is thermally dried to about 15% moisture content. The dried refuse-sludge mixture, impregnated with sodium aluminate, is then carbonized for about one hour at 480-570°F.

The carbonization process takes place in a rotary kiln and converts the dried waste to a char and a fuel gas. The proposed rotary kiln consists of inner and outer cylinders with a plenum between the two. The inner cylinder is divided into five chambers, with the first, third, and fifth chambers containing small round holes. The carbonized material tends to be brittle and is pulverized during the rotation process. The pulverized char falls through the openings in chambers three and five and is collected at an exit port. The pyrolysis gases flow up through the refuse-sludge mixture and exit through the small openings in chamber one. The gas was reported by Dr. Harendza-Harinxma to have the following average composition by weight: H_2 , 2%; CH_4 , 2%; CO , 11%; CO_2 , 70%, and N_2 , 15%. From 15,000 to 24,000 cubic feet of gas are produced per ton of refuse. The char represents from 20-40% of the starting weight (400-800 lbs/ton MSW). According to data provided by Dr. Harendza-Harinxma, the gas produced from a ton of refuse is calculated to have a

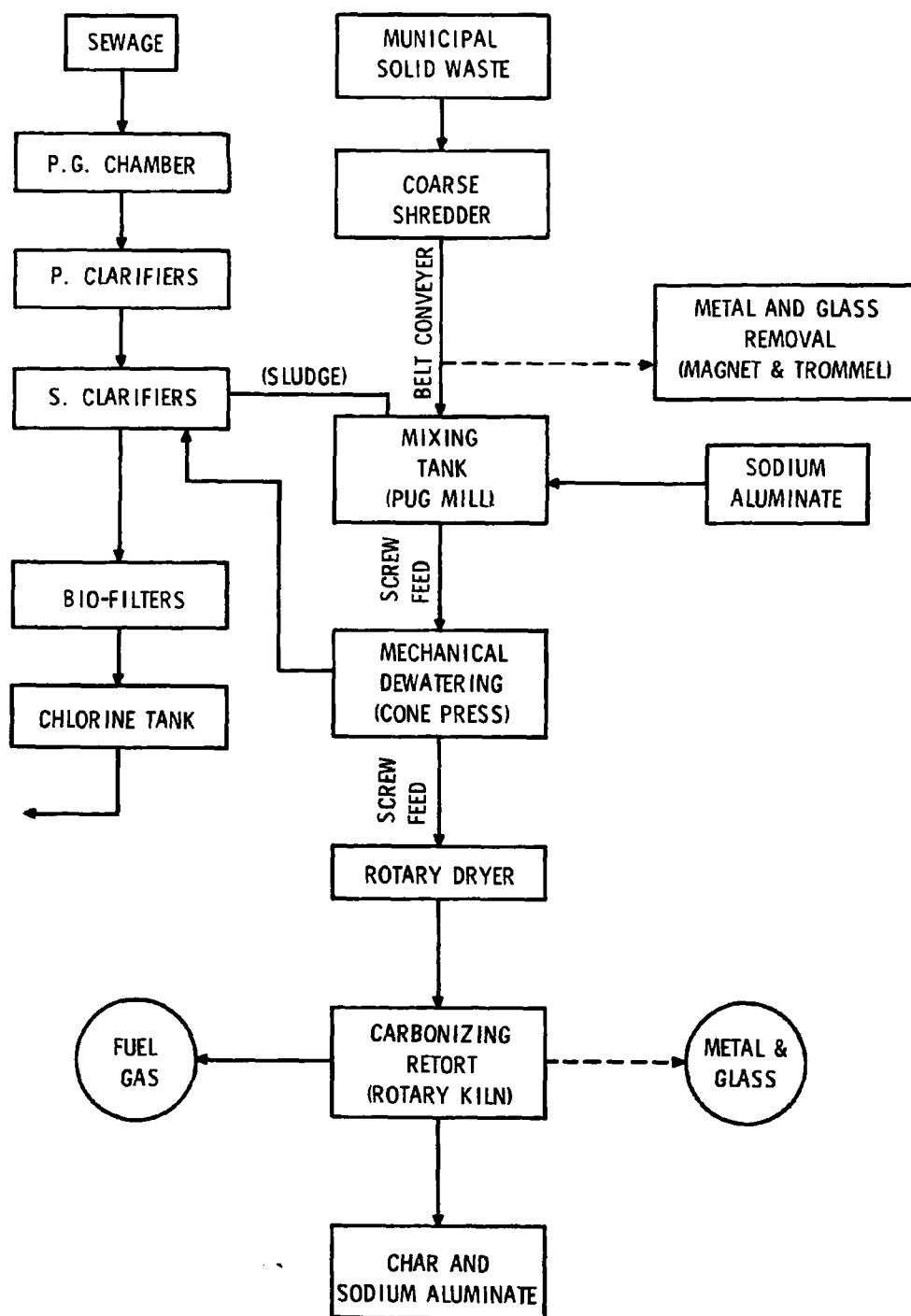


Figure 2. Basic Flow Plan for Harendza-Harinxma Process.

heat content of 3.1×10^6 Btu (127 Btu/ft^3) which would classify it as a low Btu gas. The char produced contains about 30% inert and about 15% volatile materials. A University of Dayton Research Institute (UDRI) analysis of the char showed a carbon content of 56% and a hydrogen content of 3.5%. The heat value of the char ranged from 8,000 to 11,000 Btu/lb depending on the specific composition. Samples of char measured at UDRI had an average heat content of 10,000 Btu/lb. An analysis of the inert fraction of the char residue is given in Table 6.

TABLE 6. ANALYSIS OF THE INERT FRACTION IN THE CARBON CHAR

Crystalline Compounds Identified

1. $\text{CaSiO}_4 \cdot \text{H}_2\text{O}$
2. $\text{Na}_2\text{Al}_2\text{O}_4$
3. $\text{Ca}_4\text{Al}_6\text{O}_{13} \cdot 3\text{H}_2\text{O}$
4. Other possible phases - $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$
5. Elements present in concentrations greater than 1/2% - Na, Al, Si, K, Ca, Ti, and Fe.

In his most recent plan, Dr. Harendza-Harinxma proposed the use of a pug mill for mixing the shredded refuse and the sludge-sodium aluminate solution. To convey this mixture to the dryer a screw conveyor was suggested. It is believed that this proposed processing plan has several drawbacks.

a. The presence of the metal and glass in the screw feed system and the pug mill could cause considerable maintenance and material handling problems (glass is abrasive and metal can become lodged between the wall and auger).

b. A 50% waste slurry is very viscous and this would also present materials handling problems.

c. The design for the rotary kiln is not well defined and might be difficult to develop or purchase as described. The perforation of the rotary drums at the initial state of carbonization would result in the loss of the fines prior to carbon conversion. In addition, the metal and glass would likely cause considerable clogging.

The basic concept in Dr. Harendza-Harinxma's process is the production of large quantities of carbon char at temperatures considerably lower than those normally employed in pyrolysis processes (570°F versus 1100°F). It is felt that a more effective processing plan can be devised for this concept.

One possibility would be to use the Black Clawson wet process for Dr. Harendza-Harinsma's concept (Figure 3). In the Black-Clawson process the refuse is pulped and the metal and glass are removed by wet processing techniques. The organic fraction is dewatered and the paper fiber can be recovered or the entire fraction can be used as a fuel. This RDF fraction (40-50% solids) could be mixed with a sewage sludge solution of sodium aluminate and the slurry could then be mechanically dewatered. This semidried (50% solids) material could then be further dried thermally. The refuse and sludge impregnated with sodium aluminate could be carbonized in a rotary kiln. The resultant pyrolysis gas could be used for the thermal drying process after it is cleaned. Using this general flow plan a theoretical material and energy balance was developed and is presented in Figure 4. A summary of the assumptions and calculations employed for this theoretical process is presented in Table 7. All assumptions were based on the information furnished by Dr. Harendza-Harinxma, laboratory results at the University, and information from the pyrolysis literature. The calculated efficiency for this process is approximately 44%.

5.4 The Market Potential for Carbon Char

As described, pyrolysis of municipal solid waste results in the production of a solid residue (char) and a fuel gas. The residue consists of a carbonaceous material from part of the organics and inorganic fraction. A major concern is the market potential for the char residue. If large quantities are to be produced, then long term valid markets must be available.

A number of potential markets have been identified for the char resulting from the pyrolysis process:

- a. Solid fuel
- b. Feed stock for preparing gaseous or liquid fuels
- c. Substitute for the carbon now being used in carbon and graphite products (activated carbon, charcoal, carbon fillers, carbon risers, etc.)

As a solid fuel, the char would contain between 8,000 and 10,000 Btu/lb and could be a substitute for powdered coal in a suspension fired boiler. The higher amount of inert material (three times that of coal) and the volatile content (about one-half that of coal) would be a drawback in its use as a fuel. The price of coal varies from about \$0.50 to \$1.60 per million Btu (\$20 to \$40/ton). However, it is unlikely that the char could command an equivalent price with coal recognizing its higher ash content, as well as the expected fluctuations in chemical composition. It is estimated that about 1 ton of refuse would produce about one-third of a ton of char. Therefore, per ton of refuse, one might hope to obtain from \$3 to \$6

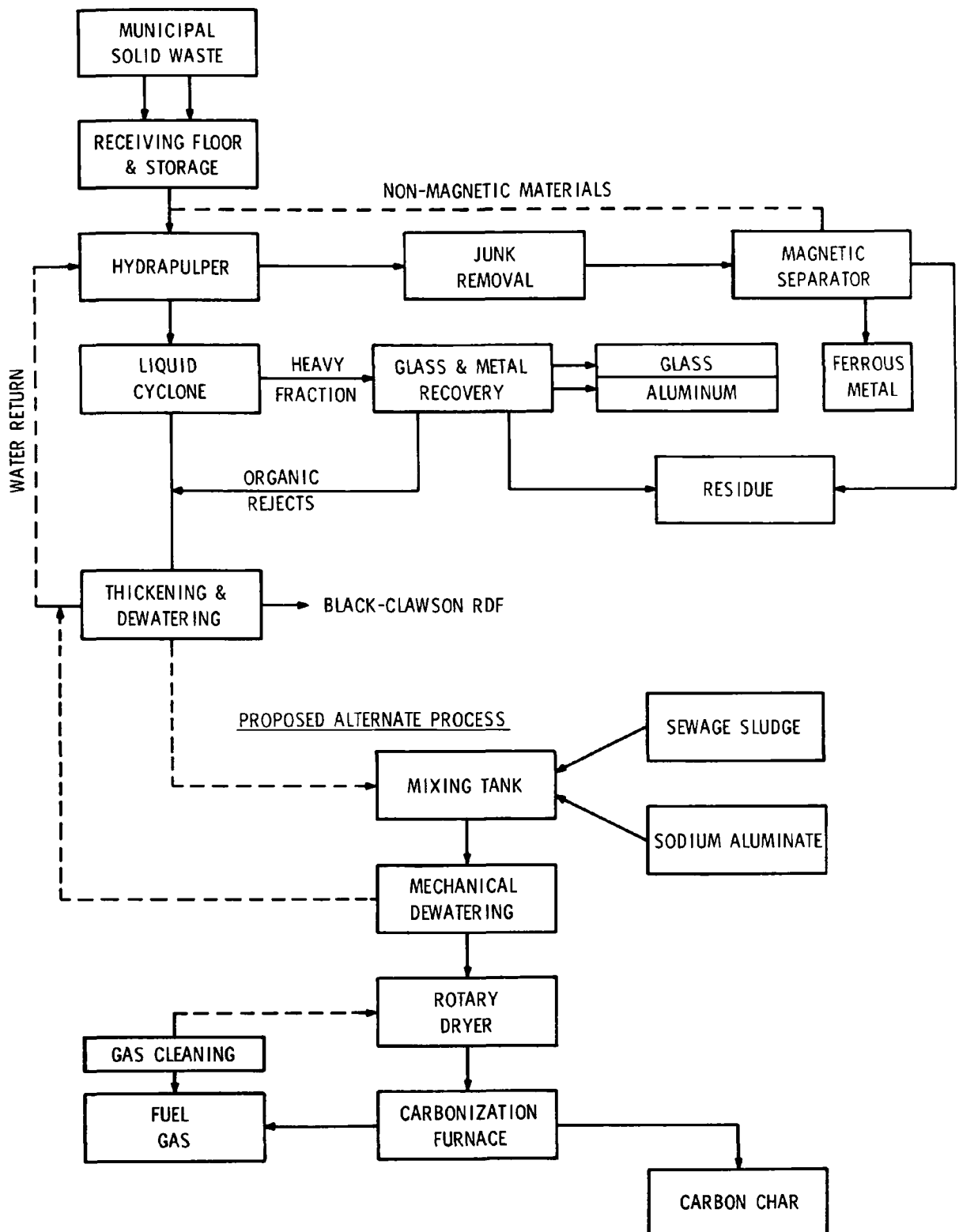


Figure 3. Modified Black-Clawson Wet Process.

