ENERGY RECOVERY FROM MIXED PAPER WASTE

FINAL REPORT

to

SUNSHARES

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SUMMARY

Municipal solid waste streams in the U. S. typically consist of 40 to 45 % of paper products which are a potential valuable source of energy. Paper waste is easy to segregate from the solid waste stream; it is free of metals, putrescibles and other noncombustible materials; it has a high heating (calorific) value; it has excellent storage characteristics when it is densified; and it has low sulfur content and low nitrogen oxides emissions.

Energy produced from the combustion of municipal solid waste is only a small portion of all energy produced today, but it is not negligible. Energy can be recovered from mixed paper waste (MPW) as heat by the incineration of unprocessed solid waste, or the paper waste can be processed into a storable refuse derived fuel, RDF. Mixed paper waste has a great potential as a fuel. Combustion of mixed paper waste produces thermal energy by means of steam or super heated water to be directly used for heating and cooling processes or electricity generation.

An important point which should be addressed for combustion systems incorporating MPW is the potential release of airborne emissions into the environment from the systems. Typical emissions that can be expected from the combustion of mixed paper waste can be grouped as metal emissions (particulate matter), organic emissions (dioxins and furans), and acid-gas emissions (sulfur dioxide (SO_2) and hydrogen chloride (HCl)) as well as nitrogen oxides (NO_x) and carbon dioxide (CO_2) emissions. These emissions can be controlled through prevention or by the installation of emission control equipment. The three ways to control possible emissions from the

combustion of mixed paper waste are:

- Prevention of pollutants from forming in the process or during the operation by obtaining complete combustion of mixed paper waste.
- Dispersion of pollutants into the atmosphere.
- Collection of pollutants just before they reach the atmosphere.

The chief characteristic that determines the quantity of energy that can be recovered from paper waste is the calorific value of the material. Calorimetric analysis of mixed paper waste gives the calorific or energy value of paper waste when all of its chemical constituents are completely oxidized at constant volume.

The laboratory analysis of the energy value of mixed paper waste depends on the degree of homogeneity of the sample. Composition of the mixed paper waste varies greatly, so it is impossible to get mixed paper waste of the same composition at different times. In order to obtain the most reproducible energy values, mixed paper waste in this study is divided into eleven groups according to the qualities of the paper. The classified groups are:

1. Newspaper
2. Boxboard
3. White office paper
4. Colored office paper
5. Envelopes
6. Treated paper (No carbon required (NCR) paper)
7. Beverage and milk boxes

8. Glossy paper
9. Kraft
10. Cardboard
11. Tissue (napkins, paper towels, bathroom tissue)

Individual energy values per unit weight of each group as well as samples of mixed paper waste are determined separately and ranges established for their calorific values. The calorific value of mixed paper waste is found to be in the range of 6002 - 6682 Btu/lb with a mean value of 6447 Btu/lb. Summary of the determined calorific values are given in Exhibit S.1.

Using the individual calorific values of mixed paper waste components, the calorific value of a typical sample of mixed paper waste was calculated to be 6504 Btu/lb. To check this value, the calorific value of the sample was determined experimentally. After the evaluation of results it is concluded that it is possible to estimate the quantity of energy obtainable from a known amount and composition of mixed paper waste by separating the sample into the eleven groups shown above and using the weight fraction and calorific value of each component. It is also possible to get the same result by separating mixed paper waste into four categories instead of eleven. Based on this work, it is concluded that laboratory calorimetry is not necessary in order to estimate the calorific value of any mixture of paper waste, since the calorific values of the individual groups can be used to calculate the calorific value of the mixture.

TYPE OF PAPER	MEAN GROSS CALORIFIC VALUE (Btu/lb)
Newspaper	7540
Cardboard	6907
Kraft	6897
Beverage and Milk Boxes	6855
Boxboard	6703
Tissue	6518
Colored Office Paper	6348
White Office Paper	6234
Envelopes	6160
Treated Paper (NCR)	5983
Glossy Paper	6370
MIXED	6477

Exhibit S.1 Summary of the Calorific Values of Paper Waste

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LIST OF EXHIBITS

ABBREVIATIONS

ASME:	American Society of Mechanical Engineers.
ASTM:	American Society for Testing and Materials.
BTU:	British Thermal Unit.
CBs:	Chlorobenzenes.
CPs:	Chlorophenols.
EPA:	Environmental Protection Agency.
ISRI:	Institute of Scrap Recycling Industries.
MPW:	Mixed paper waste.
NITEP:	The National Incinerator Testing and Evaluation Program.
NCR:	No carbon required paper.
NSPS:	New Source Performance Standards.
ORF:	Ontario Research Foundation.
PAHs:	Polycyclic aromatic hydrocarbons.
PCBs:	Polychlorinated biphenyls.
PHS:	Public Health Service.
PIC:	Products of Incomplete Combustion
PVC:	Polyvinyl chloride.
RDF:	Refuse Derived Fuel.

CHAPTER I

INTRODUCTION

Solid waste is an unwanted by-product of modern civilization. Based on Environmental Protection Agency (EPA) surveys, annual solid waste generation in the United States is more than 140 million tons. About 41 percent of this solid waste is paper (U.S. EPA 1990).

Landfills are the most common means of solid waste disposal. But, the increasing amount of solid waste is rapidly filling existing landfills, and new sites are difficult to establish. Alternatives to landfills include the use of source reduction, recycling, composting and incineration, as well as the use of landfills. Incineration is most economical if it includes energy recovery from the waste. Energy can be recovered directly from waste by incineration or the waste can be processed to produce storable refuse derived fuel, RDF, (Alter 1987).

Incineration with energy recovery has the advantage of hygienic disposal, volume reduction, and the recovery of thermal energy by means of steam or super heated water that can be used for heating, cooling, and power generation (Saullo 1977; Gagliardi 1982; Jackson 1987).

Mixed paper waste, MPW, represents a valuable source of energy for several reasons (Glaub and Trezek 1987; Energy Systems Center ORF 1982):

- it is easy to segregate from the waste stream, either by separation at source or diversion of certain commercial loads,
- it is relatively homogeneous and mostly free from metals, putrescibles and other noncombustible materials,

- it requires minimum processing to be converted into the densified form of energy suitable for direct combustion,
- its heating value is fairly high.
- when processed into densified fuel, it has excellent storage characteristics
- when properly combusted, it has a low sulfur content, and low nitrogen oxides (NO_x) emissions.

Recovered heat can result in significantly reduced energy costs (Alter 1980; Alter 1987; Porteous 1984). Gagliardi (1982) found that the most cost efficient use of mixed paper waste-recovered heat is supplemental space heating. Electricity can be generated for sale back to the local utility as second priority. Cooling is the least cost effective application, although it can also be achieved through an absorption chiller.

The purpose of this study is to determine the quantity of energy obtainable from a known amount and composition of mixed paper waste. For a waste to energy system, the heating value of waste is one of the chief characteristics that determines the quantity of energy obtainable from waste. Therefore, individual heating values of different paper groups that are present in mixed paper waste (MPW) are used to calculate the quantity of energy recoverable from a given amount and composition.

The objectives of this study are to:

- review the potential emissions from the combustion of mixed paper waste.
- identify types of paper present in mixed paper waste.
- determine the heat value of each different paper group separately.
- show that it is possible to estimate the heat value of a mixture of paper waste by separating paper into different groups and multiplying the heat values of each type of paper by the weight fraction of that type.

CHAPTER II

BACKGROUND

II.1 MIXED PAPER WASTE

Mixed paper is defined by the Institute of Scrap Recycling Industries (ISRI) in its circular PS-88 as a mixture of various papers that can be classified by the type of packing or fiber content. Some of the descriptive categories include bleachable, unbleachable, coated (glossy) or uncoated, short fiber (groundwood), and long fiber paper (newsprint and boxboard respectively). Mixed paper waste also includes contaminants such as glues, plastics, sticky labels, and food waste. ISRI also defines the grades of mixed paper as mixed paper and super mixed paper (Apotheker 1990).

Mixed paper consists of various papers not limited as to type of packing or fiber content. Its prohibited material content may not exceed 2 percent by weight and total outthrows may not exceed 10 percent. Prohibited materials are any materials that by their presence in a packing of paper stock will make the packaging unusable as the grade specified. Also any materials damaging to equipment are called prohibited materials. Outthrows are all papers manufactured or treated so as to be unsuitable for consumption as the grade specified. The total outthrows are the maximum quantity of outthrows and prohibitive materials together. Super mixed paper consists of a clean, sorted mixture of various papers containing less than 10 percent of groundwood stock, coated or uncoated. Prohibited materials and total outthrows may not exceed 0.5 and 3 percent respectively.

Mixed paper waste may be collected separate from refuse or collected by processing and separating solid waste. Europe is the technical leader in developing paper recovery methods for municipal waste, while mass burn is most used in the United States (Teeuwen 1980; Joosten 1980; Hansen 1980; Bridgwater 1980). Separation of paper from refuse can be achieved by mechanical separation techniques such as air classifiers. The higher the purity of the paper, the more efficiently it will burn (Heidenreich et al 1988). Newspapers, corrugated boxes from commercial and industrial establishments, and mixed and high-grade papers from offices are several of the grades of paper which are recoverable by source separation currently. These categories of paper constitute approximately 50 percent of the paper from residential, commercial and industrial establishments (Lingle 1974).

II.2 ENERGY RECOVERY

The magnitude of energy production from the combustion of solid waste provides only a small percentage of today's soaring power demands, but it is not negligible. Since some forms of fuel are approaching depletion, there is a need to supply energy from other resources. Today's solid waste consists of high amounts of paper products that are excellent fuels due to their high BTU content (Fernandes and Shenk 1974; Evanson 1974).

Energy can be recovered directly from solid waste as heat, or waste can be processed into a storable refuse derived fuel (RDF). Direct recovery is accomplished by mass burning, while indirect recovery is by physical and thermal processing. In physical processing the combustible and noncombustible fractions of solid waste are separated from each other. The physical characteristics of the combustible fraction are altered to enhance its utility as a fuel. The resulting combustible product is referred to as refuse derived fuel or simply RDF.

Moisture content effects the energy value of fuels. In order to have satisfactory handling and storage properties, fuel should have a density of about 60 lb/cu. ft. and a moisture content within the range of 12-20 % (by weight). The relatively high density and low moisture content eliminates biological activities that would lead to degradation of the fuel. Pelletizing operation provides a mixed paper waste fuel with these properties. In general, the moisture content of mixed paper waste is about 6-28 % (by weight). In the critical range (moisture content up to 20 %) energy values of mixed paper waste samples do not show big differences. Other words, the effect of moisture content on the energy value of mixed paper waste is minimal in this range. But, moisture contents exceeding 30 % lead to low energy value for mixed paper waste. Moisture content must also be within the critical range for shredding and or effective compaction of mixed paper waste (Gloub and Trezek 1987).

Mass burning and RDF production are regarded as having the greatest potential for energy recovery, even though several difficulties may impede full realization of that potential. Some of these difficulties are related to marketing and some are technical. However, by using heat energy to generate steam and then producing electricity, both types of difficulties can be overcome to a certain degree (Diaz, Savage, Golueke 1982). Barnes (1985) has calculated that the revenue from electricity sales can be high and that the average disposal cost of incineration with heat recovery can be significantly less than that of landfilling at a distant site.

II.2.1 ENERGY RECOVERY THROUGH INCINERATION

Incineration can be defined as the conversion of waste materials to gaseous products and solid residues through the process of combustion (Baum and Parker 1973; ASME 1988). Incineration with energy recovery reduces both solid waste weight and volume , producing a sterile residue that requires land disposal (Bridgwater 1980). Incineration with energy recovery provides thermal energy by means of steam or super heated water that can be directly used for heating and cooling processes or electricity generation.

The combustion reaction requires fuel and oxygen. The oxygen usually comes from the atmosphere. The fuel from waste materials is composed mainly of carbon and hydrogen, but also includes other components such as oxygen, sulfur, chlorine, and nitrogen as well as inorganics. In the ideal incineration process, hydrocarbon compounds of the combustible waste react chemically at the high temperatures with the oxygen in the atmosphere to form carbon dioxide and water, as steam, and leave the noncombustibles such as minerals and metals as solid residue. To simplify, the combustion reaction can be described as:

CARBON (in the waste) + OXYGEN ---------> CARBON DIOXIDE + HEAT

HYDROGEN (in the waste) + OXYGEN ---------> STEAM + HEAT

Perfect combustion can be achieved by mixing the exact amount of oxygen with exactly the right amount of fuel to be combusted. If oxygen is in excess, the combustion system is called fuel lean and the flame is oxidizing. In the case of low levels of oxygen, the system is called fuel rich or reducing. Due to imperfect mixing both of these fuel lean and fuel rich zones exist within the combustion system at the same time. Since each fuel molecule has a chance to meet an oxygen molecule before leaving the combustion chamber, a controlled amount of excess air is supplied and turbulence is induced (ASME 1988; Diaz at al. 1982). If the constituents are not completely mixed in the proper proportions, and if they are not combusted at the proper temperature for the proper length of time, the reaction will be incomplete. Undesirable products may result which are commonly referred to as products of incomplete combustion (PIC) may result.

II.2.1.1 COMBUSTION PROCESS OVERVIEW

Burning in the combustion process occurs in a diffusion flame, in which fuel molecules are supplied from one side of the flame and oxygen molecules are supplied from the other side. Oxidation of fuel molecules occurs in a narrow flame zone at which the temperature is very high and most molecules are broken down into atoms or small species called free radicals. Due to the very low activation energies of these highly reactive molecular species, the reactions between the radicals are extremely fast and take less than one millisecond to complete. This is the main reason for high destruction efficiency of organic compounds in an incinerator (ASME 1988).

Three zones can be defined in a diffusion flame: preheat zone, reaction zone, and recombination zone. Considerable molecule degradation occurs in the preheat zone and the fuel fragments leaving this zone contain lower molecular weight hydrocarbons and olefins, and hydrogen. The main constituents in the reaction zone are similar irrespective of the composition of the original fuel combustion. This is the reason why similar incomplete combustion products (PIC) exist during the combustion of any fuel such as oil, gasoline, coal, wood, paper or organic wastes.

