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Characterization Of Msw As A Feedstock Of Thermochemical Conversion

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CHARACTERIZATION OF MSW AS A FEEDSTOCK OF THERMOCHEMICAL CONVERSION

by

Harith Kumar Rojanala

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in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Department: Chemical and Bioengineering
Major: Chemical Engineering
Major Professor: Dr. Abolghasem Shahbazi

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This is to certify that the Master's Thesis of

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has met the thesis requirements of
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DEDICATION

I would like to dedicate this thesis to all the people that I’m connected to, whether it be an enemy or a friend. Most of all, to my parents and all my attaiahs for teaching me ways of how to live and love life.

BIOGRAPHICAL SKETCH

Harith Kumar Rojanala was born on December 12, 1986 in Hyderabad, Andhra Pradesh, India. In May 2007, He received his bachelor's degree in Chemical Engineering from Jawaharlal Nehru Technological University, Hyderabad, India. He joined the Master's program in Chemical Engineering in North Carolina Agricultural and Technical State University in the spring of 2009. He has received a Six Sigma Green belt Certificate from the North Carolina Agricultural and Technical State University, Greensboro, North Carolina in 2011. Mr. Rojanala has been involved on the research of biomass gasification and MSW characterization and also presented a poster on his research at the American Society of Agricultural and Biological Engineers (ASABE) of which he is a member. He is a candidate for the Master of Science degree in Chemical Engineering.

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NOMENCLATURE

TG → Thermo Gravimetric

DTG → Differential Thermo Gravimetric

DSC → Differential Scanning Calorimetry

EPA → Environmental Protection Agency

ASTM → American Society for the Testing of Materials

MSW → Municipal Solid Waste

RDF → Refuse-Derived Fuel

TGA → Thermo Gravimetric Analyzer

WTE → Waste-To-Energy

A → Pre-exponential or frequency factor (min^{-1})

E → Activation energy of the decomposition reaction ($\mathrm{kJ\ mol}^{-1)}$)

n → Order of reaction (-)

R → Universal gas constant ($\mathrm{kJ\ mol}^{-1}\mathrm{K}^{-1}$)

T → Absolute temperature (K)

t → Time (min)

TR → Temperature range (°C)

w_i → Weight of sample at time t (kg)

w_f → Weight of residue at the end of the reaction (kg)

w_0 → Initial weight of sample (kg)

X → Weight of sample undergoing reaction (kg)

$C_{p,b}$ → Specific heat capacity of biomass (J/kg K)

$C_{p,ch}$ → Specific heat capacity of char (J/kg K)

$C_{p,cr}$ → Specific heat capacity of crucible (J/kg K)

$C_{p,s}$ → Specific heat capacity of sample during TG–DSC experiment (J/kg K)

H_p → Heat flow caused by reaction heat of biomass pyrolysis (J/kg s)

M_b → Mass of biomass (kg)

m_{ch} → Mass of char (kg)

mch → Mass of crucible (kg)

m_s → Mass of sample during TG–DSC experiment (kg)

$m_{s,0}$ → Mass of sample at beginning of TG–DSC experiment (kg)

Q_p → Reaction heat of biomass pyrolysis (J)

Q → Caloric requirement of biomass pyrolysis (J)

T → Temperature of sample and crucible (K)

ΔT → Temperature change during pyrolysis (K)

t → Time of TG–DSC experiment run (s)

t_s → Time of unstable segment TG–DSC experiment run (s) about 60 s in each run

ABSTRACT

Rojanala, Harith Kumar. CHARACTERIZATION OF MSW AS A FEEDSTOCK OF THERMOCHEMICAL CONVERSION **(Major Professor: Dr. Abolghasem Shahbazi)**, North Carolina Agricultural and Technical State University

The management of municipal solid waste (MSW) has become a significant environmental problem, especially in fast-growing cities. Hence the thermo chemical conversion of Municipal solid waste (MSW) has been proven as an attractive method of waste management to recover energy from MSW. This would minimize its environmental impact and decrease disposal costs. In this thesis, the MSW is characterized to determine the feasibility for thermo chemical conversion. The samples are collected from different MSW transfer locations across North Carolina. Selected physical and chemical properties such as the moisture content, heating value, elemental composition and thermal degradation characteristics of the samples are measured to evaluate their feasibility for thermo chemical conversion. The moisture content in the samples was determined at 105 °C and it ranged between 45-55 %. Proximate analyses and Ultimate analysis are conducted to determine the contents of volatile, fixed carbon, ash and elemental composition of the samples. A TGA is used to determine the contents of volatiles under nitrogen for pyrolysis, air for combustion and carbon dioxide for gasification. The temperature ranged from 25 °C to 900 °C at a gas flow rate of 20 ml/min. It is observed that the maximum weight loss rates of samples increase obviously with the increase of heating rate. An adiabatic oxygen bomb calorimeter is used to determine the energy contents of the samples. The composition of Carbon, hydrogen, nitrogen and oxygen are measured by an elemental analyzer under combustion of the materials at 990 °C.

CHAPTER 1

Introduction

1.1 General Information

Municipal solid waste (MSW) is defined as household waste, commercial solid waste, nonhazardous sludge, conditionally exempt, small quantity hazardous waste, and industrial solid waste. It includes food waste, residential rubbish, commercial and industrial wastes, and construction and demolition debris. Tchobanoglous et al. [1] lists 10 main sources of solid wastes: residential, commercial, institutional, industrial (non-process wastes), construction and demolition, municipal solid waste (MSW), municipal services, treatment facilities, industrial and agricultural. Tchobanoglous et al. specify that MSW “is normally assumed to include all the wastes generated in a community, with the exception of waste generated by municipal services, treatment plants, and industrial and agricultural processes”. In other words, the term MSW covers the waste produced by households and commercial activities and small non-process industries located in urban areas. The US Environmental Protection Agency (EPA) simply defines MSW as “more commonly known as trash or garbage – consists of everyday items thrown away by US residents, businesses and institutions”. The importance of MSW originated from other sources than households is dependent on the degree to which waste from these sources is performed by municipal waste collection and co-collected with household waste. MSW is a major issue in today’s society. MSW is generated in enormous amounts, posing a threat to the environment and to public health. To make things worse, MSW generation continues to increase. Many countries across are confronted with the problem of how to discard large quantities of municipal solid waste (MSW). Municipal solid waste (MSW) is a domestic energy resource with the potential to provide a significant amount of energy to meet US liquid fuel requirements. Currently, about 220 million tons per year or 0.8 tons of MSW per capita are generated in the US. The composition of these wastes can vary from one community to the next, but the overall differences are not substantial.

Currently, landfills are the primary means of MSW disposal taking in approximately 60% of the residential garbage generated in the US [2]. However, rising landfill tipping fees and their proven negative environmental impacts [3], have led to the search for cleaner and less costly alternatives for municipal waste disposal. According to the United States Environmental Protection Agency (EPA), the annual national MSW production in 2006 totaled more than 251 MM short tons, which equates to greater than 4.5 lbs/person/day. Of this total, about 45% is recovered via recycling, composting, and energy production. This leaves approximately 138 MM short tons of unutilized MSW, which has about 1.4×10^{15} Btu (1.4 quadrillion Btu) fuel value associated with it. High temperature energy recovery from MSW, known as waste-to-energy (WTE), is one such alternative. Waste-to-Energy reduces the amount of materials sent to landfills, can prevent air/water contamination, improves recycling rates and lessens the dependence on fossil fuels for power generation. The two most commercially viable forms of large scale WTE are pyrolysis, combustion and gasification. Combustion is a well-established practice, while gasification is still in its early stages as a large-scale commercial industry.

Many researchers have termed MSW is a negatively priced, abundant and essentially renewable feedstock. The heat content of raw MSW depends on the concentration of combustible organic materials in the waste and its moisture content. On the average, raw MSW has a heating value of roughly 13,000 kJ/kg or about half that of bituminous coal [20]. The moisture content of raw MSW is 20% on average. In the USA, the situation is very serious with an increase of 188% in between 1960 and 2007 from 88 to 254 million tons/year (USEPA, 2008). Around the world, waste generation is very variable. In terms of kg per capita and year, it ranges from 210 in Central Asia and Central America to 520 in Southern Europe, 640 in Northern Europe and 650 in the USA.

The potential for MSW recycling is very high, both in terms of biodegradable and inert materials. However, most of the MSW is still disposed in landfill. In North America it is around 58% [4]. Landfills are waste management structures which present high risks to the environment, with the potential to pollute soils, water and air [5,6].The biodegradable fraction of MSW, mainly composed by food waste, paper and yard waste, is one of the most problematic when disposed to landfill, because its degradation generates high quantities of methane and leachate [7-10]. This problem is aggravated by the fact that this is the biggest fraction of MSW. It accounts for around 58% in the USA (USEPA, 2008). These waste management practices represent a disturbance to the natural functioning of the carbon cycle. This cycle is partially interrupted, because carbon is being stored, and its return to the ecosystems is being delayed. This represents one more negative factor to the already much destabilized carbon cycle. Thus, given its weight and polluting potential, the biodegradable fraction of MSW is an important matter of concern.

1.2. The Carbon Cycle

As previously mentioned, MSW biodegradable fraction has three main components - food waste, paper and yard waste – which, as a whole, usually represent more than a half of the total. These components are thus a major issue in MSW management and, as also mentioned, a large percentage of these components, after being utilized by man and becoming a residue, is disposed in landfills. In reality, the whole process is one of concentration: food waste, paper and yard waste are actually produced in wide land extensions but, after becoming waste, these are concentrated in landfills. In their turn, landfills are waste management infrastructures specifically prepared to receive huge amounts of waste, and store it for extended time periods. In terms of the biodegradable components, and although part of the organic matter is released mainly in the form of carbon dioxide and methane, a significant part of it is retained in the landfills. These waste management practices represent a disturbance to the natural functioning of the carbon cycle. This cycle is partially interrupted, because carbon is being stored, and its return to the ecosystems is being delayed. This represents one more negative factor to the already much destabilized carbon cycle [11].

1.3. Desertification of Soils

In line with the rationale of the previous section, and in addition to the fact that organic matter has been harvested from wide land extensions, some of these soils have been subject to highly intensive agricultural practices. This has been taken to an extent that is causing the depletion of organic matter in the soils, potentiating erosion and desertification [11-16]. Other soils are naturally poor in organic matter. This problem may be partly solved by returning organic matter to soils in the form of compost, provided this is not a vector of contamination by substances like heavy metals or organic pollutants. Compost, being a source of stabilized organic matter and microorganisms, has the ability to contribute to the health of soils and combat erosion and desertification problems [16, 17]. Portuguese soils, in this respect, are generally poor in organic matter, and hence any measures that are taken to mitigate this problem are urgent. It was estimated [18] that the increase in the organic matter content up to 1.85 % in deficient Portuguese soils would require the application of more than 116 million tons (dry matter) of MSW compost. This is a huge number, which illustrates well the organic matter requirement of a large part of Portuguese soils.

Municipal solid waste (MSW) has a negative cost at present because communities, businesses, and institutions pay a waste management facility to dispose of their refuse. This characteristic makes MSW a potentially interesting feedstock for fuels production. Hence the thermo chemical conversion of Municipal solid waste (MSW) has been proven as an attractive method of waste management to recover energy from MSW. This would minimize its environmental impact and decrease disposal costs.

CHAPTER 2

Literature Review

In this section, the historical background of municipal solid waste (MSW) management options and the possibility and essentiality of producing energy from municipal solid wastes were thoroughly reviewed. It was understood that depending on the different technical, socio-economic and environmental factors of the situation in question, one or combination of some treatment techniques could be integrated to alleviate the environmental problems caused by municipal solid wastes and to make use of resources within it.

2.1. Overview

2.1.1. What is MSW?

MSW is defined by the U.S. Environmental Protection Agency (EPA) as solid wastes that are "durable goods, nondurable goods, containers and packaging, food waste, yard wastes, and miscellaneous inorganic wastes from residential, commercial, institutional, and industrial sources” (U.S. Environmental Protection Agency, Office of Solid Waste Management Programs). This includes household trash like appliances, clothing, newspaper, etc. According to the EPA, municipal solid waste is only one of the several subcategories of wastes defined by Subtitle D of the Resource Conservation and Recovery Act (RCRA), which deals with the management of non-hazardous wastes. Agricultural, construction, and industrial wastes are not defined as MSW, but they are often discarded in the same disposal facilities along with MSW. Therefore, given the ambiguity of the EPA definition, resource assessments of MSW must be clear in defining what is included in the estimates. Municipal solid wastes characterized in the following Table 2.1 come from residential, commercial, institutional, or industrial sources.

Table 2.1. Sources of different waste and their example products

Sources and Examples	Example Products
Residential (single-and multi-family homes)	Newspapers, clothing, disposable tableware, food packaging, cans and bottles, food scraps, yard trimmings
Commercial (office buildings, retail and wholesale establishments, restaurants)	Corrugated boxes, food scraps, office papers, disposable tableware, paper napkins, yard trimmings
Institutional (schools, libraries, hospitals, prisons)	Cafeteria and restroom trash can wastes, office papers, classroom wastes, yard trimmings
Industrial (packaging and administrative; not process wastes)	Corrugated boxes, plastic film, wood pallets, Lunchroom wastes, office papers.

Since MSW resource estimates and composition studies are mostly taken from actual landfills, incinerators, and recycling centers, they include solid wastes that are not considered MSW by the EPA definition. To be consistent with most of the available data, MSW is defined in this thesis as the solid wastes that are handled in MSW processing facilities.

2.1.2. Definition of Terms.

Some frequently used terms associated with MSW are generation, recovery and disposal. *Generation* is defined as the MSW that is produced before any of it is recovered or combusted. Generated MSW is also referred to as "gross discards" in past literature. *Recovery* is defined as the MSW that is recovered for recycling or composting. Recovered material does not equal the amount of recycled and composted material because recovery processes usually produce some residues. *Disposed* MSW, also referred to as the "net discards," is the MSW that is not recovered, which is essentially all the MSW that goes to the landfill or incinerator. Incinerating MSW to generate process steam or electricity is not considered recovery (U.S. EPA, 1992).

2.2. MSW Composition and Disposal Estimates

2.2.1. Methods of Estimating MSW.

Two primary methodologies are reported in the literature for estimating the quantities and composition of the MSW generated, recovered, and disposed. The first methodology is based on taking samples, sorting and weighing the various components of MSW, which provides an estimate of the MSW composition. Records of the weigh stations at MSW disposal facilities gives the total weight of waste disposed. This methodology is good for site-specific cases and is necessary for a local waste management projects. Many samples, however, are necessary to prevent skewed results. For estimates on a national or state-wide scale, it would be very costly to take consistent samples from various places around the country over an entire year and gather weigh station data from every MSW disposal facility.

The second method is known as the material flows methodology, which has been used and developed by the EPA and Franklin Associates, Ltd. for over 20 years to estimate national MSW disposal trends (US EPA, 1992). This method uses a model based on production and end use data from the Department of Commerce, trade and manufacturing associations, and elsewhere. After adjusting for product lifetimes, imports and exports, and other factors, the model determines the total quantity of MSW generated and the average composition for a given year. MSW recovery and disposal are estimated on a material-by-'Illaterial and product-'by'-product basis and aggregated for total findings. The model results have been corroborated with various sampling studies and have shown close agreement (US EPA, 1992).

2.2.2. Composition of Feedstock.

The MSW combustible fraction mainly consists of cellulosic matter (paper, wood and wet organic fraction) and different plastics. The cellulosic matter has been divided into three different components, namely hemicellulose, cellulose and lignin, which all have different thermal decomposition characteristics. The plastic fraction constitutes of several different types with varying composition. The most common plastic types are the pure hydrocarbon plastics such as high density polyethylene (HDPE), low density polyethylene (LDPE), polystyrene (PS) and polypropylene (PP) and the chlorine containing polyvinylchloride (PVC).

On average, a pound of MSW contains an average heating value of 5,100 BTUs. However, in actuality; the amount of BTUs that can be extracted from a waste stream is dependent on the composition of the waste. MSW is a heterogeneous mixture of materials from diverse sources.

Depending on the composition of the mixture and whether and how it is separated, it will have varying biogenic content and heat value. Although there are great quantities of MSW available, only the biogenic portion (e.g., wood, yard trimmings, paper, and food wastes) would qualify as a renewable fuel source according to the amended Renewable Fuel Standard (RFS2) [19] . Biogenic wastes will vary in composition (i.e., volumes and sizes, energy, moisture, and chemical content). These characteristics will determine the energy input products. Thorough mixing of the refuse can alleviate this local irregularity, and is practiced in modern incinerators to make the MSW feedstock more homogeneous.

2.3. MSW as an Energy Feedstock

MSW is a negatively priced, abundant and essentially a renewable feedstock. Currently, about 220 million tons per year or 0.8 tons of MSW per capita are generated in the US. The composition of these wastes can vary from one community to the next, but the overall differences are not substantial. The heat content of raw MSW depends on the concentration of combustible organic materials in the waste and its moisture content. On an average, raw MSW has a heating value of roughly 13,000 kJ/kg or about half that of bituminous coal [20]. While the moisture content of raw MSW is 20% on average

[21]. Moist food and yard wastes have the lowest heating value and are better suited for composting, rather than for combustion or gasification [22]. It has a negative cost at present because communities, businesses, and institutions pay a waste management facility to dispose of their refuse. This characteristic makes MSW a potentially interesting feedstock for fuels production. High temperature energy recovery through thermo chemical conversion of MSW has been proven as an attractive method of waste management to recover energy. High temperature energy recovery from MSW, known as waste to-energy (WTE), is one such alternative. The three most commercially viable forms of large scale WTE are:

> Gasification: Gasification is a thermochemical conversion process where a solid fuel is transformed into a gaseous fuel that mainly contains H_2, CO and CH_4 (Syn gas). This gas can be used for electricity and heat production.
>
> Combustion: Combustion means oxidation of the fuel for the production of heat at elevated temperatures without generating useful intermediate fuel gases, liquids, or solids. Incineration can be done at generation site.
>
> Pyrolysis: Pyrolysis is a thermochemical conversion process where a solid fuel is heated in the absence of an oxidizing agent (in an inert atmosphere).Two technologies exist and differ on the method of heat transfer: fast pyrolysis for production of bio-oil and slow pyrolysis for production of charcoal.

