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Characterization, Heating Value Modeling and Pyrolysis Studies of Municipal Solid Wastes

Shi, Honghong

UNIVERSITY OF CALGARY

Characterization, Heating Value Modeling and Pyrolysis Studies of Municipal Solid Wastes

by

Honghong Shi

A THESIS

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Abstract

A characterization study was carried out to determine the moisture content, proximate and ultimate compositions, heating value, and thermal weight loss behavior of fourteen different municipal solid wastes (MSW).

An empirical model was developed for the high heating value (HHV) estimation of MSW: HHV (MJ/kg) = 0.350 C + 1.01 H - 0.0826 O, which is expressed in terms of weight percentages on a dry basis of carbon (C), hydrogen (H) and oxygen (O). The validation results suggest that this model was effective in producing accurate outputs that were close to the experimental values.

A series of experiments pyrolysing coffee cups were also performed using zeolite type catalysts. In the presence of Ga/HZSM-5 in the mixed bed reaction, the pyrolysis oil's effective hydrogen-to-carbon molar ratio (H/C_{eff}) was markedly increased, from 0.49 to 1.11. Valuable phenolic compounds were observed to be the main species in the pyrolysis oil.

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Dedication

This thesis is dedicated to my loving parents and husband. Their unconditional encouragement, trust and support taught me not to fear, but to embrace, the challenges I face in work and life

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
AAE	Relative Average Absolute Error
ABE	Relative Average Bias Error
Ag	Silver
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
C	Carbon
CH_4	Methane
CHP	Combined Heat and Power Process
CO	Carbon Monoxide
CO_2	Carbon Dioxide
De-NO_x	Removal of Nitrogen Oxides
De-SO_x	Removal of Sulfur Oxides
DTG	Differential Thermogravimetric Analysis
EDS	Energy Dispersive X-ray Spectroscopy
f_a	Carbon Aromaticity
FC	Fixed Carbon Content
FT	Fischer-Tropsch Process
Ga	Gallium
GDP	Gross Domestic Product
GHG	Green-house Gas
GHV	Gross Heating Value
GTCC	Gas Turbine Combined Cycle
GWP	Global Warming Potential
H	Hydrogen - Element
H_2	Hydrogen Gas
^{1}H-NMR	Proton nuclear magnetic resonance
H/C	Hydrogen to Carbon Molar Ratio
H/C_{eff}	Effective Hydrogen to Carbon Molar Ratio
HHV	High Heating Value
$HHV_{predicted}$	Predicted High Heating Value
$HHV_{experimental}$	Experimental High Heating Value
ICI	Industrial, Commercial and Institutional
IUPAC	International Union of Pure and Applied Chemistry
LHV	Low Heating Value
l	Number of Predictors in Regression Model
Mo	Molybdenum
n	Number of Samples in Regression Model
N_2	Nitrogen Gas
N_2O	Nitrous Oxide
O	Oxygen - Element
O_2	Oxygen Gas
p-value	Observed Level of Significance

PA	Proximate Analysis
R^2	Coefficient of Determination
R^2_{adj}	Adjusted Coefficient of Determination
S	Sulfur
SD	Standard Deviation
SEM	Scanning Electron Microscope
Si/Al	Silica-to-Aluminum Molar Ratio of the Zeolite
T	Temperature
t/a	Tonnes per Annual
TEM	Transmission Electron Microscope
TG	Thermogravimetric Analysis
VM	Volatile Matter Content
WTE	Waste-to-Energy
XRD	X-ray Diffraction
Zn	Zinc
ZSM-5	Zeolite Socony Mobil-5

Chapter One: **Introduction**

1.1 Overview

The world's population still maintains an upward trend. The acceleration of waste generation due to population growth and urban area expansion is still unavoidable. For example in Australia, the population rose by 22% from 1997 to 2012, the GDP increased by 63%, and waste generation dramatically increased by 145% (Senaratne et al., 2013). Population, though, is not the only reason for the fast growth of waste generation. For instance, the Europe's population increased minimally from 1995 to 2009 (European Environment Agency, 2011); however, its waste generation during the same period was accelerating, as was the region's gross domestic product (GDP), shown in Fig. 1.1. The World Bank (Hoornweg and Bhada-Tata, 2012) reported that global cities generated approximately 1.3 billion tonnes of solid waste in 2012, and this number was expected to become 2.2 billion tonnes by 2025. All these facts indicate a warning message: reducing waste generation is almost unlikely in the near future and finding ways to address waste management more effectively is very necessary. The waste management strategies can be classified as: landfilling; recycling and reusing; waste transformed to energy/chemicals by proper conversion technologies.
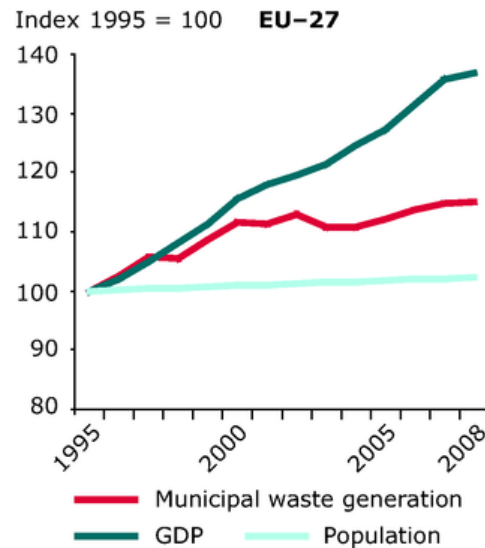
Figure 1.1 Trend of Municipal Solid Waste Generation in Europa-27 Compared with GDP and Population Growth (cited from European Environment Agency, 2011)

1.1.1 Conventional and Novel Landfilling

Conventional landfilling is the simplest way to dispose of municipal solid wastes, even though it results in negative environmental impacts. The direct disposal of wastes not only poses challenges due to land space limitation and production of leachate that would contaminate underground water, it also generates greenhouse gases - mainly CH_4 which has a global warming potential (GWP) 21 times greater than CO_2 emissions. The GHG emission from the landfills lies in the anaerobic decompositions of the organic components of the MSW. Landfills have two life stages: the operating stage, which is an open dumping period, and the closed stage, which occurs once the storage capacity is reached (Lou and Nair, 2009). The operating stage produces more methane since anaerobic degradation occurs mainly in the first few years (Fourie and Morris, 2004). However, the methane emission has the potential to last for hundreds of years (Börjesson et al., 2004). A general trend of the GHG emission during a landfill's lifetime was demonstrated in a paper by Lou and Nair (2009).

Advanced landfilling, incorporating the mechanical pretreatment and/or the integrated landfill system, produces less GHG gases in comparison with the conventional landfilling (DeWalle et al., 1978; Buivid et al., 1981; Ham and Bookter, 1982; Barlaz et al.; 1990). A typical integrated landfill contains gas collection units, wherein the captured gases are usually used as fuel gas. In 2001, there are 995 landfill facilities collecting landfill gases which is a remarkable increase over the 400 facilities that existed in 1995 (Lou and Nair, 2009). A novel landfill design (Fig. 1.2) - aerobic landfilling - can speed the degradation of the wastes by blowing air into the landfill. The initial purpose of this design is to stabilize the wastes in a shorter time and to control the leachate amount, thus improving the efficiency of energy recovery from the landfills. A series of problems related to this technology, however, were raised, warranting further discussion. For example, the recirculation of leachate has been shown to induce nitrous oxide (N_2O) production. The global warming potential (GWP) of N_2O is 310, which means that it has a 310 times larger capability than CO_2 to influence global warming. In addition, the air blowing and leachate recirculation systems need more energy input than the anaerobic landfilling. The energy consumption for aerobic landfill operations is reported as 0.198 MJ/kg of waste, whereas the consumption for conventional landfills is only 0.00399 MJ/kg of waste (Lou and Nair, 2009). Promoting this technology could be difficult in developing countries or the countries suffering from land shortage because the problem of land use is still not solved.
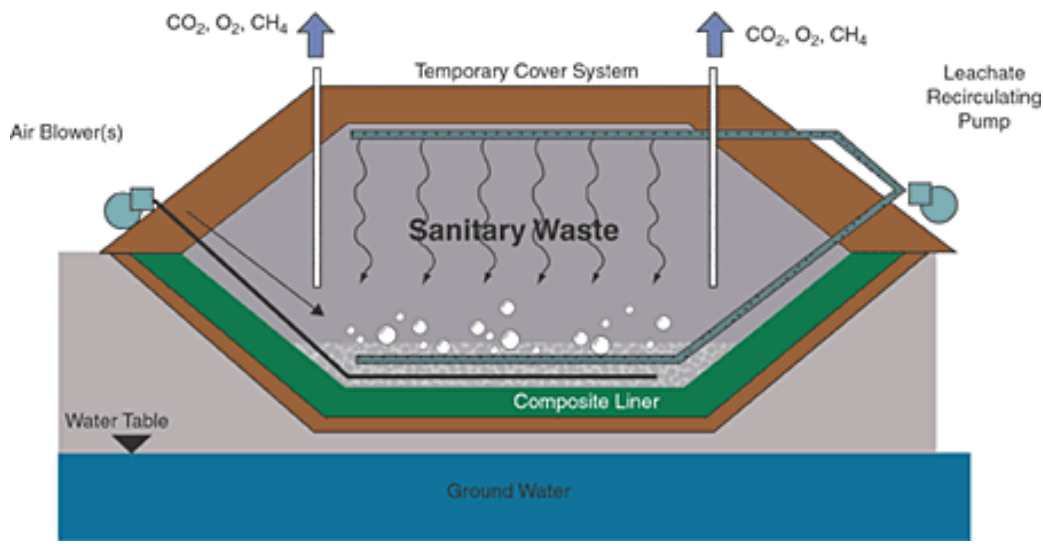
Figure 1.2 A Schematic of Aerobic Landfilling (source: http://esd.lbl.gov/ceb/landfill/)

1.1.2 Recycling

Recycling is the most effective waste management method for saving energy. Material and energy costs of manufacturing goods from the recycled material are lower than those of the virgin production. As for paper manufacturing, recycling also helps with forest protection and reduces water pollutions caused by the removal of lignin. The United States Environmental Protection Agency (EPA, 2007) proposed a methodology to estimate the benefits of waste recycling. Their results showed, based on the US national MSW recycling rate of 82 million tons in 2006, that the benefits in GHG reduction would be 182.2 million metric tons of carbon dioxide (MTCO2E). This is equivalent to taking 39.4 million cars off the road. In terms of the representation of energy content, these benefits would be 1,288 trillion British thermal units (BTU) which is equivalent to 6.8 million households' annual energy consumption or 222.1 million barrels of oil or 10.3 billion gallons of gas. Denison (1996) reviewed the environmental life-cycle studies of three MSW management systems: recycled production plus recycling, virgin

production plus landfilling, and virgin production plus incineration. Comparing the quantitative information on the four aspects of each system - solid waste output, energy use, releases of pollutants to the air and water - he concluded that the system of recycled production plus recycling provides the most environmental advantages across all the four parameters examined.

1.1.3 Waste-to-energy/chemical Technologies

Waste-to-energy (WTE) or waste-to-chemicals processes generate energy or chemical products using municipal solid waste. Not only are these methods positive alternatives to other MSW disposal methods, but they also provide promising options for the use of traditional fossil fuels. Building a new collecting or transporting system for MSW, as has been done for other fuels, is unnecessary because the system is already in place. In addition, MSW has no competition with food supplies or other human demands. The current landfill or open-dumping sites have opportunities to become a temporary storage station rather than the final solution. Modern waste-to-energy/chemicals technologies can be broadly classified as either biochemical or thermochemical processes.

Biochemical technologies are useful to convert bio-degradable wastes with high moisture contents into natural gas, ethanol, or composts. The development and applications, however, are limited due to the relatively low efficiency in energy recovery and minimal economic competitiveness. In addition, separation of large amounts of non-beneficial water from the products causes additional problems.

In contrast, thermochemical conversion has many advantages, such as reduced water use and easier continuous operation. Thermochemical conversion technologies fall into three broad categories: incineration, pyrolysis (if conducted at a low temperature, pyrolysis can also be called torrefaction) and gasification. Over the span of many years, various thermal technologies have been developed independently. Recently, the number of integrated WTE plants, incorporating two or more technologies of pyrolysis, gasification and incineration, are increasing. The flow from research of the processes, to their actual demonstration and even so far as to commercialization, is becoming apparent (Malkow, 2004).

Incineration only produces heat or electricity, while the other technologies have diverse by-products such as syngas and bio-oil. The Biofuels Digest (2013) summarized the operating/in-project bio-fuel facilities worldwide: only 25 facilities/plants out of the total 955 plants are using municipal solid waste material as the feedstock. Of those, the feedstock of 12 plants is comprised of wood waste. Gasification (occasionally accompanied with steam reforming), fermentation and hydrolysis (acid or enzymatic) were employed by these plants to convert wastes into the syngas that consist primarily of hydrogen and carbon monoxide. In turn, syngas is converted into ethanol, drop-in fuels, or biodiesels by the Fischer-Tropsch process. More details about the above mentioned biochemical and thermochemical technologies are introduced in the Literature Survey section of this chapter.

1.1.4 Global MSW Management Situation

Based on data reported by the World Bank (Hoornweg and Bhada-Tata, 2012), the United States produces the most MSW; its total MSW generation rate (624,700 tonnes/day) is only slightly lower than the sum total of 27 countries in Europa (664,195 tonnes/day). The second

largest waste producer, China, produces 520,548 tonnes/day. Fig. 1.3 shows the current proportions of each MSW management method globally and also the development trend in the United States, China and Europa over the last few years or decades. As we can see from the Fig. 1.3 (a), landfilling is still the primary choice internationally for the current stage. The alternatives, recycling and WTE, won more applications than composting, worldwide. It is worth mentioning that the most primitive method – dumping – still occupied a considerable proportion.

In the United States, MSW management, as seen in Fig. 1.3(b), refers to landfilling plus a small portion of recycling during the period before and up to 1970. Incineration grew quickly during 1980-1990. By the early 1990s, more than 15% of the MSW was combusted in the US. This fast growth, however, did not continue due to strict environmental legislation and political pressures (Psomopoulos et al., 2009). Composting appeared on the scene later than incineration but has shown an almost stagnant growth since 2003. Currently, recycling is still the most important waste management method, next to landfilling. In addition, the proportion of recycling is increasing continuously. In Europa-27 (Fig. 1.3(c)), composting, incineration and recycling grew together during 1995-2008. By 2008, more than 50% of the generated MSW were not landfilled. The growth rate of incineration, upon close observation, is smaller compared to those of the composting and recycling.
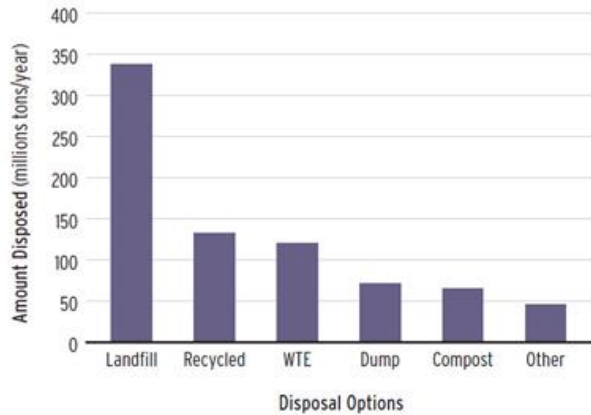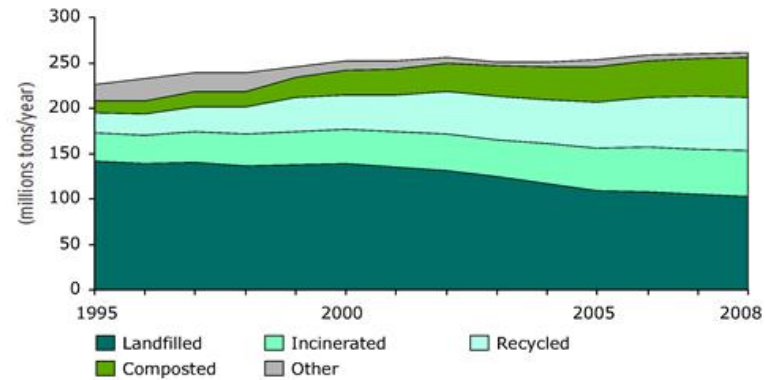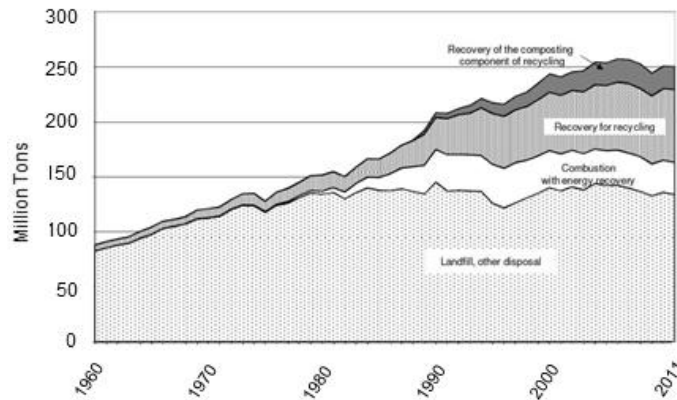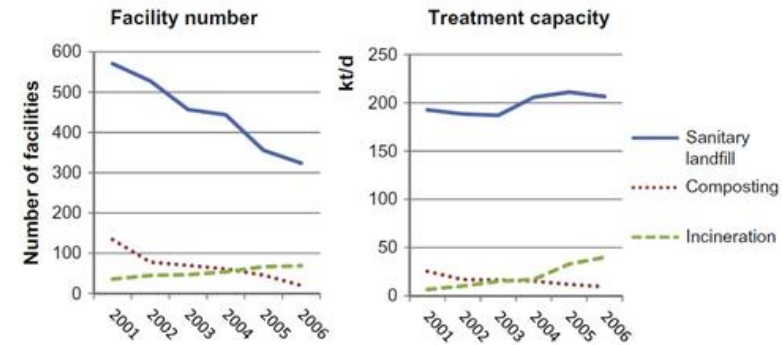
Figure 1.3 Development of Municipal Solid Waste Management in Europa-27, United States, China and the Worldwide Trend

(adapted from Hoornweg and Bhada-Tata, 2012; European Environmental Agency, 2010; United States Environmental

Protection Agency, 2011; Chen et al., 2010)

In China, from 2001 to 2006 (Fig. 1.3(d)), the landfill facilities declined in number considerably (more than 250). Of note is that the capacity and quality of the landfills both improved because of increasing support from international organizations and private investors (Chen et al., 2010). The number and capacity of incineration facilities have grown steadily, especially after 2004, the year in which China became the country to generate the most MSW for the first time. In contrast, composting facilities became difficult to site and their capacity dropped. According to the research of Chen et al. (2010) the decline in China was attributed to: (1) food and other wastes that are proper for composting are not source-separated which elevates the costs of manual work; (2) farmers in China have psychological resistance to compost products derived from the waste material, which leads to a decline in market demands; (3) composting's low profitability, due to the previous two reasons, makes it hard to attract new private investors for financial support.

Although landfilling plays an important role in many countries worldwide, it is not a priority of waste management strategies for some countries, such as Singapore or Japan. In 2000, MSW via incineration took up to 87% of the total waste disposed of in Singapore; for Japan, this number was 74% in 1996 in contrast with a rate of 5.48% in Canada and 16% in the US at the same year (Bai and Sutanto, 2002). Japan is a high population density country with about 71% of the total land area comprised of uninhabitable mountain areas, making the location of landfill sites more challenging as compared with other countries (Ecke et al., 2000). According to the report by the Ministry of the Environment of Japan (2014), the total waste production of 2013 is 44,870,000 ton; only 10% of this is from landfilled zones and 20.6% are recycled. A total of 1,172 waste incineration plants in Japan generate 1,770,000 kilowatts of power as of that year

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(Ministry of the Environment of Japan, 2014). In Singapore, land scarcity is also the main reason that drives waste management towards less landfilling. Recycling has proven to be a costly method in Singapore, where metal is the only material that is successfully recycled with a rate of more than 85%. In addition, the practice of biological treatment of organic wastes has also not been widely adopted (Bai and Sutanto, 2002). Incineration is selected as the principal MSW management strategy for these two countries due to its high efficiency in reducing the waste's volume.

1.1.5 Characterization of MSW

Characterization study is an important part of MSW management that provides necessary information for the recycling industry and other waste disposal alternatives. For most of the MSW case studies, characterization refers to the collection of wastes' physical composition. A vast of literature are available for the MSW's physical composition data globally (Hoornweg and Bhada-Tata, 2012; Troschinetz and Mihelcic, 2009; Zhang et al., 2010). However, as mentioned by Hoornweg and Bhada-Tata (2012), the definitions and methodologies for measuring these data are sometimes not clear and not standardized, for instance, the definition of organic wastes are not always provided.

Only a small number of publications also focused on the study of wastes' chemical composition. (Kathirvale et al., 2003) reported the proximate analysis data, elemental composition, heavy metal content and net calorific value of MSW in Kuala Lumpur, Malaysia. However, these data were measured using a representative sample of the local wastes. The values may change with the physical composition of the representative sample so that their repeatability could be low. A possible solution to this problem is to classify the waste stream into several

categories according to the material type; and to measure the features of each category. Then the overall feature can be conveniently calculated with the help of physical composition data.

The heating or calorific value is one of the most important chemical characteristics of MSW since it determines the wastes' energy content. It is approximately inversely proportional to the capacity of a WTE furnace/boiler (Reddy, 2011) and is either measured by a bomb calorimeter or calculated by an empirical model. It is critical to have accurate and reliable heating value data for the design, operation and maintenance of a WTE plant. However, not all MSW management facilities are equipped with bomb calorimeters in order to determine the heating values. Moreover, the experimental measurement of the heating value is tedious and requires advanced technical skills in the handling of equipment (Kathiravale et al., 2003).

Besides the physical composition and chemical composition, other characteristics such as the surface area of MSW are seldomly discussed in the literature. Recently, the agricultural and forest biomass wastes are reported as the potential bio-adsorbents for the industrial wastewater treatment (Bilal et al., 2013). Similarly, the MSW may also be attractive for uses in this area, due to its cheap nature and bulk availability. However, explorations on whether it has the porous feature and mono to multilayer adsorption behaviours are still not available. In addition, the current characterization studies do not pay enough attention to the industrial, commercial, institutional (ICI) wastes that take up the largest fraction of the collected MSW in most cities globally (Hoornweg and Bhada-Tata, 2012). The physical difference between some types of the ICI wastes and residential wastes was briefly discussed by Zhang et al. (2010), yet the chemical difference has still not been assessed in literature.

1.1.6 Summary

In a summary, the waste management patterns differ from country to country. A nation's economic development, population density, land size, human cost, and market demand of waste-derived products all have impacts on a government's decision. The conventional landfilling causes a plenty of environmental problems while the novel landfilling technologies are still not mature for widespread use. Recycling is a great way to manage the MSW, however, is only suitable to limited types of wastes. By contrast, conversion of wastes into energy or chemical products has many advantages. Most of the biochemical and thermochemical conversion technologies are still under development, and need contributions from relevant research works. The currents studies on the MSW characterization are insufficient in providing reliable data of chemical composition and other features. In particular, the chemical difference between the ICI wastes and the residential wastes have not been discussed in the previous studies.