In the reaction zone, reactions are of the free radical type and, due to short residence times, they do not reach true equilibrium. The oxidation ends up with carbon monoxide rather than carbon dioxide even though enough oxygen is present. Carbon monoxide is an intermediate product of combustion that is thermally stable and is difficult to oxidize.

Slower recombination reactions which lead to further release of heat occur in the post-flame or recombination zone. In this zone, carbon monoxide is oxidized to carbon dioxide. Organic radicals having no chance to meet an oxygen or hydroxyl radical may recombine in several routes to form different incomplete combustion products. This is why many different compounds can be formed in any combustion process.

Formation of these products of incomplete combustion can be minimized with a proper supply and mixing (turbulence) of oxygen molecules, enough residence time and proper combustion temperature. Turbulence, time, and temperature factors are known as the three T s of combustion.

Since in a complete combustion process, the combustion temperature is high, organic molecules cannot survive. The equilibrium combustion products are the function of a fuel composition only, and are not a function of a fuel structure. Therefore, under equilibrium conditions, any chemical waste which has the same elemental composition as that of fossil fuel produces the same complete combustion products.

Equilibrium condition is seldom reached due to two reasons: a) kinetic limitation, slow reaction rates with relation to the time available; or b) imperfect mixing. Reactions associated with inorganics, such as hydrogen chloride, HCl, chlorine, Cl, sulfur dioxide, SO_2, sulfur trioxide, SO_3, nitrogen oxides, NO and NO_2, are slower and then the combustion products may deviate from equilibrium. At equilibrium, all carbon in the organics is converted to carbon dioxide, with a trace amount of carbon monoxide. All hydrogen is converted into water, as steam, or some inorganic acids, and all chlorine is converted into hydrogen chloride, HCl, and chlorine gas, Cl_2. Sulfur is converted to sulfur dioxide, SO_2, and sulfur trioxide, SO_3. Nitrogen is converted into nitrogen oxides such as nitrogen monoxide, NO, or nitrogen dioxide, NO_2, and nitrogen gas, N_2, in the flue gas.

Organics are decomposed into lower molecular weight species at high temperature in the flame zone. When some of these smaller species meet with oxygen and hydroxyl radicals, some combustion intermediates such as aldehydes, ketones, alcohols, and acids are formed. In incomplete combustion, further oxidation of these intermediates is hindered due to flame quenching by cold air, water, or by a cold surface, or lack of additional oxygen. Therefore these intermediates are emitted from the flame zone as products of incomplete combustion.

II.2.1.2 ENERGY RECOVERY TECHNOLOGY

The generalized layout for an incineration system with heat recovery is shown in Exhibit II.1. An actual heat recovery system contains an incinerator, a boiler (the heat recovery unit), and an emission control unit. The solid effluent discharge is the sterile residue of unburned materials and ash (ORF 1982).

In an incineration system, energy is recovered in the boiler as heat in the form of steam or super heated water. The steam or hot water is used in heating, cooling or for generating electricity. In the cooling process, hot water from the boiler is routed to an absorption chiller unit which produces refrigerated water for cooling purposes. The absorption chiller uses hot water from the boiler for evaporation and chills the water for space cooling. Heat recovery water that cools in incinerator furnaces has the added advantage of reducing the volume of gas to be cleaned, and reducing the particulates entering either the emission control unit or the stack.

In electricity generation process, steam from the boiler is used to operate the steam turbine generator (Gagliardi 1982). Exhibit II.2 shows a generalized flow diagram for heating, cooling, and electricity generation processes.

Gagliardi (1982) has studied the incineration of mixed paper waste with heat recovery and examined the three alternatives of heating alone, both heating and cooling, and heating, electric generation and cooling together. He believes that the economic analysis is more favorable for larger systems. He also concludes that paper waste incineration is a disposal method in which everybody benefits. Utilities benefit from decreased gas and electricity demand and communities extend the life of landfills.

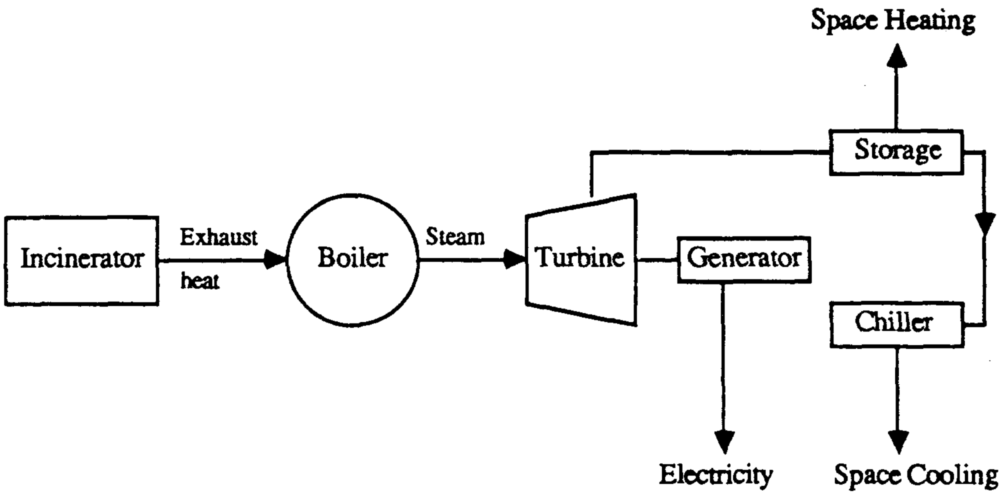

Exhibit II.1. Generalized Flow Diagram of Waste to Energy Incineration System.

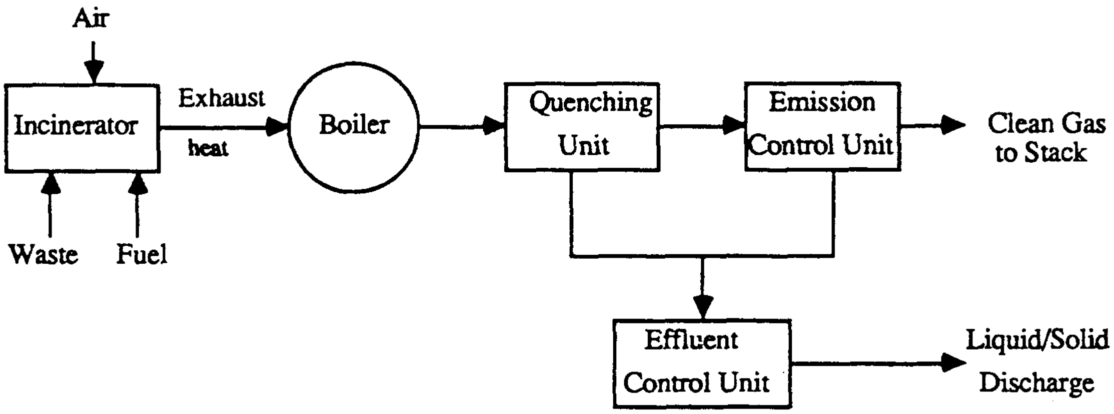

Exhibit II.2. Generalized Flow Diagram for Heating, Cooling and Electricity Generation Processes

II.2.2 ENERGY RECOVERY THROUGH CONVERSION INTO FUELS

Mixed paper waste separated from municipal solid waste can be used to produce other fuels. Recovery through chemical conversion into fuel can be achieved through hydrogenation, bioconversion, or pyrolysis, while densified RDF can be produced by various methods such as baling press, container press, briqueting, cubing and pelletizing (Bunsow and Dobberstein 1987; Gloub and Trezek 1987; Hardtle et al 1987). The purpose of some additional processing steps is to upgrade the fuel by increasing its calorific value or improving handling (Alter 1980).

Producing steam by burning fossil fuels has an efficiency of 85 percent. The efficiency of producing steam by burning paper is 60 percent. This means that 1 Btu of paper provides 0.6 Btu of steam and 1 Btu of a fossil fuel provides 0.85 Btu of steam. Therefore 1 Btu of paper replaces 0.7 Btu of a fossil fuel (Gunn 1978).

The reason for the low efficiency is that undensified paper waste burns hot and quickly. The densification process produces longer lasting fuel with limited surface area and good storage properties. Anderson et al. (1982) suggest that if pellet densities are in the range of 60 to 80 pounds per cubic foot, and in an appropriate system, the consumer should be satisfied with the rate of heat release and durability of RDF.

Williams et al. (1989) have used a computer model to predict the profitability of a plant making fuel pellets from mixtures of domestic refuse, paper waste, and coal. Originally they studied pelletized fuel from paper waste and later paper and anthracite duff together. Williams et al. (1989) and Grant (1982) recorded that the domestic market for fuel pellets can be profitable, especially when these fuels are enhanced by coal dust to increase their calorific values. Golden (1987) has studied a fluidized bed, hot gas generator burning RDF in the form of pellets. He reports that the quality (composition, density, moisture content, etc.) of pellets is very important in determining the efficiency of the incinerator. He also concludes that the fluidized bed combustion is an appropriate technology for pelletized RDF in hot gas generators and boilers.

CHAPTER III

EMISSIONS FROM THE COMBUSTION OF MIXED PAPER WASTE

III.1. POLLUTANT GENERATION

An important point which should be addressed for incineration systems is the potential release of pollutants into the environment. The purpose of this section is to provide an overview of possible airborne emissions from the combustion of mixed paper waste.

Typical emissions that can be expected from the combustion of mixed paper waste are particulates, carbon dioxides, carbon monoxides, water, oxygen, nitrogen, oxides of sulfur, oxides of nitrogen, ammonia, hydrocarbons as hexane or methane, aldehydes as HCHO, and organic acids as CH_3COOH (Carotti and Smith 1974, Hagenbrauck 1964).

In general, the municipal waste combustor emissions can be grouped as metal emissions (particulate matter), organic emissions (dioxins and furans), and acid gas emissions (SO_2 and HCl) as well as NO_x emissions (US EPA 1989). Gaseous emissions from the combustion of municipal solid waste are representative of several classes of organic and inorganic substances such as aliphatic and aromatic hydrocarbons, organic acids, alcohols, keto alcohols, ketones, aldehydes, phenols, halogen and inorganic acids. Emissions of dioxins and furans as well as benzo-a-pyrene and several other specific hydrocarbons are given particular consideration due to their carcinogenic effects. In addition, potentially toxic compounds such as hydrogen chloride, hydrogen sulfide, chlorine, and orgonometallics are also considered.

New source performance standards (NSPS) proposed under Section 111 of the Clean Air Act require good combustion practices by limiting the carbon monoxide concentration in the combustion gases (50 ppm/v for modular municipal waste combustors, 100 ppm/v for mass burn waterwall, mass burn refractory, and fluidized bed municipal waste combustors, 150 ppm/v for mass burn rotary waterwall , RDF, and coal/RDF co-fired municipal waste combustors). The operating range of the combustor should be no more than 100 % of demonstrated capacity. The temperature of flue gases entering the particulate matter control device should be 450 ^{0}F (US. EPA 1989). To limit municipal waste combustor metal emissions, the NSPS requires a particulate matter emission limit and opacity limit of 0.015 gr/dscf (at 7 % oxygen), and 10% (6-minute average) respectively. To limit municipal waste combustor organic emissions, the NSPS propose a dioxin plus furan emission limit of 5 to 30 nanograms per normal cubic meter (at 32 ^{0}F and 1 atmosphere of pressure) at 7 % oxygen for large municipal waste combustion plants. The dioxin plus furan emission limit of 75 nanograms per normal cubic meter is proposed for small municipal waste combustion plants (250 nanograms per normal cubic meter for RDF plants). To limit acid gas emissions in large municipal waste combustion plants, the NSPS propose a 95 % reduction and an 85 % reduction of HCl emissions and SO_2 emissions respectively. NSPS also propose an 80 % reduction of HCl emissions and a 50 percent reduction of SO_2 emissions for small municipal waste combustion plants or an emission limit of 25 ppmv (at 7 % oxygen) for HCl emissions and 30 ppmv (at 7 % oxygen) of SO_2 emissions for both small and large municipal combustion plants. To limit NO_x emissions, the NSPS propose a limit of between 120 and 200 ppmv (at 7 % oxygen) for large municipal combustion plants.

Carotti and Smith (1974) studied gaseous emissions from the combustion of municipal solid waste. They determined the composition of municipal solid waste before combustion. Weight percent of paper ranges between 33 and 53 % of total municipal solid waste. Carotti and Smith classified paper waste into three different paper groups; newspaper, cardboard, and miscellaneous paper that consists of food cartoons, paper towels, brown paper, mail and magazine paper. At the end of emission determinations Carotti and Smith determined that emission components from combustion of municipal solid waste that contained high amounts of paper were in the range of 13-39 parts per million by volume (ppm/v) for sulfur dioxide, 9.5-410 ppm/v for total hydrocarbons as methane, 1-2 ppm/v for total acids as HAc, 0.4-4 ppm/v for total aldehydes and ketones as HCHO, 41-81 ppm/v for hydrochloric acid, 31-53 ppm/v for sulfuric acid, and 0 ppm/v for HF and HCN. They conclude that the gaseous effluent from combustion of municipal solid waste is richer in inorganics such as hydrogen chloride, sulfuric acid, and sulfur dioxide than in organics such as hydrocarbons, aldehydes, alcohols, ketones, esters, and organic acids.

III.2 CLASSIFICATION OF EMISSIONS

The emissions from waste-to-energy units vary greatly in organic chemical composition because of the design differences, variations in refuse feed composition, and operating parameters of the combustion units. Therefore, improvements in design and operation of waste-to-energy systems are very important in reducing combustion emissions (Howes et al. 1987).

