Tertiary Recycling of Waste Plastics: An Assessment of Pyrolysis by Microwave Radiation

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EXECUTIVE SUMMARY

In 2008, according to the United States Environmental Protection Agency (EPA), Americans generated more than 254 million tons of municipal solid wastes (MSW) with plastics comprising 12.1% of the total amount. Of this waste component, only 6.8% was recycled.

The traditional ways of handling non-recycled plastic wastes are landfilling and incineration. It can be argued however that neither of those approaches are adequate solutions. Landfills require large areas which may be challenged by increasing population. Furthermore, there is no energetic incentive to sequester these polymers for decades. A better approach to land filling is energy recovery via incineration, which uses the heat of combustion to generate electricity. However, the necessity for considerable pollution control, the difficulty of burning plastics, and their chemical composition suggest that some type of recycling is more valuable.

Tertiary recycling (also known as feedstock recycling) is the processing of waste into fuels or basic chemicals. Several methods of plastic feedstock recycling have been investigated in recent years (e.g. depolymerization, catalytic cracking/reforming) with the goal of either recovering original monomers or, more commonly oils and waxes.

Also known as thermolysis, pyrolysis is a process of thermal and chemical decomposition, generally leading to smaller molecules. As MSW plastics are predominately thermoplastics, they serve as a good feedstock for this process. Pyrolysis is conducted in an oxygen depleted environment. It can be operated at a wide range of temperatures in order to target specific products (typically between 400-700 ° C for predominant liquid yield; > 700 ° C for predominant C1- C3 light hydrocarbon). There is also considerable literature on different reactor designs and the influence of catalysis.

Over the past ten years, more attention has been given to microwave powered pyrolysis. The use of microwaves initiates localized, molecular heating and therefore under certain conditions serves as more efficient reactor. However, since thermoplastics like polyethylene (PE) and polyethylene terephthalate (PET) have poor dielectric properties they are not particularly useful for microwave heating unless exposed with microwave absorbent materials. When pulverized carbon is mixed with shredded or pelletized plastics, the added carbon pyrolysis absorbs the electromagnetic radiation and transports the energy to the plastics via conduction.

Although literature and process data from microwave pyrolysis applications report a high oil/wax product yield, there are concerns that its energy requirement, and subsequent carbon footprint, make this process inefficient and undesirable as an environmentally acceptable. A life cycle assessment (LCA) was performed using pilot conditions from a commercial process of microwave pyrolysis. By using the exit gas stream as a feed for an internal generator, *Climax Global Energy*'s process significantly decreases its carbon footprint by not drawing electricity from the grid. In a comparative analysis given a set of assumptions, this process was found to have an auspicious carbon footprint versus another tertiary recycling process, gasification and F-T synthesis, and versus the heat extracted from waste-to-energy.

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1. INTRODUCTION

1.1 Thesis Overview

The following paper discusses the conversion of waste plastics into useful materials via microwave radiation. More specifically, this report investigates microwave pyrolysis (MWP) as an alternate tertiary recycling process for waste plastics.

The remainder of the initial section will provide the motivation for this project. The second section introduces the current options of waste plastic management and the advantages/disadvantages of each possibility. The third section discusses the pyrolysis of waste plastics in general as a tertiary recycling process. This leads into a discussion about microwave pyrolysis. Fundamentals of MWP are addressed as well as a discussion on the current status and research. The fifth section is a life cycle analysis (LCA) of a commercialized microwave pyrolysis process. Finally, there is a concluding section with comments about potential future work.

1.2 MSW Background

Municipal Solid Waste (MSW) is comprised of items that are used in everyday life and then thrown away. It includes paper, yard trimmings, and food scraps and many other durable and non durable goods.

MSW is generated in staggering quantities in the United States, to the extent that the magnitude of the tonnage is disputed. According to the United States Environmental Protection Agency (US EPA), in their annual report on the generation and disposal of MSW, American generated about 250 million tons of trash in the year 2008. Comparatively, according to a recent

survey of 'The State of Garbage in America" conducted by *BioCycle* and the Earth Engineering Center at Columbia University, Americans generated an estimated 413 million tons of MSW in the same year. Despite this discrepancy, all analyses agree that the tonnage of MSW in America is increasing. There is more MSW generated per year than ever previously recorded. Using the conservative total MSW estimates from the US EPA, annual MSW generation has more than doubled since the 1970s and increased by more than 21% in the last 20 years as shown in figure 1.1 below.

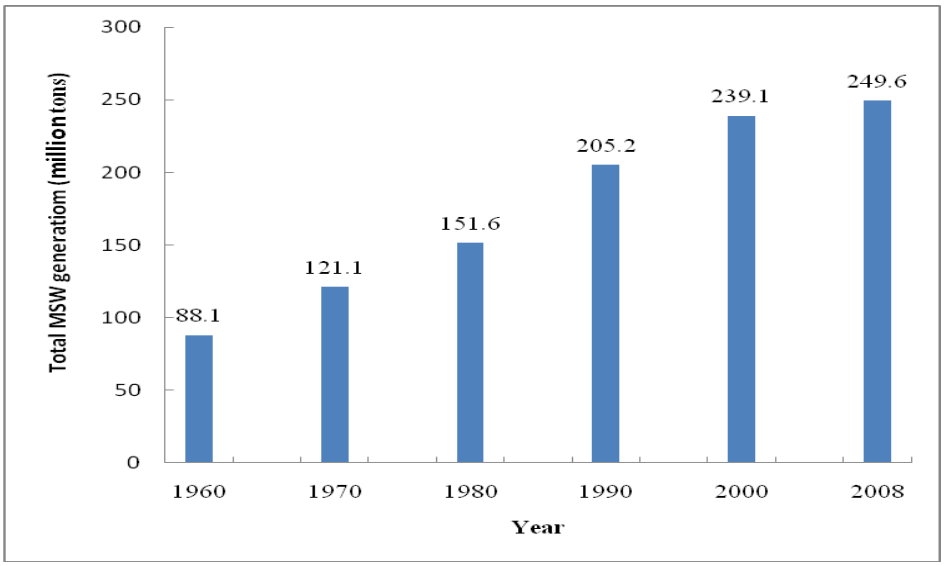


Figure 1.1. Total Annual MSW Generation for Select Years [Data: US EPA, 2009]

Furthermore, not only has the total mass of MSW increased throughout the years, but the generation per capita has maintained a more or less constant level over the past 20 years as shown in figure 1.2.

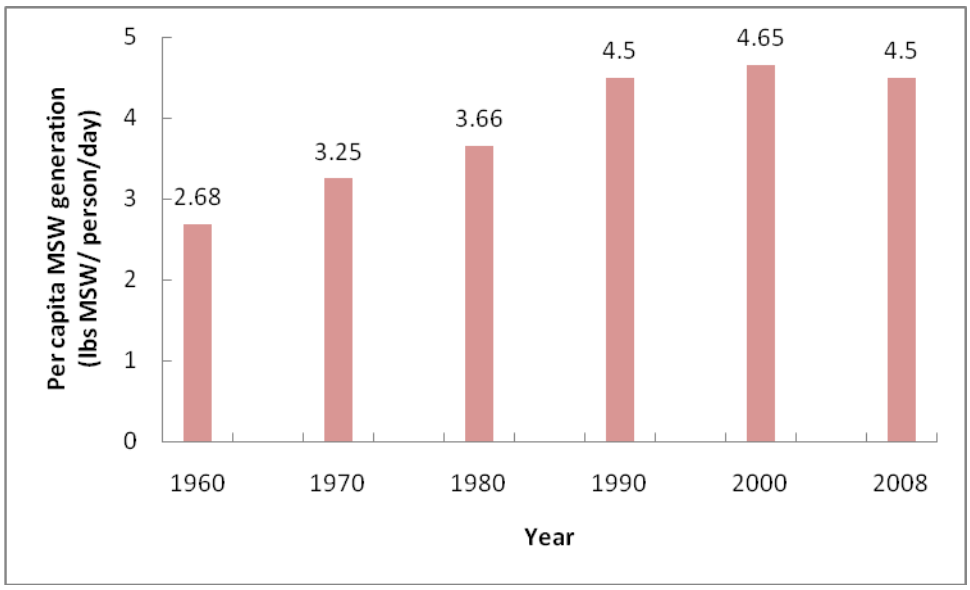


Figure 1.2. Per Capita Generation of MSW in the US [US EPA, 2009]

About 12% of all MSW consists of plastics. These are materials which cover a range of a plastics, most notably polyethylene terephthalate (PET) and high density polyethylene (HDPE). These plastics can be found in domestic products such as bottles for milk, soda, and detergent.

1.2.1 Plastics

Plastics are a generic group of materials composed of high molecular weight chains with a carbon backbone. These materials are typically defined by its monomer, which is a smaller compound that is linked together with its repeated units to form the material. Plastics have different properties depending on the different polymers. They are common in everyday life as most plastics have the same attributes. They are very resistant to chemicals, are thermal and electric insulators, are light weight, and can be processed into varying thickness and shapes (ACC 2009).

Plastics can be categorized by various criteria including chemical composition, chemical structure, stiffness, the type of application, and processing method. Of these, the most common categories are chemical composition and structure. Chemical composition classifies plastics by the type of monomer and polymerization (e.g. polyolefins, polyesters, polycarbonates and polyurethanes). Chemical structure meanwhile is associated with bonding linearity, branching, and cross-linking. Another categorization-which is considered is discussed in recycling is thermoplastics vs. thermosets, as shown in figure 1.3 below.

