PYROLYSIS OF WASTE PLASTICS TO GENERATE USEFUL FUEL CONTAINING HYDROGEN USING A SOLAR THERMOCHEMICAL PROCESS

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A thesis submitted in fulfilment of the requirements for the degree of Master of Engineering (Research)

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March, 2007
DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and is less than 30,000 words in length. To the best of my knowledge, this thesis contains no material previously published or written by another person, except where due reference has been made.

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Signature        Date
ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. Andrew Harris for his support and guidance during my research. I would also like to thank the University of Sydney for providing me the “University of Sydney Postgraduate Awards – Co-funded” scholarship and the opportunity to study in School of Chemical and Biomolecular Engineering.

I would like to thank Dr. Chris Dey and Dr. Damien Buie from School of Physics, the University of Sydney for their guidance regarding the working of solar concentrator and solar reactor design.

I would also like to thank A/Prof. Tim Langrish for his support as my associate supervisor.

I also like to thank Dr. Jeffrey Shi for helping me out during my thermogravimetric experiments.

I would like to thank Ms. Lorriane Ryan from the Learning Centre, the University of Sydney for her help and feedback on my thesis writing style.

Finally, I would like to thank my research group the Laboratory of Sustainable Technology for supporting me throughout my research.
ABSTRACT

Global warming and diminishing energy supplies are two major current concerns. Disposal of plastic wastes is also a major concern. The aim of this research is to address these three concerns by developing a solar powered process, using waste plastics as fuel to generate energy. Research into: i) solar concentrators for high temperature thermochemical processes, and ii) pyrolysis/gasification of waste plastics has been separately reported in the literature. In this study the aim was to bring these fields of research together to design a solar receiver-reactor suitable for the production of a synthesis gas, consisting of hydrogen, from waste plastics.

To achieve this aim, studies of plastic decomposition behaviour using the thermal analysis method known as thermogravimetric analysis were conducted. Solar concentrators and their potential to be used for thermochemical processes were also studied.

Firstly, the thermal decomposition behaviour of common plastics, namely low density polyethylene (LDPE), high density polyethylene (HDPE), polyethylene terephthalate (PET) and polyvinyl chloride (PVC), were studied using thermogravimetry at heating rates of 5, 10, 20, 50 and 100 ºC/min. The kinetic parameters for the decomposition were determined from these experiments.

Secondly, a simple solar receiver-reactor in which the plastic decomposition could be achieved was designed. The solar receiver-reactor designed was a quartz tube reactor which can be placed in the focus of a dish type parabolic concentrator capable of generating up to 3 kW in the focus of diameter 50 mm.

The thermogravimetric analysis of plastic samples showed that LDPE, HDPE and PET have a single-step decomposition, whereas PVC has a two-step decomposition. The first step was related to the release of hydrogen chloride from the PVC and the second step was related to the release of hydrocarbon from the polymer backbone. If PVC is pre-treated to release HCl it can be mixed with other plastics for a single step decomposition. It is likely that a single step plastic decomposition can be achieved in a directly irradiated solar receiver-reactor to generate useful gases consisting of hydrogen.
# TABLE OF CONTENTS

**DECLARATION** ........................................................................................................................................... i  
**ACKNOWLEDGEMENTS** ............................................................................................................................ ii  
**ABSTRACT** ................................................................................................................................................ iii  
**TABLE OF CONTENTS** .............................................................................................................................. iv  
**ACRONYMS AND ABBREVIATIONS** .......................................................................................................... viii  

1. **INTRODUCTION** ...................................................................................................................................... 1  
   1.1 OVERVIEW ............................................................................................................................................. 1  
   1.2 BACKGROUND ....................................................................................................................................... 1  

2. **THERMAL DECOMPOSITION OF PLASTICS** ....................................................................................... 4  
   2.1 PYROLYSIS OF PLASTICS .................................................................................................................... 4  
      2.1.1 Background ...................................................................................................................................... 4  
      2.1.2 A review of the mechanism of plastic thermal decomposition .............................................. 6  
   2.2 DECOMPOSITION PRODUCTS OF POLYETHYLENE PYROLYSIS .................................................... 10  
      2.2.1 Temperature ................................................................................................................................. 11  
      2.2.2 Temperature and Residence time ............................................................................................... 14  
      2.2.3 Heating rates ............................................................................................................................... 17  
      2.2.4 Other factors ............................................................................................................................... 18  
   2.3 POTENTIAL FOR THE PRODUCTION OF HYDROGEN FROM THE DECOMPOSITION PRODUCTS OF WASTE PLASTICS ............................................................................................................. 19  
   2.4 CONCLUSIONS ..................................................................................................................................... 20  

3. **THERMOGRAVIMETRIC ANALYSIS OF THERMOPLASTICS** .............................................................. 21  
   3.1 THERMAL ANALYSIS OF PLASTICS .................................................................................................. 21  
      3.1.1 Background ...................................................................................................................................... 21  
      3.1.2 Thermogravimetric analysis (TGA) .............................................................................................. 22
3.1.3 Reaction kinetics of plastics ................................................................. 23
3.1.4 Methods to determine activation energy (E) and pre-exponential factor (A) from TGA experiments ................................................................. 26
3.1.5 Kissinger method ............................................................................... 27

3.2 A REVIEW OF THE THERMOGRAVIMETRIC ANALYSIS (TGA) OF SELECTED PLASTICS ................................................................. 29
3.2.1 Polyethylene (low and high density) ..................................................... 29
3.2.2 Polyvinyl Chloride (PVC) .................................................................. 32
3.2.3 Polyethylene Terephthalate (PET) ....................................................... 35
3.2.4 Size and shape of plastics and its effect during thermal decomposition ...... 36

3.3 TGA EXPERIMENTS ............................................................................. 37
3.3.1 Plastic Samples ................................................................................. 37
3.3.2 TGA Equipment ............................................................................... 37
3.3.3 Experimental Procedure ................................................................. 38

3.4 RESULTS AND DISCUSSION ............................................................... 41
3.4.1 LDPE sample .................................................................................. 41
3.4.2 HDPE sample ................................................................................ 50
3.4.3 PET sample .................................................................................... 54
3.4.4 PVC Sample ................................................................................... 58
3.4.5 Comparison of various plastic samples ............................................. 63

3.5 TGA EXPERIMENTAL RESULTS AND THEIR RELEVANCE TO SOLAR THERMAL DECOMPOSITION OF PLASTICS ........................................... 70

3.6 CONCLUSIONS .................................................................................. 72

4. DEVELOPMENT OF A SOLAR REACTOR FOR HIGH TEMPERATURE THERMOCHEMICAL PROCESS OF PLASTIC DECOMPOSITION ..................... 73

4.1 INTRODUCTION TO SOLAR REACTORS .......................................... 73
4.1.1 Solar systems used for thermochemical processes ............................. 74
ACRONYMS AND ABBREVIATIONS

A – Pre-exponential factor
CFD – Computational fluid dynamics
CPC – Concentrated parabolic concentrator
DSC – Differential scanning calorimetry
DTA – Differential thermal analysis
DTG – Derivative thermogravimetry
E – Activation energy
HDPE – High density polyethylene
HHV - Higher heating value
HTF – Heat transfer fluid
KJ – Kilo Joule
LDPE – Low density polyethylene
LHV – Lower heating value
MJ – Mega Joule
MSW – Municipal solid waste
NSW – New South Wales
PE – Polyethylene
PET – Polyethylene terephthalate
PVC – Polyvinyl chloride
Syn gas – Synthesis gas
TA – Thermal analysis
TG – Thermogravimetry
TGA – Thermogravimetric analysis
tpa – tonnes per annum
VCM – Vinyl chloride monomer
CHAPTER ONE

1. INTRODUCTION

1.1 OVERVIEW

This thesis has been divided into 5 chapters.

Chapter 1 gives a brief introduction to the concept of solar hydrogen and solar thermochemical processes. Also given is the importance of studies regarding reuse of waste such as plastics to generate useful fuel.

Chapter 2 explains the decomposition mechanism of plastics in general. It also presents details on the thermal decomposition behaviour of various thermoplastics at different temperature ranges compiled from the literature. A brief discussion on the potential of generation of hydrogen from the decomposition products of plastics is also given.

Chapter 3 starts with the explanation of thermal analysis methods used in plastic decomposition studies. Then it explains Kissinger method selected for determining kinetic parameters of plastic decomposition. This chapter also provides a literature review on plastic decomposition of selected plastic samples (low density polyethylene, high density polyethylene, polyethylene terephthalate and polyvinyl chloride). The thermogravimetric experiments conducted on the above mentioned samples and the results and discussions are also presented in this chapter.

Chapter 4 presents the background required for a designing a solar receiver-reactor that can be used in plastic decomposition studies at high temperatures. It also provides details of the proposed solar reactor design.

Chapter 5 provides the conclusions based on the literature review and experiments conducted, and gives some recommendations for further research that can be conducted in this area.

1.2 BACKGROUND

Global warming and concerns about diminishing energy supplies have recently focused attention on alternative fuels and renewable energy sources in academic, social and political fields. Hydrogen was suggested as an alternate fuel, cheaper than electricity, as early as 1969 (Bockris 2002). However, hydrogen must be produced from renewable energy sources if it is to be a sustainable option.
There are numerous techniques for producing hydrogen (Momirlan & Veziroglu 2002). Some of the main techniques for production of hydrogen are steam reforming of natural gas, catalytic decomposition of natural gas, partial oxidation of heavy oils, coal gasification and water electrolysis. However most of these techniques are environmentally unsound; this in turn has led research into more sustainable hydrogen generating technologies such as solar hydrogen (Steinfeld 2005).

Production of hydrogen utilizing solar energy can be carried out using three different pathways and their combinations (Fisher & Tamme 1991 and Steinfeld 2005). These are:

i) electrochemical (eV-path)

ii) photochemical (hν-path) and

iii) thermochemical (kT-path).

In recent years there has been increased interest in the production of hydrogen using solar thermochemical processes (Steinfeld 2005). Any thermochemical process utilizing solar energy as its process heat is termed a solar thermochemical process. The solar thermochemical production of hydrogen as part of a synthesis gas involves the conversion of solar energy into chemical energy (Fischer & Tamme 1991). This conversion makes it easier for solar energy to be stored for long periods of time i.e. the same as other conventional fuels, thus overcoming the problems of long term storage and transport of solar energy (Fischer & Tamme 1991). Thermochemical processes such as pyrolysis, gasification and reformation have been studied extensively in relation to fossil fuels (Higman & Burgt 2003). Consequently, considerable experience in the design of such systems already exists. In the context of solar energy however, one outstanding requirement is to determine a suitable way to couple the thermochemical process and the solar heat source (Fletcher 2001).

Another current worldwide concern is the disposal of plastic wastes. Most of the plastics generated around the world end up in landfills (Czernik & French 2006). For instance records show that out of 1.6 million tones of plastics consumed in Australia in 2003, only 12 % were recycled (PACIA & Nolan-ITU 2004). The production of hydrogen from plastic wastes (especially polyolefins) has significant potential. But plastic wastes are not currently used as a resource for hydrogen production (Czernik & French 2006).
Research into; i) solar concentrators for high temperature thermochemical processes, and ii) pyrolysis and gasification of waste plastics have been separately reported. In this study the aim is to bring these fields of research together to develop a solar receiver-reactor suitable for the production of hydrogen via the thermal decomposition of waste plastics. Thermal decomposition of plastics is simpler than biomass (a biopolymer consisting cellulose, hemicellulose and lignin) and can be used as a model fuel in understanding the decomposition behavior. Understanding of plastic decomposition would provide necessary background in the understanding more complex decomposition behaviors of mixed plastics and biomass.

To achieve this aim, important parameters affecting the process of solar thermal decomposition of plastics to useful fuel need to be identified. Hence, firstly a literature survey on the thermal decomposition of plastics at high temperatures was conducted. Secondly, the thermal decomposition behavior of plastics was studied using thermogravimetric analysis (TGA). Finally, on the basis of the experimental results and available knowledge base, a suitable solar reactor system was designed. In this thesis, i) the outcomes of the thermogravimetric study for plastic decomposition and ii) design of solar reactor suitable for decomposition of plastics to generate a synthesis gas containing hydrogen are presented. Hence, a basis for further studies in the area of solar thermal decomposition of plastic wastes to hydrogen is established.
CHAPTER TWO

2. THERMAL DECOMPOSITION OF PLASTICS

In this chapter, the background to the concept of energy recovery from waste materials and the potential of energy recovery from waste plastics through high temperature thermal decomposition process is reviewed. Focus is placed on the study of thermoplastics, a type of plastics. The main reason for choosing thermoplastics is that they constitute the largest portion in the plastic waste stream in most parts of the world including Australia. Polyethylene is used for explanation of the decomposition behaviour of thermoplastics in this chapter due to its simplicity in polymer structure compared to other plastics. The decomposition behavior of selected thermoplastics studied using thermogravimetric experiments is explained in Chapter 3. Also discussed is the waste plastic’s suitability to be used as a feedstock for generation of useful fuel containing hydrogen. This is based on results reported in the literature.

2.1 PYROLYSIS OF PLASTICS

2.1.1 Background

There is an increase in public awareness regarding the minimization of waste and ways of conserving resources. The four basic concepts to minimize wastes and its sustainable management are i) reduction, ii) re-use, iii) recycle and iv) recovery (PACIA 2006 and Perugini et al. 2005). For instance in New South Wales (Australia), the NSW Waste Avoidance and Resource Recovery Act 2001 is one of the steps taken by NSW government to provide a legislative framework for both avoiding waste creation and recovering value from waste (Wright 2002). This example shows that energy recovery is, and will remain, as an important part of sustainable waste management process.

Plastic wastes, i) take thousands of years to degrade, ii) use up landfill sites, and iii) pollute the environment. Hence, there is a necessity to look for ways of utilizing plastic wastes to achieve environmental, economic and social benefits. For example in Australia alone about 1.5 million tonnes of plastic was consumed in 2003, of which only 12 % was recycled (PACIA & Nolan-ITU 2004). Figure 1 gives a graph of the types of plastics consumed and the amount recycled in greater detail.
A lot of plastic waste, for example medical waste, food packages, personal hygiene products and many other packaging products that make a large part of waste plastics cannot be recycled and reused. Hence, energy recovery is the only means available to utilize this type of plastic waste (PACIA 2006). A common method for energy recovery from waste plastics is incineration.

Incineration of waste plastics to produce energy for power and heating is used extensively around the world. However, this method of energy recovery has received much social resistance due to the atmospheric pollution created by combustion process (Garcia et al. 2003 and Lee & Shin in press). Hence, an alternative process known as pyrolysis is identified as a promising alternative for energy recovery from plastic wastes (Bockhorn et al. 1998 and Lee & Shin in press). Incineration of waste plastic poses problems such as formation of dioxins, nitrogen oxides and chlorinated compounds in case of polyvinyl chloride. Pyrolysis is defined as an application of heat to a feedstock in the absence of oxygen (Higman and Burgt 2003). An added advantage of pyrolysis processes is that plastic mixtures, consisting of various types of plastics can be treated without the requirement for separation (Lee & Shin in press). This process is explained in detail in the following sections starting with the decomposition mechanism of plastic waste.
during pyrolysis. An understanding of the decomposition mechanism of plastic is necessary if one is to study the decomposition products of plastics.

2.1.2 A review of the mechanism of plastic thermal decomposition

Plastics are a type of polymer. Polymers can be classified into three different groups: i) elastomers (or rubbers), ii) plastics and iii) fibers. This classification is based upon their physical properties, in particular, elastic modulus and degree of elongation (Beyler & Hirschler 2001). Plastics have elastic moduli between $10^7$ and $10^8$ N/m$^2$ and elongation between 100 to 200 %. Plastics can be further divided into two groups, namely i) thermoplastics (whose deformation at elevated temperatures is reversible) and ii) thermosets (which undergo irreversible changes when heated) (Beyler & Hirschler 2001). Plastics such as polyethylene, polyethylene terephthalate and polyvinyl chloride are thermoplastics.

Physical and chemical changes that occur in a thermoplastic when heated

The physical and chemical changes that occur when a thermoplastic is heated are summarized in Figure 2. These physical and chemical changes are important as they influence the volatile products of thermal decomposition of plastics (Beyler & Hirschler 2001).

![Physical and chemical changes during thermal decomposition of thermoplastics](image)

**Figure 2: Physical and chemical changes occurring during the thermal decomposition of thermoplastics, adapted from Beyler and Hirschler (2001).**

Beyler and Hirschler (2001) report that thermoplastics can melt without chemical reaction to form a viscous state (known as a polymer melt). When further heated, the polymer melt decomposes into smaller liquid or gaseous fragments. These liquid fragments will decompose and vaporize if further heated. As shown in Figure 2 char formation can occur during the process of melting and/or vaporization. The char can undergo further reaction to form gaseous products along with the liquid products of plastic decomposition. This shows the complex nature of plastic decomposition process.
The decomposition mechanism of thermoplastics is considered to be less complex than thermosets (Beyler & Hirschler 2001).

There are four general chemical mechanisms common in polymer decomposition (Beyler & Hirschler 2001). These are shown in Figure 3 and labeled 1, 2, 3 and 4. These mechanisms have been widely reported and are well accepted (Bockhorn et al. 1999b, 1999c, Faravelli et al. 2001, Faravelli et al. 2003, Gao et al. 2003 and Inaba & Kashiwagi 1987).

![General Polymer Decomposition Mechanism](image)

**Figure 3: General polymer decomposition mechanism, adapted from Beyler and Hirschler (2001).**

According to Beyler and Hirschler (2001), the chemical reactions occurring during decomposition of polymers can be divided into those involving atoms in main polymer chain and those involving side chains or groups. The two groups of chemical reactions are shown in Figure 3, as main chain reactions and side chain reactions. These two types of chemical reactions can again be divided into two groups as shown in Figure 3. The
decomposition of some polymers can be explained by one of these general mechanisms. But that of others involve combinations of these four general mechanisms.

For simple thermoplastics such as polyethylene, the most common reaction mechanism is the reaction involving the breaking of the bonds in the main polymer chain, termed chain scission. The eight generic types of reactions shown in Figure 3 are involved in this simple decomposition process. These eight generic reactions are i) random chain scission, ii) end chain scission iii) intramolecular H transfer, iv) intermolecular H transfer, v) unzipping, vi) termination, vii) recombination and viii) disproportionation. Chain scission can occur in the chain end (termed end chain scission, E) or at any random location in the chain (termed random chain scission, R). Random chain scissions generally result in the generation of both monomers and oligomers and a variety of other chemical species (Beyler & Hirschler 2001). Hence, the volatile products of decomposition depend on the relative volatility of the resulting molecules (Beyler & Hirschler 2001). Again, mechanisms like cross-linking and cyclization can give rise to char which is less easily volatilized (Beyler & Hirschler 2001). According to Beyler and Hirschler (2001), the thermal stability of polyolefins, such as polyethylene, is strongly affected by branching. Linear polymers are most stable and polymers with branching less stable. Studies show that the dominant decomposition mechanism for polyethylene is through random scission (Aguado et al. 2002a, Beyler & Hirschler 2001, Kashiwagi 1994 and van Krevelen (cited in Groenewoud 2001)). An explanation of random scission is given in Beyler and Hirschler (2001). A general chemical mechanism for polyethylene thermal decomposition is given by Mastral et al. (2003). This shows the complex nature of plastic thermal decomposition process which would influence the decomposition products.

**Decomposition kinetics of polyethylene plastics in support of simple model**

In the previous section; the general decomposition mechanism of plastics was presented. In the following section more details are given on polyethylene (PE) decomposition. There are two main reasons for choosing polyethylene (PE) for our initial studies. The first reason is that it has the simplest decomposition mechanism amongst plastics (Beyler & Hirschler 2001). The second reason is that it is the most widely used plastic (Beyler & Hirschler 2001); for example, 37.4 % of total plastics consumed in Australia in 2003 were PE (PACIA & Nolan-ITU 2004). PE is commonly
used in industries for applications such as pipes, cable insulation, bottles and containers, and in domestic applications such as carry bags and packaging.

It can be said that the simplest of polymers such as thermoplastics involves a complex chain of reaction mechanisms. To simplify, suppose that only a subset of these reaction types mentioned above are required for decomposition of plastics and the reaction rates are unaffected by other factors such as size of the polymer chain. Even with those assumptions, the kinetics describing the process can be quite complex (Beyler & Hirschler 2001). In engineering applications, such complex reaction mechanisms are not used. A simple overall kinetic expression is generally utilized for describing the decomposition kinetics (Beyler & Hirschler 2001).

The global kinetics of polyethylene (PE) can be described by a single step decomposition process given by Equation 2.1.

\[ \text{PE} \rightarrow \text{Volatile} \quad (2.1) \]

The validity of this mechanism has been tested by Darivakis et al. (1990). This single step approach is adequate to describe the apparent kinetics of decomposition reactions of PE (Cozzani et al. 1995 and Beyler & Hirschler 2001). The most common assumption is that the reactions can be described by an Arrhenius expression of first order in the remaining polymer mass (Beyler & Hirschler 2001). This single step decomposition of polyethylene plastics has been observed by several researchers (Lin et al. 1999, Sorum et al. 2001, Senneca et al. 2002, Heikkinen et al. 2004) in thermogravimetric (TG) experiments. Results from experiments conducted to study the kinetics of polyethylene using thermogravimetry, microreactor and conical spouted bed reactor by Aguado et al. (2002b) demonstrate that first-order kinetic fits the pyrolysis of polyethylene well in all the cases. Hence, the simple global kinetic model (Equation 2.1) is sufficient for use in engineering computations.

More complex models have been developed by some researchers (Inaba & Kashiwagi 1987, Ranzi et al. 1997 and Bockhorn et al. 1999c). However, complex models are not used in engineering applications when a simple model works reasonably well. Darivakis et al. (1990) also state that it can be possible to formulate more sophisticated models that explicitly treat mass transport and secondary reactions on volatiles release in pyrolysis. However, they emphasize that “such models should remain computationally tractable for engineering calculations and thus balance improved descriptive power.
against the increased mathematical complexity needed to achieve that capability”. This argument for the use of simpler models for engineering applications is supported by Burnham and Braun (1999). Hence, this simple model is deemed appropriate for polyethylene pyrolysis studies. This argument is important for the study of plastic decomposition for practical purpose, such as the design of a chemical reactor, where complex models do not present any benefits.

2.2 DECOMPOSITION PRODUCTS OF POLYETHYLENE PYROLYSIS

This section will briefly discuss the decomposition products of polyethylene pyrolysis and the factors affecting it. As our studies are focused on the useful gases generated from plastic decomposition, it is necessary to know and understand the effects of various factors in the decomposition products of plastic.

Polyethylene when heated decomposes to form a large number of small molecules (up to 70) of hydrocarbons and also a very small amount of monomer (Beyler & Hirschler 2001). The volatiles formed during decomposition depend upon several factors such as temperature, heating rates, residence time, size/shape of the sample and other operating conditions (e.g. pressure, reactor type, gas used and flow rates, catalysts) (Darivakis et al. 1990). According to Darivakis et al. (1990), the volatiles evolved from polyethylene consist of condensables and gases. Condensables are tar-like liquids plus higher molecular weight volatilizable matter that solidifies at room temperature. Gases are hydrocarbons that have lower molecular weights and are at gas phase at room temperature. Higher molecular weight volatilizable matter is termed wax by some authors (Williams & Williams 1999). Liquids are termed oils by some authors (Mastral et al. 2003).

Hence, there are three different products that are obtained when polyethylene decomposes.

i) Gas (hydrogen, methane, ethane, ethene, propane, propene, butane, butene)

ii) Liquid (C₅-C₈, benzene, toluene, xylene, styrene)

iii) Wax (paraffins which are alkanes CₙH₂ₙ₊₂ with n > 20)

The following sections briefly discuss the effects of various factors such as temperature, residence time and heating rates on decomposition products of plastics. Other factors
affecting the decomposition of plastics are particle (size, shape and properties), pressure, catalysts, reactor (geometry & material) and flow gas (properties & flowrates).

2.2.1 Temperature

Various studies of decomposition of plastics have been conducted in different temperature ranges, depending upon the desired products. Research shows that decomposition of polyolefin plastics, such as polyethylene, results in a mixture of various hydrocarbons ranging from methane to aromatic hydrocarbons, depending on the temperature at which decomposition occurs (Bockhorn et al. 1985, Kaminsky et al. 1995, Kaminsky et al. 1996, Sodero et al. 1999, Williams & Williams 1999, Beyler & Hirschler 2001, Aguado et al. 2002a, Mastral et al. 2003 and Walendziewski 2005). Polyethylene plastics have the highest gas yield compared to other plastics (Walendziewski 2005). In general, polyethylene starts to decompose (reduction in molecular weight) at 565 K in an inert atmosphere (Beyler & Hirschler 2001). However, extensive weight loss only occurs from 645 K.