The air pollutants emitted from combustion processes can be classified as inorganic particulate matter, combustible solids, liquids, gases, gaseous pollutants related to fuel chemistry (sulfur oxides, chlorine and hydrogen chloride, trace elements, radioactive elements), and nitrogen oxide where emission levels depend on the interactions between combustor and waste (Niessen 1978; Hahn et al. 1989).

III.2.1 PARTICULATE MATTER

Fernandes (1968) states that the primary air pollution concern is with emission of particulate matter rather than gases and odors. A big portion of particulate emission arises from the carry-over of mineral matter introduced with waste. In some conditions where the combustion oxygen is supplied from an area with high dust content, oxygen supply may be a source for particulate matter.

Niessen (1978) reports that the quantity of particulate emissions from an incinerator are the function of the waste composition and the design and operation of the incinerator.

Mixed paper waste, like all solid wastes and fuels, has substantial ash content. Some amount of the fly ash may settle in the bottom of the primary furnace or in other sections. Settlement reduces the emission rate depending on the settling rate which is related to characteristic size and weight of fly ash particles, flue gas properties, and transit time which is gas velocity relative to the chamber dimensions.

Niessen (1978) states that the ash content of waste is a major factor for the determination of particulate emission rates, and that the amount of ash carried over generally ranges between 10-20 % of the total. The actual ash percentage carried over for an incinerator depends on underfire air rate.

As evidence of the effect of ash content on particulates, the result of a study of an experimental incinerator has been published by the Public Health Service (PHS). Tests were conducted using a synthetic refuse consisting of newspaper, cardboard, wood, and potatoes and then by using a high-ash paper. The ash contents of synthetic refuse and high-ash paper were found to be 2.0 % and 7.5 % by weight respectively (Niessen 1978, Kaiser et al. 1968). Niessen and Sarofim (1970) have estimated the ash percent of paper to be 2.74 % by weight.

III.2.2 COMBUSTIBLE SOLIDS, LIQUIDS AND GASES

Combustible solid, liquid, and gas pollutants can be classified as carbon; carbon-hydrogen compounds such as methane, ethane, acetylene and other aliphatic compounds; carbon-hydrogen-oxygen compounds such as carbon monoxide and formaldehyde, ketones; and carbon-hydrogen-nitrogen compounds such as amines, N-ring compounds and other chemical species.

Some of these pollutants are harmful to plants (e.g. ethylene), animal life respiration (e.g. carbon monoxide), or they may cause cancer in human beings (e.g. benz-(a)-pyrene). Because of their health effects, these emissions should be controlled. They are as a result of incomplete combustion due to inadequate residence time to complete reaction or inadequate combustion temperature, or inadequate turbulence (lack of oxygen). With a proper incinerator design, emissions of these kinds of pollutants can be reduced and controlled.

III.2.3 GASEOUS POLLUTANTS RELATED TO THE CHEMISTRY OF WASTE/FUEL

Pollutant emissions generated by the combustion of waste appear in the gas phase as well as in the emitted fine dust (Lorber 1987). In this group, pollutants are generated by release and reaction of elements in the waste. The most common and important pollutants are sulfur oxides and hydrogen chlorides (Niessen 1978, Hahn et al. 1989). There are also some highly toxic trace metals and carcinogenic pollutants such as dioxins and furans that are of major public concern.

III.2.3.1 SULFUR OXIDES

All fossil fuels contain some sulfur. Sulfur may be in the oxidation states of S (-II) to S (VI) or in the form of sulfides, free sulfur, or sulfur in acid forms. In all of these cases, sulfur is expected to be in flue gases as sulfur dioxide or trioxide. And a very small portion of the sulfur may be released due to reduction reactions as inorganic sulfides (calcium sulfides, gypsum). Chemistry of sulfur in the fuel, the time sequence of temperature and composition of the flue gases, and the amount of catalytic ash material determine the proportion of sulfur between the dioxide and trioxide forms.

A portion of the sulfur oxide may be lost from the flue gas by gas-solid reaction depending on the alkalinity of the mineral ash residues. And some portion may also remain with ash. Typically 95 % of the sulfur can be found in the flue gases of suspension fired combustors and 70 % for mass burning systems. Bunsow and

Dobberstein (1987) have studied emissions of sulfur, chlorine, fluorine, and heavy metals generated from combustion of different RDFs. They conclude that the emission distribution of sulfur is 0.5 % in the bottom ash, 1.0 % in the fly ash, and 98.5 % in the flue gas. They also report that only the fluidized bed furnaces with 600 ^{0}C to 800 ^{0}C combustion temperatures are able to deposit 50 % of the sulfur in the bottom ash, 1.0 % in the fly ash, and 49 % in the flue gas.

Sulfur oxides have some important health effects especially when they combine with particulate matter. Sulfur oxides also have corrosive effects on solid surfaces. When sulfur trioxide reacts with water vapor, it forms sulfuric acid which is very corrosive. The importance of sulfur oxides emissions from the combustion of waste depends on the quantity of sulfur present in the waste. The average sulfur content of mixed paper waste is around 0.2 percent by weight.

III.2.3.2 CHLORINE AND HYDROGEN CHLORIDE

Chlorine can be found in the waste stream as organic compounds or inorganic salts. Mixed paper waste may contain some bleached components and these components contain chlorine and/or some chlorinated organic compounds. Chlorine content of unbleached and bleached papers are about 0.071 % and 0.007 % by mass (dry basis) respectively (Domalski et al. 1986). During combustion, chlorine is converted to hydrochloric acid (HCl), which is highly corrosive.

Organic chlorine may form some organics other than hydrochloric acid such as chlorobenzenes (CBs), chlorophenols (CPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-para-dioxins

(PCDDs), and polychlorinated dibenzofurans (PCDFs). The concentration of a majority of these compounds, all of which are suspected human carcinogens, are in the parts-per-billion or parts-per-trillion range in the flue gas for a properly designed and operated combustor (Klicius et al. 1990).

Domalski (1986) and Churney et al. (1985) studied the chlorine content of municipal solid waste from Baltimore County, MD and Brooklyn, NY. According to their results, they conclude that the major chlorine source in municipal waste is from paper and plastic fractions. They also state that the paper fraction has about one third to half of its chlorine in water soluble form while the plastic fraction has most of its chlorine in water insoluble form.

III 2.3.3 DIOXINS AND FURANS

Dioxins (PCDDs), and furans (PCDFs) which are generated from combustion of chlorine containing waste are a major public concern because of their carcinogenic properties. Almost any combination of carbon, hydrogen, oxygen, and chlorine can produce some polychlorinated dioxins and furans under suitable conditions of temperature and time (Altwicker et al. 1990, Gotoh 1987). 2, 3, 7, 8 tetrachloro-dibenzo-p-dioxin (2, 3, 7, 8 - TCDD) is one of the most toxic man-made substances known, and it results from the incomplete combustion of chlorinated compounds. PCDDs and PCDFs may be found in the precipitator fly ash and flu gas of the incinerator (Altwicker et al. 1990, Gotoh 1987, Domalski 1986).

There are two possible explanations for the presence of dioxins and furans in incinerator emissions, disregarding their presence in waste feed. The first is that

PCDDs and PCDFs are produced from related chlorinated compounds such as PCBs, CPs, or CBs. The second is that PCDDs and PCDFs are formed from chemically unrelated compounds such as polyvinyl chloride (PVC), other chlorocarbons, or from the combustion of non-chlorinated organic matter such as polystyrene, cellulose, lignin, and coal in the presence of chlorine donors (Altwicker et al. 1990).

Depending on operating conditions of the incinerator, PCDDs and PCDFs may be partially or completely destroyed. According to the work done by Altwicker they can be largely destroyed by using the most important three incineration parameters of temperature (600 - 1000 ^{0}C), residence time (0.5 - 2 s), and oxygen concentration (0.2 to 21 %). Maximum dioxin destruction is expected to occur at 600 ^{0}C, 1.5 s, and 20 % oxygen (Altwicker et al. 1990).

III.2.4 NITROGEN OXIDES

Nitric oxide (NO) is produced at the high combustion temperatures. At lower temperatures, formation of nitric oxide is limited by equilibrium and kinetics. A small portion of NO is oxidized to nitrogen dioxide (NO_2). Nitrogen oxides participate in atmospheric chemical reactions which are mostly photochemical reactions producing ozone and several oxygenated compounds that adversely affect air quality.

There are two mechanisms of nitrogen oxides generation in combustion processes. At high temperatures nitrogen oxides are generated thermally through fixation of nitrogen from the combustion of air with oxygen. At lower temperatures, nitrogen contained in the waste feed forms nitrogen oxides (Niessen 1978).

III.2.5 METALS

The bottom ash and fly ash of incinerators may contain some metals including zinc, cadmium, lead, chromium, nickel, antimony, arsenic, mercury, copper, and selenium (Jackson 1990, Klicius et al. (1990). Jackson reports that the most prevalent elements in the ash are: copper (0.04 % - 0.017 % by weight), lead (0.07 % - 0.017 by weight), and zinc (0.15 % - 6.69 % by weight). Bunsow and Dobberstein (1987) report that among the heavy metals the largest proportional carry-over is found with highly toxic mercury, cadmium, and lead emissions.

III.3 EMISSION CONTROL

Emissions from the combustion of mixed paper waste can be controlled in three ways:

- Prevention of pollutants from forming in the process or during the operation.
- Dispersion of pollutants into the atmosphere.
- Collection of pollutants just before they reach the atmosphere.

Formation of pollutants can be prevented by using one or several preventive techniques such as changing the combustion equipment, improving operation and maintenance practices of the combustor, and enclosing the operation.

It may also be possible to dilute the emission concentration to an acceptable level by raising the stack height, or by moving the plant to an uninhabited area where the emissions can be diluted by the time before they reach receptors. However, this technique does not solve a pollution problem satisfactorily.

Emission control pollutants can be trapped, changed, or destroyed before they reach the atmosphere. The methods of pollutant collection, change and destruction are called tail-end techniques since they are used after the pollutants are formed in the combustor.

III.3.1 EMISSION CONTROL EQUIPMENT

There are several types of equipment for removing contaminants from the air. The most common emission control equipment includes the settling chamber, the cyclone collector, inertial collectors, filters, electrostatic precipitators, scrubbers, absorbers, adsorbers, combustion chambers, and condensers.

Pollutant type is one of the most important factors in the selection of emission control equipment. Some of the more common control equipment for particulates and gases that are expected to be emitted from the combustion of mixed paper waste are described in the following sections.

III.3.1.1 CONTROL EQUIPMENT FOR PARTICULATES

Particulate matter removal equipment may involve either dry or wet techniques. Dry collectors involve settling chambers, inertial collectors, cloth filter collectors, and electrostatic precipitators (Crawford 1976, Walker 1975, Jackson 1974, Corman 1974).

Settling chambers can remove only large particles that are greater than 40 microns in diameter. Smaller particles settle too slowly, and therefore, this technology is not suitable for the removal of particulates from combustion of mixed paper waste.

Inertial collectors operate with inertial force as well as gravity. They can reach an efficiency of 85-95 % depending on the fineness of the particles. The most common inertial collector is the cyclone collector. In cyclone collectors, the gas rushes into a cylindrical chamber through a tangential inlet duct at the top of the cylinder. Centrifugal force carries the particulates out of the spinning gas stream onto the wall of the chamber where the particles fall into a collector hopper. Cyclone collectors can remove particulates as small as 3 microns. A high efficiency collector can remove over 95 % (by weight) of particulates.

Dynamic precipitators can remove particles over 10 microns. In dynamic precipitators, the gas stream is rushed against a series of fan blades on which the particulates are caught and then deposited in a hopper (Crawford 1976, Corman 1974).

Cloth filter collectors can be used for particles as fine as 0.4 micron. The gas stream passes through a woven fabric in which the particulates are caught. The choice of fabric is based on the temperature and chemical composition of the gas and physical and chemical characteristics of the particulate matter. Cloth filter collectors are not applicable to very hot gases. Even with properly selected fabric, very hot gases should be cooled first, or the high temperature can destroy the fabric. They are also expensive. Cloth filter collectors can remove enough particulate matter to meet the various emission standards, although they have not been widely used because of cost and operational problems.

The electrostatic precipitator is one of the most widely used types of collection equipment for particulates. Electrostatic precipitators can remove many different kinds of particulates as small as 0.1 micron. They can reach to a 99.9 % removal efficiency.

They can also operate at high temperatures and pressures with a low power requirement.

The electrostatic precipitator can not collect gaseous pollutants (McDonald and Dean 1982). Electrostatic precipitators have a small diameter negative electrode and a grounded positive electrode plate. A one-dimensional electric field is set by a strong electric charge from the negative electrode. The particulates passing through the field are negatively charged and are drawn to the positive collecting surface. The drawn particles are then collected in a hopper.

Wet collectors have a disadvantage in that as they eliminate air pollution, they can create water pollution. It is important to figure out how to dispose of the resultant contaminated liquid or sludge. They also have corrosion and freezing (in cold weather) problems. For these reasons they are not the most suitable equipment for particulate removal. The most common wet collectors include wet electrostatic precipitators, wet dynamic precipitators, gravity spray towers and scrubbers. Electrostatic precipitators remove particulates by washing them off the electrode plate. Dynamic precipitators spray water on the blades of a fan. They can remove particles from 15-50 microns in diameter. Gravity spray towers trap the particulates riding upward on the gas stream by water drops sprayed from above. They can remove particles as small as 2 microns.

Scrubbers are widely used although they have many drawbacks. Like other wet collectors, they create waste water and their power requirements are high and they are noisy. They are also less effective than electrostatic precipitators or filters in the removal of very fine particulates. The most common types are centrifugal spray scrubbers and Venturi scrubbers. In centrifugal spray scrubbers the gas stream is sent spinning, while a liquid is sprayed against the stream to wet the gas and the scrubber chamber walls. Wetted particles are thrown against walls by centrifugal force and are wasted downward. Removal efficiencies of centrifugal scrubbers can reach 96 % for 2 or 3 micron particles. In Venturi scrubbers, gas stream passes through a Venturi tube. A water spray is injected at the throat of the tube where the particles are trapped. Their removal efficiencies can reach over 99 % of particles as small as 0.5 microns.