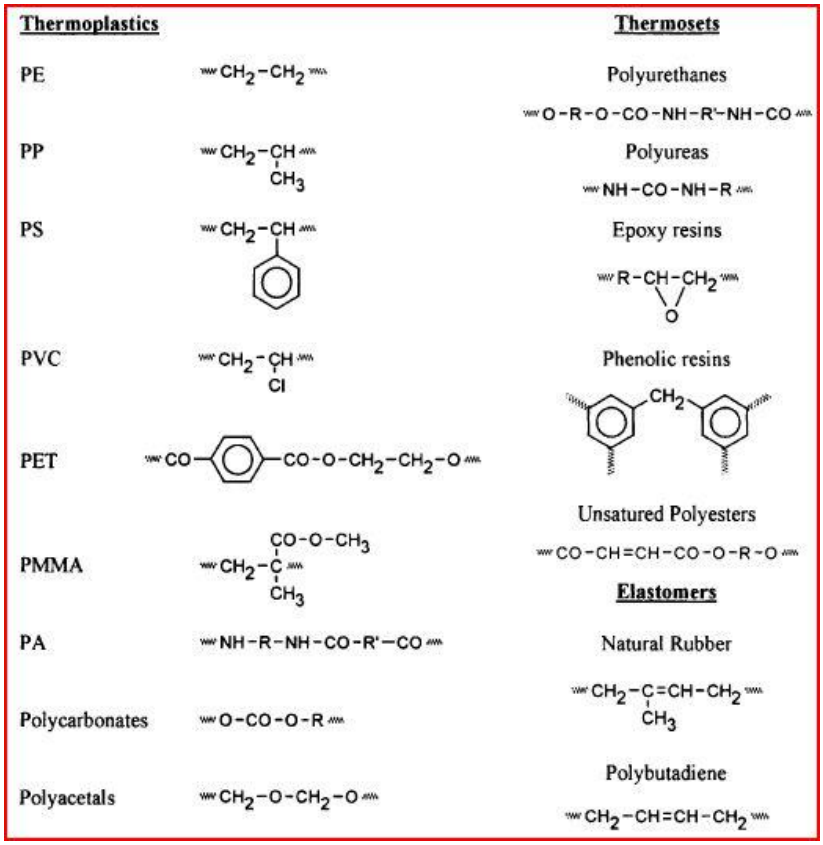


Figure 1.3. Examples of Thermoplastics and Thermosets

[Adapted from *Feedstock Recycling of Plastic Wastes.* J. Aguado]

Thermoplastics, which are most commodity plastics like HDPE or PET, soften when heated since there is little bonding when the molecular chains. Thermosets meanwhile, which are plastics found in circuit boards and epoxy resins, thermally decompose while heating (which has implications later in this paper). In general however, according to the EPA, the vast majority (99%) of MSW plastics are thermoplastics. A typical MSW plastic stream can be considered as the following (% by tonnage/mass) 48% HDPE not from milk bottles, 26% PET from soda bottles, 21% unpigmented HDPE from milk bottles, 2% PET not from soda bottles and, 2% PVC.

1.3 Plastic Waste Management

Given the importance of plastics in everyday life and the large quantities with which it is disposed, it is critical to evaluate how plastics are managed as they are accumulated in municipal solid waste streams. Primary (mechanical) recycling, which reuses plastic in a similar application as its initial use provides the highest value but is by and large uncommon, only 6.8% of all plastics according to the US EPA. In fact, it has been estimated that only 15-20% of all MSW plastics can be effectively recycled by conventional mechanical recycling technologies--i.e. sorting/grinding/washing/and extrusion (Kaminsky 2006). Beyond this level, plastics are mingled with and contained by extraneous materials such as soil, dirt, aluminum foils, papers labels, and food remnants. 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 and therefore cannot be recycled and reused (PACIA 2006).

In the following section, options of plastic waste management are discussed.

2. PLASTIC WASTE MANAGEMENT METHODS

2.1 Recycling

In general, materials recycling can be divided into three (or four) general levels: primary, secondary, and tertiary. Primary recycling processes materials into a product with physical and chemical characteristics similar to the original product. Secondary recycling turns waste into products with characteristics that are less demanding than the original. Tertiary recycling (also known as feedstock recycling) - the processing of waste into fuels or basic chemicals (Hind 1999). It should be noted that incineration is sometimes considered recycling where the heat recovery is considered a product in the same way a monomer or oil would. In this context of this report, incineration is considered different than recycling.

Primary recycling of post-consumer plastics packaging gained momentum in the United States during the 1980s as a result of state level bottle deposit programs, which produced a consistent supply of returned PET bottles. HDPE milk jugs were added to the deposit programs later that decade. Since then, plastic recycling has grown steadily (Hind 1999).

It has been estimated that about 60 percent of the U.S. population (~148 million people) have access to a plastics recycling program. The first step is collection of post-consumer use. This commonly exists in two forms: (1) curbside collection - where consumers place designated plastics in a special bin to be picked up by a public or private hauling company and (2) drop-off centers - where consumers take their recyclables to a centrally located facility. Most curbside programs collect both PET and HDPE (Aguado 1999).

To make sorting and thus recycling easier, the American Society of Plastics Industry developed a standard marking code to help consumers identify and sort the main types of plastic. These types and their most common uses are shown in table 2.1 below.

Table 2.1. Main Types of Plastics and Common Uses [Adapted: American Plastics Council]

Number	Type of plastic	Common packaging uses	Amount recycled in 2004	Common recycled use
#1	Polyethylene terephthalate (PETE or PET)	Beverage and food bottles and containers	22 percent	Textiles, including clothing and carpet; film, food, and beverage containers; luggage.
#2	High density polyethylene (HDPE)	Beverage and food bottles and containers; dish and laundry detergent bottles; grocery, trash and retail bags	26 percent	Nonfood containers, including laundry detergent, shampoo, conditioner, and motor oil bottles; plastic lumber, pipe, buckets, crates, flower pots, film, recycling bins, floor tiles.
#3	Polyvinyl chloride (PVC or vinyl)	Food and non-food packaging; medical tubing; siding, window frames, floor tiles and carpet backing	less than 1 percent	Packaging, loose-leaf binders, decking, paneling, gutters, mud flaps, film, floor tiles and mats, electrical equipment, traffic cones, garden hoses, mobile home skirting
#4	Low density polyethylene (LDPE)	Dry cleaning, bread and frozen food bags, squeezable bottles	less than 1 percent	Shipping envelopes, garbage can liners, floor tile, plastic lumber, film, compost bins, trash cans
#5	Polypropylene (PP)	Food and medicine containers and bottles	3.2 percent	Automobile battery cases, signal lights, brooms, brushes, ice scrapers, oil funnels, bicycle racks, rakes
#6	Polystyrene (PS)	Cups, plates, cutlery, compact disc jackets, egg cartons	(data not available)	Thermometers, light switch plates, thermal insulation, egg cartons, vents, rulers, license plate frames, foam packing and dishware
#7	Other (often polycarbonate (PC))	Reusable water bottles, beverage and food bottles	(data not available)	Bottles, plastic lumber

After collection, the plastics are delivered to a material recovery/recycling facility (MRF) for sorting into single resin streams to increase product value. The sorted plastics are then baled to reduce shipping costs to reclaimers. During this, reclamation plastics are chopped into flakes, washed to remove contaminants and sold to end users to manufacture new products (e.g. bottles, containers, clothing, carpet, plastic lumber) (Aguado 1999).

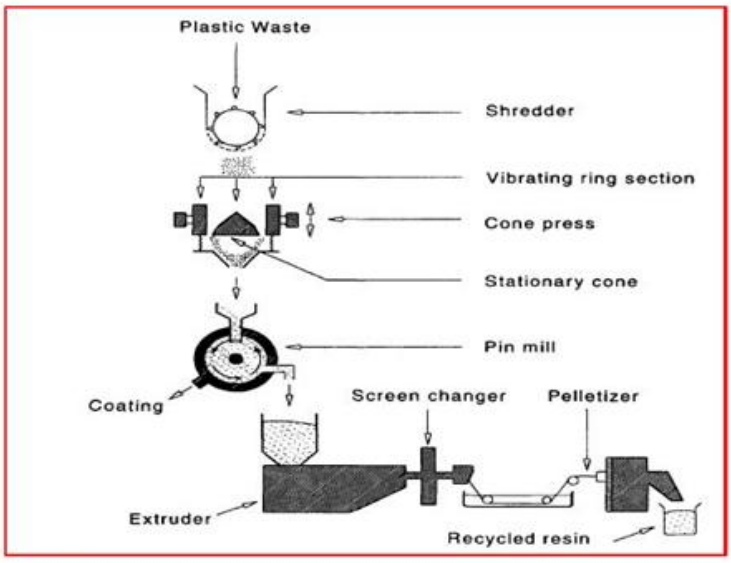


Figure 2.1. Typical Reclamation Process of Plastic Recycling [Adapted from Aguado 1999]

2.2 Landfilling

If plastics are not recycled, by and large they will end up being transported to landfills for long term storage. According to the EPA, the United States has more than 3,000 active landfills and over 10,000 municipal landfills. In a typical landfill, based on average MSW streams it is estimated that plastics will make up 7% of the landfill waste by weight, and 18% by volume (Decker 1997). Unlike several waste components sent to landfills, MSW plastics will not release any methane or light gases for energy recovery. Therefore, there is no immediate impact from landfilling waste plastics; a longer term impact is assessed by comparing land use or the amount of crude oil that is saved by recycling previous plastics as opposed to using crude oil as a feedstock for the production of new polymers.