The following Table 2.2 tells about the generation and recovery of materials in MSW in 2009.

Table 2.2. Generation and recovery of materials in MSW, 2009 ((in millions of tons and percent of generation of each material)

Material	Weight Generated	Weight Recovered	Recovery As Percent Of Generation
Paper and paperboard	68.43	42.50	62.10
Glass	11.78	3.00	25.50
Metals			
Steel	15.62	5.23	33.5
Aluminum	3.40	0.69	20.3
Other nonferrous metals	1.89	1.30	68.80
Total metals	1.89	1.30	68.80
Plastics	29.83	2.12	7.1
Rubber and leather	7.49	1.07	14.30
Textiles	12.73	1.90	14.90
Wood	15.84	2.23	14.10
Other materials	4.64	1.23	26.50
Total materials in products	171.65	61.27	35.70
Food, others	34.29	0.85	2.50
Yard trimmings	33.20	19.90	59.90
Miscellaneous inorganic wastes	3.82	Negligible	Negligible
Total other wastes	71.31	20.75	29.10
Total municipal solid waste	242.96	82.02	33.8

The following Figure 2.1 gives us the information about the heating values of various fuels.

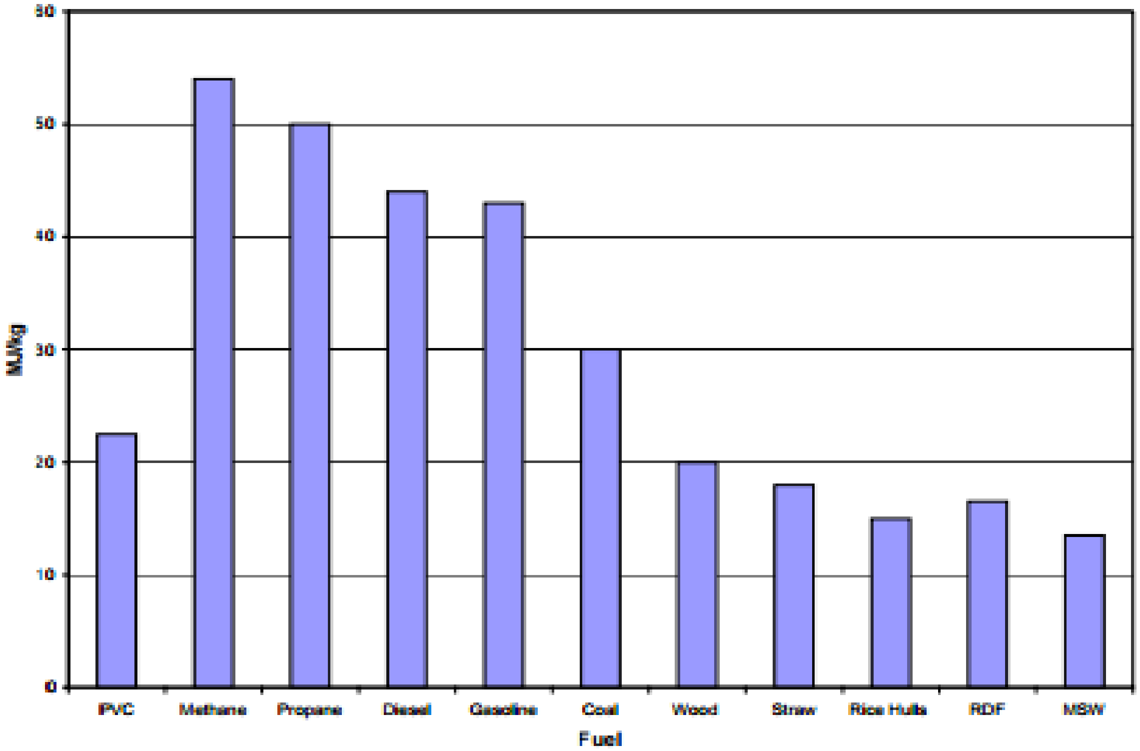

Figure 2.1. Heating values of various fuels (Source: ECN website 2002)

2.3.1. Gasification.

Gasification is a special case of pyrolysis where pyrolysis is the destructive decomposition of waste - using heat - into charcoal, oils, tars and a burnable gas. Oils and tars are produced when pyrolysis takes place at temperatures below 1,100 °F. In the case of gasification, all the solid wood waste is intrinsically converted into a combustible gas; there are no oil, tar or charcoal byproducts, unlike combustion where oxidation is substantially complete in one process. The burnable components of the gas are, typically, carbon monoxide, hydrogen and methane. A common name for this gas is "producer gas" or the “synthesis gas” or simply “syn gas”. The producer gas can be standardized in its quality and easier and more versatile to use than the original biomass in the power gas engines and gas turbines, or used as a feedstock in the production of liquid fuels.

Even though incineration of MSW with energy recovery, air emission control and proper waste disposal (ash, particles, waste water) is the overwhelmingly used thermal treatment, two other thermal techniques are promising and currently under development/early stage of industrial scale use and interesting alternatives for MSW or at least some selected/sorted MSW fractions. Gasification is one of them. Gasification is a thermochemical conversion process where a solid fuel is transformed into a gaseous fuel that mainly contains H_2, CO and CH_4. This gas can be used for electricity and heat production. The following equations summarize the principle of gasification; the produced gas then could be used for electricity and heat production through turbine, engine or boiler.

Gasification reactions:

$$C + H_2O + \text{heat} \rightarrow CO + H_2 \qquad (2.1)$$

$$C + CO_2 + \text{heat} \rightarrow 2CO \qquad (2.2)$$

The design principles of the gasifier unit are of three main kinds: fixed-bed gasifier (updraft or downdraft), fluidized bed gasifier (bubbling or circulating) and pressurized (fluidized bed) reactor which can be connected to gas turbine [23]. Waste can be used for gasification, it does not need specific sorting but it must be crushed and pelletized to increase the energy density. Produced gas composition depends on the biomass type and the gasifiying conditions (and the eventual presence of catalysts for reforming).

Gasification is of particular interest for the biomass fraction of MSW but also biomass residues and woody biomass after pre-treatment (drying, particle size, pelletizing) but mostly on a small to medium scale. However several constraints associated with gas conditioning make gasification difficult and still not very attractive: hot gas cleaning (particle and H_2S removal, etc), H_2/CO ratio (quality of gas), CH_4 and tar reforming and first and foremost efficient and economical removal of tar [18]. Association of a gasifier to a turbine is particularly difficult as a turbine is intricate and delicate machinery that require a very clean gas with low levels of contaminants (alkali, etc). Furthermore other technical problems are to be expected such as feeding difficulties, ash slagging and corrosion. Environmental aspects comparable to the one faced with combustion are also to be expected [24].

2.3.2. Combustion.

Combustion means oxidation of the fuel for the production of heat at elevated temperatures without generating useful intermediate fuel gases, liquids, or solids. Combustion normally employs excess oxidizer (air) to ensure maximum fuel conversion. Products of combustion processes include heat, oxidized species (e.g. CO_2, H_2O), products of incomplete combustion (e.g. CO and hydrocarbons), other reaction products (most as pollutants), and ash. Electricity can be produced using boilers and steam-driven engines and turbo generators, or through organic Rankine, Brayton (gas turbine), and combined cycles [25]. Separation of the hazardous substances before the process will be an issue in this method.

2.3.3. Pyrolysis.

Pyrolysis is a thermochemical conversion process where a solid fuel is heated in the absence of an oxidizing agent (in an inert atmosphere). It is the initial step in combustion and gasification processes and can therefore bring useful information about the primary products of these processes. Pyrolysis, as a conversion process, yields 3 products: (i) a gas mixture; (ii) a liquid (bio-oil/tar); (iii) a solid residue (char). The proportion and composition of the various fractions will depend on a variety of parameters. Each fraction may have a commercial potential in spite of some limitations/constraints. Pyrolysis is of particular interest for the biomass fraction of MSW. Two technologies exist and differ on the method of heat transfer: fast pyrolysis for production of bio-oil and slow pyrolysis for production of charcoal.

2.3.4. Biological Treatment of MSW.

Biological treatment will require longer time than thermal conversion as biological processes takes days, weeks or even months to be carried out fully. These processes may be particularly suited for some MSW fractions i.e. niche applications and will therefore contribute to the expansion of the MSW treatment arsenal.

2.3.5. Composting.

Composting of MSW has been defined as “the biological decomposition of the biodegradable organic fraction of MSW under controlled conditions to a state sufficiently stable for nuisance-free storage and handling for a safe use in land applications” [1].

Several specificities of composting are immediately arising from this definition: (1) this process is limited to the organic fraction of MSW and separation of other fractions is a prerequisite; (2) this process is carried out under controlled conditions and is not a mere dump; (3) the resulting decomposition product, i.e. compost or humus, has to comply with safety and quality standards before further agricultural use [1]. This technology will therefore achieve a twofold goal: reduction of waste volume and mass, and production of a valuable by-product.

Practically, various microorganisms (bacteria, fungi, etc) break down the organic matter to produce CO_2, water, heat and a stable and nutrient-rich organic product useable for soil amendment. The decomposition process goes through different phases with change in the microorganisms' population and activity of decomposition. The different phases can be followed by the temperature profile in the composting matter. To optimize the process (i.e. fast process), many parameters are of importance: C/N ratio (nutrition of the microorganisms), particle size/surface area exposed (the smaller the particle, the easier for microorganisms to work), oxygen/aeration, moisture content, pH level, temperature.

Different technical solutions exist for composting of vast amounts of waste. Traditionally, windrow systems (outdoor row of protected/unprotected waste) were used but today preference is given to in-vessel systems (i.e. large incubators) as they allow easier and more efficient control of the process. To ensure fast, efficient and safe decomposition, "active (or fast, hot) composting" operation is preferred to passive composting where no maintenance is applied. Active composting requires the follow-up and optimization of aeration, moisture and C/N ratio throughout the composting matter.

On top of the care required for the optimization of the process by providing ideal conditions for the microbial activity several problems are to be expected. The main challenges associated will be: pre-processing of the MSW, pathogen control (health hazard posed by the propagation of microorganisms into the air), leaching to underground water (need for an impermeable surface), odor control, fly and rodent attraction, fire risks (spark or self-ignition), contaminants presence (heavy metals). Health and safety constraints are therefore a hindrance for the establishment of vast composting systems and their commercial viability. However, “backyard” composting remains a good waste treatment for organic wastes such as yard clippings or food scraps.

2.3.6. Anaerobic Digestion.

Anaerobic digestion can be described as composting in the absence of oxygen and therefore require a closed reactor system, i.e. a digester. Anaerobic digestion is especially well adapted for high-moisture wastes. The products of anaerobic digestion are a biogas (CH_4, CO_2 and acid gases), a liquid (“oil”) and a solid residue (mostly lignin and chitin). However, the energy density of the gas has to be increased (removal of CO_2) as well as to be cleaned before eventual use for electricity generation. The liquid fraction may be used as a fertilizer if it does not concentrate contaminants (pesticides, heavy metals), while the solid residue may be further composted. The obvious limitations make this technique little appealing and economically viable except in some specific niche applications such as waste water treatment (sludge digestion) and farm slurries [23].

2.3.7. Fermentation.

Fermentation is of interest for the biomass fraction of MSW and more generally biomass residues. This process includes two steps: (1) lignocellulosic materials are first hydrolyzed to sugars with the help of enzyme and/or acid hydrolysis [26] and thereafter (2) converted into ethanol through fermentation. Ethanol production from lignocellulosic materials (not only corn but woody biomass) is a hot topic as development of a car fuel blend including 85% of ethanol and 15% gasoline known as E85 is a serious alternative to conventional gasoline. The trend now is for the production of Flexible Fuel Vehicles that can function either on gasoline or on E85. An overview of ethanol production (potentials, constraints and technologies) from waste and biomass residues can be found in [27].

2.4. Previous Research

Unlike single material such as coal and wood, the fundamental study of MSW has received less attention due to its complexity. Some studies [28-32] on single materials have been reported. These Studies were mostly concerned with the thermal decomposition of single composition, such as paper, plastics and so on. There have been some researchers who studied the combustion characteristics of MSW and had mixed conclusions. Yong-hua Li et al. as said that combustion of MSW mixed with coal would change its characteristics. It would increase the ignition point of the MSW with percentage of mixed coal but apparently the average activation energy would decrease. Some of the previous studies mostly focus on the larger devices and the processing for thermochemical treatment of MSW [33, 34]. Only few studies were carried out on the fundamental Thermochemical reaction and kinetic parameters.

During MSW combustion the reaction mechanism with different MSW compositions is not the same. Some composition such as waste plastics, paper and cotton complies with the two step kinetics model; the activation energy (E) and pre exponential factor (A) within higher temperature range are much greater than that within lower temperature range, while other six MSW compositions can be expressed with certain one step model [35]. Garcia et al. also studied the pyrolysis of MSW by TGA and a correlation model which considered independent reactions was applied to simulate the process [35]. There are little errors between the experimental and predicted value of sample weight loss during the combustion. It is easier for high volatile MSW composition to burn than that one with lower volatile content. Dwi Aries Himawanto et al. in his paper [36] has concluded that even though there are many kinetic equations which can be used to calculate the pyrolysis activation energy, his method has found a global kinetic method that can be applied to calculate the pyrolysis activation energy. Lin et al. calculated the global pyrolysis reaction rate from key component fractions paper, LDPE, HDPE, PS, and PVC of RDF using the weighed sum method. Jin et al. made a detailed analysis on the pyrolysis of the single component of MSW [37]. These researches revealed that pyrolysis may be complicated by the fact that the MSW is a poor thermal conductor and heterogeneous material.

There are numerous papers that complement the fact that complex hydrocarbon structures such as the Styrofoam have high thermal stability when compared to other compounds such as lignocellulosic blends and organic wastes. Even the activation energy of the latter compounds is very low when compared to complex hydrocarbon structures such as Polyvinyl chloride (PVC), High density polyethylene (HDPE), Polyethylene terephthalate (PET), Low density polyethylene (LDPE), Linear Low density polyethylene (LLDPE), Polypropylene (PP), Polystyrene (PS) and others [36, 38].

Researchers have also looked into the effect of heating rate on the reactions and have concluded that it has very little effect on pyrolysis, but the increase in terminal temperature will cause the pyrolysis percentage to rise [26]. But higher heating rates would lead to “Thermal lag”. Szabo et al. [39] have sorted out the discrepancies in TG kinetics due to the differences in measured and actual sample temperature. “Thermal lag”, as that difference is called, has attributed to the heat and mass transfer resistance as well as to the endothermic characteristics of pyrolysis reactions. The use of small samples and low heating rates is hence generally recommended to limit this phenomenon. This paper has provided a platform to even understand them at a broader prospect. Generally, it has been observed that the earlier the volatile matter is released, the lower will be the ignition temperature and the greater will be the time lag between the two temperatures.

The lack of value in many cases can be related to the mixed and often, unknown composition [40] of the waste. Separating the materials in waste generally leads to a value increase for these potential recovering substances.

2.5. Foreword

Combustion, pyrolysis and gasification are the three main thermo chemical methods. A lot of attention is being given to gasification technology as one of the most efficient methods for utilizing woody biomass [41, 42] since the usage of CO_2 has been leading to many global issues. Gasification is a robust proven technology that can be used to convert a low value and highly distributed solid biomass to a uniform gaseous mixture. It can be further used as an industrial feedstock for heat and power generation, H_2 generation and synthesis of liquid fuels.

A design of an ideal gasifier requires understanding of the influence of fuel and operating parameters on plant performance namely the biomass type, gasification medium, the producer-gas composition, gas efficiency and the gasification temperature and pressure. Thermo gravimetic Analyzer (TGA) has been used as an ideal gasifier. A TGA measures the changes in weight of a body as a function of temperature and time, under controlled atmosphere. The main use of a TGA is the measurement of thermal stability of a particular body.

In order to understand pyrolysis, combustion and gasification of MSW at a broader prospect, this thesis studies the thermal decomposition of MSW with the objective to obtain the characteristics and kinetics of the MSW under different conditions using different equipment, to understand the effects of the heating rate and components on MSW pyrolysis, combustion and gasification and to obtain basic data which can be applied in practice. The motivation for the TGA experiments was to try to establish a relationship between chemical kinetics and the chemical composition of MSW components. The Differential Scanning Calorimetry (DSC) is helpful as an auxiliary technique since it provides abundant information about some phenomena that do not lead to the mass losses.

CHAPTER 3

Materials and Methods

In this study, the MSW and the simulated waste samples were thermally degraded in a combined Thermo gravimetric Anlayser (TGA) & Differential Scanning Calorimeter (DSC), Q-600 from TA instruments. In addition to the TGA, a bomb calorimeter and a CHN elemental analyzer were used to find out the different engineering properties and elemental composition of the MSW samples respectively.