1.2 Literature Survey

Composting, anaerobic digestion, fermentation and hydrolysis belong to the biochemical technologies; incineration, gasification and pyrolysis/torrefaction are the commonly used thermochemical technologies. A summary of recent publications of the mentioned processes is presented in the next paragraphs.

1.2.1 Composting

Composting is defined as a controlled aerobic decomposition process of organic wastes that generates biologically stable end-products for use as a soil conditioner, fertilizer, bio-filter material, or fuel (Jördening and Winter, 2006). The primary objective of composting is to biologically stabilize the organic compounds in the waste. Modern composting, also known as

aerobic digestion, is a controlled process evolved from the conventional open-air composting with odours reduced or eliminated by covering the facility, using bio-filters to purify the exhaust air, or using composting reactors. Around two thirds of the bio-waste continues to be composted in conventional open-air windrows (Ludwig et al., 2012) because of this method's high economic efficiency.

The source separation of the organic compounds before composting is of great importance, particularly with regard to wastes that contain heavy metals, to ensure the compost product is safe for agricultural use. This tendency was highly marked in Germany, Holland, Austria and Switzerland, where the agricultural use of compost from unsourced MSW has been forbidden since 1986 (Ludwig et al., 2012).

1.2.2 Anaerobic Digestion, Fermentation and Hydrolysis

Anaerobic digestion and fermentation are quite similar that they both involve the decomposition of organic compounds under anaerobic conditions, that is to say, the micro-organisms access oxygen from the waste itself instead of from the ambient air. Their main differences are the end products and the microorganism species.

In an anaerobic digestion process, organic compounds in the wastes are decomposed by bacteria, producing a gaseous product that can be upgraded into high quality natural gas for dimensional use or can be used directly as a fuel gas for electricity supply. The overall efficiency of electricity production through the anaerobic digestion is reported as 10-16% (McKendry, 2002; Basu, 2013).

The conversion of sugars using yeasts and bacteria is the essence of a fermentation process. Its main production is liquid, usually ethanol. The bioethanol production from starch and sugar-based feedstock, such as corn and sugarcane, has been fully commercialized. The commercial production of lignocellulosic bioethanol, in turn, has not been practiced due to its low ethanol yields and high costs (Banerjee et al., 2010). Economic studies showed that the processes (i.e. pretreatment, enzyme production and hydrolysis) necessary to break down the cellulose and hemicellulose into simple sugars before fermentation take up to 40-45% of a project's total cost (Banerjee et al., 2010). This bottle-neck makes the total fermentation process of MSW less competitive on the economic side.

As mentioned, hydrolysis is able to transform the cellulose fractions of a feedstock into sugars for subsequent fermentation. The current hydrolysis technologies can be classified into two types: acid hydrolysis and enzymatic hydrolysis. Acid hydrolysis can be performed using either inorganic acid or organic acids, such as maleic acid and fumaric acid (Kootstra et al., 2009). Li et al. (2007) conducted experimental works to convert MSW – carrot and potato peelings, grass, newspaper, scrap paper – into the glucose by different pretreatment methods (steam and microwave) and hydrolysis conditions (dilute acids and enzymes). In their study, the dilute acid hydrolysis, followed by steam treatment, proved to be the most efficient means of processing the selected MSW's conversion.

1.2.3 Incineration

Incineration (controlled combustion) is one of the oldest thermal technologies and remains to be a generally used method to treat MSW, whereas other thermochemical technologies, such

as gasification and pyrolysis, are still under development. In the past, incineration was a simple process without any energy recovery or pollution controls. Its primary goal was to reduce the volume (about 80-90%) and mass (up to 70-80%) of the wastes in order to save landfill space (Lombardi et al., 2015). By the early 1980s, a notable amount of chlorides, dioxins, sulfur oxides, heavy metals and particulates produced from the MSW incinerators were found to contribute substantially to air pollution (Ludwig et al., 2012). Since then, the incinerator operators were forced by stringent legislations to raise investments on developing environmental technologies. At the same time, energy recovery from waste became a secondary, but increasingly important, goal (Ludwig et al., 2012). Saturated steam is generated if the energy recovery only pursues thermal energy production; otherwise, the superheated steam would be generated during a Combined Heat and Power (CHP) process for both heat and electricity production (Lombardi et al., 2015).

Current designs of MSW incinerators are classified into: grate incinerator, rotary kilns and fluidised bed, of which the grate incinerator is a dominant choice. Their benefits, limitations and operation conditions are summarized and listed in Table 1.1.

Table 1.1 A Comparison of Grate, Rotary Kiln and Fluidised Bed Incinerators (Van Caneghem et al., 2012; Lombardi et al., 2015)

Gasifier Type	Benefit	Limitation	Operation temperature	Value of excess air
Grate incinerator (mobile/fixed)	Simplicity; relatively low capital cost; high treatment capacity, especially for mobile type grate incinerator		Around 1250°C	Low

Rotary kiln incinerator	Being able to process any type of waste (even the liquid wastes)	Large flue gas flow rate influences the energy recovery performance and entails large costs of flue gas cleaning	Around 1400ºC	High
Fluidised bed (bubbling fluidised bed – BFBC, rotating fluidised bed – RFBC, circulating fluidised bed – CFBC)	High turbulence resulted in more efficient heat transfer and uniform mixing that promoted the combustion	Feedstock preparation - size reduction, ash content reduction, alkali metal removal, mixing - is a requisite; homogeneous particle size is preferential	Around 800-900ºC	Low

Most of the traditional MSW incineration facilities were considered to have lower electricity efficiency (13-24%) than the ones of burning fossil fuels (Malkow, 2004). Modern WTE plants are attempting to narrow this gap through improving the boiler/steam turbine design or optimizing the operation conditions as follows.

- Large sized plants (＞250,000 t/a) were proven to have better overall efficiency compared with the small sized plants (＜100,000 t/a) (Reimann, 2009). In addition, the large plants, which have considerable thermal input, ensure the auxiliary devices' performance and promote steam turbine efficiency (Consonni and Viganò, 2012).

- Increase the boiler's operating temperature and pressure to a certain extent but not to the level of causing corrosion problems.

- Use water-cooled condenser to take the place of the air-cooled condenser for lower condenser pressure, hence improving efficiency (Gohlke, 2009; Pavlas et al., 2011).

- Optimize the boiler design and its combustion conditions. A WTE plant in Germany applied a new boiler and stoker unit that reduced the value of excess air from

1.9 to 1.39, promoted the boiler efficiency to 87.65% and allowed an electricity efficiency of about 26.63% (Lombardi et al., 2015).

- Integrate the incineration and gas turbine combined cycle (GTCC), which involves using cleaner gaseous fuel, such as natural gas, to superheat the steam instead of using the flue gas, to allow for high steam temperatures without the concern of corrosion risk. The configurations of WTE/GTCC proposed in a number of publications (Qiu and Hayden, 2009; Poma et al., 2010; De Souza-Santos and Ceribeli, 2013a-b) showed relatively high electricity efficiency (30-46.3%), depending on the ratio of natural gas inputs, boiler type, feedstock characters and other design conditions.

Although these technology improvements will increase costs, a compromise should be established between the higher investments and the profits related to the expected efficiency increase.

1.2.4 Gasification

Unlike incineration, the oxidant supply in a gasification process is insufficient (lower than the amount for the stoichiometric combustion). In other words, gasification is a partial oxidation process, with controlled use of air, oxygen, carbon dioxide, steam (H_2O) as the gasification medium (also known as gasifying agents). In particular, using steam achieves hydrogen-rich gas product. The product gas of gasification can be directly used as fuel gas for heat or power generation because of its considerable energy content. Although the gasification-based WTE plants usually have lower electricity efficiency and higher ranges of operating/capital costs than those of incineration-based WTE plants, they still have a number of advantages related to gas clean-up, ease of control and higher reliability (Arena, 2012). By now, gasification has been

proposed as another alternative, in addition to conventional incineration, for energy recovery from MSW. This is supported by years of success in gasification-based WTE plants operating in Japan and the emerging projects in Korea and Europe (Malkow, 2004; Arena, 2012). Different types of gasifier – downdraft/updraft fixed bed, bubbling fluidized bed, circulating fluidized bed, entrained flow, rotary kiln, moving grate, plasma – used for the gasification process are reviewed by Arena (2012). Of all these technologies, the fluidized bed is considered as one of the most promising due to its numerous advantages: almost uniform isothermal conditions throughout the reactor; highly efficient mass and heat transfer; allows short residence times at lower temperature; reliable process control; good operating flexibility (Mastellone and Arena, 2008).

Another important application of product gas is to extract and convert its syngas part (hydrogen plus carbon monoxide) into a series of downstream chemicals or hydrocarbon fuels through the famous Fischer-Tropsch process. Introducing steam and increasing the gasification temperature can both enhance the conversion of feedstock and improve the syngas yield (Guan et al., 2009; He et al., 2009; Wang et al., 2012). Excessive steam, however, lowers the quality of the product gas (Wang et al., 2012). The optimized steam to carbon ratios (S/C) are reported in a wide range: 0.42-2.41 (Guan et al., 2009; He et al., 2009; Wu and Williams, 2010; Luo et al., 2012; Wang et al., 2012), mainly due to differences of feedstock. Luo et al. (2012) found that adjusting the steam-to-carbon ratio can significantly influence the ratio of hydrogen to carbon monoxide (H_2/CO) in the product gas. Advantageously, syngas of different H_2/CO ratios can be produced to fulfill the various downstream demands. For example, syngas with H_2/CO of 1-2 is suitable for liquid fuel production, whereas syngas with higher H_2/CO can be used for synthetic ammonia or fuel cell production (Luo et al., 2012).

During gasification, tar within the product gas is a major concern; it not only contains a large amount of energy content that should be in the gases, but also has the potential to cause severe damage to pumps or create other operational problems. Tar is a mixture of complex condensable hydrocarbons that includes aromatics with single to multiple rings (Mastellone and Arena, 2008). The experimental results of a pilot-scale bubbling fluidized bed gasification by Arena et al. (2007) revealed that the average tar content within the exit gas was of the order of 100 g/m^3; this amount makes the gas not possible for direct use in the internal combustion systems that require loads lower than 100 mg/m^3 or in the industrial gas turbines that requires tar contents of about 1 mg/m^3 or less (Mastellone and Arena, 2008). A number of natural or synthesised catalysts were reported to remove the tar almost completely in the laboratory research stage, so as to improve the product gas quality and, especially, to increase hydrogen yield greatly - up to 50.8-55.78 vol/% (Guan et al., 2009; He et al., 2009; Luo et al., 2012; Wang et al., 2012). In addition, a number of catalysts with similar functions have been extensively studied for tar removal during biomass gasification due to their ability to promote cracking or steam reforming reactions.

1.2.5 Pyrolysis and Torrefaction

Pyrolysis is the thermochemical decomposition of organic material in absence of oxygen which produces three products: gas, liquid and solid. It is typically carried out in a temperature range of 300-650ºC compared to 800-1000ºC for gasification (Basu, 2013). The product gas can be used as a fuel gas after proper cleaning processes. Char, the solid residue of pyrolysis, is usually carbon-rich. The liquid products of pyrolysis have been widely considered to have potential in fuel or chemical production. However, seldom existing pyrolysis technologies are

commercialized for producing oils as outputs (Chen et al., 2014). Most of the pyrolysis technologies are currently combined with gasification or incineration for heat or power generation (Chen et al., 2014) such that the pyrolysis acts as an intermediate step to promote the overall fuel gas production and increase the operation's stability. Chen et al. (2014) explained that current information on the technology's development, especially in the area of product analysis, is not sufficient to support its commercialization. In addition, the complex composition of MSW and insufficiency of its characteristics also causes difficulties. For instance, the RWE-ConTherm plant in Hamm, Germany (Chen et al., 2004) was equipped with a rotary kiln type reactor and a shredder in front for a pyrolysis process. The plant has not been operational since 2009, after an accident caused by the non-conformance between the design process and the feeding wastes, resulted in an operating temperature beyond the tolerable range (Chen et al., 2014). As for the reactor design, a rotary kiln reactor has more large-scale applications than other reactors used for pyrolysis, whereas a tubular reactor can be competitive for small/medium size plants. The characteristics and application status of different pyrolysis reactor are listed in Table 1.2.

Table 1.2 A Summary of Various Pyrolysis Reactors (cited from Chen et al., 2014)

Reactor type	Fixed-bed	Rotary kiln	Fluidised-bed	Tubular
Application status	Operation in batch; only for the laboratory reseach	Most common	Only for laboratory research; no practical experience for MSW	A few
Requirements on feedstock preparation	Almost no requirement	Not rigid	Very rigid	Rigid

Capacity	Small, up to several tons per day	Large, up to 150,000 tons/y	Large (in theory)	Medium, up to 50, 000 tons/y
Requirements on operation and maintenance	Batch operation demands more labour working	Low to medium	Highest	Medium to high
Flexibility to operational parameters' change	Excellent flexibility	Good flexibility	Limited flexibility to the waste particle size change	Limited flexibility to the waste particle size and temperature changes

Several factors influence the products' distribution and their qualities during a pyrolysis process: temperature, heating rate, residence time, waste species, and catalyst. It is generally thought that using a high heating rate, a moderate final temperature and a short gas residence time would maximize the liquid production, whereas using a slow heating rate, plus a high final temperature (700-900ºC) and a long gas residence time would promote gas production (Basu, 2013). The composition of the liquid product is highly dependent on the feedstock material. Islam et al. (2005) found that the waste paper derived pyrolysis oil is similar to that of biomass derived oils and is highly oxygenated. Demirbas (2004), however, conducted non-catalytic pyrolysis experiments of plastic wastes in a fixed-bed tubular reactor at different temperatures (650-875K) and observed that the liquid products were hydrocarbons belong to the gasoline range that would be ideally suitable for transportation fuel production after further processing. Moreover, a number of publications (Sharratt et al., 1997; Buekens and Huang, 1998; Pinto et al., 1999; Lin and Yang, 2007) introduced different catalysts to improve the gasoline selectivity of the plastic derived oil. These catalysts can be categorized as the cracking catalysts or reforming catalysts that have also been generally used in the petroleum refining industry. Attempts have

been reported to commercialize this plastic-to-gasoline technology but have not been successful so far, mainly due to economic factors (Buekens and Huang, 1998). Buekens and Huang (1998) analyzed that for an industrial-scale plant with a capacity of 25,000 t/a, the treatment costs of plastic wastes would be $250/t, while the produced oil, that has a quality similar to naphtha from crude oil, is only worth $180/t. This large price gap makes the process non-profitable. In addition, the plastics are recyclable wastes. Consequently, comparing pyrolysis to recycling is worthwhile to arrive at a better solution.

Torrefaction, a thermal treatment step in the relatively low temperature range of about 225-300°C in an oxygen-free atmosphere (Prins et al., 2006), is also considered as a mild pyrolysis process. Because torrefaction removes water from the material, it reduces the power requirement for the wastes' storage and transportation costs. It is also a technically feasible method for converting raw material into high energy, dense, and hydrophobic matter, which can be easily ground into solid char particles used for subsequent thermochemical processes (Vincent, 2013) such as gasification or incineration.

1.3 Problem Statement and Research Motivation

Due to several reasons that discussed above, the research interests of this thesis focus on the thermochemical conversion of MSW, in particular, the pyrolysis process. The development of MSW pyrolysis currently lags behind other thermal technologies such as incineration and gasification, mainly due to the inhomogeneity of MSW, insufficient information about the feedstock characteristics, complex end-products and the resulting technical difficulties. The abundant products from the pyrolysis process, however, could be value added. The current MSW characterization studies mainly refer to the physical composition determination that cannot

provide enough information for the pyrolysis technologies' development and other needs in the waste management. In particular, the previous studies did not provide reliable data on the chemical natures including the heating values of different waste materials. Moreover, the characters of the ICI wastes are seldom discussed and compared with the common residential waste, however, should be warranted in future work. The introduction of catalysts to a pyrolysis process has numerous benefits, such as increasing the selectivity of the ideal products. But studies on the topic of catalytic pyrolysis are still limited. Thus, there is a need for an improved understanding of the MSW feedstock's characteristics; and a necessary of developing suitable catalysts to promote the selectivity of high-value chemicals in the end products.

1.4 Objectives

The overall research goal of this thesis is to fill the current data gap on MSW characterization and to explore the possibility of producing value-added products from these wastes. To achieve this goal, the research works demonstrated in this thesis were conducted in accordance with the following specific objectives:

- Obtain a comprehensive characterization of the municipal solid wastes to evaluate their potential use for the thermochemical conversions
- Establish an empirical model to obtain the heating value of municipal solid waste accurately
- Develop a particular pyrolysis process, with the addition of suitable catalysts, for renewable chemical production from the municipal solid waste

1.5 Thesis Organization

This thesis is composed of five chapters. In Chapter One, an overall scenario of the global municipal solid waste management situation and the development of various waste-to-energy/chemicals technologies are reviewed. Based on all the discussions, the motivation for this study is delivered and the objectives are stated.

Chapter Two presents the characterization studies of the municipal solid waste. Different municipal solid waste samples were tested and evaluated with an emphasis on their potential in thermochemical conversions. In addition, a preliminary study of pyrolysis and torrefaction of these samples were conducted using a thermogravimetric analyzer that provides information about the thermal weight loss behaviour of each material and elemental analysis of the produced chars.

Chapter Three deals with the objective of estimating the heating value of MSW accurately by an empirical model. The collected experimental data was divided into two subsets, for model establishment and model validation, respectively. Multiple linear regression and step-wise regression methods were used to establish the statistical model and error analysis was conducted to evaluate its accuracy level.

Chapter Four presents the investigation of producing high-value chemicals from the waste coffee cups via catalytic pyrolysis. The catalyst synthesis method and the pyrolysis reaction apparatus were described in details. Various analytical technologies were used to acquire the composition knowledge of the gas and liquid products. The catalysts were characterized by the XRD, SEM-EDS and TEM to discuss their catalytic mechanism.

The conclusions and suggests for future work are discussed in Chapter Five.

Chapter Two: **Characterization of Municipal Solid Wastes**

2.1 Introduction

MSW is often quantified and characterized by the source of generation or the type of material that provides its physical composition. However, in the design of a WTE facility, it is also important to consider other factors such as the moisture content, the volatile and fixed carbon contents, the proportion of non-combustibles, and the sulfur content. These characteristics are crucial for the selection of the technology, the capacity determination of the furnace/boiler, and the design of auxiliary facilities, such as flue gas cleanup equipment.

2.2 Material and Methods

2.2.1 Sampling

The sampling of 14 different landfill wastes was conducted at the City of Red Deer's Waste Treatment Facility in Alberta, Canada. The physical composition of the landfill waste from the City of Red Deer is shown in Fig. 2.1. The samples were in their original conditions that did not experience any washing or cleaning process. All samples were dried immediately after sampling to obtain their true moisture contents. After drying, these samples were separately sealed and contained within plastic bags or bottles with a desiccant agent based on the relevant category.

According to the material properties, the samples were divided into 7 categories: wood waste, rubber/leather/multiple/composite organic material, non-recyclable paper, carpet waste, rigid plastic, textile waste, and film/styrofoam waste. Each category contained two samples from different sources: residential; and ICI (industrial, commercial and institutional).

This sampling range covered almost all types of organic landfill MSW, except waste water sludge, food wastes, human fecal matter, hospital wastes, manures and animal wastes. These organic wastes were not considered in this work due to their possible biohazardous properties, since the sampling, storage, pretreatment and experimental handling of these wastes require special disinfection or bio-protection instruments. Inorganic components or recyclable wastes, such as glass or metal, were not considered in our sampling range.
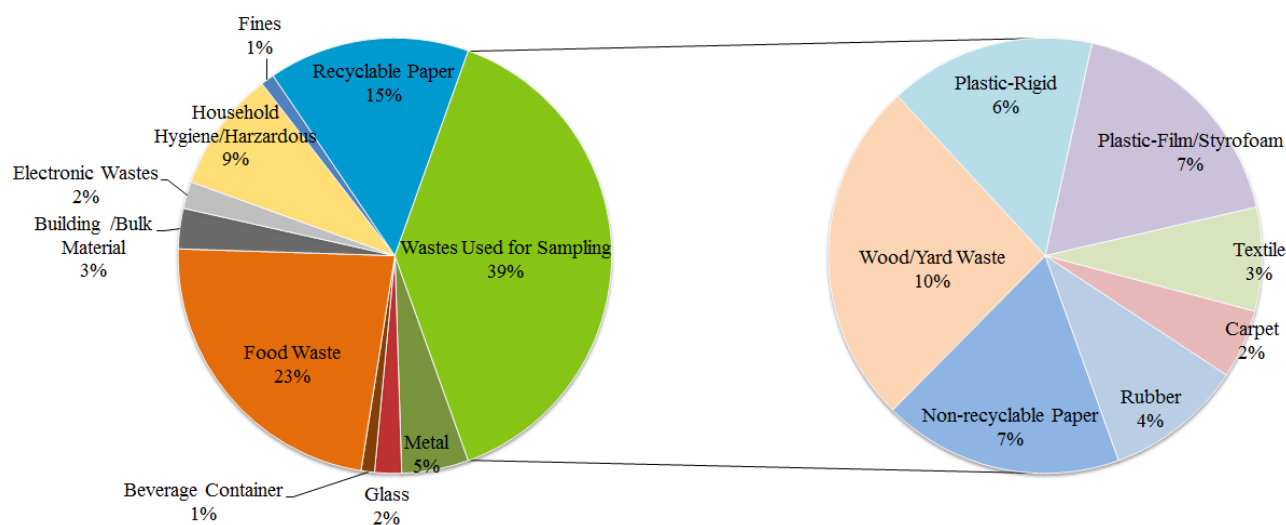
Figure 2.1 Physical Composition of Landfill Wastes from the Red Deer City (calculated on as-received basis)

2.2.2 Basic Characterization

Basic characterization in this study refers to five types of measurements: moisture content determination, proximate analysis, ultimate analysis, surface area and heating value determination. Every sample was tested three times for each type of the measurement; then, an average value was calculated and used to represent the sample's characteristic result.

The moisture content was measured using an oven drying procedure, with the specimen weighed outside of oven, according to ASTM D1348-94(2008). The samples were dried in an oven at 70°C to a constant weight.

After the determination of their moisture contents, the dried samples were ground by grinder at room temperature. Paper, textile and carpet samples turned into wool-like material that can't be sieved. Other samples became particles that can be easily sieved into three diameter ranges: 0-425 µm; 425 µm-1 mm; 1-5 mm for the triple repeated measurements respectively.

