AQUEOUS PYROLYSIS
OF SOLID WASTES

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PREFACE

The method of aqueous pyrolysis was investigated as an alternative for treating solid waste materials. The benefits of this treatment process were the production of gaseous products containing hydrocarbon gases, the reduction of volatile organic matter, volume reduction, and the destruction of toxic pollutants. The waste material processed by this method included raw municipal wastewater sludge, newsprint paper, grain dust, and a rubber waste.

I wish to express my gratitude to all the people who have assisted me in this study. I especially appreciate the assistance of my major adviser, Dr. Don F. Kincannon, and for his guidance, concern, and invaluable help.

I also appreciate the assistance of Dr. William L. Hughes, who provided much of the equipment and facilities used in this work, and for providing information from previous work on aqueous pyrolysis.

Special thanks are due to Barney Grau of Induction Systems Engineering, Inc. who assisted me with the induction heating process,and also to Ali Torabian who assisted me with the GC analysis and development of standard curves for phenols.

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CHAPTER I

INTRODUCTION

The disposal or treatment of solid waste materials presents many problems with the current methods of solid waste handling practiced. Large quanities of solid waste materials are generated continuously from residential, commercial, agricultural, and industrial sources. The production of wastewater sludge from wastewater treatment plants is another source of solid wastes. These waste materials require adequate space for storage or disposal. Solid waste materials are usually disposed of in sanitary landfills which must be permitted and require large amounts of land. The land for a sanitary landfill must be acceptable with good soil characteristics, a good location near the sources of the solid waste generated, and minimal endangerment to the groundwater of the local area. Proper treatment or disposal is required to reduce the risks of pollution of the environment or to prevent public health hazards. Some waste materials, such as wastewater sludges, require treatment before disposal to reduce health hazards, while other wastes such as untreated hazardous wastes may require special containment before disposal. The handling and transportation of these solid wastes to disposal sites can be very costly and uneconomical. A problem that exists with most solid waste disposal sites is the opposition of the public to the location of new disposal facilities. This opposition is based upon concerns about health, pollution, odors, and other unpleasant aesthetics, with the opinion that such facilities should not be located in their vicinity.

Aqueous pyrolysis was studied as an alternative method for the treatment of solid waste materials. The objective of the study was to determine if aqueous pyrolysis of selected solid waste materials provided adequate reduction of volatile solids, reduction of volume, and production of reuseable hydrocarbon gases, which could make this treatment alternative feasible for future use. The solid waste materials selected consisted of wastewater sludges, some common solid wastes, and some priority pollutants, which were used to investigate the effect of aqueous pyrolysis on the destruction of hazardous materials. This study compares the aqueous pyrolysis treatment method to the different treatment unit processes and methods of storage and disposal of solid wastes currently used.

CHAPTER II

REVIEW OF LITERATURE

Types and Quantites of Solid Wastes

Solid wastes are defined by Tchobanglous, Theisen, and Eliassen (1) as all of the discarded solid wastes from human and animal activities that are considered to be useless or unwanted. Solid waste materials are catgorized by the source of the waste materials such as residential, commercial, agricultural, industrial, and municipal wastes.

Quantities Generated

Jackson (2) estimated that by the year 1980 over 340 million tons of solid wastes would be produced in the United States each year, which would be equivalent to nearly one ton of solid wastes generated for each person annually. Sorg (3) reported that studies have indicated that the rate of solid wastes generated is about 100 pounds per person per day. Of this 100 pounds, 10 pounds of all solid wastes are generated from residential, commercial, industrial, and municipal sources. Of these 10 pounds, six pounds per person per day are municipal solid wastes and three pounds per person per day are industrial wastes. Tchobanoglous, Theisen, and Eliassen (1) have reported that estimated quantities of solid wastes generated in the United States average about 4.4 billion tons each year, which consists of 640 million tons of agricultural wastes, 230 million tons of municipal wastes, 140 million tons of industrial wastes, and 1.7 billion tons of solid wastes from mines, minerals, and animal wastes.

Municipal Solid Wastes

Municipal solid wastes, including residential and commercial wastes, consists mostly of organic biomass such as paper, wood, textiles, rubber and food. These organic materials comprise approximately 75 percent of the total mass of municipal solid wastes that are disposed.(1) Municipal solid wastes also include wastewater sludge.

Wastewater Sludge

Wastewater sludge is the suspended solid matter which is removed from wastewater at sewage treatment facilities. The concentration of suspended solids entering sewage treatment facilities generally ranges from 100 to 300 mg/L.(5) More suspended solids are generated from the excess growth in biological treatment processes which also must be removed. It has been estimated that sewage treatment plant solids are generated at a rate of 0.5 pounds per person per day. (1) Wastewater sludge is handled as a solid waste although as much as 95 percent of the mass of the sludge consists of water. There are two main objectives in the treatment of wastewater sludge: to reduce the volume by removing much of the liquid portion, and "to decompose the highly putrescible organic matter to relatively stable or inert organic and inorganic compounds" which eliminates pathogenic organisms and facilitates sludge dewatering processes.(6)

Industrial Wastes

Sorg (3) explained that industrial wastes could be catagorized by two ways: process and nonprocess wastes. Nonprocess wastes consist of wastes generated by packaging and shipping, and office wastes, which are common to most industries. Nonprocess wastes are similar to municipal wastes in composition. Process wastes are more specific to the industry, its process and products. Process industrial wastes are more likely to be hazardous than most other solid wastes due to the materials used in the industrial processes and the byproducts that are generated.

Hazardous Wastes

Hazardous wastes are defined as solid wastes that due to the "quantity, concentration, or physical, chemical, or infectious characteristics may cause or significantly contribute to an increase in mortality or ... illness", or are "potentially hazardous to human health or to the environment when improperly handled". Solid wastes are classified as hazardous under the Resource Conservation and Recovery Act of 1976 if the waste material exhibits one or more characteristics identified by the Environmental Protection Agency which are ignitability, corrosivity, reactivity, and toxicity.(7)

Treatment and Disposal of Solid Wastes

Wastewater Sludge

There are many available methods for the treatment and disposal of wastewater sludge. These processes are used to thicken, stabilize, condition, dewater, reduce, and dispose of the suspended solids removed from wastewater.

Sludge Thickening

Sludge thickening removes water, reduces sludge volume by increasing the solid concentration, increases the post process efficiencies, and blends the sludge which facilitates the sludge stabilization and dewatering processes.(5) The sludge blending process is usually accomplished in the primary settling tanks.(8) The methods used for sludge thickening are gravity, dissolved air flotation, and centrifuge.

Gravity Thickening. Gravity thickening involves the separation of solids from wastewater by gravity settling. The sludge settles to the bottom of the settling basin, compacts, and is gently collected at the center of the bottom of the basin from where it is pumped to digesters or dewatering equipment.(8) Gravity thicking is efficient and economical because it requires very little energy input.

Dissolved Air Flotation. Air flotation thickening is a process of separating solids from wastewater in an upward direction by attaching pressurized small diameter air bubbles to the particles of suspended solids. The thickened sludge forms a sludge blanket at the surface which is removed by surface skimming equipment. Flotation thickening is generally used whenever the solid particles are more likely to float than to settle by gravity.(5)

Centrifuge Thickening. Centrifuge thickening is primarily used when a particular sludge cannot be effectively removed by gravity settling or dissolved air floatation. Centrifuges can have substantial costs for maintainance and power and therefore there has been limited use of this process.(5) Centrifuges are used to both dewater and thicken sludge, and its use in thickening is usually limited to waste activated sludge.(8)

Sludge Stabilization

The sludge stabilization process reduces the pathogenic organism content, reduces the volume and weight of the sludge, controls offensive odors, controls the potential for putrefaction, and can produce gases that are reusable as an energy source.(5) Metcalf and Eddy (8) define the four means to eliminate offensive and unsafe characteristics of sludge as "the biological reduction of volatile content, the chemical oxidation of volatile matter, the addition of chemicals" which makes the sludge unsuitable for microorganisms to survive in, and "the application of heat to disinfect or sterilize the sludge." Process methods for sludge stabilization include anaerobic digestion, aerobic digestion, composting, and lime treatment.

Anaerobic Digestion. The anaerobic decomposition of any complex organic substance is explained by De Renzo (4) as a two stage process that consists of a first stage that envolves "the breakdown of the complex organic materials by acid forming bacteria into organic acids with the production of carbon dioxide" gas, and a second stage in which bacteria known as methane formers act upon the volatile organic acids to produce methane and carbon dioxide gases. The methane gas can be collected and reused for heating or other energy needs. The process is devoid of oxygen bearing air because the process is controlled by anaerobic methane forming bacteria, which grow at low rates, are very sensitive to pH, temperature, sludge composition, and are highly active in mesophilic ($80^{o}F$ to $110^{o}F$) and thermophilic $113^{o}F$ to $149^{o}F$ ranges. Methane formation ceases and there is no decrease of sludge organic content when the pH drops below 6.0. (5) De Renzo (4) reported that studies show that the production of gas from anaerobic digestion ranges from 1.40 cubic feet per pound of dry solid at $95^{o}F$ with a retention of four days to 4.96 cubic feet per pound of dry solid at a temperature of $140^{o}F$ with a 30 day retention time. The gas produced by anaerobic digestion was found by De Renzo (4) to contain about 70 percent methane at low temperatures and short retention times, while at high temperatures the methane content dropped to a range of 50 to 55 percent with carbon dioxide accounting for the remainder of the gas produced. This study also showed that the destruction of volatile solids was 17.4 percent at 95°F and retained for only four days and destruction of volatile solids increased with an increase of temperature and retention time with a 61.8 percent destruction reported for a temperature of 140°F and 30 days retention time.(4) Similar results have been reported by Carrio, Lopez, Krasnoff, and Donnellon (9) where thermophilic anaerobic digestion volatile destruction ranged from 55 to 71 percent.