Figures 4, 5 and 6 show the product composition from the pyrolysis of polyethylene across various temperature ranges. These graphs are based on data obtained from the literature. In general there is an increase in gas yield (wt %) with an increase in temperature. The liquid composition increases up to 873 K and starts decreasing from this temperature onwards till 1053 K. The amount of wax decreases with an increase in temperature. The increase in liquid around 1053 K is due to secondary reactions which generate aromatics. This increase in liquid around 1053 has been explained by Mastral et al. (2003). The experimental results of Mastral et al. (2003) were from fluidized bed reactors and hence the volatiles from the decomposition of polyethylene have sufficient time to undergo secondary reactions. However, in a solar reactor there is a rapid quench effect once the volatiles move away from the focus preventing the secondary reactions. This will lead to the decrease in aromatics which is seen in fluidized bed reactor. The rapid quench effect of solar receiver-reactors has been explained by Ferrer and Lede (1999). The solar receiver-reactors suitable for plastic decomposition are explained in detail in Chapter 4.

Some discrepancy between liquid and wax fractions when comparing figures 4 and 5 and figures 5 and 6 are due to the differences in polyethylene samples, sample size, experimental set up and product analysis method used.
Figure 4: Product composition of pyrolysis of polyethylene at temperature range 643 - 703 K, adapted from Walendziewski and Steininger (2001).

Figure 5: Product composition of pyrolysis of polyethylene at temperature range 773 - 973 K, adapted from Williams and Williams (1999).
Walendziewski and Steininger (2001) have used waste polyethylene samples (unspecified) of 25-100 g in autoclaves for their experiments and analysed the products using gas chromatography. Williams and Williams (1999) have used virgin pellets of low-density polyethylene samples of 2-3 mm diameter in fluidised bed pyrolysis reactor and analysed the products using gas chromatography, Fourier transform infra-red (FTIR) and liquid chromatography. Mastral et al. (2003) have used virgin pellets of high-density polyethylene samples of 0.222 mm diameter in fluidised bed reactor and analysed the products using gas chromatography and mass spectroscopy.

Figure 7 shows the yield (%) of some products of pyrolysis of polyethylene as a function of temperature (°C). This graph (Figure 7) is obtained from the results of experiments conducted by Kaminsky (1985) using a laboratory scale fluidized bed (0.1 kg/hr feed rate) between 873 – 1173 K (600 – 900°C). This graph also shows the dependence of decomposition products on pyrolysis temperature. There is an increase in hydrogen with the increase in temperature. The increase in hydrogen with temperature was also reported by Mastral et al. (2003) in their fluidized bed experiments in temperature range of 913 – 1123 K. The aromatics such benzene, toluene and cyclopentadiene starts decreasing at around 1073 K (800°C). This is explained in detail in Section 2.2.2.
In Figure 7, 1 = Methane, 2 = hydrogen, 3 = ethylene, 4 = propene, 5 = cyclopentadiene, 6 = benzene, 7 = toluene, 8 = benzene and toluene.

2.2.2 Temperature and Residence time

In this section, the effects of temperature and residence time on the products of polyethylene decomposition will be discussed. Apart from temperature, residence time is also an important factor in determining the product constituents of plastic decomposition (Sodero et al. 1996 and Serrano et al. 2005). The following discussion is based on results obtained from fluidized bed reactors where the sample particle is introduced at the given temperature, unless otherwise stated. The residence time discussed in this section is the length of time the pyrolysis product gases spend inside the reactor.

Temperature range: 673 – 873 K

Literature show that heating polyethylene in the temperature range of 673 – 873 K results in an increase in gaseous products and a decrease in liquid and wax. For example, studies conducted by Walendziewski (2005) on polyethylene cracking show that at temperatures between 693 – 713 K, the product yield (weight percentage), was 84.5% liquid hydrocarbon, 10.2 % gas and 5.1 % solid carbon residue and when the temperature was increased from 713 K to 773 K, the gaseous products increased from 5.1% to 10 %. The liquid hydrocarbons found were mainly mixtures of paraffinic and olefinic C₅-C₂₅ hydrocarbons and the gases were mainly C₁ – C₅ hydrocarbons. Similar observations were made by Kaminsky et al. (1995) and Aguado et al. (2003) in their
experiments. They also found that there was an increase in gaseous products with an increase in temperature from 773 to 873 K. In their experiments, they found that an increase in the temperature of decomposition would decrease the wax yield almost linearly.

*Temperature range: 873 – 1073 K*

Literature show that heating of polyethylene from 873 K to 1053 K results in an increase in gaseous products and a decrease in liquids and waxes. However, beyond 1053 K there is an increase in aromatics (liquids) (Figure 6), which is explained in the following paragraphs.

Serrano et al.’s (2005) pyrolysis experiments on LDPE samples at 973 K show that the products of decomposition consisted of a wide range of smaller molecular weight species (C$_2$ – C$_5$), linear and branched paraffins, olefins and aromatic compounds. However, the formation of aromatic species such as benzene or toluene was reportedly low at 973K. Similar results were obtained by Kaminsky and Kim (1999), Williams and Williams (1999) and Aguado et al. (2002a). Serrano et al. (2005) stated that if the product gases were retained in the reactor longer, they may undergo further reactions. These reactions can be cracking, recombinations, cyclization and aromatisation reactions which increases the amount of aromatics. The increase in aromatics due to longer residence time was observed by other authors (Kaminsky & Kim 1999 and Williams & Williams 1999) as well.

Aznar et al. (2006) explain that the formation of aromatics at high temperatures occur due to lighter hydrocarbons such as ethene and propene reacting to form aromatic compounds as benzene and toluene. They report that that at higher temperatures ethene and propene are unstable. This was reported by Kaminsky (1985) as well. In Serrano et al.’s (2005) view the increase in aromatics in the product can be the effect of residence time. They came to this conclusion by comparing their results to that obtained from a larger sized reactor. The larger sized reactor according to them had longer residence time and in this reactor, higher levels of aromatics were observed. The effect of residence time on the product composition was also reported by Westerhout et al. (cited in, Aznar et al. 2006). The increase in aromatics formation with the increase in residence time might be due to secondary reactions as explained by Darivakis et al.
(1990) that can occur if the volatiles generated from plastic decomposition remains near the substrate.

_Temperature range: > 1073 K_

When polyethylene plastics are heated beyond 1073 K there is a decrease in gaseous products and an increase in aromatics (liquids) (Figure 6). Kaminsky (1985) and Mastral et al. (2003) report the increase in hydrogen with the increase in temperature during their experiments conducted at temperature range of 873 K – 1173 K. However, Kaminsky (1985) reports a decrease in methane (CH₄) with the increase in temperature from 1053 K to 1098 K (Figure 7). Mastral et al. (2003), however report an increase in methane with the increase in temperature in temperature range of 973 to 1123 K (Figure 8).

![Variation of Hydrogen and Methane with pyrolysis and gasification technique](image)

**Figure 8: Variation of H₂ and CH₄ production with pyrolysis and gasification temperature, adapted from Mastral et al. (2003).**

In Kaminsky’s (1985) experiments, there is a subsequent decrease in ethene and increase in propene at temperature range 1053 – 1098 K, indicating that the decrease in methane might be due to secondary reactions occurring between methane and ethene to produce propene with the release of hydrogen. The reason for this secondary reaction could be the longer residence times for Kaminsky’s experiments. But, Kaminsky has not mentioned the residence times for his samples in the fluidized bed reactor.
experiments. The residence time reported by Mastral et al. (2003) is between 0.81 and 1.45 s. This short residence time may be the reason for preventing methane from undergoing secondary reactions unlike in Kaminsky’s (1985) experiments. Aguado et al. (2002a) also report that if the products of pyrolysis is subsequently cracked at higher temperatures larger amount of hydrocarbon’s olefinic monomers can be produced. They also used short residence times (few seconds) in their conical spouted bed reactor experiments in pyrolysis of polyethylene. These examples show that shorter residence time favours production of methane which can be subjected to water gas shift reaction to produce hydrogen. Figure 8 shows the results of Mastral et al.’s (2003) experiment, a comparison between pyrolysis and gasification of polyethylene. When gasified in the presence of oxygen there is an increase in hydrogen and a decrease in CH₄.

All experiments on plastic decomposition have been conducted at temperatures lower then 1173 K. For the decomposition of plastics at temperatures higher than 1173K, no data is available for the product gas composition. Experiments conducted at lower temperatures shows that pyrolysis of polyethylene produces marked amount of hydrogen and methane and it increases as the temperature rises (Kaminsky 1985, Williams & Williams 1999 and Mastral et al. 2003). According to Bockhorn et al. (1985) and Westerhout et al. (cited in, Aznar et al. 2006), at temperatures about 1773 K the product mixture from decomposition of plastics would contain mainly methane and unsaturated smaller hydrocarbons. Walendziewski (2002) and Walendziewski (2005) have concluded that shorter reaction times favor larger yields of liquid and semi liquid products and longer reaction times favors larger gas yields at lower temperatures (693 – 753K). However, at temperatures greater than 873 K the effects of residence time are not well understood. But, there is an indication that shorter residence time favours higher gaseous products at temperatures greater than 873 K. Hence, further studies are recommended to understand the product gas distribution of decomposition products of polyethylene plastics at temperatures higher than 1173 K plus the influence of the residence time.

2.2.3 Heating rates

The influence of heating rate and its effect on pyrolysis/gasification has been discussed by Darivakis et al. (1990) and Higman and Burgt (2003). According to Hatakeyama and Quinn (1999), lower heating rates favors multiple reactions and at higher heating rates there is a decrease in multiple reactions. This also explains the presence of less variation
in decomposition products of polymers at higher temperatures. Darivakis et al. (1990) have studied polyethylene decomposition behaviour at 100, 1000 and 10000 K/s nominal heating rates, using an “electrical screen heater”. The heating rates were controlled by using timer-actuated relays to deliver fixed-duration AC current pulses to the electric heater screen. They have showed that with the increase in heating rate the amount of gases in the product of decomposition increases (i.e. the liquid and wax fraction decreases). However, they recommend further studies for understanding the devolatilization chemistry for heating rates higher than 1000 K/s. Likewise, in the studies of flash pyrolysis of biomass in a fluidised bed reactor, Luo et al. (2005) have found that temperature and particle size are the most important factors influencing the heating rate. In fluidised bed, heating rates of order $10^4$ K/s have been reported (Luo et al. 2005). However, they have not mentioned how those heating rates were obtained in their fluidized bed. They observed increase in heating rates with the increase in temperature when the particle size is kept constant. Hence, both the temperature and heating rates are important factors in determining the decomposition products of plastics.

2.2.4 Other factors

**Particle size**

The effect of particle size on polyethylene decomposition have been discussed by Darivakis et al. (1990). In their experiments they took two different sizes of polyethylene samples. They observed that weight loss for smaller sized particles (63-90 µm) starts from 773 K and is nearly 100% complete by 973 K; whereas for larger sized particles (271 µm thick) no volatiles release were detected below 1073 K. According to them at 1346 K the yield of volatiles was only 57% from larger particle sample. Darivakis et al. (1990) considered the volatiles yield as the total weight loss from the sample and measured the weight change in the sample. The effects of shape and size of particles in thermal analysis have been explained by Hatakeyama and Quinn (1999). The effects of particle size on heating rates have been given in Luo et al. (2005). Hence, particle size also has considerable effect on the decomposition of plastics, with smaller sized particles decomposing faster with higher volatiles evolution.
**Pressure**

Increasing the pressure inside the reactor chamber decreases the gaseous products from plastic decomposition. In studies made by Murata et al. (2004), they found that pressure effects directly on C-C links during thermal degradation of polymers. They also observed decrease in gaseous products and increase in liquid products due to increase in pressure. They suggest that pressure can be a means of controlling the decomposition products. However, more studies on pressure effects are recommended to use pressure as a means to control the decomposition products of plastics.

2.3 POTENTIAL FOR THE PRODUCTION OF HYDROGEN FROM THE DECOMPOSITION PRODUCTS OF WASTE PLASTICS

Decomposition of plastics for the production of liquid fuels through pyrolysis and gasification has been extensively studied (Czernik & French 2006). According to Czernik and French (2006), plastics especially polyolefins, have significant potential for the use as resource for hydrogen production. However, very little research has been conducted on the generation of hydrogen from waste plastics (Czernik & French 2006).

Czernik and French’s (2006) work on generation of hydrogen from plastic wastes suggests that polyethylene can be converted to a gas yielding hydrogen with up to 80% of the stoichiometric potential. Their conclusion was based on experiments conducted in a micro reactor at temperatures between 923 – 1073 K. Work by Aznar et al. (2006) using fluidized bed on decomposition of plastics also provides favorable results for hydrogen production at high-temperatures. The influence of temperature on the amount of hydrogen in product gases evolved from decomposition of plastics pyrolysis has been discussed in the previous section. Several experiments on waste plastics pyrolysis using fluidized bed at temperatures greater than 973 K report that the amount of hydrogen generated increases with temperature (Kaminsky 1985, Williams & Williams 1999 and Mastral et al. 2003). They also report the increase in other lighter hydrocarbon gas fractions (C₂ – C₆) in product gases evolved from pyrolysis of plastics (explained in earlier sections). Hence, the product gases produced from pyrolysis of plastics at high temperatures are similar to naphtha from which most commercial hydrogen is produced. The production of hydrogen from steam reforming of light hydrocarbons (naphtha) is the most widely used process (Balthasar & Hambleton 1980 and Melo & Morlanes 2005).
2.4 CONCLUSIONS

Thermal decomposition studies of thermoplastics such as polyethylene have been conducted at temperatures up to 1173 K. Literature reports show an increase in hydrogen and lighter hydrocarbon gases in the product gas composition of polyethylene plastic pyrolysis at temperatures greater than 1073 K. This product gas with light hydrocarbon gases and hydrogen can be steam gasified to produce hydrogen. However, few studies are focused on generation of hydrogen from the decomposition products of plastics.
CHAPTER THREE

3. THERMOGRAVIMETRIC ANALYSIS OF THERMOPLASTICS

This chapter presents the thermogravimetric analysis (TGA) conducted on selected plastic samples and its results. It begins with an explanation of thermogravimetric analysis and explains how TGA methods used for the analysis of plastics provide a simple technique for understanding the decomposition behaviour during heating. The chapter also elaborates on how the understanding of the decomposition behaviour of plastics can provide valuable information required in designing a chemical reactor, which can be used for accomplishing the desired decomposition using a solar thermal reactor.

The second part of the chapter is a literature review on the thermal decomposition of i) low-density polyethylene (LDPE), ii) high-density polyethylene (HDPE), iii) polyethylene terephthalate (PET) and iv) poly vinyl chloride (PVC).

The third part of the chapter describes the equipment used for TGA and selected samples.

The fourth part of the chapter presents the results and discussion based on the TGA experiments conducted on the above-mentioned plastic samples. Also discussed is the relevance of the experimental results to the decomposition of plastics in a high temperature reactor.

3.1 THERMAL ANALYSIS OF PLASTICS

3.1.1 Background

Thermal analysis is conducted by the application of heat in order to investigate behaviour of a sample as a function of temperature (Hatakeyama & Quinn 1999). The first recorded thermal analysis of plastics was conducted in 1962 (Manley 1989). This was about 10 years after plastic began being widely used in domestic and industrial sectors (APC 2006). Since 1962, the methods utilized for thermal analysis have improved; thermogravimetry (TG) in particular, is used for the qualitative analysis of plastics. Indeed, TG analysis methods are widely accepted as the basis for standards such as British, European and American Standards (Manley 1989). One of the reasons
for TG’s widespread use is its simplicity for the estimation of the reaction rate kinetics based on data acquired from TG curves (Hatakeyama & Quinn 1999). Thermogravimetry is explained in the following section.

3.1.2 Thermogravimetric analysis (TGA)

Thermogravimetry (TG) is defined as a thermal analysis method which investigates the mass change of a sample as a function of temperature or time (Hatakeyama & Quinn 1999). It provides a rapid way of determining the temperature-decomposition profile of a sample and the kinetics of its thermal decomposition (Varhegyi et al. 1997).

In thermogravimetry, the fraction of starting material consumed (\( \alpha \)) is represented by the following Equation 3.1, and is called conversion.

\[
\alpha = \frac{m_s - m}{m_s - m_f} \quad (3.1)
\]

where,

- \( m_s \) = initial mass of the sample
- \( m \) = actual mass of the sample
- \( m_f \) = final mass of the sample

This conversion \( (\alpha) \) is plotted against temperature or time to monitor the decomposition behaviour of the sample. The plot obtained is known as the thermogravimetric curve (or simply, TG curve).

Thermogravimetric analysis (TGA) can be conducted in two ways.

1. Non-isothermally: non-isothermal thermogravimetry is the measurement of changes in weight as a function of changes in temperature. This is also sometimes referred to as the “scanning” or “dynamic” mode (Hatakeyama & Quinn 1999).

2. Isothermally: Isothermal thermogravimetry is the measurement of changes in weight of sample as a function of time at constant temperature.

Thermal analysis of polymers such as plastics are carried out using non-isothermal methods. It is preferred over the isothermal analysis method in plastics sample studies the for following reasons (Hatakeyama & Quinn 1999):

i. dynamic experiments are quicker and the results are easier to interpret;
ii. the reaction process can be followed over a wide temperature range;

iii. several reaction steps can be observed in a single experiment and

iv. a number of methods of data evaluation are available.

The pyrolysis characteristics of plastic samples are generally studied using non-isothermal conditions at specified heating rates. Pyrolysis is a process of decomposition of plastics using heat in an oxygen deficient atmosphere (explained in Chapter 2). The main reason for preference of non-isothermal conditions over isothermal conditions is because of morphology and structure of plastic samples that can change during the preliminary heating stage of an isothermal experiment (Hatakeyama & Quinn 1999). These initial changes in structure are uncontrolled for most part and their occurrence greatly complicates the analysis of the isothermal curve (Hatakeyama & Quinn 1999). The definition of E and A are given in the glossary.

3.1.3 Reaction kinetics of plastics

The kinetics of plastics decomposition is considered to be heterogeneous (Hatakeyama & Quinn 1999). Heterogeneity here means the existence of more than one state during reaction, for example, the existence of reactants and/or products in solid and gas states. Heterogeneity arises in almost all solid-state reacting systems (Hatakeyama & Quinn 1999). Heterogeneity is said to increase in the case of polymer blends (mixing of two different types of polymers to form plastic) due to the addition of extra components to the system.

The various factors that cause heterogeneity in plastics are i) distribution of molecular weight, ii) tacticity, iii) cross-linking density, iv) degree of orientation, v) functional group concentration, vi) presence of plasticizers, vii) unreacted monomers, viii) residual catalysts and ix) residual stabilizers (Hatakeyama & Quinn 1999).

The rate of reaction of a heterogeneous system has the following general form (Hatakeyama & Quinn 1999):

\[
\frac{d\alpha(t)}{dt} = k(T)f[\alpha(t)]h(\alpha,T)
\]  

(3.2)

In Equation 3.2,

\[
\frac{d\alpha(t)}{dt} = \text{rate of consumption of the reactant}
\]
where,

\( \alpha \) = conversion (defined in Equation 3.1)

\( k \) = reaction rate constant, assumed to be a function of \( T \) (temperature) only

\( f[\alpha(t)] \) = function of \( \alpha \)

\( h[\alpha,T] \) = function of \( \alpha \) and \( T \)

The rate of reaction for homogenous system is given in Appendix A1 for comparison.

For many reactions the rate expression can be written as a product of temperature-dependent and composition-dependent terms (Levenspiel 1999). The above rate conversion equation (Equation 3.2) has also been defined using a temperature-dependent and composition-dependent term. \( h[\alpha,T] \) is normally taken to be equal to unity (Hatakeyama & Quinn 1999). The temperature dependent term (the reaction rate constant) has been found to be relatively well represented by the Arrhenius’ law (Levenspiel 1999). Despite Equation 3.2 being a heterogeneous system ‘\( k \)’ is usually defined using Arrhenius’ Law. Arrhenius’ Law is given as,

\[
k = Ae^{\frac{-E}{RT}}
\]

Arrhenius Law (Equation 3.3) has its own inherent assumptions (Hatakeyama & Quinn 1999).

\( f[\alpha(t)] \) has various forms depending upon the reaction system. The most commonly presumed form for a “solid-state” reaction is (Coats & Redfern 1964, Salin & Seferis 1993, Hatakeyama & Quinn 1999):

\[
f[\alpha(t)] = (1 - \alpha)^n
\]

\( n \) = order of reaction (also termed “reaction order”)

The solid-state reaction is given as:

\[
aA (s) \rightarrow bB (s) + cC (g) \quad \text{(Coats & Redfern 1964)}
\]

The reaction order is assumed to be constant for the duration of the reaction.
With \( h(\alpha, T) = 1 \), the rate of reaction of heterogeneous reacting system (Equation 3.2) takes the form as given below:

\[
\frac{d\alpha(t)}{dt} = k(T)f[\alpha(t)]
\]

Now, with \( k \) (rate constant) as given by Arrhenius’s Law and \( f[(\alpha(t)] = (1 - \alpha)^n \) the above equation takes the form:

\[
\frac{d\alpha(t)}{dt} = A e^{\frac{-E}{RT}}(1 - \alpha)^n \quad (3.5)
\]

When considering non-isothermal thermal analysis, under dynamic conditions the sample temperature is presumed to be a function of time only and equal to the furnace temperature (Bockhorn et al. 1998 and Hatakeyama & Quinn 1999). Hence, the above Equation 3.5 can be written as:

\[
\frac{d\alpha(t)}{(1 - \alpha)^n} = A e^{\frac{-E}{RT}} dt \quad (3.6)
\]

The rate of change of the furnace temperature with time (also known as the “heating rate”) for non-isothermal TGA is given by \( \beta \) (deg/min).

\[
\beta = \frac{dT}{dt} \quad (3.7)
\]

Hence,

\[
dt = \frac{dT}{\beta}
\]

Substituting this value of \( dt \) in Equation 3.6 would give the following equation for heterogeneous reacting system with a heating rate.

\[
\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} e^{\frac{-E}{RT}} dT \quad (3.8)
\]

The right hand side of Equation 3.8 cannot be integrated (Hatakeyama & Quinn 1999) and hence most methods for estimating non-isothermal kinetic parameters deal with this problem using graphical methods (Hatakeyama & Quinn 1999). For example,

1. a single curve or
2. a series of curves recorded at different heating rates.
All methods used for determining $A$, $E$ and $n$ using a non-isothermal TGA are based on the hypothesis (Hatakeyama & Quinn 1999) that “$A$, $E$ and $n$ uniquely characterize a given reaction irrespective of the experimental conditions”. These methods of determining $A$, $E$ and $n$ are discussed in Section 3.1.4.

In non-isothermal TGA runs, when the heating rates are constant, temperature dependence on time is linear and it is always a known function of time.

$$T(t) = \beta t + Tº$$  \hspace{1cm} (3.9)

$Tº$ in the above equation (Equation 3.9) is the initial temperature.

3.1.4 Methods to determine activation energy $(E)$ and pre-exponential factor $(A)$ from TGA experiments

The schemes that have been developed by various researchers for solving Equation 3.8 for $E$ and $A$ values are classified into the following types:

1. Differential methods
2. Integral methods

1. Differential methods

There are a number of differential methods that are commonly used such as Borchardt and Daniels method (Hatakeyama & Quinn 1999), Coats and Redfern method (Coats & Redfern 1964), Freeman and Carrolls method (Hatakeyama & Quinn 1999), Frieman method (Friedman 1965), Kissinger method (Kissinger 1957), Petrovic et al. method (Lin et al. 1999). Of a number of differential methods available, Kissinger method is commonly used in thermal analysis because the reaction rate is not affected by the size or shape of the sample holder and the dilution of the sample (Hatakeyama & Quinn 1999). Also this method has been generalized to include a broad range of solid-state reaction mechanisms and the temperature dependence of $A$ (Hatakeyama & Quinn 1999). A detailed explanation of this method and its advantages are given in Section 3.1.5. Some of the shortfalls of other more commonly used methods are discussed below.

Borchardt and Danials use the area of the differential thermal analysis curve to calculate the kinetic parameters. Additional assumptions are pertinent to liquid systems but extremely difficult to satisfy in solids (Hatakeyama & Quinn 1999). However, despite
this shortfall, their method has been used by many for the analysis of solid-state reactions.