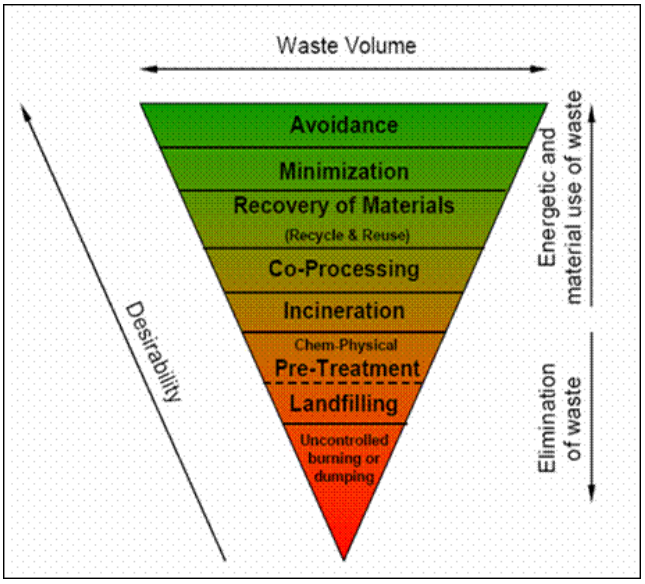


Figure 2.2 Hierarchy of Waste Management [Adapted from EnviroTech.com]

It is also worth noting the "waste management pyramids" as shown in figure 2.2 above. According to US EPA, sustainability means meeting the needs of the present generation without compromising the ability of future generations to meet their needs. The bottom line of environmentally sustainable solid waste management is to reduce the amount of trash for final disposal and then dispose of it in the environmentally safest manner. The most desirable and sustainable way of managing materials to if possible avoid and minimize if possible, and if not possible, then to recycle or reuse.

2.3 Waste-to-Energy

As of 2010, there are 87 waste-to-energy facilities in the United States, in which incineration of waste is used to produce energy for power and heating (NYT). However, this method of energy recovery has received much social resistance due to the atmospheric pollution created by combustion process (Garcia et al. 2003). While MSW plastics have excellent fuel value (on the order of 40-45 MJ/kg for HDPE and PET), in practice plastics are not used as WTE

feedstock, in part because of their recyclability, and since they are difficult to burn due at a controllable rate without additional processing. The result of the uncontrolled combustion is localized areas of oxygen deficiency-which in return affect the release products of incomplete combustion (Kamisky 2006). Incineration of waste plastic of certain plastics has been linked in the past to the formation of dioxins, nitrogen oxides and chlorinated compounds, especially in the case of polyvinyl chloride (PVC) which is ~57 wt% chlorine. Additionally, the generation of chlorine (as Cl_2 or HCl) from combustion in waste-to-energy facilities presents a major operating problem as it causes significant corrosion in the boiler system which increases operating costs and decreases the electrical output (Krause 1987).

2.4 Feedstock/Tertiary Recycling

The concept of feedstock recycling is based on thermal and sometime thermal and catalytic breakdown of polymer structure yielding monomers, oil fractions, aromatic fractions, synthesis crude or synthesis gas (Buekens 2006). "Thermal cracking" is usually considered to be pyrolysis-which will be discussed in further detail in the next section.

Feedstock recycling can be considered complementary to mechanical recycling since it is has the sensitivity to handle plastic waste streams that are unsorted and contaminated. There are several routes that can be considered which include, but are not exclusive to the chemical depolymerization, thermal decomposition, gasification, catalytic cracking and reforming, and hydrogenation, as shown in figure 2.3 below.

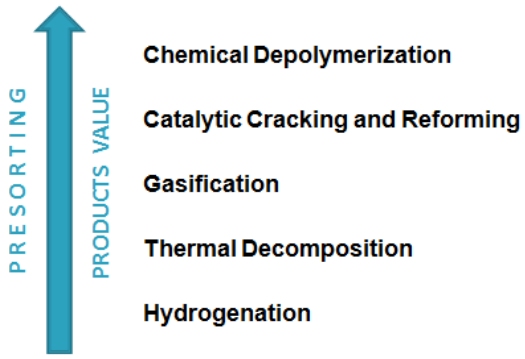


Figure 2.3. Different Forms of Tertiary Recycling

While chemical depolymerization (original monomer recovery) is the highest product value, the feed for this process requires a pure plastic stream (e.g. styrene can be recovered from polystyrene) and therefore presorting. Meanwhile, while pyrolysis (thermal decomposition) is known for a "low quality" product (a mixture of various hydrocarbons), it is an advantage to MSW plastics in that it can tolerate a mixed feed. Therefore, one can conclude that pyrolysis is an ideal route (economically) for recovering some value for mixed, unwashed MSW plastics which would not be candidates for primary recycling and otherwise reside in landfills.

3. PYROLYSIS OF MSW PLASTICS

3.1 Introduction

Simply defined, pyrolysis is the chemical and thermal decomposition of molecules in the absence of oxygen. As most thermoplastics begin to degrade above ~300 °C, plastic pyrolysis can be proceed at low (< 400°C), medium (400°C-600°), or at high temperatures (>600°C). Process pressure is generally atmospheric (Buekens 2006).

There are several major factors which help to determine the product distribution from plastic pyrolysis. Temperature is the most important operating variable, as it determines both the rate of decomposition, and the stability of reaction products (lower temperatures favors formation of larger molecules, whereas high temperature favors formation of smaller molecules). Reaction time is also important as short residence times favor primary products like monomer whereas longer times favor more thermodynamically stable products with longer times. Reactor type is also important. This determines the quality of the heat transfer, as well as the gas and liquid residence times (Kamisky 2006).

3.2 Mechanisms / Modes of Decomposition

In general, the pyrolysis of plastics follows complex routes that cannot be described by a single or a set of chemical reactions. Nevertheless, pyrolysis is well understood regarding the typical mechanisms by which these polymers degrade based on molecular composition and structure.

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 side groups. The

two groups of chemical reactions are shown in figure 3.1, as main chain reactions and side chain reactions. These two types of chemical reactions can again be divided into two groups. The decomposition of some polymers can be explained by one of these general mechanisms (Beyler and Hirschler 2001).

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 3.1 are involved in this simple decomposition process. These eight generic reactions are 1) random chain scission, 2) end chain scission 3) intramolecular H* transfer, 4) intermolecular H* transfer, 5) unzipping, 6) termination, 7) recombination and 8) 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. Hence, the volatile products of decomposition depend on the relative volatility of the resulting molecules (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).

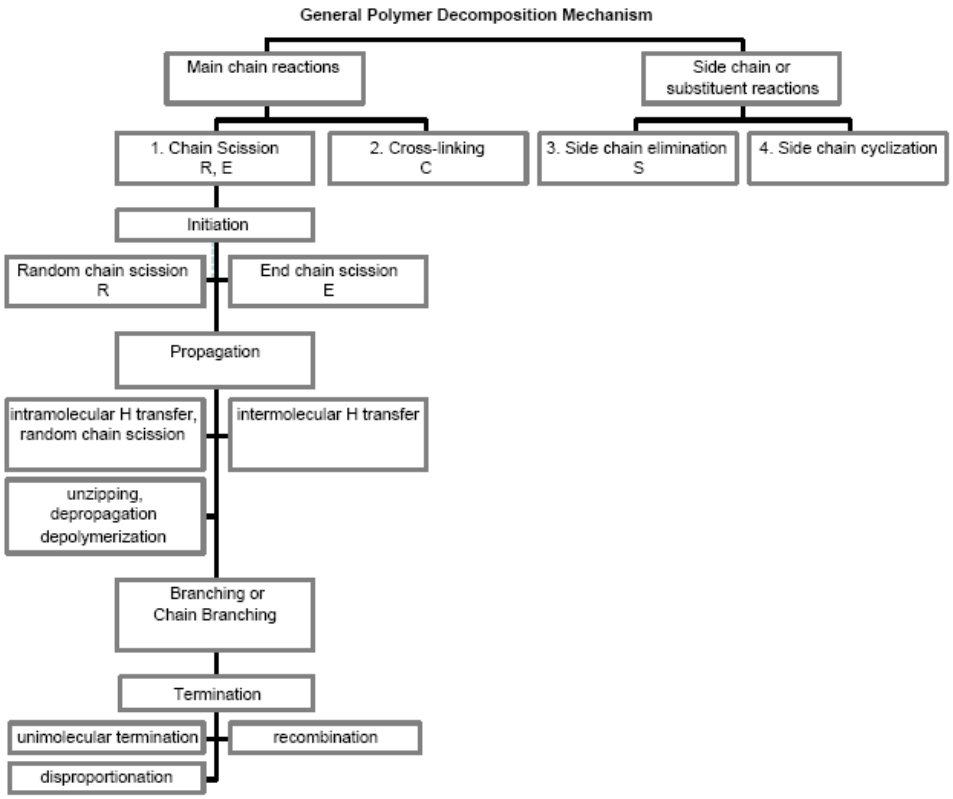


Figure 3.1. General Polymer Decomposition Mechanism

[Adapted from Beyler and Hirschler (2001)]

As a result of the complex random chain rupture, the pyrolysis of polyethylene at low temperature operations favors the production of waxes and paraffin oils and light oils and light alkanes at high temperatures. Conversely, PET, which exhibits predominantly hydrogen transfer and decarboxylation, branches off benzoic acid and vinyl terephthalate (Duncan 2000). PVC via HCl elimination favors production of benzene at lower temperatures and HCl vapor and toluene at higher temperatures.

3.3 Reactors

In regards to reactor design, compared with other methods of gas-solid contacting (e.g. fixed beds, rotary cylinders), fluidized beds have several advantages over alternative reactor designs. Fluidized beds have rapid and good mixing of solids—which leads to almost uniform isothermal conditions throughout the fluidized bed. This allows for easy and reliable process control. The range of operating temperatures is generally lower than that of other gas-solid reactors. It also has a high process flexibility—making it possible to utilize different fluidizing agents (in pyrolysis nitrogen could be used), operating temperatures and gas residence times and the ability to operate with or without a catalyst (Arena 2006).