<u>Aerobic Digestion.</u> Aerobic digestion is a similar process to anaerobic digestion with the same treatment objectives but some different operational procedures. Aerobic digestion is the separate aeration of sludge in an open tank where microorganisms in the endogenous phase oxidize organic matter aerobically into carbon dioxide, water, and ammonia.(8) The advantages that aerobic digestion has over other sludge stabilization methods are that the process is a relatively simple operation, lower capital costs, no significant odor generation, reduction of pathogenic organisms to low levels, a supernatant with a lower biochemical oxygen demand, and production of an easily

dewatered sludge.(5) Reynolds (10) reported that aerobic digestion has the major disadvantages of high power costs due to the amount of aeration and mixing required and that the useful by-product of methane gas is not produced.

Sludge Conditioning

The functions of sludge conditioning are to improve the dewatering rate, improve the capture of solids, improve sludge compactability, and to stabilize the sludge. The two most common methods of sludge conditioning are heat treatment and chemical addition. Heat treatment with temperatures of 300 to 500°F and pressures of 150 to 400 psig are used to break open cellular material, which leaves behind a solid material consisting of mineral matter and cell wall debris.(5) Heat treatment can be accomplished by wet-air oxidation as in the Zimpro process or by heat exchanging and steam injection as in the Porteus process.(8) Chemical addition is used to coagulate the solids and release the water adsorbed by the sludge, and can be economical due to increased yields. The chemicals that are used include lime, alum, and organic polymers, and mixing mechanisms must be provided.

Sludge Dewatering

The dewatering of sludge is for the removal of water, to reduce the sludge volume and weight, and to change the sludge from a liquid form to a damp cake. With much of the water removed, the retention time of the drying beds is reduced and fuel requirements for incineration decreases. The methods for dewatering include vacuum filters, centrifuges, filter presses, and air drying in drying beds which is the most commonly used method. Air drying of sludge is usually limited to well-digested sludge because of the odors, insect attraction, and poor drying characteristic of raw sludge. The effectiveness of air drying is determined by such factors as the quantity and rate of precipitation, humidity, temperature, and rate of evaporation.(5) Drying beds are very effective in dewatering sludge but do require adequate land area. The reasons given by Metcalf and Eddy (8) for dewatering are that it substantially lowers the cost of transportation of the sludge from the treatment facility to the site of final disposal, dewatered sludge is easier to handle than liquid sludge, incineration processes have less energy expended on water evaporation when burning dewatered sludges, and dewatering is commonly required before sludge can be disposed of in a sanitary landfill to reduce leachate production at the landfill.

Sludge Reduction

Generally thermal processes are used for major reduction of sludge solids to accomplish a destruction of solids, removal of water, conversion of volatile organic matter to inert inorganic matter, and sterilization. Established sludge reduction processes include incineration, wet air oxidation, and heat drying. Experimental processes include pyrolysis and generation of power or steam by incineration.(5) Sludge reduction normally results in the production of ash or residue which can be disposed of in sanitary landfills.

Incineration. The incineration of a sludge involves a drying process followed by the complete combustion of all organic substances in the sludge. Incineration is accomplished by raising the temperature of the sludge to the boiling point of water (212°F) which evaporates the sludge. The water vapor and air temperature of resulting gases is increased, and then the temperature of the dried sludge volatiles is increased to the ignition point at which the sludge is oxidized. The temperature required for ignition is usually about 900°F. Incineration requires a very significant power input and adequate supply of air for oxidation.(5) One method of incinration is the fluidized bed incineration method in which a bed of sand is fluidized at temperatures of 1,400 to 1,500°F. The dewatered sludge is injected above the fluidized sand in a verticle cylinder reactor and mixes with the sand where moisture evaporation and combustion occur.(5)

Wet Air Oxidation. Organic matter is oxidized at elevated temperatures and under high pressure in the presence of liquid water in this process. This is a flameless oxidation of organics process that has been commercialized and patented as the Zimpro process.(11) Wet air oxidation is also known as wet combustion or wet incineration because it does not require dewatering or drying. The water present can be as much as 99 percent of the sludge for combustion to occur. Unlike pyrolysis, there are no useful by-product gases formed since all organic matter is oxidized to inert material and carbon dioxide gas. This process recovers heat from the oxidation for further wet air oxidation and usually uses a small steam generator for start-up heat.(5)

Pyrolysis. Pyrolysis is the process in which organic substances, upon heating in an atmosphere without oxygen, are "split by combinations of thermal cracking and condensation reactions into gaseous, liquid, and solid fractions."(8) The pyrolysis process subjects organic matter to high temperatures and pressures in the absence of oxygen which results in the conversion of the organic matter to gases consisting of methane, carbon dioxide, hydrogen, and various other gases, a liquid fraction, and a char of carbon and inert materials.(8)

Final Disposal Process

The ultimate disposal or utilization is the final process for the treatment of sludge. Sludge disposal is accomplished at sanitary landfills or by ocean disposl, while sludge utilization includes the use of treated sludge for application to cropland as a soil conditioner and for land reclaimation. For a sludge to be satisfactory for disposal in a sanitary landfill it must not contain free water because that would lead to problems with production of leachate. The sanitary landfill must be maintained with a systematic process of disposal and earth covering to control the impact to the environment within the limits of the landfill.(5) Utilizing treated wastewater sludge by application to agricultural land is very popular due to the economics and simplicity of the method. This method is limited by the content of heavy metals, which if present in the sludge, makes it unsuitable for land application. Although sludge does not have the needed amount of essential nutrients for use as a fertilizer, treated sludge is a very good source of soil conditioner. Utilizing sludge for land reclaimation is made by applying the treated sludge to minning excavations and other low-quality land.

Industrial and Hazardous Wastes

The treatment and disposal methods used for industrial wastes are dependent upon the type of waste materials produced ,but according to Sorg (3), "the common disposal alternatives for industrial waste are the same as those used for residential and commercial wastes: landfill, incineration, and in some situations, composting." The methods of landfilling and incineration are very similar to those used for the treatment of wastewater sludge as described previously. According to Sorg (3), the ideal solution is utilizing industrial wastes. Present methods are acceptable, but for many waste materials, new disposal or utilization methods are needed. This is particularly true for hard-to-handle wastes or wastes that are classified as hazardous. It is Sorg´s (3) opinion that if an industry generates these wastes, they should be the ones to develop the methods for treating these wastes.

Hazardous wastes, as explained earlier, are solid waste materials that are ignitable, corrosive, reactive, or toxic. According to Parr, Marsh, and Kla (12), the are two methods of disposing of hazardous wastes that appear to control the risks associated with these materials but which are very expensive. They are disposal in well designed and properly managed hazardous waste landfills, and incineration at high temperatures. There is a great need for inexpensive and safe methods for disposing hazardous wastes. Parr, Marsh, and Kla (12) suggest land treatment of hazardous wastes as an alternative treatment method. In this process soil is used to hold the toxic organic chemicals while microbes degrade the compounds into safer substances.

The dangers of hazardous wastes have led to strict regulations on the generation, treatment, storage, transportation, and disposal of these wastes. Improper handling of thsese wastes can lead to expensive legal fines for generators and hazards to human health and the environment.(7) The ideal situation would be to convert the hazardous waste to materials that are no longer hazardous.

Pyrolysis Processes

Aqueous pyrolysis and other methods of pyrolysis have been reviewed to compare the results and provide insight into the process. Previous research performed on the process of pyrolysis has provided helpful information in several areas of this method of solid waste treatment.

Bohn and Benham (13) in their study of biomass pyrolysis used an entrained flow tubular reactor to pyrolyze a wheat straw feedstock using steam as a carrier gas. They measured the gas yield, gas composition, and process heat of the process. There were gas yields of 91 percent measured at 950^{o}C and the process heat was measured in the range of 2,300 to 3,000 J/g of pyrolysis gas. The composition of the gases was found to be 52 percent carbon monoxide, 20 percent hydrogen, 11 percent methane, eight percent carbon dioxide, five percent ethane, and four percent other gases. Their study showed that the pyrolysis process was strongly influenced by the temperature of the reactor but not by the steam to biomass ratio.

Pyrolysis of tree bark, straw, peat, wood, and coal was performed by Rensfelt (14) in which a straight, vertical, tubular quartz reactor was heated using electrical resistance heaters to convert the feedstock into mass fractions of gas, tar, and char. The composition of the gas produced by this process was reported to be 43 percent carbon monoxide, 18 percent methane, 16 percent hydrogen, 11 percent carbon dioxide, 10 percent ethane, and the remaining two percent as other gases.

In an experiment conducted by Jackson (2) municipal refuse was pyrolyzed by fluidized bed pyrolysis to produce a variety of by-product gases. The compositon of the gases produced in this process was 37 percent hydrogen, 36 percent carbon monoxide, 16 percent carbon dioxide, and 11 percent methane.

Volume reduction of organic wastes was the objective of the pyrolysis study conducted by Kemmler and Schlich (15). This process was used for the pyrolysis of nuclear wastes and spent solvents. A volume reduction of 50 percent of the nuclear wastes was accomplished while the reduction of the mass was 20 percent. A seven percent reduction of solvent volume along with nearly six percent reduction of solvent mass was achieved by this process. There was not much reported on the composition of the off-gas in this study.

The objective of Hughes and Ramakumar (16) in the use of aqueous pyrolysis was to generate energy using biomass waste products as sources of fuel. The term "aqueous" refers to the use of water to fill all void spaces with water to prevent oxidation by air and to provide constant volume expansion heating. They found that the aqueous pyrolysis yielded a gaseous product nearly evenly divided between carbon dioxide and combustable hydrocarbon gases. The actual gas compositions were dependent upon the material pyrolyzed, and results showed that pyrolysis of newsprint produced a gas consisting of 57 percent carbon dioxide, 25 percent methane, five percent ethane, and the remainder consisting of air and other gases. A mixture of coal dust and water was pyrolyzed which produced a gas consisting of 53 percent methane, 23 percent carbon dioxide, seven percent ethylene, and the remainder consisting of air, water, and ethane. This aqueous pyrolysis method used a coil induction heater to pyrolyze such biomass as newsprint, cotton, saw dust, coal dust, and plant materials.