The proximate analysis was carried out according to ASTM D7582-12 with a thermogravimetric analyzer (TGA - STA6000, Perkin Elmer). Ceramic crucibles were used in order to minimize any thermal lag and to optimize the heat transfer. The proximate analysis includes the determination of moisture, volatile matter, fixed carbon and ash content. Fig. 2.2 describes the standard procedure of a measurement. A typical result illustration is as shown in Fig. 2.3. Since all the samples were dried in advance, the weight loss during 0-60 minutes which represents the moisture content cannot be observed.
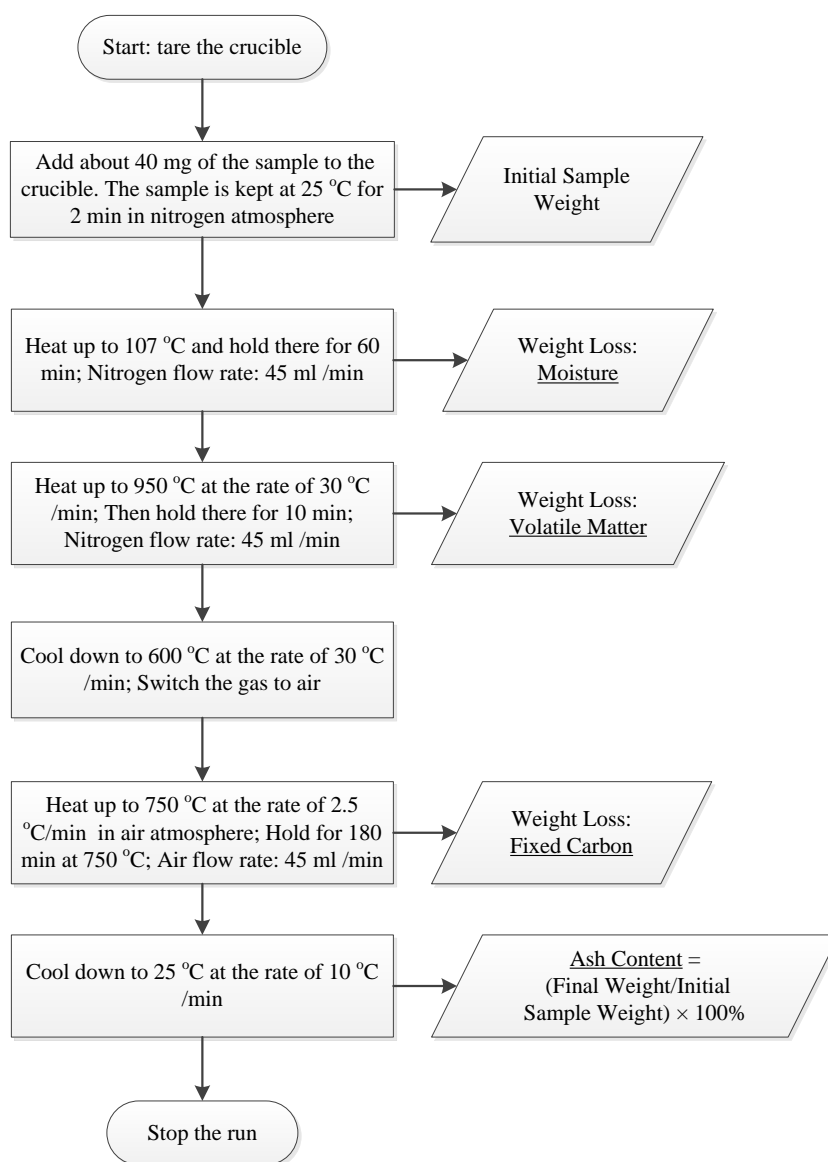
Figure 2.2 Procedure Flow of Proximate Analysis Experiments
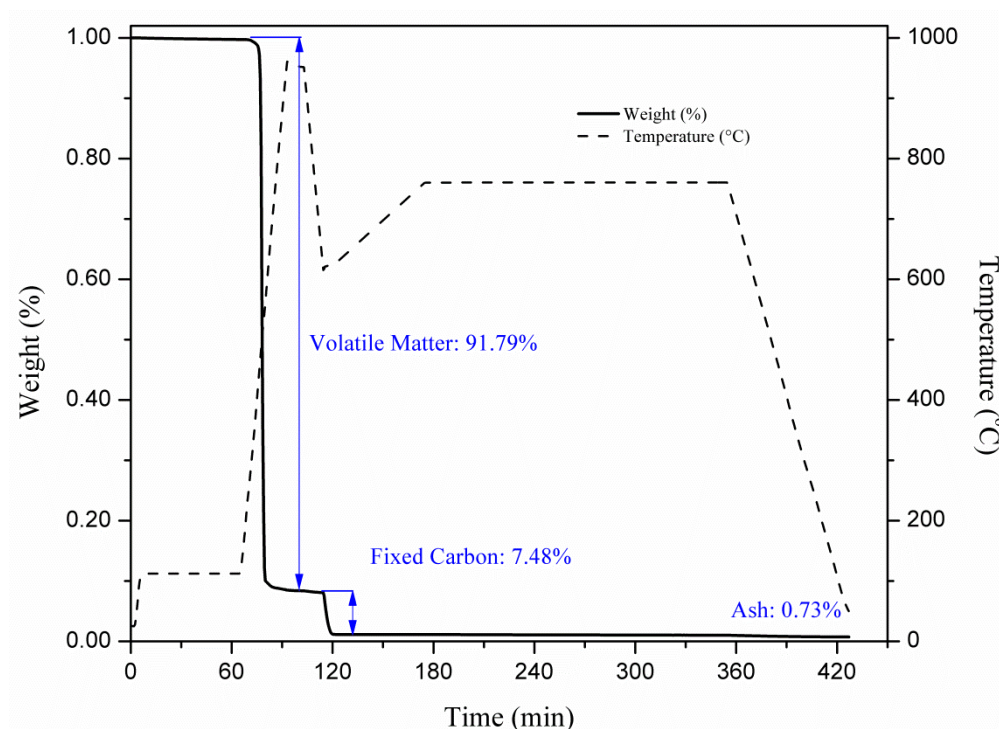
Figure 2.3 A Typical Result Illustration of Proximate Analysis (Sample: ICI-Plastic)

The ultimate analysis was performed using an elemental analyzer (2400 Elemental Analyzer, Perkin Elmer) in order to determine the carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) compositions. A standard experimental procedure of the ultimate analysis is described as follows: the system was purged with helium for 2 min, then with oxygen for 1 min. The sensors were monitored to ensure the combustion temperature to be 975°C and the reduction temperature to be 500°C. Prior to any runs, the analyzer should undergo a warm-up time of at least 2 hours (from a cold start). Blank tests and K-factors tests were carried out to obtain detector calibrating factors. In this step, cystine (provided by Perkin Elmer) is used as the analytical standard for K-factors determination. Aluminum crucibles (provided by Perkin Elmer) were used for sample preparation. After stability and repeatability of blank tests and K-factors

tests were obtained, the sample tests can be conducted. The weight range of a sample should be within 1.5 mg to 2.5 mg.

Oxygen in a feedstock consumes a significant amount of hydrogen, making the production of liquid hydrogen difficult, and generates water, which is of little benefit (Basu, 2013). Chen et al. (1986) introduced the effective hydrogen to carbon molar ratio (H/C_{eff}) with the following equation:

$$H/C_{eff} = (H - 2\ O)/C$$

where H, O and C are the moles of hydrogen, oxygen and carbon in a sample, respectively. The H/C_{eff} ratio is widely used to describe whether the economic conversion from a feedstock into hydrocarbons is possible.

The surface area of MSW was determined by using an automated porosimetry analyzer (Micromeritics ASAP 2020). Liquid nitrogen was used as a cold bath. Prior to the analysis, the sample was degased on the degas port at 70°C and with a 10 μm mercury (Hg) vacuum for 3 hours. After degasing, it was carefully moved to the analysis part for the gas adsorption measurement.

Experimental heating value measurements using a bomb calorimeter (6100 Compensated Jacket Calorimeter, Parr) were carried out according to ASTM D5468-02(2007). The experimental procedure was performed to burn the sample in a high-pressure oxygen atmosphere within a metal vessel, called a bomb, which was placed in a bucket filled with exactly two kilograms of water. A sample size of 0.5-1.0 g was used for each measurement.

After firing, the sample would be completely consumed in the bomb and was followed by a temperature rise of the water in the bucket. The heat of combustion was then calculated by multiplying the temperature rise of the water by a previously determined energy equivalent with a standard material (benzoic acid). This calculation process was automatically completed by the calorimeter. At the end of each measurement, the bomb needed to be opened to check whether the sample had been completely combusted; if not, the measurement had to be repeated.

It is worth mentioning that two forms of expression of the heating value are widely used in publications and technical reports: the high heating value (HHV), which is also called the gross heating value (GHV); and, the low heating value (LHV), which is also called the net heating value (NHV). The LHV can be calculated by subtracting the heat of water vaporization from the HHV. The water in this measurement is not the moisture content of a sample, but the water formed by the complete oxidization of hydrogen during the combustion. The bomb calorimeter used in this study was set up for measuring HHVs.

2.2.3 Thermal Weight Loss Behavior

The weight loss behavior of MSW during torrefaction and pyrolysis was studied by experiments using the TGA. Approximately 40 mg of the MSW sample was placed in a ceramic crucible to conduct the experiment. High-purity nitrogen was used as the carrier gas at a flow rate of 20 ml/min. Before heating, the sample was purged with nitrogen for 10 minutes to ensure the atmosphere in the apparatus was oxygen free.

The samples were then warmed up to 110°C at a heating rate of 20°C/min. After a drying period of 20 minutes, the samples were heated up to the desired temperature (250°C for

torrefaction and 550°C for pyrolysis) at the heating rate of 20°C/min. The samples were kept at the desired temperature for 120 minutes. The weight loss data of the MSW sample were automatically recorded as a function of time by the TGA.

2.3 Results and Discussions

2.3.1 Basic Characterization

The summaries of the basic characterization data are presented in Tables 2.1 and 2.2. Although the properties of the MSW had wide ranges, average values can still be proposed respectively for the residential and ICI wastes, using their physical compositions if determined in the future. Similarly, if the physical composition data of the residential or ICI wastes are available for a city that has similar economic development and living standards as the City of Red Deer, its representative average characteristics can also be conveniently estimated using the data in Tables 2.1 and 2.2.

As observed, the moisture content of the MSW varied significantly, depending on the type of material. As expected, paper and wood samples had the highest moisture contents, due to their stronger water sorption ability. Other materials, such as rigid plastic, styrofoam, plastic-textile and carpet, all contained small amounts of moisture, due to their hydrophobic properties. In addition, the waste source influenced the moisture contents significantly. For instance, the ICI plastic-rigid sample has a moisture content of 0.23%, whereas the residential plastic-rigid sample contains higher moisture (15.02%) due to the moisture-rich impurities (such as shampoo or laundry detergent) attached to the residential samples. As a general trend, the moisture contents of residential wastes are remarkably higher than those of ICI wastes (except the similar values of paper and carpet).

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The volatile matter (VM) content of residential wastes varied between 73.46% and 99.38%, and the VM content of ICI wastes was between 74.31% and 99.68%. These values are close to the VM content of biomass, but higher than that of coal/coke (Channiwala and Parikh, 2002). Residential plastic, styrofoam and rubber and ICI plastic, styrofoam and carpet had VM contents higher than 90%, as well as less ash by comparison with the other wastes. The waste source didn't influence the VM contents a lot as it did to the moisture contents. Most of the residential and ICI samples (except carpet and rubber) have similar VM contents.

Most of the MSW samples have low ash contents (less than 8%) that is beneficial in reducing energy consumption during transportation and facility operation. As an exception, residential carpet had the highest ash content of 24.75% due to the accumulated fine sand in the course of its using. Wood (both residential and ICI types) had the highest fixed carbon content among wastes of all categories, which may yield more solid products in thermal processing. Based on the ultimate analysis data, the H/C molar ratio, the effective hydrogen/carbon (H/C$_{eff}$) molar ratio and the O/C molar ratio of each sample were calculated and are listed in Tables 2.1 and 2.2. The H/C molar ratio of the MSW samples varied in a range from 0.86 to 1.85. Residential and ICI carpet materials had the largest H/C ratio, as well as a relatively low O/C ratio, among all 14 categories of samples.

Table 2.1 Basic Characterization Data of Residential Municipal Solid Waste

Residential MSW	Non-recyclable paper	Wood/yard waste	Plastic-rigid	Plastic-film & styrofoam	Plastic-textile	Carpet	Rubber
Moisture (wt%, dry basis)	22.48	72.57	15.02	0.45	1.07	0.19	9.30
Proximate Analysis (wt%, dry basis)							
Volatile Matter	79.00	73.46	90.62	99.38	86.13	74.36	90.61
Fixed Carbon	13.64	21.26	8.28	0.62	12.82	0.89	8.29
Ash	7.36	5.28	1.10	0.00	1.05	24.75	1.10
Ultimate Analysis (wt%, dry basis)							
C	41.64	48.75	71.23	90.38	59.37	62.49	43.94
H	5.62	5.93	7.62	7.53	4.26	9.70	5.13
N	0.34	0.60	0.08	0.69	0.07	0.36	0.18
S	0.14	0.12	0.39	0.40	0.00	0.72	0.01
O[a]	44.90	39.32	19.58	1.00	35.25	1.98	49.64
H/C Molar Ratio	1.61	1.45	1.27	0.99	0.86	1.85	1.39
H/C$_{eff}$ Molar Ratio = (H-2×O)/C	-0.01	0.24	0.86	0.98	-0.04	1.80	-0.30
O/C Molar Ratio	0.81	0.61	0.21	0.01	0.45	0.02	0.85
Empirical Formula	$C_{3.5}H_{5.6}O_{2.8}$	$C_{4.1}H_{5.9}O_{2.5}$	$C_{5.9}H_{7.6}O_{1.2}$	$C_{7.5}H_{7.5}$	$C_{4.9}H_{4.2}O_{2.2}$	$C_{5.2}H_{9.6}$	$C_{3.7}H_{5.1}O_{3.1}$
Surface Area (m^2/g, dry basis)	3.1	2.3	1.7	1.1	1.2	1.7	0.5
High Heating Value (MJ/kg, dry basis)	15.58	18.426	35.721	42.461	20.743	25.793	20.834

[a] O was obtained by subtracting the sum of the CHNS and ash contents from 100% (percentage).

Table 2.2 Basic Characterization Data of ICI Municipal Solid Waste

ICI MSW	Non-recyclable paper	Wood/yard waste	Plastic-rigid	Plastic-film & styrofoam	Plastic-textile	Carpet	Rubber
Moisture (wt%, dry basis)	24.18	8.37	0.23	0.35	0.18	0.86	0.88
Proximate Analysis (wt%, dry basis)							
Volatile Matter	79.45	77.17	99.68	97.79	88.66	93.83	74.31
Fixed Carbon	14.89	19.1	0.26	1.66	9.13	3.67	13.59
Ash	5.66	3.73	0.06	0.55	2.21	2.5	12.1
Ultimate Analysis (wt%, dry basis)							
C	42.85	41.73	85.75	85.4	56.7	61.68	53.44
H	5.79	5.39	7.18	9.67	6.36	8.71	7.2
N	0.1	1.53	0.22	3.02	0.37	5.46	3.69
S	0.12	0.14	0.31	0.78	0.21	0.55	0.38
O[a]	45.48	47.48	6.48	0.58	34.15	21.1	23.19
H/C Molar Ratio	1.61	1.54	1.00	1.35	1.34	1.68	1.61
H/C$_{eff}$ Molar Ratio = (H−2×O)/C	0.02	-0.17	0.88	1.34	0.43	1.17	0.95
O/C Molar Ratio	0.80	0.85	0.06	0.01	0.45	0.26	0.33
Empirical Formula	$C_{3.6}H_{5.8}O_{2.8}$	$C_{3.5}H_{5.3}O3.0$	$C_{7.1}H_{7.1}$	$C_{7.1}H_{9.6}$	$C_{4.7}H_{6.3}O_{2.1}$	$C_{5.1}H_{8.6}O_{1.3}$	$C_{4.5}H_{7.1}O_{1.4}$
Surface Area (m^2/g, dry basis)	1.5	1.9	1	2.7	2.3	2	1.8
High Heating Value (MJ/kg, dry basis)	17.37	19.247	43.341	47.06	26.381	28.698	22.671

[a] O was obtained by subtracting the sum of the CHNS and ash contents from 100% (percentage).

As presented in Tables 2.1 and 2.2, the H/C_{eff} ratios of residential and ICI wastes varied between (-0.30, 1.80) and (-0.17, 1.34) respectively. The H/C_{eff} ratios of plastic, styrofoam and carpet were close to or higher than 1.0, due to their petroleum-derived properties. The H/C_{eff} ratios of some samples, such as residential paper, textile and rubber and ICI wood, were negative numbers, indicating that their hydrogen contents were not sufficient to remove all the oxygen contained in the waste. The deoxygenation of these wastes will cost more in hydrogen and energy.

Table 2.3 lists the H/C_{eff} ratios of various fuels: the H/C_{eff} ratio of coal is between 0.5 and 1.1; the H/C_{eff} ratio of biomass is usually below 0.5; and, petroleum and petroleum-derived products have higher H/C_{eff} ratios: 1.48 to 2.1. (Chen et al., 1986) stated that feedstocks with an H/C_{eff} ratio of less than 1.0 are difficult to upgrade to produce premium products. Therefore, the MSW from the City of Red Deer is mainly made up of hydrogen-deficient components that have similar H/C_{eff} ratio to biomass and low grade coal, and strategies for waste-to-liquid fuel conversion must take the H/C_{eff} ratio into account. Technologies for adding hydrogen or deoxygenation should be considered.

The nitrogen content of most ICI wastes (except paper) was larger than that of the residential wastes, while the sulfur contents of ICI and residential wastes were similar. The nitrogen contents of ICI styrofoam (3.02%), carpet (5.46%) and rubber (3.69%) were remarkably higher than the same type residential wastes (due to the different quality of samples – thickness, layers, density and material use) and other categories of wastes. Proper NO_X and SO_X removal

(De-NO$_X$ and De-SO$_X$) technologies should be used to combat the environmental effects of the thermochemical conversion and reduce the degree of corrosive damage.

Table 2.3 Effective Hydrogen to Carbon (H/C$_{eff}$) Molar Ratio of Various Fuels (NETL Website, 2014)

Fuel	H/C$_{eff}$ Molar Ratio
Biomass	≤ 0.5
Coals	$0.5 - 1.1$
Peat	$1.0 - 1.5$
Asphalt & Tar Sand	$1.2 - 1.7$
Petroleum	$1.48 - 1.95$
Petroleum Distillate	$1.8 - 2.0$
Premium Products	$1.95 - 2.1$
Liquefied Petroleum Gas	≈ 2.7
Natural Gas	≈ 4.0
Hydrogen	∞

The pore volumes of all the waste were less than 0.01 cm^3/g, which indicates the non-porous property of MSW. Paper had the largest surface area among the residential wastes; and, carpet had the largest surface area among the ICI wastes. However, the Brunauer Emmett Teller (BET) surface areas of the samples were all less than 5 m^2/g, as presented in Tables 2.1 and 2.2. This suggests that raw waste materials would not be suitable as absorbent material in water pollution control or similar applications.

The heating values of plastic and styrofoam were the highest of all the samples, while the heating values of wood and paper were the lowest. All the ICI wastes had higher heating values compared to those of the residential wastes, however, their differences were not significant.

In order to roughly estimate the energy profits that could be obtained from the residential MSW, physical composition of the MSW from the City of Red Deer (data as shown in Fig. 2.1) was used as the weight coefficient of each material to calculate the representative average heating values of the residential MSW. Since the data in Fig. 2.1 is a general composition for the entire MSW, a better estimation could be made using the specific data of residential waste in the future works. As a result, the average HHV of residential wastes was 27.654 MJ/kg. The conversion formula from HHV to LHV is as follows:

$$LHV = HHV - 0.212 \, H$$

where H is the dry-basis weight percentage of hydrogen in a sample, and LHV and HHV are expressed in MJ/kg. Therefore, the average LHV of residential and at the City of Red Deer were 26.268 MJ/kg. According to the reported data (The City of Red Deer Website, 2013), the City of Red Deer's population was 97,109 in the 2013 census, and its average generation rate of residential MSW was 180 kg/cap/yr. Thus, the annual amount of residential MSW generated was about 17,479,620 kg.

Around 39% of this amount (Fig. 2.1) can be easily collected and used for producing energy or fuels by thermochemical conversion. Based on the average heating value that we calculated, this amount of waste will yield about 39,220,619 MJ of energy, which is equivalent to 1,225,644 L of gasoline based on an oil equivalent of 32 MJ/L (World Nuclear Association, 2010). This amount of energy accounts for around 1.1% of the city's total consumption of gasoline/diesel: 115, 512,866 L (the City of Red Deer, 2013). This could result in annual gross profits of about CAD $1.6 million, based on gasoline price in 2013 (Natural Resources Canada Website, 2013).