For polymer decomposition, fluidized beds are beneficial in that they have excellent heat and mass transfer that can reduce the time necessary for a reaction. They have a low tendency for clogging with molten polymer during the degradation process and have the ability to maintain a constant temperature throughout (Hernandez 2007).

There a few aspects about fluidized beds that might be considered for further study. *Conesa et al 1994* reported that yields of products obtained by fluidized bed pyrolysis come via two contributions. The first is primary degradation or cracking of the polymer which occurs in the dense bed. The second contribution is the so called secondary and ternary reactions which occur partially in the bed and partially in the freeboard. The influence of the secondary or ternary reactions could be more important for applications that do not use catalysts and may have an impact on the design of the column. For improvements in pyrolyzing plastics in fluidized beds, it may be beneficial to consider this effect.

Unfortunately one downside of fluidized bed reactor is that scale-up is not always easy to realize. As a result, even if laboratory scale tests are promising, a pilot scale is often necessary to verify that such a process can be conducted.

Over the past ten years, more attention has been given to microwave pyrolysis. Microwaves initiate localized, molecular heating and could therefore under certain conditions be advantageous a faster as more efficient reactor. The following section investigates this specific process to MSW plastics.

4. MICROWAVE PYROLYSIS OF WASTE PLASTICS

4.1 Introduction

'Microwaves' is the name given to electromagnetic radiation 1 m to 1 mm in wavelength that corresponds to a frequency of about 1 to 300 GHz as shown in figure 4.1 below. This frequency range falls between radio waves and visible light in the electromagnetic spectrum (Katz 1992). Most of the microwave frequency band is used for communications and radar, and consequently it is regulated by the Federal Communications Commission.

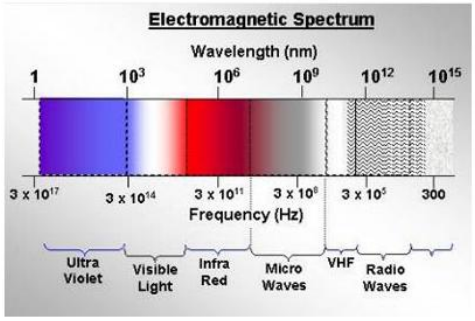


Figure 4.1. Electromagnetic Spectrum. [Adapted from EWI]

As a result, certain frequencies are allocated for exclusive industrial, scientific, and medical use, specifically 915 MHz, and 2.45, 5.85, and 20.2-21.2 GHz. Because present industrial and medical uses are based on heating water only 915 MHz and 2.45 GHz have significant application. These are the frequencies at which commercial units are designed to operate.

The practical application of microwave radiation started during the Second World War, in the course of intensive research on electromagnetic radiation in the frequency range from 500 MHz to 100 GHz in the development of high-definition radar (Meredith 1998). In reality, microwave heating is one form of electrical volumetric heating (along with ohmic, radio

frequency (RF), and conduction/induction) which is defined by all the infinitesimal elements constituting the volume of a workload being each heated individually, ideally at the same rate.

In conventional thermal processing, energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer (Thostensin 1999).

4.2 Microwave Systems

Microwave furnaces consist of three major components: the sources, the transmission lines, and the applicator. The microwave source generates the electromagnetic radiation via acceleration of charge, and transmission lines deliver the energy from the source to the applicator-where the microwaves are either absorbed or reflected.

The main part of the microwave is the source- typically a magentron- the most common microwave source, which is a vacuum tube. In this tube an anode (an electrode on which high density of electrical charge is present) is set at a high potential compared to the cathode (another electrode). The potential difference produces a strong electric field, and the cathode is then heated to remove loosely bound valence electrons. These removed electrons are the accelerated towards the anode due to the presence of the electric field. In the magnetron, as depicted in figure 4.2 below, an external magnet is used to create a magnetic field perpendicular to the

electric field and the applied magnetic field creates a circumferential force on the electron as it is accelerated to the anode. The force causes the electron to travel in a spiral direction, and this creates a swirling cloud of electrons. As electrons pass the resonant cavities, the cavities set up oscillations in the electron cloud, and the frequency of the oscillations depends on the size of the cavities. Electromagnetic energy is coupled from one of the resonant cavities to the transmission lines through a coaxial line or waveguide launcher (Thostenson 1999).

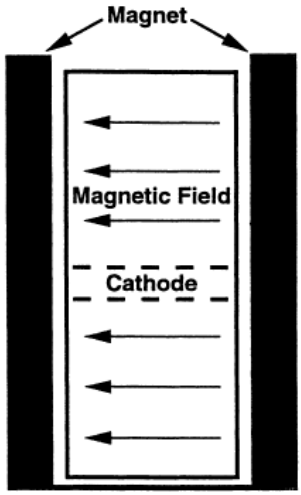


Figure 4.2. Schematic of Magnetron Microwave Tube [Adapted from Thostenson et al 1999]

The magnetron is able to generate the electromagnetic radiation with high efficiency for electrical energy, about 85% for 900 MHz and ~80% for 2.45 GHz (Meredith 1998).

4.3 Microwave Heating

When materials are exposed to a microwave field, there are essentially three different ways by which the material will be heated. These mechanisms are based on how the molecules of the material behave when subjected to the microwaves. The first mechanism is polarization-having either the electrons of individual atoms (electronic polarization) or the nuclei of the atoms themselves (atomic polarization) are displaced from their equilibrium position, which results to induced dipoles which respond to an applied field. This effect is more pronounced in molecules that have permanent dipoles from asymmetric charge distributions-like water. The second mechanism is interfacial polarization—which arises from a buildup of charge in contact areas of heterogeneous systems (heterogeneous being defined as multiple components that have different conductivities or dielectric constants). The third mechanism is via ionic conduction where some materials produce electric currents when subjected to EM fields. As the atoms of the molecules of a given material undergo one of these phenomena, the movements aligned with the EM fields cause a localized friction or heating.

The heating of materials can be further described by the following dielectric power absorption equation:

$$P = \mathrm{K}f\,\mathrm{E}^2\acute{\varepsilon}\tan\delta \qquad \text{(Thostensin 1999)}$$

where P is the power dissipation in W/cm^3, K is a constant equal to 55.61 x 10^{-14}, f is the applied frequency in Hz, E is the electric field strength in V/cm, $\acute{\varepsilon}$ is the dielectric constant, and $\tan\delta$ is the dielectric loss tangent. Both $\acute{\varepsilon}$ and $\tan\delta$ have a dependence on operating frequency and the sample temperature. In practice these values also vary with moisture content and

physical state (solid or liquid). The electromagnetic field energy dissipated as heat per unit volume is proportional to the dielectric loss factor, the square of the field strength, and the frequency of the applied field. This expression assumes that the influences upon heating rate due to the heats of the reaction are negligible (Chen 1993).

Based on the above dissipation expression, the dielectric loss factor is largely important as to whether a material can be heated and possibly pyrolyzed by microwave radiation. This quantity is directly proportional to a more common material property, the dielectric constant.

Thermoplastics (with the exception of nylons) normally have very low dielectric constants and low loss factors and are known as 'transparent' to microwaves. Therefore they have not been thought of as candidates for microwave processing in the past. For example, polyethylene, polystyrene, and polypropylene--three common polymers that belong in MSW streams--have dielectric loss factors between 0.0007-0.0008 respectively at room temperature in response to 2.45 GHz radiation—the most common microwave source—with little improvement at lower frequencies or higher temperatures up to 100 °C, as obtained from the *Engineer's Handbook of Industrial Microwave Heating*. The magnitude of this transparency can be understood by comparing those values to a dielectric loss factor of 13.0 for distilled water at room temperature (25 °C). At 2.45 GHz, substances with dielectric loss factors on order of 10 require an electric field of 4.69 V/cm to increase 11°C/min, whereas substances with dielectric loss factors of 0.01 require 148 V/cm for the same temperature rate-which are unsafe electric fields to be generated by commercial devices.

The poor dielectric properties of plastics are aggravated by the fact that when plastics are heated and have reached their melting point or gel transition, absorption of microwaves increases substantially (Chen 1993). This can result in a poorly controlled pyrolytic reaction.

In order to take advantage of microwave heating with plastics, an additional material must be intimately mixed with a microwave-absorbent material. By doing so, the plastics are not directly heated via the mechanism previously discussed above, but rather by conduction from the quickly heated-highly microwave absorbent material to the plastics. This is referred to often as "microwave-induced" or "microwave-assisted" pyrolysis where the microwaves are considered for the most part an indirect source of heat. The material that is most known for its use as absorbent is graphitic carbon since it has dielectric properties of the same magnitude as water (dielectric loss factor: ~12-15) and is cheap and highly abundant (Ludlow-Palafox 2006). Microwave heating of carbon is used commonly in sintering in the ceramics industry. Carbon accelerates the first stage of heating by applying thin coats of about millimeter depths to ceramic surfaces (Katz 1992).

4.4 Microwave Pyrolysis Literature

While there has been some published literature on the microwave pyrolysis of waste tires and biomass (e.g. corn stover), literature microwave induced pyrolysis of plastics is rare. In fact, only one group from the University of Cambridge (UK) has been found to publish work on this subject at the time of this paper.

Ludlow-Palafox et al (2001) implemented a lab scale, modified microwave furnace system which is represented by the schematic in figure 4.3 below. Plastics, in shredded or pelletized form, are fed by a hopper (3) to a quartz vessel (2) within the microwave cavity (1). Pulverized carbon is also added as the material which is susceptible to microwave heating. Nitrogen is fed into the reactor vessel to ensure the oxygen-depleted reaction environment (5). Upon pyrolysis, the products volatilize and exit the microwave system. The vapors are condensed (7) into the respective liquid (8, 9) and light gas fractions (10).