3.1. Physical and Chemical Characteristics of the MSW and Simulated Waste Samples

3.1.1. MSW Samples.

The MSW samples are collected from different MSW transfer locations situated in Greensboro, Highpoint and Winston-Salem across North Carolina. Two samples are taken from each place for obtaining best experimental values. These six samples are later dried at 105 °C for two days in order to take out the moisture content in them. The samples are weighed before and after the drying to calculate the percentage of moisture. The moisture content ranges between 39-55 % as shown in the Table 3.1. Each sample is then segregated into different components namely paper, metals, plastics, glass, wood, textile and sand and their individual weights are also recorded as shown in Table 3.2. Glass, metals and sand are not considered for the experiments since they do not carry any caloric value in them.

Table 3.1. Moisture content of each sample

City	Name of the Sample	Moisture Content, %
Greensboro	1 2	46.43 55.74
High Point	1 2	42.75 39.74
Winston Salem	1 2	42.74 39.00

Table 3.2. Percentages of Individual components in each sample

	Sample -1	Sample-2	Sample-3	Sample-4	Sample-5	Sample-6
Paper	38.82	54.40	31.87	28.27	39.30	75.63
Metals	5.09	1.51	9.25	15.44	2.08	1.86
Plastics	20.41	21.16	26.09	20.41	49.58	15.62
Glass	15.38	7.03	23.37	32.47	2.44	0.73
Textile	2.74	8.55	4.27	1.05	6.59	0.87
Wood	2.12	2.06	5.15	2.37	0.00	5.29
Sand	15.44	5.30				

The following Figure 3.1. is of a transfer station in Greensboro where all the waste from the city is collected. Paper, plastics, textile and organics (wood and food material) have been taken into consideration for the characterization and a mixture of these four compounds has been considered to calculate the calorific value for comparison with the individual compounds.

Figure 3.1. Transfer station in Greensboro

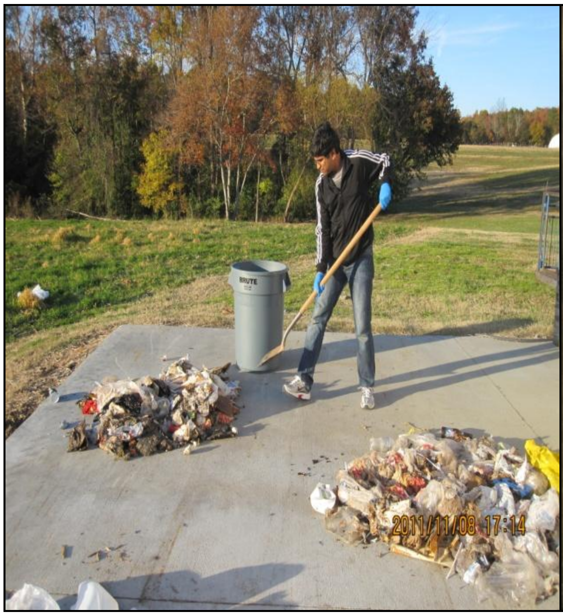

Figure 3.2. MSW collected into cans

Figure 3.3. MSW being segregated into samples

Figure 3.4. MSW samples after segregation

Figure 3.5. Simulated waste

3.1.2. Simulated Waste.

Eleven different samples from our daily use namely biomass, yard grass, vegetable peels, packaging paper, banana peels, textile, low density plastics, high density plastics, cardboard, printed paper, newspaper were collected from households and used as a simulated waste. These samples are also dried at 105 °C for two days to take out the moisture content.

Figure 3.6. IKA M-20 Universal batch mill

The above Figure 3.6. is of a batch mill which is used in the experiment. It is suitable for dry grinding of hard and brittle substances. The advantage of this equipment over others is its double-walled grinding chamber which can be cooled with water through two hose adapters. There are two hose couplings located at the rear of the grinder in order to connect the cooling brine. Cooling with tap water is usually sufficient for substances which become hot as a result of the grinding operation and are thus given to smearing or those that produce oil. Two grinding chambers can be alternately operated using one drive.

Table 3.3 Moisture content of simulated MSW samples

Name of the Material	Before Drying			After Drying		Moisture %
	Weight of the Pan	Weight of the Pan + Material	Weight of the Material	Weight of the Pan + Material	Weight of the Material	
Packaging paper	11.23	26.50	15.27	25.48	14.25	6.68
Print paper	11.11	61.71	50.60	58.86	47.75	5.64
Cardboard	11.29	23.32	12.03	22.55	11.25	6.42
Newspaper	11.18	41.34	30.16	38.56	27.38	9.21
Low density Plastics	11.27	16.62	5.35	16.59	5.31	0.64
High density Plastics	11.15	20.10	8.95	19.89	8.74	2.33
Textile	11.06	56.49	45.42	34.80	23.73	47.75
Vegetable peels	11.255	35.701	24.446	13.684	2.429	90.06
Banana peels	11.16	167.55	156.39	31.682	20.522	86.88
Yard grass	11.19	28.97	17.78	14.523	3.333	81.25
Woody biomass	11.105	44.424	33.319	42.016	30.911	7.23

The vegetable peels, banana peels and the yard grass have lost almost 80-90% of their total weight and textile, about 48% during the process of drying. The samples are then crushed and powdered with the help of IKA M-20 Universal batch mill for obtaining a homogeneous mixture.

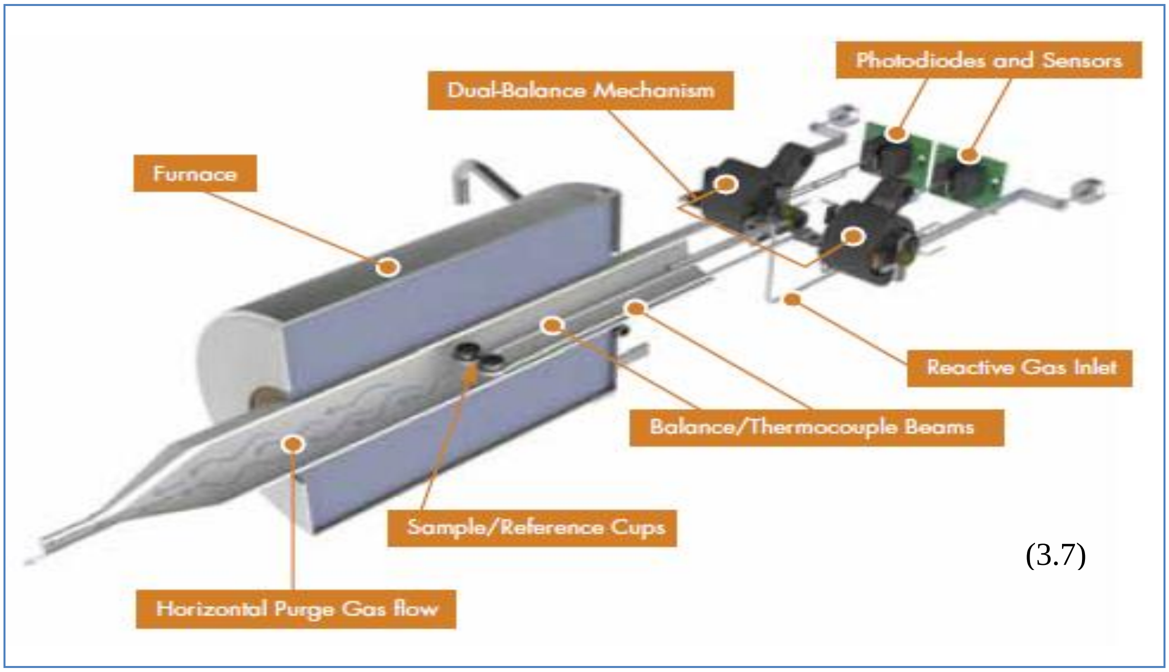

Figure 3.7. The different parts of the TA instruments Q-600

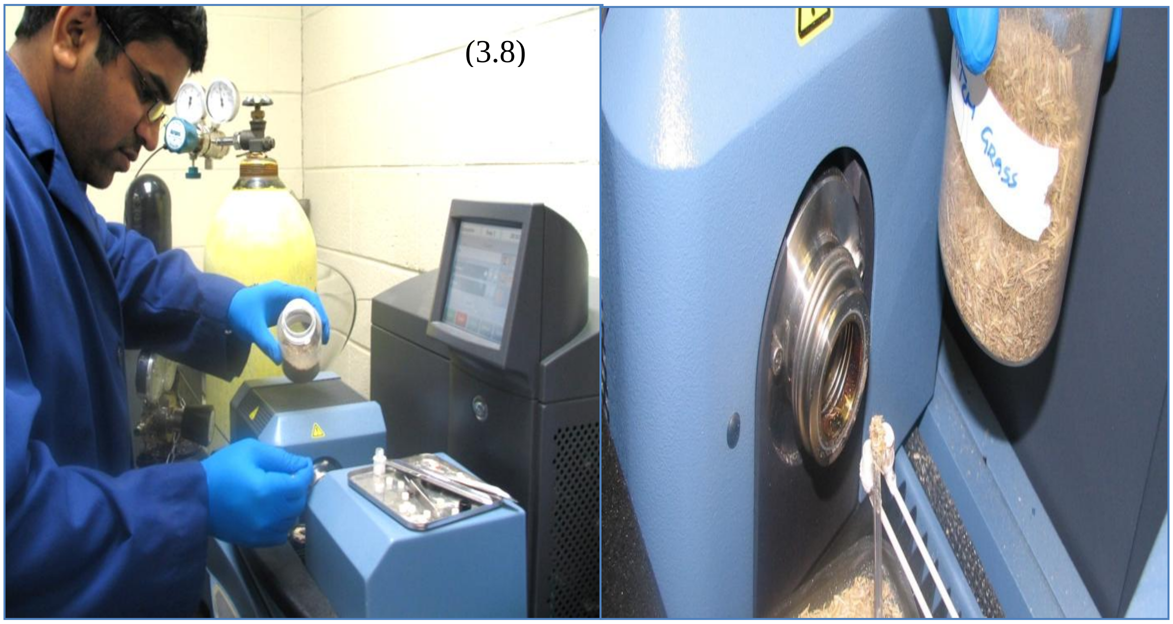

Figure 3.8. Loading of the samples into the instrument

3.2. Thermal Analysis

The samples are thermally degraded in a Thermo Gravimetric Analyzer (TGA), Q-600 by QA instruments shown in the Figure 3.7. Small samples of weight 13-16 mg were placed in the microbalance of the TGA for each analysis. Nitrogen, carbon dioxide and air were used as the purging gases for pyrolysis, gasification and combustion, respectively. An alumina crucible is used in the experiments in order to get the best possible heat transfer between the thermocouples and the crucibles and also to reduce the emissivity of the sample. The heating rate of 10 °C/min was maintained for all the samples. The gas flow rates were maintained constant at 20 ml/min. The temperature range was between 25 °C – 900 °C. The residual weights of all the biomass samples after gasification (CO_2), pyrolysis (N_2) and combustion (air) were 7-10%, 15-20% and 4-6% of the original dry mass, respectively. The TGA and DSC data are analyzed for their kinetics and heat, and are discussed in the results and discussion chapter.

3.3. Heat of Combustion

The heat of combustion is the energy released as heat when a compound undergoes complete combustion in the presence of oxygen under standard conditions. The heat of combustion, Q was determined using a 1341 Oxygen Bomb calorimeter by Parr instruments. The value is conventionally measured with a bomb calorimeter or calculated as the difference between the products and the reactants in a chemical reaction. The following Tables 3.4 and 3.5 show us the average Q values of three set of experiments.

Figure 3.9. 1341 Oxygen bomb calorimeter

The 1341 Calorimeter has a high strength, molded fiberglass jacket formed with double walls and a double cover to provide an oval chamber for the calorimeter bucket which is completely surrounded by sealed, dead air space. This simple yet effective insulating system allows very little heat transfer between the calorimeter and its surroundings. A stirring shaft and thermistor are attached to the cover and are removed with the cover when the calorimeter is opened. Stirring is provided by a small motor attached to the jacket but sufficiently removed so that it does not add heat to the system. A pair of wires with banana plugs carries the firing circuit to terminals on the bomb head. An additional ignition unit which supplies the proper electric current for firing the oxygen bomb calorimeter. If observed closely, the heat of combustion is high for the plastics due to the presence of complex hydrocarbons of Polyvinyl chloride (PVC), High density polyethylene (HDPE), Polyethylene terephthalate (PET), Low density polyethylene (LDPE), Linear Low density polyethylene (LLDPE), Polypropylene (PP), Polystyrene (PS) and others.

Table 3.4. Heat of combustion data for the MSW samples

Sample	Name of the Compound	Average Heat of Combustion, cal/g
Sample 1	Plastics	7108.81
	Textile	5117.80
	Organics	4994.34
	Paper	6629.30
Sample 2	Plastics	7057.40
	Textile	3718.27
	Organics	3918.86
	Paper	4691.75
Sample 3	Plastics	7405.89
	Textile	4138.41
	Organics	3510.54
	Paper	4210.94
Sample 4	Plastics	6109.85
	Textile	4889.77
	Organics	4828.12
	Paper	4113.14
Sample 5	Plastics	6151.20
	Textile	4361.07
	Paper	5296.04
Sample 6	Plastics	7691.55
	Textile	4018.40
	Organics	3454.10

In the above Table 3.4, it is observed that the heat of combustion is very high for plastics when compared to other compounds. And the rest of all them has the same range of 3500-5500 KJ/Kg.

Table 3.5. Heat of combustion data for the simulated MSW samples

Name of the Compound	Average Heat of Combustion cal/g
Biomass	3646.64
Yard Grass	3835.72
Vegetable peels	3391.15
Packaging paper	3998.54
Banana peels	3379.69
Textile	3384.93
Low density plastics	7827.12
High density plastics	4379.95
Cardboard	3246.27
Printed paper	2668.02
News paper	3208.63

3.4 Ultimate Analysis

The elemental composition of the all the MSW samples are determined using a PE 2400 II CHNS/O analyzer (PerkinElmer Japan Co., Ltd.). The weight used of the samples used in the experiment was about 2-3 mg.

Table 3.6. Elemental analyzer data for MSW samples

Trash Samples	Name of the Compound	C (%)	H (%)	N (%)	O (%)
Sample -1	Plastics	71.17	9.31	0.41	19.11
	Organics	38.5	3.73	5.41	52.36
	Textile	53.89	5.82	1.51	38.78
	Paper	44.86	7.25	0.97	46.92
Sample -2	Plastics	62.91	9.91	0.55	26.63
	Organics	35.45	5.23	2.54	56.78
	Textile	38.67	6.33	0.75	54.25
	Paper	44.67	7.4	0.29	47.64
Sample -3	Plastics	72.25	6.31	0.74	20.7
	Organics	37.67	6.13	3.21	52.99
	Textile	45.4	6.94	2.13	45.53
	Paper	44.28	6.99	0.22	48.51
Sample -4	Plastics	69.36	4.18	0.79	25.67
	Organics	40.01	6.5	3.57	49.92
	Textile	55.76	4.8	0.47	38.97
	Paper	45.12	7.13	0.22	47.53
Sample -5	Plastics	68.4	10.58	0.41	20.61
	Organics				

Table 3.6. Continued.

Sample -5	Textile	45.05	7.39	14.57	32.99
	Paper	42.37	6.94	0.19	50.5
Sample -6	Plastics	54.41	7.2	0.93	37.46
	Organics	45.87	6.92	1.04	46.17
	Textile	59.13	4.86	0.38	35.63
	Paper				

Table 3.7. Elemental analyzer data for simulated MSW samples

Name of the Compound	C (%)	H (%)	N (%)	O (%)
Biomass	47.33	6.82	0.12	45.73
Yard grass	54.8	8.27	6.03	30.9
Vegetable peels	39.96	6.37	8.22	45.45
Packaging paper	47.56	8.12	0.33	43.99
Banana peels	43.16	2.78	1.07	52.99
Textile	42.27	7.08	0.63	50.02
Low density plastics	90.79	8.08	0.06	1.07
High density plastics	60.76	4.42	0.04	34.78
Cardboard	42.84	2.94	0.19	54.03
Printed paper	37.67	6.22	0.1	56.01
News paper	45.38	6.7	0.13	47.79

From the preceding Tables 3.4 and 3.5, it can be inferred that the carbon content in the plastics is very high when compared to others due to the presence of large hydrocarbon chains. The value of the carbon percentage in high density plastics is relatively greater than that of the low density plastics because as the name suggests the density of the hydrocarbons per molecule is greater in the former plastics when compared to the latter one. And this property in the high density plastics is clearly evident in the above Tables 3.4 and 3.5. The rest of the samples are in the range of 35- 55 %.

3.5 Method Used for the Calculation of Thermal Kinetics

The kinetics of thermal decomposition reactions of MSW samples is complicated in that the decomposition of these materials involves a large number of reactions in parallel and series. Although TGA provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison kinetic data of various reaction parameters such as temperature and heating rate. Other advantages of determining kinetic parameters from TGA are that only a single sample and considerably fewer data are required for calculating the kinetics over an entire temperature range in a continuous manner.

Determination of the kinetic parameters from TGA data was based on the following rate expression [43, 44].

$$\frac{dX}{dt} = -Ae^{-\left(\frac{e}{RT}\right)}X^n \tag{3.1}$$

Where,

X is the weight of sample undergoing reaction (kg), t is the time (min), A is the pre-exponential or frequency factor (min^{-1}), E is the activation energy of the decomposition Reaction (kJ mol^{-1}), R is the Universal gas constant (kJ mol^{-1} K^{-1}), T is the absolute temperature (K), n is the order of reaction.