2.3.2 TG and DTG Results of Pyrolysis and Torrefaction
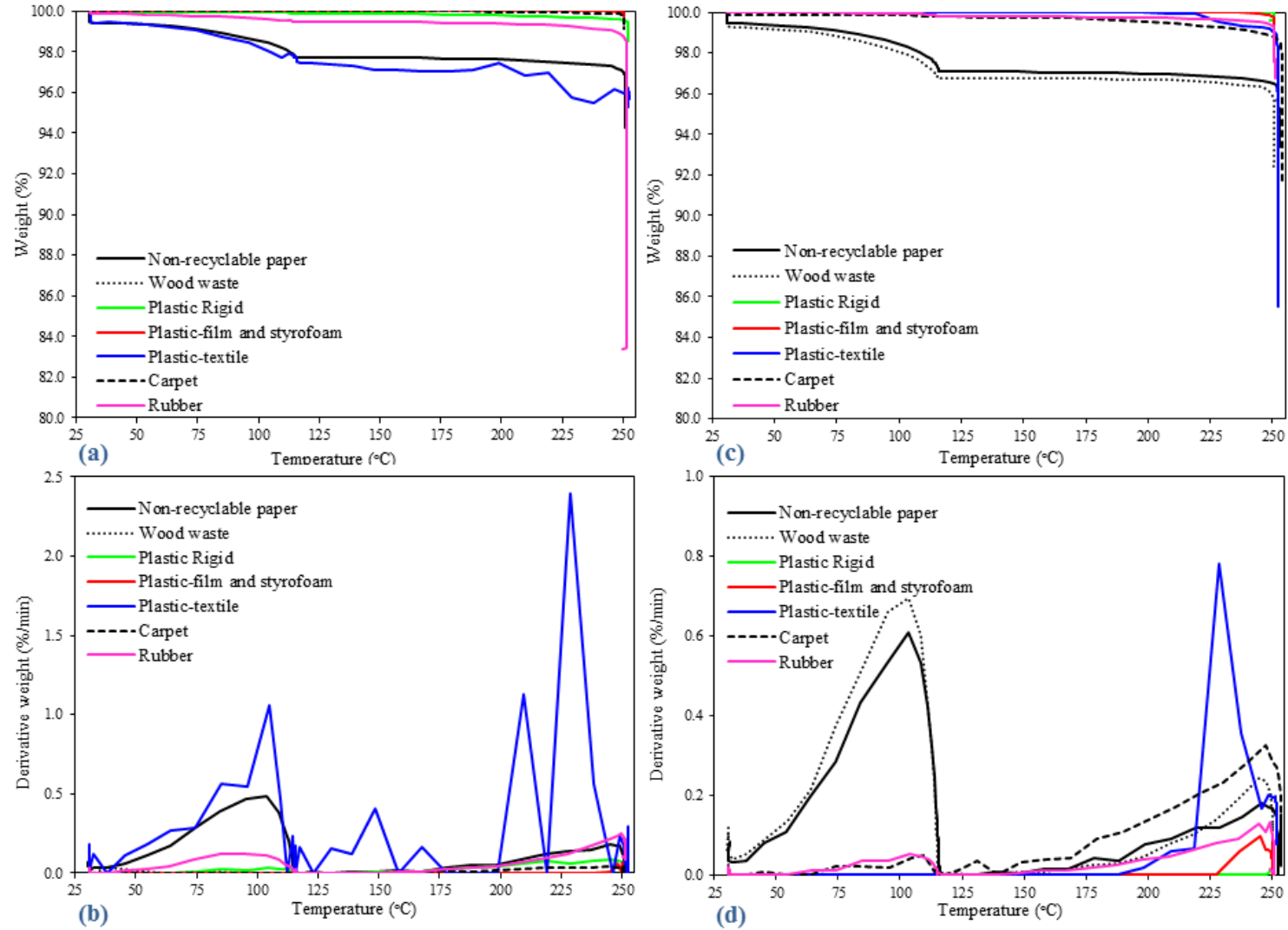
Figure 2.4 TG and DTG Curves of Torrefaction: Residential MSW – (a) (b); ICI MSW – (c) (d)

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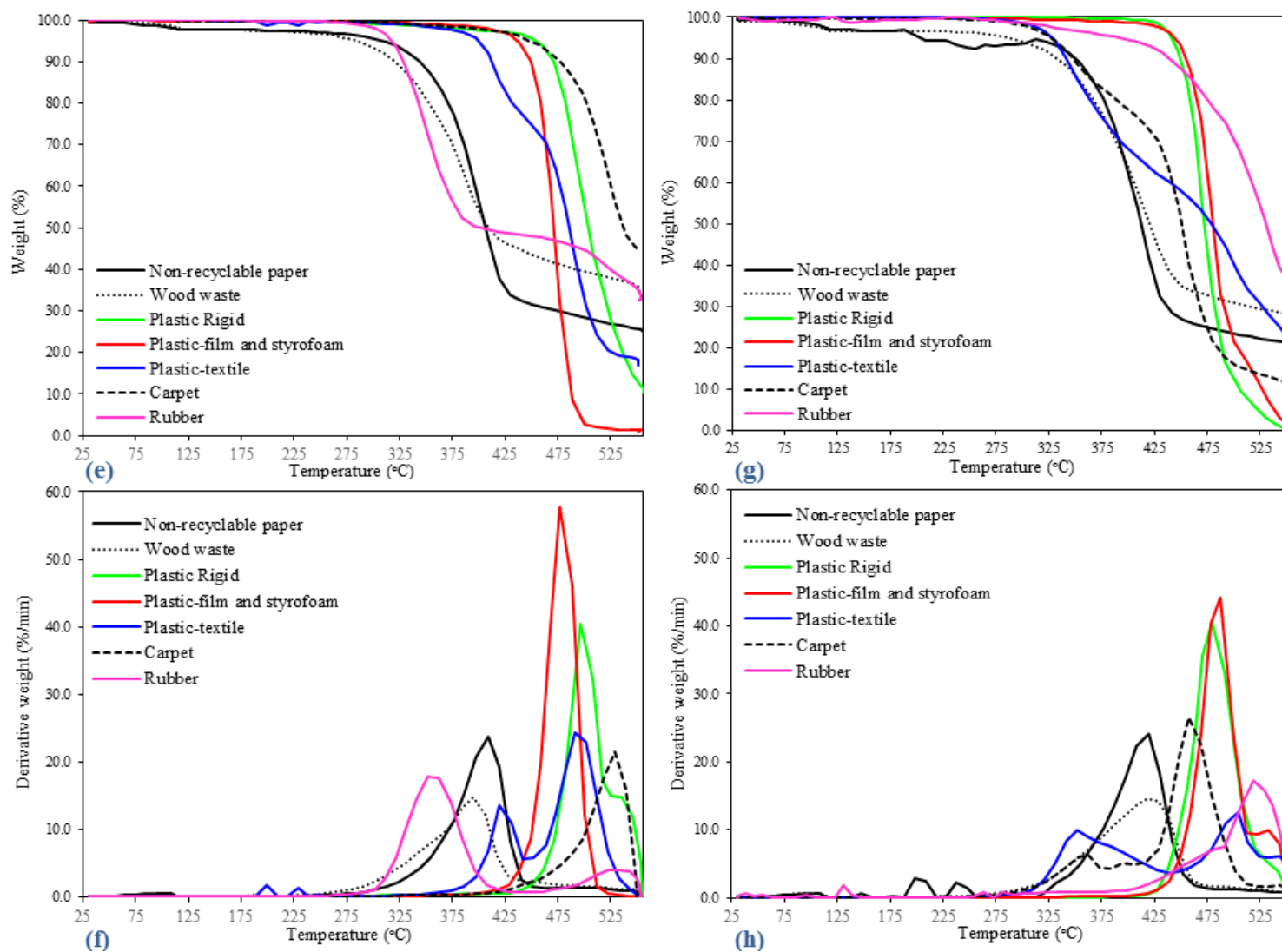
Figure 2.5 TG and DTG Curves of Pyrolysis: Residential MSW – (e) (f); ICI MSW – (g) (h)

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Torrefaction

The normalized weight loss (TG curve) and rate of weight loss (DTG curve) for torrefaction of the residential and ICI wastes are shown in Fig. 2.4. The results show that the major weight loss for all the samples occurred between 200°C and 250°C, with the maximum rate of weight losses between 235°C and 250°C. For cellulosic-based samples, such as paper and wood, the weight loss in this temperature range represents mainly the degradation of the cellulose and hemicellulose (Prins et al., 2006). For synthetic samples, the weight loss represents the loss of some short-chain hydrocarbons. The temperature of torrefaction is still too low for the decomposition of long-chain compounds or polymers.

Another significant weight loss during torrefaction occurred at about 100-120°C, especially for the following four samples: residential paper, residential textile, ICI paper and ICI wood. Since the entire sample had been dried at 70°C, the weight change that occurred was not due to the removal of the surface water; however, it could have been caused by the volatilization of the chemical bound water or some light volatiles. It is interesting to observe that the residential textile samples had four peaks in its DTG curve, with the additional two peaks at 150°C and 210°C, indicating the occurrence of significant weight loss at those temperatures.

Pyrolysis

The TG and DTG curves for pyrolysis of the residential and ICI wastes are shown in Fig. 2.5. Differences in the curve shapes largely depended on the type of the material. However, the curve shapes of the same type of material from different generation sources (i.e., residential or

ICI) were similar. For the paper and wood samples, the major weight losses occurred between 275 and 450°C, which indicate the degradation of hemicellulose, cellulose and part of lignin (Sørum et al., 2001; Zhou et al., 2014). The flat tailing section observed at temperatures above 450°C identifies the gradual degradation of the lignin.

The thermal degradation of plastic and styrofoam that mainly composed of polymer material (such as polyethylene, polypropylene or polystyrene) occurred between 425-550°C, while the two-stage degradation of textile occurred between 325-450°C and between 450-550°C due to its more complex components (cotton, nylon, polyester and acrylic, etc.). The main weight loss of residential carpet occurred between 400-550°C with one peak on its DTG curve at 525°C. However, the DTG curve of ICI carpet had two pronounced shoulders (at 360 and 400°C) prior to its major weight loss peak at 460°C.

The main weight loss of both residential and ICI rubber materials occurred between 300 and 550°C; however, the peak positions of their DTG curves were different. The DTG curve of residential rubber had two peaks, one at 350°C and the other at 520°C, as an indication of two different components – common household rubbers (kitchen gloves, man-made leather material, etc.) that may decompose at lower temperatures; and, commercial rubbers that are more resistant to heat or abrasion, such as waste tires. On the contrary, the curve of ICI rubber had only one peak at 520°C.

Char Yield and Elemental Analysis

Table 2.4 summarizes the yields of the produced chars from both the torrefaction and pyrolysis experiments. All the values were calculated on a dry ash-free basis.

The char yield of torrefaction was in the range from 82.71% to 99.4%, which reveals that the weight loss of the samples was not significant. The shape and color of the most of the samples did not change significantly after torrefaction. However, most of the samples became fragile and crisp, indicating an increase in their grindability by torrefaction.

In comparison, the char yields of pyrolysis were lower, ranging from 0% to 30.39%. The rest of the masses of the feedstocks were converted into gas and liquid products that left the TGA crucible during pyrolysis. There is no remaining solid (char) in the crucible after the experiments for residential styrofoam and ICI styrofoam and plastic, as indicated by zero reading from the TGA. This is consistent with the proximate analysis results of these samples. The char yield of residential carpet (25.14%) was significantly higher than the value of ICI carpet (7.07%). The char yields of other residential wastes were similar to the yields of the corresponding ICI wastes.

Table 2.4 Char Yield of Torrefaction and Pyrolysis of the MSW

(%wt, dry ash-free basis)	Residential MSW		ICI MSW	
	Torrefaction	Pyrolysis	Torrefaction	Pyrolysis
Non-recyclable paper	93.32	16.16	92.59	13.77
Wood waste	90.49	28.97	92.07	21.20
Plastic-rigid	98.07	8.07	99.40	0.00
Plastic-film and styrofoam	98.28	0.00	97.70	0.00
Plastic-textile	90.79	14.21	84.38	15.75
Carpet	98.35	25.14	91.13	7.07
Rubber	82.71	30.39	95.89	22.89

Tables 2.5 and 2.6 show the elemental analysis results of the MSW chars obtained from the torrefaction and pyrolysis experiments. It can be observed that the carbon contents of all the chars were higher than the carbon contents of the raw materials. In addition, the ash contents of the torrefaction chars were slightly higher than those of the original MSW feedstock, while the ash contents of the pyrolysis chars were significantly higher than the values of the original MSW feedstock.

The H/C, H/C_{eff} and O/C ratios of the chars were also calculated. When comparing these ratios with the values of the raw material, both increases and decreases were evident. Nevertheless, some statistical regularity could still be determined. In the torrefaction experiments, the H/C ratios of 11 out of 14 samples increased, and the H/C_{eff} ratios of 10 out of 14 samples

increased. Correspondingly, the O/C ratios of 10 out of 14 samples decreased or were unchanged.

The residential styrofoam and ICI styrofoam and plastic produced no char during pyrolysis, because all of the samples were volatilized. Consequently, these 3 types of samples were not taken into account for the comparison between the chars and their original materials. The H/C ratios of 9 out of 11 available samples decreased in the pyrolysis experiments, and the H/C_{eff} ratios of 8 out of 11 samples increased. The O/C ratios of 5 out of 11 samples increased, while the other 6 samples decreased. Therefore, the pyrolysis process has the opposite effect on these quality evaluation parameters (H/C, H/C_{eff} and O/C ratios) compared to torrefaction.

From these observations, it can be proposed that the torrefaction process increases the H/C or H/C_{eff} ratios, while it decreases the O/C ratios of the MSW. In contrast, pyrolysis decreases the H/C or H/C_{eff} ratios of the MSW, producing chars with high carbon contents and high heating values. Consequently, the MSW char from pyrolysis can be considered as promising feedstock for gasification or incineration.

Table 2.5 Elemental Compositions of MSW Torrefaction Char

Torrefaction Char	C	H	N	S	O[a]	ASH	H/C Molar Ratio	H/C$_{eff}$ Molar Ratio	O/C Molar Ratio
Residential Waste									
Non-recyclable paper	43.13	5.94	0.78	0.00	42.30	7.85	1.6	0.2	0.7
Wood waste	47.84	5.12	1.99	0.00	39.25	5.80	1.3	0.0	0.6
Plastic-rigid	71.40	8.84	0.69	0.39	17.56	1.12	1.5	1.1	0.2
Plastic-film & styrofoam	90.26	7.76	0.76	0.22	1.00	0.00	1.0	1.0	0.0
Plastic-textile	49.85	5.75	0.57	0.00	42.67	1.16	1.4	0.1	0.6
Carpet	39.49	4.60	0.53	0.00	30.32	25.06	1.4	0.2	0.6
Rubber	39.09	5.09	0.56	0.00	53.93	1.33	1.6	-0.5	1.0
ICI Waste									
Non-recyclable paper	46.56	6.78	0.70	0.10	39.77	6.09	1.7	0.5	0.6
Wood waste	48.58	6.03	1.52	0.00	39.83	4.04	1.5	0.2	0.6
Plastic-rigid	86.76	10.65	0.79	0.74	1.00	0.06	1.5	1.4	0.0
Plastic-film & styrofoam	82.15	13.86	1.28	1.15	1.01	0.55	2.0	2.0	0.0
Plastic-textile	60.91	7.09	0.85	0.13	28.41	2.61	1.4	0.7	0.4
Carpet	62.30	9.08	5.10	0.42	20.36	2.74	1.7	1.2	0.2
Rubber	40.19	4.54	0.92	0.72	41.08	12.55	1.3	-0.2	0.8

[a] O was obtained by subtracting the sum of the CHNS and ash contents from 100% (percentage).

Table 2.6 Elemental Compositions of MSW Pyrolysis Char

Pyrolysis Char	C	H	N	S	Oa	ASH	H/C Molar Ratio	H/Ceff Molar Ratio	O/C Molar Ratio
Residential Waste									
Non-recyclable paper	59.75	2.18	1.17	0.00	3.93	32.97	0.4	0.4	0.0
Wood waste	64.35	2.56	2.21	0.00	14.74	16.14	0.5	0.2	0.2
Plastic-rigid	83.32	3.45	1.02	0.00	0.64	11.57	0.5	0.5	0.0
Plastic-film & styrofoam	-	-	-	-	-	-	-	-	-
Plastic-textile	71.42	2.76	0.99	0.00	17.88	6.95	0.5	0.1	0.2
Carpet	12.04	0.04	0.13	0.00	31.11	56.68	0.0	-3.8	1.9
Rubber	27.09	3.28	0.45	0.00	65.65	3.53	1.5	-2.2	1.8
ICI Waste									
Non-recyclable paper	52.20	4.38	0.77	0.00	12.30	30.35	1.0	0.7	0.2
Wood waste	77.68	2.86	1.95	0.00	2.06	15.45	0.4	0.4	0.0
Plastic-rigid	-	-	-	-	-	-	-	-	-
Plastic-film & styrofoam	-	-	-	-	-	-	-	-	-
Plastic-textile	30.89	3.79	0.38	0.00	52.39	12.55	1.5	-1.0	1.3
Carpet	44.61	1.52	4.94	0.00	22.31	26.62	0.4	-0.3	0.4
Rubber	4.62	0.19	0.37	0.00	57.27	37.55	0.5	-18.1	9.3

[a] O was obtained by subtracting the sum of the CHNS and ash contents from 100% (percentage).

2.4 Summary

Basic Characterization

The moisture contents of the unaltered MSW largely depend on the material type, the sampling region and the sampling time. As expected, paper and wood have the highest moisture content, compared to other samples. The moisture contents of most Residential MSW were higher than those of the ICI MSW; while the dry samples from these two sources have similar characteristics. The volatile matter contents of both the dry Residential and ICI wastes are higher than 85%, which indicates that most of the MSW will be converted into gas or liquid products during a thermal process. As for gasification, using updraft type gasifier may carry a high risk of operational problems caused by the severe tar by-production. In this case, using the downdraft type gasifier would be a good preference. In addition, recovering most of the MSW's volatile part through a pyrolysis process; then using the obtained char for the following gasification would also reduce the operational risks and increase the recovery efficiency.

The H/C_{eff} of the MSW locates in a position close to the biomass and low grade coal. Technologies of adding hydrogen or rejecting oxygen should be considered if the liquid fuels are target products from MSW. Research on this topic could expand from the current research achievements of lignite, peat, biomass and coal. Because the MSW has non-negligible sulfur and nitrogen contents, proper De-NOx and De-SOx technologies are vital to reduce the negative environmental or health effects of a WTE facility. In addition, MSW belongs to non-porous material that is unsuitable to be used as absorbent material without treatment.

The HHV of Residential waste is in a range of 15.580 MJ/kg to 42.461 MJ/kg; the HHV of ICI wastes varies from 17.370 MJ/kg to 43.341 MJ/kg. The heating values of plastic waste and styrofoam waste are the highest, while the heating values of wood waste and paper waste are the lowest among all the samples.

Torrefaction and Pyrolysis

The weight change of MSW during torrefaction is small (less than 10% for most of the samples) and is mainly caused by the volatilization of chemical-bound water and light volatiles. Torrefaction increases the H/C or H/C_{eff} ratios of the MSW, as well as decreases its O/C ratios, which is an appropriate treatment to convert the raw MSW material into high quality solid feedstock for producing liquid products.

For pyrolysis, the shape differences of TG and DTG curves are largely related to the chemical- nature differences of the samples. The char yields of pyrolysis are much lower than the yields of torrefaction, ranging from 0% to 30.39%. Some samples were entirely volatilized during the pyrolysis experiment, leaving zero char. The pyrolysis can decrease the H/C or H/C_{eff} ratios of the MSW, but produces char of high carbon content which is a suitable feedstock for gasification.

In conclusion, a considerable amount of volatiles in the MSW are extracted during pyrolysis. Moreover, pyrolysis char is a carbon-rich fuel that can be mixed with coal or lignite as the feedstock in traditional coal gasification or incineration plants. Compared to pyrolysis, torrefaction is more like a pre-treating technology. The small amounts of extracted light volatiles

created during torrefaction are not worthy to be considered as liquid or gas products. However, torrefaction produces a solid product which is a better feedstock than original MSW materials due to its higher H/C ratio. This solid product can be used as a form of refuse-derived fuel (RDF) for further processing. Moreover, a torrefaction facility usually requires lower operating temperatures and fewer separation units. The choice between these two technical routes depends on the market demand of products, the regional economics and other relevant factors. Generally speaking, torrefaction is preferable for projects which have limited budgets and for the purpose of producing RDF for WTE plants that are not in the local area. Since the water and most microorganisms have been removed during torrefaction, the transportation and storage of the RDF becomes easier and safer than those of the original MSW material. Compared to torrefaction, pyrolysis is capable of producing more value-added products. On one hand, downstream WTE industries can be developed to produce transportation fuels or chemicals using pyrolysis oil, as well as generate electricity or synthesis gas using the pyrolysis char. On the other hand, these liquid or solid products can be sold as RDF to existing refineries, coal-fired power plants, or biomass/coal gasification companies.

Chapter Three: **Heating Value Modeling**

3.1 Introduction

The most common calculation method currently being used is the equation derived by Dulong (Kathiravale et al., 2003). However, the Dulong model was originally derived for coal and may not be suitable for the heating value estimation of MSW, due to the physical and chemical differences between coal and MSW. Other advanced models derived for coal or biomass are also not favorable choices.

Elemental compositions and heating values collected from this study and the literature were used as the input data to perform the modeling in Minitab software. The analysis of variance (ANOVA) results were generated to help select the best-fit model. Three statistical parameters, namely the relative average absolute error (AAE), relative average bias error (ABE) and adjusted coefficient of determination (R^2_{adj}), were employed to evaluate the final derived equation:

$$AAE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{HHV_{predicted} - HHV_{experimental}}{HHV_{experimental}} \right| \times 100\%$$

$$ABE = \frac{1}{n} \sum_{i=1}^{n} \left[\frac{HHV_{predicted} - HHV_{experimental}}{HHV_{experiemntal}} \right] \times 100\%$$

$$R^2_{adj} = 1 - (1 - R^2) \times \frac{n-1}{n-l-1}$$

where *n* is the number of samples and l is the number of predictors and

$$R^2 = \frac{\sum(HHV_{predicted} - \overline{HHV}_{experimental})^2}{\sum(HHV_{experimental} - \overline{HHV}_{experimental})^2}$$

The AAE is the relative average absolute error between the predicted HHV and the experimental values. A lower AAE value implies a higher accuracy of a model. Positive or negative values of ABE represent the overestimation or underestimation character of a model, respectively. The lower the absolute value of the ABE, the smaller the bias (Sheng and Azevedo, 2005).

In statistics, the coefficient of determination (R^2) is used to assess how well a statistical model fits the data. R^2_{adj} is a modified version of R^2 that accounts for the number of predictors and sample size in the model. When dealing with multiple regression models, it is suggested that R^2_{adj} be used (Levine et al., 2001).

3.2 Collection and Selection of Experimental Data

A literature survey of experimental heating values and ultimate compositions of MSW was carried out before developing the model. Similar data gathering and comparison work has been also reported in a number of publications. However, when these data were examined more closely, it could be seen that they were not always listed or compared appropriately. The easily overlooked mistakes can be summarized as:

- Data from different bases (dry-basis, wet-basis, ash-free basis, and dry ash-free basis) were listed and compared together (Yin, 2011). Data need to be consistent and may need mathematical conversion to ensure accurate comparison.
- Inconsistency was also found in the mass balance of chemical compositions. In the same table, the sums of C, H, N, S, O and ash contents of some samples were larger

than 100%, while others were equal to 100%, without explanation (Courtemanche and Levendis, 1998; Sørum et al., 2001; Patumsawad and Cliffe, 2002; Meraz et al., 2003; He et al., 2009).

- Errors occurred during data copying. The data belonging to one material in the first reference source was mistakenly categorized as another material (Becidan, 2007).

Another common problem with the reporting of heating value and composition data was: the analytical methods of data acquisition (by experiments or a model), and the basis (such as dry-basis, as-received basis, or ash-free basis) were not always stated (Kim et al., 1994; González et al., 2001). However, knowledge of the analytical method and basis is crucial for data selection and comparison.

In order to ensure the accuracy of the developed model, any HHV data with the above problems were not utilized. Table 3.1 presents the summary of the 193 data points used for this study. Appropriate unit transformation and data conversion were taken to keep the data in consistent conditions, i.e., the heating values were all HHVs obtained from bomb calorimeters and expressed in the units of MJ/kg on a dry-basis; and, the ultimate compositions were expressed in dry-basis weight percentages.