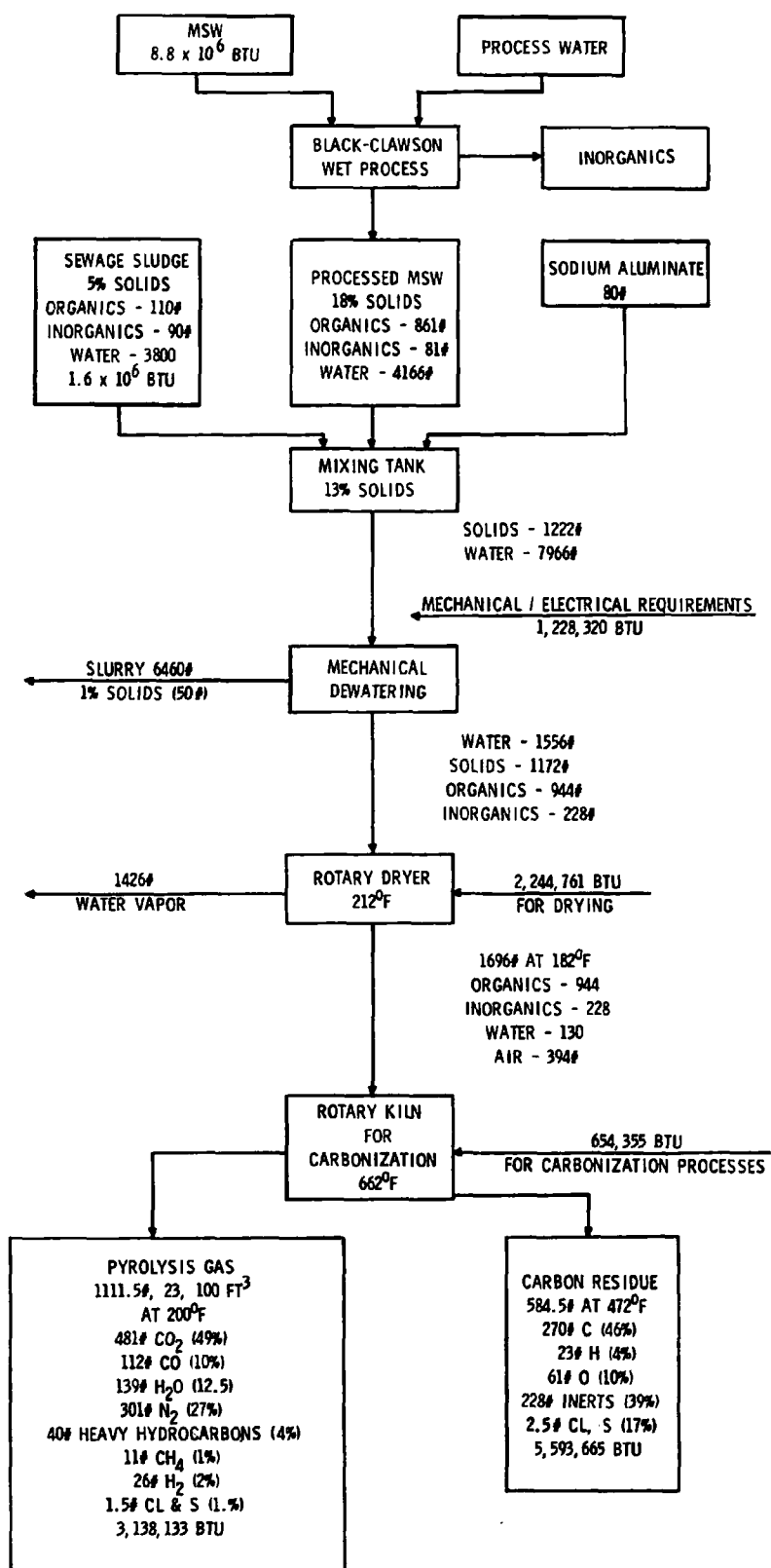


Figure 4. Material and Energy Balance.

TABLE 7. MATERIAL AND ENERGY BALANCE CALCULATION FOR
ONE TON OF MUNICIPAL SOLID WASTE

I.	Proposed Average Composition for MSW
A.	Organic Fraction
	Paper - 40%
	Other Organics - 37%
B.	Inorganic Fraction
	Metal - 11%
	Glass - 8.5%
	Inerts - 3.5%
	(moisture - 30%)
II.	Composition of the Organic Fraction from the Black-Clawson Process for 1 ton MSW ⁸
	Organic Material - 861 lbs
	Noncombustibles - 81 lbs
	Water - 4,166 lbs
III.	Composition of Sewage Sludge (5% Solids) and Sodium Aluminate
	Organics - 110 lbs
	Noncombustibles - 90 lbs
	Sodium Aluminate - 80 lbs
	Water - 3,800 lbs
IV.	Heat Content
A.	MSW as received - 4,400 Btu/lb x 2,000 lbs/ton =
	8.8 M Btu
B.	Sewage Sludge (5% solids) - 8,000 Btu/lb solids x
	200 lbs = 1.6 M Btu
C.	Total Heat Content of Wastes
	8.8 M Btu
	+ <u>1.6 M Btu</u>
	10.4 M Btu
V.	Estimated Energy Requirements for MSW Processing and Blending MSW, Sludge, and Sodium Aluminate
	Operation of all mechanical and electrical equipment -
	120 KWH
	Assuming an efficiency of 33% for the generation of electric energy gives:
	$\frac{120 \text{ KWH}}{0.33} \times 3412 \frac{\text{Btu}}{\text{KWH}} = 1,241,000 \text{ Btu} \approx 1.24 \text{ M Btu}$

TABLE 7. MATERIAL AND ENERGY BALANCE CALCULATION FOR
ONE TON OF MUNICIPAL SOLID WASTE (Continued)

VI. Composition in Mixing Tank

Organics - 971 lbs

Inorganics - 251 lbs

Water - 7,966 lbs = 9,188 lbs/ton MSW

VII. After Mechanical Dewatering

Solids - 1,172 lbs

Water - 1,556 lbs

VIII. Drying

A. Material Balance

<u>Composition</u>	<u>Quantity (M)</u>	<u>Specific Heat (Cp) Btu/lb/°F</u>	<u>Latent Heat (L) Btu/lb</u>
Organics	944 lbs	0.3	---
Inorganics	228 lbs	0.2	---
Water	1,556 lbs	1.0	970

B. Thermal Requirements: To Heat the Waste in a Dryer
from 60°F to 212°F ($\Delta T = 152^\circ\text{F}$)

$$M \times Cp \times \Delta T = \text{Btu}$$

Organics	944 x 0.3 x 152 =	43,046
Inorganics	228 x 0.2 x 152 =	6,931
Water	1,556 x 1.0 x 159 =	236,512
Water Vaporization	1,556 x 970 =	1,509,320
TOTAL		1,795,809 Btu

Allowances for heat losses - 25%

$$\therefore 1,795,809 \times 0.25 = 448,952$$

Total heat requirement for drying

$$\begin{array}{r} 1,795,809 \\ 448,952 \\ \hline 2,244,761 \text{ Btu} \end{array}$$

$$\approx 2.24 \text{ M Btu}$$

IX. Carbonization

A. Composition to Rotary Kiln

Organics - 944 lbs

Inorganics - 228 lbs

Water - 130 lbs

Entrapped Air - 394 lbs

TABLE 7. MATERIAL AND ENERGY BALANCE CALCULATION FOR
ONE TON OF MUNICIPAL SOLID WASTE (Continued)

B. Proposed Chemical Composition for Feed to Carbonization Kiln

	C	O	H	N	Cl	S	Total
Organics	472	405	57	6	3	1	944
Inerts	---	---	---	---	---	---	228
Air	---	99	---	295	---	---	394
Water	---	116	14	---	---	---	130
	472	620	71	301	3	1	1,696

Thermal Gradient ΔT from 182°F (out of dryer) to 662°F
(for carbonization) = 480°F

C. Sensible Heat

$M \times C_p \times \Delta T$

Organics	944 x 0.3 x 480	=	135,936
Inorganics	228 x 0.2 x 480	=	21,888
Water	394 x 0.25 x 480	=	47,280
Water Vaporization	130 x 1.0 x 30	=	3,900
TOTAL			209,004 Btu

D. Water Vaporization

130 x 970 = 126,100 Btu

E. Sensible Heat for Water Vapor

130 x 0.475 x 450 = 27,788 Btu

F. Carbonization Energy

291,463 Btu

G. Total Heat Requirements for Carbonization

Sensible Heat	-	209,004
Vaporization	-	126,100
Heat for Water Vapor	-	27,788
Carbonization Energy	-	291,463
		654,355 Btu

H. Carbonization Products - Carbon Char and Pyrolysis Gas

1. Carbon

C	-	270 lbs (46%)
O	-	61 lbs (10%)
H	-	23 lbs (4%)
Cl	-	2 lbs (0.3%)
S	-	0.5 lbs (0.1%)
Inerts	-	228 lbs (39%)
		584.5 lbs

TABLE 7. MATERIAL AND ENERGY BALANCE CALCULATION FOR
ONE TON OF MUNICIPAL SOLID WASTE (Continued)

2. Pyrolysis Gas

	C	O	H	N	Cl	S	Total (lbs)
CO ₂	130	351	---	---	---	---	481
CO	48	64	---	---	---	---	112
H ₂ O	---	123	16	---	---	---	139
N ₂	---	---	---	301	---	---	301
C _n H _n O _n	16	21	3	---	---	---	40
CH ₄	8	---	3	---	---	---	11
H ₂	---	---	26	---	---	---	26
Cl ₂ & S	---	---	---	---	1	0.5	1.5
TOTALS	202	559	48	301	1	0.5	1111.5 lbs

The compositions proposed for the char and pyrolysis gas are based on the data from the literature, information obtained from Dr. Harendza-Harinxma and observations from University of Dayton laboratory studies.