A technique based on the Arrhenius equation of the form proposed by Goldfarb and Duvvuri [45, 46] was used to determine the kinetic parameters from typical curves of thermogravimetric data over an entire temperature range in a continuous manner. The linearized form of the Arrhenius equation was used to determine A, E and n by applying least squares (multiple linear regression) technique. The simplified form of the linearized rate equation is as follows:

$$y = B + Cx + Dz \tag{3.2}$$

The parameters y, x, z, B, C and D in Eq. (2) are defined as follows:

$$y = \ln[\{\frac{-1}{(w_0 - w_f)}\}\{\frac{dw}{dt}\}] \tag{3.3}$$

$$x = \frac{1}{RT} \tag{3.4}$$

$$z = \ln[\frac{(w - w_f)}{(w_0 - w_f)}] \tag{3.5}$$

$$B = \ln A, C = -E, D = n \tag{3.6}$$

The values obtained from the experiment for calculated for the y, x and z values and then a method of regression has been used in Microsoft excel to calculate the values of B, C and D. Thus, the values of A, E and n are obtained.

3.6. Calculating the Caloric Requirement

Several studies have done on investigation of the heat of reaction of biomass using the TGA/DSC data and the literature shows that quantification of the reaction heat is really difficult. The main reasons for them are:

- During pyrolysis, combustion or gasification, the temperature of the sample changes greatly, the chemical state and the property of the component also changes continuously.
- At high temperatures, it is evitable that there will be interaction between the specific heat and the reaction heat and it is really impossible to detect them separately especially in TGA analyzer.

The caloric requirements of the compounds are calculated by integrating the DSC heat flow curve with the help of the following equation [47, 48]

$$Q = c_{p,b} \int m_b dT + c_{p,ch} \int m_{ch} dT + Q_p \tag{3.7}$$

For the heat flow data from the plots and by integrating the above equation, we get

$$\frac{Q}{m_{s,0}} = \int_0^t \frac{(m_s c_{p,s} \frac{dT}{dt} + m_s H_p)}{} dt \tag{3.8}$$

We know that the moisture content in the DSC peaks of the sample is influenced by the moisture (at least 6-12 %) in the sample which further influences the caloric requirement. And since this stage (moisture content) is unstable, the exact caloric requirement is really difficult to calculate. Hence, the data until the first 200 °C is omitted and then the DSC curve is integrated using EXCEL to obtain the values of caloric requirement.

CHAPTER 4

Results and Discussion

4.1. TG, DTG and DTA Curves

Figure 4.1, 4.2 and 4.3 show the weight loss (TG), weight loss rates (DTG) and temperature change (DTA) of different components in MSW i.e., Plastics, Paper, Textile and Organics, simulated MSW and mixture of MSW (equal weights) under three different gases namely air, nitrogen and carbon dioxide respectively. The TG/DTG and DTA curves of these samples exhibit completely different profiles, under the influence of different gases.

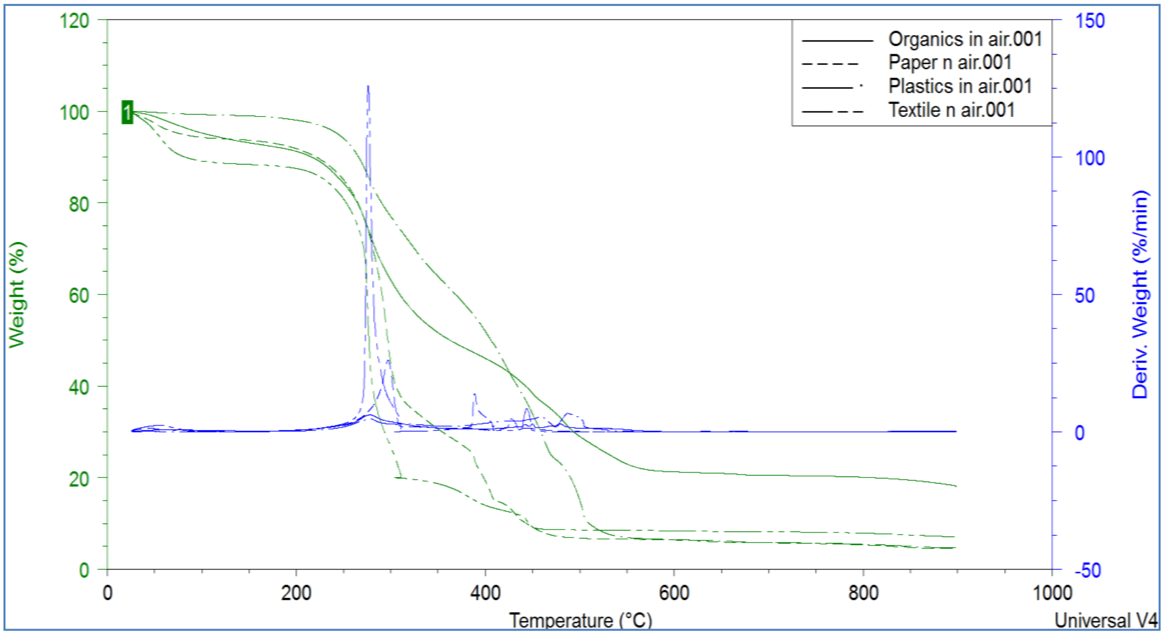

Figure 4.1. Thermo gravimetric (TGA) and weight loss (DTG) kinetics of MSW in air

The Figures 4.1 to Figure 4.6 show the same pattern for all the samples in different gases environment. The number of derivative peaks in the sample represent the number of different compounds present in the samples. If we observe carefully, two peaks were seen for organics as well as plastics due to the presence of two or more different compounds in them. The organics had bone matter in the sample. Hence, we can see that the ash percentage is bit higher when compared to the other compounds.

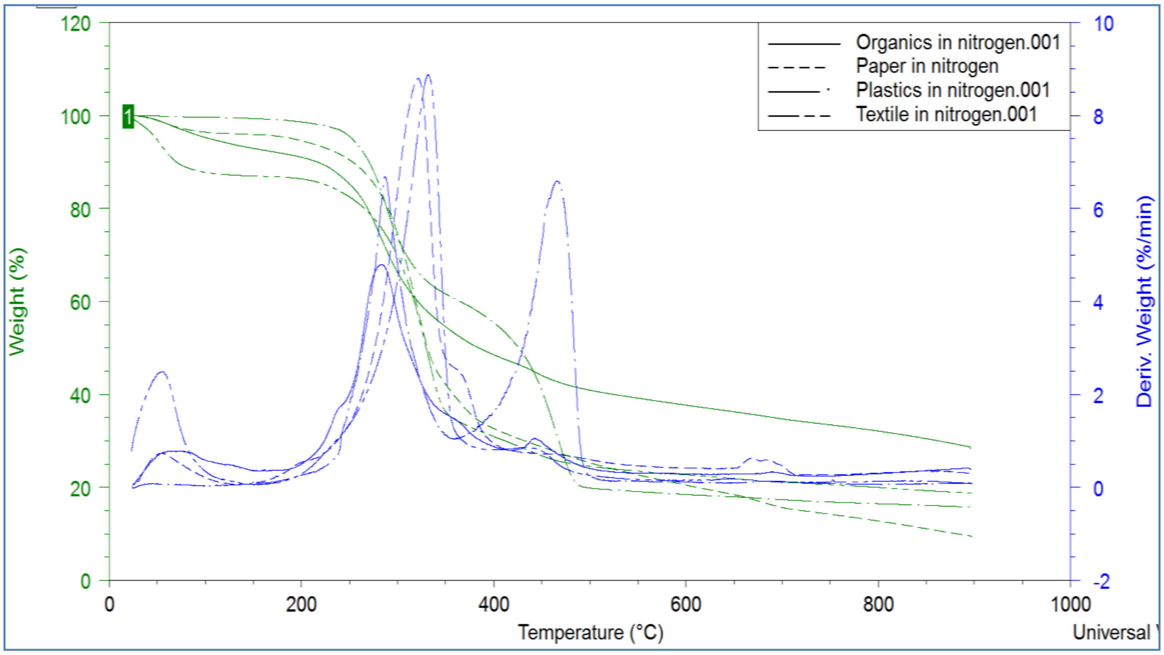

Figure 4.2. TGA kinetics of MSW in nitrogen

The thermal degradation rate data of the samples gives the possibility to establish the wastes in mixtures thermo-chemical properties in combustion, pyrolysis or gasification conditions. The solid waste submits a continuously homogenous thermal treatment process, guaranteed by the unit isothermal profile and the continuous gas flow residential time distribution. This insures an accurate dynamic process gas analysis.