Induction Heating

Induction heating occurs when an electrical conductor is shaped into a coil and an induced electrical current is passed through it, and the material having a high resistance heats up, according to Brown (17). The heating from the induction coil occurs only in the vicinity of the area enclosed by the coil; the heating is faster when the coils are closer to the working surface. The coils should be placed close together to provide an even heating pattern, and the maximum number of turns should be provided to obtain good heat distribution and the desired heat pattern. (17)

Fisher (18) stated that there are two mechanisms of heating by electrical induction. One mechanism is dielectric heating which uses displaced currents induced from an elctrical field. The other mechanism is often simply called induction heating and uses eddy currents induced by a magnetic field.

CHAPTER III

METHODS AND PROCEDURES

Process Description

Aqueous pyrolysis is the conversion of a sample of organic matter mixed with water into other substances by subjecting the material to high temperature and high pressure. The water is used to replace the air in void spaces of the material. Due to thermal fission, the process generally leads to the production of molecules of lower mass. The process results in the decomposition of the material into char, carbon dioxide, methane, and other hydrocarbon gases such as ethane and ethylene. The thermal energy input and the absence of air in the reactor vessel results in temperatures in the range of 300°C to 500°C and pressures of 8,000 to 14,000 psig being achieved. The thermal energy is provided by electrical induction heating which consists of a coil of wire wraped around an electrically-conductive reactor vessel and energized by an alternating electrical current. The resulting magnetic flux causes induced currents to circulate within the walls of the reactor and generates heat, which increases the pressure in the constant volume reactor. Many solid wastes may be processed into combustable products by aqueous pyrolysis and these products may be reused as sources of fuel for this process. Additional benefits of the aqueous pyrolysis process are the volume reduction of the solid material and the reduction of volatile organic solids.

Research Equipment

The research of this aqueous pyrolysis method involved using a technique that consisted of packing a mixture of a solid waste material into the central reaction region of a long, thin, cylindrical reactor vessel and then heating the reactor vessel by using a high frequency (approximately 1,000 Hz) induction heating process. The reactor vessel, with its contents, was quickly quenced after heating and the contents were recovered. The gaseous products formed in the process were analyzed using gas chromatography.

The Reactor Vessel

The reactor vessel consisted of a three foot long, carbon-steel tube with an outer diameter of one and one-half inches and an inner diameter of one-half inch. At one end of the reactor vessel, a pressure gauge was attached, and a valve was available through which the gaseous products could pass through and be collected. The other end of the reactor was closed by a stainless-steel bolt. Two solid, stainless-steel spacing rods, each about 15-inches long, were placed inside the reactor at both ends. The remaning space of approximatly 18 ml in volume, was the reaction region. The material that is to be processed was placed in this reaction region prior to heating. The reaction vessel is shown in Figure 1. A heating coil is arranged so that it encircles the mid-section of the reactor vessel and the reaction region. The heating coil was supplied with electrical energy at a frequency of about 1,000 Hertz (cycles per second), from an inverter system for a short period of time (usually 60 seconds), and at a constant rate of electrical input of 80 amps line current. The thermal input to the constant volume reactor and the presence of water causes a rapid build-up of pressure in the vessel. The process was characterized by a rapid pressure "kick" in which the pressure increased from about 2,000 psig to pressures measured above 10,000 psig within a period of 10 to 15 seconds. When the pressure ceased to increase, the reactor vessel was quickly removed from the heating coil and was quenched in a large container of cold water. This method of quickly cooling the reactor made the cooling time shorter, which was an improvement over an earlier used method of pouring water onto the reactor vessel. Figure 2 shows the process setup for the aqueous pyrolysis method.

Gas Collection System

The device used for the collection of gases consisted of a one-gallon capacity (at 1 Atm) stainless-steel cylinder, a vacuum/pressure gauge, a glass bottle trap (for the collection of liquids and suspended solids), and valves,

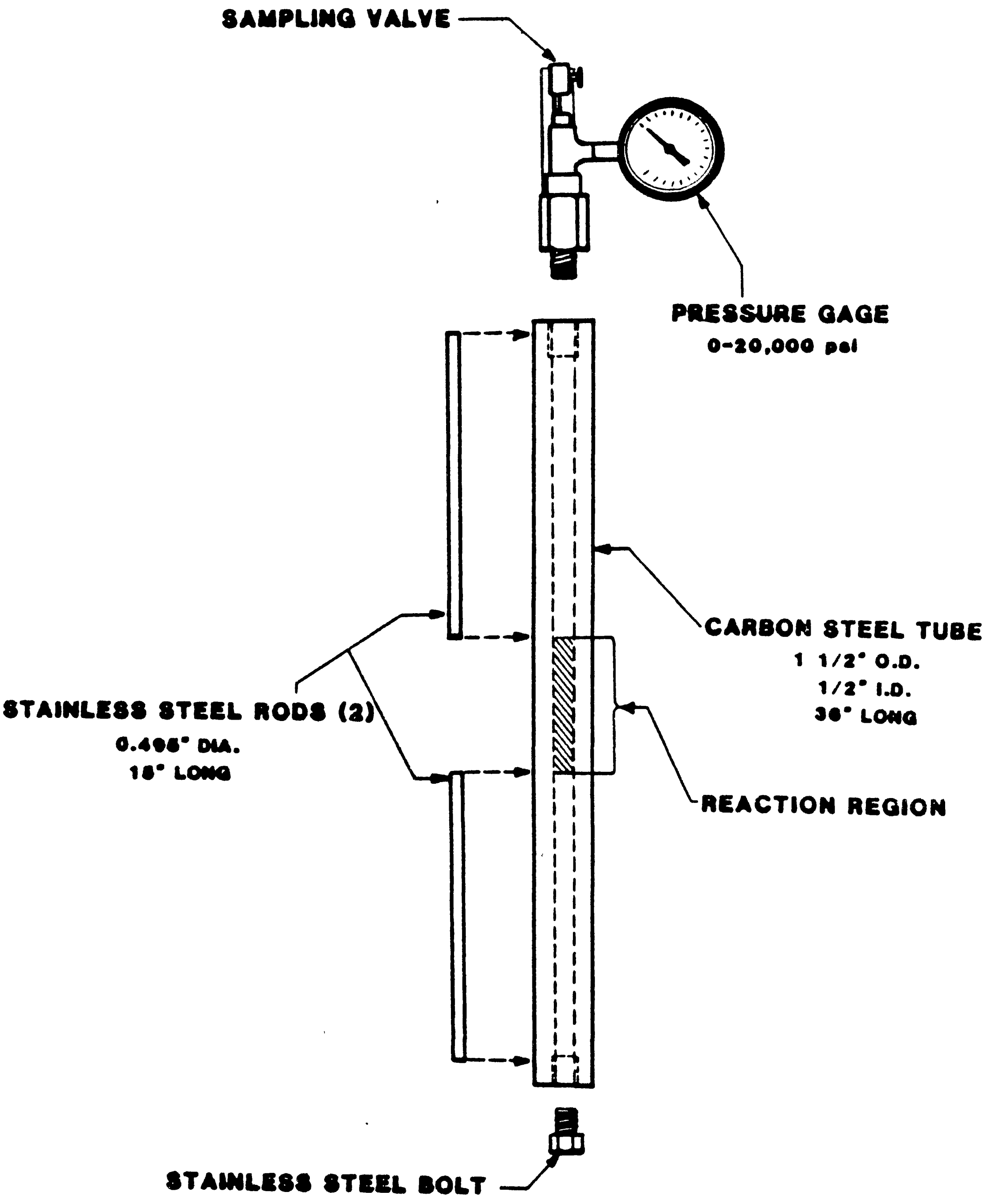

Figure 1. The Reactor Vessel

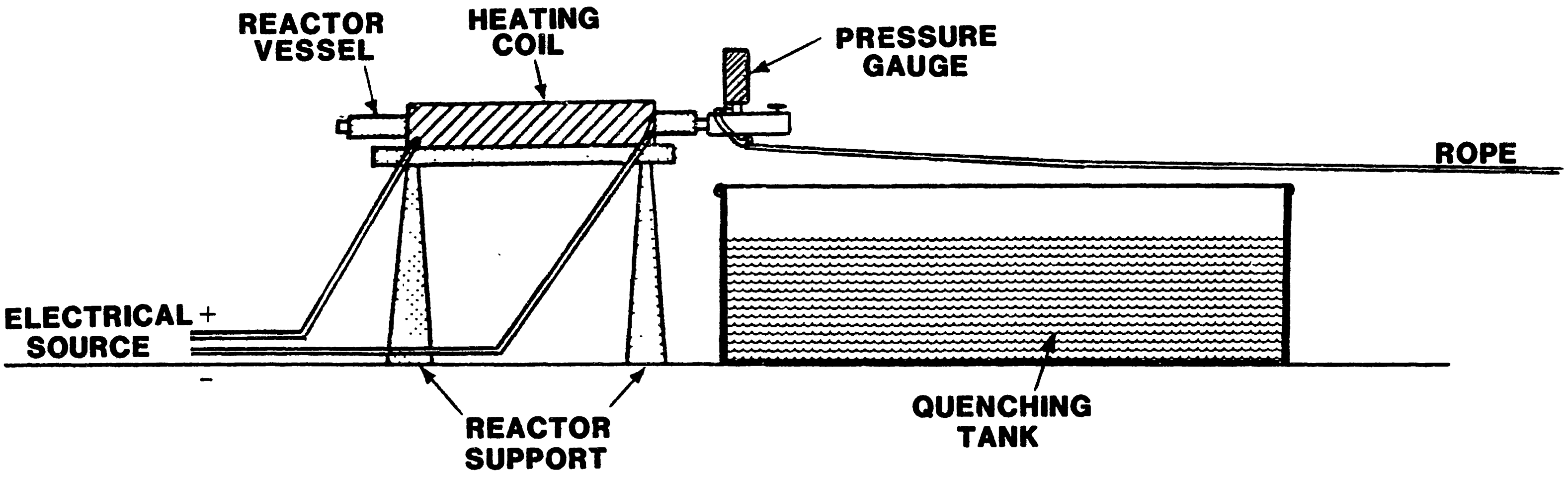

Figure 2. Diagram of the Process System.

tubing, and fittings as shown in Figure 3. The collection device was prepared for gaseous product collection by evacuation of the cylinder by using a vacuum pump and by recording the initial gauge pressure after the cylinder was evacuated. The reactor vessel, which contained pressurized gases, was attached to the gas collection device. The gases were then released into the collection system and any liquids or suspended solids present were collected in the glass bottle trap. Once the transfer of gases was complete, the final gauge pressure was recorded so that an estimate of the volume of gas produced could be made by comparing the change of pressure in the gas collection system to the volume of the system. At the gauge end of the gas collection system was a three-way valve and a sampling port from which samples were taken by using a hypodermic syringe.