3. Estimated Heat Content of Pyrolysis Products

a. Carbon Char (9,500 Btu/lb)

$$9,500 \text{ Btu/lb} \times 584.5 \text{ lbs} = 5,552,750 \text{ Btu}$$

In addition, the heat contained in the hot char exiting the kiln may also be recovered. For this calculation a specific heat of 0.175 and a ΔT of 400°F is assumed:

$$584.5 \times 0.175 \times 400 = 40,915 \text{ Btu}$$

$$\text{Total heat content of char} = 5,593,665 \text{ Btu} \\ \approx 5.59 \text{ M Btu}$$

b. Pyrolysis Gas

CO	-	112 lbs	x	4,347 Btu/lb	=	486,864
H ₂	-	26 lbs	x	61,100 Btu/lb	=	1,588,600
CH ₄	-	11 lbs	x	23,879 Btu/lb	=	262,669
C _n H _n O _n	-	40 lbs	x	20,000 Btu/lb	=	800,000
						<u>3,138,133 Btu</u>
						$\approx 3.14 \text{ M Btu}$

X. Energy Balance

Estimated Energy Content from 1 Ton MSW and 200 lbs of Sewage Sludge = 10.4 M Btu

Estimated Energy Requirements to Process MSW and Sludges:

Mechanical and Electrical Equipment 1.23 M Btu

Drying 2.24 M Btu

Carbonization 0.65 M Btu

4.12 M Btu

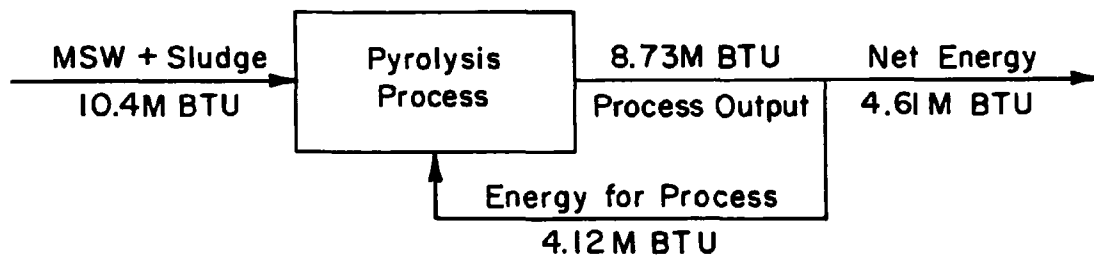
Energy Content of Pyrolysis Products

$$5.59 \text{ M Btu} + 3.14 \text{ M Btu} = 8.73 \text{ M Btu}$$

TABLE 7. MATERIAL AND ENERGY BALANCE CALCULATION FOR
ONE TON OF MUNICIPAL SOLID WASTE (Concluded)

Estimated Energy Efficiency

$$\frac{(8.73 - 4.12) \text{ M Btu}}{10.4 \text{ M Btu}} \times 100 = 44\%$$



in revenues for the sale of char as a solid fuel. Representatives from the Dayton Power and Light Company have expressed reservations about the acceptability of the char as a fuel. They felt that its low volatility would make it difficult to burn and the high ash content could be a problem. In addition the fusion temperature of the ash must be above 2550°F to minimize slagging.

The char residue could also be used to replace coal as a feedstock for the generation of synthetic liquid or gaseous fuels. Although coal has a market value of \$20-\$40/ton, char with a carbon content of 50% to 60% (versus 75% for coal) could not command identical market value. In addition, its large inert fraction and somewhat lower hydrogen content (three-fourths that of coal) further reduces its economic potential.

Another potential use for char is as a raw material for carbon and graphite products. Carbon is used for filtration, in the production of electrodes and brushes, for refractory ware, in the production of iron and steel, in the production of rubber and plastic products, in charcoal, and in asphalt products. Inquiries were made regarding the potential market for the char to the following firms:

ARMCO Steel	Ohio Rubber
Union Carbide	Premier Rubber
Dayton Walther	Akron Chemical
Inland Manufacturing	SOHIO
ALCOA	Great Lakes Carbon
Dayton Tire and Rubber	

Their assessment of the market potential for the carbon char assumed the generalized composition of the material provided by Dr. Harendza-Harinxma.

The carbon char from pyrolyzing solid waste can be activated and used for waste water filtration treatment. In studies by Stanford University⁶ it was found that the activated char from MSW pyrolysis had comparable adsorptive properties to commercial carbons for COD (chemical oxygen demand) removal in water samples. Preliminary cost analysis showed that the use of char was competitive with commercial carbon products. A more intensive study of the technical and economic factors is in progress. In addition, a market analysis is planned to determine the realistic potential and level of demand for the carbon char as an activated carbon. (Private communication, Dr. J.O. Leckie, Stanford, University.)

Discussions with other sources have indicated two problems with the activated carbon from pyrolyzed refuse:

- a. Chemical quality
- b. Limited potential demand

Representatives from the carbon industry felt that the carbon char might not satisfy the rigid chemical specifications. Soluble metal content and anticipated fluctuations of chemical composition were the two areas frequently mentioned. The second problem, potential market size, was also raised several times. At the present time the number of tertiary sewage treatment plants is limited, and the demand for activated carbon is small. A plant processing 1000 tons of refuse per day would generate 300 tons of activated carbon per day.

Another possible application for the carbon char is as a raw material for the manufacture of carbon brushes and consumable electrodes. The carbon char could serve as a partial substitute for the petroleum coke now used in these applications. Some motor brushes contain a mixture of carbon and abrasives. It is felt that the inert fraction in the carbon char could function as the abrasive. However, the lower carbon content, the varying composition and higher volatile content were found to be objectionable. The quantity of carbon used for this application was not known, however, it was felt that the carbon char would only be acceptable as a partial substitute in the raw material blend.

The aluminum industry uses large quantities of carbon for consumable electrodes in the arc melting process. About one million tons of calcined petroleum coke are used annually. The current price for high quality petroleum coke is \$100/ton (\$0.05/lb). However, the rigid specifications for these electrodes, especially the silicon, iron, and ash content would exclude the char from consideration:

SPECIFICATIONS FOR ALUMINUM ELECTRODES

<u>Property</u>	<u>Weight (%)</u>
Volatiles	0.5
Silicon	0.02
Iron	0.03
Vanadium	0.01 to 0.04
Sulfur	0.02 to 0.04
Moisture	0.5
Fixed Carbon	0.75 to 0.85
Particle Size	Minus 1 inch plus 100 mesh
Density	2.05 gm/cm ³

The feasibility of using the char as a raw material for the manufacture of carbon and graphite crucibles and other refractory ware was also explored. Based on the established specifications for these products, the char does not appear to be an appropriate raw material. The feasibility of using the char for producing calcium carbide for the production of acetylene was also investigated. Based on information from the Union Carbide Corporation, it would also appear that this would not be a feasible application for the char.

The use of the char as carbon risers in the production of steel and high carbon iron was also investigated. Carbon and graphite pellets are added to the steel and iron melts to raise the carbon content. Two to three pounds of carbon are used per ton of steel. About 100 million tons of steel are produced annually (requiring approximately 150,000 tons of carbon). About 30 to 40 lbs of carbon are used per ton of gray iron. The requirements for the carbon specify less than 0.5 percent sulfur and high density. Consequently, the carbon char would have to be densified into 1/8-inch diameter pellets. In addition, the rate of solution of the char in the ferrous melt would have to be established by laboratory tests. It appears that the carbon char could be an acceptable substitute for this application. The iron and steel industry presently pays about \$0.05/lb for scrap carbon and graphite which contain about 85% carbon.

Another application considered for the carbon char is in the production of rubber and plastic products. At the present time, about 3 billion lbs of carbon black are produced annually. About 93% is used in rubber products to provide reinforcement and abrasion resistance and the remaining 7% is used in plastics, paints, and ink. About 75% of the rubber products are used in the automotive industry, with more than half being used in the production of automotive tires.

The majority of carbon black is made from petroleum derivatives, and the small remainder is made from natural gas. The present cost of carbon black is about \$0.15/lb and all indications are that the price will be increasing. The specifications for the carbon black used in tires are very rigid and it does not appear that the char could be considered. However, in nonstructural rubber products the specifications are not so restrictive and the char might well qualify. The major requirement would be particle size which would necessitate grinding and screening the char.

Discussions with rubber producers indicated that they might accept a carbon char of proper particle size if the cost were \$0.03-\$0.05/lb. Nationwide it is estimated that 500,000 tons of carbon black are used in nonstructural rubber products. However, no single plant would require more than 10,000 to

20,000 tons of carbon a year. The costs of transportation, as well as further processing of the carbon char, would be important factors to consider in determining its applicability in nonstructural rubber products.

Charcoal briquettes represent another potential application for the use of the carbon char. Each year some 750,000 tons of briquettes are produced. An average sized plant will produce 40,000-50,000 tons per year. The current market price for raw carbon for briquetting ranges between \$40 and \$60 per ton with an average of about \$50 (2.5 cents/lb). According to a representative from the Great Lakes Carbon Corporation, the charcoal normally used for briquettes contains about 75% carbon and has about 15% inorganic ash. If the ash content is too high (above 24%), the briquettes exhibit poor burning characteristics. The lower carbon content (50-60%) and higher ash content (30-50%) of the char from MSW would make this material less desirable, however, it could be used as a partial constituent in the manufacture of charcoal briquettes. It was estimated that the char from MSW could be used for about half of the briquette composition if the price were favorable (1.5 to 2 cents/lb). Based on current estimates a ton of refuse could generate about \$9.00 worth of char.

A plant processing 1000 tons of refuse per day could generate up to 300 tons of char per day or about 79,500 tons per year. If the MSW char supplied about half of the material for the briquette production, a single MSW processing facility could supply about four average sized charcoal plants. Based on current projections it would appear that the entire charcoal briquette market would support only 4 or 5 refuse processing facilities. The potential market for the char as an ingredient in charcoal briquettes was determined in a telephone interview; however, a detailed analysis of the char by charcoal manufacturers would be necessary to more accurately define its market.

A final application considered for the char was in asphalt and asphalt products. As a partial replacement for the asphalt, the char would have a very large market potential. However, as a filler in asphalt products it would represent a very small potential market for the char. Based on a preliminary assessment of the char by SOHIO, there is considerable question about its acceptability for use in asphalt paving. The current market value for asphalt is about \$75/ton (4 cents/lb). If the char could be used for this application it is estimated that the char would have a value of 1 to 2 cents/lb.

In summary, several potential applications have been identified for the char. However, all of the identified applications are confronted with certain barriers. The major problems are the anticipated fluctuations in chemical composition

and the high quantity of inerts in the char. Its low carbon content relative to coal (56% vs. 75-85%) also reduces the market value of the char residue.

It appears that the char can be used as a solid fuel and as feed stock for synthetic liquid and gaseous fuels at a market value of about \$0.01/lb. With some additional processing the char could also be utilized as an activated carbon, a raw material for charcoal briquettes, a carbon riser in iron and steel production and as fill in nonstructural rubber products at a market value of \$0.02-\$0.04/lb. The major questions regarding these latter applications concern the availability of sufficient market demand. A plant processing 1000 tons of refuse per day could more than saturate many of the potential market opportunities identified (79,500 tons/year). It is, therefore, very apparent that each specific char-producing plant built must secure a certified market for its product from one of the applications identified.

5.5 Engineering Analysis of a Plant to Convert MSW to a Carbon Char

A preliminary engineering study of a plant to produce carbon char from MSW and sewage sludge was conducted. Based on the information accumulated, a design for a low temperature pyrolysis facility was developed. The proposed facility would process 1000 tons per 20 hour day (50 TPH) for six days per week. The basic design for this plant is based on the Black-Clawson wet processing system at Franklin, Ohio. The process flow essentially follows the Black-Clawson process to dewatering at the hydrodenser. After partial dewatering at the hydrodenser, the slurried refuse would be mixed with sodium aluminate and sewage sludge in a flash mixer. This slurry mixture is then mechanically dewatered in a cone press and dried in a rotary dryer. The dried refuse would then be pyrolyzed in a rotary carbonization kiln. A flow plan and material balance for the proposed plant is presented in Figure 5. The calculations developed for the material balance at each step of the process are presented in Table 8. The data used for the flow plan and material balance were obtained from:

- a. System Technology Corporation Report evaluating the wet processing system⁸
- b. U.S. Patent No. 3,961,025 Dr. A. Harendza-Harinxma
- c. UDRI Laboratory Studies

The calculations developed served as a basis for determining equipment sizes and operating requirements (flow rates, etc.). This information was used to develop the environmental considerations and to conduct an economic analysis for the proposed plant.