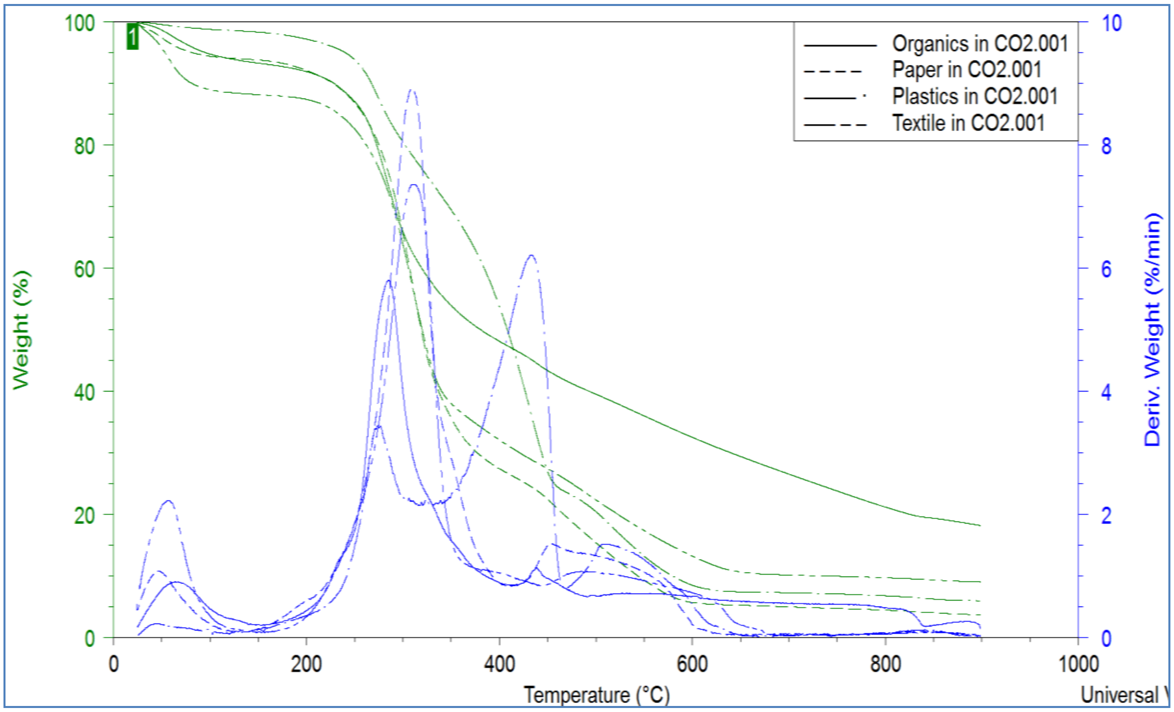

Figure 4.3. TGA kinetics of MSW in carbon dioxide

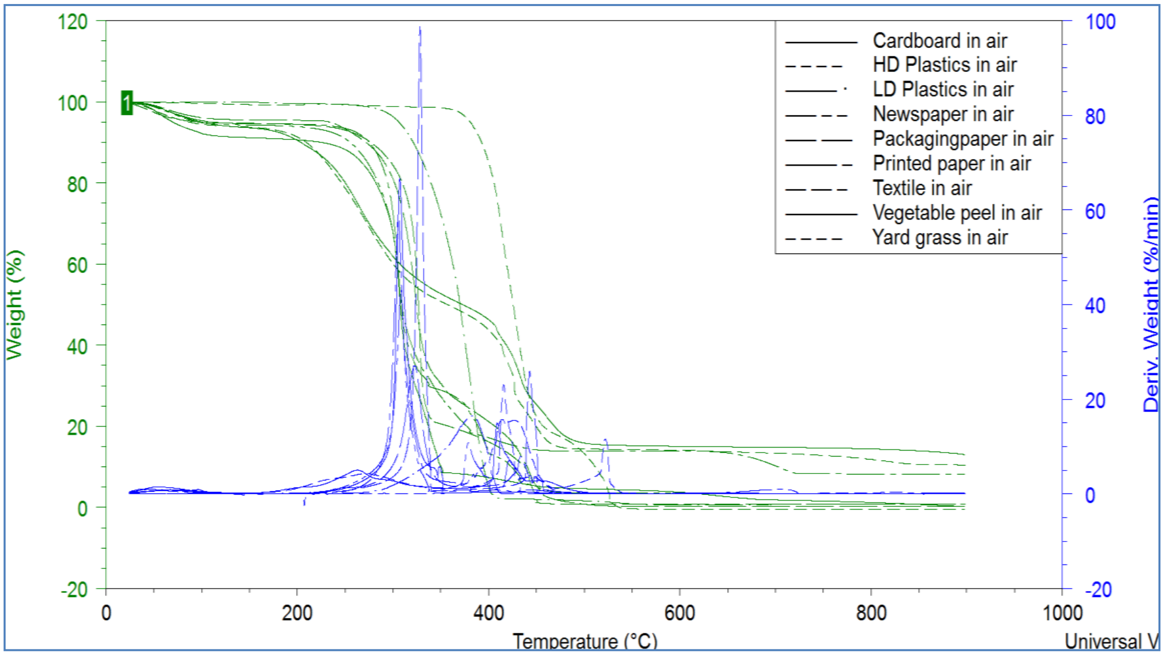

Figure 4.4. TGA kinetics of MSW (simulated) in air

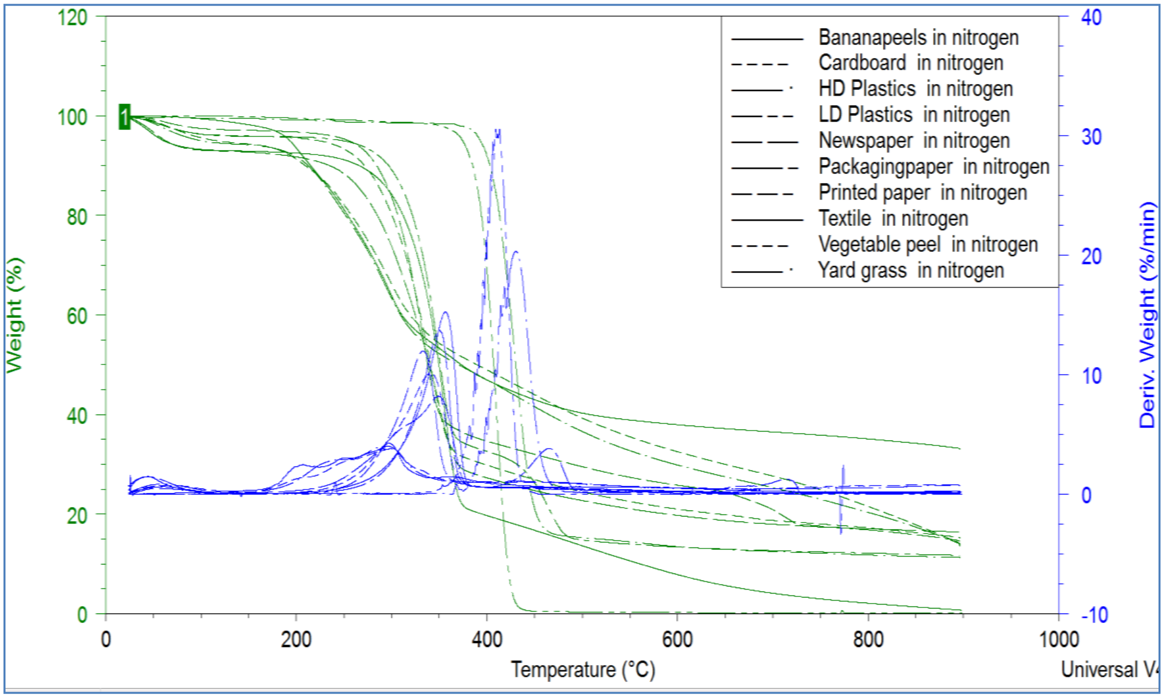

Figure 4.5. TGA kinetics of MSW (simulated) in nitrogen

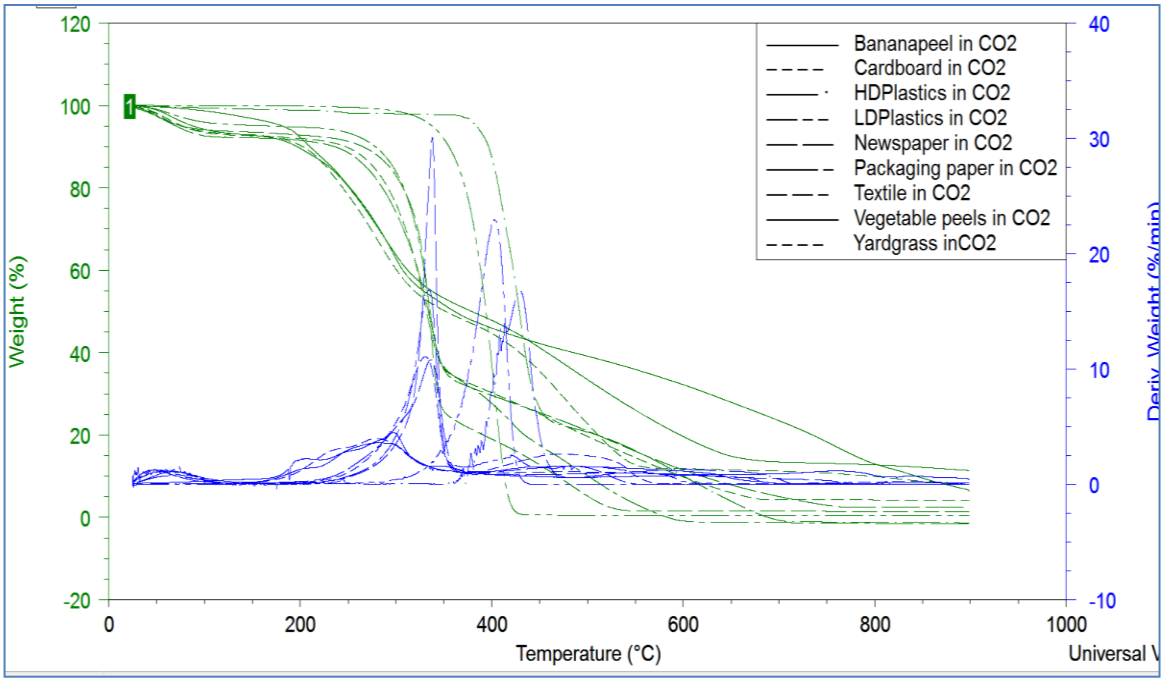

Figure 4.6. TGA kinetics of MSW (simulated) in carbon dioxide

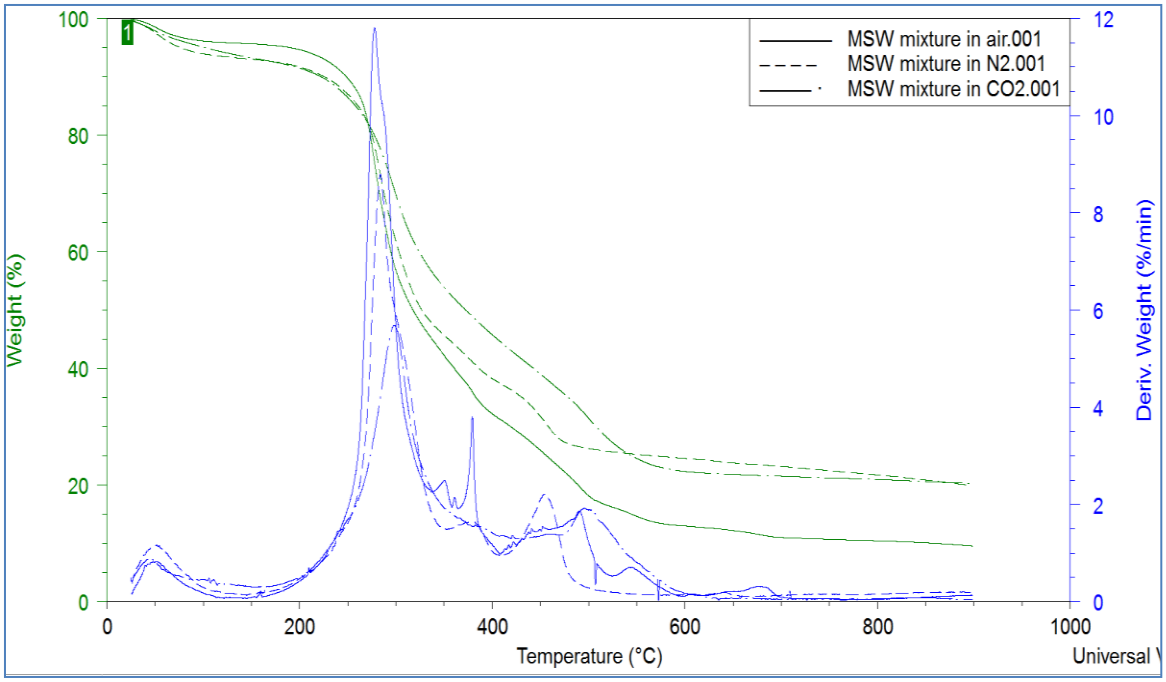

Figure 4.7. TGA kinetics of MSW mixture in air, nitrogen and carbon dioxide

In the above Figures, 4.4, 4.5 and 4.6, there is a similar pattern followed by all the samples in all the environments. The plastics, since there is no lignin content in the sample, the final weights were always lesser than all the other compounds, mostly close to zero.

In the following Tables 4.1, 4.2, 4.3 & 4.4, the thermal degradation rate for each of the samples followed the same pattern in terms of their thermal degradation rate, peak temperatures and their corresponding final weights. The final weights of all the MSW and the MSW (simulated) samples were high in nitrogen when compared to other gases. The thermal degradation rate helps us to understand where the actual reaction is taking place and this can be inferred from the following Tables 4.1, 4.2, 4.3 & 4.4. A same pattern is observed in all the three different gas environments for all the samples.

Table 4.1. Thermal degradation rates, their corresponding temperatures and final weights (MSW) in nitrogen, air and carbon dioxide

Name of the Sample	Peak 1		Peak 2		Peak 3		Final weight, %
	Thermal Degradation Rate, %/min.	Temp (°C)	Thermal Degradation Rate, %/min.	Temp (°C)	Thermal Degradation Rate, %/min.	Temp (°C)	
Nitrogen							
Organics	4.78	282.48	1.05	443.18	0.32	692.64	28.81
Paper	8.79	322.15	-	-	0.56	677.85	9.52
Plastics	6.62	285.84	6.58	466.72	0.12	675.83	15.76
Textile	8.87	332.34	0.82	445.20	0.19	645.57	18.82
Air							
Organics	6.21	277.27	2.59	451.25	0.17	669.78	18.03
Paper	8.89	297.25	13.93	388.72	4.83	427.72	4.52
Plastics	4.72	279.12	5.38	455.96	6.60	488.91	4.71
Textile	5.10	276.43	7.68	442.51	-	-	7.12
CO_2							
Organics	5.80	285.95	1.09	440.69	.65	606.11	18.29
Paper	8.90	310.05	1.50	453.27	0.1247	612.63	3.693
Plastics	3.42	274.41	6.21	432.42	1.514	508.40	5.984
Textile	7.35	310.05	1.05	478.12	0.1330	666.42	9.02

Table 4.2. Thermal degradation rates, their corresponding temperatures and final weights (MSW Simulated) in nitrogen

Name of the Sample	Peak 1		Peak 2		Peak 3		Final wt, (%)
	Thermal Degradation Rate, %/min.	Temp. (°C)	Thermal Degradation Rate, %/min.	Temp. (°C)	Thermal Degradation Rate, %/min.	Temp. (°C)	
Banana Peel	4.23	298.62	1.44	365.86	-	-	33.27
Cardboard	10.15	341.65	0.26	682.55	-	-	15.39
HD Plastics	20.28	429.73	-	-	-	-	11.32
LD plastics	29.84	412.25	-	-	-	-	0.15
Newspaper	8.18	348.38	-	-	-	-	16.44
Packaging paper	13.78	349.05	3.8	466.67	-	-	11.73
Printed paper	11.97	332.91	1.24	712.81	-	-	14.76
Textile	15.22	355.77	-	-	-	-	1.377
Vegetable peel	3.79	299.29	-	-	-	-	14.25
Yard grass	4.04	293.91	1.08	440.49	-	-	14.29

Table 4.3. Thermal degradation rates, their corresponding temperatures and final weights (MSW Simulated) in air

Name of the Sample	Peak 1		Peak 2		Peak 3		Final wt, (%)
	Thermal Degradati-on Rate, %/min.	Temp. (°C)	Thermal Degradati-on Rate, %/min.	Temp. (°C)	Thermal Degradati-on Rate, %/min.	Temp. (°C)	
Banana Peel	4.45	301.98	9.47	406.87	8.21	572.28	7.08
Cardboard	65.51	306.69	-	-	-	-	0.09
HD plastics	15.73	414.27	11.6	521.85	-	-	0.21
LD plastics	16.46	383.34	-	-	-	-	0.79
Newspaper	43.02	308.02	10.81	378.63	6.55	420.32	3.44
Packaging paper	27.11	322.82	7.98	433.77	-	-	0.3
Printed paper	56	304.67	1.87	379.88	0.8	716.17	8.13
Textile	98.71	328.2	25.77	443.18	-	-	0.85
Vegetable peel	5.02	263.65	14.86	409.56	-	-	13.02
Yard grass	4.3	271.05	22.39	407.47	-	-	12.73

Table 4.4. Thermal degradation rates, their corresponding temperatures and final weights (MSW simulated) in carbon dioxide

Name of the Sample	Peak 1		Peak 2		Peak 3		Final wt, (%)
	Thermal Degradation Rate, %/min.	Temp. (°C)	Thermal Degradation Rate,(%/min.	Temp. (°C)	Thermal Degradation Rate,(%/min.	Temp. (°C)	
Banana Peel	4.45	299.29	355	1.52	-	-	6.37
Cardboard	11.07	330.89	-	-	-	-	4.16
HD plastics	16.78	429.73	-	-	-	-	1.34
LD plastics	22.88	403.51	-	-	-	-	0.45
Newspaper	10.8	336.27	-	-	-	-	2.55
Packaging paper	16.83	333.58	2.5	421.67	-	-	0.49
Printed paper	13.48	324.84	6.77	376.62	-	-	4.11
Textile	27.79	339.63	-	-	-	-	1.36
Vegetable peel	3.59	283.15	-	-	-	-	11.36
Yard grass	3.97	279.79	2.63	475.46	-	-	8.03

4.2. Operating Conditions

4.2.1. Type of Gas Used.

There are three types of gases that are used in this experiment. They are nitrogen for pyrolysis, air for combustion and carbon dioxide for gasification.

4.2.1.1. Pyrolysis (Nitrogen).

The pyrolysis temperature ranges and the peak temperature of mixed components samples. It could be seen that the mixed component samples initial pyrolysis temperature located between the initial pyrolysis temperatures of each component with exception in organic mixed component. The initial pyrolysis temperature of organic mixed component higher than the single component pyrolysis initial temperature. It caused of synergetic reactions which occurred between the components. Pyrolysis temperature ranges of each sample could be seen in the above Tables 4.1 & 4.2, they show that the samples other than plastics were pyrolysed starting from around 220 °C and continuing until 450 °C, where the highest mass loss occurred at about 250-280 °C, while the banana leaves wastes was pyrolysed from 190 °C to 420 °C with the highest decomposition rate at 298 °C. Plastics were pyrolysed at 310 °C – 450 °C with peak temperature occurring at 420 °C.

From the experimental results, it could be concluded that all the waste samples, except the plastics started pyrolysing at almost the same temperature which as hemicelluloses decomposition temperature. Heikkinen et al. [49] explained that the maximum decomposition rates of xylan, the one of hemicelulose type, occurred at 298 °C. Based on the peak temperature, i.e. the temperature which highest devolatilization rates occurred which defined by Heikkinen et al. [49], banana leaves wastes categorized as low stability organic component (LSOC), i.e. materials which have the peak temperature around 300 °C. The peak temperature of packaging paper occurred at 349

°C, which is close to the peak temperature of milk carton [49], i.e. 354 °C. Plastic wastes have high thermal stability and have peak temperature above of 400 °C as we can see from the Figures 4.3. & 4.4. Banana waste sample begin to decompose at 175 °C and finished at 420 °C and signed with one maximum mass loss rate at 322.7 °C and one shoulder located at 273.4 °C. According to Di Blasi [50] biomass started to be decomposed at 227 °C, while Kalita et al. [51] found that bamboo dust pyrolysed at 190 °C to 365 °C.

4.2.1.2. Combustion (Air).

In the combustion process, the char formed from the previous phase of evaporation and cracking combusts rapidly, only 3-4% of the original mass of biomass is ash. Hence, we observe an obvious peak is observed in the DSC cures. The weight loss peak will also be a bit different when compared to pyrolysis and gasification. The combusting process of the primary MSW is a serial complicated chemical reaction process. In their paper, Kok et al. [52] have postulated that even though, the combustion of fuel can be initiated whenever oxygen comes into contact with the fuel, it is the temperature, the composition of the fuel and the air supply which dictate the nature of the reaction. It has been inferred here in this paper that under the influence of different fuels (gases) and the conditions, the same sample tends to behave differently. It has been also observed from the curves that the rate of mass loss is maximal at the peak temperature. When analyzing and comparing the combusting curve of the mixture of municipal solid waste, we can conclude that the combustion of municipal solid waste can be divided into three stages: First, it is the dehydration stage, which is carried out before the temperature of 200 °C. Because of the high proportion of the kitchen-left waste in primary municipal solid waste, and the high water-containing in this waste, in this stage, the weight of the waste would decrease rapidly. During 150-200 °C, TG curve almost had no change. When temperature is above 200 °C, TG curve began to decrease, which indicated the volatilization occurring. As temperature increased more, the volatile fraction began to combust. Because of the complicated waste composition, the different combusting nature, as well as the interaction among each elements, the combusting process did not reflect the three obvious stages of the volatile fraction combustion, over-combusting, fixed carbon combustion ,which, on the contrary, occurred simultaneously, which could sustain till combusting completely at about 500 °C. When it’s above 700 °C, another weight-losing process appeared. Combining with the relative DTA curve, we can conclude that during this period, some solid materials began to be melted.

After comparing the curves of all the samples, we can see that during the combusting process, activation energy in two stages have no obvious difference, and during the two stages, the combustion proportion show the same level, that is activation energy in primary municipal solid waste will decrease slightly with the temperature increasing, but not too much, less than the activation energy of the coal. The ignition point is low. The activation energy E will increase during the low temperature stages, but in high temperature, decrease the activation energy E, increase the combustion percentage, which illustrate that during this mixed proportion scope, ignition point would increase as the mixed coal increase, The average apparent activation energy shows the opposite trend, which indicate that low ignition point elements often influence the combustion nature of high ignition point elements. Because elements with low ignition point will speed up the elements with high ignition point and spread the easy-burning molecules, which would tend to decrease the ignition point. After comparing the curves of the MSW to those of simulated waste, we would find that activation energy E in the mixes municipal solid waste are low than that in the segregated solid waste as well as the simulated waste.

4.2.1.3. Gasification (Carbon Dioxide).

There is not much research done on TGA in the carbon dioxide environment even though it is the most viable process. The reason for that being that the amount of char yield at the end of the process is quite low when compared to other gases. The characteristics of all the MSW and simulated waste samples in the presence of carbon dioxide are quite similar to that of air except for the plastics. In the presence of air, the large hydrocarbon chains will have a greater chance of bonding with the available oxygen atoms hence releasing an extra amount of energy when compared to gasification and pyrolysis. However the thermal degradation rate is very high for gasification when compared to other gases and that is clearly visible from the plots.

4.2.2. Sample Size.

Although some argue that large samples can cause limitations of both heat and mass transfer, which can drastically influence the results of these experiments [53]. The results show for all the samples particle size has an effect on pyrolysis product yields and composition: smaller particle size results in higher gas yield with less tar and char; the decrease of particle size can increase H_2 and CO contents of gas, as well as the ash and carbon element contents in the char. The influence is the much more significant for sample with higher fixed carbon and ash contents, such as kitchen garbage, and less for sample with higher volatile content, plastic in the test Therefore, small samples should be used when heat and mass transfer limitations occur at higher sample masses. Chamberlain et al. suggest that both the mechanism and the activation energy of dehydration of a hydrate could be significantly influenced by sample pre-history such as particle size, sample weight, crystal defects and surface characteristics [53]. But the instrument limits the sample size to 25 mg to get admirable results. And hence, the sample size used in the TGA/DSC analyzer is between 20-25 mg.

4.2.3. Gas Flow Rate.

The gas flow rate of the purge gas can also affect the measurement curve. There are authors who have used high gas flow rates of around 100ml/min. But the samples used in these experiments are very light and there is a greater possibility for them for fly away with high purge gas flow rates. Since, weight is an important parameter in calculating the TGA/DSC characteristics; TGA purge gas flow rates are normally kept between 20 – 30 ml per minute total flow to avoid these problems. In this experiment, an optimum gas flow rate of 20 ml/min. has been used to make sure that the samples do not lose weight through gas flow.

4.2.4. Heating Rates.

Researchers have also looked into the effect of heating rate on the reactions and have concluded that it has very little effect on pyrolysis, but the increase in terminal temperature will cause the pyrolysis percentage to rise [35, 39, 54-56]. But higher heating rates would lead to “Thermal lag”. Szabo et al. [55] and Varhegyi et al. [29] have sorted out the discrepancies in TG kinetics due to the differences in measured and actual sample temperature. “Thermal lag”, as that difference is called, has attributed to the heat and mass transfer resistance as well as to the endothermic characteristics of pyrolysis reactions. The use of small samples and low heating rates is hence generally recommended to limit this phenomenon. This paper has provided a platform to even understand them at a broader prospect. Generally, it has been observed that the earlier the volatile matter is released, the lower will be the ignition temperature and the greater will be the time lag between the two temperatures. Hence, to avoid thermal lag, a heating rate of 10 °C has been used throughout the experiment for all the samples.

4.3. Thermal Degradation Kinetics (TGA Curves and Kinetics)

We can clearly observe that there is about a 10 % loss in the weight of all the samples within the temperature range of 0-200 °C, which indicate that it is not only moisture that evaporates but also some organic matter which have low boiling points. Any given sample loses most of its weight within the range of 200 to 500 °C and this stage is shown as the exothermic process in the DTA curve indicating the light compounds that are volatile from the samples. The DTG peak starts between 200-250 °C and its corresponding shoulder peak emerges at around 350-400 °C, which might be because of the decomposition reaction of some heavy compounds [56]. Organics behaves peculiarly under the presence of air, but exhibit the same characteristics in the presence of the other two gases. And after reaching 600 °C, the TA curve almost becomes horizontal. Meanwhile, the DTA curve shows a mild endothermic process, showing the decomposition reaction of remaining heavier components [57]. The main section of weight loss is within the range of 450-500 °C. In all the curves, the DTG peak occurs at around 290 °C. All the organic compounds volatilize before 225 °C. Hence, we can observe a mild endothermic curve before that temperature. About 75 % of the weight loss occurs between the ranges of 375-550 °C in all the MSW and the simulated MSW samples. According to Sorum et al, [57], Orfao et al. [58] and Varhegyi et al. [29], the lower temperature shoulder in the curves shows the decomposition of hemi cellulose and the higher temperature peak shows the decomposition of cellulose in the material. We can observe these peaks in all the samples expect the plastics which have high hydrocarbons.