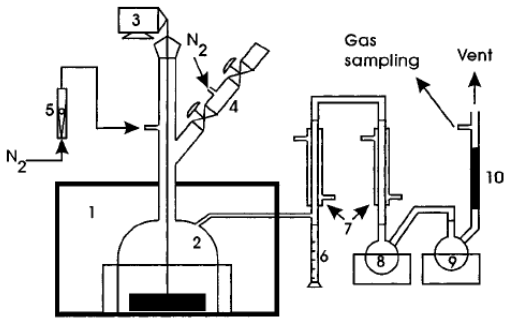


Figure 4.3. Schematic of MWP Setup

[Adapted from Ludlow-Palafox et al (2001)]

50 grams of HDPE (average density: 954 kg/m^3 and diameter: 3 mm) was mixed with a kilogram of particulate carbon. The microwave furnace (maximum operating power: 5 kW) operated at 1250 W (2.45 GHz, for 500 °C) for 350 seconds upon addition of the plastic. The carbon was heated additionally for a few minutes prior as well.

Slow agitation (6 rpm) maintained the intimate mixture between the carbon and the HDPE pellets while nitrogen was continuously flowed (1.4 L/min) to remove oxygen from the quartz chamber. After 350 seconds there was no plastic remnant within the reactor. The overall recovery was a gaseous stream (19% by mass) and an oil/liquid fraction (81%). Thermocouples measuring the temperature of the degrading plastics reported a system temperature of 500 °C.

Additional results were reported at 600 °C and 700 °C respectively. Temperature was reportedly maintained by switching on and off various magnetrons. The product stream from the condensing system was analyzed via gas chromatography-mass spectrometry (GC/MS).

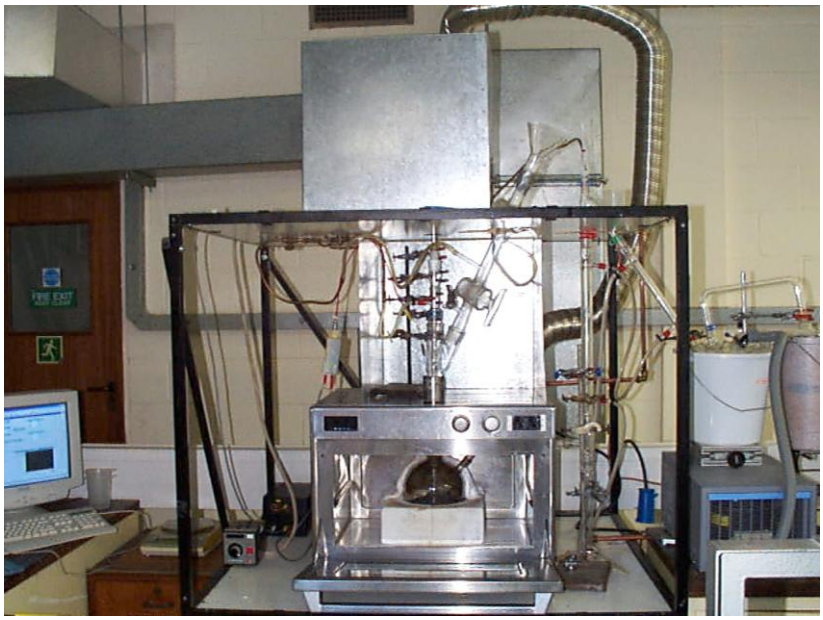


Figure 4.4. Photo of the MWP Laboratory System [Univ. Cambridge]

Ludlow-Palafox et al (2001) had several key findings. The first was that reactor temperature had the greatest effect on the rate if reaction/decomposition as shown in figure 4.5 below. This was quantified by the accumulation of volume in the main collection flask over reaction time.

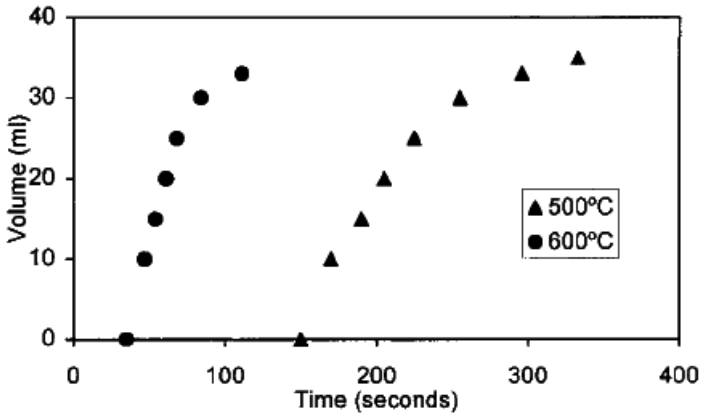


Figure 4.5. Cumulative Yield of Products for MWP of 50 grams of HDPE Over Time at 500 °C and 600 °C. [Adapted from Ludlow-Palafox (2001)]

At 600°C, no additional oils or waxes accumulated in the collection vessel after 120 seconds, suggesting that the entire 50 gram sample was pyrolyzed within that duration. It should be noted that reactions reported at 700°C were extremely fast (flash pyrolysis) and were not able to report accumulated volumes over a comparable time scale.

Table 4.1. Product Yield (wt%) from Polyethylene Pyrolysis for Various Reactors

		500°C			600°C		
Paper	Reactor	Gas	Oil/Wax	Solid	Gas	Oil/Wax	Solid
Conesa et al 1997	Batch Fluidized	~7-16	NR	NR	~18-60	NR	NR
Cozzani et al 1997	Fixed Bed	~8-12	~83-90	~2-5	~20-35	~55-74	~6-10
Williams et al 1999	Fluidized Bed	10.8	89.2	0	24.2	75.8	0
Ludlow-Palafox et al 2001	Microwave	19	81	0	20.9	79.1	0

Note: NR = not reported

In Table 4.1 above, some of the results from *Ludlow-Palafox et al* were compared versus literature of polyethylene pyrolysis for alternate reactors. From this table two conclusions can be made. First, an increase in temperature causes little difference in the liquid/gas yields of the

microwave reactor whereas it had quite an impact for the fluidized and fixed beds respectively. Secondly, the magnitude (wt%) of the oil and wax seems to be largest for the microwave pyrolysis reactor. This is a favorable result for the consideration of upgrading the pyrolysis oil/wax into a crude liquid fuel.

4.5 Possible "Microwave Effect"

As previously discussed, microwave radiation interacts differently depending on the given material and its dielectric properties. In microwave–induced pyrolysis, it is thought that the pulverized carbon (a microwave absorbent material) absorbs the microwave energy and conducts heat to the shredded plastics it is mixed with, thereby degrading the polymers. However, there are some researchers who claim there may be more than conduction of heat from the carbon to the plastic taking place. A second mechanism, a so called non-thermal effect, in which the microwave radiation may be contributing to a lowering of the apparent activation energy of the polymer molecular decomposition, manifested in a decrease of reaction rate.

In the past some organic reactions have suggested this particular phenomena. *Gedye et al* initially claimed that significant rate enhancements in hydrolysis and esterification reactions in a microwave reactor. The proposed lowering of the activation energy has been hypothesized to be the storage of microwaves in the vibrational energy of a molecule--an enthalpic effect or by alignment of molecules—an entropic effect (Marand 1992).

Arguments attempting to falsify the "microwave effect" suggest that experimental mistakes have been made by extrapolating concepts of conventional heating into microwave

heating. The possibility of reduced temperature measurements is temperature reading due to heat losses that occur because of conduction through thermocouple guards (Olmstead 1997). The debate continues to the present day.

Regardless of whether the non-thermal effect exists, the fact remains that microwave have been shown to successfully induce pyrolysis of waste plastics. In the following section, a discussion of whether a large scale implementation of this technology is feasible is made via a life cycle analysis of a patented MSW plastic microwave pyrolysis process.

5. A LIFE CYCLE ASSESSMENT OF MWP OF WASTE PLASTICS

5.1 Introduction

Although microwave pyrolysis has been shown to have similar product streams to conventional pyrolysis technologies, there are concerns that its input energy requirement, and subsequent carbon footprint, may make this process inefficient and undesirable as a large scale waste plastic management scenario. Despite its high efficiency of converting electrical energy into microwave radiation, microwaves still require electricity, which if produced via combustion of primary energy sources (i.e. coal), is produced inefficiently (~30-40%) and therefore decreases the overall process efficiency. This claim is investigated in the following chapter using a case study of a patented microwave pyrolysis technology which has been proposed to operate in Patterson, New Jersey, USA. In addition to determining the carbon footprint of the process, its impact will be weighed against the footprint determined for a rival tertiary recycling technology gasification and accompanied Fischer-Tropsch synthesis as well as incineration for the given waste stream.

Climax Global Energy (Summit, New Jersey) has commercialized a microwave pyrolysis technology that can convert landfill-bound plastics into beneficial materials, with particular interests in upgrading to produce liquid fuels. Estimated pilot-scale microwave pyrolysis data was provided for the conversion of waste plastics into Fischer-Tropsch (F-T) wax. The current operating scale is 20 metric tons of MRF plastic feed per day. A product upgrading unit has not been incorporated into their MWP systems yet, and thus, the data are only available for F-T wax as the final product. However, considering that the required product upgrading process would be

very similar to that of the F-T process, the future addition of this unit should not pose any technical difficulties for the commercialization of such technology.

Two MWP scenarios were considered the LCA study: one that exclusively employed microwaves (MWP-1) and one that integrated microwave and a hybrid thermal microwave system using the waste light off-gas (MWP-2).