Gas Chromatography

The analysis of the composition of the gases produced in the aqueous pyrolysis process reaction was made using a Perkin-Elmer SIGMA-3 gas chromatograph. This instrument was comprised of a column oven, a Supleco stainless-steel general configuration packed-column with Porapak S 100/120 packing material, a hot-wire thermal conductivity detector, a closed loop temperature control by keyboard input, a Perkin-Elmer SIGMA-10 Chromatography Data Station with a printer/plotter for recording the analysis results, and interface and control equipment.

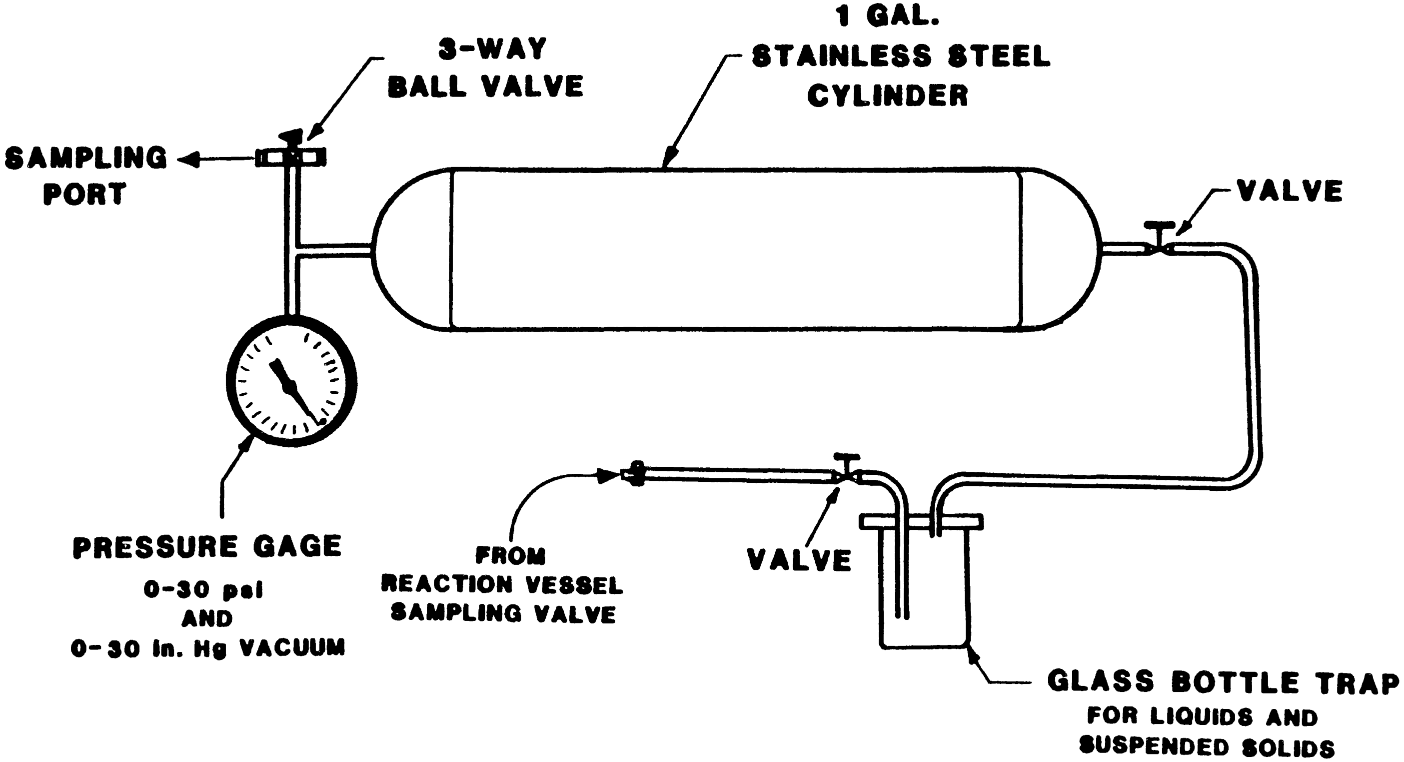

Figure 3. The Gas Collection System

A gas sample was injected into an injection port on the gas chromatograph analyzer. Using helium as a carrier gas, the gases to be analyzed were transported through the heated coil-shaped column where the different gaseous materials were separated. This enables the detection of the gases at different times. The results attained were compared to standard curves developed individually on known types and quanitities of gases that were expected to be produced by the process.

In the investigation of the destruction of priority pollutants by aqeuous pyrolysis, a Perkin-Elmer SIGMA-3B gas chromatograph was used. This instrument consisted of a column oven, a metal packed column (Supleco SP-1240-DA) which is designed to separate priority pollutant phenols, a flame ionization detector (FID), which uses hydrogen as the combustion gas, a Perkin-Elmer SIGMA-15 Chromatography Data Station with a plotter/printer, a closed loop temperature control by keyboard, interface and control equipment, and it uses nitrogen gas as the carrier gas.

Processing Waste Material

The solid waste material required some preparation before the aqueous pyrolysis process could be performed. This preparation consisted of making a mixture of the material and enough water in a combination that will produce desirable results, and packing the reactor vessel with this mixture. The weight of the solid fraction of the waste material was measured so that it could be compared to the amount of gas produced. Water was added to most of the materials except for those that already had a high water content, such as wastewater sludges. The wastewater sludges tested were dewatered by various amounts to investigate the effect of different water contents on the pyrolysis process. The packing of the waste material was done in such a manner that air would not be trapped inside of the reaction region. This was to ensure that there would be a constant volume heating reaction. The ends of the reactor vessel were applied with teflon tape, attached, and fastened tightly to prevent any unwanted emissions occuring during and after the reaction process, and to keep air from entering the reactor.

During the induction heating of the reactor vessel, the change in pressure was observed to see if there was a rapid build-up of the pressure, which usually occured between 45 and 60 seconds into the process. This was a characteristic of the pyrolysis reaction and indicated that a successful reaction had been achieved. Following the induction heating process, the gases were collected for gas chromatograph analysis, and the liquid and solid by-products were collected for further analysis.

Analysis of the recovered solids consisted of a measure of the dry solids content of the waste material and a measure of the percent reduction of volatile solids content of the material. Procedures for dry weight and volatile solids determination were those described in the <u>Standard</u>

Methods (19). The volatile solids reduction was determined by taking measured dry amounts of the waste material samples before and after the aqueous pyrolysis reaction and combusting the samples in an oven at 600°C. At this temperature, the volatile organic matter was removed by combustion, and the remaining fixed solid material was weighed to determine the amount that was volatile. The values obtained for a material before and after pyrolysis were compared to determine the extent to which the process reduced the volatile solids.

Determination of Gas Product Volume

The amount of gas produced was determined by calculating the pressure difference (in units of atmospheres) that occured in the gas collection system when the gases were collected and multipying this pressure by the volume of the gas collection system, measured at one Atm. The volume of the collection system was estimated as follows:

One-gallon cylinder	3785 ml
Glass bottle trap	147 ml
Pressure gauge, valves tubbing, fittings, etc.	14 ml
Total Volume (est.)	3946 ml

The initial and final gauge pressures were measured in units of inches of mercury (in. of Hg) and were converted to absolute pressure in units of atmospheres. An absolute vacuum is measured at a value of 0.0 atmospheres and is equivalent to -29.9 inches of mercury.

The following example shows how the volume of gas produced from the aqueous pyrolysis of a solid waste was determined:

Initial pressure .... = - 19.2 in. of Hg
= 0.3583 Atm. abs.

Final pressure .... = - 8.4 in. of Hg
= 0.7193 Atm. abs.

Net pressure change ...... = 0.7193 - 0.3583 Atm.
= 0.361 Atm. abs.

Volume of gas collected = 3946 ml/Atm x 0.361 Atm
(at 1.0 Atm. pressure) = 1425 ml

Analysis of Priority Pollutants

The determination of the concentrations of the priority pollutants phenol and 2,4-dichlorophenol present before and after aqueous pyrolysis was made using the microextraction procedure developed by Lowenbach & Sclesinger Engineering (20). In this procedure, 80 ml of a liquid sample known or suspected to contain phenols is transfered into a flask containing 30 grams of sodium chloride. Phosphoric acid (1:1 H_3PO_4:H_2O) is added until the pH is less than 2. Next 1 ml of isopropyl ether is added, and the flask is shook for two minutes to thoroughly mix the solution. A phase separation occurs in which the phenols are removed from the sample material and collected in the isopropyl ether which is less dense than the water and floats on the top. The extraction solution of isopropyl ether and phenols is then removed with a microliter syringe for analysis in the gas chromatograph.

CHAPTER IV

RESULTS AND DISCUSSION

Introduction

The solid waste materials that were processed using the aqeuous pyrolysis method were each analyzed for the total volume of gas produced, the volume of gas produced per unit weight of dry input material, the composition of the gases produced, and the reduction of volatile solids. The solid waste materials consisted of municipal wastewater sludges, newsprint, wheat dust, rubber, 2,4-dichlorophenol and phenol added to newsprint, and wastewater sludges of various amounts of water content. The waste materials were identified and are refered to in the figures by the following notation:

NP .... Newsprint
WD .... Wheat dust
R .... Rubber
NP-P ...... Newsprint with Phenols
WWS .... Wastwater sludge

Gas Production

The results of the the amount of gas produced and a comparison of the volume of gas produced to the mass of the input material are given in Table 1 and in Figures 4 and 5.