Table 3.1 Elemental Composition and HHV of Various Municipal Solid Wastes

No.	Material	Ultimate Analysis (wt%, dry basis)					Experimental HHV (MJ/kg)	Source
		C	H	N	S	O		
	Paper Waste							
1	Coated paper	30.50	4.60	2.90	1.50	37.70	12.220	(Wu et al., 1997)
2	Newspaper	51.58	5.84	0.11	0.03	41.44	19.300	(Sørum et al., 2001)
3	Cardboard	44.52	5.68	0.10	0.12	41.18	16.900	(Sørum et al., 2001)
4	Glossy paper	32.83	3.46	0.10	0.04	35.58	10.400	(Sørum et al., 2001)
5	Paper	41.44	8.19	0.11	0.34	43.20	17.680	(Siang and Zakaria, 2006)
6	High-grade paper	38.10	5.60	0.15	0.07	46.90	15.235	(Liu and Lipták, 1999)
7	Paper mixture	43.00	6.00	0.36	0.17	43.80	17.647	(Liu and Lipták, 1999)
8	Newspaper	43.80	5.90	0.29	0.24	44.40	17.987	(Liu and Lipták, 1999)
9	Corrugated & kraft	46.00	6.40	0.28	0.22	44.80	18.999	(Liu and Lipták, 1999)
10	Other paper waste	42.70	6.10	0.50	0.14	43.30	17.580	(Liu and Lipták, 1999)
11	Papers	44.49	6.58	0.57	0.00	41.29	17.018	(Gidarakos et al., 2006)
12	Magazines	35.00	5.00	0.05	0.08	39.40	13.551	(Liu and Lipták, 1999)
13	Corrugated paper	45.99	6.35	0.14	0.29	44.26	18.119	(Meraz et al., 2003)
14	Glossy paper	43.40	5.30	0.62	0.25	27.50	14.663	(Meraz et al., 2003)
15	Magazine stock	32.93	4.64	0.11	0.21	32.85	15.133	(Meraz et al., 2003)
16	Brown Paper	44.90	6.08	0.00	0.11	47.84	17.914	(Meraz et al., 2003)
17	Cardboard	49.60	6.40	0.72	0.24	35.70	18.463	(Meraz et al., 2003)
18	Corrugated boxes	43.73	5.70	0.09	0.21	44.93	17.278	(Meraz et al., 2003)
19	Junk mail	37.87	5.41	0.17	0.09	42.74	14.837	(Meraz et al., 2003)
20	Mixed paper	43.41	5.82	0.25	0.20	44.32	17.602	(Meraz et al., 2003)
21	Newsprint I	49.14	6.10	0.05	0.16	43.03	19.717	(Meraz et al., 2003)
22	Newsprint II	48.82	6.21	0.15	0.25	42.35	19.296	(Meraz et al., 2003)
23	Non-glossy paper	47.30	6.10	1.58	0.25	32.00	19.661	(Meraz et al., 2003)
24	Other paper	42.09	5.86	0.40	0.25	39.88	16.555	(Meraz et al., 2003)
25	Paper food cartons	44.74	6.10	0.15	0.16	41.92	17.978	(Meraz et al., 2003)
26	Plastic-coated paer	45.30	6.17	0.18	0.08	45.50	17.914	(Meraz et al., 2003)
27	Trade magazine	32.91	4.95	0.07	0.09	38.55	12.744	(Meraz et al., 2003)
28	Waxed milk cartons	59.18	9.25	0.12	0.10	30.13	27.281	(Meraz et al., 2003)
29	Paper	43.50	6.00	0.30	0.20	44.00	16.809	(Meraz et al., 2003)
30	Non-recyclable paper	41.64	5.62	0.34	0.14	44.91	15.580	This study
31	Non-recyclable paper	42.85	5.79	0.10	0.12	45.48	17.370	This study
	Wood Waste							
32	Block wood	46.90	6.07	0.95	0.00	43.99	18.261	(Parikh et al., 2005)
33	Wood chips	48.10	5.99	0.08	0.00	45.74	19.916	(Parikh et al., 2005)
34	Red wood	50.64	5.98	0.05	0.03	42.88	20.720	(Parikh et al., 2005)
35	Soft wood	52.10	6.10	0.20	0.00	41.00	20.000	(Parikh et al., 2005)
36	Spruce wood	51.90	6.10	0.30	0.00	40.90	20.100	(Parikh et al., 2005)
37	Subabul wood	48.15	5.87	0.03	0.00	44.75	19.777	(Parikh et al., 2005)
38	Eucalyptus saw dust	49.37	6.40	2.02	0.00	42.01	18.502	(Parikh et al., 2005)
39	Fibreboard	48.59	6.30	3.60	0.02	41.05	19.810	(Becidan, 2007)
40	Spruce wood	47.40	6.30	0.07	0.00	46.20	19.300	(Sørum et al., 2001)
41	Wood	44.76	8.81	0.28	0.45	43.82	23.010	(Siang and Zakaria, 2006)
42	Yard waste	40.47	7.47	1.53	0.44	41.85	28.570	(Siang and Zakaria, 2006)
43	Yard waste mixture	45.00	5.60	1.50	0.17	37.70	17.982	(Liu and Lipták, 1999)
44	Wood	46.70	6.00	0.71	0.16	43.40	19.608	(Liu and Lipták, 1999)
45	Yard waste - grass clippings	43.30	5.90	2.60	0.30	37.60	17.917	(Liu and Lipták, 1999)
46	Yard waste - leaves	50.00	5.70	0.82	0.10	36.00	18.678	(Liu and Lipták, 1999)
47	Yard waste - other yard waste	40.70	5.00	1.30	0.10	40.00	17.182	(Liu and Lipták, 1999)

#	Material							Reference
48	Oak wood (small branch)	46.78	6.09	2.70	0.00	40.38	19.200	(Yin, 2011)
49	Oak wood (medium branch)	47.16	6.32	2.50	0.00	41.01	19.240	(Yin, 2011)
50	Oak wood (large branch)	47.56	6.67	2.34	0.00	41.36	19.170	(Yin, 2011)
51	Bamboo wood	48.76	6.32	0.20	0.00	42.77	20.550	(Yin, 2011)
52	Forest residue	53.16	6.25	0.30	0.09	40.00	19.500	(Yin, 2011)
53	Pine chips	49.66	5.67	0.51	0.08	38.07	19.790	(Yin, 2011)
54	Wood	47.80	5.80	0.30	0.01	45.10	19.000	(Telmo et al., 2010)
55	Wood	50.30	5.60	0.20	0.00	43.60	20.300	(Telmo et al., 2010)
56	Wood	47.20	5.50	0.20	0.01	46.80	18.700	(Telmo et al., 2010)
57	Wood	47.70	6.10	0.20	0.04	45.60	19.200	(Telmo et al., 2010)
58	Wood and bark	50.46	5.97	0.15	0.05	42.37	20.063	(Meraz et al., 2003)
59	Balsam spruce	53.30	6.66	1.49	0.20	35.17	22.187	(Meraz et al., 2003)
60	Furniture wood	49.70	6.10	0.10	0.10	42.60	19.330	(Meraz et al., 2003)
61	Brush	42.52	5.90	2.00	0.05	41.20	18.400	(Meraz et al., 2003)
62	Demolition softwood	51.00	6.20	0.10	0.10	41.80	19.610	(Meraz et al., 2003)
63	Evergreen shrubs	48.51	6.54	1.71	0.19	40.44	20.316	(Meraz et al., 2003)
64	Flowering plants	46.65	6.61	1.21	0.26	40.18	18.667	(Meraz et al., 2003)
65	Grass, dirt, leaves	36.20	4.75	2.10	0.26	26.61	14.610	(Meraz et al., 2003)
66	Green logs	50.12	6.40	0.14	0.08	42.26	19.560	(Meraz et al., 2003)
67	Lawn grass I	46.18	5.96	4.46	0.42	36.43	19.330	(Meraz et al., 2003)
68	Lawn grass II	43.33	6.04	2.15	0.05	41.68	17.874	(Meraz et al., 2003)
69	Mixed greens	40.31	5.64	2.00	0.05	39.00	16.463	(Meraz et al., 2003)
70	Ripe leaves I	52.15	6.11	6.99	0.16	30.34	22.915	(Meraz et al., 2003)
71	Ripe leaves II	40.50	5.95	0.20	0.05	45.10	16.442	(Meraz et al., 2003)
72	Rotten timbers	52.30	5.50	0.20	1.20	39.00	20.232	(Meraz et al., 2003)
73	Waste hardwood	49.40	6.10	0.10	0.10	43.70	19.295	(Meraz et al., 2003)
74	Wood	49.05	5.99	0.29	0.08	41.13	19.194	(Meraz et al., 2003)
75	Wood and textiles	53.80	6.00	1.07	0.28	31.50	21.002	(Meraz et al., 2003)
76	Yard waste	42.35	5.33	1.62	0.24	31.89	16.935	(Meraz et al., 2003)
77	Wood	49.50	6.00	0.20	0.10	42.70	23.260	(Meraz et al., 2003)
78	Yard	47.80	6.00	3.40	0.30	38.00	16.283	(Meraz et al., 2003)
79	Wood	48.40	6.00	0.10	0.00	45.30	20.100	(Telmo et al., 2010)
80	Wood	47.60	5.90	0.20	0.01	45.80	19.700	(Telmo et al., 2010)
81	Wood	47.10	4.90	0.20	0.02	47.70	18.700	(Telmo et al., 2010)
82	Wood	46.20	5.80	0.20	0.02	47.20	17.600	(Telmo et al., 2010)
83	Wood	46.70	5.90	0.20	0.02	46.80	19.100	(Telmo et al., 2010)
84	Wood	48.60	5.80	0.20	0.05	45.30	18.300	(Telmo et al., 2010)
85	Wood	47.20	5.60	0.40	0.00	44.40	18.200	(Telmo et al., 2010)
86	Wood	47.80	6.00	0.20	0.03	45.40	18.800	(Telmo et al., 2010)
87	Wood	46.80	5.80	0.20	0.06	46.10	18.600	(Telmo et al., 2010)
88	Wood	50.70	6.00	0.20	0.00	40.40	20.300	(Telmo et al., 2010)
89	Wood	50.40	6.20	0.50	0.01	42.50	20.400	(Telmo et al., 2010)
90	Wood	52.30	6.10	0.20	0.03	41.30	20.700	(Telmo et al., 2010)
91	Wood	48.30	5.70	0.20	0.04	45.10	19.200	(Telmo et al., 2010)
92	Wood waste	41.73	5.39	1.53	0.14	47.48	19.247	This study
93	Wood waste	48.75	5.93	0.60	0.12	39.32	18.426	This study
	Plastic Waste							
94	Plastic-PA6/PE	79.70	13.30	2.60	0.01	4.20	39.500	(Becidan, 2007)
95	Plastic-PVC	38.00	5.00	0.00	0.00	0.00	19.200	(Courtemanche and Levendis, 1998)
96	Plastic-Polyethylene	86.00	14.00	0.00	0.00	0.00	40.500	(Courtemanche and Levendis, 1998)
97	Plastic-Polystyrene	92.00	8.00	0.00	0.00	0.00	44.500	(Courtemanche and Levendis, 1998)
98	Plastics	62.90	4.90	0.00	0.20	31.18	22.240	(Siang and Zakaria, 2006)
99	Plastic-Polypropylene	86.00	14.00	0.00	0.00	0.00	43.400	(Courtemanche and Levendis, 1998)

100	Plastic-PMMA	60.00	8.00	0.00	0.00	32.00	25.800	(Courtemanche and Levendis, 1998)
101	Plastic-LDPE	85.70	14.20	0.05	0.00	0.05	46.600	(Sørum et al., 2001)
102	Plastic-HDPE	86.10	13.00	0.00	0.00	0.90	46.400	(Sørum et al., 2001)
103	Plastic-PP	86.10	13.70	0.00	0.00	0.20	46.400	(Sørum et al., 2001)
104	HDPE bottles	81.60	13.60	0.10	0.20	1.90	43.794	(Liu and Lipták, 1999)
105	Plastic mixture	76.30	11.50	0.26	0.20	4.40	38.377	(Liu and Lipták, 1999)
106	Plastic - PET bottles	68.50	8.00	0.16	0.08	21.90	32.008	(Liu and Lipták, 1999)
107	Polystyrene	86.30	7.90	0.28	0.30	3.40	39.479	(Liu and Lipták, 1999)
108	PVC bottles	44.20	5.90	0.26	0.89	7.60	23.632	(Liu and Lipták, 1999)
109	Polyethylene bags & films	77.40	12.90	0.10	0.12	1.80	39.779	(Liu and Lipták, 1999)
110	Other plastic waste	72.90	11.40	0.45	0.24	5.50	36.662	(Liu and Lipták, 1999)
111	Plastics	79.53	10.64	0.46	0.00	6.98	39.798	(Gidarakos et al., 2006)
112	Plastic	83.93	12.84	0.00	0.00	0.80	37.000	(Meraz et al., 2003)
113	Plastics	66.39	9.17	1.00	0.34	9.47	31.699	(Meraz et al., 2003)
114	Plastic film	67.21	9.72	0.46	0.07	15.82	32.200	(Meraz et al., 2003)
115	Polyethylene I	84.54	14.18	0.06	0.03	0.00	45.972	(Meraz et al., 2003)
116	Polyethyline II	84.57	14.13	0.07	0.03	0.00	45.876	(Meraz et al., 2003)
117	Polystyrene I	87.10	8.45	0.21	0.20	3.96	38.337	(Meraz et al., 2003)
118	Polystyrene II	86.87	8.42	0.20	0.20	4.00	38.261	(Meraz et al., 2003)
119	Polyurethane I	63.27	6.26	5.99	0.20	17.65	26.162	(Meraz et al., 2003)
120	Polyurethane II	63.23	8.32	6.01	0.20	17.64	26.106	(Meraz et al., 2003)
121	Polyvinyl chloride I	45.14	5.61	0.08	0.14	1.56	22.776	(Meraz et al., 2003)
122	Polyvinyl chloride II	45.09	5.61	0.10	0.10	1.60	22.729	(Meraz et al., 2003)
123	Mixed plastics	60.00	7.20	0.00	0.00	22.60	34.092	(Meraz et al., 2003)
124	Plastics	60.00	7.20	0.00	0.00	22.80	33.229	(Meraz et al., 2003)
125	Plastic-rigid	71.23	7.62	0.08	0.39	19.58	35.721	This study
126	Plastic-rigid	85.75	7.18	0.22	0.31	6.48	43.341	This study
127	Plastic-film & styrofoam	90.38	7.53	0.69	0.40	1.00	42.461	This study
128	Plastic-film & styrofoam	85.40	9.67	3.02	0.78	0.58	47.060	This study
	Rubber and Leather Waste							
129	Scrap tyre	80.30	5.18	0.00	0.00	10.33	33.300	(Islam and Beg, 2004)
130	Waste tire	84.22	7.58	0.40	1.41	2.67	35.588	(Kim et al., 1994)
131	Tire	60.90	5.30	0.28	2.46	7.10	29.000	(Courtemanche and Levendis, 1998)
132	Rubber	52.77	9.44	0.78	0.41	13.52	25.040	(Siang and Zakaria, 2006)
133	Leather shoe	42.01	5.32	5.98	1.00	22.83	19.667	(Meraz et al., 2003)
134	Shoe heel and sole	53.22	7.09	0.50	1.34	7.76	25.938	(Meraz et al., 2003)
135	Tires	79.10	6.80	0.10	1.50	5.90	32.673	(Meraz et al., 2003)
136	Leather	60.00	8.00	10.00	0.40	11.50	22.867	(Meraz et al., 2003)
137	Rubber and leather	47.88	5.97	1.49	1.30	12.86	21.791	(Meraz et al., 2003)
138	Rubber	43.94	5.13	0.18	0.01	49.64	20.834	This study
139	Rubber	53.44	7.20	3.69	0.38	23.19	22.672	This study
	Textile Waste							
140	Linoleum	48.06	5.34	0.10	0.40	18.70	19.745	(Meraz et al., 2003)
141	Oils, paints	66.85	9.65	2.00	0.00	5.20	31.160	(Meraz et al., 2003)
142	Rags	55.00	6.60	4.62	0.13	31.20	19.778	(Meraz et al., 2003)
143	Textile	55.57	6.02	0.08	0.25	36.27	21.220	(Siang and Zakaria, 2006)
144	Textiles I	46.19	6.41	2.18	0.20	41.85	18.690	(Meraz et al., 2003)
145	Upholstery	47.10	6.10	0.30	0.10	43.60	18.679	(Meraz et al., 2003)
146	Textiles II	49.64	6.69	4.15	0.37	36.15	20.449	(Meraz et al., 2003)
147	Textiles	55.00	6.60	4.60	0.20	31.20	19.161	(Meraz et al., 2003)
148	Carpet	61.68	8.71	5.46	0.55	21.10	28.698	This study
149	Plastic-textile	56.70	6.36	0.37	0.21	34.15	26.381	This study
150	Plastic-textile	59.37	4.26	0.07	0.00	35.25	20.743	This study
151	Carpet	62.49	9.70	0.36	0.72	1.97	25.793	This study

MSW Mixture

152	MSW Thai	37.14	5.41	0.22	0.09	24.93	15.590	(Patumsawad and Cliffe, 2002)
153	Leather, wood, textile, rubber	44.99	6.01	0.55	0.00	39.59	17.980	(Gidarakos et al., 2006)
154	MSW Total	53.00	7.32	1.32	0.00	31.06	25.504	(Gidarakos et al., 2006)
155	RDF (Refuese derived fuel)	59.20	8.22	0.52	0.00	26.75	27.633	(Gidarakos et al., 2006)
156	MSW in Taiwan	40.84	6.27	0.83	0.17	27.68	18.188	(Shu et al., 2006)
157	Raw refuse	46.68	6.61	1.03	0.10	35.94	20.252	(Wilson, 1972)
158	MSW in Taiwan	38.96	5.86	1.13	0.23	25.90	16.311	(Chang et al., 2007)
159	Textiles/rubber/leather	50.30	6.40	3.30	0.33	31.30	23.202	(Liu and Lipták, 1999)
160	MSW UK	35.81	4.82	0.78	0.41	24.43	15.170	(Patumsawad and Cliffe, 2002)
161	Raw municipal refuse	47.60	6.00	1.20	0.30	32.90	19.878	(Sanner et al., 1970)
162	Processed municipal refuse	47.30	5.00	1.40	0.20	32.60	21.353	(Sanner et al., 1970)
163	Heil mill industrial refuse	33.90	4.60	0.70	0.40	22.40	13.130	(Sanner et al., 1970)
164	Gondard mill infustrial refuse	31.20	3.80	0.70	0.10	21.80	11.991	(Sanner et al., 1970)
165	MSW	51.81	5.76	0.26	0.36	35.88	22.527	(He et al., 2009)
166	MSW	41.22	9.07	1.23	0.79	24.18	22.440	(Franjo et al., 1992)
167	Raw refuse	45.93	6.28	0.54	0.24	35.34	19.597	(Wilson, 1972)
168	Raw refuse	47.18	6.23	0.44	0.22	39.82	19.390	(Wilson, 1972)
169	Raw refuse	47.16	6.38	0.60	0.14	37.92	19.636	(Wilson, 1972)
170	Raw refuse	46.75	6.35	0.67	0.10	38.05	19.485	(Wilson, 1972)
171	Raw refuse	44.27	6.25	0.75	0.20	33.87	19.055	(Wilson, 1972)
172	Raw refuse	46.33	6.02	0.75	0.20	35.54	19.071	(Wilson, 1972)
173	MSW in Taiwan	35.89	5.51	1.03	0.40	23.00	18.122	(Liu et al., 1996)
174	MSW	41.21	6.62	1.11	0.09	32.13	18.581	(Magrinho and Semiao, 2008)
175	MSW	41.07	6.55	1.09	0.09	32.07	18.489	(Magrinho and Semiao, 2008)
176	MSW	40.87	6.45	1.05	0.09	31.99	18.368	(Magrinho and Semiao, 2008)
177	MSW	40.60	6.32	1.01	0.09	31.88	18.198	(Magrinho and Semiao, 2008)
178	MSW	40.20	6.12	0.95	0.10	31.77	17.943	(Magrinho and Semiao, 2008)
179	MSW	39.54	5.79	0.84	0.11	31.45	17.521	(Magrinho and Semiao, 2008)
180	Rubber, leather, and hard plastics	53.80	8.90	0.83	0.57	23.30	25.412	(Meraz et al., 2003)
	Other Wastes							
181	BSG(Brewer's Spent Grains) Waste	49.00	6.71	3.94	0.22	35.10	20.830	(Becidan, 2007)
182	Coffee waste	47.95	6.34	2.82	0.20	36.11	19.820	(Becidan, 2007)
183	Organics/Combustibles mixture	48.60	6.80	0.94	0.22	35.00	21.292	(Liu and Lipták, 1999)
184	Other organics mixture	46.20	6.10	1.90	0.36	33.30	20.232	(Liu and Lipták, 1999)
185	Fines	37.30	5.30	1.60	0.45	29.50	16.231	(Liu and Lipták, 1999)
186	Disposable diapers	48.40	7.60	0.51	0.35	38.80	22.611	(Liu and Lipták, 1999)
187	Other organics	44.20	5.30	1.80	0.81	14.40	17.301	(Liu and Lipták, 1999)
188	Putrescribles	45.56	6.24	2.29	0.00	36.19	18.630	(Gidarakos et al., 2006)
189	Cotton residue	47.03	5.96	1.79	0.19	38.42	16.900	(Yin, 2011)
190	Steet sweepings	34.70	4.76	0.14	0.20	35.20	17.438	(Meraz et al., 2003)
191	Vacuum cleaner dirt	35.69	4.73	6.26	1.15	20.08	16.619	(Meraz et al., 2003)
192	Household dirt	20.62	2.87	0.50	0.01	4.00	9.101	(Meraz et al., 2003)
193	Other organic	34.60	4.30	1.07	0.38	41.10	16.521	(Meraz et al., 2003)

The 193 data were composed of 31 data points for paper waste (the heating value's standard deviation (SD_{HHV}) is 2.9 MJ/kg), 62 for wood and yard waste (SD_{HHV} = 1.9 MJ/kg), 35 for plastic waste (SD_{HHV} = 8.3 MJ/kg), 11 for rubber and leather waste (SD_{HHV} = 5.5 MJ/kg), 12 for textile waste (SD_{HHV} = 4.3 MJ/kg), 29 for MSW mixtures (SD_{HHV} = 3.4 MJ/kg) and 13 for other wastes (SD_{HHV} = 3.4 MJ/kg).

Among them, 32 data points − 5 for paper waste, 10 for wood waste, 6 for plastic waste, 2 for rubber and leather waste, 2 for textile waste, 5 for MSW mixtures and 2 for other wastes − were picked randomly by Excel for the model validation from the numbered whole data set. Thus, the majority of collected data (other 161 data points) were reserved for the model derivation in order to avoid the random errors and ensure the modeling's accuracy as much as possible. This data distribution proportion has also been used in the literature of similar topic (Prikh et al., 2005). The range of the considered data points revealed that the HHV contents varied between 9.101 and 47.06 MJ/kg, the carbon contents between 20.62 and 92 wt%, the hydrogen contents between 2.87 and 14.2 wt%, the nitrogen contents between 0 to 10 wt%, the sulfur contents between 0 to 2.46 wt%, and the oxygen contents between 0 to 49.64 wt% (all on dry-basis).

3.3 Model Derivation

The initial regression of HHV with five variables (C, H, N, S, and O) using the 161 data points was performed in Minitab software. The results showed that 6 data points were considered as high leverage points, which were a type of outlier that have the potential to do great harm to the regression. Although unusual residuals are generally not produced, the regression coefficients would be very different if these points were omitted. Therefore, these data points were deleted

because they may cause the derived equation to have less creditability; and, the initial regression was performed again.