The Freeman and Carroll method uses the following plot to determine $A$, $E$ and $n$.

$$\frac{d\left[\ln(d\alpha/dt)\right]}{d\left[\ln(1-\alpha)\right]} \text{ vs. } \frac{d\left[(1/T)\right]}{d\left[\ln(1-\alpha)\right]}$$

Therefore, the plot results in a straight line of slope $(-E/R)$ and intercept $n$. “$n$” and “$E$” are calculated from a single experimental curve. The problem in this method is that because the slope of the best-fit line to the data points has a very large absolute value, a small error in the estimation of the slope results in considerable uncertainty in the value of “$n$” (Hatakeyama & Quinn 1999). This often makes it impossible to distinguish with confidence between the various proposed reaction mechanisms using this procedure. Despite modifications suggested and used this method shows strong dependence on sample mass and heating rate. Hence, no physical meaning can be attributed to rate parameters obtained using this method (Hatakeyama & Quinn 1999).

2. Integral Methods

Integral methods are based on the assumption that a single non-isothermal thermogravimetric analysis (TGA) curve (weight loss vs temperature) is equivalent to a large number of comparable isothermal curves (Hatakeyama & Quinn 1999). This assumption that a single dynamic curve is equivalent to a large number of comparable isothermal curves is incorrect (Hatakeyama & Quinn 1999). Furthermore, determination of kinetic parameters from a single integral TGA curve involves cumbersome curve-fitting techniques which might give rise to misleading results (Flynn & Wall 1966). Therefore, differential methods for determining the kinetic parameters from the thermogravimetric data are much preferred over integral methods (Flynn & Wall 1966). Hence, integral method is seldom used in analysis of plastic samples to study thermal decomposition behaviour.

3.1.5 Kissinger method

Kissinger method (Kissinger 1957) is the most widely used amongst the differential methods available (Hatakeyama & Quinn 1999). It assumes that the maximum reaction rate corresponds to the point at which the differential weight loss curve is also a maximum. The method applies with good approximation to both first and $n^{th}$ order
reactions (Senneca et al. 2002). The final form of the Kissinger equation is given below (Equation 3.10). Details of its derivation are given in Appendix A2.

$$\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{R}{E} \frac{A n (1 - \alpha)}{m} \right) - \left( \frac{E R}{T_m} \right)$$  \hspace{1cm} (3.10)

In Equation 3.10, $\beta = \text{heating rate (K/min)}$, $A = \text{pre-exponential factor (s}^{-1})$, $E = \text{activation energy of the reaction (kJ/mol)}$, $R = \text{Universal Gas Constant (8.314 J/mol-K)}$, $T_m = \text{temperature at which the differential weight loss curve is at a maximum (K)}$, $n = \text{order of reaction}$, $\alpha = \text{conversion (reacted fraction, Equation 3.1)}$.

$T_m$ is measured from the differential weight loss curve obtained from the TG experiment. The differential weight loss curve is also sometimes termed DTG (derivative thermogravimetry) (Cho et al. 1998, Senneca et al. 2002).

For a single first order reaction, $n = 1$, and Equation 3.10 reduces to:

$$\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{R A}{E} \right) + \frac{E}{R T_m}$$  \hspace{1cm} (3.11)

Thus, the activation energy, $E$, can be determined from the slope of a plot of $\ln(\beta/T_m^2)$ vs. $(1/T_m)$ and the pre-exponential factor, $A$, from the intercept of the same plot. For a constant heating rate the temperature is a linear function of time.

The pyrolysis of thermoplastics such as polyethylene, polyethylene terephthalate, polystyrene, polypropylene usually occur with a single sharp peak of volatile release. This is observed as a single peak in the differential weight loss curve in thermogravimetry (TG). TG analysis studies made by various researchers (Sorum et al. 2001, Augado et al. 2002, Senneca et al. 2002 and Heikkinen et al. 2004) report this single step decomposition of plastics. Based on this, the use of single first order reaction model is considered adequate to represent the decomposition of thermoplastics, which decompose in a single volatile release.
3.2 A REVIEW OF THE THERMOGRAVIMETRIC ANALYSIS (TGA) OF SELECTED PLASTICS

In this section a literature review of TGA of selected plastics conducted in an inert gas atmosphere using non-isothermal method is presented.

3.2.1 Polyethylene (low and high density)

The polymeric structure of both low density polyethylene (LDPE) and high density polyethylene (HDPE) is a long chain of aliphatic hydrocarbons. Aliphatic hydrocarbons are hydrocarbons which do not contain benzene rings. The difference in density between LDPE and HDPE is due to its difference in chain branching. LDPE has a large degree of molecular chain branching whereas HDPE has very few or none. The difference in HDPE and LDPE molecules can be seen in Figure 9. A polyethylene monomer structure is given in Figure 10.

![Figure 9: Differences in molecules of (a) LDPE and (b) HDPE, adapted from Bibee (1990).](image)

![Figure 10: Polyethylene monomer.](image)

The density ranges for LDPE are 910 to 925 kg/m³ and that for HDPE are 940 to 965 kg/m³ (Meier 1996). All types of polyethylene are relatively soft but the hardness increases with density. The higher the density, the better the dimensional stability and
physical properties, particularly as a function of temperature. The melting of polyethylene ranges from 87.8 ºC (360.8 K) to 121.2 ºC (394.2 K) (Meier 1996). Melting in low density polyethylene begins at around 87.8 ºC, whereas in HDPE it begins only at temperatures around 121.2 ºC. This also shows that HDPE is thermally more stable than LDPE.

Polyethylene (PE) plastics have widespread use for various commercial applications such as heavy-duty sacks, refuse sacks, carrier bags, toys, electrical cable insulation and general packaging because of its lower cost in manufacturing and ease of processing (Brydson 1995, cited in Sorum et al. 2001).

*Thermal decomposition temperatures and heating rates*

The thermal decomposition temperature range in which polyethylene decomposes during thermogravimetric analysis depends on the heating rate selected. Table 1 below, compiled from available literature, shows temperature ranges at which polyethylene decomposition occurs at various heating rates. It shows that at higher heating rates the temperature range at which decomposition occurs increases.

**Table 1: Heating rate and decomposition temperature range for polyethylene decomposition in TGA.**

<table>
<thead>
<tr>
<th>Heating rate (ºC/min)</th>
<th>Polyethylene</th>
<th>Temperature range (ºC)</th>
<th>Temperature at peak (ºC)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>PE</td>
<td>370 – 520</td>
<td>470</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>10</td>
<td>HDPE</td>
<td>350 – 500</td>
<td>480</td>
<td>Sorum et al. (2001)</td>
</tr>
<tr>
<td>10</td>
<td>LDPE</td>
<td>350 – 500</td>
<td>475</td>
<td>Sorum et al. (2001)</td>
</tr>
<tr>
<td>20</td>
<td>PE</td>
<td>400 – 520</td>
<td>480</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>20</td>
<td>HDPE</td>
<td>410 – 515</td>
<td>493</td>
<td>Heikkinen et al. (2004)</td>
</tr>
<tr>
<td>20</td>
<td>LDPE</td>
<td>410 – 515</td>
<td>491</td>
<td>Heikkinen et al. (2004)</td>
</tr>
<tr>
<td>100</td>
<td>PE</td>
<td>400 – 560</td>
<td>520</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>900</td>
<td>PE</td>
<td>500 – 660</td>
<td>600</td>
<td>Senneca et al. (2002)</td>
</tr>
</tbody>
</table>

HDPE – high density polyethylene, LDPE – low density polyethylene, PE – polyethylene (HDPE or LDPE not specified)
Studies show that decomposition of polyethylene (high and low density) occurs in a narrow temperature interval of 100 to 160 °C. For instance, at the heating rate of 10 °C/min, both LDPE and HDPE samples studied by Sorum et al. (2001) decomposed in the temperature range of 350 – 500 °C. This gives a temperature interval of about 150 °C. In the studies done by Senneca et al. (2002) at a higher heating rate of 100 °C/min, decomposition occurred in the temperature range of 400 – 560 °C. This gives the temperature interval of decomposition of 160ºC. The same temperature interval was obtained for 900 °C/min heating rate (Senneca et al. 2002). Hence, it can be said that the temperature interval in which the decomposition occurs is independent of the heating rate.

In all the literature studied, the decomposition of polyethylene was seen to occur with a rapid weight loss (Sorum et al. 2001, Senneca et al. 2002 and Heikkinen et al. 2004). The weight loss is due to the release of hydrocarbons. Literature also show that pyrolysis of polyethylene plastic occurs in a single step (Sorum et al. 2001, Senneca et al. 2002 and Heikkinen et al. 2004). This rapid release of hydrocarbons is termed devolatilization.

The temperature at which the maximum devolatilization occurs is denoted as $T_{\text{max}}$. $T_{\text{max}}$ increases with the heating rate (Table 1). The $T_{\text{max}}$ values of high density polyethylene are higher than low density polyethylene showing that HDPE has higher thermal stability.

Senneca et al. (2002) observed that higher heating rates (> 100°C/min) affect the rate of plastic decomposition. The rate of plastic decomposition in an inert atmosphere is termed pyrolysis rate. The reason behind this influence of heating rate on the pyrolysis rate according to Senneca et al. is that at higher temperatures the role of conductive heat transfer inside the particles becomes important. This process of conduction of heat from the outer to the inner layers of the sample becomes important at higher heating rates. The limit to this conductive heat transfer is termed “conductive heat transfer limitation”, which starts to occur at higher heating rates. Hence, when large temperature gradients occur inside the particles (as in case of high heating rates), it becomes relevant and needs to be taken into account to predict the pyrolysis rate.
Volatility of PE

Complete decomposition of plastics occurs at temperature between 500 – 600 °C (Lin et al. 1999, Sorum et al. 2001 and Senneca et al. 2002) depending on the heating rate. LDPE and HDPE are 100 % volatile (Sorum et al. 2001, Senneca et al. 2002 and Heikkinen et al. 2004).

However, in some cases, a very small amount of ash content may be present at the end of thermal decomposition process due to the presence of additives (Senneca et al. 2002 and Heikkinen et al. 2004). The proximate & ultimate analysis and the heating values of polyethylene are given in Appendix A3.

3.2.2 Polyvinyl Chloride (PVC)

Polyvinyl chloride polymer is a homopolymer of repeating units of vinyl chloride monomer (VCM) (Gobstein 1990). Homopolymer is a polymer formed from only one type of monomers. The vinyl chloride monomer is shown in Figure 11. The properties of PVC can be changed considerably with the addition of additives (usually between 8 – 12 %) such as plasticizers, stabilizers, fillers, lubricants, biocides, flame retardants, colorants, blowing agents, UV absorbers, antiblocking and slip agents, and alloying polymers (Gobstein 1990). PVC has high chloride content which is greater than 50% (Heikkinen et al. 2004).

```
[ H   H ]
[     ]
[ C——C ]
[     ]
[ H——Cl ]
```

Figure 11: Vinyl chloride monomer (VCM).

Normally at room temperature PVC polymer is brittle, heat sensitive and difficult to process (Gobstein 1990). Commercial grades of PVC resins have a glass transition temperature (T_g) of about 81°C and above this value, the polymer is soft and flexible (Gobstein 1990). T_g is also sometimes known as second order of transition. The first order of transition, the melting point of PVC is 175°C (Gobstein 1990). PVC plastic has outstanding optical properties and can be made clear to opaque (Gobstein 1990).
PVC has a wide range of applications, ranging from packaging such as bottles and food wraps, to clothing, electrical, agricultural, toys, automobile, building and construction, etc. (Gobstein 1990).

**Thermal decomposition behaviour and heating rates**

Unlike polyethylene decomposition, polyvinyl chloride decomposition is a two step process (Heikkinen et al. 2004). The decomposition of PVC generates HCl and leads to contamination of other pyrolysis products if PVC is mixed with other plastics (Karayildirim et al. 2006). The chlorinated hydrocarbons formed can contaminate the valuable pyrolysis products that can be used as fuel (Miranda et al. 2001). Another problem related with HCl generation is its corrosive nature which can corrode the pyrolysis equipment (Miranda et al. 2001 and Karayildirim et al. 2006). The process of removal of HCl from PVC has been termed dehydrochlorination (Karayildirim et al. 2006). Hence, the use of dehydrochlorinated PVC is suggested when large amount of chlorine is contained in waste PVC (Heikkinen et al. 2004 and Kamo et al. 2006). The dehydrochlorination process to remove the HCl from PVC during pyrolysis is called stepwise pyrolysis and has been researched widely (Bockhorn et al. 1999a, Miranda et al. 2001 and Karayildirim et al. 2006).

Chlorine forms a weaker bond in the polymer chain and hence can be removed from the polymer backbone at lower temperatures of around 300°C (Miranda et al. 2001). This dehydrochlorination process is predominant up to around 350°C and a small amount of benzene and ethylene evolution has also been reported (Miranda et al. 2001). Above, 350°C, polymer backbone scission occurs, leading to the formation and evolution of various compounds (Miranda et al. 2001) depending on the heating rates.

The first step takes place at temperatures of about 300 - 350 °C corresponds to the release of hydrogen chloride (Bockhorn et al. 1998 and Miranda et al. 2001). The second step occurs at around 468 °C and is due to the decomposition of remaining hydrocarbon (Heikkinen et al. 2004). This temperature range is similar to other plastic thermal decomposition temperature range.

This two-step decomposition of PVC has been reported in other literature as well (Bockhorn et al. 1999a, Lin et al. 1999 and Karayildirim et al. 2006). However, alternative models with three and four steps of PVC pyrolysis have been suggested by some researchers (Miranda et al. 2001). The second step out of three steps as suggested
by Miranda et al. (2001) is due to the remaining chlorine content in the hydrocarbone backbone at lower heating rates. However, at temperatures higher than 375ºC, almost all chlorine is removed from the PVC polymer backbone. Table 2 below shows the temperature range obtained at different heating rates for PVC decomposition, compiled from the literature. The peak temperatures ($T_{\text{max}}$) where the maximum decomposition occurs are also listed in Table 2. As PVC decomposition is a two-step process, two temperature peaks occur during PVC decomposition which are represented as $T_{\text{max}_1}$ and $T_{\text{max}_2}$ in Table 2. The effects of the heating rate on the decomposition temperature range and the peak temperature are similar to those for polyethylene plastics.

Table 2: Heating rate and decomposition temperature range for polyvinyl chloride plastics decomposition in TGA experiments.

<table>
<thead>
<tr>
<th>PVC Plastics</th>
<th>Heating rate (ºC/min)</th>
<th>Temperature range 1 (ºC)</th>
<th>$T_{\text{max}_1}$ (ºC)</th>
<th>Temperature range 2 (ºC)</th>
<th>$T_{\text{max}_2}$ (ºC)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>200 - 330</td>
<td>280</td>
<td>350 - 500</td>
<td>430</td>
<td>Bockhorn et al. (1999b)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>184.2 – 296.8</td>
<td>255</td>
<td>356.1 – x*</td>
<td>431.9</td>
<td>Karayildirim et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>192.4 – 311.1</td>
<td>268.1</td>
<td>370.5 – x*</td>
<td>442.1</td>
<td>Karayildirim et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>212.9 – 338.3</td>
<td>283.8</td>
<td>383.1 – x*</td>
<td>456.9</td>
<td>Karayildirim et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>250 – 350</td>
<td>287</td>
<td>350 - 510</td>
<td>439</td>
<td>Miranda et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>214.3 – 339.8</td>
<td>290.6</td>
<td>390.9 – x*</td>
<td>466.6</td>
<td>Karayildirim et al. (2006)</td>
</tr>
</tbody>
</table>

$T_{\text{max}_1}$ - Temperature at the 1st peak (Step 1) where rate of weight loss is maximum, $T_{\text{max}_2}$ - Temperature at the 2nd peak (Step 2) where rate of weight loss is maximum; x* - not given in literature

Volatility of PVC

PVC is not 100 % volatile and leaves solid residue at the end of decomposition. Solid residue of about 5 to 11 % has been reported in the literature (Zevenhoven et al. 1997 and Miranda et al. 2001). The solid residues are mainly carbonaceous. About 99.6% dehydrochlorination occurs during the first step of PVC decomposition and less than 0.4
% chlorine was detected in the char remains (Bockhorn et al. 1998). They suggest that some chlorine escape during the second step of decomposition as well. Appendix A3 provides a proximate and ultimate analysis of PVC samples.

3.2.3 Polyethylene Terephthalate (PET)

Polyethylene terephthalate is a homopolymer. Figure 12 shows a PET monomer. The polymerisation process of PET involves the elimination of water. Hence, PET is called a condensation polymer (McFarlane 1990). The glass transition temperature and melting point of PET are 80ºC and 254ºC respectively. PET has good clarity and toughness and is a good barrier to gases such as oxygen and carbon dioxide (McFarlane 1990).

![Figure 12: Polyethylene terephthalate (PET) monomer.](image)

PET has numerous applications. The use of polymer is widespread in textiles, packaging, audio/video films, engineering resin applications and other miscellaneous applications such as cable wrap, etc. (McFarlane 1990).

*Thermal decomposition behaviour and heating rates*

PET is a thermoplastic and like polyethylene, melts in a narrow temperature range of about 120 – 130 ºC. PET also has a one step decomposition, similar to polyethylene giving rise to one peak in the differential weight loss curve plotted with respect to time. The heating rates, temperature range in which the decomposition occurs and $T_{\text{max}}$ are listed in Table 3. The decomposition behaviour of PET is similar to polyethylene plastic which was explained in section 3.2.1.
Table 3: Heating rate and decomposition temperature range for PET plastics in TGA experiments.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Temperature range (°C)</th>
<th>T_max (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>370 – 500</td>
<td>414</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>20</td>
<td>380 – 510</td>
<td>443</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>**</td>
<td>**</td>
<td>444</td>
<td>Heikkinen et al. (2004)</td>
</tr>
<tr>
<td>100</td>
<td>400 – 520</td>
<td>467</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td>900</td>
<td>500 - 630</td>
<td>560</td>
<td>Senneca et al. (2002)</td>
</tr>
</tbody>
</table>

** - not available in literature

Volutility of PET

PET has a char yield of about 13 % (Heikkinen et al. 2004), so has a comparatively larger charge yield than other thermoplastics. The proximate and ultimate analysis data for PET obtained from the literature is given in Appendix A3.

3.2.4 Size and shape of plastics and its effect during thermal decomposition

Studies done by Zevenhoven et al. (1997) on the combustion and gasification properties of plastics indicate that the shape of the sample has little effect on the behaviour of gasification or combustion when the mass remains constant. However, they noticed that increasing the sample mass during TGA from 10 to 70 mg showed a significant effect on the pyrolysis rate. According to Zevenhoven et al. (1997), pyrolysis rate decreases proportionally with mass to the power of 2/3 when the mass of the sample is increased from 10 mg to 70 mg. Due to this decrease in pyrolysis rate it leads to 3 to 4 times lower char burn out, giving larger char remains. This confirms that TGA of larger sample sizes will be influenced by mass and heat transfer limitations. The conductive heat transfer limitations on samples due to high heating rates have been briefly discussed in Section 3.2.1.

The effects of shape, size and volume of the sample during a thermogravimetry analysis are discussed in Hatakeyama and Quinn (1999). According to them, i) endothermic and exothermic reactions occurring in the sample cause the true sample temperature to deviate significantly from the programmed temperature (this deviation increases with the increase in the mass of the sample), ii) the evolution of the gases from the sample depends on the bulk of the sample in the sample holder and iii) thermal gradients are more pronounced for large sample masses. They also report that weight loss rates are
higher for flakes than blocks and that for powdered samples are the highest. Hatakeyama and Quinn (1999) also found that smaller particles have the best surface to volume ratio and at any given temperature the extent of decomposition is greater than samples for larger particles.

### 3.3 TGA EXPERIMENTS

#### 3.3.1 Plastic Samples

Four different plastic samples were chosen for the experiments. The choice of the plastic samples was based on the most common ones found in the waste stream from such as shopping bags, milk bottles, cream containers, beverage bottles etc (explained in Chapter 2). The plastic samples used for the experiments were obtained from various manufacturers of plastic resins (Table 4). The material properties of the samples are listed in Appendix A4. PET and PVC samples were available at the School of Chemical and Biomolecular Engineering, the University of Sydney. However, data on material properties were not available for these samples.

**Table 4: Plastic samples used for TGA experiments.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Plastic Grade</th>
<th>Manufacturer</th>
<th>Application/Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>LDPE PETLIN LD N125Y</td>
<td>Swift Co., Australia</td>
<td>Carry bags and produce bags.</td>
</tr>
<tr>
<td>2.</td>
<td>HDPE HD 5148</td>
<td>Qenos, Australia</td>
<td>Milk bottles, cream containers, fruit juice and cordial bottles.</td>
</tr>
<tr>
<td>3.</td>
<td>PET (Unknown)</td>
<td>SANWA</td>
<td>Beverage bottles and food packaging</td>
</tr>
<tr>
<td>4.</td>
<td>PVC (Unknown)</td>
<td>ICI</td>
<td>Bottles, pipe and fittings, house sliding, sheets</td>
</tr>
</tbody>
</table>

#### 3.3.2 TGA Equipment

The thermogravimetric analysis was conducted using SDT Q600 TGA equipment manufactured by TA Instruments (USA) (SDT stands for Simultaneous DSC and TGA). Q600 provides a simultaneous measurement of weight change (TGA) and heat flow (DSC) on a sample over the temperature range from ambient to 1500 ºC. The heating rates achievable from the equipment ranges from 0.1 to 100 ºC/min. The heating of the equipment is a horizontal bifilar wound furnace (Figure 13). Bifilar coil used in the furnace to generate heat is an electromagnetic coil, which contains closely spaced...
parallel windings placed horizontally. The maximum sample capacity of the equipment is 200 mg with a balance sensitivity of 0.1 µg. The calorimetric accuracy of the data measured is ± 2 %. Other specifications of SDT Q600 are given in Appendix A5.

![SDT Q600 TGA Furnace Configuration](source: www.tainstruments.com)

The DTA sensitivity is 0.001°C, which is the minimum temperature difference that can be measured by DTA. Detailed explanation of the DTA thermal analysis can be found in Hatakeyama and Quinn (1999). Heat-flux DSC is the temperature difference between the sample and reference measured as a function of temperature or time under controlled temperature conditions. The temperature difference is proportional to the change in the heat flux (energy input per unit time) (Hatakeyama & Quinn 1999).

### 3.3.3 Experimental Procedure

TGA experiments were conducted in an inert gas atmosphere using the non-isothermal method (explained in Section 3.1.2).

*Pyrolysis procedure and heating rates*

The following procedure was chosen for each experiment.

1. Isothermal for x minutes (x = 1, 3 or 15 as specified)
2. Ramp at selected heating rate ‘β’ (ºC/min) to 750 ºC.

Five different heating rates (β): 5, 10, 20, 50 and 100 ºC/min were used.

The isothermal conditions at the start (step 1) was included to ensure that the purge gas (nitrogen) purges out the remains of the cooling air from the system before the furnace begins heating the sample.

For each plastic sample five different experiments at specified heating rates were conducted. The heating starts from ambient conditions normally around 25 ºC and ramps up to 750 ºC in a specified heating rate. The maximum temperature was selected such that the thermal decomposition of the sample was complete. Once all the volatiles and gases from the plastic sample have evolved the remaining char would show no weight change even when increasing the furnace temperature.

Table 5 lists the time taken to complete each experiment at a specified heating rate. The time taken listed in Table 5 does not include the 1 min (or 3 min) isothermal conditions used in stabilizing the and purging out the residual air from the reaction chamber.

**Table 5: Heating rate and time taken for experiments.**

<table>
<thead>
<tr>
<th>Heating Rate, β (ºC/min)</th>
<th>Time taken (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>145</td>
</tr>
<tr>
<td>10</td>
<td>72.5</td>
</tr>
<tr>
<td>20</td>
<td>36.25</td>
</tr>
<tr>
<td>50</td>
<td>14.5</td>
</tr>
<tr>
<td>100</td>
<td>7.25</td>
</tr>
</tbody>
</table>

The data sampling was done at 0.5 s time intervals.

*Sample Vessel*

An alumina pan was used as the sample vessel, which is an open-type vessel. The sample and reference pan are shown in Figure 14 below. The thermocouples (Type R) measuring the temperatures are located immediately below the sample and reference pans. Type R thermocouple is Platinum/13% Rhodium (+ve terminal) vs. Platinum (-ve terminal) with the recommended operating temperature range of 227 – 1427 ºC (500 – 1700 K). The Alumina pan used for the experiment was a 40 µL pan.
Figure 14: SDT Q600 TGA equipment showing sample and reference pans, thermocouples and purge gas inlet to the furnace.