The TG curves can be categorized into three phases namely (1) the water and the lighter compound evaporation i.e., the release of the volatile compounds, (2) ignition and burning of the heavier compounds (mainly carbon) and finally (3) decomposition of the carbonate compounds [59]. The ignition and burning of these compounds can be divided further into two different stages. The first stage involves the volatilization of the light compounds and the oxidization in the gaseous phase. The second stage involves the heterogeneous combustion between the heavy compounds and the exposed gases [60]. The experiment was even carried out at higher rates and it was observed that at much higher rates of around 50 °C/min., there will be a formation of thick shell around the samples with high lignin content that prevents the diffusion of the respective gases and makes the compound more resistant towards the heat and they also cause more intense release of volatiles. Arrhenius n^{th} order rate equations were used to describe the kinetics of single reaction steps. Heat and mass transfer limitations due to transport phenomena within the sample were neglected because of the low heating rates and the small sample sizes used in experimental runs.

The TGA data is used to calculate the activation energy E (KJ/mol), the pre-exponential factor A (min^{-1}) and the order of the reaction. Agrawal performed some TG studies on some pure components of MSW and their mixtures. According to him, the pyrolysis of several cellulosic wastes take place in the same range of temperature with similar kinetic constant. The same has been observed in the experiments. The temperature range of cellulosic decomposition is 300-400 °C. And that of newspaper (high lignin content) is around 250-375 °C. Plastics have a thermal decomposition of 400-500 °C. In the following Tables 4.5, 4.6, 4.7, 4.8, & 4.9, we can see the kinetic parameters for all the MSW samples. The residual weights of all the biomass samples after gasification (CO_2), pyrolysis (N_2) and combustion (Air) were 5 %, 10-15 % and 4 % of the original dry mass respectively. The maximum rate of mass loss is directly proportional to the reactivity of the sample. It has been also observed that as the temperature in the sample increases, the weight loss peaks in the Derivative Thermo Gravimetric analysis, DTG curves shift to the higher temperature. It will also have a higher peak value and peak width at higher rates. This will not have any effect on the initial ignition temperature but the initial temperature of the volatile release and the burn up temperature shift higher. The following Tables 4.5, 4.6, 4.7, 4.8 and 4.9 give us the information of the kinetic parameters such as the pre-exponential factor A, activation energy E and the reaction order n.

Table 4.5. Kinetic parameters of MSW samples in nitrogen

Compound	Kinetic Parameters	Peak 1	Peak 2	Peak 3
Organics	Pre exponential factor, A, min-1	$3.7 \text{x} 10^7$	$3.4 \text{x} 10^7$	
	Activation energy, E, kJ/mol	84.29	183.10	
	Reaction order, n	1.12	1.17	
Paper	Pre exponential factor, A, min-1	$1.7 \text{x} 10^7$		
	Activation energy, E, kJ/mol	70.24		
	Reaction order, n	1.15		
Plastics	Pre exponential factor, A, min-1	$1.1 \text{x} 10^8$	$3.4 \text{x} 10^7$	
	Activation energy, E, kJ/mol	123.75	137.64	
	Reaction order, n	1.50	1.56	
Textile	Pre exponential factor, A, min-1	78099.98	0.86	
	Activation energy, E, kJ/mol	66.2	121.5	
	Reaction order, n	0.95	2.99	

The Tables 4.5, 4.6, and 4.7 give us the kinetic parameters of the MSW compounds. The values obtained for the pre-exponential factor and the activation energy for the organics, paper, and plastics comply with the earlier published data. There was not much research done in terms on textile but since it also has the lignin content, the values were close to that of others except plastics.

Table 4.6. Kinetic parameters of MSW samples in air

Compound	Kinetic Parameters	Peak 1	Peak 2	Peak 3
Organics	Pre exponential factor, A, min-1	$2.65x10^{7}$	$5.17x10^{7}$	
	Activation energy, E, kJ/mol	65.4	181.15	
	Reaction order, n	2.68	1.88	
Paper	Pre exponential factor, A, min-1	$4.20x10^{7}$	$2.3x10^{7}$	$3.6x10^{7}$
	Activation energy, E, kJ/mol	98.86	115.78	126.41
	Reaction order, n	2.91	1.56	1.60
Plastics	Pre exponential factor, A, min-1	$5.1x10^{7}$	732115.77	$3.9x10^{7}$
	Activation energy, E, kJ/mol	119.69	88.51	220.88
	Reaction order, n	1.61	1.60	1.33
Textile	Pre exponential factor, A, min-1	$3.4x10^{7}$	612326.18	
	Activation energy, E, kJ/mol	244.82	30.74	
	Reaction order, n	2.85	1.39	

Table 4.7. Kinetic parameters of MSW samples in CO_2

Compound	Kinetic parameters	Peak 1	Peak 2	Peak 3
Organics	Pre exponential factor, A, min-1	411383.47	742125.12	
	Activation energy, E, kJ/mol	67.89	124.77	
	Reaction order, n	2.58	2.40	
Paper	Pre exponential factor, A, min-1	495432.31	1355208.58	
	Activation energy, E, kJ/mol	66.41	91.42	
	Reaction order, n	2.88	1.75	
Plastics	Pre exponential factor, A, min-1	4335.74	$1.2x10^{7}$	$2.4x10^{7}$
	Activation energy, E, kJ/mol	53.74	128.78	172.97

Table 4.8. Kinetic parameters of MSW (simulated) samples in air

Compound	Kinetic Parameters	Peak 1	Peak 2	Peak 3
Banana peels	Pre exponential factor, A, min-1	28446.01	$3.7x10^7$	$3.24x10^7$
	Activation energy, E, kJ/mol	54.79	136.72	522.010
	Reaction order, n	1.26	1.09	1.27
Cardboard	Pre exponential factor, A, min-1	$4.1x10^7$		
	Activation energy, E, kJ/mol	324.25		
	Reaction order, n	1.27		
HD plastics	Pre exponential factor, A, min-1	$1.7x10^7$	$2.3x10^7$	
	Activation energy, E, kJ/mol	379.86	229.66	
	Reaction order, n	1.19	0.47	
LD plastics	Pre exponential factor, A, min-1	$3.1x10^7$		
	Activation energy, E, kJ/mol	424.25		
	Reaction order, n	1.31		
Newspaper	Pre exponential factor, A, min-1	$2.8x10^7$	$4.1x10^7$	$5.3x10^7$
	Activation energy, E, kJ/mol	423.25	222.499	689.75
	Reaction order, n	1.07	1.13	1.42
Packaging paper	Pre exponential factor, A, min-1	$1.3x10^7$	$4.6x10^7$	
	Activation energy, E, kJ/mol	282.74	357.68	
	Reaction order, n	0.95	1.41	
Printing paper	Pre exponential factor, A, min-1	$4.7x10^7$	$3.1x10^7$	$2.9x10^7$
	Activation energy, E, kJ/mol	229.75	198.60	238.21
	Reaction order, n	1.45	2.51	1.51
Textile	Pre exponential factor, A, min-1	$2.1x10^7$	$5.5x10^7$	
	Activation energy, E, kJ/mol	229.10	971.93	
	Reaction order, n	1.96	1.99	
Vegetable peels	Pre exponential factor, A, min-1	$3.7x10^7$	$3.8x10^7$	
	Activation energy, E, kJ/mol	189.03	273.66	
	Reaction order, n	1.82	1.77	
Yard grass	Pre exponential factor, A, min-1	$3.1x10^7$	19.26	
	Activation energy, E, kJ/mol	198.21	120.74	
	Reaction order, n	2.50	1.02	

Table 4.9. Kinetic parameters of MSW (simulated) samples in carbon dioxide

Compound	Kinetic Parameters	Peak 1	Peak 2	Peak 3
Banana peels	Pre exponential factor, A, min-1	28446.01	1.55x10^8	8.7 x10^7
	Activation energy, E, kJ/mol	54.79	136.72	122.50
	Reaction order, n	1.25	2.08	1.77
Cardboard	Pre exponential factor, A, min-1	6.12 x10^7		
	Activation energy, E, kJ/mol	135.94		
	Reaction order, n	1.76		
HD plastics	Pre exponential factor, A, min-1	1.07 x10^8	4.5 x10^7	
	Activation energy, E, kJ/mol	305.90	129.66	
	Reaction order, n	1.8	0.47	
LD plastics	Pre exponential factor, A, min-1	6.3 x10^8		
	Activation energy, E, kJ/mol	137.81		
	Reaction order, n	1.30		
Newspaper	Pre exponential factor, A, min-1	5.55 x10^7	3.55 x10^7	3.3 x10^7
	Activation energy, E, kJ/mol	113.58	222.49	689.75
	Reaction order, n	1.07	1.12	1.42
Packaging paper	Pre exponential factor, A, min-1	1.88 x10^8	2.23 x10^7	
	Activation energy, E, kJ/mol	121.91	357.68	
	Reaction order, n	1.94	1.41	
Printing paper	Pre exponential factor, A, min-1	7.06 x10^7	6.77 x10^7	2 x10^8
	Activation energy, E, kJ/mol	219.38	598.60	538.213
	Reaction order, n	1.45	1.55	1.50
Textile	Pre exponential factor, A, min-1	4.54 x10^7	2.57 x10^7	
	Activation energy, E, kJ/mol	128.85	971934	
	Reaction order, n	1.96	1.98	
Vegetable peels	Pre exponential factor, A, min-1	253 x10^7	2.51 x10^7	
	Activation energy, E, kJ/mol	88903.804	273665.2	
	Reaction order, n	1.82	1.76	
Yard grass	Pre exponential factor, A, min-1	2.64 x10^7	19.26376	
	Activation energy, E, kJ/mol	116.57	120.74	
	Reaction order, n	1.50	1.01	

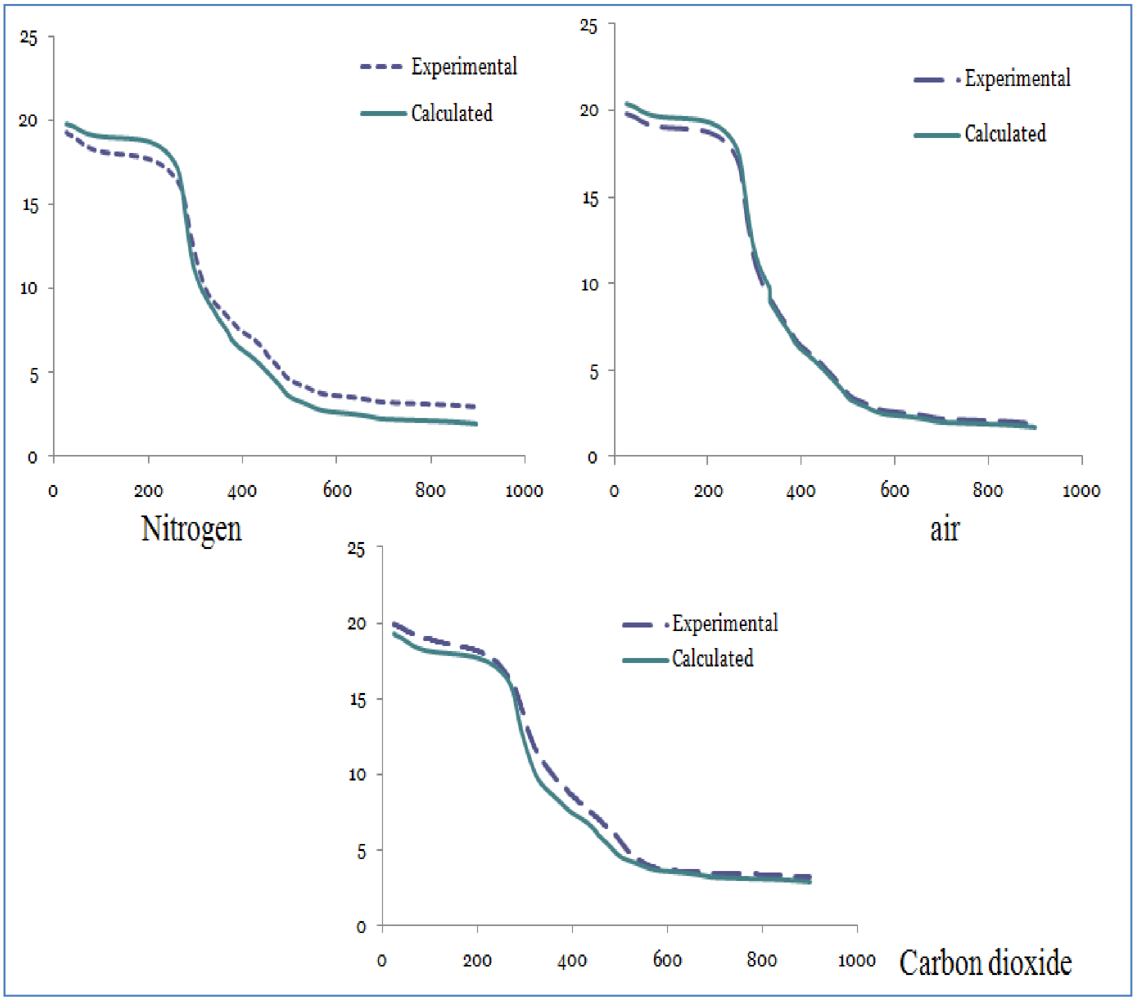

Figure 4.8. Experimental (Vs.) calculated curves for MSW mixture in N_2, air and CO_2

The Figure 4.8 shows us the plot between the experimental values and the calculated values for the MSW mixture in nitrogen, air and carbon dioxide gas environments. We can clearly infer that the values calculated with the help of the kinetic equation perfectly match with the experimental values obtained from the equipment. Activation energies, pre- exponential factors and orders of reaction computed from the model were comparable with published values. These kinetic parameters can directly be used to describe decomposition processes.

4.4. Caloric Requirement of Pyrolysis (DSC Curves and Analysis)

The caloric requirements of the compounds are calculated by integrating the DSC heat flow curve with the help of the following equation

$$Q = c_{p,b} \int m_b dT + c_{p,ch} \int m_{ch} dT + Q_p \tag{4.1}$$

For the heat flow data from the plots and by integrating the above equation, we get

$$\frac{Q}{m_{s,0}} = \int_0^t \frac{(m_s c_{p,s} \frac{dT}{dt} + m_s H_p)}{} dt \tag{4.2}$$

We know that the moisture content in the DSC peaks of the sample is influenced by the moisture (at least 6-12 %) in the sample which further influences the caloric requirement. And since this stage (moisture content) is unstable, the exact caloric requirement is really difficult to calculate. Hence, the data until the first 200 °C is omitted and then the DSC curve is integrated using EXCEL to obtain the values of caloric requirement. Precision data is really difficult to achieve by current calculation methods and the equipments because of the complexity of the samples, the lack of the property values and the difficulty in determining the heat loss of the equipments. The following Figures 4.9. to 4.15. show the caloric requirement in MSW samples, mixtures and simulated MSW samples.

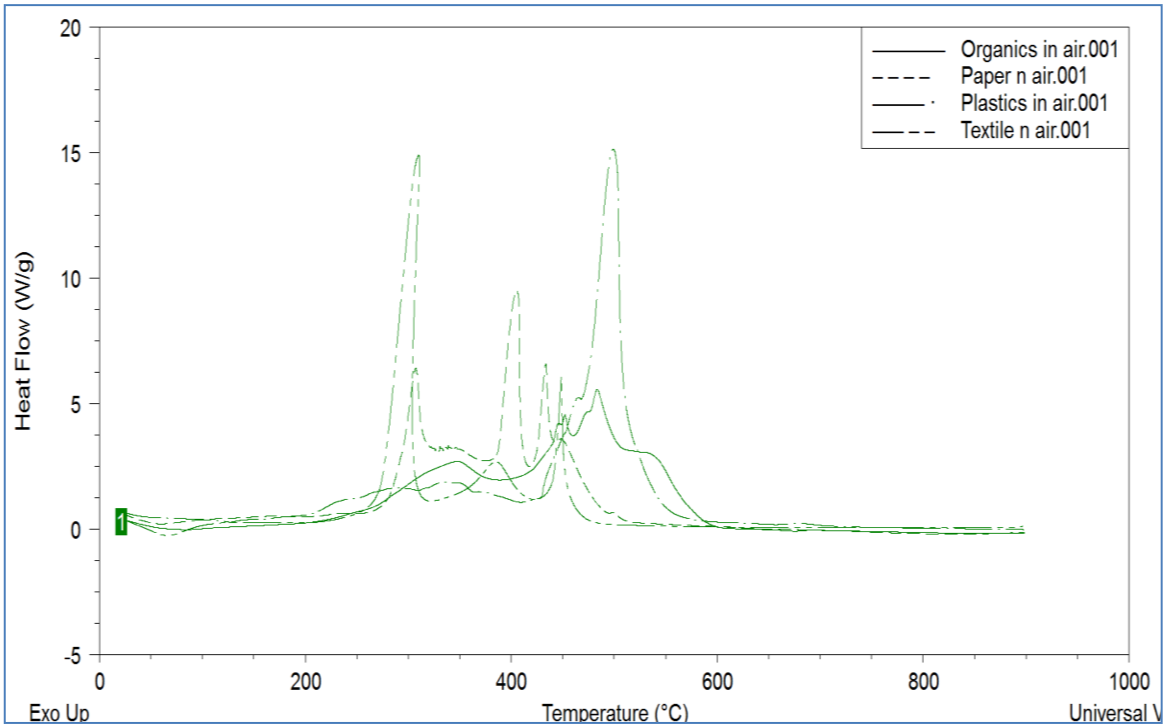

Figure 4.9. DSC curves of MSW in air

Based on the values obtained, this thesis proves that the DSC cannot be used for all the substances because in some cases, most of the substance is lost by sublimation during heating and there are cases where there is unburnt carbonaceous substance even at the end of the reaction. The organic components wastes could be categorized as low stability organics, while the packaging paper could be categorized as mixed polymer material. Styrofoam wastes could be categorized as plastic material which has high thermal stability Precision data of the caloric requirement of biomass pyrolysis is difficult to achieve by current calculation methods or by experiments on some laboratory equipments because of the complexity of MSW, the complexity of the processes, the lack of property values and the difficulty in determining the heat loss of the equipments.