This initial regression resulted in Eq. (1) which involved all the elemental predictors and allow the y-intercept, as shown in Table 3.2, with favorable R^2 and R^2_{adj} values. However, it should be noted that the p-values of three terms in this equation (constant term, nitrogen and sulfur) were higher than 0.05, indicating that these terms did not statistically contribute to the regression. Thus, stepwise regression was performed to remove the variables of less significance. Eq. (4) is the final developed model, with all the p-values equal to 0.00. During this stepwise procedure, the R^2 and R^2_{adj} values were slightly decreased. However, this trade-off allowed for the equation's conciseness and calculation convenience.

Table 3.2 Regression Statistics of the Newly Derived Models

No.	Equation	Unit	R^2	R^2_{adj}	Standard Error	Variables of p-Value > 0.05
Eq.(1)	HHV = - 1.46 + 0.361 C + 1.05 H - 0.160 N + 1.24 S - 0.0658 O	MJ/kg	93.8%	93.6%	1.9140	Constant Term, Nitrogen, Sulfur
Eq.(2)	HHV = 0.349 C + 1.01 H - 0.174 N + 0.886 S - 0.0812 O	MJ/kg	93.7%	93.5%	1.9149	Nitrogen, Sulfur
Eq.(3)	HHV = 0.353 C + 1.01 H - 0.130 N - 0.0818 O	MJ/kg	93.7%	93.5%	1.9203	Nitrogen
Eq.(4)	HHV = 0.350 C + 1.01 H - 0.0826 O	MJ/kg	93.6%	93.5%	1.9225	None (all the p-values = 0.00)

3.4 Accuracy and Comparison with Other Models in Literature

In order to confirm the accuracy of this newly derived model (Eq. (4)), the validation work was carried out by comparing the experimental and predicted HHVs for the randomly selected 32 data points from Table 3.1. The comparison results are shown in Fig. 3.1. This figure also demonstrates the best-fit line of $HHV_{experimental} = HHV_{predicted}$ and the $\pm 5\%$ relative error lines. As seen, most of the data points were close to the best-fit line and within the space between the $\pm 5\%$ relative error lines. This observation indicates the good prediction performance of Eq. (4).
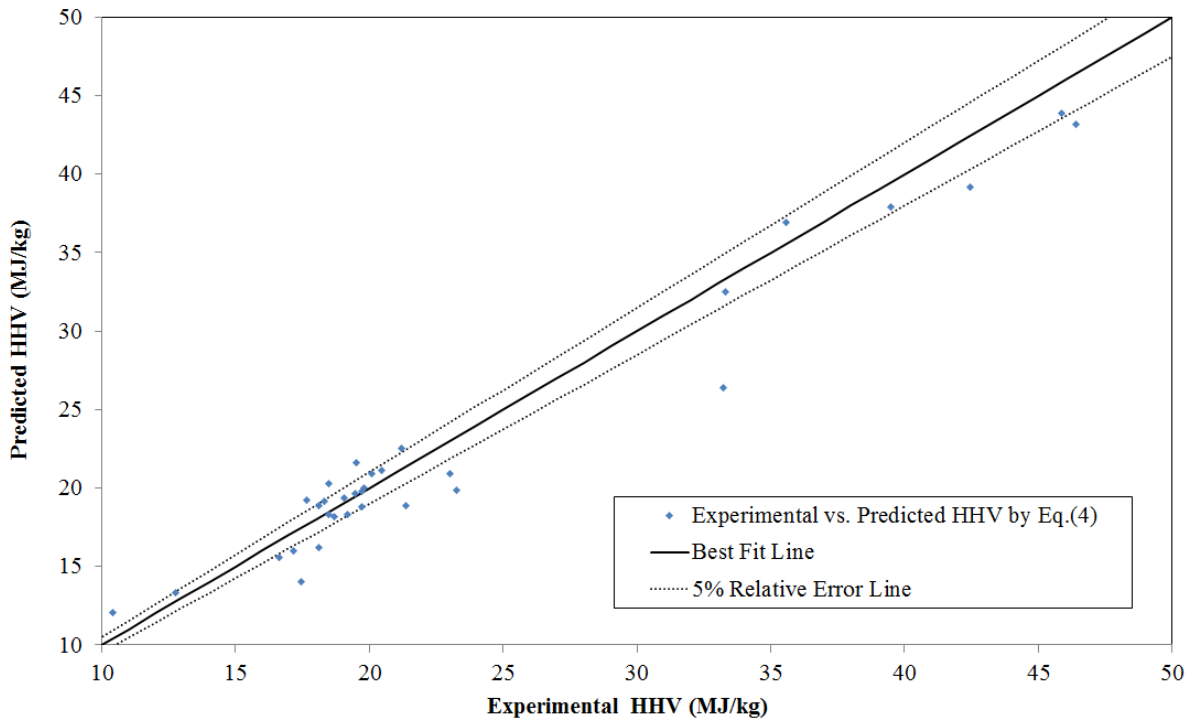

Figure 3.1 Comparison of Experimental HHVs and those Predicted by Eq. (4)

Seven available regression models based on ultimate analysis from the literature (as shown in Table 3.3) were used for comparison with the model derived in this study, i.e., Eq. (4).

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Fig. 3.2 delineates clear comparisons of the AAE and ABE values among these equations. It can be seen that Eq. (4) had the lowest AAE (6.73%), as well as the lowest absolute value of ABE (1.78%) among all the models, thereby reflecting the good prediction accuracy of the developed model. Eq. (9) overestimated the HHVs, while the remainder of the equations underestimated the HHVs. Eqs. (9) and (10), which were developed by Steuer and Scheurer-Kestner (Liu et al., 1996), also demonstrated good accuracy in predicting HHVs, as indicated by their comparable AAE and ABE values.

Attempts to discuss the wastes suitable for thermochemical conversions in this study and the application of the developed model may be limited to the organic waste categories listed in Table 3.1. Future work may shed light on the characterization and statistical studies of wet organics, such as food wastes or sewage sludge.

Table 3.3 Available Models in Literature for the HHV Prediction

No.	Equation	Unit	Application	Source
Eq. (5)	HHV = 0.2949 C + 0.8250 H	MJ/kg	Biomass	(Yin, 2011)
Eq. (6)	HHV = - 0.763 + 0.301 C + 0.525 H + 0.064 O	MJ/kg	Biomass	(Vargas-Moreno et al., 2012)
Eq. (7)	HHV = 0.416638 C – 0.570017 H + 0.259031 O + 0.598955 N – 5.829078	MJ/kg	MSW	(Kathiravale et al., 2003)
Eq. (8)	HHV = 81 C + 342.5 (H - O/8) + 22.5 S - 6 (9H +W[a])	kcal/kg	MSW	(Liu et al., 1996)
Eq. (9)	HHV = 81(C - 3×O/8) + 57×3×O/8 + 345(H-O/16) + 25 S - 6(9H + W)	kcal/kg	MSW	(Liu et al., 1996)
Eq. (10)	HHV = 81(C - 3×O/4) + 342.5H + 22.5 S + 57×3×O/4 - 6(9H + W)	kcal/kg	MSW	(Liu et al., 1996)
Eq. (11)	HHV = 1558.80 + 19.96 C + 44.30 O - 671.82 S - 19.92 W	kcal/kg	MSW	(Liu et al., 1996)

[a] W means the water content in a sample, which equals to 0 for application in this paper.
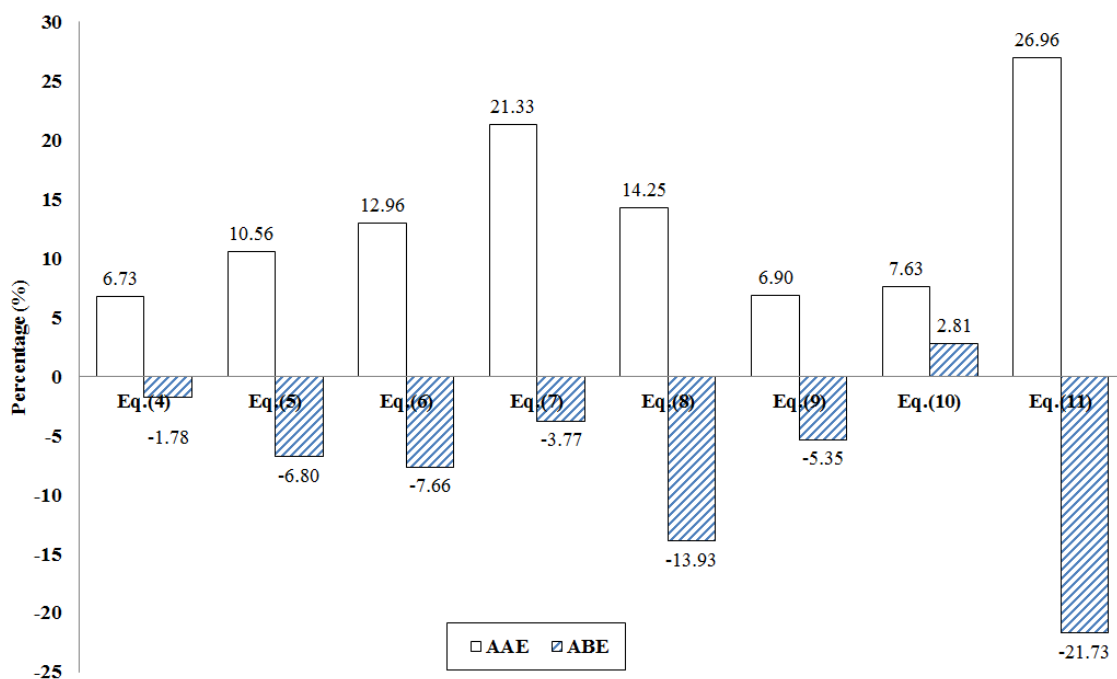
Figure 3.2 AAE and ABE of the High Heating Value Prediction Models

3.5 Summary

An empirical model with excellent heating value predictability was built using different statistical methods, with the help of analysis software – 'MINITAB'. Extraneous predictors that do not contribute statistically to the heating value were eliminated. C, H, and O were then selected to be independent predictors of the final model, which has an adjusted R^2_{adj} equal to 0.935. After comparing the output of the model with the HHV obtained by a bomb calorimeter, an average absolute error of 6.73% and a bias error of -1.78% were calculated. These error levels are significantly smaller than the values of the other seven models from the literature. The present model was derived from widely varying data points and encompassed almost all

categories of landfill wastes suitable to thermochemical conversion. This empirical model, based only on carbon, hydrogen and oxygen composition data, provides a rapid, easy and accurate estimation of the heating value. It may be of particular interest in contexts where experimental heating value measurements are not always available.

Chapter Four: **Catalytic Pyrolysis of Waste Coffee Cups**

4.1 Introduction

During the last decade, the use of biomass as a petroleum alternative to derived fuel and chemicals has attracted a vast amount of research interests. Taking the long view, wood or most other biomasses are not preferred for commercial application because we cannot provide continuous large amounts of wood in the same way we provide crude oil to a refinery. However, there is one material that is produced by each of us every day – waste. Specifically speaking, paper coffee cups. In Canada, there are three types of public garbage bins: landfill waste, beverage and paper/cardboard. Unfortunately, the beverage and paper bins do not accept coffee cups. Meanwhile, Canada's largest fast coffee server, Tim Hortons (2012), sells more than two billion cups of coffee every year in North America. This number becomes four billion every year when incorporating Starbucks (2012) consumption globally. Such a large accumulation of paper cups going to the landfill is a serious environmental problem. But if we take another view, this also could be beneficial for the waste-to-fuels/chemical technology's commercialization in the future. The consumption of coffee can result in the provision of a sustainable feedstock supply. Therefore, there is a need to develop an economically attractive process to convert the waste into value-added products.

In this study, the waste coffee cups were used as the feedstock to generate value-added products that were rich in aromatic hydrocarbons through a catalytic pyrolysis process. This process creates a practical solution that could address the oil crisis and land pollution at the same time. To our knowledge, this topic has not been studied previously. The mechanism of cellulosic feedstock to aromatics can be summarized as follows (Lin et al., 2009; Cheng and Huber, 2011):

under certain pyrolysis conditions, cellulose and hemicellulose in the feedstock are degraded into anhydrosugars; then turned into a series of furan derivatives that undergo decarbonylation, aromatization and other reactions to form aromatics.

Zeolite-based solid acid catalysts are extensively used in more than 110 commercial processes employed in the petrochemical industry (Venuto, 1994). This allows the convenient use of them in both scientific studies and commercial applications. The pore window size, internal pore space and steric hindrance play an important role in selecting the right zeolite for desired applications, due to their influence of shape selectivity. For aromatization, medium and large pore zeolites are considered to be more suitable than small pore zeolites (Guisnet and Gnep, 1996). Medium pore zeolites (ZSM-5 and ZSM-11) are reported to have the highest aromatic yield on the conversion of glucose to aromatics by catalytic fast pyrolysis and the least amount of coke because of moderate internal pore space and steric hindrance (Jae et al., 2011).

Foster and co-workers (Foster et al., 2012) tested ZSM-5 catalysts with different Si/Al ratios and observed that the optimal value is 30 for catalytic fast pyrolysis of wood. In another paper (Cheng et al., 2012), Ga/ZSM-5 (Si/Al=30) is observed to increase the yield of aromatics by 40% compared to standard ZSM-5. Actually, Ga/ZSM-5 is already known as one of the most effective bi-functional catalysts in many other aromatization processes, such as propane aromatization, transformation of short chain alkenes to aromatics, methanol to aromatics, and even activation of methane to aromatics (Guisnet and Gnep, 1996; Baba and Abe, 2003; Choudhary et al., 2005; Bhan and Nicholas Delgass, 2008). The aromatization of LPG alkanes to aromatics (mainly BTX) using Ga/ZSM-5 catalysts was commercialized in the Cyclar process developed by UOP

and BP jointly (Bhan and Nicholas Delgass, 2008). The synergism between Ga and bronsted acid sites on the zeolite is discussed in a review of the mechanism of short-chain alkane transformation over protonic zeolites (Guisnet and Gnep, 1996).

Similar to gallium (Ga), many other metals such as zinc (Zn), silver (Ag) and molybdenum (Mo) also have the ability to enhance functions of the catalysts during the aromatization process (Guisnet and Gnep, 1996; Choudhary et al., 2005; Luzgin et al., 2008; Anunziata et al., 2011; Jin et al., 2013). Among the large variety of metallic components added to ZSM-5 besides gallium, Zn has been evaluated to give the best performance in dehydrogenation and aromatization (Bhan and Nicholas Delgass, 2008). Zn cations have a significant role in the transformation of intermediate alkenes into aromatic hydrocarbons, as well as in the activation of alkanes (Ono, 1992).

The HZSM-5 of Si/Al = 30, and the gallium/zinc supported zeolites (Ga/HZSM-5 and Zn/HZSM-5) were prepared and used as the catalysts in the pyrolysis of the waste coffee cups. Various characterization technologies were employed to characterize the zeolites and discuss their structure's effect on reaction performance and coking status. The pyrolysis reactions were performed in a vertical tubular reactor at moderate temperature (400°C) and atmospheric pressure. Elemental analysis, ^{1}H-NMR and GC-MS analyses were conducted to obtain the chemical compositions of the liquid products.

4.2 Material and Methods

4.2.1 Feedstock

The waste coffee cups were collected from the University of Calgary and dried in an oven at $70^{o}C$ overnight to remove extraneous water. Proximate analysis (according to ASTM 7582-12) and ultimate analysis of the dried paper cups are shown in Table 4.1, where the oxygen content was determined by difference. An approximate chemical formula of the paper cups is $C_{6.0}H_{11.0}O_{4.3}$.

Table 4.1 Proximate Analysis and Ultimate Analysis of Waste Coffee Cups

Proximate Analysis (wt %)				Ultimate Analysis (wt %)				
Moisture	Volatile	Fixed Carbon	Ash	C	H	N	S	O
1.16	91.19	7.65	0.00	46.99	7.21	0.44	0.38	44.98

4.2.2 Catalyst

Ammonium form zeolite ZSM-5 (with a surface area of 400 m^2/g and $SiO_2/Al_2O_3 = 30$) was purchased from Alfa Aesar, and calcined at $550^{o}C$ in air atmosphere to obtain the acid form zeolite (HZSM-5). The 2.5 wt% gallium loaded zeolite (Ga/HZSM-5) was prepared by the incipient wetness impregnation method using gallium nitrate (Alfa Aesar, 99.9% metal basis) water solution. The impregnated zeolite was dried at $85^{o}C$ for four hours and then calcined at $550^{o}C$ for six hours. The 2.5 wt% Zn/HZSM-5 was prepared in a similar manner using the zinc acetate (Alfa Aesar, 99.9% metal basis) water solution.

The catalysts before reaction (fresh catalysts) were characterized by TEM (Tecnai, F20 Transmission Electron Microscope) and SEM (Philips, XL 30 Scanning Electron Microscope) incorporated with energy dispersive X-ray spectroscopy (EDX). X-ray diffraction analysis was

performed using the Rigaku Ultima III diffractometer with Cu Kα irradiation at 40 kV and 44 mA. The zeolites' diffractograms were recorded within a range of 5 to 50 degrees2θ using a 0.02° step length and a counting time of 1°/min. A thermogravimetric (TG) analyzer (Perkin Elmer, STA 6000) was used to examine the cokes deposited on the catalysts after reaction (spent catalysts). About 30 mg of the spent catalyst was placed in the ceramic crucible of the TG analyzer and heated at a rate of 10°C/min up to 750°C under air. The air flow was kept at 70 ml/min to remove the product gas continuously from the crucible. During the heating, the temperature was held at 180°C, 330°C and 750°C for one hour each, in order to obtain complete weight loss at the desired temperatures.

4.2.3 Experimental Setup

Fig. 4.1 shows the schematic of the fixed bed reactor system. Pyrolysis reactions were performed in a vertical stainless-steel tube, which has an i.d. of 2.54 cm and a length of 61 cm. Feedstock and catalysts were held in the middle of the reactor by a metal screen (150 μm). Two catalyst loading patterns - mixed bed pattern and separated bed pattern - were used and compared in this paper. A thermocouple was inserted from the upside of reactor to the top of the feedstock bed, in order to measure the temperature. The carrier gases (N_2 of 190 ml/min; and He of 10 ml/min) were injected into the reactor from the top. Helium gas was the internal standard for the gas composition calculation. The outlet line was wrapped with a heat trace controlled at 250°C and thermal insulation material to avoid coking and liquid yield reduction.

Prior to a run, the system was flushed by the carrier gases for 15 minutes to remove the air. Then the reactor was heated up to 400°C ± 1.5°C in 10 minutes and was held at the temperature

for an additional 30 minutes. In a typical run, one gram of catalyst and three grams of feedstock were used. All the runs were conducted at the atmospheric pressure. A condenser placed in the ice bath was used to trap the heavy hydrocarbons, and the light gases were analyzed every three minutes by an online gas chromatography (Agilent, Micro GC 490) equipped with thermal conductivity detectors, which can precisely measure the He, H_2, N_2, CH_4, CO and CO_2 contents. After reaction, the reactor was cooled down to room temperature and flushed by the carrier gases during the cooling. The condenser was weighted before and after a run to obtain the liquid yields. ^{1}H-NMR, elemental analysis, and GC-MS were performed to identify and analyze the condensed liquid products.
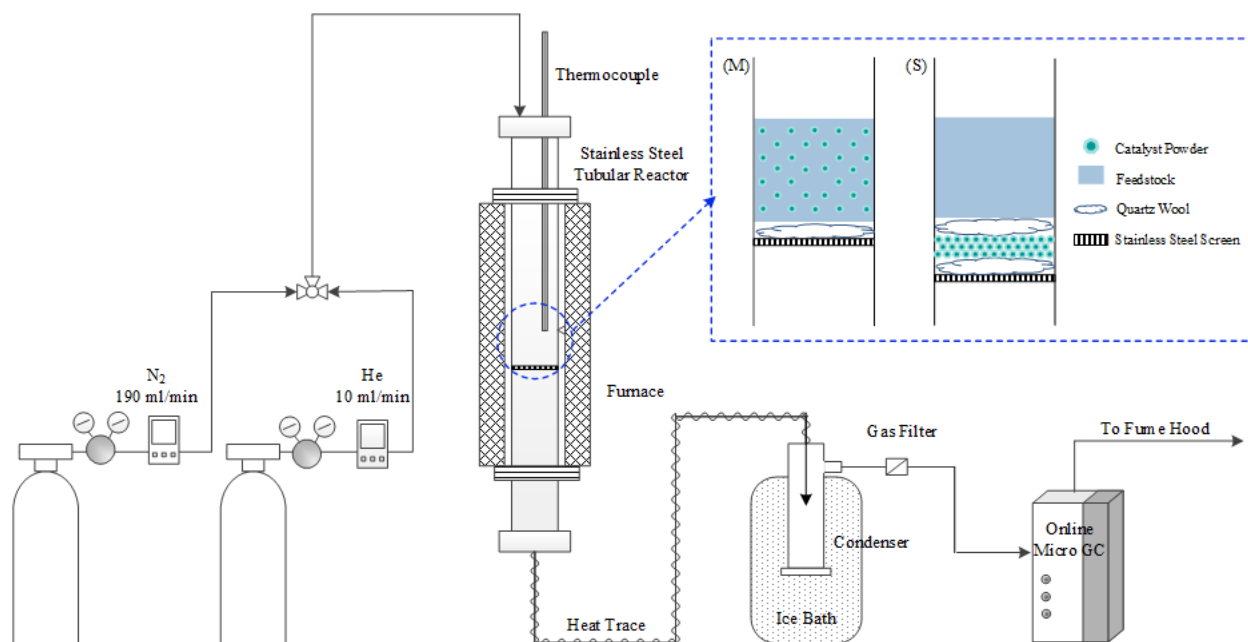

Figure 4.1 Reactor System and Different Catalyst Loading Patterns: (M) Mixed bed; (S)