MATERIAL BALANCE CALCULATIONS FOR A CARBON CHAR PRODUCTION PROCESS

[illegible]

TABLE 8 (Continued)

Components	Through Crusher to 1/2" screen	Residue Fines	To Float Separation	Nonferrous Metal Recovered	To Surge Tank	From Mechanical Dewater	To Mixing Tank	From Mechanical Dewatering	From Thermal Drying
<u>Refuse</u>	<u>183.6</u>	<u>107.1</u>	<u>76.5</u>	<u>34.1</u>	<u>706.2</u>	<u>706.2</u>	<u>748.6</u>	<u>735.6</u>	<u>522.6</u>
Organics	43.7	10.0	33.7	3.7	430.3	430.3	460.3	447.3	447.3
Metals	21.7	1.7	20.0	18.0	0.1	0.1	2.1	2.1	2.1
Glass	67.8	65.0	2.8	1.4	0.2	0.2	1.6	1.6	1.6
Inerts	32.4	20.4	12.0	6.0	0.6	0.6	6.6	6.6	6.6
Moisture	18.0	10.0	8.0	5.0	275.0	275.0	278.0	278.0	65.0
<u>Process Water</u>	<u>20</u>	<u>10</u>	<u>10</u>	<u>5</u>	<u>13,000</u>	<u>1,800</u>	<u>1,805</u>	<u>250</u>	----
Make up Water	----	----	----	----	----	----	----	----	----
<u>Sewage Sludge</u>	----	----	----	----	----	----	<u>2,000</u>	<u>348</u>	<u>98</u>
Organics	----	----	----	----	----	----	55	54	54
Inorganics	----	----	----	----	----	----	45	44	44
Water	----	----	----	----	----	----	1,900	250	----
<u>Sodium Aluminate</u>	----	----	----	----	----	----	<u>40</u>	<u>30</u>	<u>30</u>

5.5.1 Environmental Considerations

The proposed low temperature pyrolysis plant should result in significant reduction in solid waste (refuse) and sewage sludge that would have to be landfilled or incinerated. In addition, the materials recovered in the process could reduce the need for an equivalent quantity of virgin natural resources. Although the carbonization process should reduce land pollution, it can contribute to the air and water pollution. Potential pollution problems and control technologies associated with the proposed carbonization process have been considered. The areas of major concern are discussed in the following paragraphs.

5.5.1.1 Air Quality

The Clean Air Act Amendments of 1977 were signed into law by President Carter on August 7, 1977. Certain aspects of these amendments could directly apply to a carbon char plant. For example, for those areas which have not attained ambient standards, so-called "nonattainment areas," states must have an approved implementation plan revision by July 1, 1979, which provides for attainment of primary standards by December 31, 1982. This requirement is a precondition for construction or modification of major emission sources in non-attainment areas after June 30, 1979. Further, in both "nonattainment" and "nondegradation" (those cleaner than ambient standards) areas, major stationary sources may be constructed only by permit, and must, at the very least, meet new source performance standards prescribed by the law. Two sources of possible air pollution have been identified for the proposed pyrolysis facility: the combustion products from the dryer and carbonization kiln, and the water vapor and dust from the dryer. It is anticipated that the combustion products from burning the fuel gas of pyrolysis would not present any serious problems requiring environmental control equipment. The major products should be H₂O, CO₂ and N₂. In addition, minor amounts of NO_x, HCl and SO₂ may also be present as well as some unburned hydrocarbons. It is anticipated that there will not be any significant quantity of heavy metals in the exhaust gases, since they are more likely to be in the carbon char. One potential source of air pollution is likely to be the dust entrained with the water vapor driven off during drying. Dust control equipment will probably be required for cleaning the water vapor before it can be released to the atmosphere. A filter type unit or some other type of dry dust collection system is envisioned. The dust collected would be recycled back to the carbonization kiln for processing.

5.5.1.2 Water Quality

The proposed pyrolysis process for char production is basically a wet process requiring large quantities of water. Most of the water to be used would be obtained from the nearby sewage treatment plant which would also supply the sewage sludge. Most of the water used for processing would be recycled, however, about 15 percent of the process water would be returned to the sewage treatment plant each cycle and up to 5% is evaporated during the drying process. The waste water returned to the sewage treatment plant is primarily from the last mechanical dewatering step before drying. Based on the data from an analysis of the Franklin, Ohio plant it is reasonable to expect the waste water to have considerable suspended solids and BOD loading. Estimates from the Franklin, Ohio facility indicate a BOD loading of 100 lbs BOD/ton refuse and suspended solids loading of 160 lbs/ton refuse. In addition, considerable concentrations of heavy metals can also be expected. At the Franklin, Ohio facility, total metal content of the waste water (both suspended and dissolved) was found to be higher than encountered in normal domestic waste water or landfill leachates. It is evident that adequate precautions for treatment of the water from the pyrolysis facility will have to be taken at the waste water plant.

5.5.1.3 Bacteriological Considerations

There are likely to be bacteriological hazards present at all solid waste and sewage treatment facilities. It would appear that the problems at the proposed pyrolysis facility would not be any different than that found at any sewage treatment plant and airborne contaminants might be less in a wet processing system.

5.5.2 Economic Considerations

A preliminary economic analysis was prepared for the proposed pyrolysis plant. This analysis is based on the process flow plan shown in Figure 5. The proposed plant would have two processing lines each with a capacity of 25 tons per hour for a total capacity of 1,000 tons of refuse per day. It is assumed that the facility would operate 20 hours per day, 6 days per week for 52 weeks per year processing 265,200 tons of refuse annually [1000 x 6 x 52 x 0,85 (on-line availability)]. It is further assumed that an adjacent landfill would serve as a backup to the pyrolysis facility. Revenues for the facility would be provided from several sources:

- a) a tipping fee
- b) sludge disposal
- c) sale of aluminum and iron
- d) sale of carbon char

This preliminary economic analysis followed the format published in EPA document SW-1579,10. A summary of the calculations developed for the capital and operating costs are presented in Table 9 and 10 respectively. Consideration of possible revenues are presented in Table 11. The data presented in these tables show an estimated total operating cost of \$26.68/throughput ton of MSW and a potential revenue of \$17.15/throughput ton of MSW plus revenue from sale of carbon char. For the pyrolysis facility to operate profitably the carbon char would have to sell for \$0.017 per pound (\$34/ton) in order to cover the \$9.53 deficit calculated between total operating cost and identified potential revenues.

TABLE 9. ESTIMATED CAPITAL COSTS (1977 Dollars)

Land (30 Acres at \$10,000/acre)	300,000
Site preparation (35% of land cost)	105,000
Equipment, installation and facility construction	18,560,000
Engineering and Design (6% of 18,965,000)	1,138,000
Contingencies (10% of 20,103,000)	2,010,000
Start up and work capital	500,000
SUBTOTAL	<u>22,613,000</u>
Legal and financial costs (2%)	452,000
TOTAL PLANT COST	<u>23,065,000</u>
Municipal revenue bonds for project (financing costs raise bond requirements 12% above capital cost of facility)	25,833,000
Estimate life of facility - 20 years	
TOTAL INTEREST TO BE PAID (8%)	26,397,655
TOTAL CAPITAL COST	52,230,655
ANNUAL CAPITAL COST	2,611,533
ANNUAL THROUGHPUT (tons)	265,200
Capital Cost per ton	<u><u>9.85</u></u>

TABLE 10. ESTIMATED ANNUAL OPERATING & MAINTENANCE COSTS (1977 Dollars)

Salaries & Benefits	923,000
Fuel	75,000
Electricity	963,000
Water & Sewer	111,000
Maintenance	696,000
Residue Removal	190,000
Materials & Supplies	1,070,000
Taxes (.75%)	173,000
Insurance & Management Costs (\$1.00/ton)	265,000
Total Annual Operating & Maintenance Costs	<u>4,463,000</u>
Operating & Maintenance Cost per ton	<u><u>16.83</u></u>

TABLE 11. POTENTIAL REVENUE SOURCES

Revenue Source	Dollars/throughput ton
Tipping fee	\$ 8.50/ton
Sludge disposal (200 lbs @ \$50/ton)	5.00/ton
Ferrous metal (58 TPD at a net cost of \$22.55/ton)	1.31/ton
Stock for aluminum recovery 18 TPD @ net cost of \$130/ton	2.34
Sub Total	17.15
Carbon Char (295 TPD market values not established)	?

5.6 Conclusions

The use of chemical treatments to promote carbon char formation at lower pyrolysis temperatures has potential if a reliable market for the char is secured. Laboratory results clearly demonstrated that several chemical treatments can be employed to generate char by low temperature pyrolysis. Both sodium aluminate and ammonium chloride showed promise as char promoters. An analysis of the projected economics for a low temperature pyrolysis process reveals that a market providing about \$0.017 per pound for the char is necessary to make the process economically viable.

Another major reservation concerning the use of the carbon char is the lack of user familiarity with it as a product. Potential consumers are hesitant to commit themselves to an untried material. To date, the commercialization of char generated from conventional pyrolysis processes has been rather disappointing and this serves to moderate enthusiasm for a low temperature pyrolysis process designed to produce a carbon char product.

SECTION 6

POWDERED SOLID FUEL

The conversion of the organic fraction of municipal solid waste into a fine powder offers a number of advantages for using this material as a solid fuel. A number of thermal and chemical treatments have been identified that promote the conversion of the organic fraction in refuse to a fine powder. Most of these processes embrittle or degrade the cellulose wastes.

6.1 Embrittlement Studies

As part of this project, various chemicals were screened for their ability to embrittle paper. Prospective reagents that would be effective in the presence of the ambient moisture (approximately 25% of the weight of solid waste) were selected. It was felt that the ambient water may function as a coreactant with the cellulose and the reagent in question, or might serve simply as a solvent to concentrate the reagent on the cellulose surface. Other desirable properties of the ideal reagent include ease of application, recovery, reuse, and either minimum retention in the final product or, if retained, a negligible adverse effect on its utility. Gaseous reagents appeared most likely to meet our criteria.

In the presence of water, one obvious reaction to employ for degrading paper is acid-catalyzed hydrolysis. A great deal of bonding between fibers in wood pulp papers may be due to the action of hemicelluloses. To the extent that the hemicelluloses and cellulose are accessible to the aqueous acid, hydrolysis should be effective in reducing the structural integrity of the cellulosic material. However, workers at the Forest Product Laboratories have reported little advantage in treating wood with H_2SO_4 or HCl prior to milling during the preparation of microcrystalline cellulose. (Private Communication, June, 1977.) Hence, there appears to be a practical limit to the extent of hydrolytic degradation of wood. (Of course it would be pointless to strive for such finely divided material from refuse.)

Embrittlement of paper via the formation of bonds between cellulose chains (crosslinking) appeared to be another attractive possibility. The 50% decrease in the fold-strength

of paper which has been heated at 350°F for 2 to 3 days is thought to be partially due to this type of mechanism. Treatment of paper with bidentate reagents capable of promoting crosslinking under less demanding conditions therefore seemed appropriate.

At the very outset of these screening studies it was realized that the shredded newsprint selected was too dry and homogeneous to serve as a model for municipal solid waste. For many of the test runs we found it desirable to spray the paper sample with water or a liquid reagent. The spraying process was facilitated by the reactor described in the following paragraph. Later experiments with a second type of paper (computer paper) supplemented the initial studies with newsprint.

The experimental arrangement used in these studies is shown in Figure 6. A three-liter, round-bottom reactor flask, modified to provide a second opening in the bottom was used for the screening studies. This reactor flask was placed on a rotary evaporator, and, if desired, the contents could be sprayed uniformly through the second opening while the flask was rotating. When the second opening was sealed by a glass plate and an O-ring seal, the system could be vented through a glass stopcock mounted on the glass plate. A gaseous reactant could flush the entire apparatus when the stopcock was in the open position. After closing the stopcock, the reactor flask and its contents were rotated and heated (to approximately 185°F) for 10 minutes with a heat lamp. The reactor was then evacuated using a water aspirator while the heating (to approximately 250°F) and rotation was continued for an additional 10 minutes. In some instances embrittlement had been so effective that the rotation of the reactor flask had reduced some of the sample from 4 inch lengths to fragments 0.4 to 1.2 inches in length. All samples were subjected to 1 hour of ball milling. (Observations of this process would indicate that shorter ball milling times would be adequate).