Purge gas

The Q600 instrument uses a horizontal purge gas system with digital mass flow controllers. The balance is purged with 100 mL/min of nitrogen gas entering the system. This flow rate was maintained during the experiments. The sample purge can be switched from nitrogen to air with the aid of a software-controlled gas-selector. A special reactive purge gas inlet tube directly on the vicinity of the sample allows experiments requiring the use of oxidative or reactive gases. However, the reactive gases are used in conjunction with the inert purge gas such as nitrogen to reduce the reactive gases entering the sensitive balance of the TGA equipment. The recommended amount of reactive purge gas flow is 20 mL/min for Q600 TA equipment.

Data evaluation software and data collection

For evaluating the data obtained from TGA, the data evaluation software TA Universal Analysis 2000 was used. This software is a useful tool for analysis of data obtained from TGA equipment Q600 where data can be analysed with much ease.

The data collected during the experiments were stored in the TGA equipment as well as the computer that communicates with it. All the data collected during the experiments
are provided in the compact disk under the folder name “TGA Experiments” in Appendix C. This data is compatible with the TA Universal Analysis 2000 software and can be analysed using it.

3.4 RESULTS AND DISCUSSION

3.4.1 LDPE sample

_Weight loss curve_

Figure 15 below shows the change in weight of LDPE sample with temperature at various heating rates. This graph was taken from the first set of experiments (Run 1) conducted at the heating rates of 5, 10, 20, 50 and 100 °C/min. The figure for Run 2 is given in Appendix 6.

![Figure 15: Weight (%) vs. temperature (°C) for LDPE sample at various heating rates (Run 1).](image)

Data for other experimental runs are presented in Table 6. A distinct weight loss step characterizes the weight loss curve for LDPE sample at all heating rates considered. In Table 6 the heating rates (column 3) are listed against i) sample size, ii) temperature (T_max) when the rate of weight loss is maximum, iii) remaining weight % after T_max, iv) the maximum rate of weight loss which occurs at T_max, v) time at which maximum
weight loss takes place and vi) temperature range in which the decomposition occurs. In Table 6 column 9, in thermal decomposition temperature range, the lower temperature is the temperature when 1 % of the total weight of sample decomposes and the higher temperature is the temperature when 99.9 % of the total weight of the sample has been decomposed (unless otherwise stated).

Table 6: Thermal decomposition of LDPE sample at various heating rates.

<table>
<thead>
<tr>
<th>No</th>
<th>Run</th>
<th>Heating Rate (ºC/min)</th>
<th>Sample Size (mg)</th>
<th>T_max (ºC)</th>
<th>Remaining wt (%) at T_max</th>
<th>(dw/dt)_max (%/min)</th>
<th>Time when (dw/dt)_max (min)</th>
<th>Decomposition temperature range (ºC) (1% wt loss – 99.9% wt loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>22.579</td>
<td>460.75</td>
<td>40.15</td>
<td>18.10</td>
<td>89.68</td>
<td>396 – 486</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>10</td>
<td>22.641</td>
<td>478.00</td>
<td>23.18</td>
<td>30.37</td>
<td>46.42</td>
<td>398 – 500</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>20</td>
<td>24.047</td>
<td>485</td>
<td>34.48</td>
<td>54.98</td>
<td>24.9</td>
<td>426 – 637*</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>50</td>
<td>25.802</td>
<td>498.5</td>
<td>44.24</td>
<td>132.03</td>
<td>10.93</td>
<td>433.8 – 528</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>100</td>
<td>22.952</td>
<td>517.82</td>
<td>40.60</td>
<td>240.98</td>
<td>6.28</td>
<td>446 – 552.5</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>5</td>
<td>22.248</td>
<td>460</td>
<td>39.71</td>
<td>18.23</td>
<td>91.44</td>
<td>383 – 646*</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>10</td>
<td>24.865</td>
<td>466</td>
<td>44.75</td>
<td>32.74</td>
<td>46.15</td>
<td>401 – 495</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>20</td>
<td>24.616</td>
<td>485</td>
<td>39.12</td>
<td>54.53</td>
<td>26.84</td>
<td>422 – 510*</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>50</td>
<td>25.225</td>
<td>498.59</td>
<td>45.63</td>
<td>130.21</td>
<td>13.14</td>
<td>424 – 528*</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>100</td>
<td>24.632</td>
<td>517</td>
<td>41.68</td>
<td>244.08</td>
<td>8.22</td>
<td>456 – 546</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>50</td>
<td>25.527</td>
<td>498</td>
<td>43.71</td>
<td>137.13</td>
<td>12.93</td>
<td>431.5 – 528</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>100</td>
<td>25.715</td>
<td>516</td>
<td>41.69</td>
<td>239.95</td>
<td>8.33</td>
<td>447 – 549</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>50</td>
<td>24.336</td>
<td>499</td>
<td>45.67</td>
<td>130.51</td>
<td>12.83</td>
<td>432 – 622**</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>100</td>
<td>25.616</td>
<td>517</td>
<td>42.04</td>
<td>243.66</td>
<td>8.3</td>
<td>460 – 572</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>50</td>
<td>24.219</td>
<td>498</td>
<td>44.67</td>
<td>131.56</td>
<td>12.83</td>
<td>427 – 526</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>100</td>
<td>24.972</td>
<td>516</td>
<td>42.72</td>
<td>234.20</td>
<td>8.35</td>
<td>435 – 602</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>100</td>
<td>24.859</td>
<td>517</td>
<td>42.21</td>
<td>258.97</td>
<td>8.48</td>
<td>462 – 546</td>
</tr>
<tr>
<td>18</td>
<td>7</td>
<td>100</td>
<td>22.317</td>
<td>516</td>
<td>41.98</td>
<td>239.23</td>
<td>8.33</td>
<td>445 – 551</td>
</tr>
<tr>
<td>19</td>
<td>8</td>
<td>5</td>
<td>0.9280</td>
<td>456.72</td>
<td>39.85</td>
<td>12.42</td>
<td>90.0</td>
<td>401.18 – 993****</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>10</td>
<td>0.566</td>
<td>422.43</td>
<td>48.49</td>
<td>14.12</td>
<td>42.53</td>
<td>38 - 462</td>
</tr>
<tr>
<td>21</td>
<td>8</td>
<td>20</td>
<td>0.3370</td>
<td>430.91</td>
<td>34.77</td>
<td>47.36</td>
<td>23.7</td>
<td>30 - 447</td>
</tr>
</tbody>
</table>
At lower heating rates the weight loss starts at lower temperatures than higher heating rates. This was seen in literature as well. A complete thermal decomposition also occurs at lower temperatures for lower heating rates. However, at lower heating rates the time taken for complete decomposition is longer (see Section 3.3.3, Table 5).

For LDPE the start of the decomposition occurs at temperatures between 396 – 462 ºC and the end of the decomposition occurs at temperatures between 486 – 572 ºC, for heating rates between 5 – 100 ºC/min. The decomposition temperature range found in literature for polyethylene samples is 350 – 560 ºC (Section 3.2.1, Table 1) for the heating rates between 5 to 100 ºC/min. This was similar to the temperature range found in our experiments. Extensive weight loss was not observed below 396 ºC and the weight loss below this temperatures was less than 1 % of the sample weight. These low-temperature weight changes are considered to be due to scission of weak links such as oxygen incorporated into the main polymer backbone as impurities (Beyler & Hirschler 2001). These weight changes occur before rapid decomposition and without significant volatilisation.

Polyethylene decomposes via random chain scission (Bockhorn et al. 1999b and Gao et al. 2003) and does not depend on heating rate (Gao et al. 2003). LDPE being branched compared to HDPE enhances the intramolecular hydrogen transfer and results in lower thermal stability than HDPE (Beyler & Hirschler 2001) and decomposes at lower

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>8</td>
<td>50</td>
<td>0.913</td>
<td>500.61</td>
<td>41.97</td>
<td>103.83</td>
<td>12.99</td>
</tr>
<tr>
<td>23</td>
<td>8</td>
<td>100</td>
<td>0.682</td>
<td>503.20</td>
<td>34.28</td>
<td>198.41</td>
<td>8.14</td>
</tr>
<tr>
<td>24</td>
<td>9</td>
<td>20</td>
<td>0.91</td>
<td>481.79</td>
<td>33.95</td>
<td>55.40</td>
<td>26.41</td>
</tr>
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<td>25</td>
<td>9</td>
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<td>0.977</td>
<td>482.36</td>
<td>26.77</td>
<td>107.03</td>
<td>12.59</td>
</tr>
<tr>
<td>26</td>
<td>10</td>
<td>20</td>
<td>0.897</td>
<td>451.81</td>
<td>34.42</td>
<td>41.44</td>
<td>24.92</td>
</tr>
</tbody>
</table>

+ Note time includes 1 or 3 min isothermal used for purging left over air from the previous experiments while cooling of the furnace.
- In experiment 1 – 5 listed above the isothermal time is 1 minute.
- In experiments 6 – 26 listed above the isothermal time is 3 minutes.
* - at 99.5 % wt loss
** - at 98.5 % wt loss
*** - at 92 % wt loss
****- at 88% wt loss

In the underlined decomposition temperature range, the lower temperature (where 1% decomposition occurs) is quite low. Hence, this weight loss of 1% is not due to plastic decomposition as it cannot occur at such low temperatures. The reason for 1% decomposition obtained at this temperature is because of very small sample sizes taken compared to other experiments. Hence, it might be related to balance sensitivity or the moisture present on the sample.
temperatures than HDPE. The various mechanisms involved in polymer decomposition were explained in Chapter 2. However, the one step decomposition observed at all heating rates (5, 10, 20, 50 and 100 ºC/min) suggests that it follows the same decomposition mechanism.

The decomposition temperature influences the size of the volatile products (Gao et al. 2003). As the temperature increases the minimum length of the fragments which can evaporate under the prevailing conditions also increases (Gao et al. 2003). At higher heating rates the decomposition of polyethylene occurs at higher temperatures as seen in Figure 15 and Table 6. This means that the distribution of the size of volatile products will depend on the heating rate (Gao et al. 2003). This also explains the variation in decomposition products of polyethylene obtained in different temperature ranges (explained in Chapter 2). The random chain scission method for polyethylene decomposition discussed by Gao et al. (2003) and proposed by Bockhorn et al. (1999b) is given in Appendix A7.

Various attempts were made to analyse the gas samples using a mass spectroscope, which was connected to the exhaust port of the TGA instrument. A mass spectroscope can be used to detect the exhaust gas composition and this method has been successfully used in studies of polymer analysis (Lattimer 1993, Raemakers & Bart 1997, Mastral et al. 2003). However, due to problems related to blockage of the capillary tube connecting the exhaust of TGA instrument to the mass spectrometry the product gases from TGA instrument during the experiments could not be analysed successfully. Hence, Run 2 and subsequent runs were performed while trying to obtain the gas composition data from the mass spectroscope. However, due to the blockage of the capillary tube the data obtained from the mass spectrometer was flawed. Thermogravimetry-mass spectrometry analysis was not conducted later due to limited time available during the research.

Derivative weight loss curve

The temperature at which the rate of weight loss with respect to time is maximum is different for different heating rates. At lower heating rates this temperature is lower than that of higher heating rates (Table 6). In Figure 16 the peaks are the points where the rate of weight loss is maximum. This plot is a derivative of the plot given in Figure 15 (i.e. derivative weight loss). The derivative weight loss curve for Run 2 is given in Appendix 6.
Figure 16: Derivative of weight (%/min) vs. temperature (ºC) for LDPE sample (Run 1).

The highest peak corresponds to highest heating rate used during the experiment (100ºC/min) and the lowest peak corresponds the lowest heating rate (5ºC/min). The rate of weight loss at the peak for 100ºC/min heating rate is about 13 times higher then that of the peak for 5ºC/min heating rate. This shows that rapid thermal degradation occurs at higher heating rates shortening the length of time required to decompose LDPE completely.

Effects of sample sizes

The following figures (Figure 17, Figure 18 and Figure 19) show that the maximum rate of weight loss occurs at higher temperatures for larger samples than smaller samples. Hence, this indicates that larger samples do show heat transfer limitations requiring higher temperatures to decompose than smaller samples. The shift of the peak temperature was observed for all heating rates (5, 10, 20, 50 and 100 ºC/min). Graphs for 20, 50 and 100 ºC/min heating rates are given below. This supports the findings of Darivakis et al. (1990) that larger sized particles does have heat transfer limitations with higher peak temperatures and volatiles release occurring at higher temperatures. Heat and mass transfer limitations because of sample size of polymer are due to complex
transport process involving both gas and liquid phase (Kashiwagi 1994). According to Kashiwagi (1994), complex transport process can be avoided by choosing smaller samples. Hence, this complex transport process might be the cause of shift of peak temperatures towards higher temperatures for the polyethylene samples taken as seen in figures 17, 18 and 19 below.

Figure 17: Derivative of weight loss (%/min) vs. temperature (ºC) curves for LDPE samples for Run 1 and Run 10 at a heating rate of 20 ºC/min.

Figure 18: Derivative of weight loss (%/min) vs. temperature (ºC) curves for LDPE samples for Run 1 and Run 9 at a heating rate of 50 ºC/min.
Figure 19: Derivative of weight loss (%/min) vs. temperature (ºC) curves for LDPE samples for Run 1 and Run 8 at a heating rate of 100 ºC/min.

Kinetic parameters (E and A)

The activation energy (E) and the pre-exponential factor (A) for the decomposition process were determined using Kissinger method (explained in Section 3.1.5). Figure 20 represents the plot of \( \ln(\beta/T_m^2) \) vs. \( (1/T_m) \) used for determining the slope (= E/R) and intercept (= \( \ln[R\cdot A/E] \)) of the straight line determined using Kissinger equation and data from Run 1 and 2. This plot is also sometimes referred as Arrhenius plot.

Figure 20: Arrhenius plot for LDPE sample.
The kinetic parameters obtained for LDPE sample is given in Table 7. Further discussions on E and A and its comparison with other plastic samples are given in Section 3.4.5.

**Table 7: Kinetic parameters for pyrolysis of LDPE sample.**

| Activation Energy, kJ/mol | 242.62 |
| Pre-exponential factor, s\(^{-1}\) | 9.03 x 10\(^{14}\) |

Two runs for LDPE samples and other subsequent runs were performed as explained in Section 3.4.1. Run 1 and Run 2 were used to determine the kinetic parameters for the LDPE samples as both runs were conducted taking five different heating rates (See Table 6 above). The average sample sizes for Run 1 and Run 2 are 23.60 mg and 24.32 mg respectively. The activation energy and pre-exponential factor was determined using the best fit through both sets of data. The standard deviation for the activation energy was found to be ± 13.1 kJ/mol.

Flynn and Wall method (Flynn & Wall 1966) was used in determining the constancy of the activation energy and its independence to the temperature and conversion for the LDPE samples studied. This method provides a simple way via heating rates to show the independence of activation energy to the temperature and conversion. This has been explained in detail in following paragraphs using LDPE as an example.

The following table (Table 8) shows the activation energy determined for Run 1 using Flynn and Wall method at various heating rates (β) and conversions (α).

In Table 8 below, the average activation energy determined for various heating rates has an average value of 241.29 kJ/mol with a standard deviation of ± 0.308 kJ/mol. This accounts to deviation of less than 3% from the total. This shows that the activation energy is not dependent on the heating rates, suggesting that the mechanism of LDPE decomposition is independent of heating rates selected. The details of the calculation for all plastic samples studied are given in Appendix C under the file name: *Flynn and Wall method for plastics.xls*. Further details on Flynn and Wall method is given in Appendix 8.
Table 8: Activation energy (kJ/mol) obtained for LDPE sample at different conversions and heating rates (Run 1).

<table>
<thead>
<tr>
<th>α</th>
<th>Activation Energy (kJ/mol)</th>
<th>β=5°C/min</th>
<th>β=10°C/min</th>
<th>β=20°C/min</th>
<th>β=50°C/min</th>
<th>β=100°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td></td>
<td>229.97</td>
<td>229.88</td>
<td>229.64</td>
<td>229.49</td>
<td>229.33</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
<td>248.13</td>
<td>247.96</td>
<td>247.80</td>
<td>247.61</td>
<td>247.41</td>
</tr>
<tr>
<td>0.25</td>
<td></td>
<td>244.86</td>
<td>244.72</td>
<td>244.56</td>
<td>244.36</td>
<td>244.16</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td>246.45</td>
<td>246.31</td>
<td>246.16</td>
<td>245.96</td>
<td>245.73</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>244.46</td>
<td>244.30</td>
<td>244.16</td>
<td>243.96</td>
<td>243.70</td>
</tr>
<tr>
<td>0.90</td>
<td></td>
<td>244.37</td>
<td>244.22</td>
<td>244.07</td>
<td>243.85</td>
<td>243.50</td>
</tr>
<tr>
<td>0.98</td>
<td></td>
<td>233.28</td>
<td>233.07</td>
<td>232.78</td>
<td>232.57</td>
<td>232.24</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td>241.65</td>
<td>241.50</td>
<td>241.31</td>
<td>241.11</td>
<td>240.87</td>
</tr>
</tbody>
</table>

Avg. – Average

In Figure 21 below the trend lines obtained LDPE for various values of conversion using Flynn and Wall method are more or less parallel to each other. Hence, the slopes of all the lines are the same. This also shows that there is no effect on the activation energy due to conversion or temperature.

Figure 21: ln β vs. (1/T) obtained using Flynn and Wall (1966) method for LDPE samples.
There is about 3% difference between the value of activation energy determined using Flynn and Wall method for LDPE from that determined using Kissinger method.

3.4.2 HDPE sample

Weight loss curve

Figure 22 below shows the weight change of HDPE sample with temperature at various heating rates (5, 10, 20, 50 & 100 °C/min) during thermogravimetry (Run 1). The weight loss curve for Run 2 is given in Appendix 6. A distinct weight loss step characterizes the weight loss curve for HDPE for all heating rates considered. This is similar to the weight loss curves obtained for LDPE samples.

![Weight (%)](attachment:image)

**Figure 22: Weight (%) vs. temperature (°C) for various heating rates for HDPE sample (Run 1).**

From Figure 22 it can be observed that at lower heating rates the weight loss starts at lower temperatures and the complete thermal degradation occurs at temperatures lower than that of the higher heating rates. This observation is similar to that of LDPE samples.

In Table 9 the heating rates (column 3) are listed against i) sample size, ii) temperature (T_{max}) when the rate of weight loss is maximum, iii) remaining weight % after T_{max}, iv)
the maximum rate of weight loss which occurs at $T_{\text{max}}$, v) time at which maximum weight loss takes place and vi) temperature range in which the decomposition occurs. In Table 9 column 9, the thermal decomposition temperature range, the lower temperature is the temperature when 1% of the total weight of sample decomposes and the higher temperature is the temperature when 99.9% of the total weight of the sample has decomposed (unless otherwise stated).

**Table 9: Data for thermal decomposition of HDPE sample.**

<table>
<thead>
<tr>
<th>No</th>
<th>Run</th>
<th>Heating Rate (ºC/min)</th>
<th>Sample Size (mg)</th>
<th>$T_{\text{max}}$ (ºC)</th>
<th>wt % at $T_{\text{max}}$</th>
<th>$(\text{dw/dt})_{\text{max}}$ (%/min)</th>
<th>Time when $(\text{dw/dt})_{\text{max}}$ (min⁺)</th>
<th>Decomposition temperature Range (ºC) (1% wt loss – 99.9% wt loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>26.164</td>
<td>471.25</td>
<td>32.97</td>
<td>23.65</td>
<td>93.78</td>
<td>416 – 492*</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>10</td>
<td>23.458</td>
<td>472.60</td>
<td>44.60</td>
<td>42.29</td>
<td>47.65</td>
<td>377 - 496</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>20</td>
<td>38.705</td>
<td>487.67</td>
<td>49.14</td>
<td>66.84</td>
<td>26.54</td>
<td>427 – 548**</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>50</td>
<td>26.521</td>
<td>507.68</td>
<td>44.30</td>
<td>160.10</td>
<td>13.14</td>
<td>445 – 535</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>100</td>
<td>26.201</td>
<td>526.00</td>
<td>45.80</td>
<td>316.18</td>
<td>8.51</td>
<td>482 – 550</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>5</td>
<td>6.992</td>
<td>471.64</td>
<td>32.69</td>
<td>19.18</td>
<td>93.61</td>
<td>358.5 – 488</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>10</td>
<td>7.838</td>
<td>476.88</td>
<td>31.78</td>
<td>28.77</td>
<td>47.53</td>
<td>365 – 498</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>20</td>
<td>6.192</td>
<td>490.09</td>
<td>31.88</td>
<td>58.36</td>
<td>26.27</td>
<td>404 – 508</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>50</td>
<td>6.851</td>
<td>508.04</td>
<td>38.81</td>
<td>164.61</td>
<td>12.85</td>
<td>427 – 668**</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>100</td>
<td>8.408</td>
<td>523.16</td>
<td>42.16</td>
<td>287.54</td>
<td>8.29</td>
<td>428 – 548</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>5</td>
<td>0.798</td>
<td>462.71</td>
<td>33.22</td>
<td>14.29</td>
<td>91.12</td>
<td>401 – 483**</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>10</td>
<td>0.64</td>
<td>447.23</td>
<td>24.25</td>
<td>21.01</td>
<td>62.07</td>
<td>33.4 – 470</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>20</td>
<td>0.604</td>
<td>463.61</td>
<td>19.06</td>
<td>55.67</td>
<td>42.16</td>
<td>32 – 470</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>50</td>
<td>0.748</td>
<td>486.88</td>
<td>30.64</td>
<td>115.4</td>
<td>29.54</td>
<td>34.8 – 509</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>100</td>
<td>0.814</td>
<td>506.06</td>
<td>32.16</td>
<td>218.13</td>
<td>25.14</td>
<td>32 – 525</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>50</td>
<td>0.688</td>
<td>489.94</td>
<td>29.32</td>
<td>118.74</td>
<td>29.72</td>
<td>29 – 507</td>
</tr>
</tbody>
</table>

* For exp 1 – 11, Note that the time includes 3 min isothermal used for purging left over air from the previous experiments while cooling of the furnace.

12 – 16, time includes 20 min isothermal

* - at 99.75% wt loss

** - at 99.5 % wt loss

See comments in Table 6 for the underlined temperature decomposition ranges in Table 9.
The thermal decomposition of HDPE in the heating rates between 5 – 100 °C/min occurred in the temperature range of 358 to 550°C. This temperature range is similar to the range given in literature (Section 3.2.1).

*Derivative weight loss curve*

The derivative weight loss curves for HDPE samples (Run 1) are given in Figure 23 and the data for various runs are listed in Table 9. The peaks in Figure 23 denote the point where rate of weight loss with respect to time is a maximum. The derivative weight loss curve for Run 2 is given in Appendix 6.

![Derivative weight loss curve](image)

**Figure 23:** Derivative of weight (%/min) vs. temperature (°C) for HDPE sample (Run 1).

As expected the rate of weight loss at higher heating rates are higher. The highest peak corresponds to highest heating rate of 100°C/min used during the experiment and the lowest peak corresponds the lowest heating rate of 5°C/min. The rate of weight loss at the peak for 100°C/min heating rate is about 13 times higher then that of the peak of 5°C/min heating rate. These observations are similar to observations made for LDPE sample (Section 3.4.1).
Kinetic Parameters $E$ and $A$

Kissinger’s method was used in determining the kinetic parameters of HDPE decomposition. Figure 24 was obtained for experimental Run 1 using Kissinger method. The given plot of $\ln(\beta/T_m^2)$ vs. $(1/ T_m)$ was used to determine the slope and intercept as explained in Section 3.1.5.

![Arrhenius plot of pyrolysis of HDPE sample.](image)

The kinetic parameters for HDPE sample are given in Table 10.

Table 10: Kinetic parameters of pyrolysis of HDPE sample.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy, $E$: kJ/mol</td>
<td>233.60</td>
<td>260.14</td>
</tr>
<tr>
<td>Pre-exponential factor, $A$: s$^{-1}$</td>
<td>$1.53 \times 10^{14}$</td>
<td>$1.04 \times 10^{16}$</td>
</tr>
</tbody>
</table>

* Values of kinetic parameters from Run 2 are considered to be more accurate.

The difference in $E$ and $A$ observed in Run 1 and Run 2 are due to the difference in sample size. The average sample size for Run 1 was 28.0 mg compared to sample size of 7.26 mg for Run 2. This shows that there might have been mass and heat transfer effects due to larger sample sizes in Run 1. The activation energy for Run 2 is greater than Run 1. When comparing with the activation energy obtained for LDPE sample in Run 1 the activation energy for HDPE (Run 1) is lower. As HDPE is thermally more stable than LDPE this value of 233.60 kJ/mol cannot be the correct value. Hence, the value obtained from Run 2 is considered to be the correct value of the activation energy.
For HDPE samples (Run 2) the average activation energy determined using Flynn and Wall method was 245.87 kJ/mol with a standard deviation of ± 0.327 kJ/mol. The difference between activation energy obtained from Kissinger method and that from Flynn and Wall method is about 5.5 %. Note that Flynn and Wall method is just a quick method to determine activation energy where as Kissinger method provides both activation energy and pre exponential factor.