TABLE I.

QUANTITIES OF GAS PRODUCED.

Material	Dry Input Weight, gm	Volume of Gas Produced, ml	Volume per unit Mass, ml/gm
Newsprint	4.30	371	86
Wheat dust	7.73	1184	153
Rubber	9.37	1425	152
Newsprint w/ phenols	4.20	686	163
Wastewater Sludges			
6% solids	1.14	63	55
12% solids	2.14	118	55
13% solids	2.30	710	309
32% solids	5.59	276	49

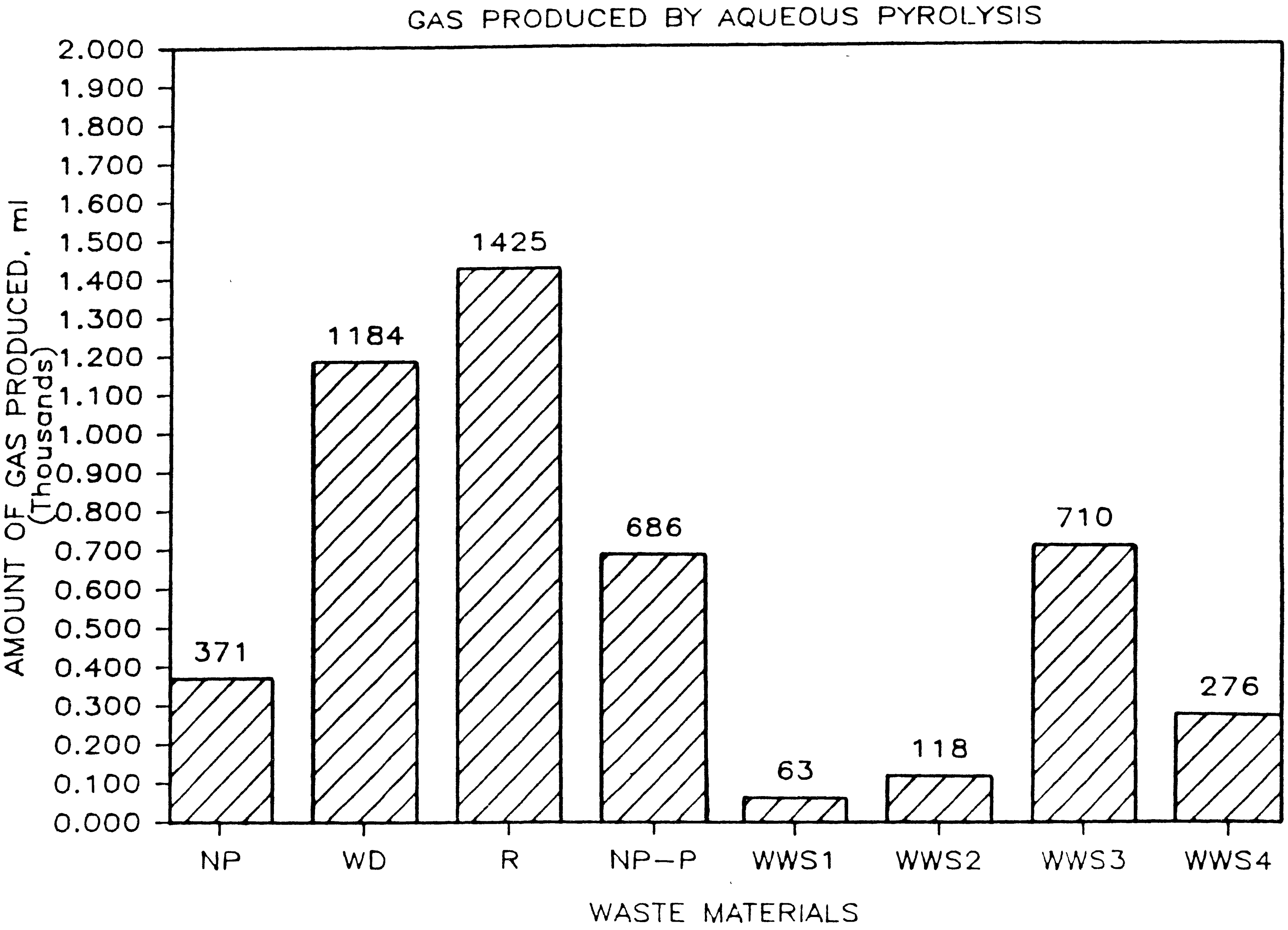

Figure 4. Volume of Gas Produced by Aqueous Pyrolysis of Wastewaters Sludges and Organic Wastes.

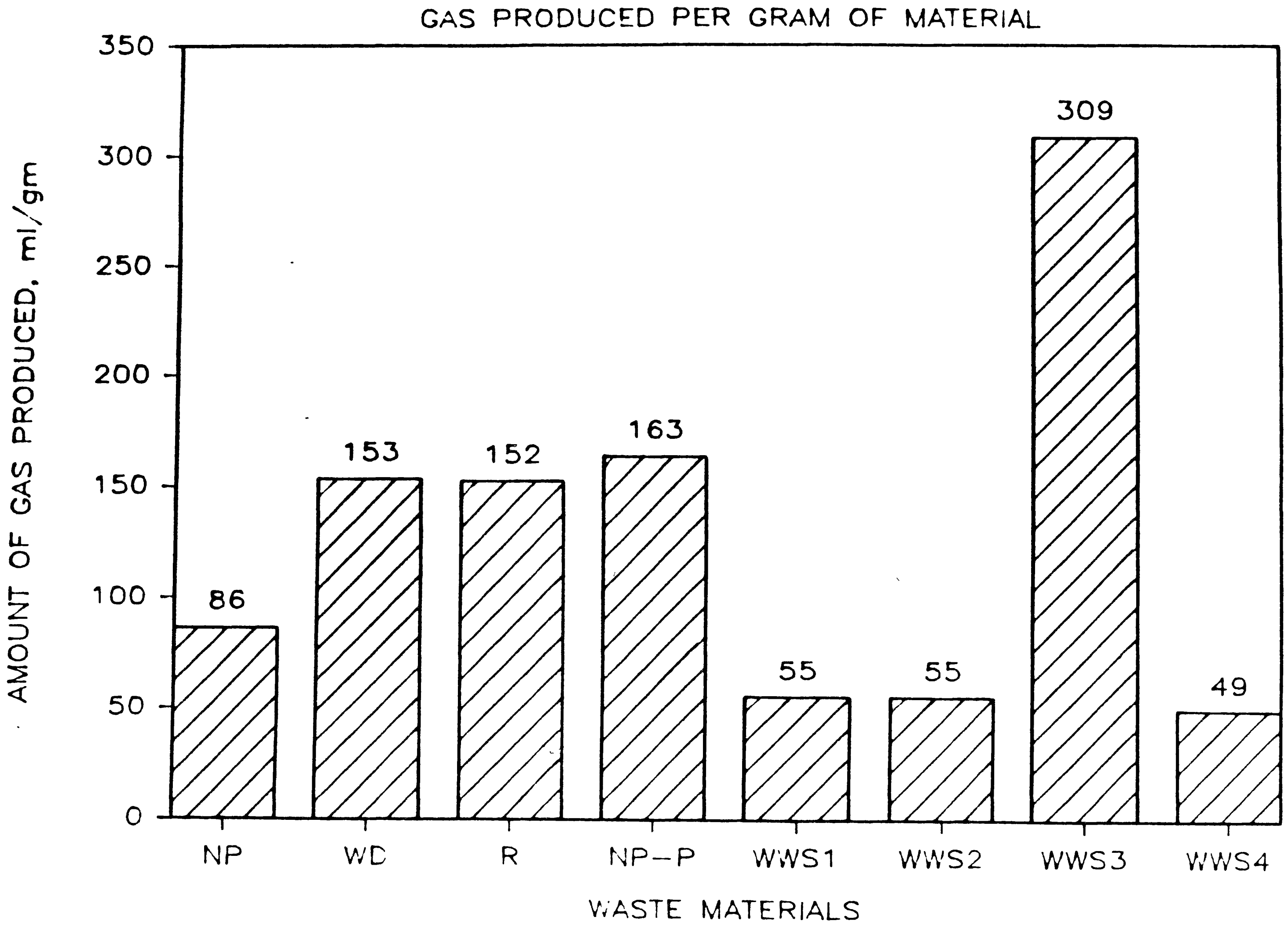

Figure 5. Volume of Gas Produced per Gram of Waste Material

Aqueous pyrolysis produced 86 ml of gas per gram of newsprint, 153 ml per gram of wheat dust, 152 ml per gram of rubber, and 163 ml per gram of newsprint/phenol mixture. The production of gases by the aqueous pyrolysis process was similar for three of the sludges with different water contents. Gas was produced at 49 to 55 ml per gram of dry weight material when the water content was high (6 and 12 percent solids) and when the water content was lower (32 percent solids). The sludge that was 87 percent water produced 701 ml of gas from 2.3 grams of dry weight input material for a production of 309 ml per gram. The total volume of gas produced was highest for wheat dust and rubber with a production of 1184 ml from wheat dust and 1425 ml from rubber. The quantity of gas produced was studied to determine if the available fuel gas could substanially contribute to meeting the input energy demand of the process.

Reduction of Volatile Solids

The reduction of the organic fraction of the waste materials, the volatile solids, was investigated as a possible benefit of the aqueous pyrolysis process. Results of volatile solid reduction by aqueous pyrolysis are given in Table 2 and in Figures 6, 7, and 8. The volatile solids of the wheat dust were reduced by 52 percent, and 40 percent were reduced from the rubber. The newsprint had a reduction of volatile solids by 15 percent, while the mixture phenol and 2,4-dichlorophenol and newsprint experienced a volatile

TABLE II.