III.3.1.2 CONTROL EQUIPMENT FOR GASES

At a properly operating incinerator, since the combustion will be complete, no visible emissions should exist except a water vapor plume. Carbon monoxide concentrations should be low and nitrogen oxide emissions should be minimal. Even with complete combustion, however, emissions from incinerators will have to be controlled because of gaseous pollutants. Sulfur oxide and nitrogen oxide are the most common gaseous pollutants.

Sulfur Oxides: The sulfur in organic compounds can be removed preventively by changing the fuel chemically. However, this method is impractical for mixed paper. Therefore, flue gas cleaning is the only way to achieve sulfur removal. There are three processes to do this:

- lime scrubbing process
- catalytic oxidation
- fluidized bed combustion with limestone or dolomite injection.

In the lime scrubbing process, dry limestone is injected into the firebox and converted to reactive lime. The reactive lime joins the gas stream and passes into a wet scrubber. Here, lime reacts with water and with fly ash and forms a slurry. This slurry and the sulfur dioxide react to form sulfite and sulfate salts, that are then disposed of. This system can remove about 75 % of the sulfur dioxide in flue gas, but there are some problems such as disposal of sulfite sludge and cooled gases.

Catalytic oxidation is another sulfur dioxide removal process. Flue gas must first be sent through an electrostatic precipitator to remove the particulates. Then, flue gas flows over a catalyst. Here, sulfur dioxide is changed to sulfur trioxide. The sulfur trioxide reacts with water vapor in flue gas and forms sulfuric acid. Sulfuric acid is condensed by cooling, and then can be sold. This system can reach up to 90 % conversion.

Fluidized bed combustion with limestone or dolomite injection is another possibility for sulfur removal. Limestone or dolomite is injected into the bed where the limestone reacts with the sulfur oxides to form easily removable calcium-sulfur salts.

Nitrogen Oxides: It is not easy to remove substantial amounts of nitrogen oxides from the flue gas. Therefore, control of nitrogen oxides emissions should be preventive. By changing the equipment and the combustion process, nitrogen oxides in the flue gas can be reduced up to 80 %. In order to reach this efficiency level, heat production will be reduced (Corman 1974).

The basic principle in the reduction of thermal nitrogen oxides formation is the reduction of temperature, oxygen level and residence time (OECD 1983). Several techniques can be used to meet the above conditions. The main techniques for the removal of nitrogen oxides are:

- Modification of operating conditions that includes combustion at a low air ratio, reduced air preheat operation, and load reduction.

- Modification of the combustion facility including off-stoichiometric combustion, two stage combustion, flue gas recirculation, water and steam injection.

- Low nitrogen oxides burners which include mixture accelerating burners, flame splitting burners, self recirculation burners, off-stoichiometric combustion burners. and two stage combustion burners.

When high removal efficiencies are required, flue gas denitrification (FGD) can be used in addition to combustion modifications. In flue gas denitrification, nitrogen oxides are decomposed to nitrogen and other substances. Flue gas denitrification processes can be grouped as dry and wet processes. The dry process is mainly applicable to flue gas free of sulfur dioxide and dust. Wet processes on the other hand require a certain amount of sulfur oxides for the treatment of flue gas from the combustion of waste. These systems can remove sulfur oxide and dust as well as nitrogen oxides. Flue gas denitrification can be conducted by installing auxiliary equipment.

CHAPTER IV

EXPERIMENTAL WORK

At an energy recovery process the chief characteristic that determines the quantity of energy obtainable from waste is the calorific value of the waste to be burned. Calorimetric analysis of paper waste gives the calorific or energy value of paper waste when all of its chemical constituents are completely oxidized at constant volume. When a fuel is burnt at constant volume, none of the energy given out is expended in doing work, and all the heat released is stored as internal energy in the products. That causes an increase in the temperature of the products. This analysis is required to determine the calorific value of paper waste which is used for the assessment of the mixed paper waste as a source of energy.

In this study calorific value of the paper waste is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The calorific values are computed by reading the temperature changes during the combustion.

IV. 1 CLASSIFICATION OF MIXED PAPER WASTE

Mixed paper is a mixture of papers having different characteristics. Paper can be classified as bleachable, unbleachable; coated, uncoated (glossy); long fiber, and short fiber. Short weak fiber paper is made from mechanical pulp to produce end products such as newspapers, magazines, and telephone directories. Long strong fiber papers are used to produce corrugated containers (cardboards), kraft grocery sacks, and boxboards. Bleachable papers are used for magazines, office papers, envelopes, tissue, and junk mail. Unbleachable papers are used in corrugated and boxboard containers. Coated papers include glossy paper, beverage and waxed milk boxes. There are also some papers which are referred to as treated paper such as no carbon required (NCR) papers. Envelopes have many contaminants such as plastic windows, sticky labels and hot melt glues, and because of this, they are categorized separately from the office papers. Clearly it can be sometimes difficult to categorize paper using the above criteria. It is more reasonable to separate mixed paper waste according to easily identifiable types and also according to their intended use.

In this study mixed paper waste is divided into eleven groups according to the use of the papers, and not necessarily by the type of packing or fiber content. Classified groups are:

1- Newspaper
2- Glossy paper
3- White office paper
4- Colored office paper
5- Envelopes
6- Tissue
7- Treated paper (NCR)
8- Beverage and waxed milk boxes
9- Kraft paper
10- Boxboard
11- Cardboard

IV.2 SAMPLE PREPARATION

The homogeneity of the sample is important in the calorimetric test of mixed paper heat value. The composition of the mixed paper varies greatly; it is impossible to get mixed paper waste with exactly the same composition at different times. Accurate categorization and adequate mixing of a large sample size before the extraction of a test sample are critical.

Samples are prepared in the form of pellets, since pellets are easier to handle than loose samples and they burn slower in the bomb, enhancing the complete combustion. Preparation of pellets requires the size reduction and mixing of the samples. The Willey Mill shown in Exhibit IV.1 is used for the grinding and mixing of the samples.

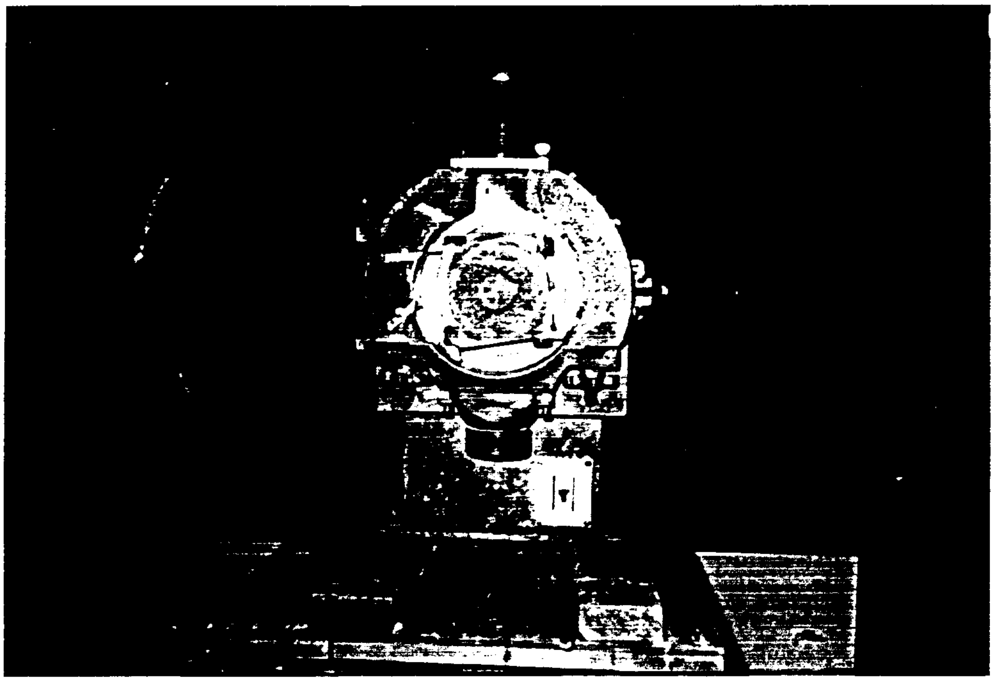

Exhibit IV.1. Willey Mill (Scale: 1 inch equals approximately 10 inches).

A 2811 Parr pellet press (Exhibit IV.2) is used to compress the powdered samples into small pellets of approximately 0.5 inch diameter (Exhibit IV.3).

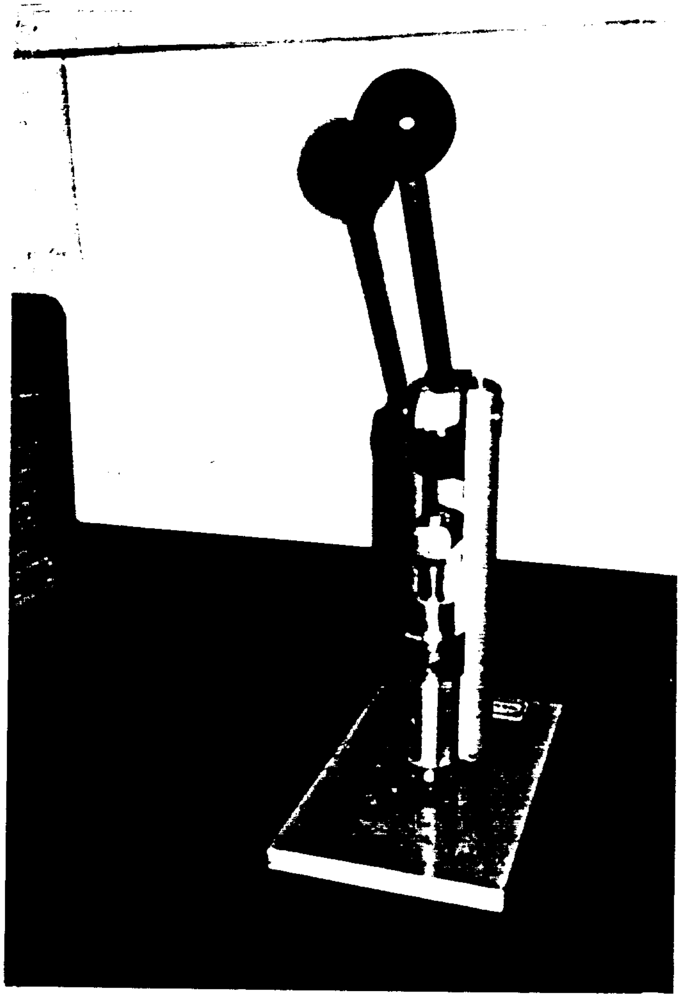

Exhibit IV.2. Parr Pellet Press (Scale: 1 inch equals approximately 3.3 inches).

For the preparation of the **mixed paper waste** sample, a sample approximately 0.5 gram (0.0011 pound) is taken from each of the eleven different groups and mixed homogeneously. Then, the mixture is compressed into small pellets smaller than 1.0 gram.

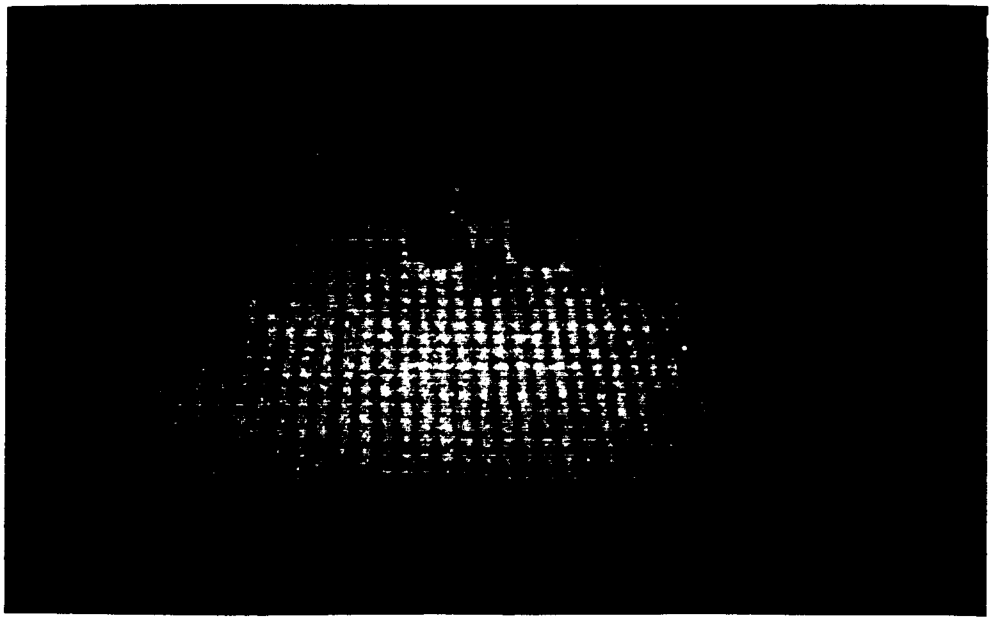

Exhibit IV.3. Paper Pellets (Scale: 1 inch equals approximately 1.8 inches).

IV. 3 TERMINOLOGY

These definitions have been extracted from ASTM Standard Test Method for the measurement of gross calorific value of refuse derived fuel with the bomb calorimetry (ASTM 1987).

Calorific value: The heat of combustion of a unit quantity of a substance under specified conditions. Calorific value is expressed in joules per gram, J/g, or in British thermal units per pound, Btu/lb, or in calories per gram.

Gross calorific value: The heat produced by combustion of a unit quantity of solid fuel, at constant volume, in an oxygen bomb calorimeter under specified conditions so that all the water in the products remains in liquid form.

Net calorific value: The heat produced by combustion of a unit quantity of solid fuel at a constant pressure of one atmosphere, under the assumption that all water in the products remains in the form of vapor. It has a lower value than that calculated from gross calorific value.

Calorimeter: Calorimeter consists of the bomb and its contents, the calorimeter vessel with stirrer, the water in which the the bomb is immersed, the thermometer and the ignition leads within the calorimeter vessel.