5.2 LCA Scope

There are a number of different measures for environmental impacts. This report presents the results of Life Cycle Analysis (LCA) in terms of greenhouse gas (GHG) emissions. Five different conversion scenarios were considered including two microwave pyrolysis processes, incineration, and two gasification/F-T processes. Figure 5.1, shown below, illustrates the system boundaries for each analyzed technology. Like in most LCA analyses, the system boundaries are very important for the meaningful comparisons. Transportation and its environmental impact are assumed to be in a similar range for all cases, and thus, not included in the LCA calculations. Also, it is important to note that due to the availability of data different products were considered for three waste management schemes. For example, the plastic incineration produces electricity as the only product, while microwave pyrolysis produces crude fuel similar to F-T wax and gasification/F-T process generate diesel as the final product within the system boundaries.

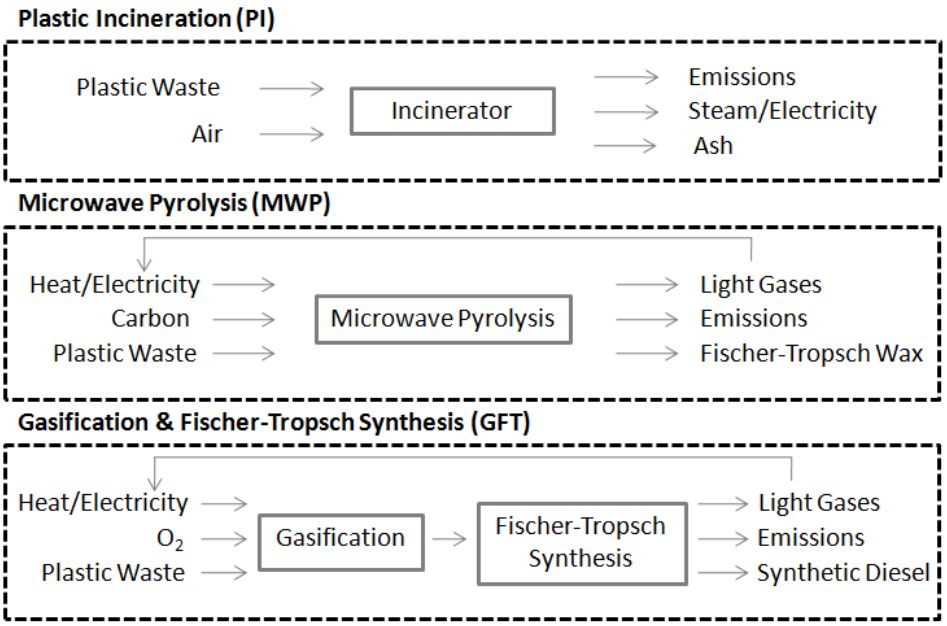


Figure 5.1. Description of Three Waste Management Schemes

It should also be noted that since this study is based on the GHG emission analysis of various waste conversion technologies, a comparison cannot be directly made with landfilling. A comparison to landfill would necessitate some considerations regarding the land use and GHG emission due to landfill gas. However, generally there is no landfill GHG emission associated with waste plastic's degradation, it is difficult to discuss the land use for the proposed technologies. Thus, only the technologies that convert non-recyclable plastics into products such as fuels, chemical and electricity were assessed as a part of this study.

5.3 LCA Process Assumptions and Calculations

MWP-1: Microwave only

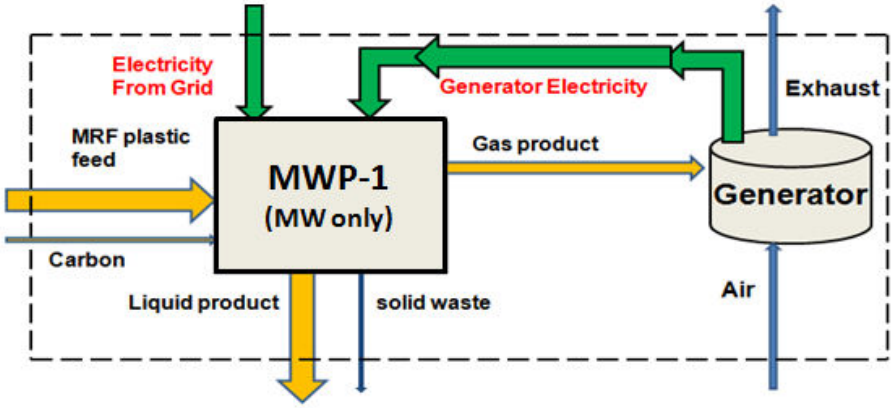


Figure 5.2. Material and energy flows of the MWP-1 process

The material and energy flows involved in the MWP-1 process are shown in Figure 5.2. For continuous operation of 20 metric tons MRF plastics per day, 687 kW of electricity was calculated in order to operate the reactor. This value considered the energy input required for the intended product yield as well as the efficiency of the magnetron and the reactive microwave efficiency. An additional 30 kW was estimated by *Climax* to operate a compressor, pumps, chillers, and plant lighting. As a result, the greatest environmental impact of the MWP-1 process is the emissions from generating 717 kW for operation,

In order to offset the electricity demand of MWP-1 process on the electrical grid, the off-gas product, consisting about 15 wt% of the product stream, could be sent to a generator. *Climax* has estimated that this off-gas stream has an energy density of 20,000 BTU/lb (similar to the energy density of propane gas). Operating at 33% efficiency, this generator provides 501 kW towards the parasitic electricity requirement for MWP-1 process. Therefore, only 216 kW is

needed from the grid. Furthermore, depending on the electricity mix of the grid, this byproduct utilization may also reduces the overall carbon footprint of the MWP-1 process.

According to a July 2000 US Department of Energy Report, "*Carbon Dioxide Emissions from the Generation of Electrical Power in the United States,"* electricity generated by coal (the largest source for base load electricity in the US), emits 2.1 lb CO_2 per kWh production. For gas supplied electricity, the value of 1.3 lb CO_2 per kWh was reported. Other pollutants were considered to be minimal in comparison to magnitude of CO_2 production. In order to calculate the GHG emission associated with the electricity coming from the grid, a location specific electricity mix is considered. Since *Climax*'s plant is located in New Jersey, the following electricity mix listed in Table 1 was considered.

Table 5.1. Fuel Electricity Generation in NJ (EIA 2009 Data)

Electricity Generation Method	**Electricity Generation (thousand MWh)**
Total Net Electricity Generation	4769
Natural Gas-Fired	1646
Coal-Fired	284
Nuclear	2711
Other Renewables	76

This shows that 56.8% of electricity in NJ is provided by carbon free nuclear power, with the majority of difference coming from natural gas fired facilities (34.5%) and only about 6% from coal fired plants. The lower carbon emission associated with the electricity mix results in a lower carbon footprint for the MWP products. For the analysis of the same MWP technologies in another state, the impact could be significantly different, as about 50% of the United States electricity today still comes from coal combustion.

MWP-2: Microwave & Thermal Treatment

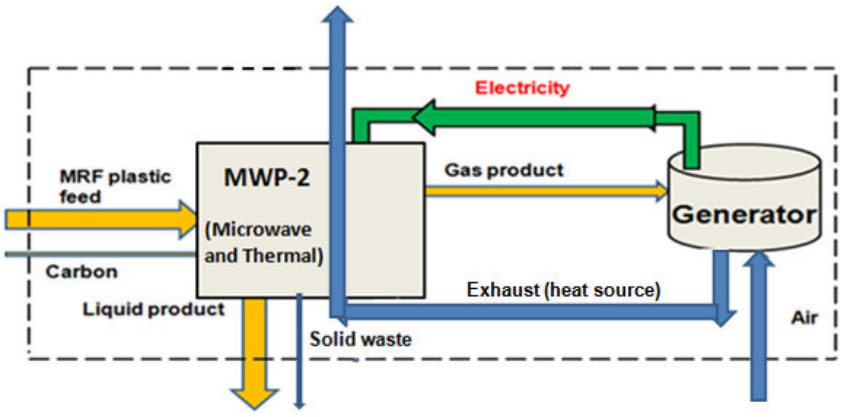


Figure 5.3. Material and energy flows of the MWP-2 process

In the second scenario (MWP-2) shown in Figure 5.3, a hybrid reactor is used with 50% of the pyrolysis energy provided by thermal heat and 50% by microwaves. The addition of thermal heat is to overcome the low microwave susceptibility of plastics during the pyrolysis process- as the permittivity of microwave radiation is increased at higher temperatures, and reduces the requirement of microwaves in the pyrolysis reactor. The rejected heat from the generated is used after start-up to liquefy the plastics and decrease the necessary microwave radiation input. In doing so, following the other assumptions and values in the MWP-1 process, 373 kW of electricity (vs. 717 in MWP-1) is required for processing 20 metric tons of MRF plastics per day. This allows for a surplus of 124 kW of electricity that is not used in the process after utilizing the 15 wt% of gaseous products for electricity. Although this is promising benefit, since this has not been currently integrated in their design, an output credit of providing electricity to the grid was not considered within the scope of this LCA.

Assuming that the electricity produced in MWP-2 scenario with 20,000 BTU/lb gas stream at 33% efficiency, the amount of heat rejected is more than four times the amount of energy necessary to incorporate into the hybrid reactor. Further heat utilization is possible, such as gasification of the solid residue stream. But given the quantity of the solid stream, conversion to a new product would be impractical in application versus, recycling. Furthermore, there is no infrastructure in place to utilize the waste heat to provide heat steam/hot water. Therefore it is assumed that all heat unused by the plastic liquefaction process is rejected and wasted.

Given the same emission analysis as MWP-1 and the emissions analysis from operating the generator, and a product energy density of F-T wax of 46.2 MJ/kg, the GHG emission for MWP-2 process was determined to be 10.1 kg CO_2 per million BTU of product.