3.4.3 PET sample

Weight loss curve

Figure 25 shows the weight change with temperature obtained for the PET samples at various heating rates using (Run 1). The figure for Run 2 is given in Appendix 6.

![Figure 25: Weight (%) vs. temperature (ºC) for PET sample at various heating rates (Run 1).](image)

It can be observed that at lower heating rates the weight loss starts at lower temperatures and the complete thermal degradation occurs at temperatures lower than that of the higher heating rates. This behaviour is similar to LDPE and HDPE samples.

In Table 11 the heating rates (column 3) are listed against i) sample size, ii) temperature ($T_{max}$) when the rate of weight loss is maximum, iii) remaining weight % after $T_{max}$, iv) the maximum rate of weight loss which occurs at $T_{max}$, v) time at which maximum
weight loss takes place and vi) temperature range in which the decomposition occurs. In Table 11 column 8, in thermal decomposition temperature range, the lower temperature is the temperature when 1 % of the total weight of sample decomposes and the higher temperature is the temperature when 20 % of the total weight of the sample has decomposed (unless otherwise stated). A value of 20 % was chosen as PET unlike polyethylene does have char remains.

Char remains of about 12.2 % in average and up to 18 % (approximately) was recorded during the experiments. Heikkinen et al. (2004) also report char yields of 13.2 % in their TGA experiments. The char yields obtained during the experiments are also listed in Table 11.

Table 11: Thermal degradation of PET sample at various heating rates.

<table>
<thead>
<tr>
<th>Run</th>
<th>Heating Rate (ºC/min)</th>
<th>Sample Size (mg)</th>
<th>( T_{\text{max}} ) (ºC)</th>
<th>wt (%) at ( T_{\text{max}} )</th>
<th>( (dw/dt)_{\text{max}} ) (%/min)</th>
<th>Time when ( (dw/dt)_{\text{max}} ) occurs (min)</th>
<th>Decomposition temperature range (ºC)</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>4.520</td>
<td>422.08</td>
<td>50.509</td>
<td>10.192</td>
<td>82.48</td>
<td>374.8 – 488.5</td>
<td>17.56</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>5.123</td>
<td>435.88</td>
<td>50.869</td>
<td>20.384</td>
<td>42.97</td>
<td>374 – 473</td>
<td>10.39</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>5.755</td>
<td>450.05</td>
<td>49.850</td>
<td>39.430</td>
<td>24.07</td>
<td>370.5 – 481.4</td>
<td>12.14</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>5.367</td>
<td>465.91</td>
<td>53.225</td>
<td>96.678</td>
<td>11.89</td>
<td>398.3 – 493</td>
<td>12.08</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>16.976</td>
<td>477.63</td>
<td>56.114</td>
<td>229.77</td>
<td>7.80</td>
<td>429 – 500</td>
<td>11.6</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>6.174</td>
<td>423.84</td>
<td>47.96</td>
<td>10.43</td>
<td>82.03</td>
<td>366.9 – 457.8</td>
<td>5.01</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>6.847</td>
<td>436.81</td>
<td>49.31</td>
<td>20.83</td>
<td>43.78</td>
<td>343.4 – 471.9</td>
<td>12.64</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>4.412</td>
<td>449.30</td>
<td>46.675</td>
<td>40.733</td>
<td>24.98</td>
<td>207.6 – 469.4</td>
<td>10.78</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>4.564</td>
<td>468.37</td>
<td>50.355</td>
<td>96.354</td>
<td>12.26</td>
<td>277.5 – 497.6</td>
<td>14.40</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>3.714</td>
<td>483.93</td>
<td>53.626</td>
<td>185.478</td>
<td>7.79</td>
<td>292.1 – 516.8</td>
<td>15.23</td>
</tr>
</tbody>
</table>

Note that the time includes 3 min isothermal used for purging left over air from the previous experiments while cooling of the furnace.

The thermal decomposition of PET sample occurred between the temperature range of 207 – 516.8ºC. The temperature ranges for PET samples at various heating rates are given in Table 11.
**Derivative weight loss curve**

The derivative weight loss curve for PET samples obtained for Run 1 is given in Figure 26. Those for Run 2 is given in Appendix 6. $T_{\text{max}}$ temperatures at lower heating rates are lower than that of higher heating rates. This is similar to other plastic samples.

![Derivative weight loss curve](image)

**Figure 26: Derivative of weight (%/min) vs. temp (ºC) for PET sample (Run 1)**

The highest peak corresponds to highest heating rate used during the experiment (100ºC/min) and the lowest peak corresponds the lowest heating rate (5ºC/min). The rate of weight loss at the peak (100ºC/min heating rate) is about 22 times higher then that of the peak (5ºC/min heating rate).

The sample sizes for all experiments were around 5.164 mg (average) except for Run 1 (heating rate 100 ºC/min). For the heating rate of 100ºC/min (Run 1) the sample size was of size 16.976 mg. For the same heating rate the sample size for Run 2 was 3.714 mg. It was observed that for a larger sample $T_{\text{max}}$ was 477.63 ºC where as for the smaller sample the $T_{\text{max}}$ was 483.93 ºC. The derivative of weight loss (%/min) was higher for the larger sized sample. For larger sample this was 229.77 %/min where as for the smaller sample this was 185.478 %/min.
**Kinetic Parameters E and A**

Figure 27 presents the graph for Run 2 derived using Kissinger method which is a plot of \( \ln \left( \frac{\beta}{T_m^2} \right) \) vs. \( \frac{1}{T_m} \) used for determining the slope (= \( E/R \)) and intercept (= \( \ln[R \cdot A/E] \)) of the straight line.

![Graph showing the relationship between 1/Tm and ln(β/Tm^2) for different heating rates.](image)

\[
y = -24932x + 24.31 \\
R^2 = 0.9995
\]

**Figure 27: Determination of kinetic parameters of pyrolysis of PET sample (Run 2).**

The kinetic parameters of pyrolysis of PET sample are given in Table 12 below.

**Table 12: Kinetic parameters of pyrolysis of PET sample.**

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activation Energy, E: kJ/mol</strong></td>
<td>221.34</td>
<td>207.28</td>
</tr>
<tr>
<td><strong>Pre-exponential factor, A: s(^{-1})</strong></td>
<td>1.84 ( \times ) 10(^{14})</td>
<td>1.05 ( \times ) 10(^{13})</td>
</tr>
</tbody>
</table>

*Values of kinetic parameters from Run 2 are considered to be more accurate.*

The difference in E and A observed in Run 1 and Run 2 might be due to the sample size difference used in the heating rate 100°C/min. The sample size for Run 1 (heating rate 100°C/min) was 16.976 mg compared to sample size of 3.714 mg for Run 2 (heating rate 100°C/min). Hence, the E and A values obtained from Run 2 was considered to be more accurate.

The activation energy determined from Flynn and Wall method for Run 2 for PET samples has the average value of 194.19 kJ/mol with a standard deviation of \( \pm 0.409 \).
kJ/mol. Compared to the activation energy determined from Kissinger method for Run 2 the value determined from Flynn and Wall is 6.3 % lower.

3.4.4 PVC Sample

Weight loss curve

Table 13 lists the sample sizes, temperature when the rate of weight loss is maximum \( (T_{\text{max}_1}, T_{\text{max}_2}) \), the weight at this point, maximum weight loss rate and time at which maximum weight loss takes place for different heating rates. PVC decomposition being a two step process has two peak temperatures \( (T_{\text{max}_1}, T_{\text{max}_2}) \). \( T_{\text{max}_1} \) is the peak temperature for step 1 and \( T_{\text{max}_2} \) for step 2. The weight loss curve for PVC is given in Figure 28 obtained for Run 1. Those for Run 2 are given in Appendix 6. First part of the table is for step 1 and the second part for step 2. The decomposition temperature range given in step 1 is the temperature at weight loss of 1 % and 55 % of total weight. The decomposition temperature range given in step 2 is the temperature at weight loss of 60 % and 85 % of total weight.

Table 13: Thermal decomposition of PVC using TGA.

**Step 1**

<table>
<thead>
<tr>
<th>Run</th>
<th>Heating rate ( (^\circ \text{C}/\text{min}) )</th>
<th>Sample size ( (\text{mg}) )</th>
<th>( T_{\text{max}_1} ) ( (^\circ \text{C}) )</th>
<th>Wt (%) at ( T_{\text{max}_1} )</th>
<th>( \left( \frac{d\text{W}}{dt} \right)_{\text{max}_1}(%/\text{min}) )</th>
<th>Time at ( \left( \frac{d\text{W}}{dt} \right)_{\text{max}_1}(\text{min}) )</th>
<th>Decomposition temperature range ( (^\circ \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>7.272</td>
<td>279.95</td>
<td>79.29</td>
<td>16.04</td>
<td>54.91</td>
<td>223.5 – 306.9</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10.333</td>
<td>293.74</td>
<td>78.61</td>
<td>24.35</td>
<td>29.35</td>
<td>240.8 – 376.2</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>9.134</td>
<td>309.04</td>
<td>77.94</td>
<td>37.32</td>
<td>17.16</td>
<td>251.8 – 337.8</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>8.892</td>
<td>330.53</td>
<td>78.10</td>
<td>61.97</td>
<td>9.52</td>
<td>274.5 – 380</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>10.128</td>
<td>350.29</td>
<td>73.82</td>
<td>92.35</td>
<td>6.72</td>
<td>264.7 – 389</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>8.176</td>
<td>277.68</td>
<td>81.85</td>
<td>17.23</td>
<td>51.04</td>
<td>234.2 – 396.8</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>8.028</td>
<td>292.50</td>
<td>79.63</td>
<td>24.95</td>
<td>30.60</td>
<td>242 – 392.8</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>6.897</td>
<td>310.22</td>
<td>77.75</td>
<td>35.15</td>
<td>17.52</td>
<td>253.4 – 400.4</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>8.075</td>
<td>336.13</td>
<td>74.80</td>
<td>58.75</td>
<td>9.66</td>
<td>271.2 – 387.3</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5.166</td>
<td>350.53</td>
<td>75.18</td>
<td>95.00</td>
<td>6.63</td>
<td>265 – 393</td>
</tr>
</tbody>
</table>
### Step 2

<table>
<thead>
<tr>
<th>Run</th>
<th>Heating Rate (°C/min)</th>
<th>( T_{\text{max}_2} ) (°C)</th>
<th>Wt (%) at ( T_{\text{max}_2} )</th>
<th>( \left( \frac{dw}{dt} \right)_{\text{max}_2} ) (%/min)</th>
<th>Time at ( \left( \frac{dw}{dt} \right)_{\text{max}_2} ) (min)</th>
<th>Decomposition temperature range (°C)</th>
<th>Residue %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>442.73</td>
<td>26.46</td>
<td>3.097</td>
<td>87.56</td>
<td>410.8 – 471.4</td>
<td>11.21</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>449.57</td>
<td>29.34</td>
<td>7.65</td>
<td>44.94</td>
<td>422.7 – 483.7</td>
<td>8.10</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>460.35</td>
<td>29.25</td>
<td>12.17</td>
<td>24.69</td>
<td>430 – 496</td>
<td>9.95</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>470.31</td>
<td>29.22</td>
<td>27.40</td>
<td>12.27</td>
<td>433.7 – 503.8</td>
<td>7.02</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>504.39</td>
<td>18.21</td>
<td>40.58</td>
<td>8.19</td>
<td>428.6 – 512.5</td>
<td>5.44</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>446.93</td>
<td>28.79</td>
<td>3.23</td>
<td>84.93</td>
<td>422.2 – 584</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>453.70</td>
<td>27.05</td>
<td>6.26</td>
<td>46.70</td>
<td>423 – 486.4</td>
<td>11.37</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>458.29</td>
<td>31.43</td>
<td>13.84</td>
<td>24.90</td>
<td>435.7 – 502.4</td>
<td>10.44</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>473.16</td>
<td>29.76</td>
<td>27.61</td>
<td>12.35</td>
<td>441.3 – 510</td>
<td>9.40</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>487.09</td>
<td>27.22</td>
<td>46.27</td>
<td>7.92</td>
<td>444.7 - 518</td>
<td>7.69</td>
</tr>
</tbody>
</table>

Note that the time includes 3 min isothermal used for purging left over air from the previous experiments while cooling of the furnace.
Figure 28: Weight (%) vs. temperature (ºC) for PVC sample at various heating rates (Run 1).

It was observed that at lower heating rates the weight loss starts at lower temperatures and the complete thermal decomposition occurs at temperatures lower than that of the higher heating rates. This is similar to other plastic samples studied.

The first step (dehydrochlorination) occurs in PVC sample between the temperature range 223 to 397ºC. The second step the degradation step occurs in PVC in the temperature range of 410 to 518 ºC.

*Derivative weight loss curve*

Two distinct peaks were obtained in the derivative weight loss curve for PVC. The first step corresponds to the release of hydrogen chloride (dechlorination) and the second the degradation of remaining hydrocarbon (as explained in Section 3.2.2). The derivative weight loss curve for Run 1 is given in Figure 29. Those for Run 2 are given in Appendix 6.
Figure 29: Derivative of weight (%/min) vs. temperature (ºC) for PVC sample (Run 1).

As expected the rate of weight loss with time at higher heating rates are higher. The highest peak corresponds to highest heating rate used during the experiment (100ºC/min) and the lowest peak corresponds the lowest heating rate (5ºC/min). The rate of dehydrochlorination (first peak) are observed to be higher then the rate of degradation (second peak). The rate of dechlorination is observed to be about 3 times higher then that of hydrocarbon decomposition observed in the second peak.

Kinetic Parameters $E$ and $A$

Assuming both dehydrochlorination and degradation steps of PVC degradation to be of first order reaction two sets of Activation Energy and Pre-exponential factors was determined.

The following graphs determined using Kissinger method taken for Run 1 (steps 1 and 2) of the experiment are shown in the figures (Figure 30 and Figure 31) below. The values of $E$ and $A$ are given in Table 14.
Figure 30: Determination of kinetic parameters of pyrolysis of PVC sample (Run 1: Step 1: Dehydrochlorination).

Figure 31: Determination of kinetic parameters of pyrolysis of PVC sample (Run 1: Step 2: Degradation).

There is a large difference seen in decomposition temperature range in Run 1 and Run 2 at heating rate 5 ºC/min in Step 2. With Run 1 having the range of 410.8 – 471.4 ºC and Run 2 having the range of 422.2 – 584 ºC. Observing the residue, it can be noted that Run 1 has higher residue compared to Run 2 (see Table 13 Step 2). The reason for this would be that the sample for Run 2 taken might have contaminants present or mixture of plastic sample giving raise to this behaviour.
Table 14: Kinetic parameters of pyrolysis of PVC Sample.

<table>
<thead>
<tr>
<th></th>
<th>Step 1 Dehydrochlorination</th>
<th>Step 2 Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run 1</strong>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation Energy, E: kJ/mol</td>
<td>112.64</td>
<td>207.19</td>
</tr>
<tr>
<td>Pre-exponential factor, A: s⁻¹</td>
<td>1.67 x 10⁸</td>
<td>7.76 x 10¹²</td>
</tr>
<tr>
<td><strong>Run 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation Energy, E: kJ/mol</td>
<td>104.49</td>
<td>320.96</td>
</tr>
<tr>
<td>Pre-exponential factor, A: s⁻¹</td>
<td>2.84 x 10⁷</td>
<td>1.5 x 10²¹</td>
</tr>
</tbody>
</table>

* Values of kinetic parameters from Run 1 are considered to be more accurate.

The inconsistency between the E and A values for Run 1 and Run 2 might be due to the presence of contaminants in Run 2 at heating rate of 5 °C/min.

The activation energy determined using Flynn and Wall method for Run 1 Step 1 is 132.97 kJ/mol with a standard deviation of ± 1.088 kJ/mol. This value is 18 % greater than the activation energy determined for Run 1 Step 1 using Kissinger method. The value for activation energy calculated for Run 1 Step 2 using Flynn and Wall method is 401.97 kJ/mol with a standard deviation of ± 0.210 kJ/mol. This value is about 94 % larger than that obtained using Kissinger method. This indicates that Flynn and Wall method might not be applicable to two step processes such as that of PVC decomposition.

3.4.5 Comparison of various plastic samples

Weight loss and derivative weight loss curves

Figure 32 shows typical results from the temperature ramp TGA experiments at a nominal heating rate of 5 °C/min for all four types of plastic (HDPE, LDPE, PET and PVC), as a plot of temperature versus mass. The plots for heating rates 10, 20, 50 and 100 °C/min are given in Appendix A9. The rate of mass loss vs. temperature plot (derivative weight loss curve) of a single first order reaction will appear as a well-defined peak (Gronli et al. 1999). This is shown in Figure 33 for the heating rate of 5°C/min. The plots for heating rates 10, 20, 50 and 100 °C/min are given in Appendix A9.
The order of stability for the plastic samples obtained from the experiments is HDPE > LDPE > PET > PVC. The higher the temperature required for the start of decomposition the higher is the stability. This order of stability can be observed in Figure 33, where T\text{max} peak for PVC is followed by that of PET, then LDPE and HDPE. A polymer is more stable if it has fewer branches. Hence, it can be said that decomposition of branched polymer would occur at lower temperatures than the unbranched ones. More details on the order of stability are given in Glossary.

The signal noise of data between 127 – 227 °C in Figure 33 is due to lower heating rate of 5°C/min and the small sampling interval of 0.5 s taken for measuring the weight loss in the TGA. However, at higher heating rates this clutter reduces noticeably with the data-sampling interval being the same (see Appendix 9).

The peaks for derivative of weight loss curve for LDPE, HDPE, PET and PVC can be distinguished clearly, which are important for deriving the kinetic parameters.

Figure 32: Sample mass versus temperature for LDPE, HDPE, PET, and PVC samples at a heating rate of 5°C/min.
Figure 33: Rate of mass loss versus temperature for LDPE, HDPE, PET, and PVC samples at a heating rate of 5°C/min.

The shift of $T_m$ with heating rates is presented in Figures 34 for samples studied. The shift of $T_m$ towards higher temperatures is true for all samples LDPE, HDPE, PET and PVC. This shows the dependence of decomposition temperature on heating rates. Similar results were obtained in experiments conducted by Cho et al. (1998). The data for Run 1 was used for LDPE and PVC whereas data from Run 2 was used for HDPE and PET. HDPE being more stable than other plastics has the highest peak temperatures. The peak temperature for step 2 of PVC decomposition was used for the graph. The hydrocarbon decomposition peak (step 2) for PVC occurs at similar temperatures than those of PET showing that the hydrocarbon backbone of remaining PVC is as stable as PET after chlorine removal.
Both polyethylene samples (LDPE and HDPE) were completely decomposed into volatiles in all experiments. These results are corroborated by the work of Bockhorn et al. (1998), Sorum et al. (2001), Senneca et al. (2002) and Heikkinen et al. (2004). The thermal degradation of PET showed a similar mass loss profile to that of polyethylene. The only difference is that PET consists up to 17% residue. Similar results were reported by Senneca et al. (2002) and Heikkinen et al. (2004) for PET.

For PVC two distinct peaks in the rate of mass loss profiles were observed. The decomposition of the residue hydrocarbon (second step) is similar to the decomposition of the other plastic materials and occurs within a similar temperature window. Approximately 11% of the PVC sampled remains as a solid residue. Again these measurements correspond with results reported in the literature (Zevenhoven et al. 1997; Bockhorn et al. 1998 & Heikkinen et al. 2004).

The implication of this two step decomposition of PVC for the design of chemical reactor to process mixed plastics to generate useful fuel is that a pretreatment step to remove chlorine will likely to be necessary before PVC can be mixed with other plastics for decomposition (explained in Section 3.2.2). As PVC has high chloride content (> 50%), the cost of this pretreatment is likely to be considerable.
**Activation energy (E) and pre-exponential factor (A)**

According to Sorum et al. (2001), the activation energy (required for determining the reaction kinetics), is influenced by the method used for calculating the activation energy, experimental equipments and procedures. Alternatively, activation energies can be estimated from transition-state theory. However, this method has poor reliability (Levenspiel 1999). Hence, it is best to estimate the activation energy from the experimental findings for reactions (Levenspiel 1999).

The activation energy and pre-exponential factors determined using Kissinger method (Kissinger 1957) for LDPE, HDPE, PET and PVC are given in Table 15. For LDPE and PVC the data from Run 1 was used and for HDPE and PET data from Run 2 was used. The selection of these runs was explained in Section 3.4.

**Table 15: Comparison of kinetic parameters for pyrolysis of different plastic samples.**

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>LDPE</th>
<th>PET (step 1)</th>
<th>PVC (step 1)</th>
<th>PVC (step 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy: kJ/mol</td>
<td>260.1</td>
<td>248.7</td>
<td>207.2</td>
<td>112.6</td>
<td>207.1</td>
</tr>
<tr>
<td>Pre-exponential factor: s⁻¹</td>
<td>1.0 x 10¹⁶</td>
<td>2.2 x 10¹⁵</td>
<td>1.0 x 10¹³</td>
<td>1.6 x 10⁸</td>
<td>7.7 x 10¹²</td>
</tr>
</tbody>
</table>

In Table 15 activation energy for HDPE is the highest and that for PVC is the lowest. The order of stability is HDPE>LDPE>PET>PVC.

In the literature activation energies for LDPE were found to be between 128.4 to 340.8 kJ/mole and for HDPE between 208 to 444.5 kJ/mole (Cozzani et al., 1995, Bockhorn et al., 1999, Lin et al., 1999, Sorum et al., 2001, Aguado et al., 2002, Senneca et al., 2002, Heikkinen et al., 2004). Pre-exponential factors between 10¹¹ and 10²¹ s⁻¹ was reported by different researchers for polyethylene (Cozzani et al., 1995, Gao et al., 2003). The results obtained from our experiments fall in this range for LDPE and HDPE samples. The difference in the values obtained for activation energies and pre-exponential factors are mainly due to differences in sample used (e.g. different molecular weight, various additives) and experimental conditions (Gao et al. 2003). The comparisons of activation energies obtained in literatures and from our experiment for LDPE and HDPE are given in Figure 35 and Figure 36 below respectively.
The activation energies and pre exponential factors in literature for PET were found to be between 217 – 242 kJ/mol and 1.349 – 8.33 x 10^{13} s^{-1}. The comparison of activation energies obtained from literature and our experiments are presented in Figure 37.

Figure 35: Comparison of activation energies for LDPE from literature

Figure 36: Comparison of activation energies for HDPE from literature
The activation energies for PVC, step 1 and step 2 were found to be in the range 123 – 190 kJ/mol and 250 – 299.2 kJ/mol respectively in literature. The pre exponential factors for step 1 and step 2 are in the range of 0.49 – 17.6 min\(^{-1}\) and 0.64 – 18 min\(^{-1}\) respectively. The values obtained for our experiments falls in this range for PVC samples studied. The comparison of activation energies obtained from literature and our experiments are presented in Figure 38 below.
The data for E and A obtained from literature for different plastic samples are listed in Appendix A10 and in the file named “kinetic parameters.xls” in Appendix C.

Plastics consists largely of C-C and C-H bonds and the chain branching structure might also consist of C=C double bonds. The dissociation energies of the C-C, C-H and C=C bonds are 347, 414 and 611 kJ/mole respectively. Weaker secondary bonds such as dipole forces, induction forces and dispersion forces are typically lower than 42 kJ/mole. These bond energies are responsible to provide the picture on the level of activation energies expected for the plastics decomposition. The differences in the chemical structures can alter the reactivity of different plastics. Hence, there were differences observed between LDPE, HDPE, PET and PVC samples. For instance, there are differences between LDPE and HDPE samples during thermal decomposition due to the differences in chain branching, which alters the distribution of the chemical bonds present (Sorum et al. 2001). Hence, variations in kinetic parameters are mainly due to differences in plastic characteristics (molecular weight, presence of weak links, chain branching etc.) and sometimes due to the choice of methods used in determining them (Cozzani et al. 1995).