The results of these screening studies, summarized in Table 12 revealed that formaldehyde (as a formalin spray or as solid polymeric material) could serve as an effective aid in the embrittlement of paper. Hydrogen chloride (HCl), a strongly acidic gas, embrittled newsprint even in the absence of formaldehyde (entry 12, 13). Weakly acidic reagents such as carbon dioxide (entry 2), formic acid (entry 4), and acetic acid (entry 5) failed to produce significant embrittlement even in the presence of formaldehyde. The nominal embrittlement of newsprint by sulfur dioxide (entry 6), however, was greatly enhanced by the inclusion of formaldehyde in the reaction mixture (entry 7, 8). The final product obtained after ball milling was a finely divided brown powder comparable in texture to the powder obtained from paper embrittled by HCl. Similar products

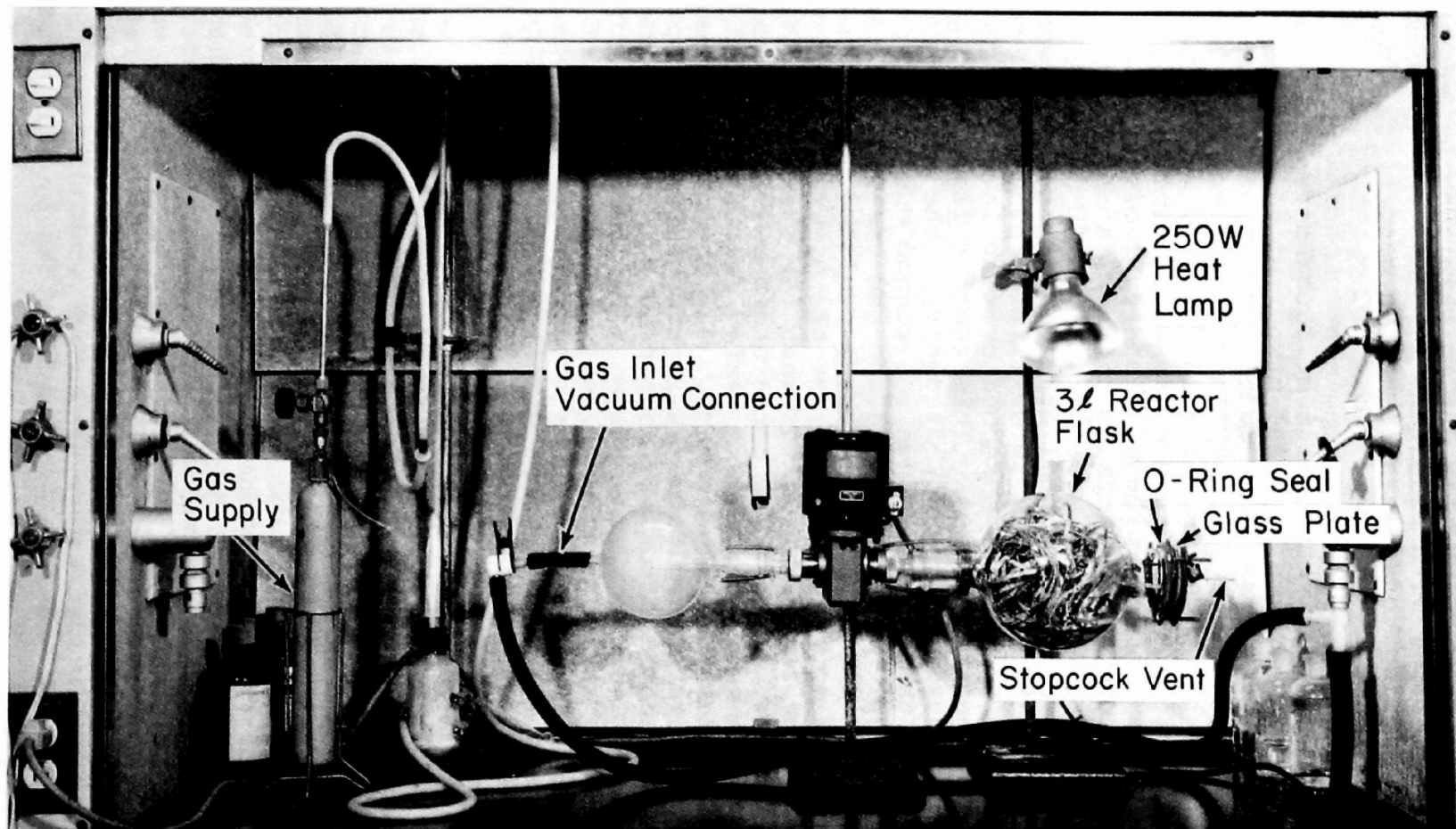
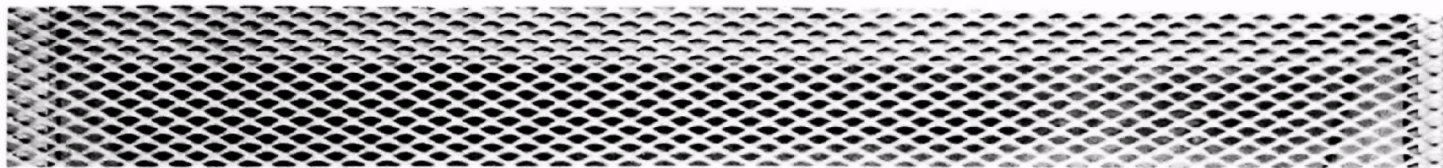


Figure 6. Experimental Arrangement Used for Embrittlement Studies.

resulted from the treatment of newsprint with either chlorine gas (Cl_2) or thionyl chloride (SOCl_2) spray.

TABLE 12. CHEMICAL EMBRITTLEMENT OF PAPER SCREENING STUDY

Entry No.	Paper Type*	Treatment	Time (min.)	Results
1	N.P.	Formalin	20	powder/fragments
2	N.P.	Formalin + CO_2	30	powder/fragments
3	N.P.	Formalin + NO_2	45	fragments
4	N.P.	Formalin + Formic Acid	20	no effect
5	N.P.	Formalin + Acetic Acid	45	powder/fragments
6	N.P.	SO_2	20	fragments
7	N.P.	Formalin + SO_2	20	powder
8	N.P.	Paraformaldehyde + SO_2	30	powder
9	N.P.	Methylal + SO_2	20	no effect
10	N.P.	Acetal + SO_2	20	fragments
11	N.P.	Formalin + HCl (gas)	20	powder
12	N.P.	HCl (gas)	20	powder
13	N.P.	HCl (gas) + H_2O	25	powder
14	N.P.	SOCl_2	20	powder
15	N.P.	Cl_2	20	powder
16	N.P.	Cl_2 + H_2O	20	powder/fragments
17	N.P.	Paraformaldehyde + SO_2^{**}	20	powder/fragments
18	N.P.	Paraformaldehyde + SO_2^{***}	20	powder/fragments
19	N.P.	Paraformaldehyde + SO_2 + $\text{H}_2\text{O}^{****}$	20	powder/fragments
20	C.P.	Formalin + SO_2	20	powder/fragments
21	C.P.	Formalin + excess SO_2	25	powder
22	C.P.	Cl_2	20	powder

* N.P. = Newsprint, C.P. = computer paper (bond)

** 1 wt. paraformaldehyde/10 wt. paper

*** 0.3 wt. paraformaldehyde/10 wt. paper

**** 0.15 wt. paraformaldehyde/10 wt. paper/3.5 wt. water

The results of combustion analysis of three of the powders (Table 13) revealed that some of the reagent was retained in each of these powders. Care should be taken not to place undue significance on these analytical data in comparing the reagents for retention in the final product. These screen-

ing studies did not allow mass balances to be conducted, nor was an attempt made to measure the concentration of the gaseous reagents at the outset of the treatments. An effort was made to maintain experimental conditions to a degree consistent with efficient screening. Assuming a degree of polymerization (DP) of 1000 for the cellulose, the data suggest the retention of 61 sulfur atoms per cellulose chain, or approximately one sulfur per 16 anhydroglucose units. Likewise the 2.18% chlorine analysis suggests about 1 chlorine per 10 anhydroglucose units, while the analysis for 5.30% chlorine indicates 1 chlorine for each 4 anhydroglucose units.

Our understanding of embrittlement mechanisms for the foregoing reagents is not extensive. A reduction in DP of the cellulose almost certainly occurs in the presence of acidic reagents. However, discussions with members of the Forest Products Laboratory and the Paper Institute assured us that paper produced from an over-pulped feedstock (lower than normal DP) would not be expected to be brittle. The extensive incorporation of chlorine in the HCl-embrittled paper suggests a more extensive involvement of HCl besides acid catalysis of the hydrolysis process. The replacement of hydroxyl groups in the cellulose by chlorine, followed by crosslinking via oxygen bridge formation may be another possible but unproven explanation.

TABLE 13. COMBUSTION ANALYSES OF PAPER POWDERS
(WEIGHT PERCENTAGE)

Reagents	Carbon	Hydrogen	Chlorine	Sulfur
HCl + CH ₂ O (*)	42.80	6.10	5.30	----
Cl ₂	41.92	5.90	2.18	----
SO ₂ + CH ₂ O (*)	36.06	5.84	----	1.20

(*) Formaldehyde

Rigidity caused by crosslinking may also be the cause for embrittlement by formaldehyde and SO₂. Viscous solutions containing more than 15% cellulose may be prepared by treating wood pulp with formaldehyde in a dimethylsulfoxide (DMSO) solution. The reaction of cellulose with formaldehyde is generally thought to result in the formation of methylol cellulose:



Methylol cellulose is expected to be capable of undergoing crosslinking and reacting with other alcohols and amines. Its failure to do so in DMSO solution led to the proposed existence of an ill-defined, cellulose-formaldehyde-DMSO complex.¹¹ The embrittlement observed in our studies might be the result of the anticipated crosslinking of the methylol cellulose. The role of SO₂ and the possible significance of the dipolar, aprotic properties of both SO₂ and DMSO would deserve further attention in a more careful, fundamental study.

Embrittlement by thionyl chloride (SOCl₂) was verified after HCl and SO₂-induced embrittlement was observed. The facile hydrolysis of SOCl₂ by ambient moisture would of course produce HCl and SO₂. In addition, however, the direct reaction of SOCl₂ with cellulose to yield chlorosulfite esters was also anticipated. Crosslinking reactions involving these chlorosulfite esters might contribute to the embrittlement process. The expense of the reagent and the experimental difficulty of obtaining anhydrous cellulose (to minimize HCl formation) discouraged us from pursuing this process beyond the stage of simple observation.

The embrittlement produced by chlorine gas may be fundamentally different in cause than that of the three foregoing reagents. Oxidative decomposition of the lignin matrix in groundwood paper (newsprint) may be at least partially responsible for the observed effect of chlorine. The reaction of chlorine with the cellulose itself may give rise to hypochlorites:



Simple alkyl hypochlorites are thermally unstable and decompose to a variety of products. In the case of cellulose, these decomposition reactions may possibly lead to a decrease in DP and to an increase in the number of carbonyl groups. Crosslinking reactions between these carbonyl groups and adjacent cellulose chains may contribute to rigidity and embrittlement.

The possible applications for a refuse-derived powder might include uses such as a fuel for suspension-fired boilers, a feedstock for cellulose hydrolysis or hydrogenation reactions, and as a low density filler in building materials such as wall-board which do not require load-bearing properties. The unique properties of such a powder include a high surface area to mass ratio, which is an obvious advantage in heterogeneous reactions such as combustion, hydrolysis, and hydrogenation.

6.2 Thermal Treatment

Thermal processing can be employed to obtain solid fuels. As described earlier, pyrolysis processes have been

used for generating carbon char as well as liquid and gaseous fuels. Similarly, heating in air at moderate temperatures (212-390°F) can cause cellulose degradation. It has been found that in some respects heat can have a more degrading influence on cellulose than a mild acid or oxidizing agent. Free water adsorbed by the cellulose effectively functions as a plasticizer. The major effect of the heat treatment is dehydration, however, some oxidation and depolymerization also occurs. The dehydration process causes increased intermolecular hydrogen bonding and the formation of chemical linkages between adjacent cellulose molecules. These effects promote cellulose embrittlement, which facilitates the production of powdered fuel from solid waste. Dehydration and cellulose embrittlement is observed at 300°F. Prolonged heating above 390°F results in the complete loss in fiber integrity. It would appear that hot ball milling of the shredded light fraction of MSW in a Hardinge-type mill (air swept conical ball mill) might well be an effective means for obtaining a powdered fuel.