5.4 Compared Processes

5.4.1 Gasification and Fischer-Tropsch Synthesis of MSW Plastics (GFT-1 and GFT-2)

Author's note: This values obtained for the LCA for gasification and FT synthesis and incineration were performed with and co-authored by Kyle Fricker (kjf2123@columbia.edu), junior research associate of the Earth and Engineering Center at Columbia University.

Gasification is a thermochemical process that converts the carbonaceous material to synthesis gas (syngas) – an energetic gaseous fuel composed primarily of carbon monoxide, hydrogen, carbon dioxide, and methane that can be used in power generation or chemical/liquid fuel synthesis. By varying reaction parameters and further processing it is possible to fine tune the syngas composition for certain applications (Tijmensen 2002). The syngas can be used to generate electricity, yet, for this study, the syngas will be further processed into a liquid fuel

using Fischer-Tropsch technology (Huber 2006). Prior to alkane synthesis, several reforming and conditioning steps are needed to purify the syngas. After the catalytic transformation of syngas to Fischer-Tropsch crude oil/wax, the product is upgraded to produce primarily synthetic diesel fuel and naphtha.

During gasification numerous chemical phenomena occur concurrently. Partial oxidation is most important because it is responsible for producing the syngas, yet pyrolysis and hydrogenation are also occurring. The process is very flexible in its feedstock – any carbon-containing material can be gasified including materials in municipal solid waste. The products, shown below in equation (1), will vary with different feedstocks, and the syngas can be further adjusted through manipulation of operating conditions and downstream gas treatment (Higman & van der Burgt 2008, Yung 2009).

Carbonaceous Material (thermoplastics) + Oxidant (O2, H2O) (1)

→ CO, H2, CO2, H2O, CH4, hydrocarbons

→ tar, char, ash

→ HCl, NH3, sulfur species

The overall Fischer-Tropsch (FT) reaction is represented by equation (2) below. The appropriate H_2/CO ratio is maintained through governing the kinetics of the reversible water gas shift (WGS) reaction (3) below. The Anderson-Schulz-Flory (ASF) polymerization model predicts the distribution of alkane chain products ranging from C1 to C50. The process was developed early in the 20th century, yet catalysts are still being developed to select the desired product range. The methane produced during F-T synthesis, usually larger quantities than

predicted by the ASF model, can be used to generate electricity or heat and improve the overall process efficiency (Huber 2006).

$$CO + 2H_2 \rightarrow \quad C_nH_n + H_2O \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

The products of FT synthesis are either olefin- or paraffin-rich depending on the operating conditions and the catalyst choice. Long carbon chained paraffin products (C12-C19) form at low reaction temperatures and produce FT waxes and synthetic diesel fuel. The shorter carbon chain olefins (C5-C10) occur at high reaction temperatures and can be further processed to make gasoline and other chemicals.

Since plastic gasification is an emerging research field, literature on gasification of pure plastics is not readily available, emissions calculations are based on coal gasification data. This is an acceptable assumption since the carbon content (wt%) in the plastic residue is similar to that of coal (Oak Ridge National Laboratory Data: HDPE : ~85 wt% C, PET: 62 wt%, coal: ~75 wt%).

Assuming that GFT can achieve a similar product distribution from Climax's pilot design, F-T diesel (LHV: 123,600 Btu/gal, Norton *et al.* 1998), two GFT scenarios were considered. GFT-1 is a base case, in which all CO_2 is vented to the atmosphere and all off-gas from the F-T reactor and the product upgrading unit is flared (similar to MWP-1). GFT-2 is designed so that nearly all the process off-gas is used for the cogeneration of heat, steam, and/or electricity (analogous to MWP-2). In doing so the impact was determined to be 107.3 kg CO_2-eq

per million Btu of product (which is mostly diesel) for GFT-1, and 72.96 kg CO_2-eq per million Btu of product for GFT-2 respectively.

5.4.2 Incineration (PI)

The carbon footprint of incineration (LCA scenario-PI "plastic incineration') was determined using methodology and values presented by Johnke (2010) in section 2, which provides an empirical relationship to calculate the emission from the incineration of municipal solid waste streams.

5.5 LCA Discussion

For this study, the GHG emissions for five selected waste conversion processed based on the system boundaries were estimated and illustrated in Figure 5.1. The LCA results are summarized in Figure 5.4 (in terms of kg CO_2-eq per million Btu of products) and Figure 5.5 (in terms of ton of CO_2-eq per day of operation).

Compared to the traditional waste-to-energy scheme of incineration, both MWP-1 and MWP-2 resulted in less GHG emission per MBtu of products. The difference is not as significant as between MWP and GFT processes but it is important to note that the microwave pyrolysis technologies are capable of producing F-T wax which can be a feedstock for various fuels and chemicals, whereas the incineration method only provides electricity. It should be also noted that the further upgrading of F-T wax to liquid fuels such as gasoline and diesel has been omitted in this study due to the lack of data availability. Further, the combustion (end use) of upgraded liquid fuel has been left out of the GHG comparison since both MWP and GFT produce fuels

with similar combustion characteristics. However, overall the conversion of plastic wastes into F-T wax via *Climax*'s microwave technology seems to be quite efficient.

When MWP-1 and MWP-2 were compared to two of the gasification/F-T schemes (GFT-1 and GFT-2), their benefits seem to be more significant in terms of kg CO_2-eq per million Btu of products. However, this can be misleading since GFT-1 and GFT-2 are considered for the production of diesel while MWP-1 and MWP-2 are designed to produce a mixture wax. Therefore, without the incorporation of product upgrading process for the microwave-based technologies, it is not fair to compare these technologies directly. While GHG emission data was not available for such a product upgrade process, it is a well-known technology such that we do not anticipate any technological difficulties with the development of efficient product upgrading process for the MWP-1 and MWP-2 processes.

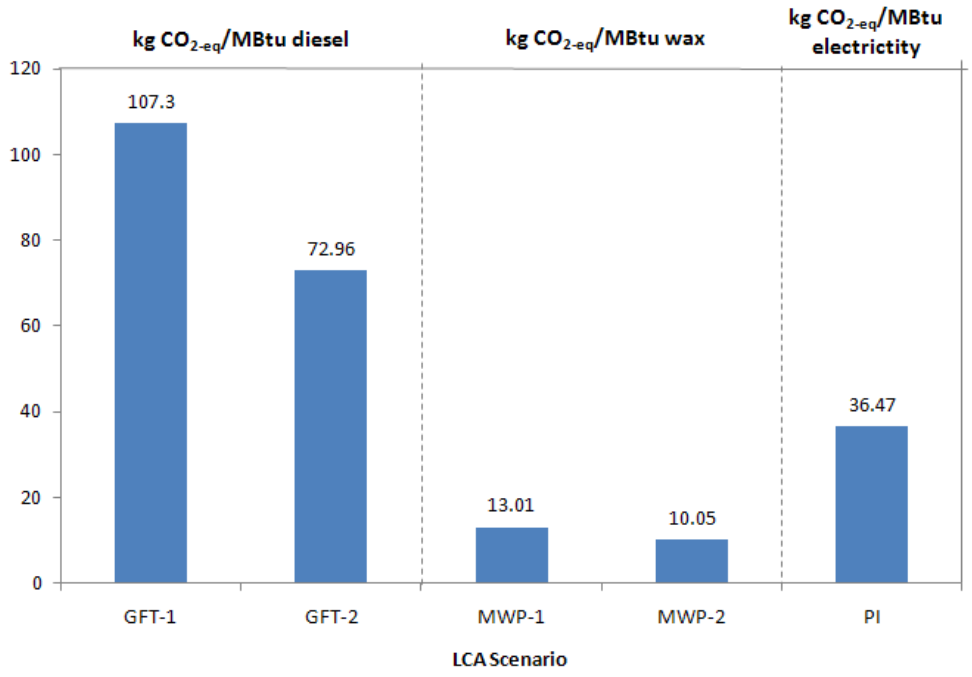


Figure 5.4. Comparison of Estimated Greenhouse Gas (GHG) emissions in terms of kg CO_2-eq per million Btu of products

The results shown in Figure 5.5 illustrate how much carbon in waste plastics is transferred to the fuels during the process. As expected, most of carbon in waste plastics was used to generate liquid fuels in MWP and GFT technologies, while a significant amount of carbon was emitted as CO_2 during the incineration of plastics.

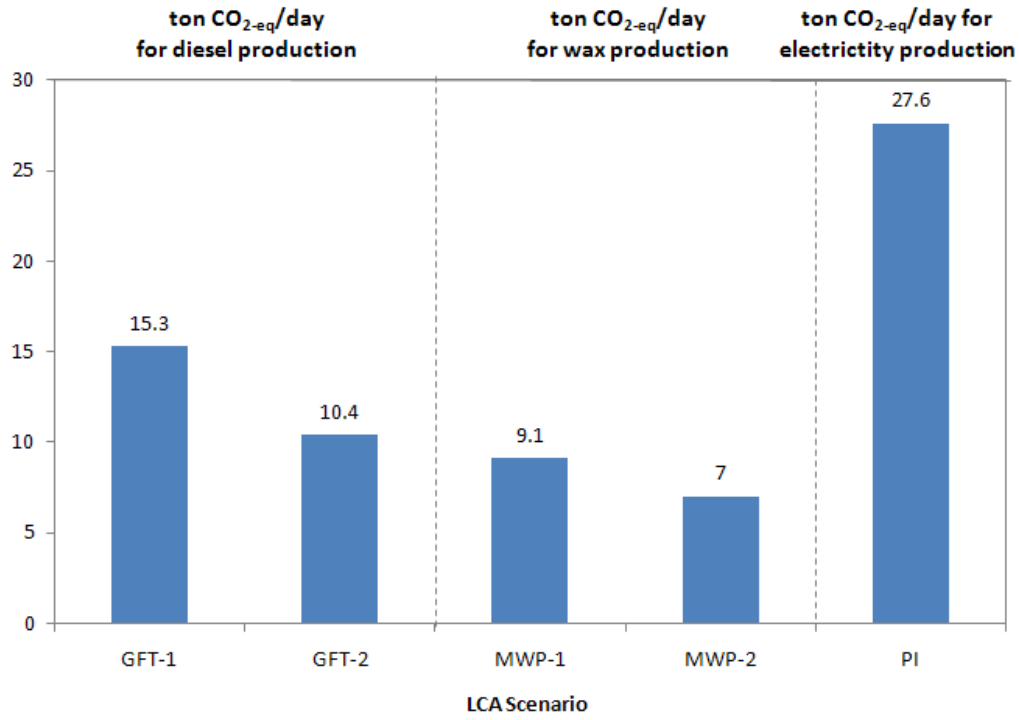


Figure 5.5. Comparison of Estimated Greenhouse Gas (GHG) emissions in terms of ton of CO_2-eq per day of operation with the feed rate of 20 metric tons of waste plastics

Based on this evaluation, *Climax*'s microwave pyrolysis technologies seem to be competitive with the gasification/F-T technologies for waste management. Among the five selected process scenarios, the microwave pyrolysis with the utilization of thermal energy from

the off-gas seems to be the option with the most potential at this point in terms of GHG emissions.