Corrected temperature rise: Change of temperature of calorimeter caused by the process occurring inside the bomb.

Energy equivalent: Energy required to raise the temperature of calorimeter system one arbitrary unit per gram of sample.

IV.4 APPARATUS

The experimental apparatus shown in Exhibit IV.4 includes a Parr oxygen bomb, a Parr calorimeter with a jacket, a mercury-in-glass thermometer, Parr 45 C 10 nickel alloy firing wire and oxygen gas as oxidizer.

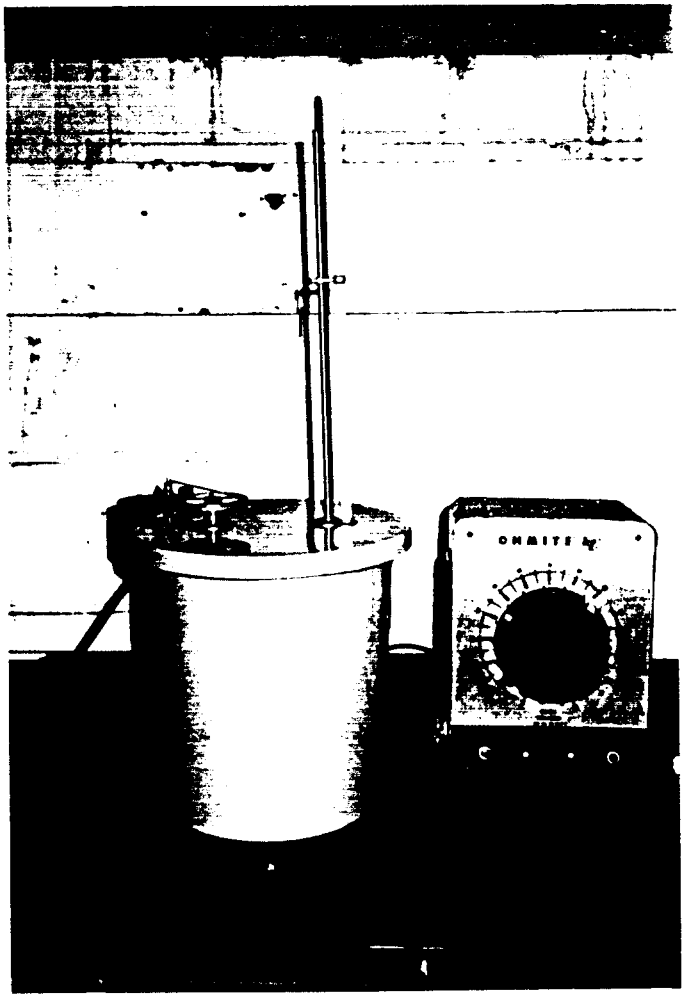

Exhibit VI.4. Experimental Set-Up (Scale: 1 inch equals approximately 7 inches).

Oxygen Bomb:	1108 Parr oxygen bomb (Exhibit III.5) with a removable head and a closure that can be sealed by turning a knurled cap. When the bomb is pressurized, sealing force increases. After the pressure has been released, the cap is unscrewed and the head is lifted from the cylinder. Two valves are installed in the bomb head. There is a check valve on the inlet side of bomb. This check valve opens when the pressure is applied and closes automatically when the supply is cut off. On the outlet side there is an adjustable needle valve from which the gases are released passing through a longitudinal hole in the valve stem and discharging from a shorthose nipple at the top.
Calorimeter:	The Parr calorimeter is made of metal with a tarnish-resistant coating. The calorimeter has a mixing device to stir the water thoroughly and uniformly with a minimum heat input. The calorimeter includes a jacket as a water bath.
Firing Wire:	Parr 45C10 nickel alloy wire.
Ignition Unit:	Ohmite ignition unit operates from 115 volt, 50 or 60 Hz line to provide the low voltage current for igniting the fuse wire (firing wire) in the oxygen bomb.

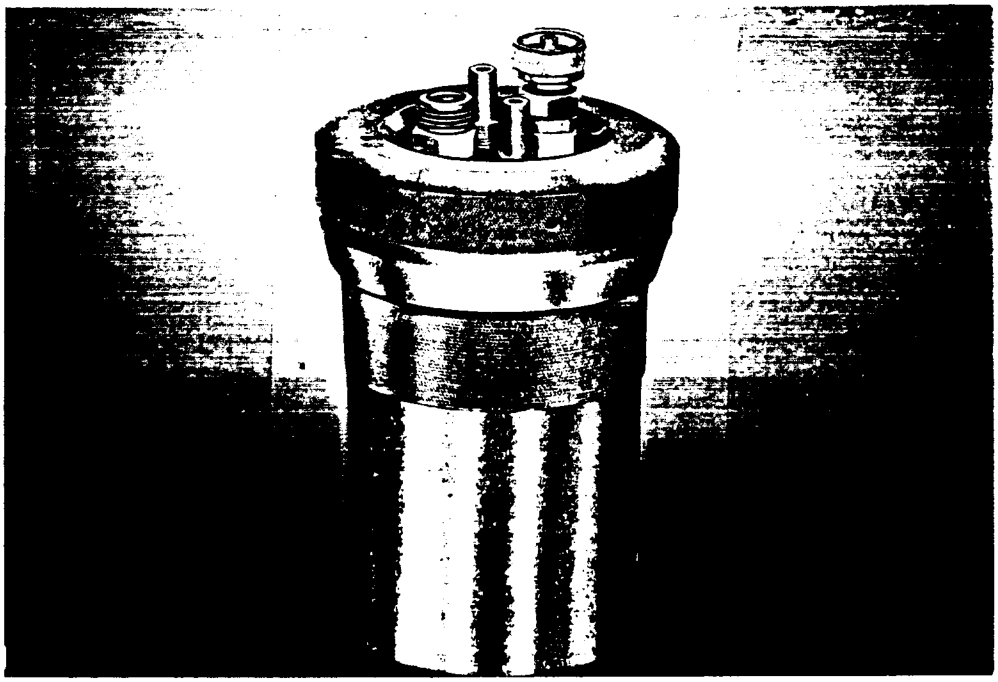

Exhibit IV.5 Parr Oxygen Bomb (Scale: 1 inch equals approximately 2 inches).

IV.5 PROCEDURE

Before starting the measurements of heat values of papers, the calorimeter is standardized to determine the energy equivalent of the calorimeter as an average of a series of individual runs. To be acceptable, the standard deviation of series are 6.5 Btu/^{0}C or less (ASTM 1987). For this purpose benzoic acid pellets of 0.9 to 1.3 grams are burned, and their heat values and corrected temperature rise are determined in accordance with the procedure described below. The energy equivalent of the calorimeter is calculated as :

$$E = [\ (H)\ (g) + e_1 + e_2\ ] \times T \qquad (1)$$

where:

E = energy equivalent, Btu/^{0}F (J/^{0}C)

H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards certificate, Btu/lb (J/g)

g = weight of benzoic acid, lb (g)

T = corrected temperature rise, ^{0}F (^{0}C)

e_1 = correction for the heat of formation of HNO_3, Btu (J)

e_2 = correction for the heat of combustion of the firing wire, Btu (J)

Since the sulfur and nitrogen contents of the mixed paper waste are minimal, the exclusion of the corrections e_1 and e_3 would have very little effect, if any, upon the calorific value results. The sulfur correction (e_3) is about 2.266 cal/mg of sulfur while, the nitric acid formation correction (e_1) is about 1.434 cal/ml of 0.1 N nitric acid. The sulfur content of mixed paper waste is about 0.2 % by weight. Then the sulfur correction may change the result only about 0.001 - 0.0015 %. Correction for the heat of combustion of firing wire (e_2) is about 1400 cal/g of Parr 45C10 nickel alloy wire. Wire correction has also little significance such that, it can change the final result by an average of only 0.8 %. This change is not important compared to the changes sourced from the calorimetric analysis of the mixed waste paper which is a difficult material to test as a homogeneous fuel. Repeating calorimetric tests of the same mixed waste paper sample yield a much larger variation.

In order to determine the heat values of various waste paper samples, paper pellets are prepared by means of pellet press and they are weighed by a precise balance taking care that the weight of pellets is less than 1.0 gram. A weighed amount of firing wire is connected to the loop electrode, by the help of a support stand, with enough slack to allow the firing wire to maintain contact with the sample. Then, the sample capsule carrying the pellet is placed in the loop holder and the firing wire is bent down to touch the surface of the pellet to keep it from sliding against the side of the capsule. Exhibit III.6 shows the connected form of the firing wire.

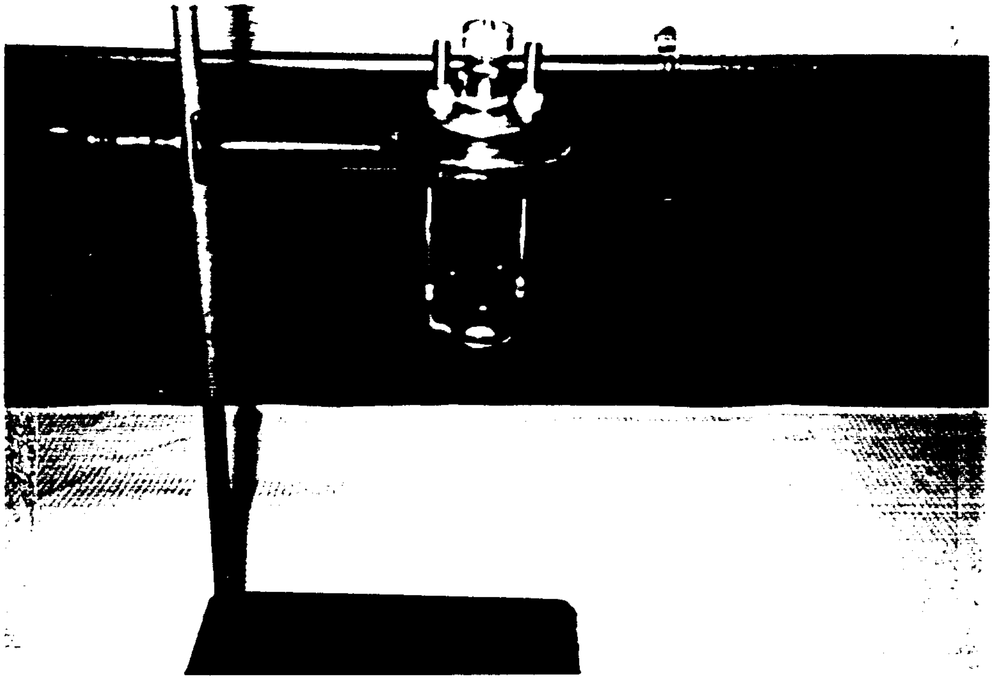

Exhibit IV.6. Connection of Firing Wire (Scale: 1 inch equals approximately 3.8 inches).

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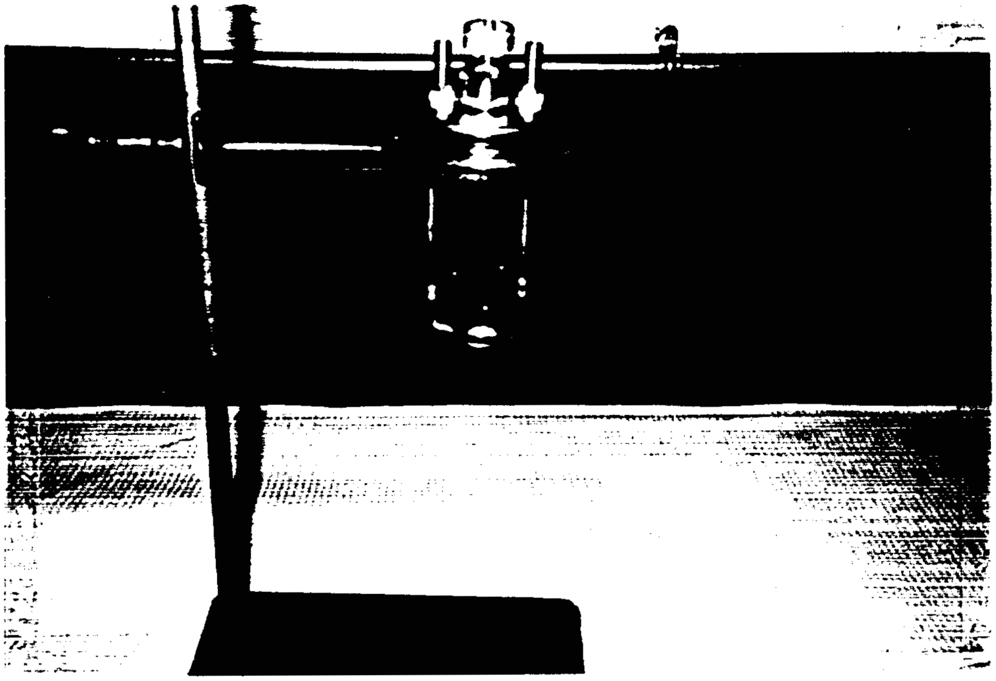

Exhibit IV.6. Connection of Firing Wire (Scale: 1 inch equals approximately 3.8 inches).

One milliliter of distilled water is pipetted into the bomb as a sequestering agent to maintain a water saturated atmosphere in the bomb and to dissolve all the gaseous combustion products. Care is taken not to disturb the sample when moving the bomb head from the support stand to the bomb cylinder. The head is slid into the cylinder and pushed down as far as it will go. The screw cap is set on the cylinder and turned firmly by hand.