During this phase of the program a series of experiments were performed to study the effects of thermal treatments alone, and in combination with ball milling. Samples of shredded newsprint and bond paper, both dry and in a moistened condition, were exposed to temperatures of 212°F, 300°F, and 390°F for periods of 15 minutes and 30 minutes. For this series of thermal exposures the samples were placed in a ceramic crucible and heated in a Leco glo-bar furnace. In addition, a furnace was designed and constructed to encompass a set of rollers and a ceramic ball mill jar to permit hot ball milling of shredded paper samples at temperatures of 212°F, 300°F, and 390°F.

At 212°F no apparent change was observed in any of the paper samples. At 300°F, oxidation of the paper samples had begun for the 15 minute exposures and was more pronounced for 30 minute exposures. At 390°F oxidation was rather extensive for the 15 minute exposures and almost complete throughout the samples for the 30 minute exposures. The rate of sample oxidation was more rapid with the newsprint sample. The moisture content of the samples did not seem to be a factor in the oxidation rate. The degree of oxidation was judged by the change in sample color and the degree of sample embrittlement. It was also observed that the longer the samples were exposed to temperatures above 300°F the greater the degree of degradation.

Ball milling the shredded paper samples at 340-385°F for two to three hours resulted in the conversion to a fine powder. Grinding times of less than one hour were not very effective. Because of the apparent need for extended grinding times it may not be feasible to process shredded refuse by hot ball

milling alone. A more practical approach may be to combine chemical embrittlement and hot ball milling.

6.3 Engineering Analysis of a Plant to Produce Powdered Fuel

A limited engineering analysis was conducted for a plant to produce a powdered fuel from refuse. The first phase of this study was the development of a design for a plant to process 1,000 tons of refuse per day. The proposed facility would contain two processing lines (each 30 ton/hr capacity) and would operate 20 hours per day, six days per week. In the flow plan developed, the incoming refuse would be screened in a trommel to separate the minus 4" fraction and open the trash bags. The oversized (+4") would be shredded and both fractions passed under magnetic separators to recover the ferrous metal. The nonferrous fraction would be screened in a trommel to separate out the fine fraction (minus 1/2") prior to air classification. The heavy fraction from the air classifier and the fines from the 1/2" Trommel are burned in an incinerator and provide the thermal energy required for embrittlement. If aluminum and glass recovery are desired, this would be accomplished by further processing the heavy fraction collected from the air classifier. Aluminum can also be recovered from the incinerated residue but it would not be of as high a quality. The light fraction obtained from air classification would be embrittled and powdered in an air swept ball mill (Hardinge Mill). The embrittlement is accomplished by treating the light fraction with a heated reagent like HCl or Cl₂, etc., in the Hardinge Mill. The powdered material would be swept from the mill entrained in the reactant gas when it is of the appropriate size. The data used for developing the flow plan for the proposed facility were obtained from University of Dayton studies¹², Combustion Equipment Associates data reported in U.S. Patent 3,961,913¹³, and NCCR studies for New Orleans¹⁴. The flow plan established for a facility to produce fine powdered fuel from refuse is presented in Figure 7. The calculations developed for the material balance used in the flow plan are presented in Table 14. The flow plan and material balance developed in this phase of the program served as the basis for determining equipment specifications and operating requirements. This information in turn was used to develop the environmental considerations and the economic analysis for the proposed plant in a subsequent phase of the program.

6.3.1 Environmental Considerations

Recovery of powdered fuel and ferrous metal results in a reduction of solid waste for disposal and the associated environmental problems. However, processing, use and disposal of the products from this proposed facility could re-

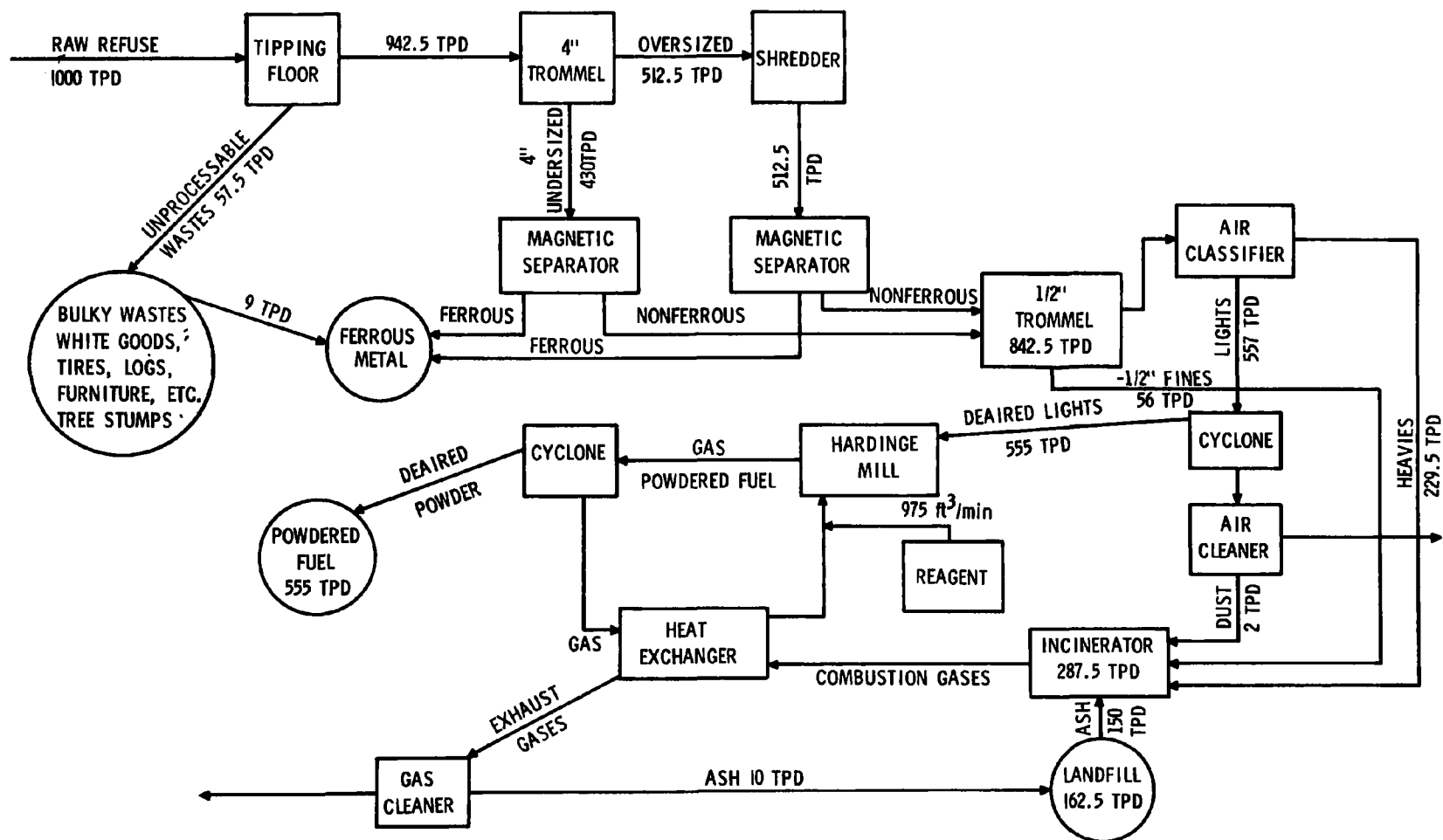


Figure 7. Resource Recovery Plant to Produce Powdered Fuel.

TABLE 14. MATERIAL BALANCE FOR A POWDERED FUEL PROCESS

	Incoming (100 TPD)	Unprocessable Waste- (57.5)	Trommel 4"		Magnetic Separation		Trommel 1/2"		Air Classification				
Refuse			-4" (430)	+4+ (512.5)	Ferrous (100)	Nonferrous (842.5)	-1/2" (56)	+1/2" (786.5)	Lights (557)	Heavies (229.5)	Incineration (287.5)	Landfill (162.5)	Powdered Fuel (555 TPD)
Organic Fraction	750	40	225	485	22	688	45	643	553	90	135	10	553
Metal	100	10	67	23	76.5	13.5	0.5	13	3.5	9.5	11.5	11.5	2
Ferrous	85	9	57	19	75	1	-	1	-	1	1	1	-
Nonferrous	15	1	10	4	1.5	12.5	0.5	12	3.5	8.5	10.5	10.5	2
Glass and other inerts	150	7.5	138	4.5	1.5	141	10.5	130.5	0.5	130	141	141	-

sult in environmental pollution problems. Waste to energy conversion facilities and the products generated can contribute to land, water, and air pollution.¹⁵ The potential pollution problems and associated control technologies for this proposed embrittlement process have been considered and the areas of major concern are discussed in the following section.

6.3.1.1 Air Quality

Several potential pollution problems which have been identified for the proposed process include dust, and gas emissions from incineration.

Dust emissions are a problem that plagues most phases of solid waste processing. Shredding, air classification and screening are major sources of dust emission. Bacteria and virus emissions are closely associated with dust since both generally reside on the surface of dust particles. Effective dust control for the processing requirements of the proposed facility does not appear to be a problem. Care must be taken to enclose all processing equipment and conveyors. In addition, effective exhaust systems must be utilized at the processing equipment and for the plant in general. Fabric filtration units (baghouses) can be readily employed for cleaning the exhaust gases, since the gas is at ambient temperature and the dust is not very abrasive. Pilot studies demonstrated that 99.9% particulate removal efficiencies can be obtained with the use of fabric filters.¹⁶

The other cause of air pollution is the exhaust gases from incineration of the heavy and fine fractions which provide the heat source for embrittlement. The uncontrolled emissions from this process should be similar to those reported for most incinerator operations: particulates, HCl, SO₂, NO_x, CO, and unburned hydrocarbons. CO, NO_x, SO₂ and unburned hydrocarbons do not appear to be a problem nor are any special controls anticipated for these pollutants. HCl removal can be achieved with a scrubber unit, however appropriate materials selection in the design are necessary to inhibit acid corrosion. Particulate control would probably require an electrostatic precipitator. In addition, since up to 30% of the particulates could be less than 1 μ m, the use of a fabric filter system may also be required. Disposal of the fly ash collected is also of concern due to the presence of trace elements (Cl, Pb, Cu, Zn, etc.) found in the fly ash.

6.3.1.2 Water Quality

The proposed facility for producing a powdered fuel relies primarily on dry processing. The only

water required is for quenching the incinerator residue and washing down processing equipment. These waters pick up a considerable amount of contaminants and organics, trace metals, acids, etc., and will require treatment at a waste water facility.

6.3.1.3 Solid Wastes

The residue from the proposed facility will come from the incineration process and is relatively inert. The captured fly ash and quenched bottom ash will contain a very small amount of unburned organics (2.5%) and some trace elements (Be, Hg, Cl, Pb, etc.) requiring proper sanitary landfill procedures for its disposal.

6.3.1.4 Environmental Impact of the Powdered Fuel

The powdered fuel obtained by the embrittlement process can cause environmental problems in its use. Combustion of this powdered fuel will produce air pollutants (particulates, trace metals and gaseous emissions) similar to those described for the incineration of the heavies and fine fraction. Of particular concern are the fine particulates, trace metals and the acid vapors. Similar precautions as those described for incineration will have to be taken to control these pollutants.

A problem with the powdered fuel which should also be addressed although it is not usually covered under environmental concerns is the explosive potential of the powdered fuel. Fine powders can readily detonate and great care must be exercised in handling and storage of the powdered fuel. Several explosions were experienced by A.D. Little and CEA in their work with powdered fuels. It was reported that the explosive power of the powdered cellulose was equivalent to half that attributed to powdered grain. The standard safety practices established for grain should be followed in the handling of powdered fuels. In addition to the hazards of explosion by the dust, there may be a hazard if significant amounts of metal are in the waste being treated and the embrittlement reagent is an acid. The hydrogen released by this type of reaction could present an additional danger and should be avoided. One means of avoiding this problem would be the use of Cl_2 or some other nonacid as the embrittlement reagent.