3.5 TGA EXPERIMENTAL RESULTS AND THEIR RELEVANCE TO SOLAR THERMAL DECOMPOSITION OF PLASTICS

The experiments of Bockhorn et al. (1998) and Senneca et al. (2002) confirm that pyrolysis at higher temperatures would increase devolatilization rate, and it increases with increasing heating rate. Rapid devolatilization in an inert atmosphere is called flash pyrolysis and it is widely used for maximizing the gaseous yields from plastic decomposition (Aguado et al. 2002). This was explained in detail in Chapter 2. According to Aguado et al. (2002), there is a decrease in the yield of wax during pyrolysis when temperature increases. They also observed that this decrease in wax yield is almost linear to the temperature increase. No differences were observed between pyrolysis of LDPE and HDPE. Thus, high temperature pyrolysis supports the formation of gaseous products more rapidly. Hence, higher heating rates would promote faster pyrolysis or even flash pyrolysis.

From TGA it was observed that a complete pyrolysis of plastics is possible at temperatures as low as 500ºC (Lin et al. 1999, Sorum et al. 2001 and Senneca et al. 2002) depending on the heating rate. The lower temperatures for complete degradation
are observed for heating rates between 5 to 10 °C/min. When the heating rate is high it was found that the complete degradation takes place at temperatures around 650°C (at heating rate of 900°C/min) (Senneca et al. 2002). Lower heating rates lower the temperature at which the thermal degradation of polyethylene starts.

This shows that heating rate plays a significant role in the polymer degradation process. Hence, TGA alone might not be able to predict the true characteristics of thermal degradation processes involved in direct irradiation of concentrated solar radiation where high temperatures and heating rates are involved. The complexities on predicting the nature of reactions at high heating rates were observed by Senneca et al. (2002). The single first order reaction model used by them to describe the kinetics of plastic degradation had a good fit to the experimental curves at low heating rates (100°C/min) however the fit is lost at higher heating rates (900°C/min). Lin et al. (1999) also found that the pyrolysis temperature is the key factor for determining the desired product distribution. Hence, both temperature at which degradation takes place and the heating rates are equally important in determining the chemical kinetics involved.

Thermogravimetric analysis shows that plastic decomposition in an inert atmosphere is a single step process. The mechanism of decomposition remains the same at different heating rates and it has been suggested that the product composition might vary due to the effects of temperature alone. This means that the mechanism for plastic pyrolysis is likely to be same at high temperatures and heating rates as suggested by TGA experiments.

Solar reactors can achieve high temperatures as well as heating rates and are suitable for flash pyrolysis. A number of research have been conducted in the area of flash pyrolysis of coal and biomass samples using solar reactors (Antal et al. 1983, Beattie et al. 1983, Hofmann & Antal 1984 and Boutin et al. 2002). The advantages using solar reactors for flash pyrolysis are discussed in Chapter 4.

There are complexities on predicting the nature of reactions at high heating rates (Senneca et al. 2002). However, a single first order reaction model is found to have a good fit to the experimental curves at low heating rates (up to 100°C/min has been tested). However, proper thermal analysis at higher heating rates (> 100°C) is not possible with TGA. Lin et al. (1999) found that the pyrolysis temperature is the key factor for determining the desired product distribution. Hence, both temperature at
which decomposition takes place and the heating rates are equally important in determining the chemical kinetics involved. Proper kinetic evaluation will be required to understand the thermal decomposition of plastics under direct high temperature concentrated sunlight to understand the decomposition characteristics of plastics. Literature suggests that the process of flash pyrolysis is economic to generate useful fuel from feed such as biomass and coal. Hence, more research in sustainable ways of waste plastic decomposition looks promising.

A possible experimental set up for thermal analysis of flash pyrolysis of plastic samples using solar radiation is discussed in Appendix 11. However, before conducting experiments, it is recommended that the behaviour of plastic decomposition be modelled to be familiar with the influencing parameters of the process.

Chapter 4 discusses the use of solar energy and solar reactor design that can be used in conducting a solar thermal analysis of plastic decomposition.

3.6 CONCLUSIONS

Thermogravimetric analysis of LDPE, HDPE and PET samples confirmed literature reports that the thermal decomposition of these materials occurs in a single step. The decomposition of PVC is a two-step process. The decomposition range for polyethylene samples (LDPE and HDPE) for the heating rates between 5 – 100 °C/min were found to be between 383 – 551 °C. The decomposition temperature range for PET between 207 – 516.8 °C. For PVC the decomposition temperature range was found to be between 223 – 397 °C (1st step) and 410 – 518ºC (2nd step). This shows that the decomposition of plastics occurs in a temperature interval of about 100 – 300 ºC.

The decomposition of all plastic samples generated a large quantity of volatiles. For HDPE and LDPE samples the volatiles release was 100 %. For PET and PVC samples the volatiles release were 87.9 % and 91.5 % respectively. These values are consistent with the literature. The activation energies and pre-exponential factors measured during the study for all plastic samples were in the range found in the literature.

Further studies using thermogravimetric analysis coupled with evolved gas detection methods are recommended to determine the composition of the evolved volatiles as a function of temperature.
CHAPTER FOUR

4. DEVELOPMENT OF A SOLAR REACTOR FOR HIGH TEMPERATURE THERMOCHEMICAL PROCESS OF PLASTIC DECOMPOSITION

This chapter starts with an introduction to solar concentrators and solar reactors. It also provides a brief background to the procedure used in designing a solar reactor system followed by solar reactor concepts. Solar reactor concepts are related to studies of the coupling of a solar technology with a chemical reactor. A brief literature review of the solar thermochemical processes available for hydrogen production is also given in this chapter. The advantages of using a solar reactor in the pyrolysis of wastes such as plastics are also given.

The second section of this chapter provides the details of a solar reactor designed for the current project based on the literature and the available solar concentrator available in the University of Sydney, School of Physics.

4.1 INTRODUCTION TO SOLAR REACTORS

Any thermochemical process utilizing solar energy as its process heat is termed a solar thermochemical process. Hence, solar reactors are one of the main components of a solar thermochemical system.

Solar reactors are different from conventional reactors and their heat transfer characteristics differ significantly from conventional ones. For instance, existing energy conversion techniques to utilize heat were developed for much cooler (long wavelength) heat sources where radiation is less important (Hunt 1986). Therefore, conventional methods of heat exchange are not necessarily the best method for converting sunlight to heat (Hunt 1986). Hence, to design a solar reactor to conduct a thermochemical process, an understanding of complex interactions between solar flux, reactor geometry, optics, heat transfer, reactant feed conditions and chemical kinematics is necessary (Hunt 1986 and Palumbo et al. 2004). The complexity is further compounded due to the limitation in the number of working hours available in a solar reactor (Levitan et al. 1989). A number of solar reactor concepts have been developed depending on requirements such as temperature, processes, feed (solid, liquid, gas) etc. The design of a solar reactor is
thus always an iterative process as the physical processes involved in the thermochemical process are interrelated (Hunt et al. 1986). Solar reactor design will involve tradeoffs between performance and the cost of the reactor, requiring a balance between the two (Hunt 1986).

The following sections give a brief description of the solar concentrator technologies and solar reactor concepts available, and identifies and explains the most suitable solar reactor concept for high temperature solar thermochemical processes. Solar reactors are categorized on the basis of operating temperatures as low temperature (up to 350°C), medium temperature (>350°C and up to 800°C) and high temperature (>800°C) (Effelsberg et al. 1990). For example, in terms of waste utilization in the low temperature range, the removal of solvents and water from the waste is possible. In the medium temperature range, the carbon contents can be carbonised. In high temperature range, the material to be detoxified can be fused.

4.1.1 Solar systems used for thermochemical processes

High temperature solar concentrators are usually based on one of the three optical configurations using parabolic reflector systems (Steinfeld 2005). These configurations are: i) trough ii) tower and iii) dish. The three systems are shown in Figures 39(a), (b) and (c) (Tyner et al. 2001).

Figure 39: Parabolic solar concentrator configurations: (a) the trough system, (b) the tower system and (c) the dish system.
Detailed descriptions of these systems are given by Winter et al. (1991). For high temperature solar research (such as solar thermochemical processes), the parabolic dish and tower concentrators are typically used. This is because they have higher mean flux concentration ratios. The mean flux concentration ratio is simply the capability of solar concentrators to concentrate sunlight. The mean flux concentration ratio ($C$) over a targeted area $A$ [m$^2$] at the focal plane, normalized with respect to the incident normal beam insolation $I$ [Wm$^{-2}$], is given by Equation 4.1 (Steinfeld 2005).

$$C = \frac{Q_{\text{solar}}}{IA} \quad (4.1)$$

In the above equation, $Q_{\text{solar}}$ [W] is the solar power intercepted by the target.

The greater the concentration ratio, the greater the achievable temperature at the solar receiver (Steinfeld 2005). A detailed explanation of the concentration ratio and its relation to the temperature of receiver operation is provided by Duffie and Beckman (1991). Typical concentration ratios for trough, tower and dish systems are 100, 1000 and 10 000 respectively (Steinfeld 2005). Some typical characteristics of the three solar systems are given in Table 16.

**Table 16: Solar collector types vs. their characteristics**

<table>
<thead>
<tr>
<th>Solar Collector Type</th>
<th>Solar flux concentration ratio$^1$ (suns)</th>
<th>Peak efficiency$^2$</th>
<th>Annual efficiency$^2$</th>
<th>Annual capacity factor$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Trough Systems</td>
<td>30 – 100</td>
<td>21%</td>
<td>10 to 12%(p)</td>
<td>24% (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14 to 18%(d)</td>
<td>25 to 70% (p)</td>
</tr>
<tr>
<td>2. Tower Systems</td>
<td>500 – 5000</td>
<td>23%</td>
<td>14 to 19% (p)</td>
<td>25 to 70% (p)</td>
</tr>
<tr>
<td>3. Dish Systems</td>
<td>1000 – 10,000</td>
<td>29%</td>
<td>18 to 23% (p)</td>
<td>25% (p)</td>
</tr>
</tbody>
</table>

$^1$ Steinfeld & Palumbo (2001), $^2$ Tyner et al. (2001), d = demonstrated, p = projected, based on pilot-scale testing

Annual capacity factor refers to the fraction of the year the technology can deliver solar energy at the rated power.

suns = concentration ratio, when incident solar radiation ($I$) is taken as 1000 W/m$^2$.

For small-scale solar research experiments, dish type systems are recommended. This is because their smaller size and high achievable temperatures are suitable for small-scale research work (Diver et al. 1983). According to Duffie and Beckman’s (1991) calculations, temperatures greater than 1773 K can be attained in the receiver of a
parabolic dish concentrator. The peak efficiencies of dish type systems are higher as well (Table 16).

4.1.2 Procedure to design a solar reactor system

The basic steps involved in designing a solar reactor system are described by Palumbo et al. (2004). A brief description of those steps is given below.

Step 1: Determine the kinetics of the reactions involved

To design a reactor, it is necessary to determine the reactions involved in the chemical process. This is often done by using experimental procedures because information on chemical kinetics for specific processes is not always available and the chemical kinetics depends on the feedstock used. For example, in plastics decomposition studies, Sorum et al. (2001) have tried characterizing the pyrolysis and chemical kinetics of the components of MSW using thermogravimetric analysis (TGA). Hence, TGA is one of the methods used in determining the kinetics of the reactions involved. A general description of the procedures that can be used in estimating the chemical kinetics and testing them with the experimental data can be found in Levenspiel (1999). However for a particular reactor design only particular types of chemical reactions might be possible. Some examples of evaluation of chemical reactions suitable to be conducted in a solar reactor are given by Hunt (1986).

Step 2: Develop a reactor concept

A balance between performance and cost is important while developing a reactor concept. Some reactor concepts available for high temperature thermochemical processes are discussed in Section 4.1.3. The reactor concept should also be “scaleable” so that it can be upscaled for industrial purposes if required. Things such as mechanical boundary conditions, reactor construction materials and their availability are important for good scalability. Apart from scalability, there are other factors involved in the design of a solar reactor.

To improve the performance of a solar reactor, some of the factors that are considered are i) the design of the reactor for low activation energy to favour kinetics (Steinfeld & Palumbo 2001), ii) the design of the reactor to ensure large enthalpy change to maximize energy conversion capacity (Steinfeld & Palumbo 2001), iii) the design of the reactor for a small molar volume of products to minimize handling/storage volume and iv) the selection of a proper heat transfer fluid (HTF) if using heat exchanger type solar
reactor (Becker & Vant-Hall 1991). These factors related to chemical thermodynamics and kinetics of reaction are important because they might place constraints on the size, type, materials of construction, and modes of operation of a reactor.

**Step 3: Modelling of the reactor concept**

Modelling of the reactor concept is important to evaluate the reactor’s potential performance and to identify areas for improvements. Various methods are used in modelling the reactor concept depending upon the requirements. For example, i) models of fluid mechanics have been used to predict flow patterns in the reactor, ii) heat transfer models have been used to predict the reactor temperature, product production rate, partial pressures of products and reactor efficiency and iii) chemical kinetics models are used to understand the chemical process taking place within the reactor and to optimise the process. According to Rubin et al. (2004), experience and information obtained from modelling plays a crucial role in the parametric evaluation and design necessary for optimising the reactor and system performance. Modelling has helped them to increase the energy efficiency of the system through a better choice of materials for the construction of a high-temperature high-pressure reactor. Emphasis must be placed on the modelling of the reactor concept developed in order to obtain better performance and efficiency from the system studied. Modelling for improving the performance of solar reactors is seldom reported and hence in most high temperature solar reactors, the thermal efficiencies are less than 1% (Bilgen & Galindo 1981). Some methods to optimise process control and conditions involved in solar reactor systems are discussed by Effelsberg et al. (1990). Therefore, this step is also an important one in the development of a solar reactor system. Some examples of modelling used in solar reactor design are given in Appendix B1.

**4.1.3 Solar reactor concepts**

There are two basic approaches used to couple the solar heat source with a chemical reactor for thermochemical processing (Fischer and Tamme, 1991). They are integrated systems and separated systems.

i) Integrated systems

In an integrated system the solar thermal conversion and the endothermic process are conducted within the same vessel. Integrated systems are commonly known as receiver-reactors. There is a direct coupling of solar energy with the internal chemical processes.
Hence, the chemical reactor is integrated within the solar receiver. An example of an integrated system coupled with a fluidized bed reactor is given in Figure 40(a).

When the receiver-reactor has opaque external walls which are exposed to concentrated solar radiation, it is known as an “indirectly-irradiated” receiver-reactor. The walls transfer the absorbed heat to the chemical reactants located within the reactor cavity. The indirectly irradiated reactor concept is well-established (Epstein & Spiewak, cited in Steinfeld & Palumbo 2001). Various designs can be found in the literature depending on the type of application such as the single tube reactor used for ammonia dissociation (Luzzi & Lovegrove 1997), the tubular laminar flow reactor for biomass pyrolysis (Antal et al. 1983) and the two cavity reactor (Osinga et al, cited in Steinfeld 2005).

If the chemical reactants are directly exposed to concentrated solar radiation, those receiver-reactors are called “directly-irradiated” receiver-reactors. Only a limited number of studies have been conducted in the area of direct absorption of solar energy to conduct chemical reactions (Sasse & Ingel 1993). Sasse and Ingel (1993) argue that using the direct absorption method in the solar gasification of carbonaceous fuels such as coal, oil shale, biomass, organic wastes etc. is very favourable due to their good solar radiation absorption capabilities. One of the major advantages of the directly-irradiated reactor is its inherent high efficiency in light absorption, short time required to obtain desired reaction temperatures (Sasse & Ingel 1993) and its high temperature capabilities (Steinfeld 2005). This type of reactor operates as a direct heat exchanger (Becker & Vant-Hull 1991).

ii) Separated systems

In a separated system, the chemical reactor is separate from the solar receiver. This system and its operation are identical to systems which use fossil fuels to heat the chemical reactor. The only difference is the heat source. Instead of fossil fuel, solar energy is used to supply the heat required to operate the chemical reactor. The chemical reactor receives the required heat via a heat transfer fluid (HTF) (Effelsberg et al. 1990), which is heated by the solar receiver using heat exchangers. This type of indirectly-irradiated reactor uses heat exchanger tubes and operates as a recuperative heat exchanger (Becker & Vant-Hull 1991). An example of a separated system coupled with a fluidized bed reactor is given in Figure 40(b).
Fischer and Tamme (1991) report that integrated systems have the following advantages over separated systems:

i) it is possible to work at elevated temperatures and high energy densities as a result of radiant heating directly onto the reactants (Sasse & Ingel 1993);

ii) integrated systems eliminate the inherent losses occurring due to heat exchangers, and thus higher conversion efficiencies can be attained (Levy et al. 1989 and Becker & Vant-Hull 1991); and

iii) it is possible to generate strong temperature gradients giving rapid heating (Sasse & Ingel 1993).

Birke and Reimert (1987)’s studies on an integrated solar system comprising a circulating fluid bed reactor coupled to a solar receiver suggest that an integrated system is suitable for high temperature thermochemical gasification processes and can be upscaled to an industrial size. Muller (1987) found that integrated systems performed better compared to separated systems during his experiments on methane reformation. Other studies on the direct absorption receiver concept and its usefulness are discussed by Becker and Vant-Hull (1991). A review of technologies conducted by Edwards et al. (1995) for the use of solar energy in CO_2/CH_4 reforming show that integrated systems have the potential to be cheaper and more energy efficient than separated systems.
According to Edwards et al. (1995), separated systems involve a complicated heat transfer circuit and have greater heat losses. Birke and Reimert (1987) emphasize that experimental and theoretical work should be conducted simultaneously to achieve better understanding of the working of solar receiver-reactors. Therefore, it can be said that integrated systems are suitable for high-temperature processes such as solar thermochemical processes for fuels and chemical production. However, further studies in the use of integrated systems to conduct thermochemical processes are recommended.

4.1.4 Solar thermochemical processes for hydrogen production

Solar thermochemical processes for the production of hydrogen have been reviewed by Steinfeld (2005) and Fletcher (2001). These authors have identified four different pathways for hydrogen production using solar thermochemical processes. They are;

i) Hydrogen from water by “solar thermolysis”

ii) Hydrogen production involving metal oxide redox reactions

iii) “Carbothermal reduction” of metal oxide using carbonaceous material

iv) Hydrogen by “decarbonization” of carbonaceous materials (includes solar cracking, reforming and gasification)

Of these processes, two are suitable for the synthesis of hydrogen from carbonaceous wastes. These are:

1. “Carbothermal reduction” of metal oxide using carbonaceous material (Steinfeld, 2005) and

2. Hydrogen by “decarbonization” of carbonaceous materials (includes solar cracking, reforming and gasification) (Steinfeld, 2005)

A comprehensive review of solar thermochemical processes to generate hydrogen from carbonaceous wastes has been given by Antal et al. (1976), Epstein et al. (1994) and Steinfled (2005). Appendix B2 lists several studies that have been conducted in the generation of useful fuel such as hydrogen or synthesis gas from carbonaceous wastes. Plastic wastes are carbonaceous wastes and can be subjected to “carbothermal reduction” and “decarbonization” processes for the production of hydrogen. However, none of the literature has reported on the generation of hydrogen from waste plastics using a solar receiver-reactor, despite its immense potential. The potential of waste plastics for the generation of hydrogen is explained in Chapter 2.
4.1.5 Advantages of using solar reactors for pyrolysis of plastics

Some advantages of using solar reactors for pyrolysis of plastics are listed below.

i) Plastic decomposition at high temperatures (> 700 °C) generates large quantities of volatiles. These volatiles typically consist of gases such as H₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈, C₄H₁₀ with much lower quantities of higher-hydrocarbons. These gases formed from plastic decomposition can be used in generating hydrogen (explained in Chapter 2). Concentrated solar receiver-reactors are capable of generating high temperatures (> 700°C) and can be utilized in pyrolysis processes (Boutin et al. 2002, Hofmann & Antal 1984). Observations made by Ferrer & Lede (1999) and Hofmann & Antal (1984) show that the volatiles evolved from pyrolysis encounter a lower temperature zone of the solar reactor once they pass the focus of the solar concentrator. The advantage of this effect in volatiles passing from the hot zone to a cooler zone is a quick cooling (sometimes termed quenching). Quenching stops the high temperature gas phase reactions normally seen in pyrolysis (Hofmann & Antal 1984) by minimizing the secondary reactions and preventing the formation of higher-hydrocarbons (normally liquids). Hence, the two-temperature effect in a solar receiver-reactor can be considered as an advantage in increasing the amount of useful gases in the volatiles released. Studies on the two-temperature effect of solar reactors using biomass samples (Boutin et al. 2002, Hofmann et al. 1984) also point out this advantage. Numerical simulations conducted by Blasi (1999) on plastic decomposition suggest that the product distribution in volatiles is affected by secondary reactions at slow heating rates. Thus, the high heating rates and high temperatures achievable in solar reactors would favour larger quantities of useful gas.

ii) The heat required for the thermal decomposition process is obtained from the sun, which allows all of the raw materials (e.g. plastics, biomass) available as feedstock to generate useful gases. In conventional processes of waste pyrolysis a part of the feedstock is used as the fuel to generate the process heat required for pyrolysis. This reduces the amount of waste available for pyrolysis and in the same time causes pollution, as the waste is combusted to generate required heat. Hence, using solar energy maximizes the amount of feed available and reduces pollution at the same time.

iii) Solar fired pyrolysis reactors are capable of faster start up and shut down compared to conventional reactors (Hofmann & Antal 1984).
The use of solar thermochemical processes to decompose plastics also provides a suitable means of storing solar energy in the form of chemical energy. A major problem with utilization of solar energy is the dearth of economical storage technologies available (Hofmann & Antal 1984). Chemicals in the form of gaseous fuel make it easier for the solar energy collected to be stored and transported.

4.2 SOLAR REACTOR DESIGN BASED ON THE AVAILABLE PARABOLIC SOLAR CONCENTRATOR

The solar reactor is clearly one of the most important components of a solar thermochemical gasification system. A very simple quartz reactor, illustrated in Figure 41, was designed to enable the study of reaction kinetics and the measurement of important heat and mass transfer parameters. This quartz tube reactor is a directly irradiated solar receiver-reactor (discussed in Section 4.1). The designed reactor can be coupled with the receiver of a parabolic solar concentrator. The reactor, a quartz tube, has an inside diameter of 0.0028 m. The initial design is based on the parabolic solar concentrator dimensions obtained from the School of Physics at The University of Sydney. Details of design are given in Appendix B3. The design is based on the direct normal insolation (DNI) for the month of October for Sydney. The DNI data was obtained from the University of Sydney, School of Physics (Dey 2005). Figure 42 gives the DNI for Sydney for 24 hours in October. The related calculations are given in Appendix B4. The reactor will be located at the focal point of the parabolic solar concentrator (Figure 41, a and b).

The concentrator is capable of achieving heat fluxes of 600 kW/m² with six mirrors each of a concentration ratio of 100 (Dey 2005). Higher fluxes than this are achievable by adding more mirrors (total up to 18 mirrors) (Dey 2005). More concentrating mirrors can be added due to the parabolic dish’s modular design. Therefore, the flux levels achievable from this concentrator are between 60 to 180 W/cm². The highest temperature that this solar receiver can attain is 1800 K (approximately). The gas yields from direct solar pyrolysis at flux levels > 100 W/cm² are found to be high enough to sustain an economically viable solar coal gasification process (Beattie et al. 1983). The economics of plastic pyrolysis (which is simpler than coal pyrolysis) in a solar reactor are viable if the flux levels that can be obtained from solar reactors are significant enough. Plastic pyrolysis is simpler than coal pyrolysis because coal or biomass
decomposes in more than one step unlike plastics, which usually is a one step decomposition process. The use of solar reactors for flash pyrolysis of biomass and similar feedstock was shown to be advantageous due to rapid heating rates and the quench effect shown by the solar reactors in the literature (Hofmann & Antal 1983 and Lede et al. 2002). The modeling work done by Beattie et al. (1983), Gregg et al. (1980) and Hofmann & Antal (1983) suggests that solar flash pyrolysis can be economically competitive even in larger scale applications.

Figure 41: a) Sketch of the quartz reactor and concentrator, b) photograph of the focus of the parabolic concentrator located at the School of Physics, University of Sydney.
A quartz tube was incorporated into the design instead of a metal tube to enable direct irradiation. Commercial high temperature metal tube materials are suitable for a heat flux limited to about 200 kW/m² and an operating temperature of about 1000K (Bilgen & Galindo 1981). However, for the designed reactor, solar fluxes after concentration are about 600 kW/m² (around 1.2 kW in the 50 mm diameter spot where the sample is placed not considering the losses).