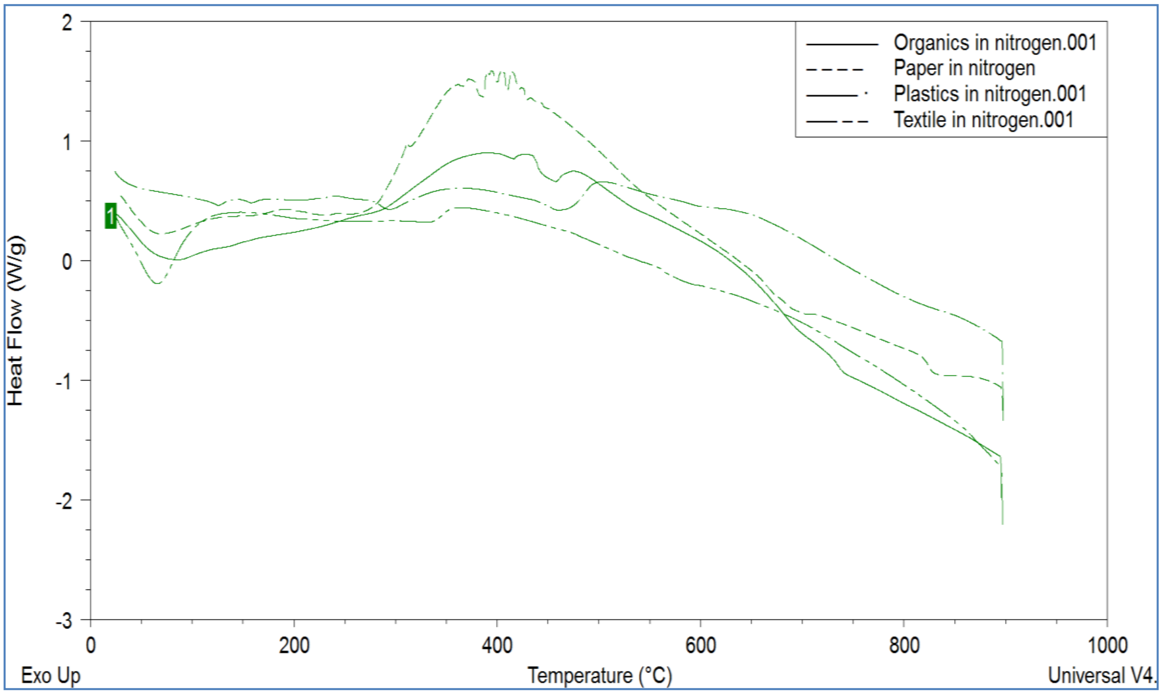

Figure 4.10. DSC curves of MSW in nitrogen

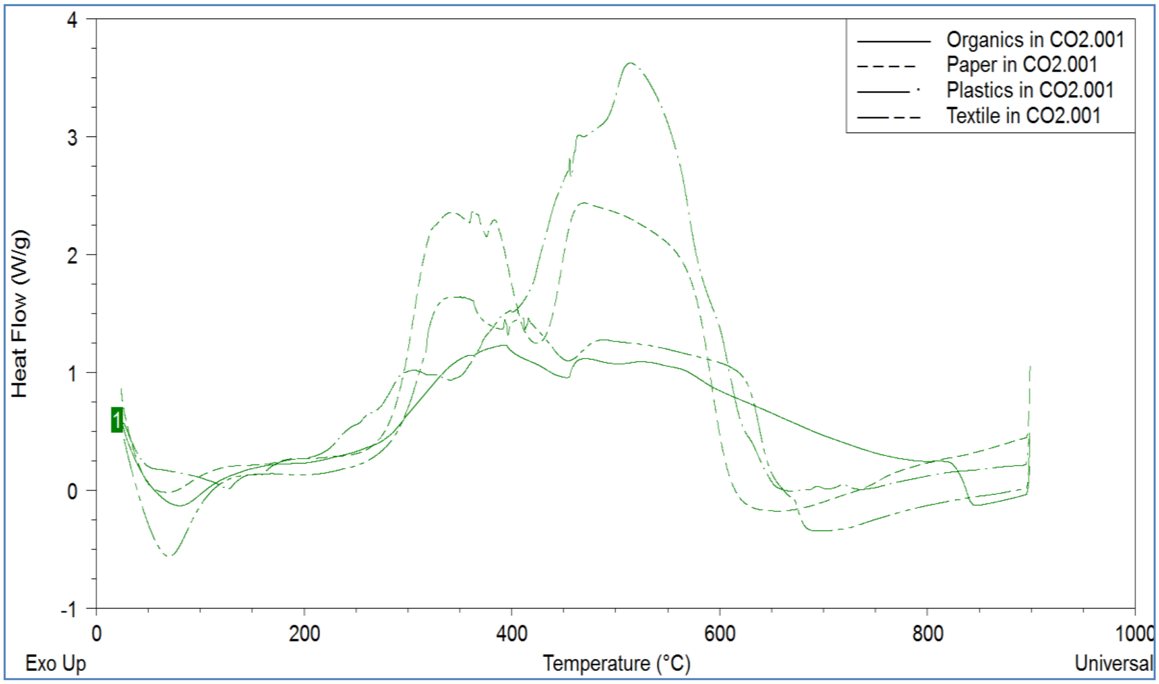

Figure 4.11. DSC curves of MSW in carbon dioxide

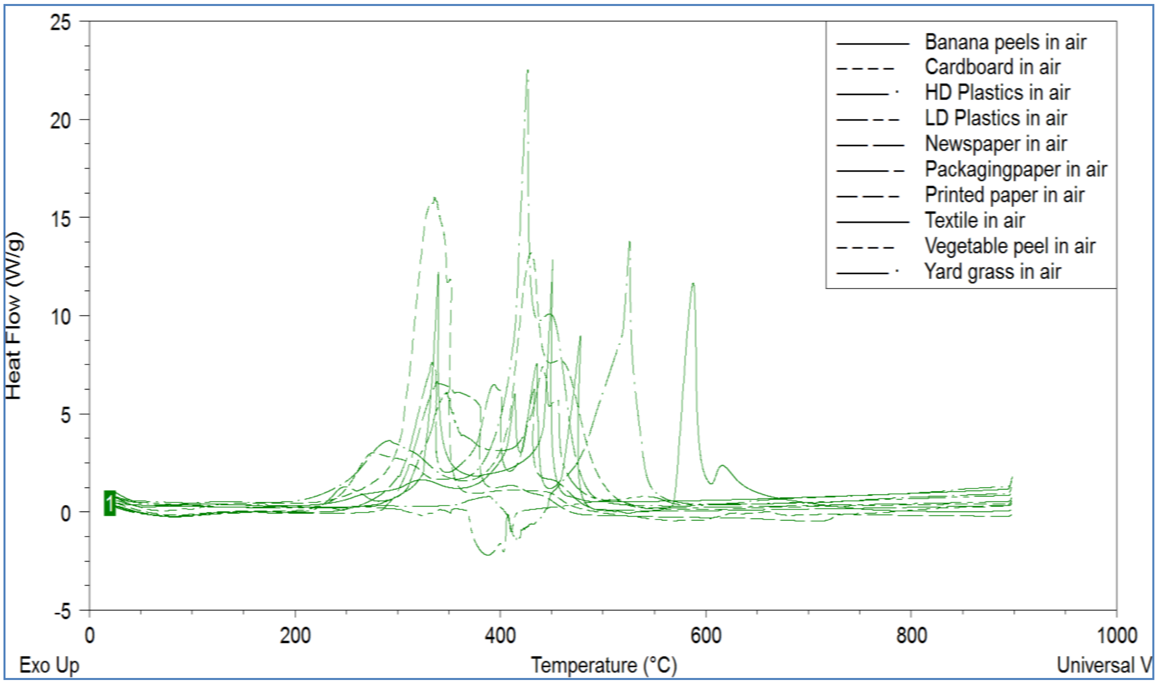

Figure 4.12. DSC curves of MSW (simulated) in air

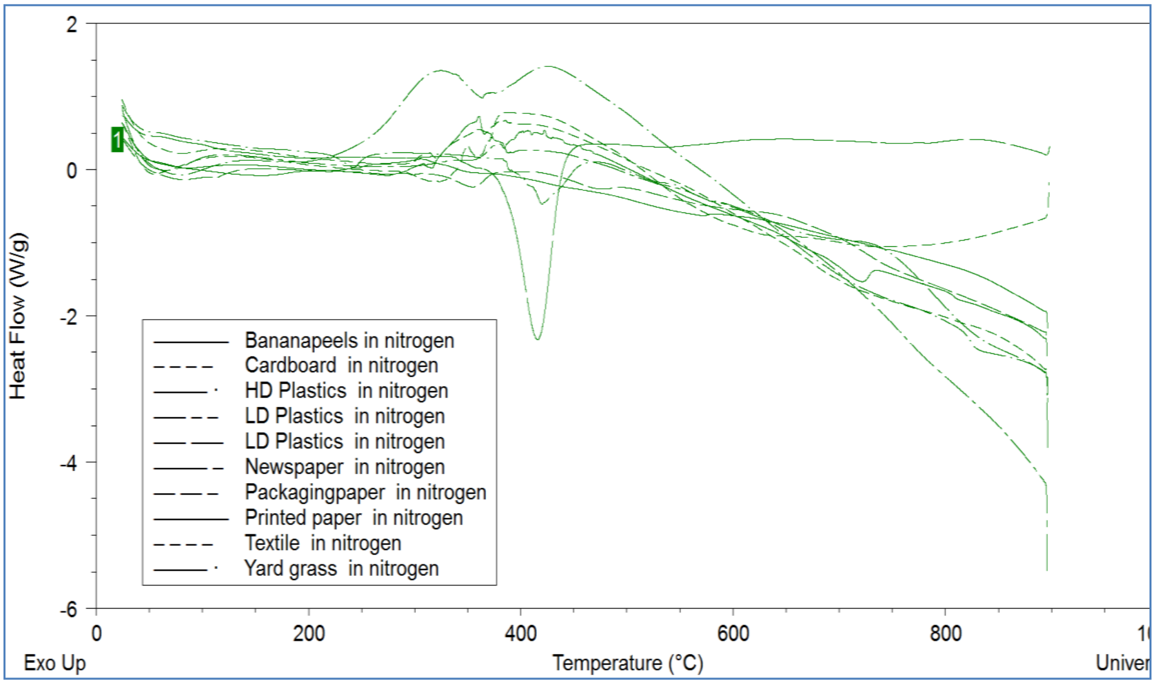

Figure 4.13. DSC curves of MSW (simulated) in nitrogen

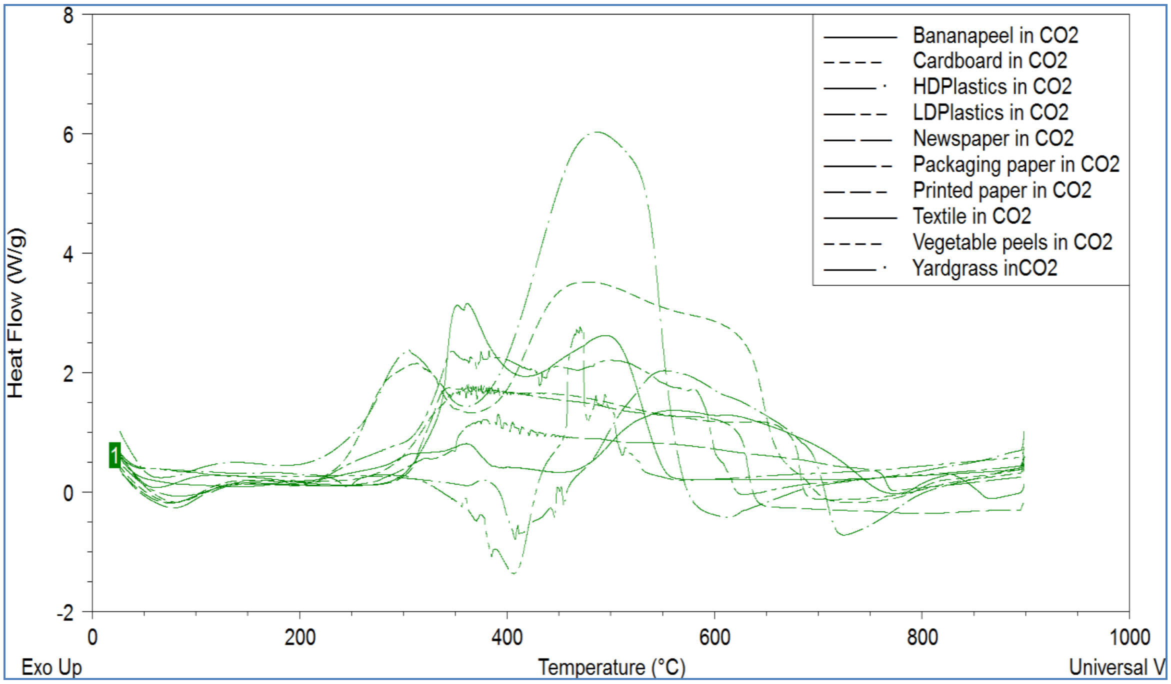

Figure 4.14. DSC curves of MSW (simulated) in carbon dioxide

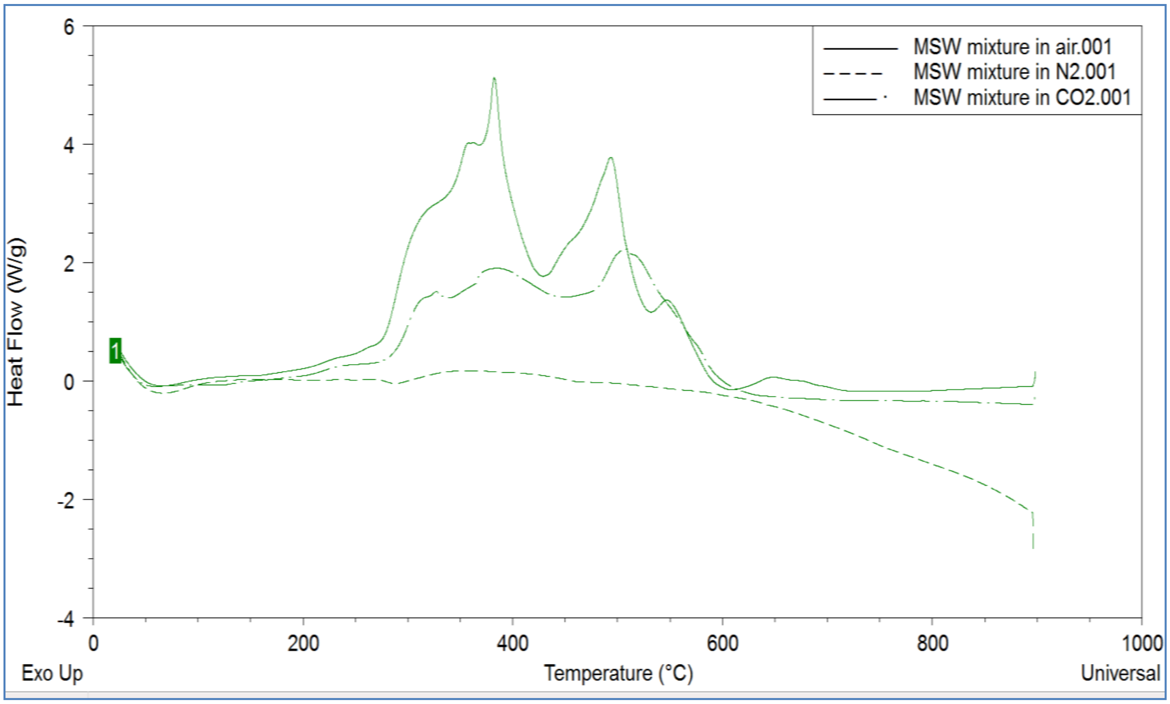

Figure 4.15. DSC curves of MSW mixture in air, nitrogen and carbon dioxide

Table 4.10. Relationship of caloric requirement with temperature of mixture

Temperature, °C	Caloric Requirement, J/g		
	Nitrogen	**Air**	**Carbon Dioxide**
50	34	50	38
100	-12	37	15
150	-12	57	1
200	-4	100	14
250	1	202	73
300	1	483	195
350	33	1346	611
400	82	2589	1142
450	110	3231	1620
500	105	4122	2102
550	79	4631	2665
600	25	4787	2844
650	-74	4770	2788
700	-248	4765	2699
750	-521	4718	2601
800	-898	4666	2501
850	-1372	4623	2396
900	-2027	4598	2280

In the above Table 4.10, the total caloric requirement for nitrogen is negative (endothermic) and it is positive (exothermic) for the mixture in the other two gases.