Another approach to handling the powdered fuel would be to suspend the treated light fraction in a light fuel oil. Grinding and storage of the treated organics in a light fuel oil will inhibit explosions and facilitate in-

troduction of the powder into the combustion system of a furnace or boiler.

6.3.2 Economic Considerations

A preliminary economic analysis was prepared for the powdered fuel process. The analysis is based on the process flow plan developed (Figure 7). The proposed facility would operate 20 hours per day, 6 days per week for 52 weeks per year (265,200 TPY). It is assumed that an adjacent land fill is available to serve as a backup to the facility. Revenues are anticipated from:

- a) tipping fee
- b) sale of recovered metals
- c) sale of powdered fuel

The format followed in preparing this economic analysis was taken from EPA document SW-157.6.¹⁰ A summary of the calculations developed for the capital and operating costs are presented in Tables 15 and 16 respectively. A summary of potential revenues are presented in Table 17.

From the analysis developed a total operating cost per throughput ton of MSW was calculated to be \$21.11. A potential revenue of \$10.44/throughput ton was calculated for the sale of ferrous and the tipping fee. To break even the powdered fuel would have to sell for about \$0.01/lb or about \$1.33/million Btu.

6.4 Conclusions

The use of powdered fuel prepared from the embrittlement of cellulose waste offers a number of advantages:

- a) It is more compatible with powdered coal fired boilers and will have better combustion characteristics than conventional RDF.
- b) It is more readily densified into pellets and will produce less wear on the extrusion dies.
- c) It can be slurried with oil for firing in oil fired units.
- d) It can be used as the feed stock for further chemical or thermal treatments like hydrolysis, hydrogenation, gasification, etc.

In the work to date we have identified a number of chemical treatments for cellulose embrittlement and evaluated

TABLE 15. ESTIMATED CAPITAL COSTS (1977 Dollars)

Land (30 Acres @ \$10,000/acre)	\$ 300,000
Site Preparation (35% of land cost)	105,000
Equipment, Installation & Facility Construction	15,456,000
Engineering & Design (6% of 15,681,000)	952,000
Contingencies (10% of 16,813,000)	1,681,000
SUB TOTAL	18,494,000
Legal & Financial Costs (2%)	<u>370,000</u>
TOTAL PLANT COSTS	\$ 18,864,000
Municipal Revenue Bonds for the Project (1.12 plant cost)	\$ 21,128,000
Annual Interest Rate for 20 years @ 8%	1,095,534
Total Interest to be paid	21,910,669
Total Capital Cost	43,038,669
Annual Capital Cost	2,151,934
Capital Cost Per Ton	<u>8.12</u>

TABLE 16. ESTIMATED ANNUAL OPERATING
AND MAINTENANCE COSTS (1977 Dollars)

Salaries and Benefits	\$ 872,000
Fuel	100,000
Electricity	437,000
Water and Sewer	3,000
Maintenance	666,000
Residue Removal	250,000
Materials and Supplies	711,000
Taxes (.75%)	142,000
Insurance and Management Costs (\$1/ton)	<u>265,000</u>
Total Annual Operating & Maintenance Cost	3,446,000
Operating and Maintenance Cost Per Ton	<u>12.99</u>

TABLE 17. POTENTIAL REVENUE SOURCES

Revenue Source	Dollars/Throughput Ton
Tipping Fee	8.50
Ferrous Metal (86 TPD @ a net cost of \$22.55/ton)	1.94
Powdered Fuel (550 TPD)	??
Cost/ton	21.11
Cost needed for sale of fuel to break even	10.67
\$.01/lb of powdered fuel @ 7,500 Btu/lb - 1.33/M Btu	

their effectiveness in laboratory studies. In addition a preliminary design for a resource recovery plan to produce powdered fuel was developed. This design plan was the basis for a preliminary economic analysis. From the data developed it was calculated that the powdered fuel would have to sell for about \$.01/lb for a facility having a tipping fee of \$8.50.

SECTION 7

LIQUID AND GASEOUS FUELS FROM THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

A number of processes have been developed for obtaining liquid and gaseous fuels from refuse. The literature contains descriptions of a wide range of liquefaction and pyrolysis processes in full scale operation, in demonstration, in pilot plant development, and in the laboratory. The major processes have been identified and are described in the background section of this report. During this project two laboratory processes were also reviewed:

- a) the Worcester Polytechnic Institute (WPI) hydrogenation-liquefaction process; and
- b) the Wright-Malta Corporation (WMC) steam injection pyrolysis process.

Although both of these processes offer an interesting potential, their scale-up at the present time poses a number of difficulties. In the WPI process the organic fraction of solid waste is converted to a fuel oil. In this hydrogenation reaction one ton of solid waste generates 2.15 barrels of oil. The Wright-Malta Corporation has developed an interesting steam pyrolysis process for garbage and sewage sludge in a rotary kiln. In the WMC process, gaseous and liquid fuels are obtained.

7.1 The Worcester Polytechnic Institute Process

Kaufman and Weiss of Worcester Polytechnic Institute (WPI) conducted pilot plant studies on the hydrogenation-liquefaction of cellulose.¹⁷ A 20 wt percent slurry of shredded paper (cellulosic material) in mineral oil was subjected to 1029 psia H_2 at 845°F for 15.1 min in the presence of 0.04 wt percent $Ni(OH)_2$ catalyst. Under these conditions 1 lb of newsprint in 4.4 lbs of oil produced 4.9 lb of product oil, 0.1 lb CO , 0.07 lb CO_2 , 0.001 lb CH_4 , 0.07 lb $C_2 - C_4$ hydrocarbons and 0.2 lb of solid residue. The product oil, projected to be 2.15 bbl/ton of refuse, had a heating value of 17682.2 - 18527.6 Btu/lb and an oxygen content below 1 percent. Analysis of the solid residue indicated its composition to be 58.5 percent C, 4.75 percent H, 19.8 percent O, and 16.95 percent others (by difference).

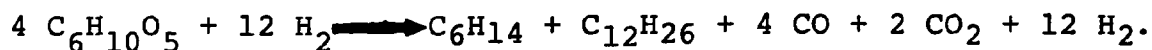
The conversion of cellulose to volatile products is thought to proceed via consecutive reactions.²⁰ (Cellulose \longrightarrow pyrobitumens \longrightarrow oil \longrightarrow gas). Formation of pyrobitumens as a first step in the conversion is well known, and involves thermal dehydration, depolymerization, and removal of CO. The WPI process is therefore in reality the catalytic hydroliquefaction and/or hydrogasification of pyrobitumens, which are defined as benzene-insoluble materials containing C, H, and O in varying proportions.

The reaction of organic compounds with hydrogen may involve the addition of hydrogen across a double bond (called hydrogenation) as in the conversion of ethylene to ethane, or it may require the replacement of an atom or group of atoms by hydrogen (called hydrogenolysis). Both processes are very slow in the absence of catalysts at room temperature and low pressure. Inclusion of catalysts such as Ni, Pd, Pt, Rh, or Ru frequently permits the desired reaction to proceed easily and rapidly under the foregoing conditions. Reaction is thought to occur on the metal surface. Since all hydrogenation reactions of carbon-double bonds are exothermic ($4.5 \times 10^4 - 5.4 \times 10^4$ Btu/lb mole), activation energies (E_{act}) may become quite low with suitable catalysts. Gupta, Kranich, and Weiss calculate E_{act} for the catalytic hydrogenation of α -cellulose to be 3.09×10^4 Btu/lb mole.

The conversion of cellulose to a hydrocarbon requires that hydrogen replace the oxygen atoms in cellulose. Such replacement may occur by direct substitution (i.e. hydrogenolysis), or by initial dehydration followed by addition of hydrogen across the double bond (i.e. hydrogenation).

Kaufman and Weiss reported DTA (differential thermal analysis) results showing hydrogenation exotherms between 390°F and 480°F. This temperature range is curiously close to the temperature range of initial water evolution during cellulose pyrolysis experiments. Infrared spectral data¹⁹ suggest the formation of anhydrocellulose at 410°F during pyrolysis. In addition, hydrogenolysis reactions are not common with saturated compounds (no double bonds) such as cellulose. (See Figure 8).

According to Kaufman and Weiss (p. 138),¹⁷ a crude approximation of the stoichiometry for the WPI process is:



Their flow plan is presented in Figure 9.