The heat losses from a solar receiver are very important. When the receiver-reactor temperatures are high, the losses have a tendency to increase as well, unless the reactor is suitably designed. In a solar environment, radiation concentration results approximately in a Gaussian distribution of energy on the receiver if all sun rays are concentrated on one aim point (Becker & Vant-Hull 1991). This is the case for the designed solar receiver-reactor. The concentrated solar radiation falls on a focus with a diameter about 50 mm. Small geometry and high concentration is equivalent to high efficiency and as a consequence high technical usefulness (Becker & Vant-Hull 1991).

The same principle was kept in mind when designing the quartz tube solar receiver-reactor.

The technology used in thermochemical processes using fossil fuel as a source to fulfil the thermal energy needs of a process is relatively mature, with several decades of
experience. However, the convection, conduction and radiation mechanism of heat transfer that occurs in a solar receiver-reactor are quite different from conventional technologies. This is because concentrated sunlight is an intense source of purely radiant energy and has quite different characteristics from the less intense and longer wavelength radiation emitted by fossil fuel combustion (Hunt et al. 1986).

4.3 CONCLUSIONS

The solar thermal pyrolysis/gasification of waste materials shows promise as a technique to generate hydrogen for a future hydrogen economy. Both solar energy and waste plastic feedstock are abundantly available in Australia.

An integrated solar receiver-reactor is likely to be suitable for the high-temperature conversion of waste plastics to a synthesis gas containing hydrogen. There are few reports in the literature of the development of such solar receiver-reactors.

A simple solar receiver-reactor for bench scale experiments on pyrolysis/gasification of wastes such as plastics can be easily constructed. Further, research on the potential use of solar receiver reactors for the decomposition of wastes to useful gases is recommended, with the inclusion of modeling tools for a better understanding of the solar thermochemical process.
CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

The focus of this research was on solar thermal energy applications, where solar energy is used to provide the heat required for carrying out thermochemical processes involved in generating a synthesis gas containing hydrogen from waste plastics. Research into; i) solar concentrators for high temperature thermochemical processes, and ii) pyrolysis and gasification of waste plastics were separately reported in the literature (details in Chapter 3 and 4). In this study the aim was to bring these fields of research together to design a solar receiver-reactor suitable for the production of hydrogen via the thermal decomposition of waste plastics. Thermal decomposition of plastics is simpler than for biomass fuel and hence plastics were used as a model fuel in understanding decomposition behaviour.

To achieve this aim, some important parameters affecting the process of solar thermal decomposition of plastics to useful fuel were identified through the literature and the thermogravimetric analysis (TGA) of selected plastic samples. Finally, on the basis of the experimental results and available knowledge base, a suitable solar reactor system was designed. The conclusions and recommendations drawn from the research are given in the following sections.

5.1 CONCLUSIONS

i) Thermal decomposition studies of thermoplastics such as polyethylene have been conducted at temperatures up to 900 °C. Literature reports show an increase in hydrogen and lighter hydrocarbon gases in the product gas composition of polyethylene plastic pyrolysis at temperatures greater than 700 °C. This product gas with light hydrocarbon gases (methane, ethane, ethene, propane, propene, butane and butene) and hydrogen can be steam gasified to produce hydrogen. However, few studies are focused on generation of hydrogen from the decomposition products of plastics.

ii) Thermogravimetric analysis of LDPE, HDPE and PET samples confirmed literature reports that the thermal decomposition of these materials occurs in a single step. TGA also confirmed that the decomposition of PVC is a two-step process. The first step in PVC decomposition is related to the release of hydrogen chlorine (HCl) and the second step is the release of hydrocarbons from the polymer backbone. This suggests that a pre
treatment to remove HCl is necessary if PVC is to be mixed with other plastics for decomposition.

iii) The stability of the plastic samples depends on their structure. The stability was found to be in the order HDPE>LDPE>PET>PVC, as HDPE had the highest decomposition temperature range and PVC the lowest.

iv) The solar thermal pyrolysis/gasification of waste materials shows promise as a technique to generate hydrogen for a future hydrogen economy. Both solar energy and waste plastic feedstock are abundantly available in Australia. An integrated solar receiver-reactor is likely to be suitable for the high-temperature conversion of waste plastics to a synthesis gas containing hydrogen. The capability of a solar receiver-reactor to achieve high temperatures and heating rates provides an advantage in the decomposition of plastics into useful gases containing hydrogen. There are few reports in the literature of the development of such solar receiver-reactors. Integrated solar receiver-reactors with direct irradiation have several advantages such as cleaner operation, faster start up/shut down and two-temperature effect (advantageous for higher gaseous products from plastic decomposition).

5.2 RECOMMENDATIONS

i) Further studies of plastic decomposition behaviour using thermogravimetric analysis coupled with evolved gas detection methods are recommended. These methods would provide additional information on the composition of evolved gases as a function of temperature enabling better understanding of the plastic decomposition mechanisms.

ii) Experiments on pyrolysis/gasification of waste such as plastics using a solar receiver-reactor are recommended to understand the nature of the decomposition of plastics in concentrated sunlight. However, before conducting the experiments, modeling of the solar thermochemical process would be necessary.

iii) The required background on the characteristics of high temperature plastic decomposition was established in this study through literature and experiments. A simple solar receiver-reactor was designed. However, modeling the thermochemical process occurring in the solar receiver-reactor will enable the identification of the most important parameters which govern the mechanism of plastic decomposition.
6. REFERENCES


Dey, C 2005, pers. comm., The University of Sydney, School of Physics, 15 Sept.


APPENDICES

Appendix A1: Reaction systems

Reacting systems can be divided into two types:

1. Homogeneous reacting systems
2. Heterogeneous reacting systems

In case of homogeneous reaction systems, the rate of reaction is determined by measuring isothermally the decrease in concentration of reactant or the increase in concentration of the product (Hatakeyama & Quinn 1999). The rate of reaction for homogeneous systems is given by the following equation.

\[
\frac{dx}{dt} = -kf([x])
\]  \hspace{1cm} (A1)

where,

\([x]\) = concentration of the reactant

\(k\) = the rate coefficient (s\(^{-1}\))

The rate coefficient ‘\(k\)’ is given by Arrhenius Equation.

\[k = Ae^{\frac{-E}{RT}}\]  \hspace{1cm} (A2)

Here,

\(A\) = frequency factor (also called as pre-exponential factor), (s\(^{-1}\))

\(E\) = activation energy of the reaction (kJ/mol)

\(R\) = gas constant = 8.314 J/mol.K

\(T\) = temperature (K)

References:

Appendix A2: Derivation of Kissinger’s equation

Kissinger’s method was originally proposed for calculating kinetic parameters for a reaction of type “Solid → Solid + Gas” using DTA experiments (explained in Section 3.1.4) (Hatakeyama & Quinn 1999). This method assumes that the reaction rate is described by equation 3.5 (rate of reaction for heterogeneous reacting systems, solid-state). Hence, Kissinger method is derived by taking the time derivative of equation 3.5.

The additional assumptions made in this method are (Hatakeyama & Quinn 1999):

1. The maximum in DTA curve occurs at the same temperature as the maximum reaction rate. DTA (Differential Temperature Analysis), which takes the difference in temperature between the sample and reference over the reaction interval (i.e. $\Delta T/\Delta t$).

2. Reaction proceeds at a rate which varies with temperature. Therefore, the position of DTA peak is a function of heating rate.

Hence, from the variation of peak temperature with the heating rate, ‘E’ can be calculated for any value of ‘n’. The advantage of Kissinger method (constant heating rate method) is that it is applicable to variable heating rate data as well. None of the other constant heating rate methods is applicable to variable heating rate data (Salin & Seferis 1993). In Kissinger Method, heating rate is not necessarily a constant and has been successfully used for variable heating rates (Salin & Seferis 1993). However, time and temperature derivatives are no longer linearly related. The variable heating rate methods has been applied to determine reaction kinetics of complex polymer systems (Salin & Seferis 1993).

The maximum reaction rate occurs when:

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = 0 \quad (A3)$$

When heating rate is constant, time and temperature derivatives of weight loss rate are linearly related. As a result, data can be plotted as a function of time or temperature, and then analysed using Kissinger Method (Salin & Seferis 1993).

Hence, differentiating Equation 3.5 (Section 3.1.3) with respect to time.
\[ \frac{d}{dt} \left( \frac{d\alpha}{dt} \right) = \frac{d}{dt} \left( Ae^{\frac{E}{RT}} (1-\alpha)^n \right) \]  \hspace{1cm} (A4)

At DTA peak, the above equation would be:

\[ \frac{d}{dt} \left( Ae^{\frac{E}{RT_m}} (1-\alpha)_m^n \right) = 0 \]  \hspace{1cm} (A5)

The subscript ‘m’ denotes maximum. \( T_m \) is the maximum rate temperature. From equation A5 the following equation is obtained when solving.

\[ \frac{E\beta}{RT_m} = An(1-\alpha)_m^{n-1} e^{\frac{E}{RT_m}} \]  \hspace{1cm} (A6)

\( T_m \) = Maximum-rate temperature

Equation A6 can be rearranged giving the following equation.

\[ \frac{\beta}{T_m^2} = \frac{R}{E} An(1-\alpha)_m^{n-1} e^{\frac{E}{RT_m}} \]  \hspace{1cm} (A7)

Now taking natural logarithmic on both sides.

\[ \ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{R}{E} An(1-\alpha)_m^{n-1} e^{\frac{E}{RT_m}} \right) \]  \hspace{1cm} (A8)

Or,

\[ \ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{R}{E} An(1-\alpha)_m^{n-1} \right) - \frac{E}{T_m} \]  \hspace{1cm} (A9)

The Kissinger method assumes that the product \( n(1-\alpha)_m^{n-1} \) is independent of \( \beta \). Therefore a plot of \( \ln (\beta/ T_m^2) \) versus \( 1/T_m \) gives the activation energy for each degradation step (Nam & Seferis 1991).

Now for 1st order reaction.

\( n = 1 \)

Hence, for 1st order reactions putting \( n = 1 \) in Equation A9 would give us.
\[
\ln \left( \frac{\beta}{T_m^n} \right) = \ln \left( \frac{RA}{E} \right) + \frac{E}{RT_m} \quad \text{(A10)}
\]

This method for 1st order reaction has been used by various researchers to determine E and A (Teng et al. 1997 and Stolarek & Ledakowicz 2001).

Hence, \( E \) is estimated from the slope of the plot of \( \ln (\beta/T_m^2) \) versus \( (1/T_m) \). And \( A \) is estimated using the intercept of the same plot.

Kissinger method assumes that (Hatakeyama & Quinn 1999),

\[
\frac{d\alpha}{dt} = \left( \frac{\delta \alpha}{\delta t} \right)_T + \left( \frac{\delta \alpha}{\delta T} \right) \left( \frac{dT}{dt} \right) \quad \text{(A11)}
\]

Therefore, the size and shape of the sample holder and the dilution of the sample do not affect the reaction rate. When the heating rate is constant, time and temperature derivatives of weight loss rate are linearly related (Salin & Seferis 1993). As a result of this data can be plotted as a function of time or temperature, and then analysed using the above stated method (Kissinger method).

References:


Appendix A3: Proximate & ultimate analysis of plastic samples and their heating values

A more detailed table is given in the compact disk at the end of the thesis in the excel file: Proximate and Ultimate analysis.xlsx

Table 17: Proximate and Ultimate Analysis of Plastics and their Heating Values compiled from literature

**LDPE and HDPE**

<table>
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<tbody>
<tr>
<td></td>
<td>LDPE</td>
<td>HDPE</td>
<td>Polyethylene</td>
<td>HDPE</td>
</tr>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile Matter (wt%)</td>
<td>100.0</td>
<td>100.0</td>
<td>99.97</td>
<td>98.57</td>
</tr>
<tr>
<td>Fixed-C (wt%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.03</td>
<td>1.40</td>
</tr>
<tr>
<td><strong>Ultimate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>85.7</td>
<td>86.1</td>
<td>85.67**</td>
<td>83.73**</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>14.2</td>
<td>13.0</td>
<td>14.3**</td>
<td>15.52**</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>0.05*</td>
<td>0.90*</td>
<td>0.0**</td>
<td>0.00**</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.05</td>
<td>0.0</td>
<td>0.0**</td>
<td>0.01**</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0**</td>
<td>0.00**</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.03**</td>
<td>0.00**</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>46.6</td>
<td>46.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>-</td>
<td>-</td>
<td>44.6</td>
<td>42.20</td>
</tr>
</tbody>
</table>

* obtained by mass balance

** dry basis
**PVC and PET**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>PVC</td>
<td>PET</td>
<td>PET</td>
<td></td>
</tr>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile Matter (wt%)</td>
<td>92.3</td>
<td>94.82</td>
<td>88</td>
<td>86.83</td>
</tr>
<tr>
<td>Fixed-C (wt%)</td>
<td>7.5</td>
<td>5.19</td>
<td>12</td>
<td>13.17</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>&lt; 0.05</td>
<td>0.00</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.18</td>
<td>0.74</td>
<td>-</td>
<td>0.61</td>
</tr>
<tr>
<td><strong>Ultimate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>40.1</td>
<td>42.52**</td>
<td>62.8**</td>
<td>62.51**</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>5.1</td>
<td>6.16**</td>
<td>4.3**</td>
<td>4.19**</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>0.65</td>
<td>0.00**</td>
<td>32.79**</td>
<td>33.30**</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>-</td>
<td>0.00**</td>
<td>0.07**</td>
<td>0.00**</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>-</td>
<td>0.00**</td>
<td>-</td>
<td>0.00**</td>
</tr>
<tr>
<td>Cl (wt%)</td>
<td>53.8</td>
<td>51.31**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn* (wt%)</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>-</td>
<td>0.01**</td>
<td>0.04**</td>
<td>-</td>
</tr>
<tr>
<td><strong>HHV (MJ/kg)</strong></td>
<td>21.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>LHV (MJ/kg)</strong></td>
<td>-</td>
<td>22.26</td>
<td>23.2</td>
<td>22.07</td>
</tr>
</tbody>
</table>

* Sn is a stabilizer in PVC, ** dry basis

**References:**


Appendix A4: Data for various plastic samples

LDPE Sample: PETLIN LD N125 Y

Molecular weight

Mw = 185 x 100000

Mn = 18 x 100000

Note: The GPC testing is very sensitive, data may vary from one machine to another.

This data was obtained from Mr G Wotherspoon from Swift and Company Ltd.,
Australia through email on 16 August 2005.

Physical Appearance and Properties

Appearance & Odour: Colourless opaque granules. No odour.

Melting/softening point: Melts in a range about 104-115ºC.

Boiling point and vapour pressure: Decomposes before boiling at 100kPa.

Volatile materials: No specific data. Expected to be low at 100ºC.

Flashpoint: Not flammable.

Flammability limits: Not applicable. This product is not flammable.

Specific gravity: 0.915-0.935 (bulk density 0.55 – 0.63)

Solubility in water: Insoluble

Corrosiveness: Not corrosive

Decomposition Temperature: > 330ºC

Autoignition Temperature: > 360ºC

Vapour Pressure: Expected to be very low at 20ºC

Additional Information can be obtained from the manufacturers: Swift and Company
Ltd., 1st Floor, 372 Wellington Road, Mulgrave, VIC 3170, Ph (03) 8544 3100.
**HDPE Sample: HD5148**

Physical Appearance and Properties

Appearance: Translucent pellets or powder.

Melting point: 107 – 130°C

Boiling point: None allocated

Melt Index @ 190 °C, 2.16 kg: 0.85 g/10 min

Vapour pressure: None allocated

Specific gravity: None allocated

Flash Point: None allocated

Flammability limit LEL: None allocated

Form: Solid

Density range: 0.910 – 0.970 g/cm³

Water solubility: Negligible

Tensile Strength at Yield: 28 MPa

Elongation at break: 600 %

Secant Modulus: 700 MPa

Ingredients

<table>
<thead>
<tr>
<th>Ingredients Name</th>
<th>CAS</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>9002-88-4</td>
<td>98 – 100 %</td>
</tr>
<tr>
<td>Proprietary Additives</td>
<td></td>
<td>0 – 2 %</td>
</tr>
</tbody>
</table>
**Appendix A5: Q600 TGA Equipment Specifications**

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace Type</td>
<td>Horizontal, Bifilar Wound</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>Ambient to 1500°C</td>
</tr>
<tr>
<td>Temperature Calibration</td>
<td>Metal Standards (1 to 5 points)</td>
</tr>
<tr>
<td>Heating rate – Ambient to 1000°C</td>
<td>0.1 to 100°C/min</td>
</tr>
<tr>
<td>Heating rate – Ambient to 1500°C</td>
<td>0.1 to 25°C/min</td>
</tr>
<tr>
<td>Auto-Stepwise TGA</td>
<td>Included</td>
</tr>
<tr>
<td>Thermocouples</td>
<td>Platinum/Platinum-Rhodium (Type R)</td>
</tr>
<tr>
<td>Furnace Cooling</td>
<td>Forced Air (1500 to 50°C in &lt;30 min)</td>
</tr>
<tr>
<td>Sample Capacity</td>
<td>200 mg (350 mg including sample holder)</td>
</tr>
<tr>
<td>Balance Design</td>
<td>Dual Beam Horizontal</td>
</tr>
<tr>
<td>Balance Sensitivity</td>
<td>0.1 µg</td>
</tr>
<tr>
<td>Calorimetric Accuracy/Precision</td>
<td>± 2% (based on metal standards)</td>
</tr>
<tr>
<td>DTA Sensitivity</td>
<td>0.001°C</td>
</tr>
<tr>
<td>Mass Flow Controller with Automatic Gas Switching</td>
<td>Included</td>
</tr>
<tr>
<td>Vacuum</td>
<td>To 7 Pa (0.05 torr)</td>
</tr>
<tr>
<td>Reactive Gas Capability</td>
<td>Included – separate gas tube</td>
</tr>
<tr>
<td>Sample Pans</td>
<td>Platinum: 40 µL, 110 µL</td>
</tr>
<tr>
<td></td>
<td>Alumina: 40 µL, 90 µL</td>
</tr>
<tr>
<td>Dual Sample TGA</td>
<td>Included</td>
</tr>
</tbody>
</table>
Appendix A6: Weight loss and derivative weight loss curves for various plastic samples at different heating rates

*Weight loss curves at various heating rates for selected plastic samples for Run 2*

**LDPE**

![Weight loss curve for LDPE](image)

*Figure 43: Weight (%) vs. temperature (°C) for LDPE sample at various heating rates (Run 2)*

**HDPE**

![Weight loss curve for HDPE](image)

*Figure 44: Weight (%) vs. temperature (°C) for HDPE sample at various heating rates (Run 2)*
Figure 45: Weight (%) vs. temperature (°C) for PET sample at various heating rates (Run 2)

Figure 46: Weight (%) vs. temperature (°C) for PVC sample at various heating rates (Run 2)
Derivative weight loss curves at various heating rates for selected plastic samples for Run 2

**LDPE**

![Graph](Image)

*Figure 47: Derivative of weight (%/min) vs. temperature (ºC) for LDPE sample (Run 2)*

**HDPE**

![Graph](Image)

*Figure 48: Derivative of weight (%/min) vs. temperature (ºC) for HDPE sample (Run 2)*
**PET**

Figure 49: Derivative of weight (%/min) vs. temperature (ºC) for PET sample (Run 2)

**PVC**

Figure 50: Derivative of weight (%/min) vs. temperature (ºC) for PVC sample (Run 2)
Appendix A7: Random chain scission mechanism of polyethylene plastic


initiation:

\[ \text{P} \xrightarrow{k_1} \text{R}_p^* + 2 \text{R}_p^* \]

(propagation:

\[ \text{R}_p^* \xrightarrow{k_2} \text{R}_p^* + \text{CH}_2=\text{CH}_2 \]

hydrogen transfer, intramolecular

\[ \text{R}_p^* \xrightarrow{k_3} \text{R}_p^* + \text{R}_s^* \]

\[ \text{R}_s^* \xrightarrow{k_4} \text{R}_p^* + \text{CH}_2=\text{CH}_2 + \text{CH}_3=\text{CH}_2 \]

hydrogen transfer, intermolecular

\[ \text{R}_p^* + \text{R}_q^* \xrightarrow{k_5} \text{CH}_3=\text{CH}_2 + \text{CH}_3=\text{CH}_2 \]

termination:

\[ \overset{\dot{\text{CH}}_2}{} + \overset{\dot{\text{CH}}_2}{} \xrightarrow{k_6} \overset{}{\text{CH}_2=\text{CH}_2} \]
Appendix A8: Flynn and Wall method

Flynn and Wall method is a quick method used in the determination of activation energy from thermogravimetric data and can also be used in testing the constancy of $E$ with respect to $\alpha$ and $T$. Flynn and Wall method is widely used in polymer decomposition studies (Ballice 2001, Liu et al. 2003).

Assumptions used in Flynn and Wall method (Flynn & Wall 1966) are:

1. $A$, $f(\alpha)$ and $E$ are independent of $T$.

2. $A$ and $E$ are independent of $\alpha$.

Equation for heterogeneous reaction is given by Equation FW1.

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT \quad \text{(FW1)}$$

 Integrating both sides of Equation FW1.

$$\int_0^\alpha \left( \frac{d\alpha}{f(\alpha)} \right) = \left( \frac{A}{\beta} \right) \int_{t_0}^T e^{-\frac{E}{RT}} dT \quad \text{(FW2)}$$

$$F(\alpha) = \left( \frac{AE}{\beta R} \right) \left( \frac{e^{-\frac{E}{RT}}}{E/RT} \right) + \int_{-\infty}^{-\frac{E}{RT}} e^x \frac{dx}{x} \quad \text{(FW3)}$$

where, $x = \frac{E}{RT}$

$$F(\alpha) = \left( \frac{AE}{\beta R} \right) p \left( \frac{E}{RT} \right) \quad \text{(FW4)}$$

Taking natural logarithmic of both sides of Equation FW4, we obtain:

$$\ln[F(\alpha)] = \ln \left( \frac{AE}{R} \right) - \ln \beta + \ln[p \left( \frac{E}{RT} \right)] \quad \text{(FW5)}$$

Doyle (1962) has found that for $\frac{E}{RT} \geq 20$, $\ln[p \left( \frac{E}{RT} \right)]$ may be approximated using the following equation. This approximation is termed Doyle approximation (Flynn 1983).

$$\ln[p \left( \frac{E}{RT} \right)] \approx -5.3305 + 1.052 \left( \frac{E}{RT} \right) \quad \text{(FW6)}$$
In Equation FW6, \(-20 > \left( \frac{E}{RT} \right) > -60\)

Combining Equations FW5 and FW6 we obtain the following equation.

\[
\ln[F(\alpha)] \cong \ln (\frac{AE}{R}) - \ln \beta - 5.3305 + 1.052 \left( \frac{E}{RT} \right) \quad (FW7)
\]

Therefore, if a series of experiments are performed at different heating rates \(\beta_1, \beta_2, \beta_3, \ldots, \beta_j\) and \(T_{k,j}\) is the temperature at which fraction of conversion, \(\alpha_k\), was reached at heating rate, \(\beta_j\), then the plot of \(\ln \beta_j\) vs. \((1/T_{k,j})\) for each of \(k\) fractions of conversion, \(\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_k\) will yield \(k\) isoconversional lines whose slope is given below (Flynn 1983),

\[
\text{slope} \cong 1.052 \frac{E}{R} (\alpha = \alpha_k) \quad (FW8)
\]

Thus, the activation energy at any degree of conversion, \(\alpha_k\), is calculated from a plot of \(\ln \beta_j\) vs. \((1/T_{k,j})\). The linearity of the slope for three or more values of \(\beta\) is a test of the constancy of \(E\) with respect to temperature, and any change in \(E\) with respect to conversion may be observed by comparison of slopes at various \(\alpha_k\).

Corrections for Doyle approximation when \(\frac{E}{RT}\) falls outside the interval \(-20 > \left( \frac{E}{RT} \right) > -60\) is given by Flynn (1983).