The bomb is charged slowly with oxygen to a consistent pressure of approximately 25 atmospheres. The same pressure is used for all tests. The bomb is set into a jacket containing 2000 ml water at a temperature slightly below that of the laboratory air (Exhibit IV. 7). If there is any leakage, the procedure is repeated. Then, the lead wires from the binding posts on the ignition unit are pressed into the terminals on the bomb head, and the stirrer is started. Before ignition, the temperature of the water in the jacket is adjusted to be equal or slightly lower than that in the calorimeter and run for a 5 minute period to obtain equilibrium. Then, the jacket temperature is adjusted to match the calorimeter with +/- 0.01 ^{0}C and held for 3 minutes. The initial temperature is recorded and the firing button is depressed for 5 seconds to burn off the firing wire. A longer period may melt the wire while a lesser period may not be enough to ignite the wire. Calorimeter readings are taken at 30 second intervals until the same temperature is observed for three consecutive readings. This is called the final temperature.

The bomb is removed and the pressure is slowly released at constant rate. The depressurizing process must take more than one minute. The bomb interior is examined for residues and if unburned residues or sooty deposits are found, the test is discarded and repeated again.

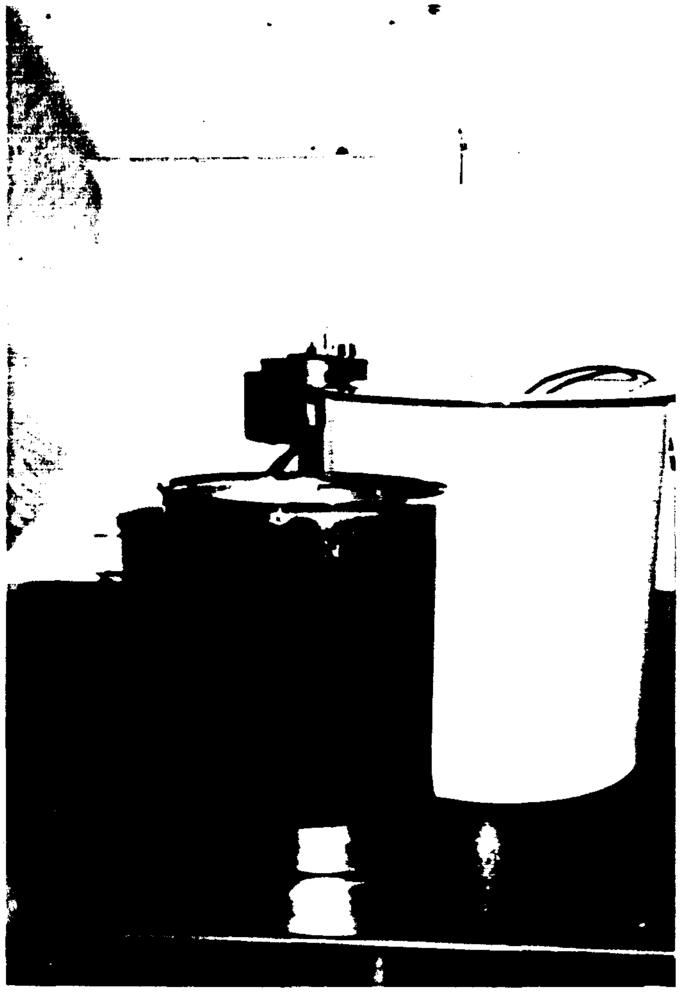

Exhibit IV.7. Calorimeter Jacket (Scale: 1 inch equals approximately 4.7 inches).

The time / temperature data are plotted as shown in Exhibit IV.8, and the temperature rise in the calorimeter is computed as follows (Exhibit IV.8):

$$T = T_c - T_a - r_1 (b - a) - r_2 (c - b) \qquad (2)$$

where:

T = corrected temperature rise, ^{0}C.

a = time of firing, minutes.

b = time when the temperature rise reaches 60 percent of the total rise, minutes.

c = time at beginning of period in which the rate the rate of temperature change with time has become constant (after combustion), minutes.

T_a = temperature at time of firing, ^{0}C.

T_c = temperature at time c, ^{0}C.

r_1 = rate at which temperature was rising during 5 minute period before firing, ^{0}C/min.

r_2 = rate at which temperature was rising during 5 minute period after time c. If the temperature is falling, r_2 is negative and the quantity r_2 (c - b) is positive, ^{0}C/min.

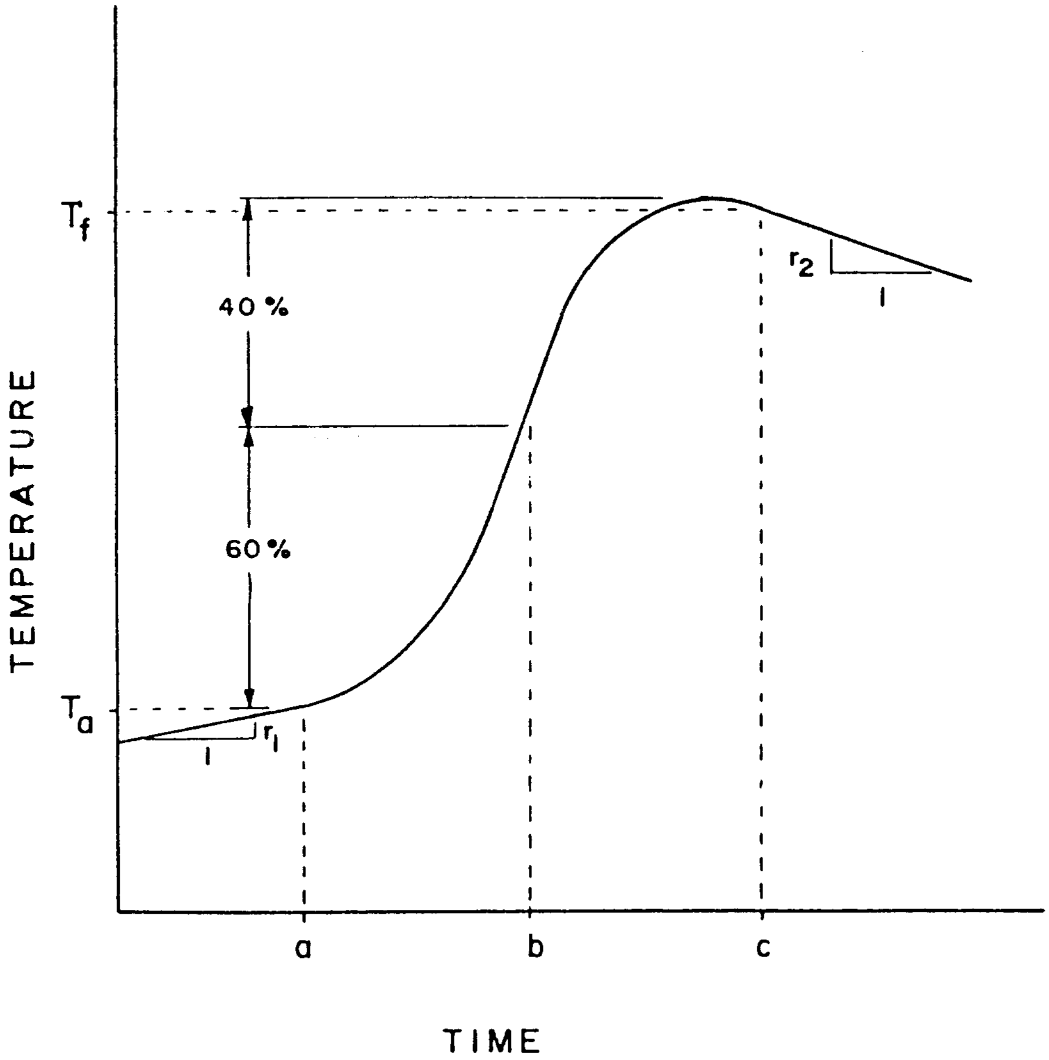

Exhibit IV.8. Example Temperature/ Time Relationship.

In Parr bomb calorimeter the heat produced from the combustion of fuel is absorbed by a water bath; however, not only the water but all other parts of the apparatus absorb heat. It is convenient for calculation of calorific values to express the heat absorbing capacity of the solid parts of a calorimeter in terms of that of an equivalent amount of water. That is the calorimeter will absorb the same amount of heat as the equivalent amount of water and it is very convenient to add this quantity to the amount of water present to give the total equivalent weight of water. The total equivalent weight of water which multiplied by the correct temperature rise will give the calorific value of the fuel.

. The gross calorific value of the samples is then calculated as:

$$GCV = [(E \times T) - e_1 - e_2 - e_3] / g \qquad (3)$$

where:

GCV = gross calorific value, Btu/lb.

E = energy equivalent, Btu/ ^{0}F.

= 1 Btu/lb ^{0}F x W

W = water equivalent of the bomb, 2442 g for the Parr bomb used in this study, lb.

T = corrected temperature rise, ^{0}F.

e_1 = correction for the heat of formation of HNO_3, Btu

e_2 = correction for heat of combustion of firing wire, Btu

e_3 = correction for the heat of formation of H_2SO_4, Btu

g = weight of sample pellet, lb.

It should be noted that since the thermochemical corrections mentioned in Equations (1) and (3) are quite small, they do not appreciably affect the accuracy of test values, as previously discussed. The equation used for all calorific value calculations is therefore:

$$GCV = (E \times T) / g \tag{4}$$

CHAPTER V

RESULTS

In this section, the results of calorimetric tests of the mixed paper waste pellets are discussed. Calorific values of individual types of mixed paper waste were determined separately, as were calorific values of a sample of mixed paper waste.

Mixed paper waste was divided into eleven categories as previously described. These eleven different types of mixed paper waste components (newspaper, boxboard, white office paper, colored office paper, envelopes including plastic windows, glue, and stickers, treated paper such as NCR paper, beverage and waxed milk boxes, glossy paper, kraft, cardboard, and tissue) were examined for their calorific values. At least four calorimetric tests were run for each sample. The temperature/time data for each test is given in Exhibits A.2 to A.14 in Appendix. Typical temperature profiles of the mixed paper waste and its components are given in Exhibits V.1 through V.12.

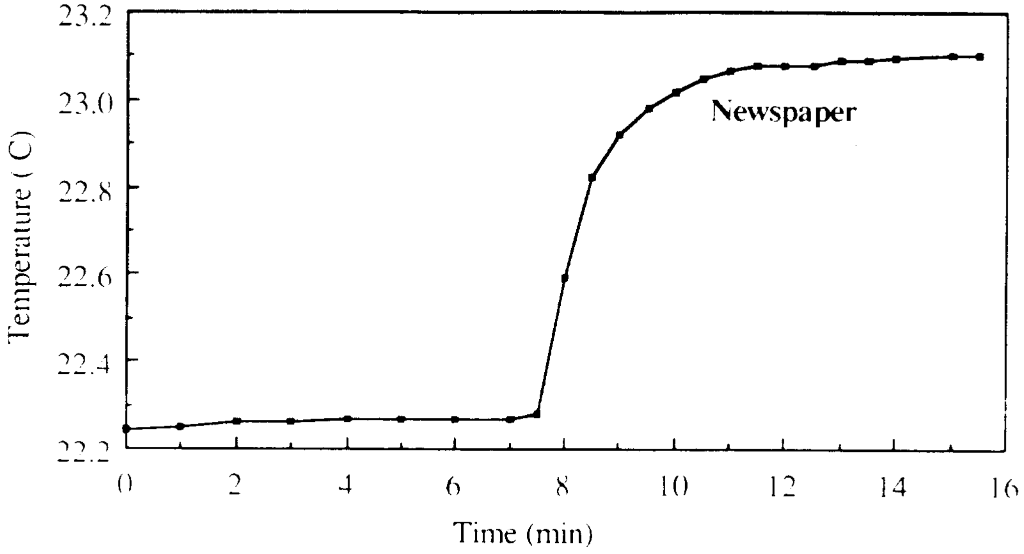

Exhibit V.1 Typical Temperature Change in the Calorimeter due to the Combustion of Newspaper.

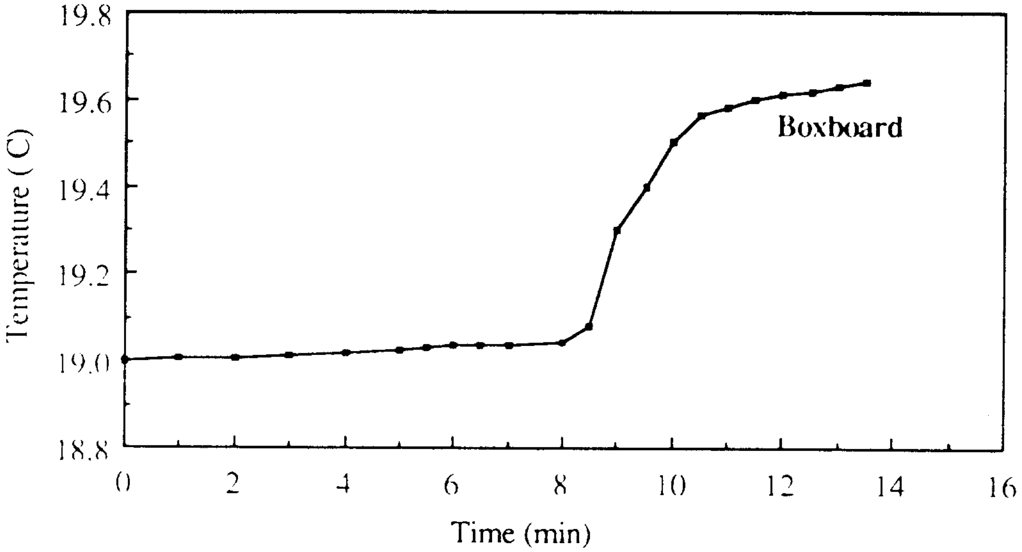

Exhibit V.2 Typical Temperature Change in the Calorimeter due to the Combustion of Boxboard.