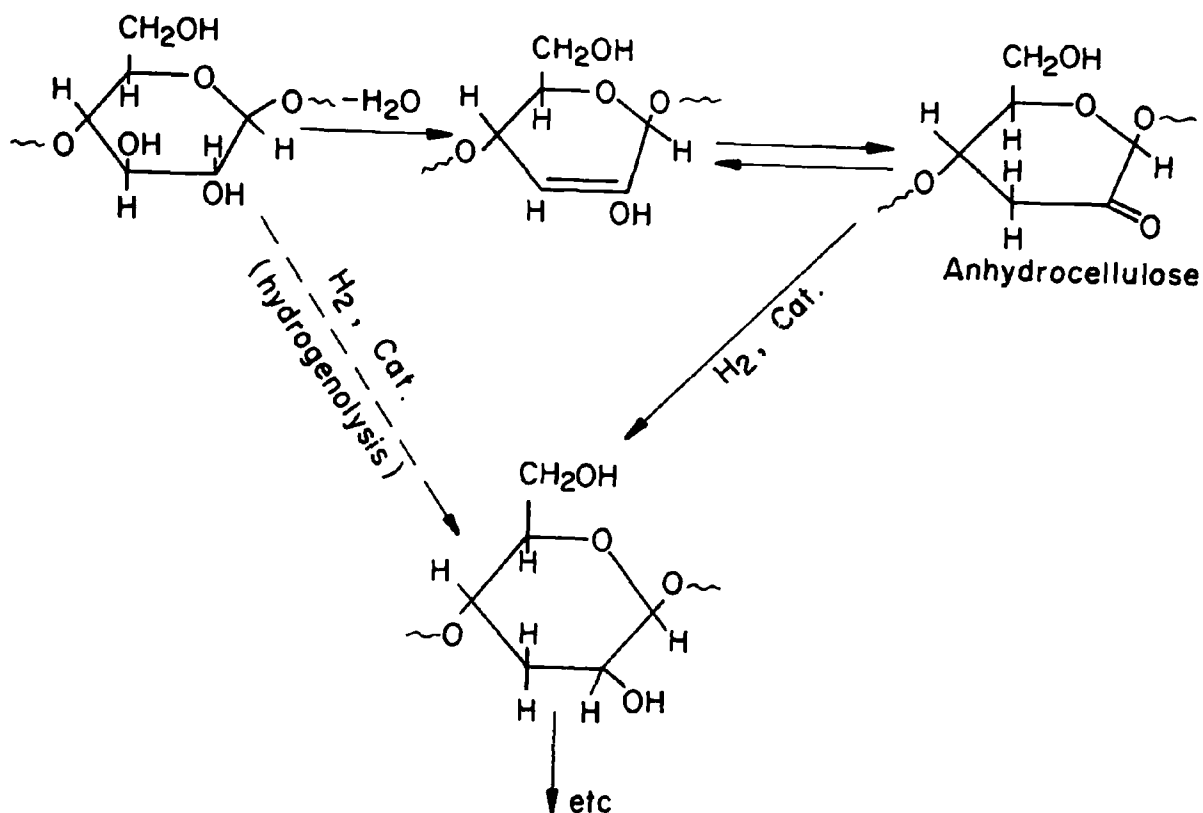
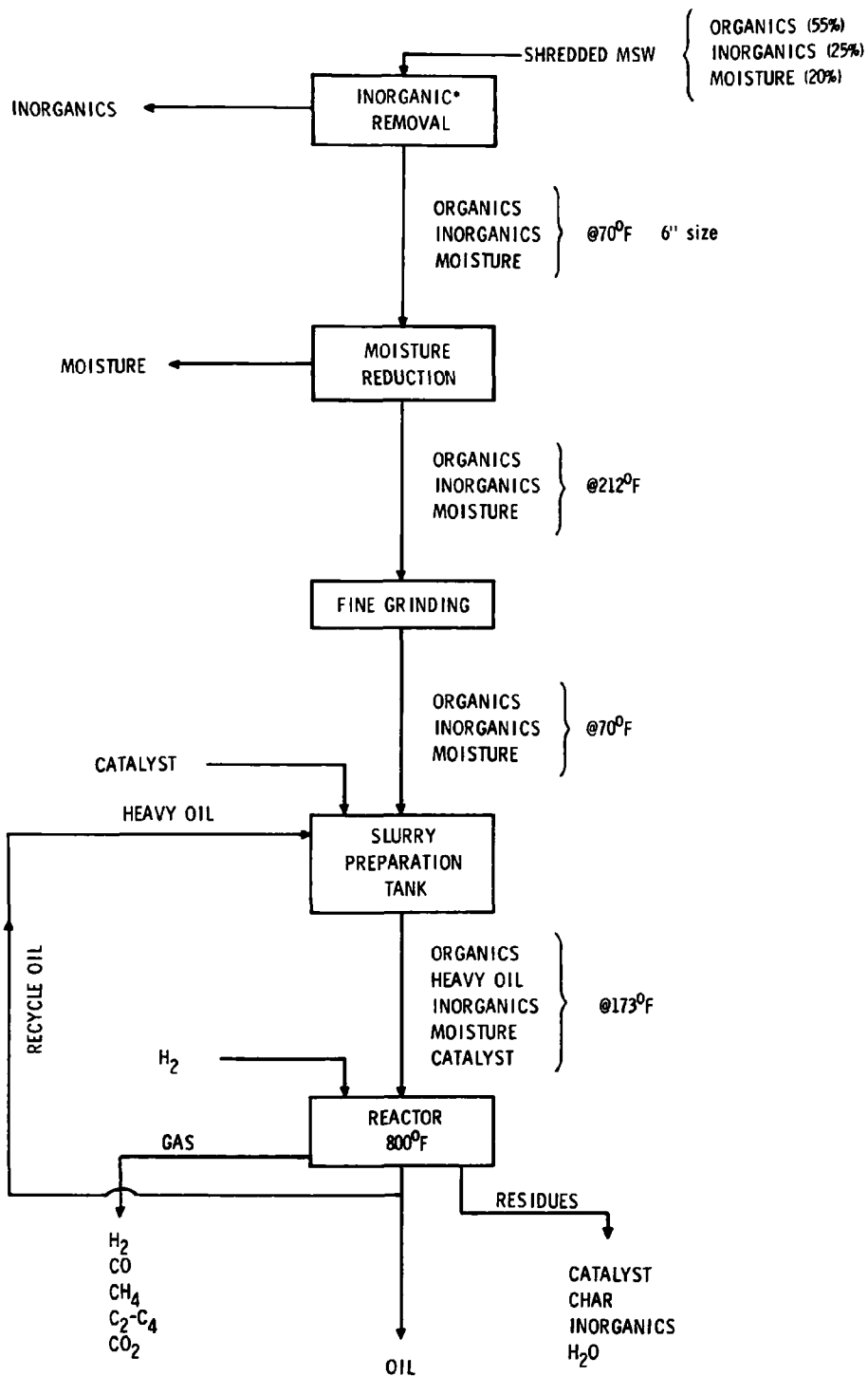


Figure 8. Cellulose Hydrogenation

The WPI investigators proposed a 36 ton/day plant for Holden, Massachusetts designed to process a 50 wt percent refuse-oil slurry. Inorganics and organics were to be source-separated. The organics were to be treated in a hammermill prior to being slurried with oil. The upper limit to particle size was never determined, but the investigators were interested in investigating chemical embrittlement to produce a powdered feedstock. Due to lack of funding, the Holden, Massachusetts, facility was never built. Cost of oil production in a proposed 36 ton/day pilot plant was projected to be \$24.77/bbl. It was estimated that plants processing 500-2,000 tons daily could produce oil for \$4.00 to \$5.92 per barrel. This projection would appear to be extremely optimistic, based on available information.

The chief advantage of the WPI method is the production of a high quality heating oil which should be readily marketable. Among the disadvantages one must consider are:

- a) high capital costs for a high pressure, hydrogenation system, and the associated maintenance problems, anticipated scale-up problems,



*INORGANIC REMOVAL MAGNETIC SEPARATION, TROMMEL SCREEN & AIR CLASSIFIER

Figure 9. Flow Plan for the WPI Process.

- b) inherent danger involved in a large scale use of hydrogen under pressure,
- c) the need to reduce the refuse to fine particles for the reaction, and
- d) the disposal of the residue (20 weight percent of the starting material) and the liquid effluents.

The source of the CO and CO₂ in the WPI process is proposed to be the water gas shift reaction which produces as a third product sufficient H₂ to supply about 50% of that required for hydrogenation. An examination of the product composition (tables, p. 129; chromatograms, p. 112, and 133)¹⁷ indicates that the suggested stoichiometry is indeed a very crude approximation. Besides neglecting numerous minor products, the equation postulates the formation of saturated non-cyclic hydrocarbons as the major products. Hexane would have the composition 83.63% C, 16.3% H, and the hydrogen: carbon ratio would be 2.33:1. Dodecane would be 84.61% C, 15.39% H, and would have a hydrogen: carbon ratio of 2.17:1. The WPI product oils have H:C ratios which are too low to be non-cyclic, saturated hydrocarbons (1.82-1.97, p. 131). The carbon contents are 2-3% too high, and the hydrogen contents are too low by similar amounts. The H:C ratios for the WPI oils indicate that they might better be represented by formulas such as C₁₀H₁₈ or C₁₀H₂₀ (i.e., 2-4 hydrogen atoms less than required for saturation). These distinctions are only important if one requires a balanced equation for subsequent thermochemical calculations. Such calculations are fraught with difficulties owing to the complexities of the reactions (many products, some of undetermined composition). A flow plan, material balance, and economic evaluation were prepared by Kaufman and Weiss for their process.

7.2 The Wright-Malta Corporation Process

Injection of steam during the pyrolysis of municipal solid waste was undertaken by the Wright-Malta Corporation.²⁰ Their studies have been limited to small scale laboratory experiments with an electrically heated desk-top rotary kiln, temperatures to 1112°F and 441 psia steam. Evolution of CO and CO₂ begins at 300°F, followed by condensable liquids. Methane evolution begins at 570°F. The gas mixture will burn when the pyrolysis temperature rises to 750°F, and by 1112°F the gas is nearly pure CO₂ and H₂ in a 1:2 ratio as required by the stoichiometry of the water-gas reaction.



The WMC workers found that the inclusion of 10 wt percent Na₂CO₃ (soda ash) resulted in a decrease in the amount of char residue, and in a tendency for the liquid pyrolysate to be less soluble in water. At 14.7 psia steam, for example, the char residue

decreased from 23 wt percent to 15 wt percent in the presence of soda ash. A six percent char residue was obtained with 441 psia steam, 930°F, and a heating time of 1.5 hr. In the projected plant, coarsely shredded refuse would be introduced through a double lock hopper into the high end of an inclined rotary kiln. Heat would be supplied by a counterflow of superheated steam, the temperatures ranging from 100°F at the high end to 1112°F at the low end. The tumbling action of the kiln, enhanced by cans, bottles, rocks, or intentionally added "breakers", would reduce the refuse to gas and a solid residue.

The expected fuel gas emerging from a projected plant would be 70% H₂O vapor, 14% steam, and 15% combustible gases. Its heating value would be about 140 BTU/scf. The residue is expected to represent 30-40% of the original mass and 10% of the original volume. It could be processed to reclaim glass and metals.

Pilot studies actually conducted in the desk-top kiln did not use counter-current steam heating, nor was the process continuous. A batch process was employed, and the temperature was raised uniformly by electrical heating. As a result, liquid pyrolysate was obtained (57-84% of the original mass by difference) in addition to gases (10-20%) and a char residue (5-23% of the original mass). The liquid was not analyzed.

The benefits as stated by WMC include:

1. no fine shredding, drying, or classifying is necessary;
2. sewage sludges may be employed as part of the feed-stocks;
3. a theoretical system efficiency of 40-45% is achieved, which claimed to be comparable to that of the best combined cycle systems operating on natural gas or liquid fuels.

In reviewing the Wright-Malta process, the following potential problem areas have been identified:

1. maintenance on the necessary rotating seals and interlocks;
2. corrosion induced by decomposition of chlorinated polymers (e.g. PVC)
3. the availability of a market for the product fuel gas. (Perhaps the liquid pyrolysate would be more desirable.)

7.3 Conclusions

In this phase of the project two laboratory processes for liquefaction/gasification described in the literature were reviewed. Although both processes were considerably different than the conventional pyrolysis processes, they appeared to offer some interesting potential for enhanced fuel recovery. In studying these processes the major problems for commercial scale-up were identified. In addition to the technical problems anticipated it is believed that the economics of either process would not be viable at this time.

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APPENDIX I

B I B L I O G R A P H Y

CONCEPTS FOR IMPROVING FUEL FRACTION OF SOLID WASTE

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TABLE OF CONTENTS

	<u>Page</u>
COMBUSTION THEORY FOR SOLID WASTES	71
PYROLYSIS OF SOLID WASTES	71
PYROLYSIS PATENTS	75
THERMAL DECOMPOSITION OF CELLULOSE	75
CARBONIZATION PATENTS	80
HYDROLYSIS	81
RENEWABLE FUELS	82
LIQUEFACTION	83
BIO-CONVERSION	84
OZONE TECHNOLOGY	85
ALLIED INDUSTRIAL PROCESSES	86
PAPER RECYCLING	87
FIBER RECOVERY	87
INDUSTRIAL WASTES	89
SHREDDERS	91
GRAVITY SEPARATION	92
UNIT OPERATIONS	92
WASTE MANAGEMENT REPORTS TO CONGRESS	93
ECONOMICS OF WASTE MANAGEMENT	94
GENERAL RESOURCE RECOVERY ARTICLES	95
AKRON	102
AMAX	102
AMES, IOWA	102
BUREAU OF MINES	103
COLUMBUS, OHIO	103
COMBUSTION EQUIPMENT ASSOCIATES - ECO FUEL	103
CONNECTICUT	104
C.P.U.	104
FOSTER WHEELER COPROATION - LIVINGSTON, N.J.	104
FRANKLIN	104
FT. WAYNE & G.M. - CUBETTES	105
NCRR	105

TABLE OF CONTENTS (Concluded)

	<u>Page</u>
NEW YORK	105
ST. LOUIS - UNION ELECTRIC	105
TULSA, OKLAHOMA	107
OTHER RESOURCE RECOVERY PROJECTS	107
CONFERENCES	108

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16. ABSTRACT <p>Although a number of resource recovery from refuse programs have been effective, the quality of the products recovered could be enhanced to improve their marketability. The purpose of this study was to investigate the potential of known processes that could improve the quality of the fuels or other products derived from the organic fraction in refuse.</p> <p>Possible processes for improving the quality of products from the organic fraction derived from municipal solid waste (MSW) were determined, and descriptions were developed for each process. An analytical framework for technical and economic assessment was developed to serve as a guide for analysis. Major thermal and chemical processes used in the pulp and paper, wood, textile, and resource recovery industries were identified.</p> <p>This study concentrated on those processes designed to produce a carbon char, a powdered fuel, and liquid and gaseous fuels from the municipal solid waste. The chemical and thermal treatments of most interest were the Worcester Polytechnic's hydrogenation-liquefaction process, Wright-Malta's steam injection pyrolysis process, and cellulose embrittlement.</p> <p>Basic requirements were defined for producing a fine powdered fuel from the organic fraction of MSW. More quantitative measurements of the embrittlement process parameters are recommended.</p>				
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