Overall, it appears that microwave pyrolysis may be a promising technology with a great potential for environmental sustainability. However, further LCA is recommended once the process is scaled up and more plant data is collected, since the GHG emission assessment is only accurate as the input data.

6. CONCLUSIONS AND FUTURE WORK

Based on the life cycle analysis of *Climax Global Energy*'s process in Chapter 5, microwave pyrolysis seems to have a promising future as a prospective tertiary recycling method. Further inquiries are necessary however, before it has any real future in large scale applications.

As is true in any life cycle analysis, the results are only as reliable as the quality of the initial data and scope/boundary conditions. Climax's estimation that its average oil/wax stream can be approximated as a type of F-T wax (~C25) is a very loose assumption. In *Ludlow-Palafox et al 2001,* the main components of the oil/wax fraction (from a 100% HDPE) yielded compounds as small as C3 and as large C56. Furthermore, F-T wax itself does not have a market of 16 metric tons a day, which by mass balance is about what would be expected based on the MWP-1 and MWP-2 LCA conditions. Upgrading, however from controlled cracking of wax to either diesel or to commodity oils may be an appealing alternative. However, those process requirements, which were not determined and included in the LCA previously would certainly increase the overall greenhouse emissions. That addition could change the comparison against the other waste management processes.

While the available information released by Climax was enough to establish the power requirements and the greenhouse gas emissions, one important variable which was excluded was process temperature. While the measuring of temperature in a microwave system is somewhat difficult-as exhibited by the conflicting studies of the non-thermal microwave effect, it is evident in conventional pyrolysis studies that process temperature has a direct relationship to the type of product. A higher process temperature, manifested by either an increase in heated carbon or in magnetron power would raise the effective temperature to which the polymers are exposed and .

In terms of experimental work there a number of studies that can be done to further the microwave pyrolysis of plastics experimental work initiated by *Ludlow-Palafox et al (2001).* Since MSW plastics often include LDPE, PET, PVC, and sometimes PS along with high density polyethylene, it would be worth investigating mixed stream pyrolysis. It should not be anticipated that the results of these experiments coincide with results of mixed streams in other pyrolysis reactors. As seen in Table 4.1, the influence of temperature, which compared MWP of HDPE versus fixed bed and fluidized bed yielded an almost constant liquid/gas wt% despite 100° increase in process temperature.

Additional process conditions that may be worth investigating in a microwave reactor include (1) vary the mass of pulverized carbon added per unit mass of plastic feed – find the optimal ratio; (2) consider the change in quality of the product and the rate of reaction vs. the diameter of the shredded/pelletized plastic; and (3) the change in quality of the product vs. the particle diameter of the carbon. All of those studies can provide further hints at the mechanism that is occurring which allows the plastics to thermally degrade despite their transparencies to microwaves.

Lastly, another interesting application that may be of interest to explore further is the removal of aluminum laminates which are attached to polypropylene wrappers, commonly found in the food, beverage, and toiletry industry. One particular example is *Tetrapack*, a European company whose drink cartons consist of a variety of types of laminates which contain ~6-30 micrometer width linings of aluminum (Ludlow-Palafox 2006). Microwave pyrolysis can be able to simultaneously recover this metal sheet while generating olefins via low temperature degradation of polypropylene.

7. REFERENCES

Aguado, J. and D. Serrano, *Feedstock Recycling of Plastic Wastes*, The Royal Society of Chemistry, Cambridge, UK (1999).

Aguado, J. *et al*. 2002a, 'Polyethylene Pyrolysis in a Conical Spouted Bed Reactor', in AV Bridgwater (ed), *Pyrolysis and Gasification of Biomass and Waste*, CPL Press, Strasbourg, France.

APC, 2006, The History of plastic, American Plastics Council, Virginia, USA, http://americanplasticscouncil.org (Accessed on April 26, 2010).

Arena, U. and M.L. Mastellone, "Fluidized-Bed Pyrolysis" Chapter 16 *Feedstock Recycling and Pyrolysis of Waste Plastics*, Wiley, Hoboken, New Jersey, (2006).

Beyler, CL & Hirschler, MM 2001, 'Thermal decomposition of polymers', In PJ Dinenno (ed), *SFPE Hanbook of Fire Protection Engineering*. 3rd ed., Quincy, Boston.

Buekens, A.G. "Introduction to Feedstock Recycling of Plastics" *Feedstock Recycling and Pyrolysis of Waste Plastics*, Wiley, Hoboken, New Jersey, (2006).

Chen, M. *et al*., Basic Ideas of Microwave Processing of Polymers, *Polymer Engineering and Science,* **33**, 1092-1109 (1993).

Conesa, J.A. *et al*. Comparison Between the Pyrolysis of Two Types of Polyethylenes in a Fluidized Bed Reactor, *Journal of Analytical and Applied Pyrolysis,* **30**, 101-120 (1994).

Cozzani, V. *et al.,* Influence of Gas Phase Reactions on the Product Yields Obtained in the Pyrolysis of Polyethylene, *Industrial and Engineering Chemistry Research,* **36,** 1955-1964 (1997).

Duncan, M.P. *et al.,* Thermogravimetry of Polymers, in *Encyclopedia of Analytical Chemistry,* R.A. Meyers (ed.) pp 8094-8105 Chichester: John Wiley & Sons, Ltd. 2000.

Gedye, R.N., W. Rank, and K.C. Westaway, *Canadian Journal of Chemistry,* 1991, **69**
M. del Remedio Hernandez, A. Garcia, and A, Marcilla, *Journal of Analytical and Applied Pyrolysis* 78 (2007) 272-281.

Hind, J. *Recycling of Polymers*, Plastics Consultancy Network, 1999 http://www.pcn.org/Technical%20Notes%20-%20Recycle1.htm (Accessed on May 1, 2010).

Huber, G.W., S. Iborra, A. Corma, ―Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, *Chemical Reviews*, **106**, 4044-4098, (2006).

Johnke, B. "Emissions from Waste Incineration," *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, Conference Paper 455, 455-468, Research, http://www.ipcc-nggip.iges.or.jp/public/gp/bgp/5_3_Waste_Incineration.pdf (Accessed on January 11, 2010).

Katz, J.D., Microwave Sintering of Ceramics, *Annual Review of Materials Science,* **22**, 153-170 (1992).

Kaminsky, W., *Feedstock Recycling and Pyrolysis of Waste Plastics*, Wiley, Hoboken, New Jersey, (2006).

Krause, H.H. "Hot corrosion in boilers burning municipal solid waste." Metal Handbook, Ninth edition, Vol. 13: Corrosion, ASM International, 1987, p. 997-998.

Ludlow-Palafox, C. and H. Chase, Microwave-Induced Pyrolysis of Plastic Wastes, *Industrial and Engineering Chemistry Research.* **40** (22) 4749-4756 (2001).

Marand, E. *et al., Macromolecules*, **25,** 2243, (1992).

Marano, J.J. & J.P. Ciferno of Energy and Environmental Solutions, LLC, *Life-Cycle Greenhouse-Gas Emissions Inventory For Fischer-Tropsch Fuels*, Prepared for U.S. Dept. of Energy, (2001).

R. Meredith, *Engineers Handbook of Industrial Microwave Heating*, The Institution of Electrical Engineers, London, UK, 1998.

Olmstead, W.E, and M.E. Brodwin, A Model for the Thermocouple Sensitivity During Microwave Heating, *International Journal of Heat and Mass Transfer,* **40**, 1559-1565 (1997).

PACIA 2006, Plastics and Chemicals Industries Association, Australia, www.pacia.org.au/ (Accessed on May 1, 2010).

Rosenthal, Elisabeth, "Europe Finds Clean Energy in Trash, But US Lags" NY Times April 12, 2010, *Environment,* http://www.nytimes.com/2010/04/13/science/earth/13trash.html (Accessed May 1, 2010).

M.J.A. Tijmensen, A.P.C. Faaij, C.N. Hamelinck, M.R.M. van Hardeveld, ―Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification, *Biomass and Bioenergy, **23**,* 129-152, (2002).

Thostenson, E.T. and T.-W. Chou, Microwave Processing: Fundamentals and Applications, *Composites: Part A,* **30** 1055-1071 (1999).

U.S. Environmental Protection Agency (US EPA), "Municipal Solid Waste in the United States: 2007 Facts and Figures," EPA530-R-08-010, (November 2008).