REDUCTION OF VOLATILE SOLIDS

Material	Volatile Solids Before Pyrolysis	Volatile Solids After Pyrolysis	Percent Reduction
Newsprint	99%	85%	15%
Wheat dust	87%	42%	52%
Rubber	44%	26%	40%
Newsprint w/phenols	99%	65%	34%
Wastewater Sludges			
6% solids	72%	62%	14%
12% solids	73%	55%	25%
13% solids	73%	39%	46%
32% solids	73%	65%	11%

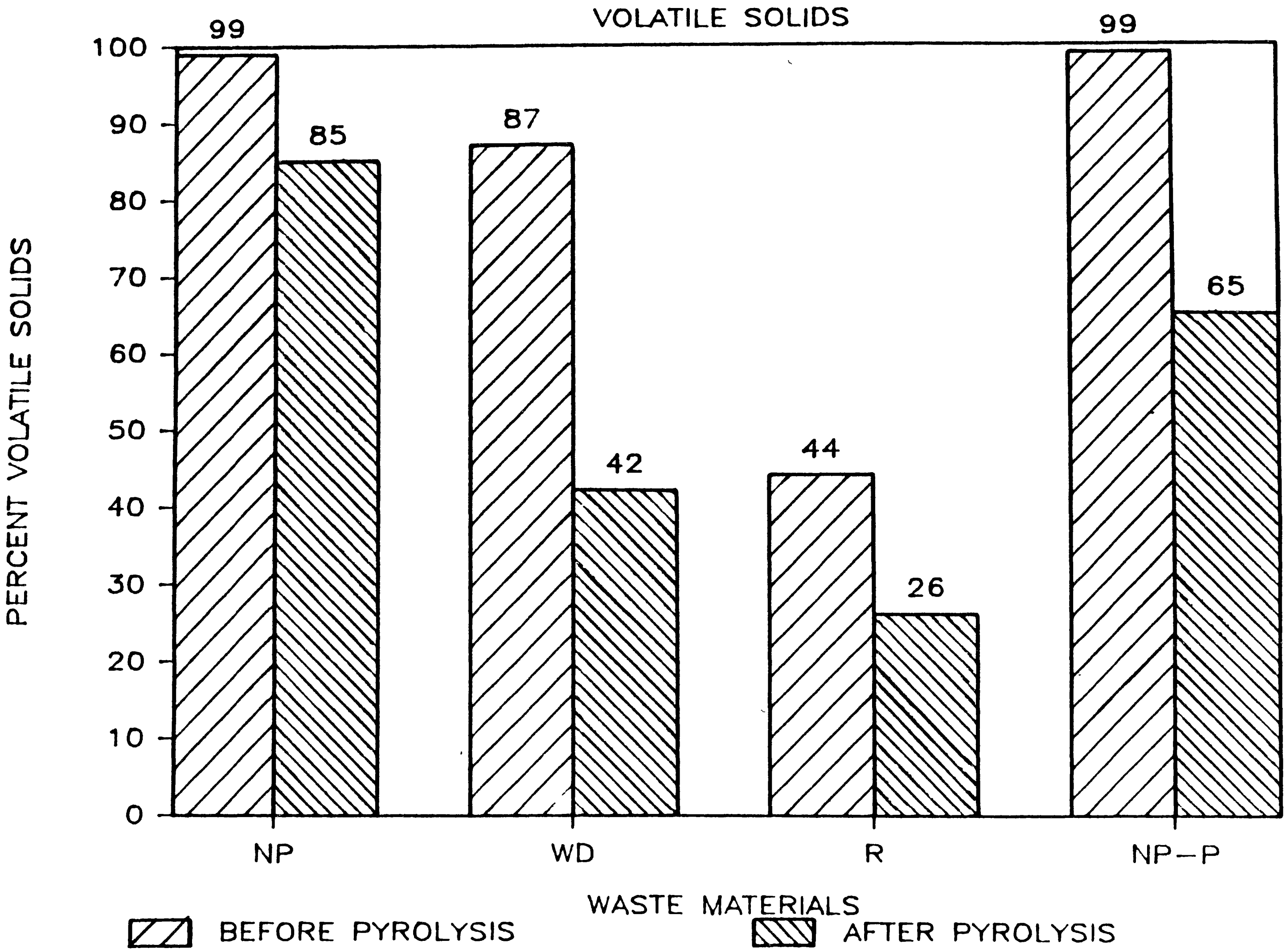

Figure 6. Percent Volatile Solids of Waste Materials

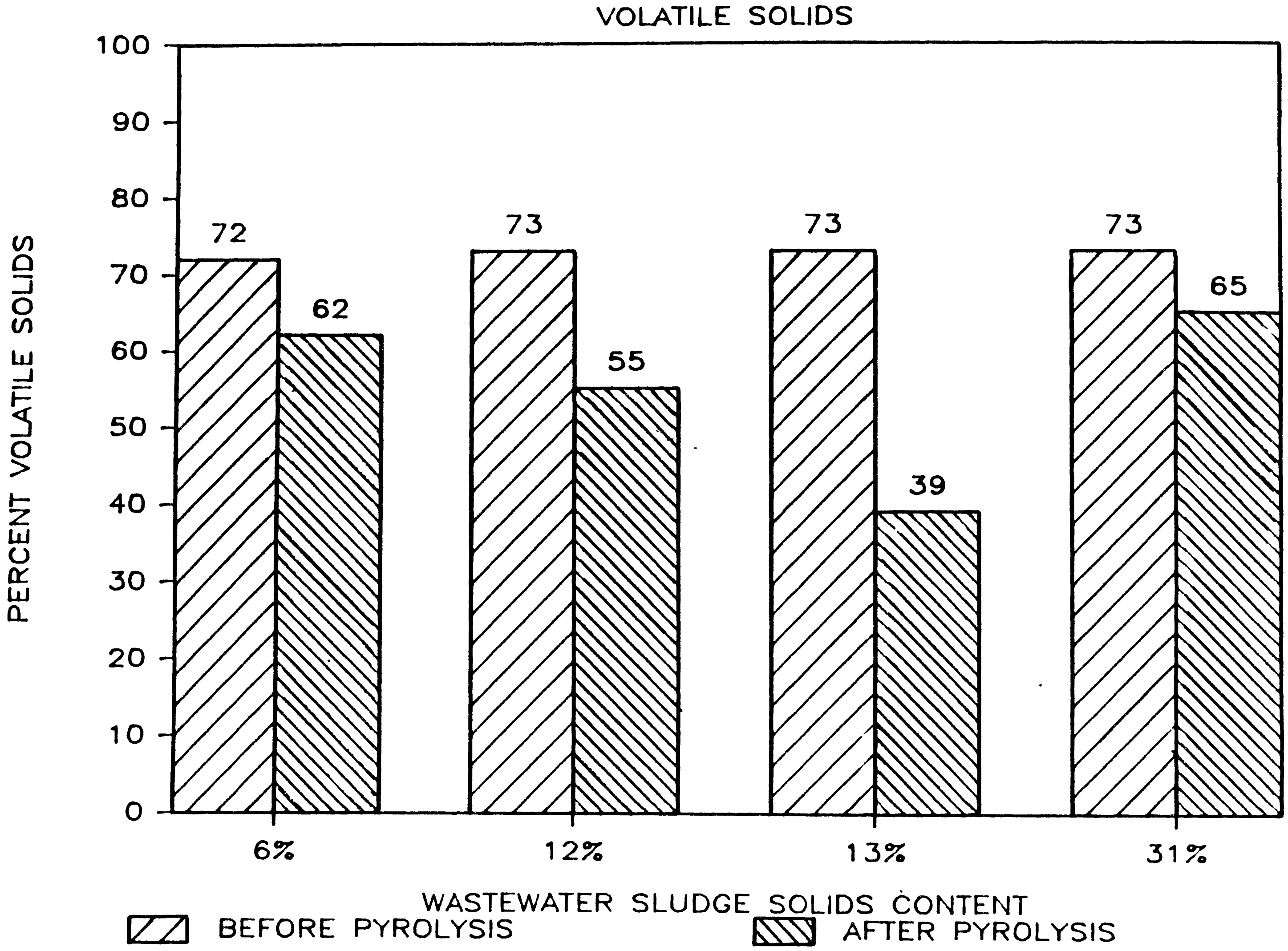

Figure 7. Percent Volatile Solids of Wastewater Sludges

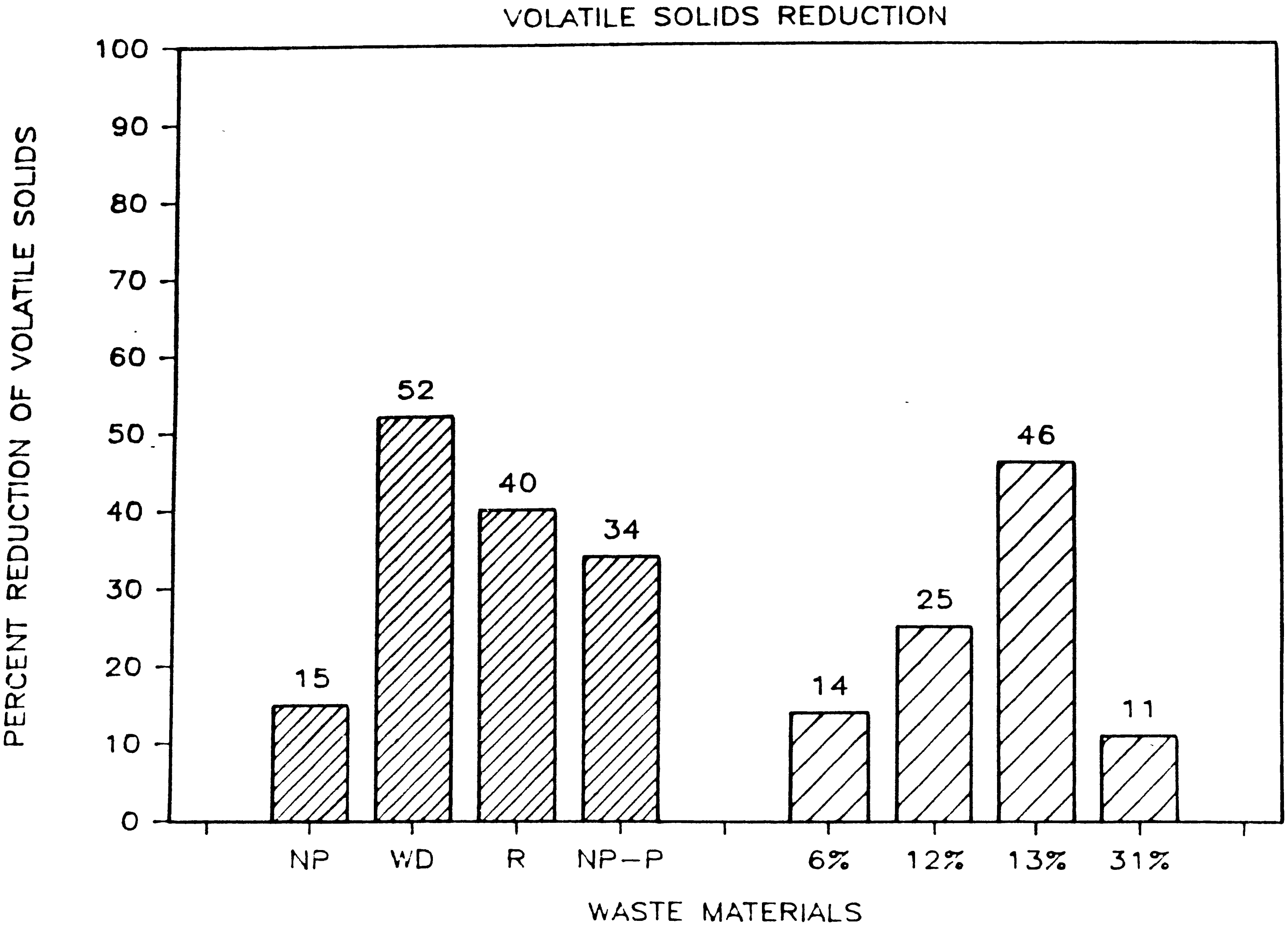

Figure 8. Percent Reduction of Volatile Solids

solid reduction of 34 percent. Volatile solid reduction results in a reduction of the overall volume of the waste material which is advantageous because there is less material that has to be disposed.

The reduction of volatile solids in wastewater sludge was dependent upon the water content of the sludge. The reduction increased as the amount of water was decreased, however as the water content was decreased to less than 68 percent, the volatile solids reduction percentage also decreased. Low reduction of volatile solids could be due to high water content and due to some air being traped in the reactor when the 32 percent solids sludge was processed.

The sludges having solid contents of 6, 12, 13, and 32 percent solids experienced a reduction of volatile solids by 14, 25, 46, and 11 percent respectively. To ensure that there is good volatile solids reduction there must not be any air in the system, and the amount of water must not be too much that a good pyrolysis reaction will not occur.

Gases Product Composition

The composition of the gases produced in the process was determined using a gas chromatograph and the results were compared to standard curves developed for several gases that were expected to be produced. The gases that were most likely to be produced were carbon dioxide, methane, ethane, ethylene, and possibly some small amounts of other hydrocarbons. Air that was detected in the analysis was neglected because it existed in the gas collection system prior to the collection of the gases. The air was not completely removed from the system because it was difficult to evacuate the system to a pressure of absolute vacuum of 0.0 Atm. Another method of removing the air would have been to replace the air with helium, since helium was used as the carrier gas in the gas chromatograph instrument and would not have been detected during the analysis.

The gases produced consisted of carbon dioxide, methane, and ethane along with a trace of other gases. The results are given in Table 3 and Figures 9 and 10. The imporatance of the production of hydrocarbon gases is that if they are abundently present they could possibly be reused as a source of fuel for an aqueous pyrolysis system. The waste material that had the highest content of hydrocabon gases was the rubber waste which produced a gas consisting of 95 percent hydrocarbons. The composition was 69 percent methane, 24 percent ethane, 1 percent ethylene, and the remaining 5 percent was carbon dioxide. The pyrolysis of wheat dust produced a gas composed of 54 percent hydrocarbon gases, with 41 percent methane, 13 percent ethane, and 46 percent carbon dioxide. The gas produced from the aqueous pyrolysis of newsprint was 76 percent carbon dioxide, 19 percent methane, and 5 percent ethane. The aqueous pyrolysis of the mixture of phenol and dichlorophenol on newsprint produced a gas that consisted only of carbon dioxide. The gas produced from pyrolyzing wastewater sludges consisted of carbon

TABLE III.

COMPOSITION OF GASES PRODUCED

Material	Methane	Carbon Dioxide	Ethane	Ethylene
Newsprint	19%	76%	5%	0%
Wheat dust	41%	46%	13%	0%
Rubber	69%	5%	24%	1%
Newsprint w/phenols	0%	100%	0%	0%
Wastewater Sludges				
6% solids	0%	94%	6%	0%
12% solids	0%	75%	25%	0%
13% solids	0%	70%	30%	0%
32% solids	0%	90%	10%	0%