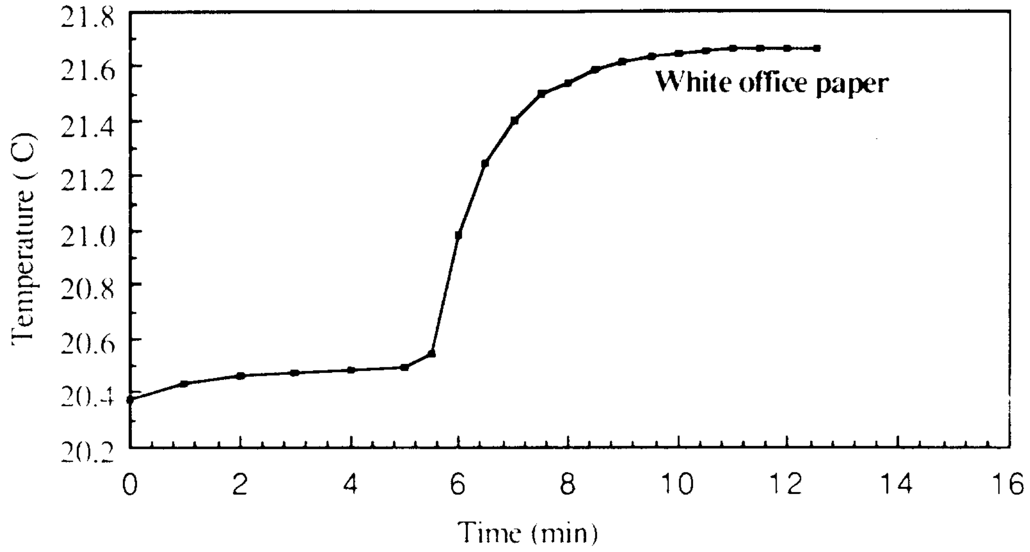

Exhibit V.3 Typical Temperature Change in the Calorimeter due to the Combustion of White Office Paper.

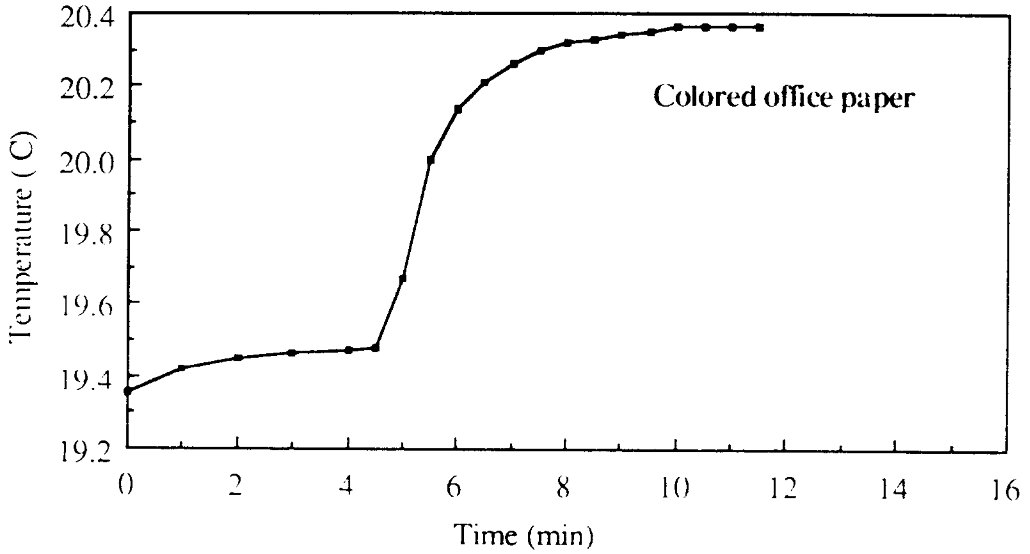

Exhibit V.4 Typical Temperature Change in the Calorimeter due to the Combustion of Colored Office Paper.

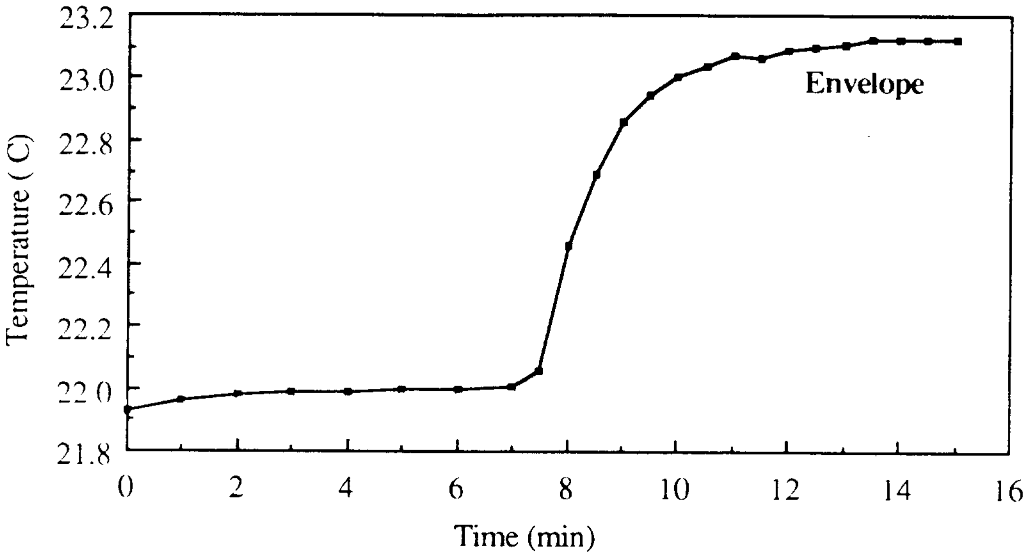

Exhibit V.5 Typical Temperature Change in the Calorimeter due to the Combustion of Envelopes.

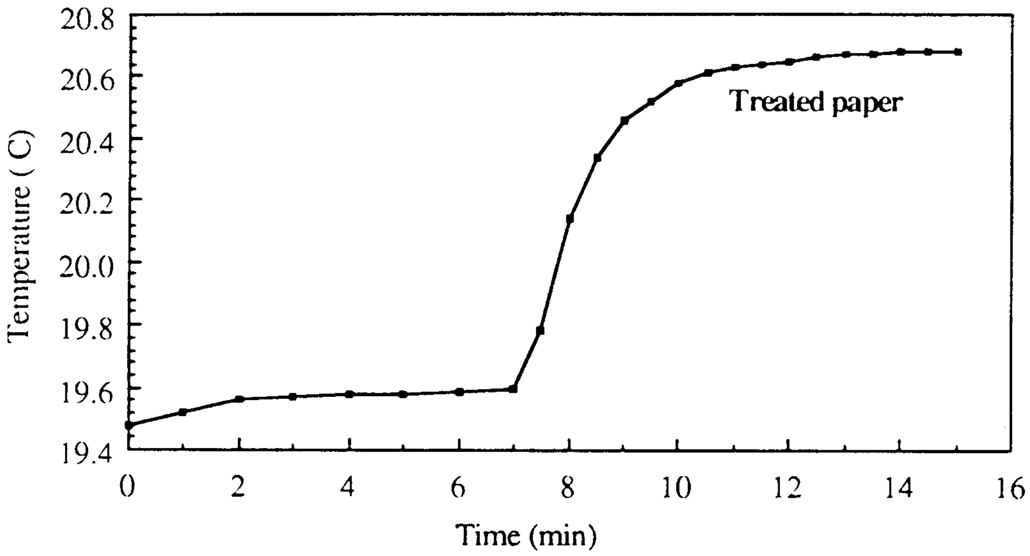

Exhibit V.6 Typical Temperature Change in the Calorimeter due to the Combustion of Treated Paper (NCR Paper).

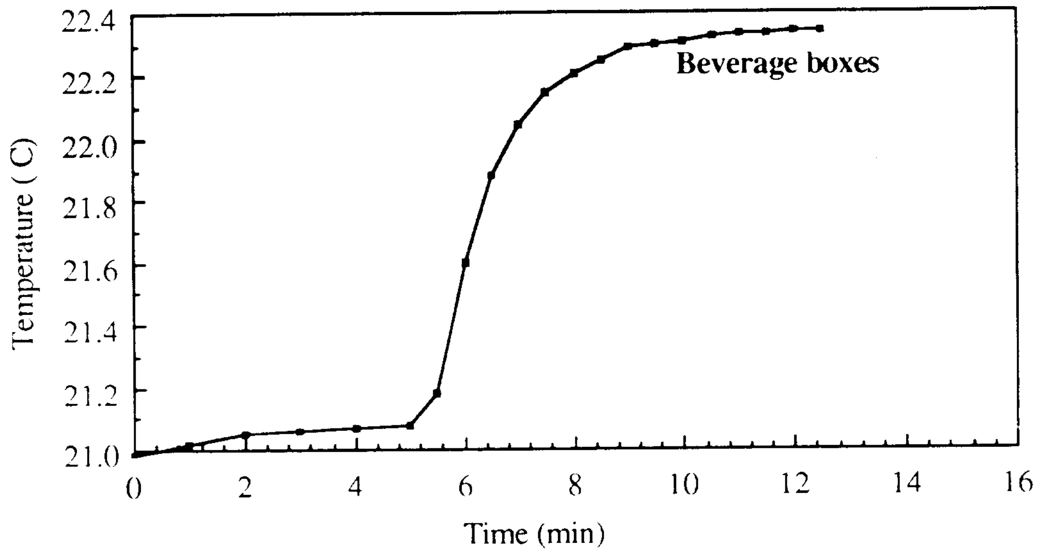

Exhibit V.7 Typical Temperature Change in the Calorimeter due to the Combustion of Beverage and Milk Boxes.

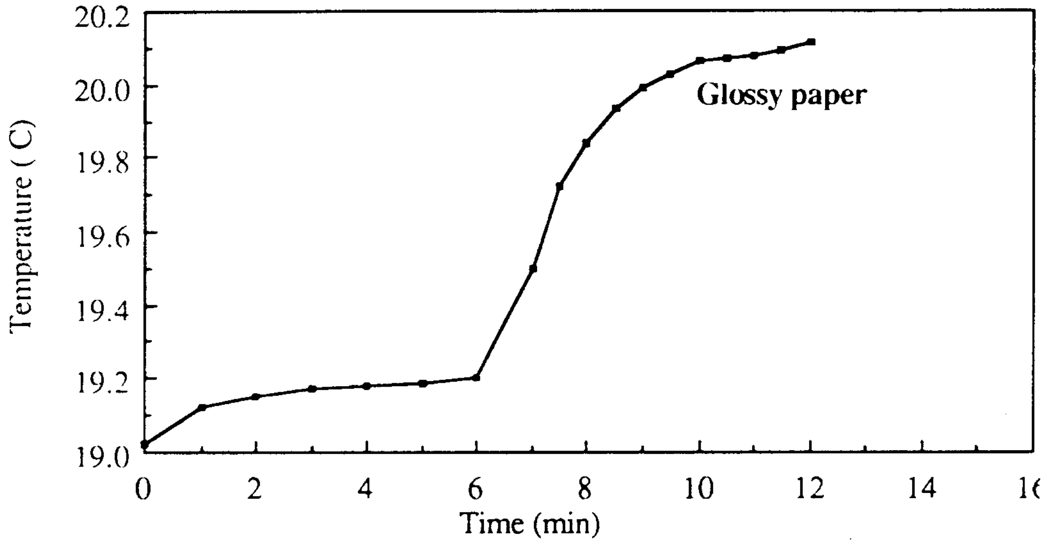

Exhibit V.8 Typical Temperature Change in the Calorimeter due to the Combustion of Glossy Paper.

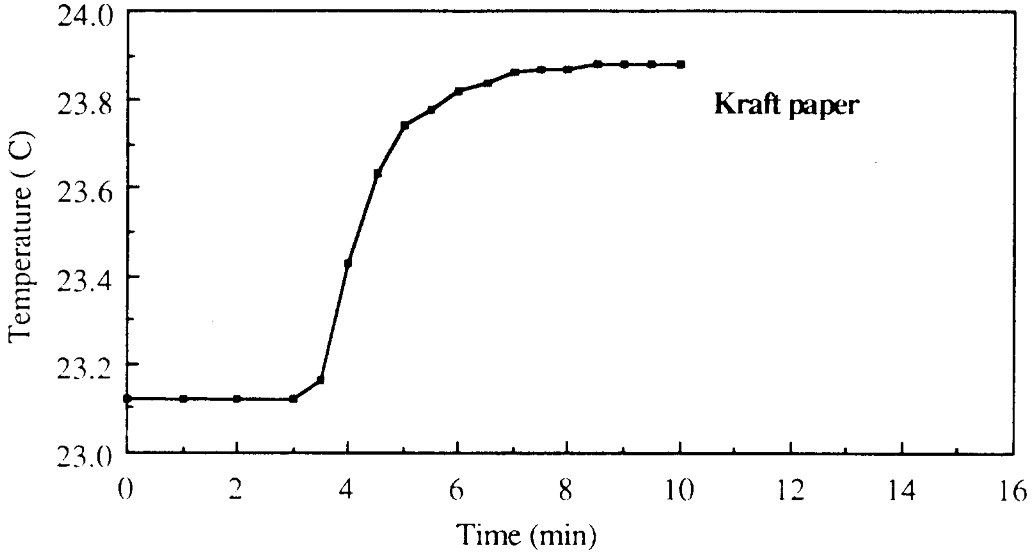

Exhibit V.9 Typical Temperature Change in the Calorimeter due to the Combustion of Kraft.