Separated bed

69

4.3 Results and Discussions

4.3.1 Characterization of Catalysts before Reaction

The X-ray diffraction (XRD) patterns of the HZSM-5, Ga/HZSM-5, and Zn/HZSM-5 (Fig. 4.2) were analyzed using the software MDI Jade 5.0. The XRD did not detect any amorphous material in the catalysts. The peaks were all sharp and well resolved, which reveals the high crystallinity of the catalysts. Aside from the peaks of HZSM-5, additional peaks ascribed to the bulky ZnO, Ga_2O_3 of other metallic oxides were not discovered. The isolated Zn^{2+}/Ga^{3+} ions and/or Zn-O-Zn/Ga-O-Ga framework clusters were expected to form on the zeolite that performs as the active site. The loading of gallium on the HZSM-5 resulted in slightly lattice distortion as evidenced by the rightwards shifting of most peaks in the pattern of the Ga/HZSM-5; but shape or intensity changes were not obvious. The loading of zinc caused lower diffraction intensities but the peak shifting phenomenon was not observed in the pattern of the Zn/HZSM-5.
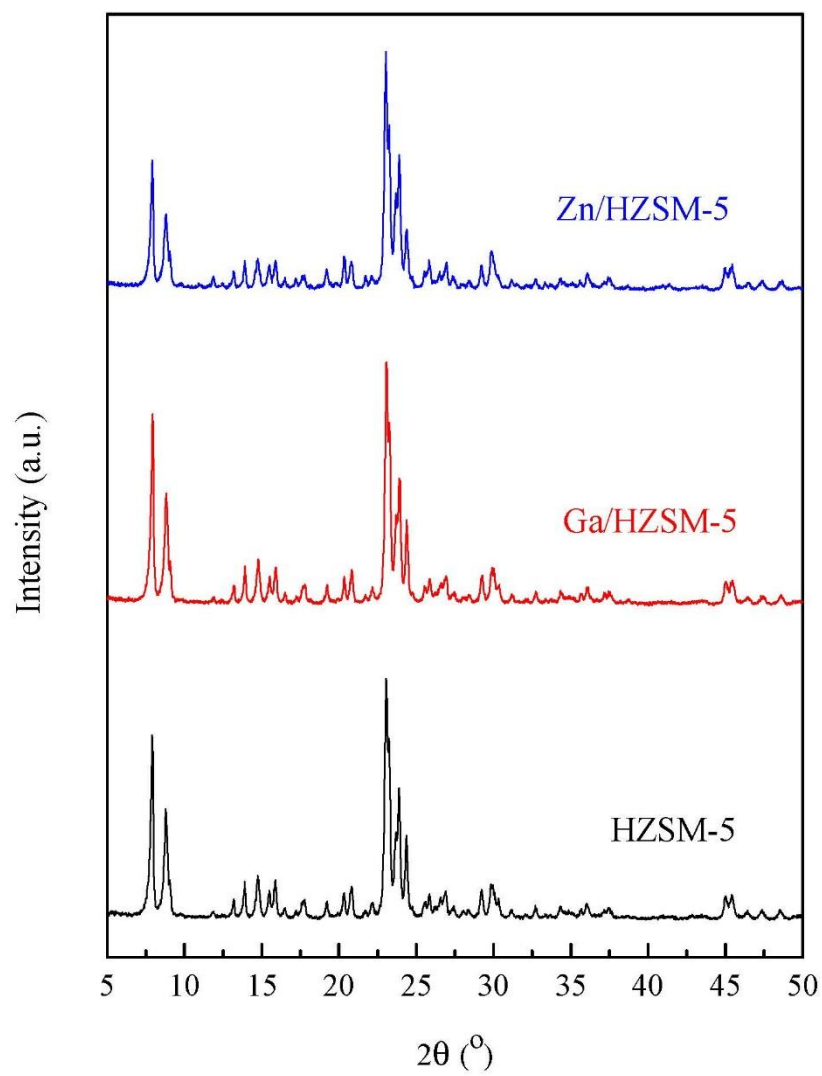
Figure 4.2 XRD patterns of HZSM-5, Ga/HZSM-5 and Zn/HZSM-5 catalysts

By using SEM-EDS technology, the element compositions were determined six times each for both the Ga/HZSM-5 and Zn/HZSM-5. The average weight percentage of the gallium and zinc was around 2.7% and 3.0% (Fig. 4.3), respectively. These values were higher than the expected level (2.5%), which indicates the metal loss was negligible under the calcination condition used in this paper. The distribution of the gallium was more uniform than that of the zinc, which is demonstrated from the obvious length difference of their interval bars. However, the average composition of the gallium and zinc compositions is not significantly different in statistics because the two interval bars overlapped.
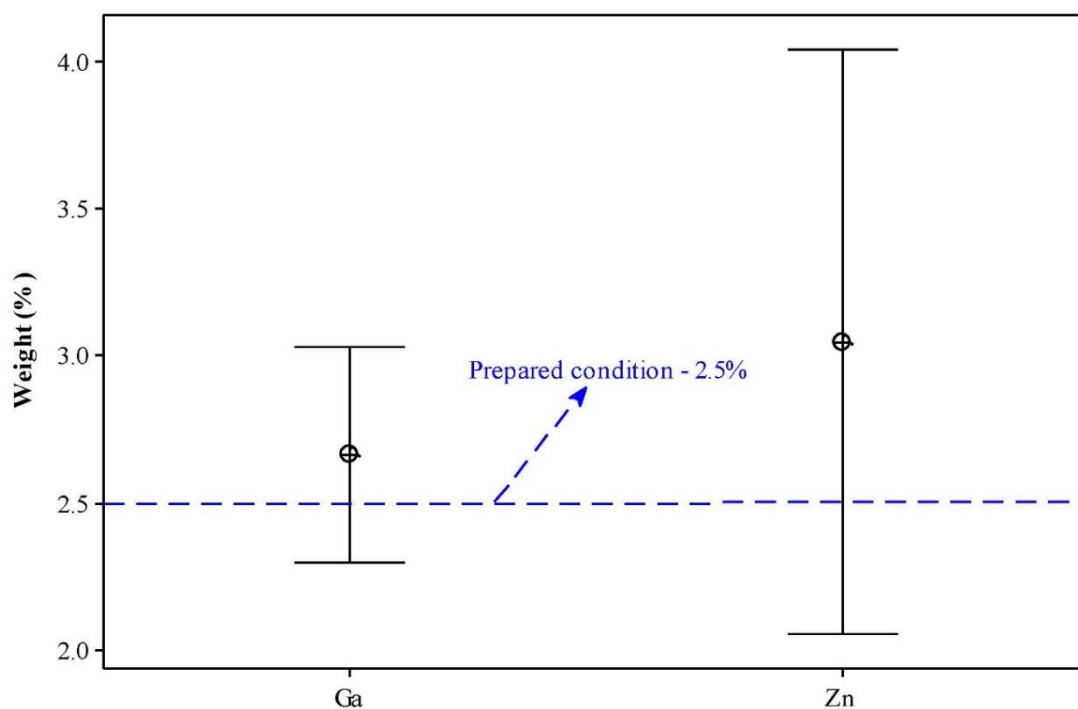

Figure 4.3 Composition of gallium and zinc loaded on the zeolites

As can be seen in Fig. 4.4a, the catalyst support exhibited various shapes and dimensions that ranged from 50 nm to hundreds of nanometers. Fig. 4.4b clearly shows the support's well-organized zeolite structure with micropore channel of around 1 nm. All the gallium particles were observed to be uniformly distributed and small ($\leq$ 1nm), which indicates it was possible to migrate into the channels of the zeolite to perform as the active sites.

By contrast, the dispersion of zinc particles was highly inhomogeneous. Dense and uniform metal distribution (Fig. 4.4e), uneven distribution or even the non-existence of zinc particles (Fig. 4.4d) appeared concurrently on the support. Some zinc particles were small (Fig. 4.4f), but some particles were too large (2-5 nm) to enter the zeolite channels and could only stay on the exterior surface of the zeolite.
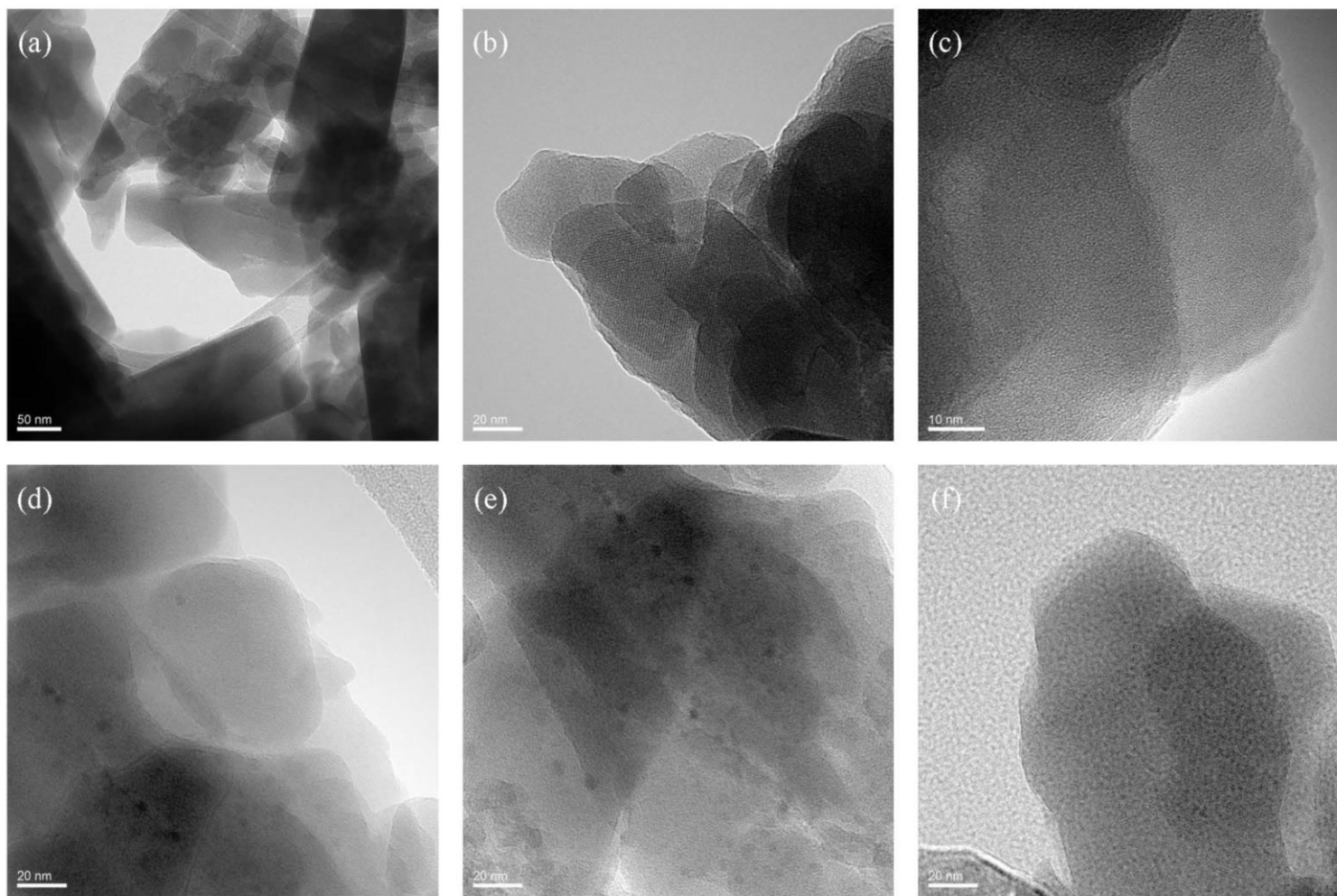
Figure 4.4 (a-c): TEM Photos of Ga/HZSM-5 Catalyst; (d-e): TEM Photos of Zn/HZSM-5 Catalyst

4.3.2 Gas Compositions

Table 4.2 Selectivity of Hydrogen and C_1 Compounds of Gas Products

	No Catalyst	HZSM-5 (S)	Ga/HZSM-5 (S)	Zn/HZSM-5 (S)	HZSM-5 (M)	Ga/HZSM-5 (M)	Zn/HZSM-5 (M)
H_2	0.8%	0.9%	1.8%	1.6%	0.7%	0.9%	0.7%
CH_4	1.5%	1.7%	1.2%	1.2%	0.9%	0.8%	0.8%
CO	31.6%	31.1%	39.2%	40.7%	48.0%	48.9%	55.1%
CO_2	66.2%	66.3%	57.8%	56.5%	50.3%	49.4%	43.4%

The hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) compositions of the pyrolysis reactions are shown in Table 4.2. CO and CO_2 accounted for most of the produced gases (more than 97%). Using the different catalysts or different catalyst loading patterns, the distribution of CO and CO_2 showed systematic changes. In composition with the separated bed reaction of a same catalyst, its mixed bed reaction delivered more CO (16.9% increase for HZSM-5, 9.7% increase for Ga/HZSM-5, and 14.4% increase for Zn/HZSM-5), and less CO_2, H_2 and CH_4 production simultaneously. Regarding the mixed bed reactions or separated bed reactions, the CO production sequences of the catalysts were the same: Zn/HZSM-5 > Ga/HZSM-5 > HZSM-5.

4.3.3 Reaction Yields and Elemental Analysis of Pyrolysis Oils

Compared with petroleum-derived oil, the waste/biomass pyrolysis oil is significantly unstable due to its high oxygen content. The costly follow-up deoxygenation steps made the utilization of pyrolysis oil less economic. Therefore, using the conventional hydrogen-to-carbon molar ratio (H/C), which does not take the oxygen content into account, is not appropriate to

compare the waste/biomass-derived oils with petroleum products. In order to evaluate whether a feed can be economically converted into high quality hydrocarbon products, (Chen et al.) suggested to use the effective hydrogen-to-carbon molar ratio (H/C$_{eff}$), which is expressed as the equation below:

$$H/C_{eff} = (H - 2O)/C,$$

where H, O, and C are the moles of hydrogen, oxygen and carbon in a material, respectively.

In this paper, the H/C$_{eff}$ of the feedstock and the pyrolysis oils were calculated and are presented with the oil yields in Fig. 4.5. Without the presence of the catalyst, pyrolysis reaction converted 49 wt% of the waste coffee cups into an oil product. This pyrolysis oil showed an H/C$_{eff}$ (0.49) of 20% higher than that of the feedstock (0.41). However, it would still be difficult to be upgraded into the premium products due to its H/C$_{eff}$ less than 1.0 (Chen et al., 1986). Using the catalysts reduced the oil yields but enhanced the H/C$_{eff}$ growths significantly (more than 51%). The highest H/C$_{eff}$ of 1.11 was observed in the mixed bed reaction using the catalyst Ga/HZSM-5. As for the HZSM-5 and Ga/HZSM-5 catalysts, the mixed bed reactions demonstrated higher H/C$_{eff}$ of oil, in comparison with the separated bed reactions. However, the different loading patterns of Zn/HZSM-5 did not influence the oil's H/C$_{eff}$ significantly. After the catalyst loading pattern was switched from the separated bed to the mixed bed, the oil yields were decreased, with a reduction of 3.6 wt%, using HZSM-5; 7.8 wt%, using Ga/HZSM-5; and 12.4 wt% using Zn/HZSM-5.
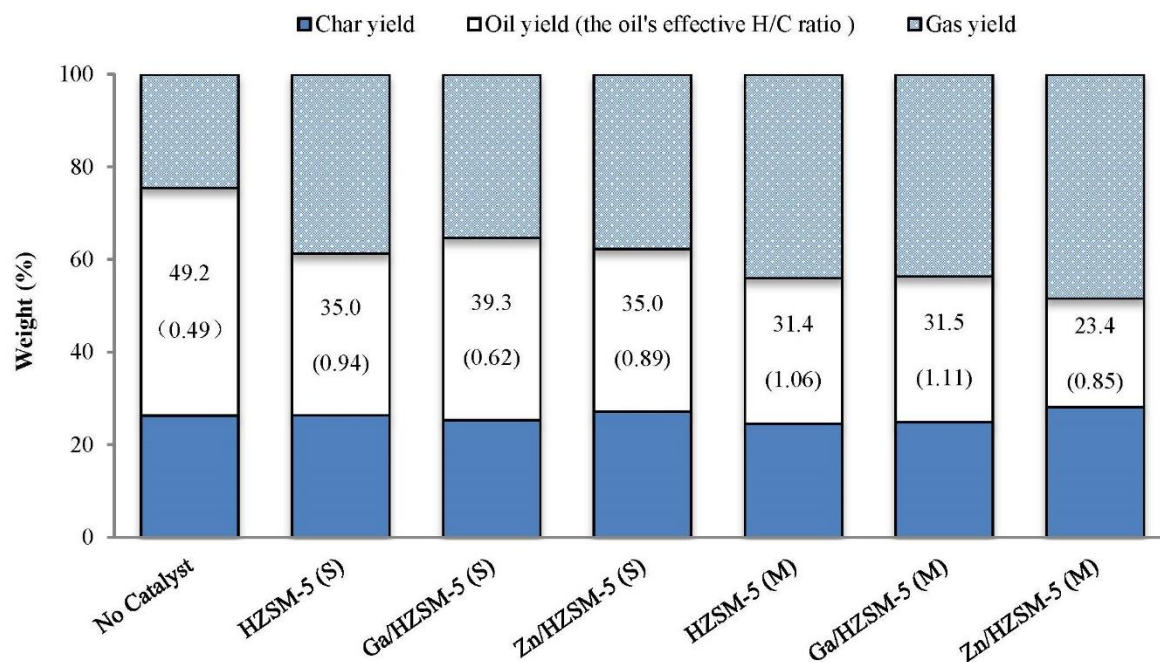
Figure 4.5 Product Distribution and Effective Hydrogen-to-Carbon Ratios of the Pyrolysis Oils

4.3.4 ^{1}H-NMR and GC-MS Analysis of Pyrolysis Oils

An apparent water peak centered at 4.79 ppm was observed in the oils' ^{1}H-NMR spectra, indicating a considerable amount of water content. A water suppression technique was utilized to help obtain the integration results without the water peaks. Assignment of the ^{1}H-NMR bands was derived from several publications based on works involving biomass-derived pyrolysis oils (Pindoria et al., 1997; Özbay et al., 2001; Pütün et al., 2001, Pütün, 2002, Wildschut et al., 2009). Table 4.3 shows the oils' quality change in terms of structural hydrogen distribution. Aliphatic hydrogen, especially the protons in α positions attached to naphthene or an aromatic ring, is the dominant hydrogen type. The hydroxyls, ring-join methylene, methane or methoxyl

hydrogens also occupied a large proportion (probably due to the contained cellulose fragments in the oil). Both aliphatic hydrogen and aromatic hydrogens were increased, in expense of the hydroxyl hydrogens, after the introduction of catalysts to the pyrolysis. The reaction using a mixed bed pattern Ga/HZSM-5 obtained an oil of the highest hydrogen aromaticity (11.7%), as well as relatively high aliphatic hydrogen content (56.25%).

The catalyst loading pattern has a significant effect on the oil's hydrogen distribution. Compared with loading the feedstock and catalyst separately, mixing them together produced oils with higher aromatic hydrogen contents and aliphatic hydrogen contents, as well as lower hydroxyl hydrogen contents. However, the aldehyde contents were also increased for the mixed bed pattern reactions. These observations were consistent with the trend of the oils' product distribution and elemental analysis results. Overall, the mixed bed loading pattern enhanced the catalyst's function in cracking and aromatization. Because of the more intensive collisions between the reactant/intermediate molecules and the catalyst in the mixed bed reactions, more feedstock was involved in the cracking, decarbonylation/decarboxylation, aromatization and other reactions to form gases. However, this trade-off of liquid yields resulted in better oil quality in terms of higher H/C_{eff} and more aliphatics/aromatics.

Carbon aromaticity, f_a, was widely applied in the evaluation of the petroleum-derived liquids or coal extracts. It can be calculated by either the 13C-NMR method or the Brown and Ladner method, expressed in the following formula: $f_a = \frac{\left(\frac{C}{H}\right) - \left(\frac{H_\alpha}{2} + \frac{H_\beta}{2} + \frac{H_\gamma}{3}\right)}{\left(\frac{C}{H}\right)}$ (Escallon, 2008), where C/H is the carbon-to-hydrogen mole ratio of a fuel and H_α, H_β, H_γ are the contents of the

protons in the α, β, γ positions to an aromatic ring respectively. In this paper, the $(C/H)_{eff}$ which is the reciprocal of the $(H/C)_{eff}$ and the $(H_\alpha, H_\beta, H_\gamma)$ contents listed in the Table 4.2 were used to calculate the f_a of the seven pyrolysis oils. The results were in the range of 0.70 to 0.88 and were similar to the numbers of decant oils reported in the literature (Escallon, 2008).