Table 4.11. Relationship of caloric requirement with temperature of organics

Organics			
Temperature, °C	**Caloric Requirement, J/g**		
	Nitrogen	**Air**	**Carbon Dioxide**
50	56	45	64
100	69	48	41
0	99	72	72
200	159	127	136
250	245	257	219
300	366	589	353
350	562	1283	622
400	824	1949	977
450	1078	2733	1296
500	1290	4113	1619
550	1438	5048	1943
600	1519	5327	2233
650	1524	5330	2457
700	1406	5313	2624
750	1164	5292	2740
800	839	5258	2821
850	447	5211	2858

Table 4.12. Relationship of caloric requirement with temperature of paper

Temperature, °C	Caloric Requirement, J/g		
	Nitrogen	**Air**	**Carbon Dioxide**
50	70	79	87
100	148	161	95
150	253	291	152
200	373	441	225
250	492	612	310
300	636	987	478
350	961	2211	1093
400	1404	3115	1760
450	1833	4774	2193
500	2165	5312	2904
550	2378	5398	3579
600	2488	5442	4041
650	2509	5456	4028
700	2422	5452	3983
750	2275	5426	3977
800	2079	5379	4027
850	1817	5321	4112
900	1493	5268	4261

Table 4.13. Relationship of caloric requirement with temperature of plastics

Temperature, °C	Caloric Requirement, J/g		
	Nitrogen	Air	Carbon Dioxide
50	127	100	73
100	298	230	120
150	447	333	142
200	598	472	206
250	754	754	323
300	900	1206	553
350	1060	1724	847
400	1239	2162	1229
450	1395	2664	1817
500	1547	4641	2719
550	1732	6397	3768
600	1883	6529	4436
650	2011	6595	4609
700	2096	6660	4613
750	2110	6690	4619
800	2051	6706	4642
850	1935	6713	4689
900	1731	6712	4761

Table 4.14. Relationship of caloric requirement with temperature in textile

Textile			
Temperature, °C	**Caloric Requirement, J/g**		
	Nitrogen	**Air**	**Carbon Dioxide**
50	44	31	23
100	37	0	-99
150	147	74	-81
200	262	152	-40
250	364	266	8
300	462	763	121
350	563	2573	524
400	692	3217	967
450	795	3811	1367
500	860	4022	1729
550	874	4066	2100
600	833	4095	2443
650	752	4116	2676
700	624	4133	2626
750	430	4152	2535
800	158	4173	2481
850	-200	4194	2455
900	-709	4218	2466

In the above Tables 4.10, 4.11, 4.12, 4.13, the total caloric requirement for nitrogen is negative (endothermic) and it is positive (exothermic) for the mixture in the other two gases. There is an exception for plastics for paper and plastics. This is because of large hydrocarbons in the samples. And it is the same even for the MSW (simulated) samples. The above data is really important as it helps us in calculating the caloric requirement of 1 gram of the sample to increase the temperatures.

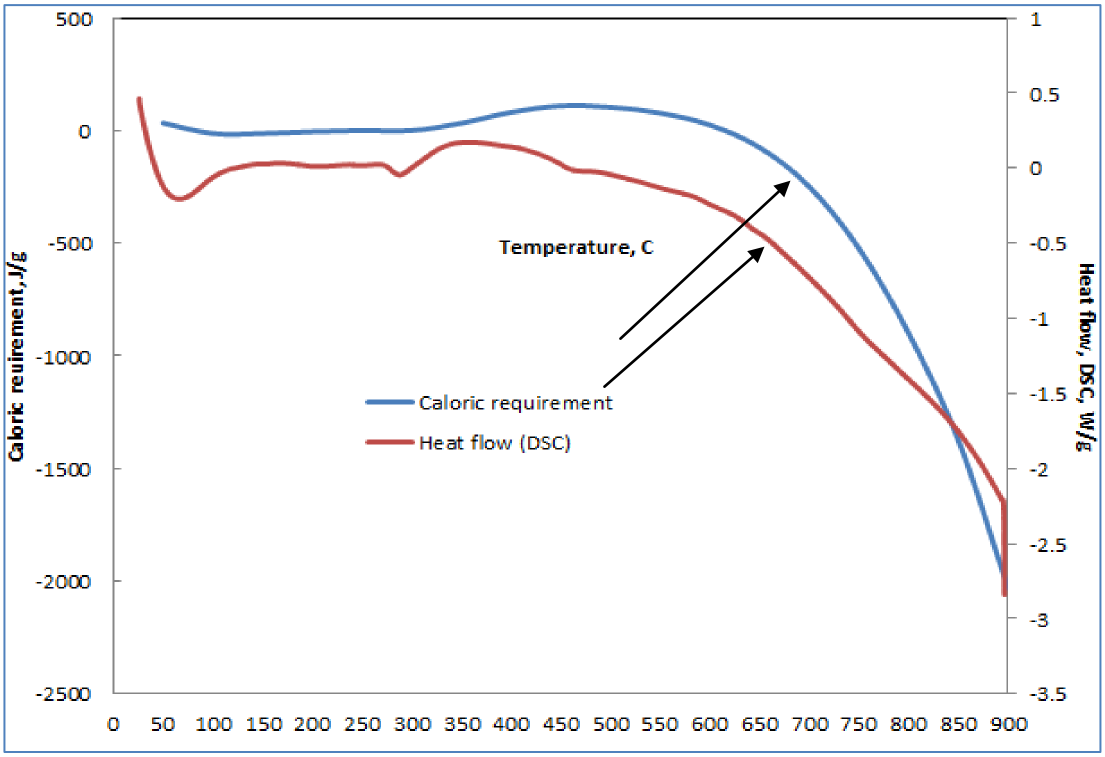

Figure 4.16. DSC curve and caloric requirement curve for the MSW mixture in nitrogen

These curves show us the heat flow and the caloric requirement (the heat required for the reaction to complete) in the three gas environment. The data from the Figures 4.16., 4.17., and 4.18., can help us predict the caloric requirement of the MSW samples at the desired temperatures. This data is really helpful in modeling an actual plant even though there are other factors such as the atmospheric and the operating conditions, energy losses etc., that are to be taken into consideration. Precision data of the caloric requirement of biomass pyrolysis is difficult to achieve by current calculation methods or by experiments on some laboratory equipments because of the complexity of MSW, the complexity of the processes.

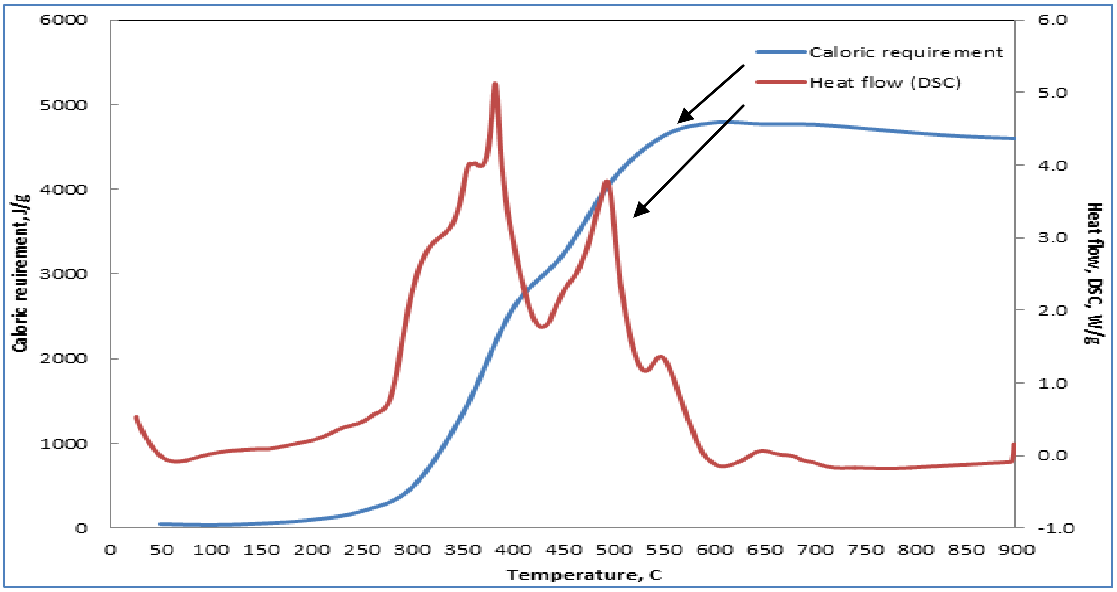

Figure 4.17. DSC curve and caloric requirement curve for the MSW mixture in air

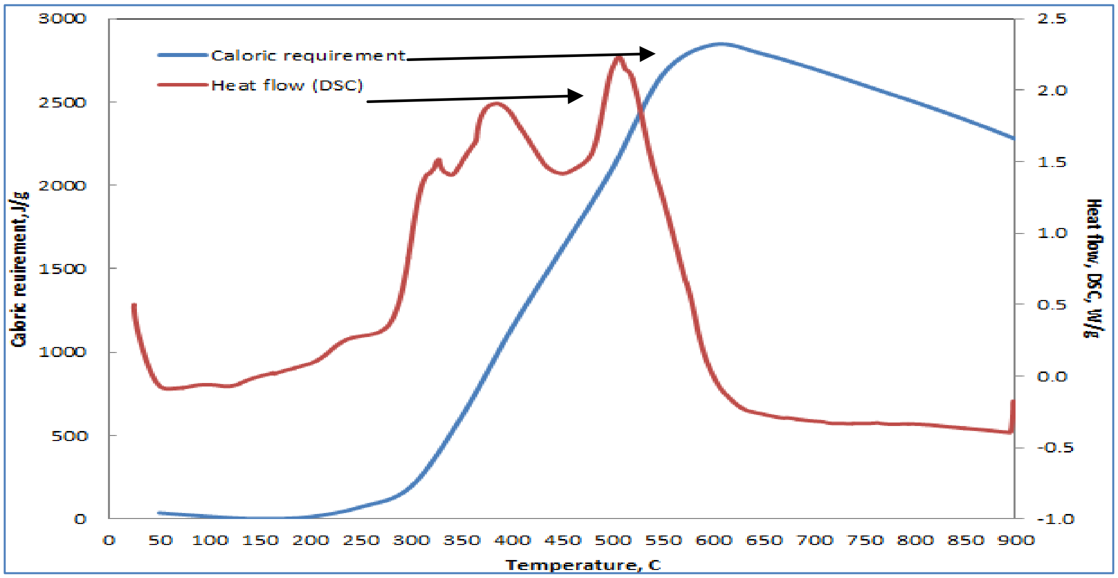

Figure 4.18. DSC curve and caloric requirement curve for the MSW mixture in carbon dioxide

A DSC is used to measure the heat flow into or out of a sample as it is exposed to a controlled thermal profile. The DSC curves and their corresponding caloric requirement curves in the Figures 4.15, 4.16 & 4.17 agree with previous data published by other authors. [47]. The caloric requirement for the MSW (simulated) and the MSW in the all the three gases i.e., nitrogen, air and carbon dioxide are shown in the following Tables 4.14, 4.15 & 4.16. As we can see, the values are negative for all the samples in nitrogen and they are all maximum in air when compared to other gases.

Table 4.15. Caloric requirement for MSW (simulated) in nitrogen, air and carbon dioxide

Compound	MSW (Simulated) in Nitrogen	MSW (Simulated) in Air	MSW (Simulated) in Carbon Dioxide
	Caloric Requirement, J/g	Caloric Requirement, J/g	Caloric Requirement, J/g
Banana peels	-2559	5657	2643
Cardboard	-2368	5371	3518
HD plastics	-2321	4989	2334
LD Plastics	1076	1696	1751
Newspaper	-3815	4288	2348
Packaging paper	-2848	1594	4297
Printed paper	-2409	2351	2385
Textile	-1272	5671	3910
Vegetable peels	-2051	7169	6321
Yard grass	-1230	9649	7102

Table 4.16. Caloric requirement for MSW in nitrogen, air and carbon dioxide

Compound	MSW in Nitrogen	MSW in Air	MSW in Carbon Dioxide
	Caloric Requirement, J/g	Caloric Requirement, J/g	Caloric Requirement, J/g
Organics	-46	5156	2842
Paper	-1493	5268	4261
Plastics	1731	6712	4761
Textile	-709	4218	2466

4.5. Technical, Economic and Environmental Analysis of Energy Production

MSW is a potential gasifier feedstock that presents an opportunity to produce alternative liquid fuels because of its availability in significant amounts at current landfills and because it is a predominantly biomass derived material that, like conventional biomass feed stocks such as wood, is a renewable resource. The viability of MSW as a gasifier feedstock for liquid fuels synthesis depends on several factors. Foremost is the availability of MSW in sufficient quantities to meet the minimum process scale required for economic feasibility. Based on this review, the process scale may be as large as 3,300 short tons per day of as received MSW, based on the anticipated scale required for conventional biomass feed stocks. Conventional biomass feed stocks are market based and are a cost to the process, averaging nearly $45 per dry short ton, whereas MSW is charged to the supplier as a tipping fee to dispose of the material. Historically, landfills receiving MSW and processing it to produce heat and energy using incinerators and gasifiers charge about $30 per short ton (as received basis) additional fee beyond that typically charged to just landfill the material. The effect of the extra charges on process economics and, in turn, minimum process scale for economic feasibility needs to be further examined.

A review of available information on the number and size of various landfill sites around the country identified 47 sites that processed 3,300 short tons per day or more (as received basis) of MSW (U.S EPA, 2008). Together these sites could potentially produce enough liquid fuel to meet approximately 1.4% of current transportation fuel demand (about 113 MM bbl/year of liquid fuel). A greater contribution could be attained if smaller scale facilities are found to be feasible due to latitude in the tipping fee charged to MSW producers. Another important issue deals with the quality of MSW as a feedstock. MSW is a heterogeneous feedstock containing materials with widely varying sizes, shapes, and composition, which can lead to variable gasification behavior if used in an as received condition. It is expected that some minimal size reduction and sorting will need to be performed to make MSW suitable as a feedstock for MSW gasifiers. RDF (Refuse Derived Fuel) is a processed form of MSW where significant size reduction, screening, sorting and, in some cases, pelletization is performed to improve the handling characteristics and composition of the material to be fed to a gasifier. There is a trade-off between the increased costs of producing RDF from MSW and potential cost reductions in gasifier design and operation. The chemical make-up of MSW includes significant quantities of chemical constituents that can create problems in downstream processes. While the concentrations of these contaminants are greater than those found in conventional biomass feedstocks, they are roughly comparable to those found in coal.

The commercial and demonstration gasifiers are currently available in sizes that range from 24 to 660 short tons per day MSW processing capability and will likely require multiple gasifiers to meet the minimum processing scale requirement for a liquid fuels synthesis plant. Further investigation is needed to determine the trade-offs between using many relatively small scale gasifiers that may be built as packaged systems or a few larger field erected gasifiers to minimize gasifier capital and operating costs. In addition, there are a large number of gasifier designs with a range of capacities that are at the pilot scale level of development. These were not examined closely and may ultimately be suitable for syngas applications. Overall, this study concludes that MSW should be considered as a potentially viable gasifier feedstock for liquid fuels synthesis. A review of feedstock availability, composition, and handling characteristics, along with commercially available MSW specific gasifiers, did not identify any obvious insurmountable technical or economic barriers to commercialization. However, further research into the economic issues surrounding tipping fees and process scale is needed to verify economic viability and the appropriate plant scale for economic viability.

CHAPTER 5

Conclusion

TGA was used to determine the thermal degradation characteristics and kinetic parameters of DGS residue and the simultaneous thermal analyzer (TG–DSC) can be used to investigate the caloric requirement for MSW in nitrogen, air and Carbon dioxide. TGA indicated that the starting temperatures of pyrolysis of DGS in nitrogen and oxidation in air increased with the increase of heating rate and initial moisture content. The residual weights of all the biomass samples after gasification (CO_2), pyrolysis (N_2) and combustion (air) were 7-10 %, 15-20 % and 5-7 % of the original dry mass respectively. The maximum rate of mass loss is directly proportional to the reactivity of the sample. It has been also observed that as the temperature in the sample increases, the weight loss peaks in the Derivative Thermogravimetric analysis, DTG curves shift to the higher temperature. It will also have a higher peak value and peak width at higher rates. The reaction kinetic model representing the process gave good agreement with the experiment al data. Activation energies, pre-exponential factors and orders of reaction computed from the model were comparable with published values. The data and model appear to be useful in the design of MSW processing systems.

The results of this research showed that the organic components wastes could be categorized as low stability organics, while the packaging paper could be categorized as mixed polymer material. Styrofoam wastes could be categorized as plastic material which has high thermal stability. The lignocellulosic blends pyrolysis gave the lower activation energy if compared with their component. Inorganic wastes blends showed lower activation energies than their components. The caloric requirements of the process can be achieved by integrating the differential scanning calorimetry (DSC) curves. Precision data of the caloric requirement of biomass pyrolysis is difficult to achieve by current calculation methods or by experiments on some laboratory equipments because of the complexity of MSW, the complexity of the processes, the lack of property values and the difficulty in determining the heat loss of the equipments.

Based on the values obtained, this thesis proves that the DSC cannot be used for all the substances because in some cases, most of the substance is lost by sublimation during heating and there are cases where there is unburnt carbonaceous substance even at the end of the reaction. Precision data of the caloric requirement of biomass pyrolysis is difficult to achieve by current calculation methods or by experiments on some laboratory equipments because of the complexity of MSW, the complexity of the processes, the lack of property values and the difficulty in determining the heat loss of the equipments.

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