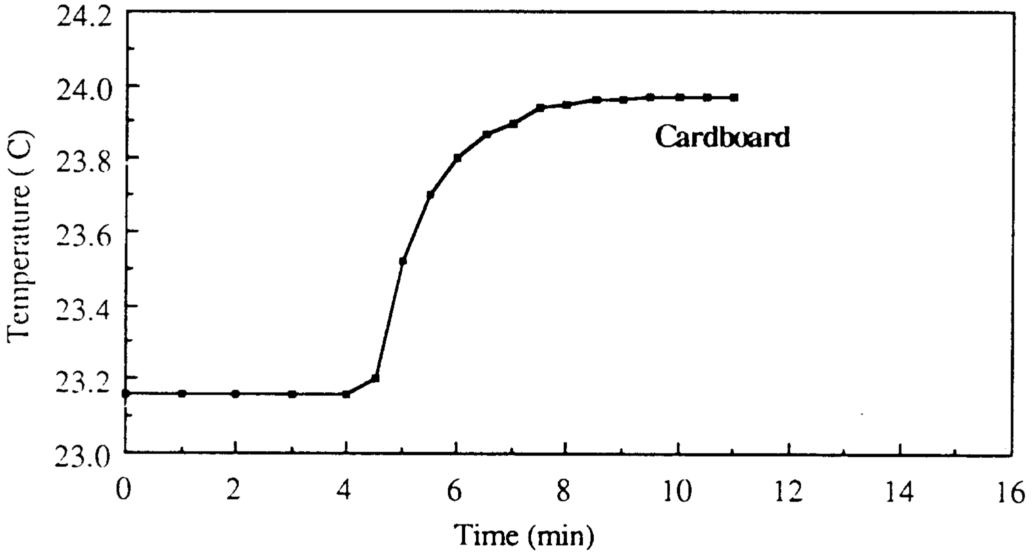

Exhibit V.10 Typical Temperature Change in the Calorimeter due to the Combustion of Cardboard.

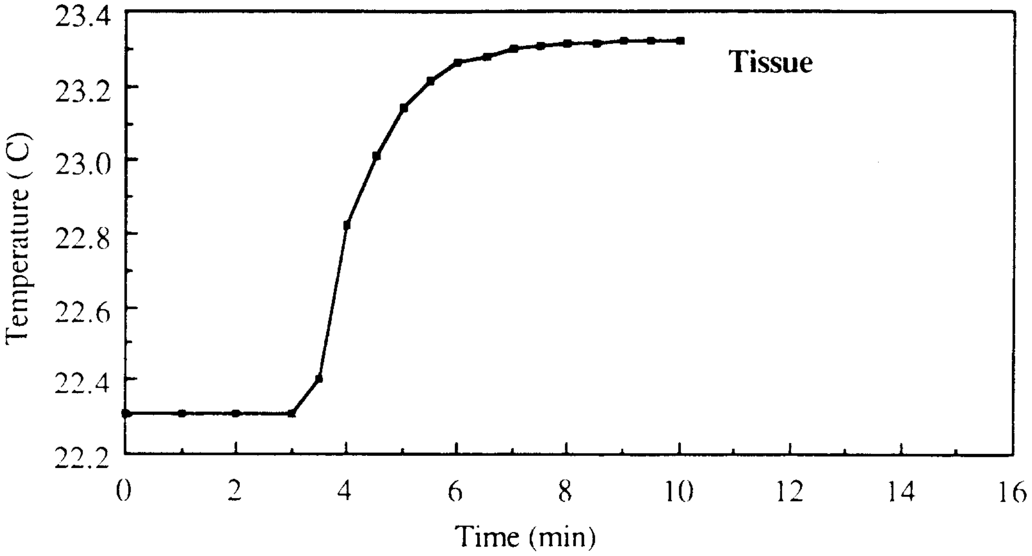

Exhibit V.11 Typical Temperature Change in the Calorimeter due to the Combustion of Tissue Paper.

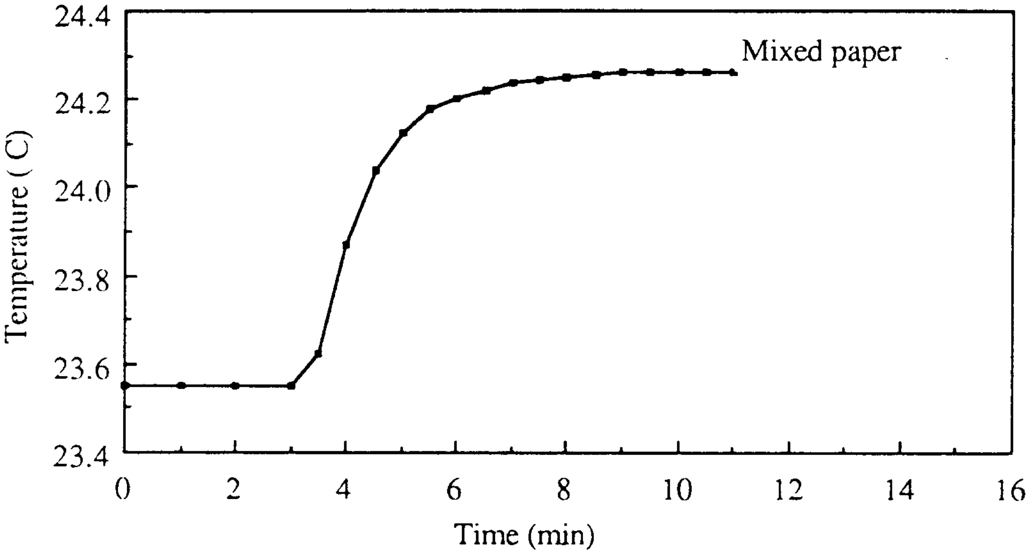

Exhibit V.12 Typical Temperature Change in the Calorimeter due to the Combustion of Mixed Paper Waste

Exhibit V.13 shows the summary of the experimental results. A complete compilation of the results is shown in Exhibit A.1 in the Appendix.

TYPE OF PAPER	GROSS CALORIFIC VALUE (Btu/lb)	
	RANGE	MEAN
Newspaper	7294 - 7803	7540
Cardboard	6867 - 6921	6907
Kraft	6767 - 7074	6897
Beverage and Milk Boxes	6479 - 7147	6855
Boxboard	6666 - 6782	6703
Tissue	6166 - 6698	6518
Colored Office Paper	6195 -6547	6348
White Office Paper	6110 -6240	6234
Envelopes	6024 - 6350	6160
Treated Paper (NCR)	5622 - 6380	5983
Glossy Paper	5228 - 5479	5370
MIXED	6002 - 6682	6447

Exhibit V.13 Summary of Calorific Values of Paper Waste.

According to the results obtained from the experimental determination of calorific values of paper samples, the highest calorific value was obtained for newspaper. The calorific value of newspaper was found to be in the range of 7297 - 7803 Btu/lb with the mean value of 7540 Btu/lb. The lowest calorific value, on the other hand is obtained for glossy paper. Glossy paper has a calorific value in the range of 5228 - 5479 Btu/lb. Its mean calorific value is 5370 Btu/lb. Calorific value of mixed paper waste is in the range of 6002 - 6682 Btu/lb with the mean value of 6447 Btu/lb. Glossy papers contain a coating (filler) material that improve the brightness, the opacity, the smoothness and printing quality of the surface. Clay is the most common white coating pigment and it has an inorganic structure. The pigments of greatest importance are kaolin clay, attapulgite, bentonite (Montmorillonite) clays, and calcium carbonate. Titanium dioxide, satin white, aluminum trihydrate, and composite pigments are also used to contribute high opacity and brightness (Browning 1977, Britt 1970). Usual combinations of pigments in coatings are as follows:

- clay 50 to 85 %, carbonate 50 to 15 %.
- clay 65 to 90 %, titanium dioxide 35 to 10 %.
- clay 65 to 90 %, titanium dioxide 20 to 5 %, aluminum trihydrate 15 to 5 %.
- clay 75 to 90 %, satin white 25 to 10 %.

Kaolin clay, the most widely used coating material (filler), consists of an inorganic structure based on a single sheet of silica tetrahedrons combined with a single sheet of alumina octahedrons (Craig1987, Bowles 1984, Lambe and Whitman 1979). Being inorganic, kaolin clay does not combust, and the chemicals do not oxidize. Hence, the glossy papers containing clay pigments give lower calorific (energy) values than other types of papers.

By comparison the calorific value of alternative fuels are listed in Exhibit V.14

(Johnson and Auth 1951; Spiers 1962; IPS 1975; Cheremisinoff 1980; Clemens at al. 1981). Since the average calorific value of **mixed paper waste** is in the range of 6002 - 6682 Btu/lb, it compares favorable to wood and brown coal.

FUEL	AVERAGE GCV (Btu/lb)
Wood	4000 - 9000
Peat	7000 - 10000
Brown Coal	5000 - 9000
Bituminous Coal	12000 - 15500
Anthracite Coal	11500 - 15000
Fuel Oil	17000 - 21000
Natural Gas	19000 - 23000

Exhibit V.14. Typical Calorific Values for Alternative Fuels

The expected calorific value of any unknown sample of mixed paper can be calculated using the calorific values of each of the eleven different types of paper and the weight fraction of each in a mixed paper sample. By adding the calorific values, Btu/lb, which are multiplied by the sample weight, and dividing the total value by the total weight of paper samples, the calorific value of any mixture of **mixed paper waste** can be estimated without conducting calorimetric experiments.

In order to test this hypothesis, weighed samples were taken from each group and mixed thoroughly to simulate a mixed paper sample. The calorific value of this mixture was determined and compared to the estimated value.

The calorific value of the mixed paper waste mixture, obtained by calculating the weighed calorific value of eleven components, was found to be 6504 Btu/lb. The calculations are shown in Exhibit V.15.

The eleven components of mixed paper waste can also be reduced to four different groups according to the ranges established for the individual calorific values of these eleven groups. These four groups can be classified as:

- Group 1: Newspaper.
- Group 2: Boxboard, beverage and milk boxes, kraft, cardboard.
- Group 3: White and colored office papers, envelopes, treated paper, tissue.
- Group 4: Glossy paper.

The mean calorific value of mixed paper waste estimated from the individual calorific values and weight fractions of the four groups is found to be 6500 Btu/lb. Calculations are shown on Exhibit 16. This value is nearly the same value of 6504 Btu/lb that estimated from eleven different mixed paper waste components. This means that it is possible to get the same result by separating mixed paper waste into four categories instead of eleven. This is easier and cheaper without sacrificing accuracy.

The calorific values 6500 Btu/lb and 6504 Btu/lb, obtained from four and eleven different paper categories respectively, closely matches the mean calorific value of 6447 Btu/lb that was obtained by averaging the results of seven calorimetric tests. The calculations are shown in Exhibit V.14. This means that it should be possible to calculate the amount of energy obtainable from a known amount of mixed paper waste without doing any calorimetric determinations and simply using the categories and their individual calorific values.

TYPE OF PAPER	GCV) (Btu/lb)	Weight Fraction of Type of Paper in Mixed Sample	
	a	b	a x b
Newspaper	7540	0.091	686
Boxboard	6703	0.091	610
White Office Paper	6234	0.091	567
Colored Office Paper	6348	0.091	577
Envelopes	6160	0.091	560
Treated Paper (NCR)	5983	0.091	544
Beverage and Milk Boxes	6855	0.091	624
Glossy Paper	5370	0.091	488
Kraft	6897	0.091	627
Cardboard	6907	0.091	628
Tissue	6518	0.091	593
		Σ = 1.000	Σ = 6504

Exhibit V.15. Estimation of the Calorific Value of an Unknown Sample of Mixed Paper Waste

TYPE OF PAPER	GCV (Btu/lb)	Weight Fraction of Type of Paper in Mixed Sample	
	a	b	a x b
Group 1	7540	0.25	1885
Group 2	6840	0.25	1710
Group 3	6248	0.25	1562
Group 4	5370	0.25	1343
		$\Sigma = 1.00$	$\Sigma = 6500$

Group 1: Newspaper.

Group 2: Boxboard, beverage and milk boxes, kraft, cardboard.

Group 3: White and colored office papers, envelopes, treated paper, tissue.

Group 4: Glossy paper.

Exhibit V.16. Calorific Value Estimation of Mixed Paper Waste by using Four Different Paper Groups.

CHAPTER VI

CONCLUSIONS

- Incineration of mixed paper waste with the production of steam for heating or electric power production is an accepted method of energy recovery.

- Mixed paper waste can be categorized into eleven easily identifiable types of papers. These eleven components of mixed paper waste can be reduced to four different paper groups according to the ranges established for the individual calorific values of these eleven components.

- The calorific value of mixed paper waste is in the range of 6002 - 6682 Btu/lb with the mean value of 6447 Btu/lb.

- Of the eleven components, newspaper has the highest calorific value in the range of 7297 - 7803 Btu/lb while glossy paper containing kaolin clay has the lowest calorific value in the range of 5228 - 5479 Btu/lb. The mean calorific values of newspaper and glossy paper is 7540 Btu/lb and 5370 Btu/lb respectively.

- The calorific value of mixed paper waste estimated from the individual calorific values and weight fractions of the eleven components is found to be 6504 Btu/lb which closely matches the value determined experimentally as 6447 Btu/lb.

- The calorific value of mixed paper waste estimated by separating the paper into four groups and calculating the weighed calorific value of these groups is found to be 6500 Btu/lb. This value is nearly the same value of 6504 Btu/lb that estimated from the eleven components. It is then possible to obtain same result by separating mixed paper waste into four categories. The value 6500 Btu/lb also closely matches the the value determined experimentally as 6447 Btu/lb.

- Since the calorific value of mixed paper waste estimated from individual calorific values of its components closely matches the calorific value determined experimentally, it is concluded that the quantity of energy obtainable from a known amount and composition of mixed paper waste can be estimated without conducting calorimetric experiments.

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APPENDIX

Type of paper	Gross Calorific Value (Btu / lb)			
	I	II	III	IV
Newspaper	7725	7297	7335	7803
Boxboard	6782	6666	6676	6689
White Office	6240	6335	6110	6250
Colored Office	6195	6278	6517	6400
Envelope	6024	6066	6350	6200
Treated	6380	5920	5622	6008
Beverage Box	6897	6897	7147	6479
Glossy	5228	5444	5328	5479
Kraft	6896	6850	7074	6767
Cardboard	6887	6867	6921	6951
Tissue	6602	6605	6166	6698
Mixed Paper I	6513	6334	5479	6002
Mixed Paper II	6682	6459	6593	6549

* The value 5479 Btu/lb is extremely lower than the calorific value of mixed paper waste obtained from different tests due to some experimental errors. Since it is not a representative value, it is omitted during the mean calorific value calculation of the mixed waste paper.

Exhibit A.1 The Complete Compilation of the Calorific Value Results