Table 4.3 Hydrogen Distribution of Pyrolysis Oils From the ^{1}H-NMR Spectra

Type of Hydrogen	Chemical shift (ppm)	No Catalyst	HZSM-5 (S)	Ga/HZSM-5 (S)	Zn/HZSM-5 (S)	HZSM-5 (M)	Ga/HZSM-5 (M)	Zn/HZSM-5 (M)
CH$_3$ γ or futher from an aromatic ring (H$_γ$)	0.5-1.0	8.06	5.22	8.52	6.78	7.10	7.89	8.70
CH$_3$, CH$_2$ or CH β to an aromatic ring (H$_β$)	1.0-1.5	9.17	7.15	8.88	7.92	8.39	8.24	9.33
CH$_2$ and CH attached to naphthene; CH$_3$, CH$_2$ and CH α to an aromatic ring (H$_α$)	1.5-3.0	32.80	36.66	36.33	40.77	38.82	40.12	42.22
Total Aliphatics	*0.5-3.0*	*50.02*	*49.03*	*53.73*	*55.47*	*54.31*	*56.25*	*60.25*
Hydroxyls, ring-join methylene, methine or methoxy	3.0-4.5	33.13	30.99	26.98	25.97	24.13	22.91	21.48
Phenols, non-conjugated olefins	4.5-6.0	5.84	5.82	5.05	6.65	7.56	5.69	4.97
Aromatics, conjugated olefins	6.0-9.0	8.30	8.08	6.70	9.99	11.40	11.10	10.23
Aldehydes	9.0-10.0	1.93	1.56	1.49	1.71	2.39	2.62	2.28

Table 4.4 Identification of Compounds in Oil Product (catalyst: mixed bed loaded Ga/HZSM-5)

Peak No.	R.T. (min)	Name of Compound	Area% of total	Formula
1	1.689	Acetaldehyde, hydroxy-	3.11	$C_2H_4O_2$
2	1.815	Acetic acid	5.79	$C_2H_4O_2$
3	2.137	Acetol	2.29	$C_3H_6O_2$
4	2.342	2,3-Pentanedione	1.35	$C_5H_8O_2$
5	2.446	Propanoic acid	1.75	$C_3H_6O_2$
6	3.179	1-Hydroxy-2-butanone	1.36	$C_4H_8O_2$
7	3.420	Di-n-propyl ether	1.55	$C_6H_{14}O$
8	4.130	Furfural	6.64	$C_5H_4O_2$
9	4.506	2-Butanone	0.86	C_4H_8O
10	4.657	Hydroquinone	1.23	$C_6H_6O_2$
11	5.404	Ethanone, 1-(2-furanyl)-	1.96	$C_6H_6O_2$
12	5.676	1,2-Cyclopentanedione	1.59	$C_5H_6O_2$
13	6.335	2-Furancarboxaldehyde, 5-methyl-	5.91	$C_6H_6O_2$
14	6.687	Pyrazine, methyl-, 4-oxide	1.14	$C_5H_6N_2O$
15	7.006	Oxazolidine, 2,2-diethyl-3-methyl-	2.01	$C_8H_{17}NO$
16	7.419	3-Octene, (Z)-	2.67	C_8H_{16}
17	7.773	Octane, 4-ethyl-	1.08	$C_{10}H_{22}$
18	7.871	Phenol, 2-methyl-	1.02	C_7H_8O
19	8.282	Orcinol	1.34	C_7H_8O2
20	8.443	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	2.72	$C_6H_8O_3$
21	8.648	2-Nonen-1-ol, (E)-	1.00	$C_9H_{18}O$
22	8.839	Maltol	2.12	$C_6H_6O_3$
23	9.432	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	1.08	$C_6H_8O_4$
24	10.114	1-Decanol, 2-methyl-	11.57	$C_{11}H_{24}O$
25	10.505	1,4:3,6-Dianhydro-α-d-glucopyranose	4.26	$C_6H_8O_4$
26	10.664	5-Hydroxymethylfurfural	8.03	$C_6H_6O_3$
27	11.750	Naphthalene, 2-methyl-	0.67	$C_{11}H_{10}$
28	14.079	2H-1,5-Benzodioxepin, 3,4-dihydro-3-methylene-	0.47	$C_{10}H_{10}O_2$
29	14.591	2,3-2H-Benzofuran-2-one, 3,3,4,6-tetramethyl-	1.84	$C_{12}H_{14}O_2$
30	14.901	d-Mannose	0.96	$C_6H_{12}O_6$
31	15.628	Benzene, ethylpentamethyl-	0.64	$C_{13}H_{20}$
Total Area			80.02	

Table 4.5 Identification of Compounds in the Acetone Elute of Condenser Outlet Gas

(catalyst: mixed bed loaded Ga/HZSM-5)

Peak No.	R.T. (min)	Name of Compound	Area% of total	Formula
1	5.051	Cyclohexanol	0.05	$C_6H_{12}O$
2	6.566	Phenol	0.06	C_6H_6O
3	8.441	Phenol, 2-methoxy-	0.19	$C_7H_8O_2$
4	9.598	Phenol, 2,3,4,6-tetramethyl-	0.66	$C_{10}H_{14}O$
5	10.106	Naphthalene	0.14	$C_{10}H_8$
6	10.500	Phenol, 3-cyclohexyl-	0.17	$C_{12}H_{16}O$
7	11.124	Benzene, 1,2-dimethoxy-4-(1-propenyl)-	0.23	$C_{11}H_{14}O_2$
8	11.742	Naphthalene, 1-methyl-	0.29	$C_{11}H_{10}$
9	11.899	Phenol, 3-cyclohexyl-	0.37	$C_{12}H_{16}O$
10	12.094	Benzenemethanol, 4-(1,1-dimethylethyl)-	0.44	$C_{11}H_{16}O$
11	12.932	1,2,3,4-Tetrahydrodibenzofuran	0.10	$C_{12}H_{12}O$
12	13.143	Benzene, 1-methoxy-4-methyl-2-(1-methylethyl)-	0.41	$C_{11}H_{16}O$
13	14.495	1-(5,5-Dimethyl-2-methylene-5,6,7,7a-tetrahydro-2H-cyclopenta[b]pyran-4a-yl)-ethanone	0.32	$C_{13}H_{18}O_2$
14	18.111	2-Biphenylcarboxylic acid	0.79	$C_{13}H_{10}O_2$
15	18.802	1,1'-Biphenyl, 2-methyl-4,5-methylenedioxy-	1.74	$C_{14}H_{12}O_2$
16	19.280	Phenol, 4,4'-methylenebis-	0.97	$C_{13}H_{12}O_2$
17	19.426	Phenol, 2,2'-methylenebis-	2.27	$C_{13}H_{12}O_2$
18	19.594	Phenol, 2,2'-methylenebis-	2.86	$C_{13}H_{12}O_2$
19	19.712	Phenol, 4,4'-methylenebis-	0.94	$C_{13}H_{12}O_2$
20	19.781	Phenol, 2-[(4-hydroxyphenyl)methyl]-	2.19	$C_{13}H_{12}O_2$
21	20.333	Phenol, 4,4'-methylenebis-	5.27	$C_{13}H_{12}O_2$
22	20.431	Phenol, 4,4'-methylenebis-	4.63	$C_{13}H_{12}O_2$
23	20.577	2-Norbornene, 7-methoxy-7-(p-methoxyphenyl)-, stereoisomer	2.93	$C_{15}H_{18}O_2$
24	20.693	Phenol, 2-methoxy-6-[(2-pyridinylamino)methyl]-	3.40	$C_{13}H_{14}N_2O_2$
25	20.926	9-Oxabicyclo[4.3.0]non-6-en-8-one, 7-[2-methylenebicyclo[3.3.0]octane-3,6-dione	1.89	$C_{17}H_{18}O_4$
26	21.098	Chapter Cinco: Benzo[e](1H)indene, 1,2,3a,4,5,9b-hexahydro-7-methoxy-3-oxo-3a,9b	3.48	$C_{16}H_{20}O_2$
27	21.336	Habranthine	10.16	$C_{17}H_{21}NO_4$
28	21.725	Habranthine	6.09	$C_{17}H_{21}NO_4$
29	21.957	Tetrahydrocortisol	2.09	$C_{21}H_{34}O_5$
30	22.335	Methenolone	4.56	$C_{20}H_{30}O_2$
31	22.552	1α-Methyltestoterone	6.13	$C_{20}H_{30}O_2$
32	22.776	Androst-4-ene-3,6,17-trione	5.05	$C_{19}H_{24}O_3$
Total Area			70.84	

The GC-MS analysis of the oil obtained from the reaction using mixed bed loaded Ga/HZSM-5 is given in Table 4.4. In order to identify the hydrocarbons that were not trapped by the condenser, this reaction (mixed bed Ga/HZSM-5) was repeated; and the condenser outlet was connected to a vessel containing acetone rather than to the normal online Micro-GC. The acetone solution was then analyzed by the GC-MS and is presented in Table 4.5. Thus, the data shown in Table 4.4 and Table 4.5 together represent the total composition of the pyrolysis liquid product. The most important compounds forming this liquid product were phenolic compounds (especially bisphenols) and furan derivatives (especially furfural, furananol, and furancarboxaldehyde), indicative of the product's potentially high economic value. In addition, considerable amounts of the naphthalene were identified in the liquid product.

Bisphenols are important intermediates for high-grade thermosets, thermoplastics, and as antioxidants for rubber, plastics, oils, and fats. The importance of bisphenols has increased continuously from the late 1930s due to the growth of the plastics industry (Ullmann, 1985-1996). Other phenolic compounds existed in the pyrolysis product, such as alkylphenols, cycloalkylphenols, and hydroquinone, which are also widely used as starting materials in the synthesis of antioxidants, pharmaceuticals and agrochemicals. Furfural is widely used as a selective solvent in the production of high quality motor oils, lubricant oils, and phenolic resins, as well as a decoloring agent (Ullmann, 1985-1996). Naphthalene and its derivatives have a diverse utilization in the chemical industry in the production of phthalic, surfactants, dyes, solvents and others.

A small amount of the olefin and paraffin hydrocarbons (C_8H_{16}: 2.67%, and $C_{10}H_{22}$: 1.08%) were observed in the pyrolysis oil (Table 4.4). As a whole, the liquid product is unsuited for use

in the production of automotive fuels due to the undesirable chemical structure, although the carbon range of this total liquid was C_2 - C_{21}, which is comparable to that of gasoline and diesel. However, the production of phenolic compounds, furfural, and naphthalene were all based on petroleum or coal-tar in the current stage. The use of technology in recovering these chemicals from waste coffee cups via catalytic pyrolysis would be a great alternative to the use of fossil fuels and would be economically beneficial.

4.3.5 Coke Deposited on Spent Catalysts

The coke deposition type and amount were determined by the TG profile after heating the spent catalyst in air. The coke was classified into (Sahoo et al., 2004) three types according to its oxidation in different temperature regions: water and volatile species in Region I (T $<$ 180°C); soft coke in Region II (180°C $<$ T $<$ 330°C); and hard coke in Region III (330°C $<$ T $<$ 750°C). The soft coke is interpreted by (Sahoo et al., 2004) as a carbonaceous material with more mobility, such as the reaction side products or physisorbed products, while the hard coke is more bulky carbon.

As can be seen in Fig. 4.6, hard coke was the main coke species for all the catalysts, probably due to the fast flow rate of carrier gases, which prevented the physisorption of the by-products/products to some extent. HZSM-5 zeolite had the largest amount (10.8%) of coke deposition and the Ga/HZSM-5 had the lowest amount (8.6%). However, the TG profiles of HZSM-5 and Ga/ZSM-5 in Regions I and II almost overlapped, i.e. the difference in their total coke deposition was caused by the hard coke.

The hard coke amounts deposited on the HZSM-5 and Zn/HZSM-5 were about the same. However, less water/volatiles and soft coke deposition was observed in the TG profile of Zn/ZSM-5, compared with that of the HZSM-5. This indicates that the loading of Ga on the zeolite hindered the hard coke formation on the catalyst; and the loading of Zn on the zeolite reduced the water/volatiles and soft coke deposition.
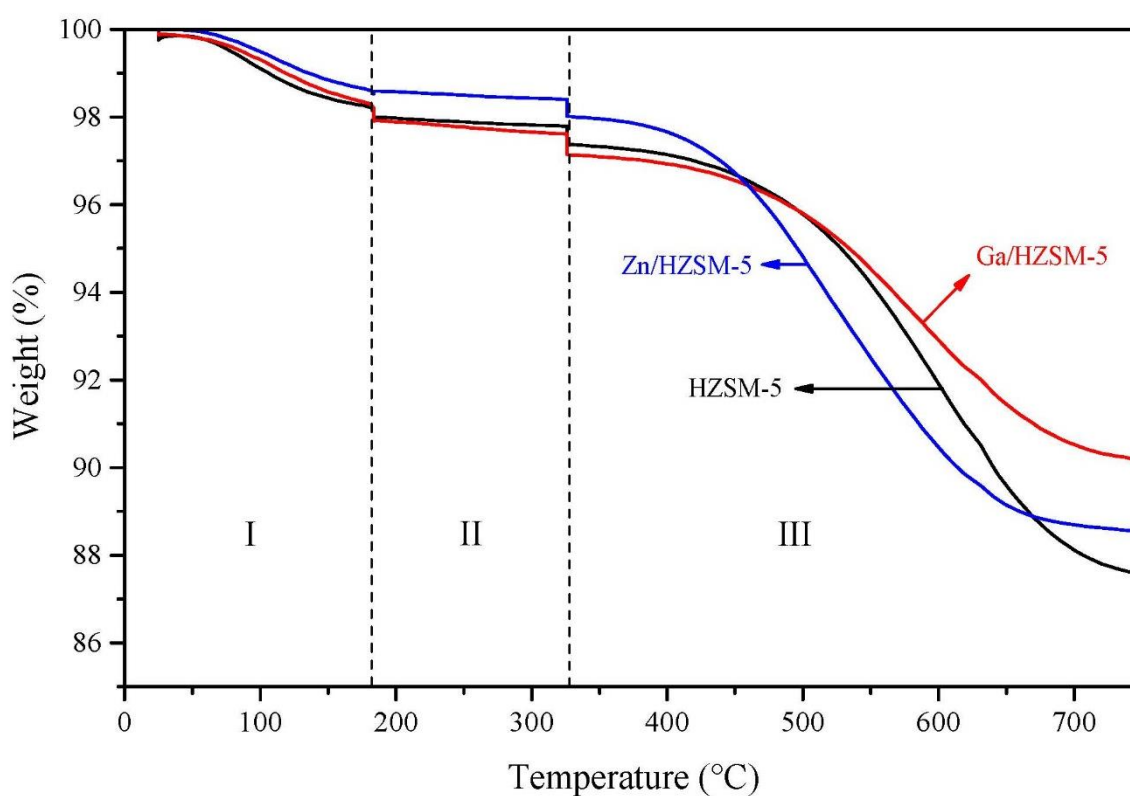

Figure 4.6 TG Profiles of Spent Catalysts

4.4 Summary

In the present work, the Ga/HZSM-5 and Zn/HZSM-5 were proven to act as bifunctional catalysts that promote the H/C_{eff} of the pyrolysis oil. This improvement largely reduces the technical difficulty and hydrogen cost of subsequent oil upgrading. Structure characterization of the catalysts showed that the gallium particles were uniformly distributed on the zeolite. The small particle size allowed their migration into the zeolite pore channel to become active sites. The zinc particles' distribution, however, was highly inhomogeneous and their migration into the pore channel was not detected by the XRD. The structure difference of the catalysts influenced the reaction results and the coke formation status significantly. Compared to the HZSM-5 or Zn/HZSM-5, the Ga/HZSM-5 proved to have the best performance in increasing the pyrolysis oil's H/C_{eff} and the aromatic and aliphatic hydrogen contents, with regards to hydrogen distribution, with less hard coke formation on the catalyst after reaction. Different catalyst loading patterns have significant effects on the catalyst's performance. The mixed bed pattern enhanced the catalyst's cracking and aromatization functions by creating more molecular collisions between catalyst particles and feedstock/intermediate reactants. Additional research could shed light on the catalytic pyrolysis of waste coffee cups using a fluidized bed reactor.

The pyrolysis oil obtained from the pyrolysis of waste coffee cups using the mixed bed Ga/HZSM-5 was mainly composed of phenolic compounds and furan derivatives that can be extracted to produce high-value chemicals. Because of its undesirable low olefin and paraffin contents, commercial production of automotive fuel from the pyrolysis oil of waste coffee cups does not seem to be viable in the near future.

Chapter Five: **Conclusions and Suggestions for Future Work**

5.1 Conclusions

The physical and chemical compositions, surface area and thermal weight loss data of MSW, based on 7 residential wastes and 7 ICI wastes gathered from the City of Red Deer, were obtained in the present study. Several conclusions of their characteristics can be drawn:

(1) The moisture content of the MSW samples largely depended on the type of material. The residential wastes were observed to have more moisture than the ICI wastes. The chemical properties of the dry residential wastes, however, were similar to those of the dry ICI wastes, containing high volatile matter contents (>85%) and low fixed carbon contents (<10%). All the MSW samples had small surface area values.

(2) The ultimate analysis results show that the MSW had an H/C_{eff} ratio similar to biomass and low grade coal. Research on the topic of WTE could extend from the use of these materials. In addition, the MSW samples had non-negligible amounts of nitrogen and sulfur. Proper De-NOx and De-SOx technologies are essential to reduce the negative environmental or health effects of a WTE facility.

(3) The shapes of TG and DTG curves are largely related to the chemical nature of the samples. Torrefaction did not change the nature of the MSW samples, but did increase their grindibility. Pyrolysis converted the MSW samples into chars. Torrefaction increased the H/C or H/C_{eff} ratios of the MSW and decreased its O/C ratio, which allows opportunity for the raw MSW material to be converted into high quality RDF (refuse derived fuel). Pyrolysis can decrease the H/C or H/C_{eff} ratios of the MSW, producing chars with high carbon content.

A new empirical model based on ultimate analysis has been developed in the present work for calculating the HHV of municipal solid waste: HHV (MJ/kg) = 0.350 C + 1.01 H - 0.0826 O, which is expressed in terms of weight percentages on a dry basis of carbon (C), hydrogen (H) and oxygen (O). The data used for the derivation of this equation were adequate and trustworthy, resulting in a favorable degree of accuracy compared to other existing models. Application of this model allows for the rapid, easy and accurate prediction of MSW heating values if the chemical composition is known.

The pyrolysis oil (bio-oil) of the waste coffee cups is highly oxygenated. Introduction of ZSM-5 type catalysts dramatically increased the oil's H/C_{eff} from 0.49 up to 1.11. In comparison with the HZSM-5 or Zn/HZSM-5, the Ga/HZSM-5 showed the best performance in increasing the oil's aromatic and aliphatic hydrogen contents thus increasing its H/C_{eff}, and with less hard coke formation on the catalyst after reaction. The mixed bed pattern enhanced the molecular collisions between catalyst particles and feedstock/intermediate reactants, hence producing better quality oils than the separated bed pattern. The pyrolysis oil produced by using Ga/HZSM-5 of the mixed bed loading pattern is mainly composed of phenolic compounds and furan derivatives that can be extracted to produce high-value chemicals.

5.2 Suggestions for Future Work

Based on the results and findings in this study, several recommendations for future research in this field are proposed:

(1) Multiple samplings drawn throughout the year are suggested, in order to obtain more accurate moisture content data for future work. Performing sampling monthly or at least

seasonally is essential because the moisture content depends largely on weather conditions and the season.

(2) Collect more experimental characteristics of the MSW by laboratory measurements or from literature would greatly add to the prediction accuracy of the empirical model built in this report. The required experimental characteristics include the high heating values of the MSW, as well as the elemental compositions in dry basis.

(3) Develop a fluidized bed reactor system to explore the possibility of continuous feeding and operation for the pyrolysis of waste coffee cups. Add a series of cold traps at the outlet of reactor to capture the heavy products more efficiently.

(4) Optimize the catalyst formulation by reducing the metal loading amount to make the process more economic or adjusting the Si/Al ratio of the zeolite support to discern the effect of the zeolite acidity.

(5) Make the catalyst undergo several reaction-regeneration cycles to test its stability in order to explore the deactivation mechanism

(6) Collect more information about the pyrolysis gas and liquid products. In addition to the composition information provided in this thesis, various analysis data of the products are required as they are found to be inadequate in literature. The viscosity, density, PH value, flash point, and pour point of the pyrolysis oil are critical parameters to compare the oil quality with traditional petroleum-derived oil. Moreover, there might be considerable amounts of C_2-C_4 hydrocarbons in the pyrolysis gases, which have not been discussed in this work.

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Appendix: Comparison of Ash Contents Obtained from Different Methods

Aside from the proximate analysis, the ash content of MSW can also be determined by using the muffle furnace. In the muffle furnace method, two gram of the test sample was placed in a clean crucible in the muffle furnace (Lindberg Blue). The heating rate was controlled as slow (30°C/min) to avoid flaming and to protect the crucible from strong drafts. Duration of combustion was 6 hours after the setting ignition temperature was reached. Preliminary tests were conducted to make sure this duration was long enough that all the combustible matter was eliminated for each sample. Two final ignition temperatures were tested for each sample: 550°C and 900°C, respectively. The selection of these two temperatures was according to various standards: ASTM E1755-01(2007), ASTM D1102-84(2013), ASTM D5630-13, ASTM D4574-06(2012).

Compare the values on Table A-1 with those of Table 2.1 and Table 2.2; it is easy to see that the ash contents of Residential-rubber and ICI-(textile and rubber) from the muffle furnace method are noticeably different from the results of proximate analysis. The two sets of muffle furnace ash contents at different temperatures are different, yet demonstrate the same trend.

Table A-1 Ash Contents of MSW by Muffle Furnace Method at 550°C and 900°C

(wt%, dry basis)	Residential MSW				ICI MSW			
	550 $^{\circ}$C		900°C		550 $^{\circ}$C		900°C	
Non-recyclable paper	9.31	(2.57)	8.19	(0.68)	9.47	(3.24)	7.63	(3.62)
Wood waste	9.13	(0.93)	7.64	(1.37)	4.11	(0.11)	3.91	(0.11)
Plastic-rigid	0.53	(0.43)	1.02	(0.78)	0.28	(0.17)	0.24	(0.21)
Plastic-film & styrofoam	0.00	(0.00)	0.00	(0.00)	0.85	(1.02)	0.29	(1.04)
Plastic-textile	0.77	(0.20)	0.63	(0.18)	7.42	(0.49)	4.51	(0.25)
Carpet	29.52	(3.16)	18.73	(1.93)	2.14	(0.64)	1.57	(0.23)
Rubber	18.33	(0.93)	11.72	(0.51)	26.73	(8.87)	22.69	(9.53)

The standard deviations of measurements are shown in brackets, in percentage.

However, we still cannot generally conclude the three different ash determination methods (proximate analysis - PA; muffle furnace method at 550 °C – MF550; muffle furnace method at 900 °C- MF900) will result in the same or different ash contents. Therefore, the hypothesis testing is used to help draw conclusions about possible differences between the population means of the three methods. Because the three sets of data for comparison are essentially the repeated measurements for the same substances, paired t test method should be used.

Thus three comparison groups were defined as following:

'Group A'– the comparison of MF550 and MF900;

'Group B' – the comparison of MF550 and PA;

'Group C' – the comparison of MF900 and PA. The null hypothesis is that no difference exists between the means of these two related populations, illustrated as

$$H_0: \mu_D = 0 \ (where \ \mu_D = \mu_1 - \mu_2)$$

Thus the alternative is that the means are not the same

$$H_1: \mu_D \neq 0$$

The following t-test statistic is computed.

$$t = \frac{\bar{D} - \mu_D}{\frac{s_D}{\sqrt{n}}}$$

where

$$\overline{D} = \frac{\sum_{i=1}^{n} D_i}{n}$$ is the mean of sample difference;

and

$$s_D = \sqrt{\frac{\sum_{i=1}^{n}(D_i - \overline{D})^2}{n - 1}}$$

The test statistic t follows a t distribution with (n-1) degrees of freedom. The sample size of each group (n) is 14. Choosing a level of significance, α, of 0.05, and assuming the differences are normally distributed, the decision rule is as follows:

$$Reject\ H_0\ if\ t < -t_{critical} = -2.1604\ or\ if\ t > t_{critical} = +2.1604;$$

$$otherwise\ do\ not\ reject\ H_0$$

The Software - Microsoft Excel was used to accomplish this procedure; the result is shown in Table A-2. Both the t values of 'Group A' and 'Group B' are larger than the critical t values, while the t value of 'Group C' is smaller than the critical one. Therefore, conclusion can be made that there is no evidence of a difference in ash content obtained from MF900 and PA. However, MF550 has proven to be different from the other two methods.

The above observation is caused by the difference of combustion temperature. The temperature of combustion stage in PA is 750°C, while MF550 and MF900 temperatures of combustion are 500°C and 900°C, respectively. One possible reason of the lower ash contents obtained at higher temperature (750/900°C) is that the combustible part of the sample is consumed more completely during the heating process. When the sample is placed at a higher temperature, it would be easier to collapse and melt. The interior part of the bulk material is able to be more exposed to the oxygen atmosphere. Thus the oxidization of the combustible part of a

material is more completely. Another possible reason is that a portion of the low boiling point ash can be volatilized at higher temperatures, resulting in a smaller value of ash content.

Therefore, in obtaining the general knowledge of ash content of MSW, either the PA or MF900 methods would give out similar results. But as for collecting local MSW data for a particular WTE facility, the ash contents are suggested to be measured under a particular combustion temperature according to the design purpose of the facility.

Table A-2 Results Comparison of Muffle Furnace Method and Proximately Analysis

t-Test: Paired Two Sample for Means	Group A		Group B		Group C	
	550 ºC	900 ºC	550 ºC	Proximate	900 ºC	Proximate
Mean	8.47	6.34	8.47	4.82	6.34	4.82
Variance	96.58	51.03	96.58	44.38	51.03	44.38
Observations	14	14	14	14	14	14
Pearson Correlation	0.98		0.84		0.80	
Hypothesized Mean Difference	0.00		0.00		0.00	
df	13.00		13.00		13.00	
t Stat	2.53		2.44		1.31	
P(T<=t) two-tail	0.03		0.03		0.21	
t Critical two-tail	2.16		2.16		2.16	
Judgement of Population Means	Different		Different		The Same	