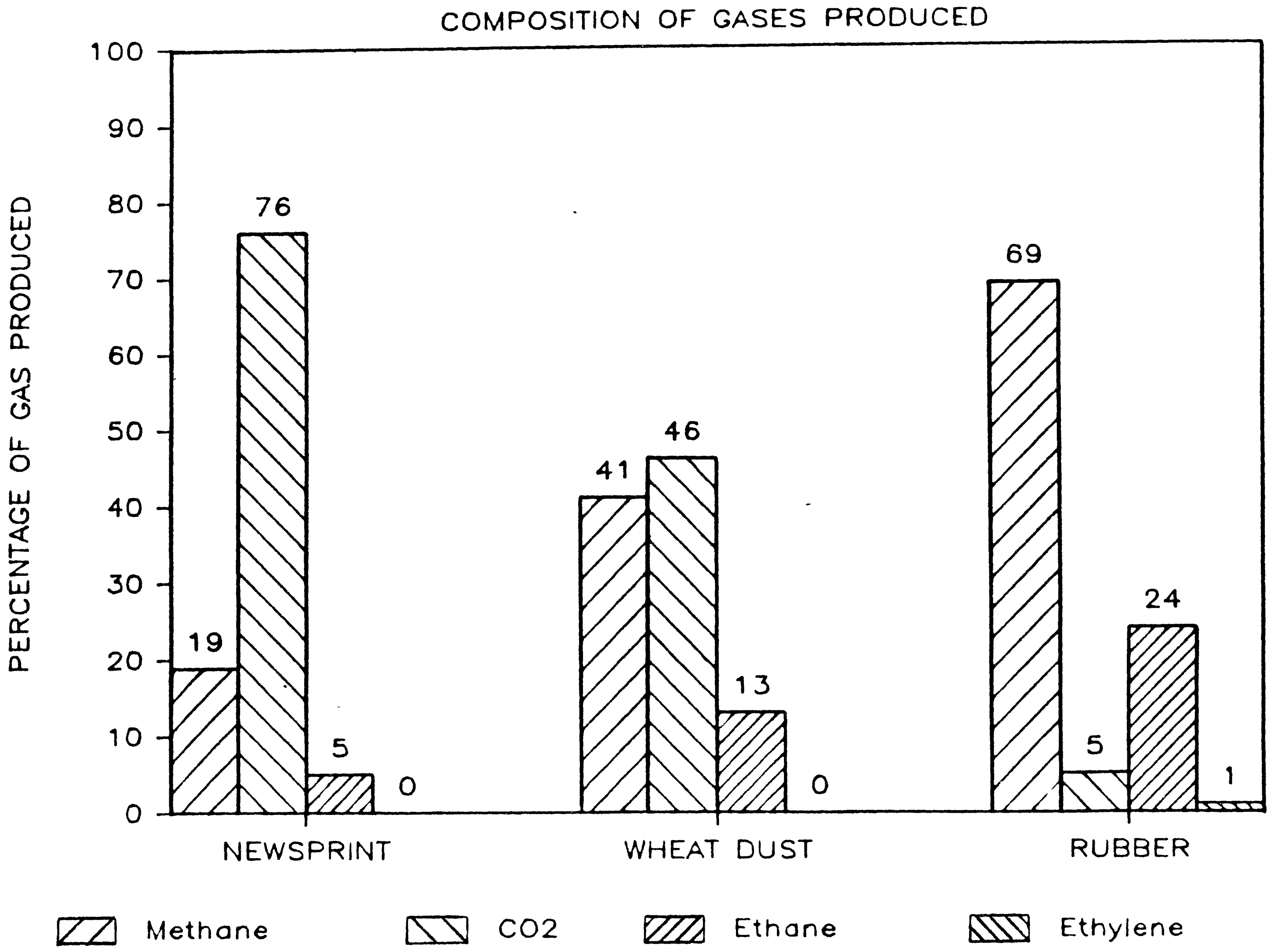

Figure 9. Composition of Gases Produced from Waste Materials

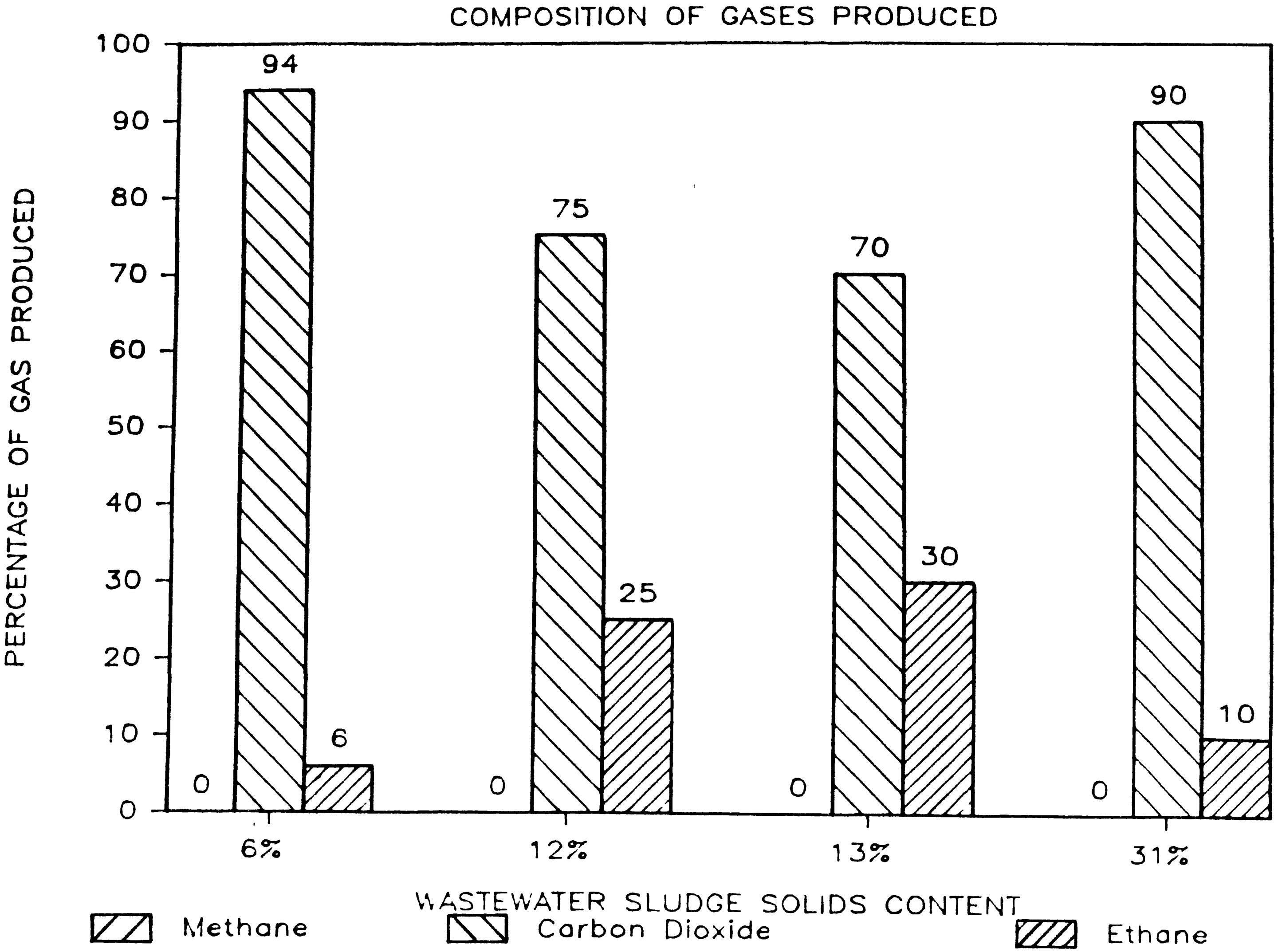

Figure 10. Composition of Gases Produced from Wastewater Sludges

dioxide and ethane. The percentage of the gas that was ethane correlated with the percent reduction of volatile solids. The percent of ethane gas produced increased with a decrease in the water content of the sludge except for the sludge with 32 percent solids where the percent ethane decreased. The amounts of ethane produced for the 6, 12, 13, and 32 percent solids content sludges were 6, 25, 30, and 10 percent ethane respectively. The only other gaseous product produced other than carbon dioxide, methane, and ethane, was ethylene which was detected in the analysis of the gas produced by the pyrolysis of the rubber waste.

Destruction of toxic pollutants

The aqueous pyrolysis process was investigated as a method for the destruction of toxic pollutants such as phenol and 2,4-dichlorophenol. The phenols were added to a newspaper and water mixture and the samples were analyzed before and after pyrolysis to determine if the phenols were destroyed. The microextraction method was used to extract the phenols from a sample for analysis using a gas chromatograph. The proceedure was conducted on a control sample of newsprint and phenols to determine the recovery attained by the microextraction method. It was found that 75 percent of a known amount of phenol was recovered and 56 percent of the 2,4-dichlorophenol was recovered. In the processed sample, it was found that the toxic pollutants were destroyed but that many other compounds were formed.

The other compounds that were formed were not identified, and this is an area that should be further investigated.

Discussion of Results

The results of the research conducted on the aqueous pyrolysis process have shown that this process produces gases that contain hydrocarbons, reduces volatile organic matter, and destroys toxic pollutants. The results of the investigation of the effect of aqueoue pyrolysis of wastewater sludges tend to show that as the water content is decreased there is an increase in the production of gas, an increase in the hydrocarbon production, and reduction of volatile solids. It appears that either there is an optimum point between a solids content of 13 percent and 32 percent where the best results can be achieved, or that due to the difficulty encountered in loading the 32 percent solids sludge, some air was trapped in the reactor and good results for the material were not obtained. It may be that the best results should be obtained at lower water contents. The lower water content wastewater sludge was difficult to pack into the reactor vessel because the material was very viscous and had a gel consistancy which had a tendency to trap air in the material. The higher water content sludges were easier to pack into the reactor because they could be poured into the vessel.

The difference in the results of the newsprint and the mixture of newsprint and phenols was greater than expected.

The amount of newsprint was the same for both samples, and the quantity of the phenol and 2,4-dichlorophenol was very small. The only major difference was in the processing of the material. The newsprint sample was mixed with water using a blender to make a slurry that could be poured into the reactor, while the sample containing the toxic pollutants was processed by stirring together the phenols with small pieces of shredded paper and adding water. The latter sample was not processed in the same manner as the newsprint because there was concern that the small quantity of phenols may not be fully accounted for after the blending of the slurry.

The production of ethane rather than methane was an interesting result of the gas composition of the gas produced from the aqueous pyrolysis of wastewater sludge. The sludge would be expected to be more likely to produce methane since this is the primary gas produced from sludge in anaerobic digestion. The chemical composition of the raw unprocessed sludge was not determined but could have a great influence on the results of the process.

The reduction of the volatile solids of the wastewater sludge by aqueous pyrolysis was comparable to that of anaerobic digestion. The aqueous pyrolysis process reduced volatile solids by 11 to 46 percent as compared to values from anaerobic digestion reported by De Renzo (4) of 17 to 62 percent, and 55 to 71 percent volatile solid reduction reported by Carrio, Lopez, Krasnoff, and Donnellon. (9)

There were some difficulties and problems encountered in the research of the aqueous pyrolysis method which provided helpful information concerning the process. The pyrolysis process was sucessful when the waste material were packed into the reactor with an adequate amount of water, no air was allowed in the reactor, the ends of the reactor were fastened tightly, the electrical induction heating system was operated properly, and the reactor was quenched in cold water immediately after the induction heating.

In preliminary process runs conducted on newsprint to establish the operating procedure and in an attempt to reproduce some of the results obtained by Hughes and Ramakumar (16), the process was operated with a larger reaction region (12 inch long spacer rods were used), a lower line current (60 amps), and the reactor was cooled by pouring water over the reactor instead of using a quenching tank. In these earlier attempts the rapid pressure jump, characteristic of a good pyrolysis reaction, was not observed, so changes were made which eventually resulted in better process results.

The spacer rods were cleaned of any excess residue and polished to facilitate easy removal. Because of the small clearance between the rods and the inner wall of the reactor, a residue buildup would make the removal of the rods and the char material remaining difficult to accomplish. The inside of the reactor was cleaned for the same reason.

To ensure that air did not enter the reactor or that any of the gases produced could not escape, teflon tape was applied to the gauge and end bolt which were fastened tightly and not loosened until the gaseous products were collected. In a few of the failed attempts, gas escaped from the reactor before it could be analyzed. Once, there was a pressurized emmision of material and water during the induction heating process at a point where the pressure had reached 10,000 psig. This emmision was due to an inadequate amount of teflon tape at the threaded connection of the pressure gauge assembly and the reactor pipe.

Safety precautions were taken because of the high pressures and high temperatures. The process was conducted outside of a building which contained the electrical source for the induction heating. The electrical operator was stationed inside of the building while the process operator was positioned behind heavy machinery in the event of a physical failure of the reactor. The pressure calculated on the end bolt was determined to have been as high as 100,000 pounds of force (20,000 psig acting on a 1/2 inch diameter surface). The possible danger of the reactor led to the referal to the reactor as a "bomb". Fortunatley the study was conducted safely, and serious malfunctions occurred. Quenching of the reactor was managed by pulling the reactor out of the heating coil and into a tank of water containing 100 to 150 gallons of water using a rope attached to the gauge assembly of the reactor.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The aqueous pyrolysis process is a promising method for the treatment and volume reduction of solid wastes. The objective of this study was to investigate the use of this treatment method as a means for processing solid waste materials so that they could be ultimately disposed of in an acceptable and economical manner. From this study several conclusions can be made with regard to the aqueous pyrolysis solid waste treatment method:

1. Aqueous pyrolysis of solid wastes produces a gaseous product that contains hydrocarbons that could be reused as a source of fuel for the process.
2. The percent reduction of the volatile solids of the solid waste material was compariable to the reduction achieved by anaerobic digestion of wastewater sludges.
3. Aqueous pyrolysis is a possible alternative for the treatment of hazardous wastes, but only if the by-products of the process are not also hazardous materials.

Recommendations for Further Research

Although much information was obtained from this study of aqueous pyrolysis of solid wastes, there remain several areas of this process which need to be studied and developed. Further research of the compounds produced by the aqueous pyrolysis of hazardous wastes is needed. If these materials produced are also hazardous, this method may not work for hazardous wastes.

An investigation of the composition of the solid and liquid materials remaining after the pyrolysis process should be made. It is very possible that the solid material may have enough energy content to be used as a source of fuel. The use of a calorimeter has been planned to determine the energy content of these solid products. This has not been done yet due to the difficulty experienced in obtaining a calorimeter that will work properly.

The development of a continous flow system that recovers heat and reuses fuel products produced is needed to make the process economically feasable for use on a larger scale.

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