**References:**


Appendix A9: Weight loss and derivative weight loss curves for various plastic samples

*Heating rate 10 °C/min*

![Weight loss curve for heating rate 10°C/min](image1)

![Derivative weight loss curve for heating rate 10°C/min](image2)

**Figure 51:** Weight loss curve for heating rate 10°C/min

**Figure 52:** Derivative weight loss curve for heating rate 10°C/min
Heating rate 20°C/min

Figure 53: Weight loss curve for heating rate 20°C/min

Figure 54: Derivative weight loss curve for heating rate 20°C/min
Heating rate 50°C/min

Figure 55: Weight loss curve for heating rate 50°C/min

Figure 56: Derivative weight loss curve for heating rate 50°C/min
Heating rate 100ºC/min

Figure 57: Weight loss curve for heating rate 100ºC/min

Figure 58: Derivative weight loss curve for heating rate 100ºC/min
## Appendix A10: Kinetic parameters for various plastics from literature

### Table 18: Kinetic evaluation of polyethylene

<table>
<thead>
<tr>
<th>Type of PE</th>
<th>E (kJ/mole)</th>
<th>Log A</th>
<th>c (wt %)</th>
<th>n</th>
<th>DTG Peaks (Tmax, °C)*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>340.8</td>
<td>21.98</td>
<td>96.3</td>
<td>1</td>
<td>472 (10)</td>
<td>Sorum et al. (2001)</td>
</tr>
<tr>
<td>LDPE</td>
<td>128.4</td>
<td>0.42</td>
<td>n/a</td>
<td>n/a</td>
<td>468 (3-9)</td>
<td>Lin et al. (1999)</td>
</tr>
<tr>
<td>LDPE</td>
<td>262 ±21</td>
<td>1.17 x 10^{16} (s^{-1})</td>
<td>n/a</td>
<td>1</td>
<td>500-600</td>
<td>Aguado et al. (2002)</td>
</tr>
<tr>
<td>LDPE (Transparent, film)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>491 (20)</td>
<td>Heikkinen et al. (2004)</td>
</tr>
<tr>
<td>HDPE (Hard, shredded)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>493 (20)</td>
<td>Heikkinen et al. (2004)</td>
</tr>
<tr>
<td>HDPE</td>
<td>260 ±23</td>
<td>1.20 x 10^{16} (s^{-1})</td>
<td>n/a</td>
<td>1</td>
<td>500-600</td>
<td>Aguado et al. (2002)</td>
</tr>
<tr>
<td>HDPE</td>
<td>445.1</td>
<td>29.1 (log s^{-1})</td>
<td>98.2</td>
<td>1</td>
<td>479 (10)</td>
<td>Sorum et al. (2001)</td>
</tr>
<tr>
<td>HDPE</td>
<td>277.8</td>
<td>0.85 (min^{-1})</td>
<td>n/a</td>
<td>n/a</td>
<td>470 (3-9)</td>
<td>Lin et al. (1999)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>268 ±3</td>
<td>17.78</td>
<td>n/a</td>
<td>0.8</td>
<td>430 – 480 (this is temp range not DTG, in this case)</td>
<td>Bockhorn et al. (1999a)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>290.0</td>
<td>46.74</td>
<td>n/a</td>
<td>1</td>
<td>465 (5)</td>
<td>Senneca et al. (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>485 (20)</td>
<td>The data analysis was made for heating rate 100°C/min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>525 (100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>595 (900)</td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>248.0</td>
<td>1.1 x 10^{17} (s^{-1})</td>
<td>0.3</td>
<td></td>
<td>450 – 500 (this is temp range not DTG, in this case)</td>
<td>Cozzani et al. (1995)</td>
</tr>
</tbody>
</table>

* The heating rates (°C/min) corresponding to the DTG Peak Temperature are given within ( ) next to the Tmax.

n/a = not available in related literature

**References:**


Appendix A11: Proposed thermal analysis set up for studying flash pyrolysis of plastics using concentrated solar energy

Experimental Set Up and Experiments

The experimental set up for conducting studies on flash pyrolysis of plastics using solar energy is presented in the Figure 59.

Figure 59: Proposed scheme of the experimental set-up for studying plastic decomposition.

Solar Reactor

A quartz tube reactor was designed for coupling with the parabolic solar concentrator available in the School of Physics (Details presented in Section 4.2). The plastic pellet will be placed inside this transparent quartz tube reactor (Appendix B4) and adjusted at the focus of the concentrator. The base for holding the sample is made from quartz as well. The reactor tube can be decoupled for inserting the sample inside it. The brackets holding the reactor can be moved via a motor. This allows the reactor to be moved which enables the sample to be placed directly on the focus of the solar concentrator. The electric motor can be controlled using a computer (Buic 2005). The reactor is continuously fed by a flow of nitrogen.

Inert gas

Inert gas nitrogen can be used for rapidly diluting and cooling the volatiles evolved from the sample during decomposition. This rapid diluting minimizes the secondary reactions of volatiles after they separate from the substrate. Hence, the exact composition of the volatiles can be determined.
**Product Recovery Device**

One end of the reactor tube can be connected to a metal hose which goes into a filter made of quartz fibre and a bed of packed zeolite particles. These devices (filters and zeolite) traps condensable species in the volatiles (Boutin et al. 2002). The quantity of condensable trapped in these filters can be calculated from the weight measured before and after the gases are passed. A similar technique has been used in gas analysis by Boutin et al. (2002) and Mastral et al. (2003). The gaseous products formed during the reaction can be recovered in gas-sampling bags. The composition of these gaseous products diluted in the carrier gas nitrogen can be determined using gas chromatography. This gas analysis technique has been used in applications such as identification of polymer additives, evaluation of thermal stability/quality assurance, study of degradation kinetics of polymeric materials and evaluation of structural/chemical kinetics (Serrano et al. 2005). The condensates collected in the filters can be analysed using mass spectroscopy or gas chromatography.

**Video Camera and Infra Red Camera**

A video camera can be used for recording the overall pyrolysis process and the time taken. With the use of a recorder it is possible observe the sample located at the focus of the concentrator. The focus of the solar concentrator cannot be viewed by naked eyes as it can cause severe damage. Use of video recorder has been employed in combustion and gasification properties studies of plastic particles to observe and record time taken for the process (Zevenhoven et al. 1997).

An Infra Red (IR) Camera can also be used along side with the normal video camera. This will provide additional details such as temperatures and temperature gradients observed in the sample versus time. The use of IR camera is essential as it is not possible to measure surface temperatures of the sample situated inside the quartz tube reactor. IR cameras have been successfully used for thermal imaging of heat fluxes inside a reactor where thermocouples cannot be used. This technique using IR cameras for studies of plastic decomposition has not been used in the past.

**References:**


Buie, D 2005, pers. comm. 18 Feb.


## Appendix B1: Examples of computer models used for modelling of solar thermochemical processes

Table 19: Computer models used for simulation of biomass/waste gasification processes

<table>
<thead>
<tr>
<th>No.</th>
<th>Gasification/Other $H_2$ generation process</th>
<th>Models</th>
<th>Laboratory where the model was developed</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| 1.  | ASPEN Plus simulator | Lawrence Livermore National Laboratory (LLNL)  
Ref: Wallman et al. (1998) | Model encompasses both pre-treatment and gasification.  
Provides means of evaluating the overall process with respect to major inputs and outputs and changes in operating strategies.  
Model is based on chemical equilibrium calculations. |
| 2.  | Two computer codes for calculation involving the chemistry of gasification | Lawrence Livermore National Laboratory (LLNL)  
Ref: Thorsness & Rozsa and Thorsness & Sherwood, cited in Gregg et al. (1980) | One code assumes equilibrium chemical compositions and is used when quick estimates are needed. For temp. above 1000 K this code is believed to be reasonably valid. This code is used when quick estimates are required.  
The second code takes into account the temp. dependency of chemical reaction rates and gives more accurate predictions in low temperature regions. |
| 2.  | Heat transfer modelling for solar receiver reactor system for solar gasification using low expanding fluidized bed | DLR (Stuttgart, Germany) and Weizmann Institute (Germany)  
Ref: Sasse & Ingel (1993) | A detailed heat transfer model that has been developed for  
Work described, an attempt to evaluate the effect of the optical properties of the particles and their temperature dependence, upon the solar driven chemical reaction was carried through. The particles investigated were oil shale particles |
| 3.  | Computational Fluid Dynamics (CFD) general-purpose code CFDS-FLOW3D was used for simulation. Simulation is used for design and optimisation of a novel high temperature solar chemical reactor used for solar thermal water splitting and reduction of metal oxide | Paul Scherrer Institute (Switzerland)  
Ref: Meier et al. (1996) | General purpose CFD code CFDS-FLOW3D was used to simulate the fluid flow and heat transfer in particle-cloud reactor.  
Modeling is done in several steps to and the model validated with the the fluid flow calculations with experimental data. |
| 4.  | NASA CET-85 | Solar Research Facilities Unit, Weizmann Institute of Science, Israel  
Ref: Kogan & Kogan | The thermochemical equilibrium calculations of the (C, $H_2$) thermochemical water splitting system was done using this computer program. |
5. Numerical simulation of the reactor performance

<table>
<thead>
<tr>
<th>Princeton University, NJ, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref: Antal et al. (1983) and Hofmann &amp; Antal (1984)</td>
</tr>
</tbody>
</table>

Model developed to simulate heat transfer within the solar reactor. The simulation uses finite difference technique to solve for particle, fluid, and wall temperatures of each of the n segments (reactor tube sub-divided for modelling) into which the reactor length was divided. Simulation also takes into account chemical reactions.

### References:

## Appendix B2: Solar thermochemical processes

Table 20: Types of solar thermochemical process studied in regards to decomposition of various wastes (recent work at the top under each heading).

<table>
<thead>
<tr>
<th>Waste or fuel (feedstock)</th>
<th>Temperature range (K)</th>
<th>Catalyst (if used)</th>
<th>Remarks</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbothermal Reduction of Metal Oxides using carbonaceous materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO with CH₄</td>
<td>Up to 1200</td>
<td></td>
<td>Solar tower with CPC</td>
<td>Steinfeld et al. (1995)</td>
</tr>
<tr>
<td><strong>Hydrogen by decarbonization of carbonaceous materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Solar Reforming</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>Up to 1373</td>
<td>ZnO</td>
<td>Infrared furnace</td>
<td>Matsunami et al. (1999)</td>
</tr>
<tr>
<td>Cellulose (Wood shavings)</td>
<td>973 - 1023</td>
<td>Pt/Al₂O₃</td>
<td></td>
<td>Rustamov et al. (1988)</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>Up to 1233</td>
<td>1. Nickel, 2. Ru on S.S, 3. Rh/Pt on Alumina and 4. 0.5% Rh on Alumina</td>
<td>Solar tower with best results obtained for 0.5% Rh on Alumina</td>
<td>Levitan et al. (1989)</td>
</tr>
<tr>
<td><strong>Solar Gasification</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal (Peat, lignite, bituminous &amp; anthracite)</td>
<td>1200 - 1500</td>
<td></td>
<td>Solar tower system with CPC. The syn gas was subjected to water gas shift reaction to generate hydrogen.</td>
<td>Zedtwitz &amp; Steinfeld (2003)</td>
</tr>
<tr>
<td>Gaseous</td>
<td>673 - 773</td>
<td>Fluidized</td>
<td>Solar tower with CPC</td>
<td>Meier et al.</td>
</tr>
<tr>
<td>Material</td>
<td>Temperature Range</td>
<td>Catalyst</td>
<td>Description</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Hydrocarbons (CH₄ and C₄H₁₀)</td>
<td></td>
<td>bed with Al₂O₃ and catalyst Ni/Al₂O₃ or Co/MgO</td>
<td>used. Experiments to produce filamentous carbon from hydrocarbons and CO.</td>
<td>(1999) and Steinfeld et al. (1997)</td>
</tr>
<tr>
<td>Coal (anthracite)</td>
<td>1273 - 1373</td>
<td>ZnO</td>
<td>Experiments were conducted using an electric heater.</td>
<td>Tsuji et al. (1996)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1050 - 1600</td>
<td></td>
<td>Work on both opaque and transparent fluidised bed reactors with bead materials: pure tabular alumina and crushed platinum or alumina catalyst. 4.2 m solar furnace used. Details given in Murray and Fletcher (1994).</td>
<td>Murray and Fletcher (1994)</td>
</tr>
<tr>
<td>Biomass (lignin, sawdust etc.)</td>
<td>773 - 973</td>
<td></td>
<td>Windowed free fall reactors have been developed and used, which act as a cavity receivers for the focussed radiant energy and provide means for direct use of radiation to rapidly pyrolyze the entering biomass.</td>
<td>Antal et al. (1983)</td>
</tr>
<tr>
<td>Sub-bituminous</td>
<td>Below 975</td>
<td>Solar tower used.</td>
<td></td>
<td>Gregg et al.</td>
</tr>
</tbody>
</table>
coal, activated carbon, coke and mixture of coal

References:


Appendix B3: Proposed solar reactor design

The box is an Aluminum box of given dimensions. There are 2 holes of 28 mm diameter at two sides exactly opposite each other at given heights (see diagram). The bottom of the box is open. The curved parabolic mirror which forms the bottom should be located as shown.

Reactor Design
Scale = 1:4
All dimensions in mm

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13 Sept 2005

Cross Section at X-X looking towards the back.
Details of materials used are given in the following figure with the basic heat loss mechanism from the receiver-reactor.

The basic loss mechanism from a receiver-reactor (adapted from Becker & Vant-Hull 1991)

concentrated energy $\Rightarrow$ atmospheric attenuation + spilled + intercepted energy

intercepted energy $\Rightarrow$ reflected + absorbed energy

absorbed energy $\Rightarrow$ reradiated + convected + conducted + delivered energy

delivered energy $\Rightarrow$ sensible energy (local temperature increase)

local temperature increase $\Rightarrow$ absorber rise + wall + fluid film + local heat transfer fluid temperature increase

heat transfer fluid temperature $\Rightarrow$ inlet temperature + sensible temperature

Reference:

Preliminary quartz tube reactor design

ESTIMATED Temperatures
Quartz tube inner 1000°C
Da of the Tube 25 mm
Length of the tube 250 mm
Thicknes of tube 1.5 mm

FIG: Quartz tube reactor
Appendix B4: Solar receiver-reactor design calculations

Design parameters

Concentration ratio per mirror (C) = 100
No. of mirrors = 6
Mirror reflectance = 0.88
Outer diameter of the quartz tube = 0.025 m
Thickness of the tube = 0.002 m
Reflectance of the receiver surface (i.e. quartz tube surface) = 0.06
An approximate value for reflectance can also be determined using Fresnel equation (Becker & Vant-Hull 1991) which is given by, reflectance = [(n-1)^2]/[(n+1)^2], where ‘n’ is the refractive index.
The refractive index for quartz (n) = 1.5442, giving the reflectance for quartz tube = 0.05 (approximately).
Emissivity (E) of quartz tube = 0.96 (a conservative figure)
Ambient temperature (T_amb) = 300 K
Stefan Boltzmann constant = 5.67 x 10^-8 W/m^2K^4
Spot diameter of the concentrated solar radiation (d) = 0.05 m

Calculation of the convective heat transfer coefficient on the outside surface of the quartz tube reactor

Assumptions:
Natural convection occurs on the outside surface of the quartz tube reactor
The flow is laminar and the reactor tube is oriented horizontally.
Surface temperature of the reactor tube is 1000 K
For horizontal bodies and laminar flow the convection coefficient is given as:

h = Nu * k / x
k = thermal conductivity (W/mK)
Nu = 0.5 (Gr Pr)^0.25 with 10^4 < Gr Pr < 10^9
Nu = Nusselt number
Gr = Grashoff number
Pr = Prandtl number
Gr = g*β*(T_wall – T_ambient)*x^3/ϑ^2
g = acceleration due to gravity (m/s^2)
β = bulk expansion coefficient (1/K)
T_wall = surface temperature of the wall (K)
T_amb = ambient temperature (K)
x = diameter of the reactor tube (in this case), (m)
ϑ = kinematic viscosity (m²/s)

Pr = ϑ/α

α = thermal diffusivity (m²/s²)

**For reactor design**

g = 9.8 m/s²

β = 3.01 x 10⁻¹ 1/K (for quartz)

T_wall = 1000 K (assumed)

T_amb = 300 K

x = 0.025 m

α = 2.74 x 10⁻⁵ m²/s²

ϑ = 1.89 x 10⁻⁴ m²/s (for air)

Gr = 9.04 x 10⁵

Pr = 6.89 x 10⁻¹

Nu = 14

k = 2.89 x 10⁻² W/mK (for quartz)

h = 16.3 (W/m)

The excel file for the related calculation is provided in the compact disk (Appendix C) attached to the end of the thesis under the file name: *solar reactor calculation.xls*

**References:**

Appendix C: Compact disc with data and other files

Please read the “Read me.doc” file for information regarding the files and folders contained in the CD.
LIST OF FIGURES

Figure 1: Plastic waste in Australia in 2003 (Source: PACIA). ........................................... 5

Figure 2: Physical and chemical changes occurring during the thermal decomposition of thermoplastics, adapted from Beyler and Hirschler (2001). ................................. 6

Figure 3: General polymer decomposition mechanism, adapted from Beyler and Hirschler (2001). ............................................................................................................... 7

Figure 4: Product composition of pyrolysis of polyethylene at temperature range 643 - 703 K, adapted from Walendziewski and Steininger (2001). ........................................ 12

Figure 5: Product composition of pyrolysis of polyethylene at temperature range 773 - 973 K, adapted from Williams and Williams (1999). .................................................... 12

Figure 6: Product composition of pyrolysis of polyethylene at temperature range 913 - 1123 K, adapted from Mastral et al. (2003). .............................................................. 13

Figure 7: Yield (wt. %) of some product components as a function of temperature (°C) for the pyrolysis of polyethylene (Kaminsky, 1985). ................................................. 14

Figure 8: Variation of H2 and CH4 production with pyrolysis and gasification temperature, adapted from Mastral et al. (2003). .............................................................. 16

Figure 9: Differences in molecules of (a) LDPE and (b) HDPE, adapted from Bibee (1990). ...................................................................................................................... 29

Figure 10: Polyethylene monomer. ...................................................................................... 29

Figure 11: Vinyl chloride monomer (VCM). ....................................................................... 32

Figure 12: Polyethylene terephthalate (PET) monomer. ..................................................... 35

Figure 13: SDT Q600 TGA Furnace Configuration (Source: www.tainstruments.com). ................................................................................................................................. 38

Figure 14: SDT Q600 TGA equipment showing sample and reference pans, thermocouples and purge gas inlet to the furnace. ...................................................... 40

Figure 15: Weight (%) vs. temperature (°C) for LDPE sample at various heating rates (Run 1). ..................................................................................................................... 41

Figure 16: Derivative of weight (%/min) vs. temperature (°C) for LDPE sample (Run 1). .................................................................................................................. 45
Figure 33: Rate of mass loss versus temperature for LDPE, HDPE, PET, and PVC samples at a heating rate of 5°C/min. ................................................................. 65

Figure 34: Decomposition temperature dependence on the heating rate for various plastics (LDPE, HDPE, PET and PVC). ................................................................. 66

Figure 35: Comparison of activation energies for LDPE from literature .................. 68

Figure 36: Comparison of activation energies for HDPE from literature ............... 68

Figure 37: Comparison of activation energies for PET from literature ............... 69

Figure 38: Comparison of activation energies for PVC from literature ............... 69

Figure 39: Parabolic solar concentrator configurations: (a) the trough system, (b) the tower system and (c) the dish system. ................................................................. 74

Figure 40: a) The Integrated and b) Separated Systems concept for Solar Energy/Reactor Linkage, adapted from Edwards et al. (1995). ......................... 79

Figure 41: a) Sketch of the quartz reactor and concentrator, b) photograph of the focus of the parabolic concentrator located at the School of Physics, University of Sydney. ............................................................................................................. 83

Figure 42: Direct normal insolation (W/m²) for October (Sydney, Australia)........ 84

Figure 43: Weight (%) vs. temperature (ºC) for LDPE sample at various heating rates (Run 2) .................................................................................................................... X

Figure 44: Weight (%) vs. temperature (ºC) for HDPE sample at various heating rates (Run 2) .................................................................................................................... X

Figure 45: Weight (%) vs. temperature (ºC) for PET sample at various heating rates (Run 2) .................................................................................................................... XI

Figure 46: Weight (%) vs. temperature (ºC) for PVC sample at various heating rates (Run 2) .................................................................................................................... XI

Figure 47: Derivative of weight (%/min) vs. temperature (ºC) for LDPE sample (Run 2) ........................................................................................................................... XII

Figure 48: Derivative of weight (%/min) vs. temperature (ºC) for HDPE sample (Run 2) ........................................................................................................................... XII
Figure 49: Derivative of weight (%/min) vs. temperature (°C) for PET sample (Run 2)
..............................................................................................................................XIII

Figure 50: Derivative of weight (%/min) vs. temperature (°C) for PVC sample (Run 2)
..............................................................................................................................XIII

Figure 51: Weight loss curve for heating rate 10°C/min............................................ XVII

Figure 52: Derivative weight loss curve for heating rate 10°C/min ......................... XVII

Figure 53: Weight loss curve for heating rate 20°C/min.......................................... XVIII

Figure 54: Derivative weight loss curve for heating rate 20°C/min .......................... XVIII

Figure 55: Weight loss curve for heating rate 50°C/min ......................................... XIX

Figure 56: Derivative weight loss curve for heating rate 50°C/min ........................... XIX

Figure 57: Weight loss curve for heating rate 100°C/min ...................................... XX

Figure 58: Derivative weight loss curve for heating rate 100°C/min .......................... XX

Figure 59: Proposed scheme of the experimental set-up for studying plastic decomposition...........................................................................................................XXIII
LIST OF TABLES

Table 1: Heating rate and decomposition temperature range for polyethylene decomposition in TGA. ................................................................. 30

Table 2: Heating rate and decomposition temperature range for polyvinyl chloride plastics decomposition in TGA experiments.......................................................... 34

Table 3: Heating rate and decomposition temperature range for PET plastics in TGA experiments............................................................................................................. 36

Table 4: Plastic samples used for TGA experiments.......................................................... 37

Table 5: Heating rate and time taken for experiments.................................................... 39

Table 6: Thermal decomposition of LDPE sample at various heating rates. ............... 42

Table 7: Kinetic parameters for pyrolysis of LDPE sample........................................ 48

Table 8: Activation energy (kJ/mol) obtained for LDPE sample at different conversions and heating rates (Run 1)................................................................. 49

Table 9: Data for thermal decomposition of HDPE sample.............................................. 51

Table 10: Kinetic parameters of pyrolysis of HDPE sample........................................ 53

Table 11: Thermal degradation of PET sample at various heating rates......................... 55

Table 12: Kinetic parameters of pyrolysis of PET sample............................................. 57

Table 13: Thermal decomposition of PVC using TGA.................................................. 58

Table 14: Kinetic parameters of pyrolysis of PVC Sample........................................... 63

Table 15: Comparison of kinetic parameters for pyrolysis of different plastic samples. 67

Table 16: Solar collector types vs. their characteristics ................................................... 75

Table 17: Proximate and Ultimate Analysis of Plastics and their Heating Values compiled from literature.........................................................................................V

Table 18: Kinetic evaluation of polyethylene............................................................... XXI

Table 19: Computer models used for simulation of biomass/waste gasification processes .................................................................................................................XXV

Table 20: Types of solar thermochemical process studied in regards to decomposition of various wastes (recent work at the top under each heading).........................XXVII

XL
GLOSSARY

Activation Energy (E) – energy that must be overcome for a chemical reaction to occur

Devolatilization – rapid release of volatiles (mainly hydrocarbons) during heating of plastics

DSC Curve – differential scanning calorimetry curve (heat flux curve based on the difference in heat absorbed by reference and the sample pan)

DTA Curve – differential thermal analysis curve (temperature difference curve based on the reference and the sample pan temperature difference)

DTG Curve – differential thermogravimetric curve also known as the differential weight loss curve

Higher heating value (HHV) – Maximum amount of energy that can be obtained from the combustion of a fuel, including the energy released with steam produced during combustion

Homopolymer – it is a polymer formed from only one type of monomers

Lower heating value (LHV) – Same as HHV, but without including the energy contained in the steam

Order of stability – Thermal stability of polyolefins is strongly affected by branching, with linear polyethylene most stable and polymers with branching less stable. The order of stability is illustrated as follows:

\[
\begin{align*}
    & \text{H}  \quad \text{H}  \\
    & \text{C} \quad \text{C}  \\
    & \text{H}  \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
    & \text{H}  \quad \text{CH}_3  \\
    & \text{C} \quad \text{C}  \\
    & \text{H}  \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
    & \text{H}  \quad \text{R}  \\
    & \text{C} \quad \text{C}  \\
    & \text{H}  \quad \text{R} \\
\end{align*}
\]

\[
\begin{align*}
    & \text{H}  \quad \text{R}  \\
    & \text{C} \quad \text{C}  \\
    & \text{X}  \quad \text{Z} \\
\end{align*}
\]

where R is any hydrocarbon group larger than a methyl group.

Pre-exponential factor (A) – it is also sometimes termed frequency factor, it indicates how many collisions between reactants have the correct orientation to lead to the products

Proximate analysis – Analysis that gives the moisture content, amount of volatiles, fixed carbon and ash present in a sample
TG Curve – thermogravimetric curve also known as the weight loss curve

Ultimate analysis – Analysis that gives the elemental composition of a sample

References: