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Plasma Energy Recycle and Conversion of Polymeric [MSW] Waste

A Final Report

Submitted to the U.S. Department of Energy

by

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Table of Contents

LIST OF TABLES.....	v
LIST OF FIGURES	vi
Executive Summary	1
1. ABSTRACT	2
2. INTRODUCTION	3
3. PLASMA TECHNOLOGY AND WASTE TREATMENT.....	5
3.1 Definition of Plasma.....	5
3.2 Plasma Characterization	5
3.3 Generation of Thermal Plasmas.....	7
3.3.1 <i>DC Arcs</i>	7
3.3.2 <i>RF Discharges</i>	8
3.4 Industrial Applications of Thermal Plasma Technology.....	9
3.5 Plasma/Waste Technology: Current Status	9
4. PROPOSED REACTION MECHANISMS.....	12
5. METHODOLOGY	19
5.1 Reactor and Process Description.....	19
5.2 Materials Selection.....	23
5.3 Analytical Techniques.....	24
6. RESULTS AND DISCUSSION.....	26
6.1 Polyethylene Depolymerization.....	26
6.1.1 <i>Process Parameters and Experimental Matrix</i>	26
6.1.2 <i>Mass Balance</i>	31
6.1.3 <i>Effect of Process Variables on Ethylene Concentration</i>	32
6.1.4 <i>Solid Residues</i>	37
6.2 Polypropylene Depolymerization	40
6.2.1 <i>Process Parameters and Experimental Matrix</i>	40
6.2.2 <i>Mass Balance</i>	44
6.2.3 <i>Effect of Process Parameters on Propylene Concentration</i>	44
6.2.4 <i>Solid Residues</i>	50

6.2.5 <i>Economic Projections</i>	53
6.3 Polyethylene Terephthalate Depolymerization.....	54
6.4 Plasma Pyrolysis of a PE and PP Mixture.....	56
7. CONCLUSIONS AND FUTURE WORK	60
7.1 Conclusions.....	60
7.2 Recommendations for Future Work.....	61
8. PUBLICATIONS AND PRESENTATIONS FROM THIS PROJECT	66
9. REFERENCES	66
APPENDIX A: Feed Particle Size Distribution and Powder Feed Rate Calibration	
Charts	74
APPENDIX B: Design-Ease TM : Experimental Matrix and Statistical Analysis	
Description	79
APPENDIX C: Sample Gas Chromatograms.....	86
APPENDIX D: Carbon Nanotubes	88
APPENDIX E: Economic Projections of PP Recycling Using ICP Technology.....	92
APPENDIX F: SEM Micrographs of Pure Polymer Powders and Carbonaceous	
Residues	94
APPENDIX G: FTIR Spectrum of Gas Products from PET Depolymerization.....	98
APPENDIX H: Residence Time Estimation.....	100
APPENDIX I: Mass Balance Calculations	102
APPENDIX J: Bomb Calorimetry Calculations.....	104

LIST OF TABLES

2.1	Composition of a typical MSW stream [EPA, 1998].....	3
4.1	Calculated $-\Delta G^0_{1000}$ and $-\Delta G^0_{8000}$ [kJ/mol] values for pyrolysis reactions of n-alkanes and 1-alkenes.....	15
4.2	Bond dissociation energies of C-C and C-H bonds [kJ/mol]: $R_1-R_2 \rightarrow R_1+R_2$ [Flynn and Florin, 1985].....	14
5.1	Various quench nozzles used.....	23
5.2	Physical and thermal properties of the polymer feedstocks [Frank, 1968; Kevorkian, 1963; Kroschwitz, 1986].....	24
6.1	Process parameters varied in the depolymerization of PE	27
6.2	PE Depolymerization: standardized effects and regression coefficients as computed by Design-Ease TM using ethylene concentration as response.....	28
6.3	PE Depolymerization: product distribution at optimum conditions [Vol. % on an Ar-free basis]	31
6.4	PE Depolymerization: mean particle size, calorific value and elemental composition of solid residue.....	39
6.5	Process parameters varied during the depolymerization of PP	41
6.6	PP Depolymerization: product distribution at optimum conditions [Vol. % on an Ar-free basis]	44
6.7	PP Depolymerization: mean particle size, calorific value and elemental composition of solid residue.....	51
6.8	Economic projections of PP recycling: summary of balance sheet	54
6.9	PET Depolymerization: mean particle size, calorific value and elemental composition of solid residue.....	56
6.10	PE + PP Mixture Depolymerization: run parameters and product distributions	57
6.11	PE Depolymerization: run parameters and product distributions.....	57
6.12	PP Depolymerization: run parameters and product distributions	58
6.13	PE + PP Mixture Depolymerization: product distribution as predicted from depolymerization of the individual pure polymers.	58
B.1	PE Depolymerization: experimental matrix	80

B.2	PE Depolymerization: analysis of variance data	80
B.3	PE Depolymerization: factorial model estimates.....	81
B.4	PP Depolymerization: experimental matrix	84
B.5	PP Depolymerization: standardized effects and regression coefficients as computed by Design-Ease TM using propylene concentration as the response.....	85
I.1	PE Depolymerization: mass balance analysis.....	102
I.2	PP Depolymerization: mass balance analysis.....	102
I.3	PET Depolymerization: mass balance analysis	102
I.4	PE + PP Mixture Depolymerization: mass balance analysis.....	103

LIST OF FIGURES

3.1	Classification of plasmas [Boulos, et al., 1994]	6
3.2	Schematic of typical RF ICP torch	8
4.1	Schematic of polymer chain scission mechanism.....	12
5.1	Schematic of PL-35 ICP torch [Boulos, 1995].....	20
5.2	Schematic of the reactor	21
5.3	Schematic of the quench nozzle layout	22
6.1	PE Depolymerization: normal probability vs. standardized effect for different parameters: A-plasma plate power input; B-sheath gas flow rate; C-central gas flow rate; D-quench gas flow rate; E-probe gas flow rate; F-powder feed rate; AD-interaction of parameters A and D	29
6.2	PE Depolymerization: effect of (a) plasma plate power input and (b) interaction between plasma plate power input [A] and quench gas flow rate [D] on ethylene concentration.....	30
6.3(a)	PE Depolymerization: product distribution at different plasma plate power inputs. The remaining parameters were held constant at: 5 g/min powder feed rate; 40 slm central gas flow rate; and 0 slm quench gas flow	33
6.3(b)	PE Depolymerization: propylene concentration at different plasma plate power inputs. The remaining parameters were held constant at: 5 g/min powder feed rate; 40 slm central gas flow rate; and 0 slm quench gas flow	34
6.4(a)	PE Depolymerization: product distribution at different central gas flow rates. The remaining parameters were held constant at: 10 kVA plate power input; 5 g/min powder feed rate; and 0 slm quench gas flow.....	34
6.4(b)	PE Depolymerization: propylene concentration at different central gas flow rates. The remaining parameters were held constant at: 10 kVA plate power input; 5 g/min powder feed rate; and 0 slm quench gas flow.....	35
6.5(a)	PE Depolymerization: product distribution at different quench gas flow rates. The remaining parameters were held constant at: 5 g/min powder feed rate; 10 kVA plasma plate power input; and 40 slm central gas flow.....	36

6.5(b)	PE Depolymerization: propylene concentration at different quench gas flow rates. The remaining parameters were held constant at: 5 g/min powder feed rate; 10 kVA plasma plate power input; and 40 slm central gas flow	37
6.6	PE Depolymerization: effect of quench nozzle size and position on ethylene concentration in the product gas. [Legend: A = quench nozzle position A; B = quench nozzle position B; Orf. = orifice; MAP = maximum passage diameter] ...	38
6.7(a)	PE Depolymerization: product distribution at different powder feed rates. The remaining parameters were held constant at: 10 kVA plasma plate power input; 40 slm central gas flow; and 0 slm quench gas flow	38
6.7(b)	PE Depolymerization: propylene concentration at different powder feed rates. The remaining parameters were held constant at: 10 kVA plasma plate power input; 40 slm central gas flow; and 0 slm quench gas flow.....	39
6.8	Enlarged view of a carbon nanotube covered with several graphene layers as shown by TEM analysis of solid residue from the bottom of the reactor [Courtesy Dr. K. Lafdi, Center for Advanced Friction Studies, Southern Illinois University]	41
6.9	PP Depolymerization: normal probability vs. standardized effect for different parameters: A-plasma plate power input; B-sheath gas flow rate; C-central gas flow rate; D-quench gas flow rate [Position A]; E-probe gas flow rate; F-powder feed rate; G-quench gas flow rate [Position B].....	42
6.10	PP Depolymerization: effect of (a) plasma plate power input, (b) powder feed rate, and (c) interaction between power input and sheath gas flow rate on propylene concentration	43
6.11(a)	PP Depolymerization: propylene and ethylene distributions at different plasma plate power inputs. The remaining parameters were held constant at: 1.5 g/min powder feed rate; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A].....	45
6.11(b)	PP Depolymerization: other product distributions at different plasma plate power inputs. The remaining parameters were held constant at: 1.5 g/min powder feed rate; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A].....	45

6.12	PP Depolymerization: product distributions at different sheath gas flow rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 0 slm quench gas flow [A]	47
6.13	PP Depolymerization: product distributions at different central gas flow rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A]	48
6.14(a)	PP Depolymerization: propylene and ethylene distributions at different quench gas flow rates [Position A]. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 40 slm sheath gas flow rate	48
6.14(b)	PP Depolymerization: other product distributions at different quench gas flow rates [Position A]. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 40 slm sheath gas flow rate	49
6.15(a)	PP Depolymerization: propylene and ethylene distributions at different powder feed rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow rate	49
6.15(b)	PP Depolymerization: other product distributions at different powder feed rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow rate	50
6.16	SEM microphotograph of solid residue collected from the filter upstream of the eductors during PP plasma depolymerization	51
6.17	PP Depolymerization: bright-field TEM image of the carbonaceous residue showing different novel carbon structures	52
6.18	Nucleus of a developing carbon nanotube formed during PP depolymerization ...	53
7.1	Schematic of a thermal plasma recycling process	63
A.1	PE powder particle size distribution	74

A.2	PP powder particle size distribution.....	75
A.3	PET powder particle size distribution	75
A.4	Particle size distribution of PE + PP mixture	76
A.5	PE powder feed rate calibration.....	76
A.6	PP powder feed rate calibration	77
A.7	PET powder feed rate calibration	77
A.8	Feed rate of calibration PE + PP mixture	78
B.1	PE Depolymerization: effect of (a) central gas flow rate [C] and (b) probe gas flow rate [E] on ethylene concentration	82
B.2	PE Depolymerization: effect of (a) quench gas flow rate [D] and (b) powder feed rate [F] on ethylene concentration.....	83
B.3	PE Depolymerization: effect of interaction between plasma plate power input [A] and central gas flow rate [C] on ethylene concentration.....	84
C.1	GC calibration chromatogram	86
C.2	Sample gas chromatogram.....	87
D.1	Drawing of a nanotube capped with a C ₆₀ hemisphere [Harris, 1999].	88
D.2	TEM image of multi-walled nanotubes. Scale bar 10 nm [Harris, 1999].	89
D.3	Carbon onions prepared by electron irradiation of polymer-derived carbon. Scale bar 5 nm [Harris, 1999].....	90
D.4	SEM picture of carbon nanobead [Sharon et al., 1998].	91
F.1	SEM micrograph of pure polyethylene particles	94
F.2	SEM micrograph of pure polypropylene particles.....	95
F.3	SEM micrograph of pure polyethylene terephthalate particles	96
F.4	PP Depolymerization: SEM micrograph of solid residue collected in the hood.	97
G.1	PET Depolymerization: FTIR spectrum of gas sample.	99
H.1	Residence time of the reactor at different power levels: RGA measurements.	101
H.2	Residence time vs. gas flow rates.	101

FINAL REPORT: Grant # DE-FG02-97ER12205 "Plasma Energy Recycle and Conversion of Polymeric (MSW) Waste."

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EXECUTIVE SUMMARY: The technical feasibility of using an atmospheric pressure thermal plasma process, driven by an induction-coupled RF plasma torch, for the depolymerization of some of the polymeric constituents of the municipal solid waste [MSW] stream has been successfully demonstrated. High recoveries of [ethylene + propylene] and propylene monomers have been demonstrated from polyethylene and polypropylene feedstocks, respectively. High yields of acetylene were obtained from PET feedstocks. Treatment of mixed polymers has also been studied, and monomer yields from [polyethylene + polypropylene] mixtures in proportions similar to those in the MSW stream were in accordance with predictions based on the results from the individual polymers, consistent with the rule of mixtures. Solids conversions were typically in the 60-90% range. Possible reaction mechanisms explaining the experimental observations were also identified.

An additional and exciting discovery made during this work was the presence of carbon nanotubes and other novel, potentially high value, carbon forms in the solid residues. While the primary goal of this work was the recovery of monomers from polymers, the latter discovery offers the possibility of a new high yield production route for the synthesis of this new class of materials, for which many new applications have been touted, ranging from nano-electronics to hydrogen storage to delivery of therapeutics.

The major academic/educational accomplishments during this project were:

- Graduation of one Ph.D. student and publication of his thesis.
- Publication of two [2] refereed journal papers.
- Presentations at two [2] conferences.
- Filing of one [1] patent application.
- Publication of press releases in several trade magazines.
- Presentation of the findings to several interested industrial contacts.

1. ABSTRACT

A three-year investigation was carried out to investigate the recycling of polymeric wastes using thermal plasma. A significant, valuable, percentage of today's municipal solid waste [MSW] stream are polymeric materials, for which no economic recycling technology currently exists. This polymeric MSW is generally incinerated, landfilled, or recycled into low-grade applications such as synthetic lumber. Thermal plasma technology was proposed as a potentially viable and economic means of recycling these materials more efficiently by converting them either back into monomers which could be directed back into the polymer production cycle, or into other useful compounds which could be the starting materials for other chemical syntheses.

A major limitation to the thermal plasma recycling of polymers prior to this work was the lack of understanding of the reactions occurring during the process, knowledge of the quenching conditions necessary to "freeze" the products before complete pyrolysis, and an understanding of the influence of the process parameters on the reactions occurring and the yields obtained. The completed research has addressed this lack of understanding.

Drexel University's Department of Chemical Engineering together with the Center for the Plasma Processing of Materials [CPPM] in the Department of Materials Engineering have extensive experience in the areas of chemical reactors, reactor design, process diagnostics, sampling and analysis; and thermal plasma technology and the thermal plasma processing of materials, respectively and collaborate closely with industry on applied concerns.

This project had two major goals:

[i] To understand the chemical reactions occurring in a thermal plasma heated reactor during the rapid thermal processing [partial pyrolysis + rapid quenching] of polymeric materials.

[ii] To determine and understand the effect of variations in thermal plasma reactor operating parameters [input power, gas flow rate/residence time, and quenching conditions] on the conversion of selected "model" polymeric materials to monomers or other organic compounds.

These goals have led to increased knowledge of chemical reactions under plasma conditions and to an enhanced understanding of the process parameters and reactor design required to carry out controlled depolymerization reactions.

Model single material polymer systems, including polyethylene [PE], polypropylene [PP] and Polyethylene Terephthalate [PET] were studied; analytical techniques utilized included design of experiments for process optimization; residual gas analysis and gas chromatography for gaseous product analysis; and FTIR, SEM and TEM analysis of solid residues.

This research has completed a processing study which will contribute directly to a strategically important, rapidly developing technology by successfully demonstrating the depolymerization of polymeric materials back to the monomers or other useful precursor chemicals. Preliminary economic analysis has also shown that a scaled-up process should prove to be more economical than current alternatives - landfilling and incineration.

2. INTRODUCTION

Today's society uses, and often quickly discards, a large volume of an increasingly diverse range of polymeric materials. According to an EPA report, "plastics" account for 9.4 % by weight [19.8×10^6 tons] of the total municipal solid waste [MSW] generated in the U.S. in 1997 [EPA, 1998]. Of this only 5.3 % [1.1×10^6 tons] is recycled either through direct reuse such as milk and beverage bottles or through remolding and blending with other pure polymers into low-grade applications such as synthetic lumber for park benches [EPA, 1998; Tesoro and Wu, 1995]. The rest is either incinerated or landfilled. Most conventional chemical methods cannot deal with MSW due to the diversity of its composition, which ranges from simple thermoplastics to complex thermosets and composites. A typical composition of polymeric materials in MSW is summarized in Table 2.1.

Table 2.1: Composition of a typical MSW stream [EPA, 1998].

Materials	Wt. % in MSW
Polyethylene [LDPE/LLDPE]	25.4
Polyethylene [HDPE]	20.9
Polypropylene [PP]	13.1
Polystyrene [PS]	10.1
Polyethylene Terephthalate [PET]	8.6
Polyvinyl Chloride [PVC]	6.2
Other	15.8

The need to recycle MSW plastics is becoming increasingly important because:

1. The cost of landfilling in many areas now exceeds \$100/ton, largely due to increasingly stringent federal and state regulations and resulting reduced land availability.
2. Polymers from petrochemical sources have a very slow rate of biodegradation.
3. Disposal by incineration is generally associated with the generation of NO_x and other hazardous emissions, including dioxin and furans.
4. The manufacture of most polymers often uses non-renewable resources.

The low-grade use of plastic recycled materials has led to research into alternative processing methods to produce higher value products. Pyrolysis and gasification processes are receiving increased attention as a route for the disposal of large quantities of plastic wastes. The advantage of these processes over incineration is a reduction of the volume of product gases by a factor of 5 - 20, which leads to considerable saving in the gas recovery equipment. Furthermore, NO_x and other toxic compounds are not generated.

The pyrolysis of plastics waste has been the subject of numerous other studies. Conventional rotating kilns, fluidized beds [Conesa, et al., 1994; Conesa, et al., 1997; Garcia, et al., 1995; Pearson, et al., 1995; Simon, et al., 1996; Williams and Williams, 1999] and screw-fed tubular reactors [Wheatley, et al., 1993] were used to pyrolyze polymers at temperatures of 450 - 750°C. The composition of the product stream was complex and very sensitive to the temperature of the process. The primary product was either oil or a waxy solid. The liquids were a mixture of alkenes and alkadienes with chain lengths of 8 to 23 carbon atoms, along with some aromatics. The yield of oils and waxy products decreased with increase in pyrolysis temperature, but the aromatic and polyaromatic hydrocarbons [PAH] content increased significantly [Conesa, et al., 1997; Wheatley, et al., 1993]. Many investigators have also studied the effect of process

parameters on the product yield and chemical kinetics of low temperature polymer pyrolysis using techniques such as thermogravimetric analysis [TGA], differential scanning calorimetry (DSC) [Cozzani, et al., 1997; Faravelli, et al., 1999, Westerhout, et al., 1997a] and laser ablation [Blanchet, 1996; Blanchet and Fincher, 1996; Fanter, et al., 1972]. Use of a fast fluidized-bed reactor [Scott, et al., 1990] and other techniques using different fast particle heating rates [up to 1000 K/s] [Fanter, et al., 1972; Zevenhoven, et al., 1997] at increased temperatures [600 - 1000°C], and decreased residence times [a few milliseconds to seconds], not only increased the amount of gaseous product but also increased the olefinic composition of the product and thus increasing the value of the products formed. Milne, et al. [1999] achieved about 90 wt.% gas conversion by treating low density polyethylene in an internally circulating fluidized-bed reactor operating at temperatures between 780 - 860°C with residence times of 400 - 600 ms. The gaseous products were composed of 20 - 40 wt.% C₄'s and C₅'s [both olefins and paraffins]. The gaseous products formed were quenched with atomized water in a secondary column. Westerhout, et al. [1997b] showed that with slow heating and quench rates [10 to 1000 K/s] would allow secondary reactions such as recombination and cyclization to occur and yield a broad range of products. With better control over the heating and quenching rates, a narrow product composition could be achieved.

Pyrolysis of mixed polymers either from MSW [Garcia, et al., 1995; Kaminsky and Kim, 1999; Kim, et al., 1997; Pearson, et al., 1995; Simon, et al., 1996] or pure polymer sources [Bharwaj, et al., 1988; Westerhout, et al., 1997b] were reported. Westerhout, et al. [1997b] observed that no significant differences existed in kinetics and conversion rates in pyrolysis of polymer mixtures from pure sources as compared to that of pyrolysis of pure polymers. Steam cracking of polyolefins from MSW by Simon, et al. [1996] yielded 60 - 75 wt. % of gaseous products containing a wide range of olefins [C₁ - C₆'s]. A wide range of products were obtained due to the low heating rates [of the order of 100 K/s], low reactor temperatures, high residence times and slow or non quenching of the products formed.

Thermal plasma technology is a potentially viable means for recycling polymeric materials more efficiently either by converting them into monomers, which can be directed back into the polymer production cycle, or into other useful compounds. The chief advantages of thermal plasma processes over competing technologies are their ability to process solid, liquid and gaseous materials; their rapid thermal response and quenching; and their low off-gas emission compared with combustion-driven incinerators. Scale-up to the multi-megawatt power levels required to treat large throughputs of waste on a commercial basis could be achieved either through the use of higher power plasma torches or the use of multiple torches operating at lower individual powers. This research program focused on an investigation of thermal plasma technology for recycling and recovery of polymeric waste.

The main objectives of this work were to:

1. Determine the technical feasibility of converting polymeric waste into monomers or other useful compounds using an Induction-Coupled Plasma [ICP] reactor.
2. Determine the effect of variations in thermal plasma reactor operating parameters on the conversion of selected "model" polymeric materials to monomers or other compounds suitable for reuse.
3. Develop an understanding of the chemical reactions occurring in a thermal plasma reactor during the rapid thermal processing [partial pyrolysis + rapid quenching] of polymeric feedstocks.
4. Compare plasma pyrolysis of individual polymers and mixed polymers.

5. Optimize the process for the generation of specific products.

Section 3 of this report begins with the description of plasma, followed by a review of the various methods of generating plasmas. Applications of plasma technology and especially the current status of plasma waste treatment technology are discussed in the following sections. Section 4 focuses on the depolymerization mechanisms.

Section 5 begins with a detailed description of the torch, reactor and process used in this work, followed by a section on the model polymers selected and one on the various analytical techniques used.

The results and discussions are presented in Section 6. After a brief description of the "design of experiment" technique used, the experimental results on depolymerization of the individual polymers are presented. The statistical analysis used to generate the experimental matrix and to study the effects of variations in the process parameters is presented in the appendix. The section ends with a short discussion on the plasma treatment of mixtures of polyethylene and polypropylene powders.

A summary of the results and conclusions of the entire study and recommendations for future work are presented in Section 7. Section 8 lists the publications arising from this work.

3. PLASMA TECHNOLOGY AND WASTE TREATMENT

3.1 Definition of Plasma

The "plasma" state is frequently referred to as the "fourth state of matter," and consists of a mixture of electrons, ions and neutral particles. Positive and negative charges balance out and overall the plasma is electrically neutral. The presence of ions and electrons, however, results in the plasma medium being highly electrically conductive, and also because of the high energy content in the plasma, many of the neutral particles are also in excited states. The transition of these particles from the excited to ground state and electron/ion recombination to form neutral particles and photons accounts for the plasma's high luminosity.

3.2 Plasma Characterization

Plasmas can be classified into based on their electron temperature and electron densities [Boulos, et al., 1994]. Figure 3.1 shows a general classification of some plasmas. Glow discharge and electric arc discharges are two common plasmas. Glow discharges are generated in a pressure range from 10^{-4} to 1 kPa and have electron temperatures on the order of 10^4 K but the bulk gas temperature is close to room temperature. An arc is a discharge of electricity between two electrodes which is intensely hot [> 6000 K], luminous and self-sustaining [Knight, et al, 1991]. Plasmas can also be classified as "Cold" or thermal plasmas based on the difference between electron and bulk particle temperatures [Boulos, et al., 1994].

"Cold" plasmas are characterized by large differences between the bulk gas temperature and the electron temperature [$T_g \ll T_e$]. Because of this difference there exists a strong deviation from kinetic and thermal equilibrium, and hence, such plasmas can be termed "non-equilibrium" plasmas. Cold plasmas are usually generated at low pressures [< 10 kPa] by glow discharges. The average electron temperatures are in the range of 1-10 eV [1 eV $\sim 7,400$ K] and relatively low densities [usually $< 10^{20}$ particles/m³]. Cold plasmas are typically used in industrial applications such as plasma etching, plasma deposition and plasma surface modification and in fluorescent lamps.

Figure 3.1: Classification of plasmas. [Boulos, et al., 1994]

Thermal plasmas are usually generated at relatively high pressures [100 kPa to a few atmospheres] and are characterized by almost equal gas and electron temperatures, which are in the range of 10,000 K - 25,000 K. The electron densities are much higher than those of cold plasmas [10^{21} - 10^{26} particles/ m^3]. Thermal plasmas are commonly in a state of local thermodynamic equilibrium [LTE] [LTE by definition is both kinetic [$T_e \equiv T_{ions}$] and chemical equilibrium].

The composition and thermodynamic properties such as specific heat, enthalpy and entropy exhibit very strong nonlinear variations with temperature [Boulos, et al., 1994]. Transport properties such as viscosity, thermal conductivity and thermal diffusivity are of primary importance for thermal plasmas as they characterize the flow, temperature and composition of the plasma which would be needed to model plasmas. The viscosity increases up to a temperature of 10,000 K and is about one order of magnitude higher than that at ambient temperature [Fauchais, et al., 1987]. According to kinetic theory of gases the viscosity of the gases is proportional to square root of temperature leading to stronger attractive forces between those particles. Formation of thermal and electrical boundary layers can account for the increase in viscosity. However, viscosity decreases beyond the ionization temperature as Coulombic forces become stronger than the attractive forces. Thermal conductivity controls the energy losses in the arc of the discharges and thus the heat transfer to the particle [to be treated in a plasma] in flight. Thermal plasmas are used in applications such as plasma spraying, plasma synthesis of fine particles, plasma melting, smelting and metallurgy, plasma waste treatment, etc. [Boulos, et al., 1994; Knight, et al., 1991; Knight and Smith, 1998; Taylor and Pirzada, 1994].

3.3 Generation of Thermal Plasmas

Thermal plasmas can be generated in several ways; passing direct current [DC] or alternating current [AC] through a gas in free burning arc/constricted-arc plasma generators, utilizing either consumable graphite or non-consumable water-cooled metallic electrodes, electrodeless radio-frequency [RF] discharges, microwaves, shock waves, high-energy particle beams, etc. [Fauchais and Vardelle, 1997; Spencer, 1999]. High-intensity arcs and inductively coupled RF discharges are the two most widely used electrical methods of producing thermal plasmas.

3.3.1 DC Arcs

DC plasma torches are commonly operated at current levels of $I > 50$ A and pressures $P > 10$ kPa. These torches can be scaled-up to power levels of ~ 6.0 MW. The electrodes carry the arc current and the cathode emits electrons in sufficient numbers to sustain the plasma. Hot and cold cathode emissions are two basic processes of electron generation [Fauchais and Vardelle, 1997; Knight, et al., 1991]. Hot cathodes emit electrons when heated to temperatures greater than 3500 K. Tungsten, zirconium and hafnium are examples of metals which can be used as thermionic cathodes. The presence of highly localized electric fields close to the surface of a cathode can also pull electrons out of the metal. "Cold" cathode emission is based on this phenomenon. Water-cooled copper, copper-chromium or copper-zirconium alloys can all be used as cold cathodes. Electrode erosion of these cathodes can be reduced by distributing the thermal loading on them through magnetic and/or gas dynamic rotation of the arc attachments over the electrode surfaces. Thermionic cathode torches are used for power levels up to few MW, whereas cold cathode torches are used at higher powers. In some DC torches graphite electrodes are used at all power levels [Boulos, 1996; Fauchais and Vardelle, 1997]. DC arcs are classified based on their methods of stabilization, i.e., by the mechanism used to control the arc column movement in a well-defined pattern [Pfender, et al., 1987]: [1] free-burning, [2] wall-stabilized, [3] gas-stabilized through axial or vortex gas flows, [4] stabilization through use of magnetic rotation, [5] stabilization through segmented electrodes and [6] water-stabilization.

Free-burning arcs do not need any external spatial stabilizing mechanisms. A bell shaped free-burning arc is observed when the cathode jet impinges on an anode placed normal to the cathode axis. Welding and arc furnaces are examples of free-burning arcs. A rotationally symmetric long arc coaxially placed in a narrow circular water-cooled copper tube is stabilized by increased thermal conduction and associated secondary effects and is known as a wall-stabilized arc. The highest allowable heat flux that can be withstood by the wall determines the highest temperature that can be sustained in such arcs. Stabilization of the arc through a superimposed convective vortex flow is another important mechanism. Convective heat transfer from the arc to the surrounding cold gas acts similarly to that of conduction to the wall in wall-stabilized arcs. Temperatures up to 25,000 K can be achieved using hydrogen as the plasma gas. Magnetically stabilized arcs are the latest development in DC arcs [Boulos, et al., 1994]. An externally-applied magnetic field confines the arc to the center of the column. These types are typically used in arc gas heaters for material processing.

DC torches can be operated in three modes [Boulos, et al., 1994; Knight, et al., 1991]: [1] Non-transferred, [2] Transferred and [3] Superimposed arc. In the non-transferred mode an arc is established between the gas flow constricting nozzle and the cathode and is commonly used in plasma spraying and in gas heaters. In the transferred mode an arc is established between the cathode and an external workpiece such as a bath of molten metal and this is used for fabrication processes [cutting and welding] and melting. In the superimposed mode arcs are "superimposed"

with an additional AC or DC power supply connected between the nozzle of the torch and the workpiece and this arrangement has been used for gas heating applications and for substrate preheating/cleaning in plasma spray.

3.3.2 RF Discharges

Induction discharges or plasmas were discovered by Hittorf in 1884 while performing experiments on the conduction of electricity through rarefied gases [Eckert, 1974]. However, a major contribution to the development of the induction torch was begun when Reed [1961] showed that a plasma could be generated in an open tube with streaming gas and could thus be used as a heating source.

RF thermal plasma discharges are characterized by the absence of electrodes. The plasma is generated and sustained either by capacitive or inductive coupling methods. In capacitive coupling, a high-frequency electric field [E-field] is used to maintain the discharge. In an inductively coupled discharge, a time-varying magnetic field [H-field] generated by an RF current flowing through a coil induces an electric field and, hence, drives a current directed opposite to the current in the primary coil. Inductively coupled plasmas [ICP] are more important than capacitive discharges as they can be generated at much lower frequencies than capacitive discharges. Metal wall and ceramic wall torches are two principal variations of the ICP torch design [Figure 3.2].

Figure 3.2: Schematic of a typical RF ICP plasma torch.

In both these designs an axial sheath gas flow reduces the heat flux to the reactor walls. The plasma is confined to the center of the torch by a water-cooled ceramic or quartz tube. ICP torches typically operate in a wide range of power levels: 3-4 kW [analytical ICP's] to 4-6 MW.

ICP torches can be operated using a wide range of plasma gases: argon, nitrogen, hydrogen, air and even pure oxygen. Their energy efficiency is of the order of 40-50 %, but is continually being improved through developments such as the use of solid-state [SCR and GTO] power supplies, and improved torch designs which reduce radiative losses from the plasma to the torch

walls and cooling water [Tuszewski, 1994] and by increased coil:plasma coupling efficiency by eliminating the inner quartz tube [Boulos, 1995; Jurewicz and Boulos, 1993]. The inductively-coupled plasma has proven to be very attractive tool for the thermal treatment of powders, for spheroidizing and for materials synthesis. The use of inert atmospheres and the absence of electrodes produce very "clean" plasmas that are essential for some processing applications. In addition, induction plasmas are typically much larger and have more uniform temperature fields than thermal plasmas generated by constricted DC arcs.

3.4 Industrial Applications of Thermal Plasma Technology

Thermal plasma processing has a very wide range of applications ranging from spraying of coatings to waste treatment. In general, plasma applications can be categorized [Boulos, et al., 1994; Taylor and Pirzada, 1994; Fauchais and Vardelle, 1997] as:

1. Plasma Deposition - The spraying of coatings and films for surface modification to improve thermal and wear resistances including densification and sintering of materials [Knight and Smith, 1998; Smith and Knight, 1996].
2. Plasma Metallurgy - The refining and remelting of metals/alloys and extraction of metals from ores, scrap and wastes [Knight, et al., 1991].
3. Plasma Synthesis of Advanced Materials - The synthesis of fine powders [TiO_2 pigments, high-purity SiO_2 , production of acetylene], thermal plasma chemical vapor deposition [TPCVD], plasma enhanced chemical vapor deposition [PECVD] and thermal plasma physical vapor deposition [TPPVD] [Taylor and Pirzada, 1994].
4. Plasma Treatment of Wastes - The destruction of hazardous and toxic wastes including radioactive waste and their volume reduction [Boulos, 1996; Heberlein, 1999; Hoffelner and Funfschilling, 1995; Paul, 1996].
5. Plasma Recycling - Recovery of catalysts from auto engines and recovery of precious metals such as cadmium, nickel, molybdenum etc. from iron and steel industrial wastes [Hoffelner and Funfschilling, 1995].
6. Spectrochemical Elemental Analysis - ICP quadrupole mass spectrometers are widely used as on-line systems to detect metals during waste treatment, particle synthesis, etc.
7. Plasma Welding and Cutting.

3.5 Plasma/Waste Technology: Current Status

Plasma processes have significant potential for the recycling of high added-value polymeric waste streams, which are difficult to recycle by conventional means. To date, the focus of plasma/waste technology [Boulos, 1996; Heberlein, 1999; Paul, 1996] has largely been on the destruction of hazardous chemical wastes such as chlorinated and fluorinated hydrocarbons [Breitbarth, 1997; Glocker, et al., 1998; Han, et al., 1993; Huhn, et al., 1997; Lachmann, et al., 1994; Mosse and Kusnetzov, 1994; Sekiguchi, 1993; Tock and Ethington, 1988], the extraction of metals from industrial waste [Hoffelner and Funfschilling, 1995; Montgomery, 1993; Taylor and Pirzada, 1994], the volume reduction/vitrification of nuclear waste [Blutke, et al., 1996; Girolid, et al., 1996; Hoffelner and Funfschilling, 1995; Hoffelner, et al., 1996; Munz and Chen, 1989] and the destruction of military wastes [Smith, et al., 1994 and 1995]. The majority of thermal plasma waste processes developed to date have used DC transferred-arc plasma generators [torches] and have focused on waste destruction, rather than recycling. The importance of ICP systems has, however, been reported by many others [Boulos, 1991; Boulos,

1995; Huhn, et al., 1997; Smith, et al., 1994; Stratton, et al., 1999]. Yargeau, et al. [1998] treated liquid wastes using an ICP and achieved destruction efficiencies as high as 99 %.

DC thermal plasma systems for waste treatment are ultimately limited in applicability because:

1. DC plasma melting and waste treatment systems are generally implemented as batch processes because of relatively short electrode lifetimes. Commercially viable waste treatment processes require at least semi-continuous operation. Torch/electrode lifetimes ranging from ~30 to 1000 hours [i.e., a maximum of only 41 days] have been reported [Goodwill and Schmitt, 1996; Hanus, 1996] for high power [MW range] DC torches with rod or "button" type tungsten cathodes and copper anode nozzles. These factors necessitate periodic shutdowns, removal of the torch[es] from the furnace or reactor, and replacement of the cathode and/or anode electrodes. Torches with tungsten cathodes are the most common and can only be used reliably with inert [non-oxidizing] plasma forming gases, including Ar, Ar/H₂, Ar/He, Ar/N₂ etc. Such torches cannot be operated using air or O₂ as plasma forming gas for more than very short periods, since the cathode would oxidize and be consumed very rapidly. This also precludes the use of oxidizing plasmas and process chemistries. Various commercial torch designs utilizing hollow, cold cathode, copper and alloy electrodes have also been developed [Cheek, et al., 1996; Eschenbach, et al., 1996], but these too are subject to electrode erosion. While the erosion can be more effectively reduced through the use of vortex gas flows and/or magnetic fields to rotate and translate the arc attachments over the electrode surfaces in order to distribute the thermal loading over much larger areas, the electrode erosion cannot be entirely eliminated. Air and O₂ can be used as plasma forming gases with these torches, although in this case consumption of the copper-based electrodes would also likely increase.
2. DC torch systems are also more prone to "stray-arcing" which has, in at least one commercial installation [Chapman, et al., 1996; Goodwill and Schmitt, 1996], reportedly led to sufficient leakage of torch cooling water into the furnace to warrant replacement of the DC torch by a simpler hollow graphite electrode.
3. Scale-up of DC torches beyond 1-5 MW is limited by the aforementioned electrode erosion and until fairly recently also by DC power supply technology. Few commercial DC torch designs suitable for use in furnace/reactor systems rated at power levels in excess of 1 MW currently exist.
4. Product contamination can also occur due to electrode erosion. This has prevented conventional DC torches with refractory metal [tungsten] cathodes from being widely used for the transferred-arc melting of reactive metals such as Ti. The possibility of tungsten inclusions in the melt is unacceptable in materials being remelted for aerospace [turbine] applications.
5. The design of transferred and non-transferred arc DC torches does not favor the injection of large amounts of feedstock materials directly into or through the plasma region. Excessive "loading" of constricted plasma jets can lead to physical and electrical instabilities in the arc and even arc extinction. Several novel "center-feed" hollow- or multi- cathode DC torches have been developed for plasma spray coating applications [Delcea and Sexsmith, 1996; Moreau, et al., 1995]. These designs have not yet been scaled up to the power levels required for processing waste, and the ability to feed large amounts of material through the cathode[s] without affecting the stability of the arc is questionable. The less constricted toroidal discharge regions in ICP torches, on the other hand, typically generate larger

volumes of plasma and are thus considered to be more suitable for applications requiring large volumes of material to be injected into the plasma region, as in the case of waste processing or gas-phase chemical syntheses.

ICP torches are, in contrast, *electrodeless*, allowing use of a wider range of plasma forming gases, including air, O₂, H₂ and even hydrocarbons such as methane, along with Ar, Ar/H₂, Ar/He, Ar/N₂ etc. ICP torches can also be more readily scaled up to the high power levels [>1 MW] required for high throughput commercial systems. Their continuous operation is unaffected by the electrode erosion and current carrying/cooling limitations of DC torches. Axial injection of the reactants to be treated into ICP torches allows better mixing of the reactants. The gas velocity in ICP torches is 20 – 30 times lower than in DC torches due to the larger cross section, allowing longer residence times and, hence, larger throughputs of reactants than in DC torches [Fauchais and Vardelle, 1997]. ICP torch and power supply efficiencies [40-50 %] are, however, generally lower than those of DC plasma systems [50-90 %]. This is due primarily to the inherently lower energy transfer efficiency of induction heating and the lower efficiency of the high frequency power supplies used. High frequency [MHz range] ICP systems often utilize vacuum tube driven Class C tuned oscillators, which have inherent efficiencies of <50 %, although more efficient solid-state power supplies operating at frequencies up to ~ 450 kHz are now being used in some of the newer high power ICP designs. It is likely that future improvements in both ICP torch and power supply design will continue to improve the overall efficiency of ICP systems.

This study had the aim of recovery rather than destruction; to recover, from polymeric waste, the monomers from which they are originally formed. There are long-term benefits to monomer recovery, both in terms of resource conservation and environmental benefits due to the reduction in landfilled waste, which is largely non-biodegradable, and by reducing incineration, with its associated generation of NO_x and other hazardous emissions.

A major limitation in the thermal plasma recycling of polymers is the lack of understanding of the reactions occurring during the process, including those during the quenching period necessary to "freeze" the product[s] before complete pyrolysis to carbon and hydrogen occurs. The influence of process parameters on the reactions occurring and on the yield of reaction products also need to be understood. Treatment of mixed polymers, typical of the actual MSW stream composition [Table 1.1], would likely involve a very large number of reactions and complex interactions among the different components and species, making understanding of the fundamental reaction mechanisms very difficult. The present study was, therefore, aimed at understanding these factors by treating individual "model" polymers, selected to represent materials typically found in MSW streams. In particular, ultra-high molecular weight [UHMW] polyethylene [PE], polypropylene [PP], polyethylene terephthalate [PET] and a mixture of PE and PP, were used as feedstocks.

4. PROPOSED REACTION MECHANISMS

Polymer pyrolysis in an ICP involves decomposition of high molecular weight polymers into monomer molecules in a very short time [~ 1 s] and in a single reactor [Merkhour, et al., 1997; Wei, et al., 1988]. Mechanistically this process can be divided into four parts:

1. Gas phase dynamics that includes the gas flow field, temperature field, and coupling to the electromagnetic field.
2. Particle dynamics including heating of the particles passing through a plasma.
3. Condensed-phase degradation reactions in the polymer particles.
4. Gas-phase pyrolysis reactions of evaporated hydrocarbons.

Several authors have modeled the dynamics of the gas flow, thermal and electromagnetic fields in ICP plasma reactors [Merkhour, et al., 1997; Wei, et al., 1988; Vardelle, et al., 1998; Ramasamy and Selvarajan, 1999]. The primary drawback of these models is the lack of experimental data to verify the results of the simulations. Validation of reaction mechanisms is extremely difficult at the high temperatures likely in thermal plasmas and intense turbulence because:

1. Many possible reaction mechanisms can occur simultaneously because of the high kinetic energy species such as radicals, ions and electrons present in a plasma system.
2. Determination of kinetic data from the condensed phase reactions is very difficult.
3. The number of reaction parameters required to be determined is very large.
4. Flow conditions and the mixing of gases are very important and, hence, the combination of a hydrodynamic model and chemical kinetics model would be needed.

A simplified polymer particle can be represented by a group of polymer chains entangled with each other. As a solid polymer particle passes through the plasma zone it is heated and breaks into smaller fragments by scission reactions. Eventually, the fragments would become small enough to evaporate. This polymer "unzipping" leads eventually to the formation of volatile products. Such a mechanism can be presented schematically as shown in Figure 4.1.

Figure 4.1: Schematic of polymer chain scission mechanism.

Several authors have proposed a critical chain length below which the products can evaporate [Westerhout, et al., 1997; Wall, et al., 1954; Kiang, et al., 1980]. The chain length of volatiles is temperature-dependent and has been determined from the normal boiling points of hydrocarbons. This approach provides a clear cut-off between which species remain in the liquid phase and those which evaporate.

The *Fourier* number [Fo] and *Biot* number [Bi] for the polymer particles fed into the plasma reactor was estimated based on the following assumptions [Petrovicova, 1999]:

1. Plasma gas velocities of 10 to 20 m/s [Wei, 1987].
2. Bulk plasma gas temperature = 3000 K. At this temperature argon plasma density, viscosity and thermal conductivity were 0.16 kg/m^3 , $1.2 \times 10^{-4} \text{ kg/m-s}$ and $9.4 \times 10^{-2} \text{ W/m-K}$, respectively [Boulos, et al., 1994].
3. Mean particle diameter = 30-100 μm .
4. Residence time of 0.1 to 1 s [Wei, 1987].

The Fo and Bi numbers were calculated to lie in the range of 6 to 100 and 0.2 to 0.4, respectively. These values indicated that transient plasma to particle heat transfer behavior could be neglected. This also indicated that polymer particles larger than 100 μm in diameter could be fed into the reactor and would be completely vaporized.

Unlike many of the pyrolysis studies cited above, evaporating products in an ICP process do not stop reacting. The gas temperatures in an ICP are much higher [up to 10,000 K] than the temperatures normally used for the thermal pyrolysis of polymers [up to 1200 K]; so thermal pyrolysis of hydrocarbons will continue in the gas-phase in a plasma heated process leading to low molecular weight reaction products.

Pyrolytic reactions have been broadly classified into four groups [Flynn and Florin, 1985; Albright, 1983]: [1] random main-chain scission; [2] depolymerization; [3] carbonization and [4] side group reactions.

Random chain scission is the breaking of large polymer chains to produce smaller polymer molecules of random sizes. Depolymerization is the successive removal of monomer units from the chain by a free-radical unzipping mechanism. Carbonization and side group reactions include those reactions which lead to cross-linking, straight chain polymer formation by elimination of side chains, cyclization and aromatization by dehydrogenation. Both chain scission and depolymerization mechanisms involve initiation, propagation, chain-transfer and termination reactions according to free radical chain theory.

Initiation can take place either by abstracting a hydrogen atom or by homolytic cleavage of a carbon-carbon bond either at the chain ends or within the polymer chain. Argon was used as the plasma forming gas. At the conditions at which the plasma reactor was operated argon undergoes partial ionization. The degree of ionization of argon is of the order of 1 % at 10,000 K [$\sim 1 \text{ eV}$] and 100 kPa and falls very rapidly with decrease in temperature [to 0.01% at 7500 K] [Boulos, et al., 1994]. Also, only a small region of the plasma will be at this temperature. Most of the initiation reactions would be due to thermal mechanism rather than ionic reactions since the ion concentration will be very low at temperatures [$\sim 3000 \text{ K}$] estimated for the bulk of the gas flow. Due to high heating rates, strong internal stresses could be generated within the polymer particle and this could lead to ablation of polymer particles. This physical process could also lead to initiation of depolymerization reactions.

The standard Gibbs free energy changes for the reactions listed below in Table 4.1 were calculated using a thermochemical calculator [Thermochemical Calculator, 1997]. From the reactions in the table, it can be concluded that the bond energy requirement for carbon-carbon

bond cleavage is lower than that for hydrogen abstraction. This predominance is even more evident with increase in molecular weight of the hydrocarbon. It can also be concluded that, at a given temperature, chain scission of C-C bonds would be more probable at the ends of molecules than at the center of the molecule. However, with increasing molecular weight of the hydrocarbon, ΔG^0 difference between chain scission of C-C bonds in molecule ends and molecule center is reversed [Table 4.1].

By comparing the bond dissociation energies of C-C and C-H bonds [Table 4.2 [Wampler, 1995; Flynn and Florin, 1985; Albright, 1983]], it can be seen that the C-C and C-H bonds to the allylic carbon are weaker than the corresponding bonds in a pure saturated chain. In a polymer chain having the bonding shown below [reaction 4.1], it is easier to break the bonds indicated than any others. These bonds are β -bonds with respect to the double bond and their scission is known as β -scission. The difference in bond energies, which leads to β -scission, increases with increasing temperature [Table 4.1].

Initiation of this process in a plasma reactor will result from collisions between the polymer molecules and ions or excited molecules from the plasma.

Table 4.2: Bond dissociation energies of C-C and C-H bonds [kJ/mol]:
 $\text{R}_1 - \text{R}_2 \longrightarrow \text{R}_1 + \text{R}_2$ [Flynn and Florin, 1985]

R1	R2							
	n-alkyl				Branched	Alkyl	Radical	Sp ² radical
	CH ₃	C ₂ H ₅	n-C ₃ H ₇	n-C ₄ H ₉	i-C ₃ H ₇	t-C ₄ H ₉	CH ₂ =CHCH ₂	CH ₂ =CH
H	435.2	410	408.4	408.4	395.4	381.2	363.2	435.2
CH ₃	369.9	353.6	355.2	354.4	356	336.8	307.9	392.1
C ₂ H ₅		341.4	340.6	340.6	335.6	321.8	294.2	376.6
n-C ₃ H ₇			340.6	339.8	334.7	321.3	294.2	413
i-C ₃ H ₇					325.1	307.1	283.3	283.7
t-C ₄ H ₉						282.9	-	339.3
CH ₂ =CHCH ₂							251.1	328
CH ₂ =CH								425.5

Table 4.1: Calculated $-\Delta G^{\circ}_{1000}$ and $-\Delta G^{\circ}_{8000}$ [kJ/mol] values for pyrolysis reactions of n-alkanes and 1-alkenes.

<u>Reaction</u>	$-\Delta G^{\circ}_{1000}$ [kJ/mol]	$-\Delta G^{\circ}_{8000}$ [kJ/mol]
$\text{CH}_4 = 0.5 \text{ C}_2\text{H}_4 + \text{H}_2$	-40.0	455.2
$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$	-8.2	898.0
$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{H}_2$	9.4	943.8
$\text{C}_4\text{H}_{10} = \text{C}_4\text{H}_8 + \text{H}_2$	8.9	837.1
$\text{C}_5\text{H}_{12} = \text{C}_5\text{H}_{10} + \text{H}_2$	7.5	898.4
$\text{C}_6\text{H}_{14} = \text{C}_6\text{H}_{12} + \text{H}_2$	7.4	1263.0
$\text{C}_3\text{H}_8 \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	52.9	881.2
$\text{C}_4\text{H}_{10} \longrightarrow \text{C}_3\text{H}_6 + \text{CH}_4$	69.0	917.2
$\quad \quad \quad \longrightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	40.6	846.4
$\text{C}_5\text{H}_{12} \longrightarrow \text{C}_4\text{H}_8 + \text{CH}_4$	70.4	1591.5
$\quad \quad \quad \longrightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6$	58.7	852.6
$\quad \quad \quad \longrightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_8$	38.1	807.4
$\text{C}_6\text{H}_{14} \longrightarrow \text{C}_5\text{H}_{10} + \text{CH}_4$	69.9	948.7
$\quad \quad \quad \longrightarrow \text{C}_4\text{H}_8 + \text{C}_2\text{H}_6$	61.0	822.9
$\quad \quad \quad \longrightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$	60.1	919.7
$\quad \quad \quad \longrightarrow \text{C}_2\text{H}_4 + \text{C}_4\text{H}_{10}$	44.0	883.7
$\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$	-50.6	888.2
$\text{C}_4\text{H}_8 = 1,3\text{-C}_4\text{H}_6 + \text{H}_2$	1.4	625.5
$\text{C}_3\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	-7.1	826.2
$\text{C}_4\text{H}_8 \longrightarrow 2 \text{ C}_2\text{H}_4$	23.6	907.3
$1,3\text{-C}_4\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	-28.4	1169.9
$\text{C}_5\text{H}_{10} \longrightarrow 1,3\text{-C}_4\text{H}_6 + \text{CH}_4$	64.3	508.5
$\quad \quad \quad \longrightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$	43.1	852.2
$\text{C}_6\text{H}_{12} \longrightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_2\text{H}_6$	55.0	185.3
$\quad \quad \quad \longrightarrow \text{C}_4\text{H}_8 + \text{C}_2\text{H}_6$	45.5	457.8
$\quad \quad \quad \longrightarrow 2 \text{ C}_3\text{H}_6$	62.1	599.8
$\text{C}_3\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	-7.1	826.2

Propagation occurs through a series of reactions which convert the polymer fragments into progressively smaller segments and subsequently to final products through radical decomposition, radical isomerization, hydrogen transfer and/or radical addition. Chain transfer reactions are classified into two types: [1] Intermolecular, where a radical is exchanged between molecules and [2] Intramolecular, where a radical is transferred between two carbon atoms of the same polymer chain. Termination reactions occur when two radicals combine or disproportionate to form stable products. Termination could also occur due to third body interactions, such as interaction at the walls of a reactor and/or interaction with quench gas molecules.

Polypropylene, PP, is a good example to explain the mechanisms of depolymerization. PP can be depolymerized by chain scission along the polymer backbone [Mechanism I] or by hemolytic scission [Mechanism II] of the methyl side groups.

Mechanism I

According to this mechanism, Polypropylene undergoes chain scission along its main backbone, resulting in two polymer fragments [R₁] and [R₂], each having a free radical at the site of the scission according to reaction [4.2]:

[R₁] has a radical on a primary carbon atom, whereas [R₂] has one on a secondary carbon atom. Each of these two radicals can undergo C-C scission at other positions along the chain, but the radicals formed would be similar to those shown in reaction [4.2]. [R₂] can further react according to the β-scission mechanism to give propylene and another [R₂] radical as shown in reaction [4.3]. Some [R₂] radicals in the very high temperature zone of a plasma could simply break next to the radical to give ethylene and [R₁] as shown in reaction [4.4].

[R₁] could react further in three ways as shown below:

Two $\dot{\text{C}}\text{H}_3$ radicals from reaction [4.5] can combine together give ethane or abstract an H to form methane. Since primary radicals are more stable at higher temperatures reaction [4.6] is most probable at high temperatures [>1500 K]. The stable product molecule in reaction [4.5] is similar to any small chain PP and could undergo further decomposition like any other PP chain. The chain transfer reaction [4.7] is more probable at slightly lower temperatures [~ 700 K] because tertiary radicals [similar to the one in R_3] are more stable than primary radicals. $[\text{R}_3]$ would react further according to the β -scission mechanism to give isobutene and $[\text{R}_2]$ as shown in reaction [4.8].

Hence, both $[\text{R}_1]$ and $[\text{R}_2]$ would react to give mainly propylene, ethylene, methane, ethane or either $[\text{R}_1]$ or $[\text{R}_2]$ radicals.

Mechanism 2

According to this mechanism, C-C hemolytic scission takes place at the methyl side group resulting in a methyl radical and polymer radical as shown in reaction [4.9].

The methyl radical would form methane by abstracting a hydrogen atom from the polymer chain, or by combining with other methyl radical to form ethane, whereas the polymer radical would undergo a β -scission reaction to give propylene and $[R_2]$. $[R_2]$ would further react according to mechanism [1].

Polymer decomposition under thermal plasma conditions is likely to take place according to both these mechanisms. In all cases, however, the main products of the primary reactions will likely be propylene, ethylene, methane, ethane and hydrogen. Since the temperature in the plasma region is so high, many secondary reactions are also possible. Some of the prominent ones are listed below:

Polyethylene [PE] decomposes through similar mechanisms and likely to form propylene, ethylene and methane as primary products. Branched PE would decompose in a manner similar to PP. Linear high density PE would undergo main chain scission followed by β -scission.

Reaction [4.15] depicts the depolymerization of polyethylene terephthalate [PET]. Since PET is manufactured through condensation polymerization, plasma depolymerization would not lead to the formation of monomers as in the case of PE and PP. Many additional products are possible for this polymer owing to the presence of the benzene ring and substituent groups. Possible products include C_2H_4 , C_2H_2 , C_6H_6 , CO, CO_2 , H_2 , O_2 , H_2O and other such as $HCOOH$.

5. METHODOLOGY

5.1 Reactor and Process Description

A Tekna [Model No. PL-35] ICP torch was used in conjunction with a Lepel Corporation [Model T-15-3-MC5-TL1] ~15 kW, 2-4 MHz vacuum tube power supply to generate the thermal plasma jet used in the study. By inducing an oscillating magnetic field in a flowing gas, the ICP torch heats and ionizes the gas, which generates an extremely hot [8,000 - 10,000 K] plasma jet at nominally atmospheric pressure. The plasma was ignited using a high voltage [~50 kV] Tesla coil, momentarily applied to the rear of the central probe. Argon was used as the plasma gases. At these temperatures and atmospheric pressure argon would be singly ionized and the particle densities of Ar and Ar^+ are of the order of 10^{24} and 10^{22} m^{-3} respectively [Boulos, et al., 1994]. The degree of ionization is ~1 % and falls very rapidly with decrease in temperature.

A schematic of the PL-35 ICP torch is shown in Figure 5.1 [Boulos, 1995]. The torch has an internal diameter of 35 mm and a 4-turn coil cast into a water-cooled ceramic body. For this torch a minimum cooling rate of 16 l/min is required. The upper part of the torch comprises of a brass gas distribution head used for the injecting different gas flows required to stabilize the plasma: the sheath and the central gas flows. The central gas flow provides the main plasma-forming gas. The sheath flow surrounds the central gas flow and protects the torch walls from being melted by the intense heat transferred from the plasma. The sheath gas also protects the walls of the reactor from being contaminated by feed material. Probe gas flow is introduced through a 2.4 mm internal diameter, 200 mm long, water-cooled double-walled stainless steel tube located on the torch axis. The probe can be moved axially and, hence, can be used to vary the injection location and residence time of particles injected into the plasma. In order to keep the chemistry of the depolymerization studies as simple as possible argon was used as sheath, central and probe gas throughout this study. A minimum power is required to sustain the plasma discharge, dependent on the frequency of operation of the torch and the plasma gas composition. For a torch operating at high frequencies [2-3 MHz] and using monatomic plasma-forming gases such as argon the minimum sustaining power of the order of ~6 kVA.

Figure 5.1: Schematic of PL-35 ICP torch [Boulos, 1995]

Figure 5.2: Schematic of the reactor.

The reactor [Figure 5.2] was designed to enable rapid reactant heating and quenching [10^6 K/s] and consisted of a series of four 143 mm long x 152 mm ID, double-walled, water-cooled, stainless steel spool pieces, with Viton® gasket seals between the section flanges. The top two sections of the reactor, located immediately beneath the torch, had four equally spaced 70 mm ID flanged side arms. These side arms were fitted with standard Conflat™ vacuum flange seals and provided access for viewing, quenching and/or sampling, as required. The spool piece located immediately beneath the torch had a Pyrex™ glass windowed side arm for direct viewing of the plasma jet exiting the torch. The reactor walls were water cooled to ~ 283 K during operation.

Figure 5.3: Schematic of the quench nozzle layout.

The gas exiting the reactor was passed through a filter [a stainless steel mesh supporting a NOMEX® cloth with a mesh size ~ 10 μm] to collect solids before entering the air-driven venturi pumps [eductors]. Pressure within the reactor was controlled by three eductors by varying the flow of compressed air, which both ensured dilution and cooling of the reactor off-gas stream. The exhaust flow from the eductors was directed through a filter [vacuum cleaner filter bag made of paper] to remove the solids before the gases were discharged into a fume hood. The reactor pressure was monitored using a diaphragm type pressure gauge [with a differential pressure range of ± 25 kPa (~ 100 " of water)].

The high temperature plasma jet exiting the torch can be quenched by an argon gas jet at approximately room temperature. Based on previous experience with quench nozzles, a full cone wide-angle [$120 - 125^\circ$] nozzle [Spraying Systems, Inc., Type 1/8 GA 316SS-8W] was located at position "A" [Figure 5.3], such that the quench gas flow directly opposed the plasma jet. The stainless steel nozzle had an orifice diameter of 2.38 mm [$3/32$ "] and was designed for a flow rate of 71.6 slm of argon gas at an inlet pressure of 69 kPa [10 psi]. Based on the results of

preliminary scoping experiments, it was proposed that quenching the hotter regions of the plasma jet tail-flame would increase the monomer concentration in the product gas. An identical quench nozzle was, therefore, located at position "B" [Figure 5.3] with the flow of quench gas directed perpendicular to the plasma stream. The gas flow rates through both nozzles were controlled using critical orifices [#56 or #47] at flow rates of up to 80 slm and ≥ 60 slm, respectively. Quench nozzles with different orifice diameters and maximum free passage diameters were used to study the effect of quench velocity on product selectivity. The different types of nozzles used are listed in Table 5.1. Maximum free passage diameter is defined as the maximum particle diameter that can pass through the nozzle without clogging the nozzle.

Table 5.1: Various quench nozzles used.

Nozzle Type	Nominal Orifice Diameter [mm]	Maximum Free Passage Diameter [mm]	Flow Rate at an Inlet Pressure of 0.69 kPa [slm]
GA-316SS-8w	2.38	1.27	71.6
GG-316SS-8w	2.38	1.27	71.6
GG-316SS-5.8w	2.38	1.02	51.2
GG-316SS-2.8w	1.60	1.02	26.1

5.2 Materials Selection

"Model" pure, single polymers were processed in the ICP reactor, rather than a MSW mixture. Polyethylene [PE], polypropylene [PP] and polyethylene terephthalate [PET] were used as feedstocks. These polymers represent about 69 wt.% of the polymers in MSW [Table 2.1]. In addition, the decomposition products of mixtures of PE and PP were also studied. Experiments were carried out to determine the effect of reactor parameters and quench conditions on the composition of the reaction products obtained. Argon was chosen as the plasma and quench gases because it would be easier to understand the complex polymer pyrolysis reactions in an inert media.

Ultra high molecular weight [UHMW] PE [Mol. Wt. = 30,000 kg/kmol, Mean Particle size = 63 μm], obtained from Ticona, LLC, PP [Mol. Wt. = 80,000 kg/kmol, Mean Particle Size = 38 μm], obtained from Clariant Co. and PET [Mean Particle Size = 48 μm], obtained from DuPont were used as feedstocks. The molecular weight of UHMW PE quoted by the supplier was much less than typical values for these polymers. It would be difficult to achieve high molecular weight polymers as powders in micron range. The mean particle size chosen was appropriate for this system because smaller PE particles [Mean size = 5 μm] could not be fed through the feeder as the feed particles were caking and blocking the feed nozzle and larger particles would lead to clogging of the probe. The physical and thermal properties of the model polymer systems are listed in Table 5.2.

Table 5.2: Physical and thermal properties of the polymer feedstocks [Frank, 1968; Kevorkian, 1963; Kroschwitz, 1986].

Properties	Polymer Types		
	PE	PP	PET
Molecular Weight	30,000	80,000	N/A
Melting Point [K]	410	440	545
Specific Gravity	0.93	0.91	1.3
Thermal Conductivity [W/m-K]	0.47	0.12	0.29
Specific Heat Capacity [kJ/kg-K]	1.88	1.88	1.2
Degradation Temperature [K]	625	540	575

A PE and PP mixture was prepared in the same weight ratio as these materials occur in MSW [Table 2.1] by blending 250 g of PE with 75 g of PP in a "Vee-blender" for 60 hours. The mean particle size of this mixture was 55 μm , which was between the particle sizes of the individual polymer powders.

5.3 Analytical Techniques

The particle size distribution of the polymer feedstock powders was analyzed by a laser scattering particle size distribution analyzer [Horiba Ltd., Model LA-910]. The particle size distributions for each polymer are shown in Figures A1-A4. The polymeric powders were fluidized in a flow of argon carrier gas and fed from a slotted rotating disk type volumetric feeder [Plasmadyne, Model No.1252B] into the center of the ICP torch *via* the water-cooled stainless steel probe. To calibrate the powder feeder, the hopper and rotating disc assembly of the feeder were thoroughly vacuum cleaned. Polymeric powder was fed and collected in sample bottles for 5 minutes at different disc RPM's and carrier gas flow rates. Each of these calibration runs was repeated 3-5 times. The mean powder feed rates in grams per minute are plotted against RPM of the disc, as shown in Figures A5 -A8.

A nominal 3.175 mm [1/8"] OD stainless steel sampling tube, connected to a diaphragm pump, was used to withdraw gas samples from the reactor [Figure 4.2] for analysis. Samples were collected in Tedlar™ gas sample bags [Supelco Co., Part No. 24634]. The sample bags were filled, evacuated and then refilled to ensure sufficient dilution of residual air. Samples were later analyzed off-line using gas chromatographs [GC], Shimadzu, Model GC-14A and GC-9A, fitted with a 23 % sp-1700 on 80 % Chromosorb™ PAW column [Supelco Co., Part No. 12809-U] and 80/100 Carbopack™ B/3 % SP 1500 column [Supelco Co., Part No. 11813-U], respectively. The GC-14A unit was run at 70 °C. Gas samples were injected splitless at 100 °C and detected using an FID detector at 110 °C and 25 ml/min of He was used as the carrier gas. The GC-9A unit was heated from 75 °C to 225 °C at a rate of 4 °C/min. Gas samples were injected splitless at 150 °C and detected using an FID detector at 200 °C and 20 ml/min of N₂ was used as carrier gas. Each sample bag was analyzed three times usually within 1 to 5 hours of collection. The GC column was calibrated using a standard gas mixture containing light hydrocarbons C1-C6 n-paraffins [Supelco Co., Part No. 330200] and acetylene, CO₂, CO and propylene.

Liquids entrapped in the solid residue were extracted using solvents CH₂Cl₂ or CCl₄. The extract was concentrated by blowing Ar gas. The concentrated liquid extract was then analyzed

using a Varian Saturn 2000 GC/MS fitted with a Chromopack CP-Sil 8 CB column. The samples were injected splitless at 280 °C. The GC oven was kept at 50 °C for 3 minutes and was then raised to 280 °C at 7 °C/min and held at 280 °C for 20 minutes. 1ml/min of He was used as carrier gas. 50 – 350 amu were scanned at 1 scan/s.

The elemental analyses of pure polymers and solid residues collected from the reactor were done at the University of Pennsylvania Chemistry Lab. The calorific value of the solid residue collected from the reactor was measured using a Parr [Model 1341] oxygen bomb calorimeter. The solid residue structures were studied using an Amray [Model 1830] scanning electron microscope [SEM] and JEOL [Model 100 CX II] transmission electron microscope [TEM]. The identification of elements in the SEM samples was made using an Oxford Instruments [Model LINK ISIS] EDS.

6. RESULTS AND DISCUSSION

Polyethylene [PE], polypropylene [PP], polyethylene terephthalate [PET] and a mixture of polyethylene and polypropylene were the four model polymer systems selected to investigate the technical feasibility of depolymerization of waste polymers using an induction-coupled plasma reactor. The plasma was ignited and operated using argon as the sheath, central and probe gases. Once the plasma was stabilized, process parameters were adjusted to the desired conditions and polymer powder was fed into the center of the plasma region.

A series of experiments was carried out to determine the dependence of the monomer concentration in the product stream on the process parameters. With the help of a commercial statistical software package [Design-EaseTM], a 2-level factorial experimental matrix was designed in order to determine the principal parameters affecting the product yield. From an initial series of experiments, Design-EaseTM was used to determine the standardized effect of each parameter and of the parameter interactions. The interaction of primary variables could be defined in terms of the effect of the combined change in two independent variables [such as power, gas flow rates, etc.] on the dependant variable [such as monomer concentration] when that change was either greater or less than the sum of the responses expected from either of the parameters alone [Box, et al., 1978]. A plot of the standardized effect vs. normal probability showed a straight line through the majority of the points. For proper use of the normal probability plot, the effects must have a common error variance. Missing data or altered independent factors can cause the variance associated with the estimated effects to differ. The effects must, therefore, be standardized to correct for this [Box et al., 1978]. Standardized effects were computed using Design-EaseTM in conjunction with equation [6.1], where A represents the first variable considered.

$$\text{Standardized Effect}_i = [\text{Coefficient}_i][2][\text{Std. Error}_A/\text{Std. Error}_i] \quad [6.1]$$

Those factors, which were significantly off the line, were the variables of statistical significance. The details of the Design-EaseTM analysis are summarized in Appendix B.

The key parameters influencing the monomer concentration in the depolymerization experiments for each of the polymer systems are discussed in the following sections of the chapter.

6.1 Polyethylene Depolymerization

6.1.1 Process Parameters and Experimental Matrix

Thirteen process variables were identified as being likely to affect the yield of monomers from a polyethylene feedstock. These are listed in Table 6.1 along with the ranges over which they were varied. ICP plasmas have a minimum sustaining power, typically around 5 kVA when using Ar as the plasma gas, as in this study. However, in order to maintain a stable plasma discharge when polymers were fed into it, plasma plate power inputs of ~8 kVA were required. A lower power limit of 10 kVA was therefore selected. Similarly, a plate power input of ~20 kVA was selected as the upper limit based on the capacity of the power supply used [22 kVA]. The limits for other plasma parameters were defined based on similar equipment considerations and limitations. Argon was used as both the plasma and quench gases. Reactor pressure was maintained at atmospheric pressure. Quench nozzle type and quench nozzle location were fixed.

The remaining six parameters were optimized with respect to monomer yield, within the ranges of the parameters as discussed above.

Table 6.1: Process parameters varied in the depolymerization of PE.

Process Parameter	Range	Optimum
Plasma plate power [kVA]	10 - 20	10
Sheath gas flow [slm]	40 - 60	40
Central gas flow [slm]	15 - 40	40
Quench gas flow [slm]	0 - 155	0
Probe gas flow [slm]	7 - 9	9
Powder feed [g/min]	1.5 - 5	5
Probe tip location	114.3 mm from rear of torch	Not varied
Reactor pressure [atm]	~1	~1
Mean particle size [μm]	63	Not varied
Quench nozzle	Described earlier	Not varied
Quench nozzle location	Position A, [Figure 1]	Not varied
Quench gas	Ar	Not varied
Plasma gas	Ar	Not varied

A 2-level factorial experimental matrix [Table B.1] was designed to determine the principal parameters affecting the product yield. Ethylene concentrations from these experiments were used as response for the analysis. The factorial analysis was performed with the assumption that the quench nozzle was fixed in position "A" [Figure 5.3] and that the injection probe was located 114.3 mm from the rear of the torch. This location of the probe would give maximum residence time for the particles in the plasma zone as particles would be injected into the center of the plasma. Placing the injection probe above the plasma zone would not ensure entrainment of the particles into the plasma due to counter flow and high density of the plasma torus. Placing the probe exit close to the downstream edge of the plasma region would reduce the average residence time. Eight experiments were required to study the effects of the six parameters [see Table 6.2], and an additional eight experiments were needed to separate the main effects from interactions.

Data from the initial set of experiments was analyzed by Design-EaseTM to determine the standardized effects of the parameters [and interactions] on the concentration of the ethylene produced. The results are shown in Table 6.2. A plot of standardized effect vs. normal probability showed a straight line through the majority of the points [Figure 6.1].

Table 6.2: PE Depolymerization: standardized effects and regression coefficients as computed by Design-Ease™ using ethylene concentration as the response.

Parameter	Coefficient	Standardized Effect	Sum of Squares
A: Plasma plate power input	-1.6	-3.2	40.1
B: Sheath gas flow rate	0.2	0.3	0.3
C: Central gas flow rate	1.5	2.9	33.0
D: Quench gas flow rate	-0.5	-0.9	3.3
E: Probe gas flow rate	1.1	2.1	17.9
F: Powder feed rate	2.8	5.6	122.6
AB	0.3	0.5	1.1
AC	-1.6	-3.2	41.8
AD	2.8	5.6	126.6
AE	-0.2	-0.5	0.8
AF	-0.7	-1.4	7.4
BC	-0.2	-0.4	0.6
BD	-0.5	-0.9	3.1
ABC	0.1	0.1	0.1

Figure 6.1: PE Depolymerization: normal probability vs. standardized effect for different parameters: A-plasma plate power input; B-sheath gas flow rate; C-central gas flow rate; D-quench gas flow rate; E-probe gas flow rate; F-powder feed rate; AD-interaction of parameters A and D.

Those factors which were significantly off the line were the variables of statistical significance. These were: plasma plate power input [A], central gas flow rate [C], probe gas flow rate [E], powder feed rate [F], and the interaction between the plasma plate power and quench gas flow rate [AD]. Even though the plot indicated that the latter was not very significant, it was selected in order to study the interaction. The range of gas flow rates for the probe gas [E] was limited since a minimum of 7 slm through the probe was required to convey the feed material. An optimum value [9 slm] for the probe gas was determined during the preliminary experimental runs, and was kept constant during all subsequent experiments.

Figure 6.2 (a) shows the influence of plasma plate power over the range from 10 to 20 kVA on the production of ethylene. The mean ethylene concentration at low power level [indicated by A-] while varying the other variables from high to low levels [Table B.1] is defined as the response. This response was calculated at both power levels. There was an ~40 % reduction in the ethylene concentration as the plasma plate power input was increased from 10 to 20 kVA. Since power level also interacted with other variables [Figure 6.1], no generalization could be made from this result. Figure 6.2 (b) shows the interaction between the plate power input [A] and quench gas flow rate [D]. At the low level of A, moving from the low to high level of D resulted in a large decrease in the ethylene concentration. At the high power input [A+], however, moving

from a low to high level of quench gas flow rate resulted in large increase in the ethylene concentration. This indicated that there was a strong interaction between the quench gas flow rate and plate power input and, hence, would have to be considered when the individual parameters were studied. The "I beam" symbol on the plot indicates the 95 % confidence level for the plotted points.

Figure 6.2: PE Depolymerization: effect of (a) plasma plate power input and (b) interaction between plasma plate power input [A] and quench gas flow rate [D] on ethylene concentration.

Those points falling outside the range were unlikely to be caused by random error alone. From the plot [Figure 6.2 (b)] it could be deduced that at the higher plasma plate power level a higher quench gas flow rate was required to produce higher concentrations of ethylene. This indicated that the higher mean temperature of the plasma region, when less quench gas was used, favored the production of other species, such as propylene. Similar plots [Appendix B] for the other main and interacting variables led to the determination of optimum values for the variables within the limitations of the equipment, as listed in Table 6.1.

6.1.2 Mass Balance

At the optimum conditions, PE powder was fed into the clean ICP reactor for 45 minutes. The total amount of polymer fed into the reactor was carefully measured. Solid residues were carefully collected from different locations of the reactor and measured. This mass balance analysis indicated that 68 ± 2.5 wt.% of conversion was achieved. Conversion is defined as the percentage of the total amount of solid polymer that was converted into gaseous products. A conventional mass balance would have involved condensation of all gaseous products formed and weighing them along with the amount of solid residues. Detailed calculations are shown in Appendix I. The gaseous products were mostly ethylene and propylene, together with small percentages of methane, acetylene and butanes. Hydrogen, other alkynes, hexanes, etc. could not be detected by the gas chromatograph used for analysis of the gas samples. A sample GC chromatogram is shown in Figure C.2. The product distribution at the optimum conditions for ethylene recovery on an Ar-free basis is listed in Table 6.3. The actual product concentrations were less than 1 % [vol.].

Table 6.3: PE Depolymerization: product distribution at optimum conditions [Vol. % on an Ar-free basis].

Product	Concentration [Vol. %]
Propylene	64.2
Ethylene	20.1
Methane	5.5
Acetylene	4.4
1,3-Butadiene	2.0
Total	96.2
Wt % of Polymer Solids Converted into Gas	~68

Although ethylene concentration was the parameter used for optimizing the variables, propylene was found to be present in the product gas stream by a factor of 2.4 times greater than ethylene. Other hydrocarbons were present to a lesser extent [10 to 25 % of the ethylene concentration]. This indicated that the chain scission mechanism followed by "unzipping" mechanism as described by reactions [6.2] - [6.4] [also in Section 4] likely played a predominant role during the conversion of the polyethylene to monomers.

6.1.3 Effect of Process Variables on Ethylene Concentration

The variations in the concentrations of ethylene and propylene with plasma plate power are shown in Figures 6.3 (a) and (b). The probable error of the mean value plotted in these graphs was calculated using equation [6.5] [Livingston, 1943].

$$\text{Error} = 0.674 \times \sqrt{\frac{1}{N(N-1)} \sum_i r_i^2} \quad [6.5]$$

where

N = total number of data points

r_i = residual = $S_i - m$

[6.6]

S_i = experimental data point

m = arithmetic mean of N data points

The ethylene concentration decreased from 22 % to 10 % when the plasma power input was increased from 10 to 20 kVA [Figure 6.3 (a)]; propylene concentration increased from 53 % to 79 % for the same change in power input [Figure 6.3 (b)]. Methane concentration decreased at a much slower rate. If the C_3H_6 formed through a decrease in the gas phase C_2H_4 , according to reaction [6.7], then the concentrations of both ethylene and methane would be decreased on a mole-per-mole basis. This provides strong evidence in support of the proposed "unzipping" hypothesis.

[6.7]

Furthermore, the changes in propylene and ethylene concentrations were +26 and -12 %, respectively, supporting the unzipping mechanism rather than the gas phase reaction mechanism. The concentration of more reactive compounds - acetylene and 1,3-Butadiene - also decreased indicating changes in product composition due to secondary reactions as discussed earlier in Section 4.

Figure 6.4 (a) shows the variation of the product concentrations as the flow rate of central gas [Ar] was increased from 15 to 40 slm. Ethylene concentration increased by 35 % over the flow range studied. More scatter was observed in this data than in Figures 6.3, likely due to increased turbulence in the plasma zone at the higher gas flow, which would indicate a shorter residence time of the materials in the plasma region [Appendix H], and a greater variation in the effective temperature. Wei [1987] and Shy, et al. [1998] reported that increased central gas flows decreased the temperature of the plasma zone along the axis of the plasma and that the temperature gradients were very steep [2000 K/mm]. Figure 6.4 (a) showed a small increase in methane concentration. Acetylene concentration increased from ~1 % at 15 slm to 5.5 % at 40 slm. The 1,3-butadiene concentration increased from 1.5 % at the lower flow rate to 2.5 % at the higher one. In Figure 6.4 (b) the propylene concentration decreased from 71 to 52 %, a 25 % decrease over the same range of variation in central gas flow rate.

Due to the steep temperature gradients in the plasma reactor most of the reactions would be quenched naturally. But hydrocarbon pyrolysis reactions could undergo secondary reactions such as cyclization and coking reactions even at 500 K. Hence, cold argon gas was used as a quench gas to "freeze" the monomers before complete combustion into carbon and hydrogen occurred.

Figure 6.3 (a): PE Depolymerization: product distribution at different plasma plate power inputs. The remaining parameters were held constant at: 5 g/min powder feed rate; 40 slm central gas flow rate; and 0 slm quench gas flow.

Figure 6.3 (b): PE Depolymerization: propylene concentration at different plasma plate power inputs. The remaining parameters were held constant at: 5 g/min powder feed rate; 40 slm central gas flow rate; and 0 slm quench gas flow.

Figure 6.4 (a): PE Depolymerization: product distribution at different central gas flow rates. The remaining parameters were held constant at: 10 kVA plate power; 5 g/min powder feed rate; and 0 slm quench gas flow.

Figure 6.4 (b): PE Depolymerization: propylene concentration at different central gas flow rates. The remaining parameters were held constant at: 10 kVA plate power; 5 g/min powder feed rate; and 0 slm quench gas flow.

The influence of quench gas flow rate on product concentrations is shown in Figures 6.5 (a) and (b). As the quench gas flow rate was varied from zero to 155 slm, the ethylene concentration peaked at 23 % at a quench gas flow rate of 29 slm and then dropped rapidly to 7 % at a quench gas flow rate of 155 slm. This indicated presence of a threshold for quench gas flow rate above which significant back mixing occurred leading to decrease in the bulk gas temperature. This would have increased the probability of secondary radical and, hence, increased the propylene concentration. Again there was increased scatter in the data at the higher quench gas flow rates, which indicated that increased turbulence led to variations in the mean jet temperature, and, hence, in conversion.

The ratio of quench gas flow rate to the combined sheath, central and probe gas flow rates was a maximum of 1.75. The quench gas flow rate and the direction of its injection did not visibly affect the physical structure or stability of the plasma except in the tail-flame region of the plasma jet. Ethylene concentration decreased with increasing quench gas flow. If it is assumed that the gas exiting the plasma zone had mean temperature of 8000 K, and that the thermal conductivity of the gas was approximately equal to that of argon at the maximum quench rate, the temperature of the gas would decrease to ~3100 K, indicating that increased quench gas flow rate would favor the chain transfer reaction [6.3], leading to the formation of increased propylene through reaction [6.4]. The maximum in the ethylene concentration curve at low quench gas flow rates could have been due to quenching of secondary reactions occurring in the hot gases exiting the plasma zone.

In some experiments, the quench nozzle was relocated to position "B" [Figure 5.3] in order to determine the effect of quench gas on the hotter portion of the plasma. Quench nozzles with different throat diameters were also used to determine whether the quench velocity, rather than the total quench gas flow, was the controlling variable. The variations of ethylene concentration for various quench nozzle sizes are shown in Figure 6.6. As the quench gas velocity was increased by decreasing the nozzle throat diameter, the quench flow rate producing maximum ethylene concentration decreased because the velocity of the quench gas increased for the same volumetric flow rate and, hence, increased back-mixing even at lower quench gas flow rates. However, the peaks varied over a very narrow range of ethylene concentration.

Polyethylene [PE] particle feed rates were varied from 1.5 to 5.0 g/min. The ethylene concentration approximately doubled, i.e. from 12 to 22 %, as the powder feed rate increased from the minimum to the maximum [Figure 6.7 (a)]. As the feed rate was increased, the residence time of the particles should remain essentially unchanged, but the number of polymer particles passing through the plasma zone would increase [a 330 % increase going from 1.5 to 5 g/min, assuming equal bulk density]. This would increase the probability of the particles being carried away by the turbulent plasma to different plasma regions and, due to steep temperature gradients in this region, would allow some of the particles to unzip in a different temperature zone through reactions similar to the one shown in equation [6.8].

Figure 6.5 (a): PE Depolymerization: product distribution at different quench gas flow rates. The remaining parameters were held constant at: 5 g/min powder feed rate; 10 kVA plasma plate power input; and 40 slm central gas flow.

Figure 6.5 (b): PE Depolymerization: propylene concentration at different quench gas flow rates. The remaining parameters were held constant at: 5 g/min powder feed rate; 10 kVA plasma plate power input; and 40 slm central gas flow.

By treating yttrium oxide and using visualization techniques Trassy and Proulx [1998] showed that particulates were carried to the plasma periphery by the recirculation eddies in the coil region. The probability of polymer particles being carried away to the plasma periphery would be even higher as they are less dense than yttrium oxide and would have less momentum to overcome the backflow caused by the eddies.

Particle loading, beyond a certain feed rate, would significantly affect the plasma torch flows and temperature profiles [Trassy and Proulx, 1998; Wei, 1987; Wei, et al., 1989]. Since the depolymerization reactions are endothermic reactions, the temperature and, hence, flow profiles could be affected even at low feed rates. This would also lead to unzipping of the polymer particles in different temperature zones. The influence of powder feed rate on the concentration of other products is shown in Figure 6.7 (a) and (b). Concomitant to the ethylene production, the solids recovered from the reactor increased from 15 % [wt.] of those fed at the 1.5 g/min level to 50 % [wt.] at the 5 g/min feed rate.

6.1.4 Solid Residues

Carbonaceous residues were collected from different parts of the reactor: [1] the reactor walls, [2] the uncooled bottom reactor section, [3] a 10 μm NOMEX[®] filter located between the reactor and the eductors and [4] a paper filter in the fume hood. The calorific values of the solids collected in the hood were analyzed using a bomb calorimeter [details are shown in Appendix J]

Figure 6.6: PE Depolymerization: effect of quench nozzle size and position on ethylene concentration in the product gas. [Legend: A = quench nozzle position A; B = quench nozzle position B; Orf. = orifice; MAP = maximum allowable passage diameter].

Figure 6.7 (a): PE Depolymerization: product distribution at different powder feed rates. The remaining parameters were held constant at: 10 kVA plasma plate power input; 40 slm central gas flow; and 0 slm quench gas flow.

Figure 6.7 (b): PE Depolymerization: propylene concentration at different powder feed rates.
The remaining parameters were held constant at: 10 kVA plasma plate power input; 40 slm central gas flow; and 0 slm quench gas flow.

and were found to be very close to those of pure carbon [Table 6.4], indicating that these residues were primarily carbon. This was verified by doing elemental analysis on the pure polymer particles and solid residues. Elemental analysis was done by a complete combustion of a known mass of the sample and measuring the total amount of carbon dioxide and water formed. Agglomerated particles were found in the residues collected from the reactor walls and the bottom section of the reactor. The calorific values of these solids indicated that some untreated polymers could be present in the bottom section of the reactor.

Table 6.4: PE Depolymerization: mean particle size, calorific value and elemental composition of the solid residue.

Solid Type	Particle Size [μm]		Calorific Value [kJ/kg]	Elemental Analysis	
	Mean	Range		C %	H %
Polyethylene	63	25-150	46,376	86.07	14.58
Residue from Reactor Walls	362	1-890	42,738	90.08*	9.92*
Residue from Uncooled Bottom Section of the Reactor	74.6	0.30-400	45,372	87.57*	12.43*
Residue from Filter before Eductors	4.9	0.2-30	38,532	94.71*	5.29*
Residue from Hood	3.7	0.1-20	34,867	98.74	1.26
Carbon [Smith and Van Ness, 1987]	--	--	32,903	100	--
Hydrogen [Smith and Van Ness, 1987]	--	--	143,398	--	100

* Interpolated using calorific data.

Transmission electron microscopy [TEM] analysis of these residues, collected during the mass balance runs, revealed various carbon structures, ranging from highly oriented crystalline structures through turbostratic to completely amorphous. Some carbon nanotubes [Figure 6.8] were also detected, indicating that this plasma process may have additional applications - namely the production of high value-added carbon materials from polymeric or hydrocarbon feedstocks. A brief background on carbon nanotubes and related structures, along with a listing of their potential applications, is described in Appendix D.

These results provided strong evidence that chain scission followed by unzipping was the likely mechanism in the plasma decomposition of polyethylene, and that significant amounts of gaseous ethylene and propylene could be produced, along with lesser amounts of other hydrocarbons. The propylene concentration was much higher than expected and could be explained by the β -scission reaction mechanism. Ethylene concentration was highest when no quench gas was used, indicating that natural quenching due to the steep temperature gradients within the reactor yielded the highest monomer concentration.

The results discussed in section 6.1 have been published in the journal *Plasma Chemistry and Plasma Processing* [Guddeti, et al., 2000a]

6.2 Polypropylene Depolymerization

6.2.1 Process Parameters and Experimental Matrix

Key process parameters likely to affect the yield of monomers were identified [Table 6.5]. An experimental matrix [Table B.4], similar to that described in Section 6.1.1, was designed and the experiments were carried out to determine the principal variables and interactions of variables that affected the yield of propylene. Quench gas flow rate from a nozzle located at position B [Figure 5.3] was included in the statistical analysis. Analysis of the results showed that plasma plate power input [A], sheath gas flow rate [B], central gas flow rate [C], quench gas flow rate from position A [D], powder feed rate [F] were the principal process variables. The normal probability plot [Figure 6.9] shows that interactions of plate power [A] with sheath gas flow rate [B] and solids feed rate [F] with sheath gas flow rate [B] were the principal interactions. The amount of interactions between these variables were indicated by the degree of deviation from the curve of Figure 6.9

Figure 6.10 (a) shows the mean propylene concentration at two different plasma power levels for different combinations of the other parameters considered. However, when significant interactions between two or more parameters occurred, these main effect graphs need to be interpreted together with an interaction plot similar to that shown in Figure 6.10 (c). Figure 6.10 (a) indicates that higher power levels favored higher propylene concentrations in the gaseous product stream.

Table 6.5: Process parameters varied during the depolymerization of PP.

Process Parameter	Range	Optimum
Plasma plate power [kVA]	10 - 20	20
Sheath gas flow [slm]	40 - 60	40
Central gas flow [slm]	15 - 40	15
Quench gas flow-Position A [slm]	0 - 155	0
Quench gas flow-Position B [slm]	0 - 155	0
Probe gas flow [slm]	7 - 9	9
Powder feed [g/min]	1.5 - 5	1.5

Figure 6.8: Enlarged view of a carbon nanotube covered with several graphene layers as shown by TEM analysis of solid residue from the bottom of the reactor [Courtesy Dr. K. Lafdi, Center for Advanced Friction Studies, Southern Illinois University].

Figure 6.9: PP Depolymerization: normal probability vs. standardized effect for different parameters: A-plasma plate power input; B-sheath gas flow rate; C-central gas flow rate; D-quench gas flow rate [Position A]; E-probe gas flow rate; F-powder feed rate; G-quench gas flow rate [Position B].

Figure 6.10: PP Depolymerization: effect of (a) plasma plate power input, (b) powder feed rate, and (c) interaction between power input and sheath gas flow rate on propylene concentration.

Figure 6.10 (b) indicates that lower powder feed rates yielded higher propylene concentrations. Similar plots for the other variables led to the optimum values for the process variables within the limits of the experiment are listed in Table 6.5. Figure 6.10 (c) shows the interaction between the power input [A] and sheath gas flow rate [B]. At the low level of A, moving from the low to high level of B resulted in a large increase in propylene concentration. At the high level of A, however, moving from the low to high level of B produced little or no change in the propylene concentration.

6.2.2 Mass Balance

At the optimum conditions listed in Table 6.5, PP powder was fed into the carefully cleaned ICP reactor for 45 minutes. The total mass of polymer fed into the reactor and the total mass of solid residue accumulated in the reactor were measured. This mass balance analysis indicated that 78 % [wt.] of the total PP fed into the reactor was converted into gaseous products. Detailed calculations including the amount of solid residues from different locations of the reactor are presented in Appendix J. The products were mostly propylene, together with small [<5 %] percentages of methane, ethylene, acetylene and butanes. Hydrogen, other alkynes, hexanes, etc. could not be detected by the gas chromatographic column used for analysis. The gaseous product distribution at the optimum conditions for propylene recovery on an Argon-free basis is listed in Table 6.6. However, the actual gaseous concentrations were in the order of 1 % [vol.].

Table 6.6: PP Depolymerization: product distribution at optimum conditions [given as Vol. % on an Ar-free basis].

Product	Concentration [Vol. %]
Propylene	93.7
Ethylene	1.7
Methane	2.6
Butanes & Butenes	1.3
Solids Conversion	~78

6.2.3 Effect of Process Parameters on Propylene Concentration

The variations in product distribution with plasma plate power input are shown in Figures 6.11 (a) and (b). As the power input was increased to 20 kVA, the energy density in the system increased, which in turn increased the plasma discharge zone, but the maximum temperature achieved in the discharge zone would only increase slightly due to increased loss of discharge energy as radiation [Wei, et al., 1988]. Wei, et al. [1988] also observed that the length of an ICP plasma zone along the centerline, greater than a temperature of 9000 K, increases with increasing power input, resulting in longer residence times for injected particles in the high temperature zone. Therefore, each polymer particle was likely to have reached a higher temperature, hence, there is an increased probability of primary radical formation and increased propylene yield via a β -scission mechanism. Reaction [4.6] shows one possibility. The acetylene peak in Figure 6.11 (b) could be due to secondary reactions, similar to the reaction [4.12].

Figure 6.11 (a): PP Depolymerization: propylene and ethylene distributions at different plasma plate power inputs. The remaining parameters were held constant at: 1.5 g/min powder feed rate; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A].

Figure 6.11 (b): PP Depolymerization: other product distributions at different plasma plate power inputs. The remaining parameters were held constant at: 1.5 g/min powder feed rate; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A].

The effect of sheath gas flow rate on product selectivity was studied by increasing the sheath gas flow rate from 40 to 60 slm [Figure 6.12]. As predicted by the statistical analysis using initial results [Figure 6.10 (c)], at high power levels the effect of sheath gas on propylene concentration was negligible. A small decrease in propylene concentration from 94 to 92 % and a corresponding increase in ethylene [2.0 to 2.4 %] and methane [2.5 to 3.6 %] concentrations were observed. Increased sheath gas flows likely decreased the bulk temperature of the plasma gas. Due to higher stability of the tertiary radical as compared to the primary radical at lower temperatures [TRC Thermodynamic Tables, 1986], increased sheath gas flow would likely lead to a shift of radical position from the primary carbon to the tertiary carbon atom on some of the radicals [reaction 4.7] and, thus, a slight decrease in the propylene concentration, as observed.

In order to study the effect of the central gas flow rate [Figure 6.13], the argon flow rate was increased from 15 to 40 slm with the other parameters kept constant at the optimum conditions. Product gas concentration remained essentially constant at 94 % propylene, 2 % ethylene, 2.5 % methane and the rest being C4's. The influence of quench gas flow rate [position A], where the quench flow was counter to the feed and plasma flow direction, is shown in Figures 6.14 (a) and (b). The propylene concentration peaked at approximately 94.5 % at a quench flow rate of 40 slm. The quench gas flow rate, at its maximum, was 1.75 times greater than the combined sheath, central and probe gas flow rate. Thus, high quench gas flow rates would likely increase the mixing of cold quench gas with the hot plasma stream and, hence, would tend to decrease the bulk gas temperature, favoring chain transfer [reaction 4.7], and leading to the formation of more butanes *via* β -scission as shown by reaction [4.8].

The longer residence time due to the back mixing induced by the quench flow would also likely lead to increased concentrations of ethylene, methane and acetylene [reaction 4.12]. The maximum in the propylene concentration and minimum in the ethylene concentration curves at low quench gas flow rates could be due to quenching of secondary reactions occurring in the hot gases exiting the plasma zone.

Figure 6.12: PP Depolymerization: product distributions at different sheath gas flow rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 0 slm quench gas flow. [A].

Figure 6.13: PP Depolymerization: product distributions at different central gas flow rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow [A].

Figure 6.14 (a): PP Depolymerization: propylene and ethylene distributions at different quench gas flow rates [Position A]. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 40 slm sheath gas flow rate.

Figure 6.14 (b): PP Depolymerization: other product distributions at different quench gas flow rates [Position A]. The remaining parameters were held constant at: 20 kVA plasma plate power input; 1.5 g/min powder feed rate; 15 slm central gas flow rate; and 40 slm sheath gas flow rate.

Figure 6.15 (a): PP Depolymerization: propylene and ethylene distributions at different powder feed rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow rate.

Figure 6.15 (b): PP Depolymerization: other products distributions at different powder feed rates. The remaining parameters were held constant at: 20 kVA plasma plate power input; 15 slm central gas flow rate; 40 slm sheath gas flow rate; and 0 slm quench gas flow rate.

As the polypropylene feed rate was varied over the range 1.5 to 5.0 g/min, propylene concentration decreased from 94 % to 88 % [Figure 6.15 (a) and (b)]. Ethylene concentration increased from 1.5 % to 4.5 %. Over the same feed rate range the methane concentration increased from 2.5 % to 4 % and the solids recovered from the reactor increased from 22 % to 35 % of the feed [given on a mass basis]. Increased powder feed rate would not change the residence time but would decrease the specific energy to each particle and likely decrease the mean temperature attained by each particle, leading to decreased propylene concentrations and increased polymer/carbon residues.

6.2.4 Solid Residues

Carbonaceous residues were collected from different parts of the reactor as described in the section 6.1.4. The calorific values of the pure polymer and solid residues were determined using a Parr Bomb Calorimeter. The details of the measurement procedure and sample calculations are presented in Appendix J. The calorific values of the solids collected in the hood and from the filter upstream of the eductors were very close to those of pure carbon [Table 6.7]. This implied that some gaseous products formed were reacting further to give elemental carbon. Elemental analysis of pure polymer and the solid residues verified that the solid residues were mainly made of carbon. The carbon weight percentage, for the residues which were not analyzed for elemental composition, were interpolated using the calorific values of the residues and pure carbon and hydrogen. Comparing the elemental compositions of the solid residues from PP depolymerization to that of the residues from PE depolymerization, it can be seen that at high power and low feed rate conditions most of the polymer particles were completely depolymerized and the solid residues were a result of complete decomposition of polymers into carbon.

Table 6.7: PP Depolymerization: mean particle size, calorific value and elemental composition of solid residue.

Solid Type	Particle Size [μm]		Calorific Value [kJ/kg]	Elemental Analysis	
	Mean	Range		C %	H %
Polypropylene	38	5 - 95	46,304	85.67	14.33
Residue from Reactor Walls	10.7	0.15 - 59	36,775	98.89*	2.11*
Residue from Un-cooled Bottom Section of the Reactor	6.6	0.15 - 29	40,303	97.78	2.22
Residue from Filter before Eductors	7.6	0.15 - 29	34,926	99.47*	0.53*
Residue from Hood	5.6	0.15 - 26	34,926	99.47	0.53

* Interpolated using calorific data

Figure 6.16 shows an SEM microphotograph of the solid residue collected from the filter located between the reactor and the eductors. These submicron [70-250 nm] particles were spherical and agglomerated. A previous study on characterization of coke formed in the pyrolysis of polyethylene identified such spherical structures as being formed from a gas phase secondary reaction mechanism [Cozzani, 1997]. The possible stoichiometries of such mechanisms are shown in reactions [4.14] and [6.9]. EDS analysis of these samples indicated that the solid residue contained only carbon. Hydrogen could not be detected by the EDS detector. SEM micrographs of particles collected from other regions of the reactor are shown in Appendix F.

Figure 6.16: SEM microphotograph of solid residue collected from the filter upstream of the eductors during PP plasma depolymerization.

TEM analysis showed that the individual particles were in the nano-scale size range but were agglomerated [Figure 6.17]: arrows [1] and [2] denote ring-shaped nanotubes; arrows [3]-[5] denote individual straight nanotubes; arrows [6]-[8] denote polyhedral particles similar to carbon black particles. No significant structural differences were found between residues collected from different locations in the reactor. Particles collected in the hood filter [5.6 μm] were approximately half the size of those collected from the reactor walls [summarized in Table 6.7].

Figure 6.17: PP depolymerization: bright-field TEM image of the carbonaceous residue showing different novel carbon structures.

Figure 6.18 shows the nucleus of a growing nanotube. A carbon nanotube growth starts with the development of a C_2 molecule into a carbon cluster due to collisions of C^* molecules either in the plasma jet or at the stainless steel surface of the reactor wall [Gamaly, 1997; Harris, 1999]. The details of several other modes of carbon nanotube formation are summarized in Appendix D.

Figure 6.18: Nucleus of a developing carbon nanotube formed during PP depolymerization.

6.2.5 Economic Projections

The results presented in this report relate only to a lab-scale process, which obviously would not be economically viable or suitable for actual recycling on an industrial scale. Moreover, the process parameters were optimized for highest monomer yields rather than for highest profitability. Some preliminary economic analysis, however, indicates that a 600 kW system processing 270 kg of PP/hr would be profitable. The basis for these economic predictions is summarized in Appendix E. The balance sheet on a yearly basis is summarized in Table 6.8. The detailed calculations are presented in Appendix E.

The ratio of polymer mass fed into the reactor to the energy input for the laboratory scale reactor was in the range of 5 to 35×10^{-3} kg/kWh and 0.45 kg/kWh for the projected scaled-up plant. From these values it can be seen that the mass of waste to energy input would be higher and, hence, would also have a profitable process. Process economics would be improved if the landfill costs increase, at better torch efficiencies and/or at lower electricity costs.

Table 6.8: Economic projections of PP recycling: summary of balance sheet.

Capital Costs	\$ 211,818
Operating Costs	\$ 448,000
Total Annual Cost	\$ 659,818
Revenue from Monomers	\$ 594,457
Revenue from saved Landfilling costs	\$ 112,000
Net Profit	\$ 47,139

These results indicated that polypropylene could be selectively depolymerized into its monomer and small quantities of other hydrocarbons [$< 5\%$] at high power, low feed rate and low gas flow rates. The results also indicated that random chain scission followed by unzipping of radicals through β -scission was the likely mechanism in the plasma pyrolysis of polypropylene.

The results discussed in section 6.2 have been published in the journal *Industrial and Engineering Chemistry and Research* [Guddeti, et al., 2000b]. The results from section 6.1 and 6.2 were also presented at the *ACS Annual Meeting, Anaheim, CA* [Guddeti, et al., 1999].

6.3 Polyethylene Terephthalate Depolymerization

The process parameters listed in Table 6.5 would represent the conditions with high power and low feed rates and also longer residence times due low gas flow rates. Hence, these conditions were used to study the thermal plasma pyrolysis of polyethylene terephthalate [PET]. PET powder was fed into the clean ICP reactor under these conditions for 30 minutes. The total mass of polymer fed into the reactor and the total mass of solid residue collected from the different parts of the reactor and downstream filters were measured. A mass balance analysis indicated that 74.6 % [wt %] of the total PET fed into the reactor was converted into gaseous products and the rest to carbonaceous solid residue.

The gaseous products were identified using two GC columns as described in section 5.3. The gaseous products were mainly acetylene along with small percentages [$<10\%$] of $\text{CO}_2/\text{C}_2\text{H}_4$ and CO/CH_4 as analyzed using a GC fitted with a ChromosorbTM column. Analysis of the gaseous sample using a CarbowaxTM column showed the presence of C_2H_2 , CO , CO_2 , and two unidentified peaks.

Since the ester bond is the weakest [Ohtani and Tsuge, 1995], PET should start decomposing on heating according to reaction [6.10]. A given polymer chain could break at many ester bond positions due to the high energy provided by the plasma. Each of these radicals would react further according to reactions [6.11] - [6.16], forming low molecular weight molecules such as C_2H_2 , C_2H_4 , etc. Their presence was confirmed by the GC analysis.

Carbonaceous residues were collected from different parts of the reactor as described in section 6.1. The mean particle size, the elemental composition and the calorific values of these solid residues are shown in Table 6.9. The elemental balance, based on the total masses of solids collected at different positions of the reactor, indicated that the analysis of gaseous samples was not complete. Non-hydrocarbon species such as O_2 , H_2O were not detected because an FID detector was used for analysis of hydrocarbons.

[PET]

[6.10]

[6.11]

[6.12]

[6.13]

[6.14]

[6.15]

[6.16]

FTIR analysis of the gaseous sample indicated the presence of small quantities of substituted acetylene, aliphatic aldehydes and substituted aromatic rings [Appendix G]. Further specific identification of the products would be difficult with a simple FTIR because (i) the concentration of the hydrocarbons was very low and (ii) the peaks of most of these hydrocarbons overlapped each other. A high sensitivity GC/FTIR would be a more suitable instrument for identifying the species formed during the depolymerization of PET.

Table 6.9: PET Pyrolysis: mean particle size, calorific value and elemental composition of solid residue.

Solid Type	Particle Size [μm]		Calorific Value [kJ/kg]	Elemental Analysis		
	Mean	Range		C %	H %	O %
Polyethylene Terephthalate	48	2-200	23,195	59.85	4.02	36.13
Residue from Reactor Walls	356	1-890	30,438	77.29	2.54	20.17
Residue from Uncooled Bottom Section of the Reactor	27	0.4-100	29,726	84.45	1.81	13.74
Residue from Filter before Eductors	8.8	0.3-26	32,947	87.68	1.48	10.84
Residue from Hood	5.3	0.15-20	33,375	91.85	1.57	6.58

A "cold finger" made of glass was placed in the sampling line so as to condense any alcohols, aldehydes, ketones or carboxylic acids formed during PET plasma pyrolysis. Dry ice [250 K] was used as the refrigerant. No significant condensation was observed. Since the concentration of these condensable species would be on the order of few ppm, better cooling techniques such as a jacketed copper tube with liquid nitrogen as refrigerant would be needed. The cold finger was washed using methylene chloride solvent and the extract was analyzed using a GC/MS. No peaks were detected. This could be either because of lack of good heat transfer between the dry ice and the cold finger or because no condensable species were formed during the process.

The soluble extract from the solid residue was concentrated by blowing cold argon gas through it and then analyzed using a GC/MS, which showed the presence of aromatics such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzoic acid, p-diacetyl benzene and biphenylene. Some of the aromatic radicals shown in reactions [6.11] and [6.12] would combine with other similar radicals to give simple polycyclic aromatic hydrocarbons [PAH's] as indicated by the GC/MS analysis.

These results indicated that ICP processing of condensation polymers would not yield monomers but would result in the formation of low molecular weight hydrocarbons such as acetylene which could be used in the synthesis of other useful chemical compounds such as vinyl chloride [monomer in PVC manufacturing], acetaldehyde, acetic anhydride and neoprene rubber.

6.4 Plasma Pyrolysis of a PE and PP Mixture

Two hundred and fifty [250] grams of PE powder was mixed with 75 grams of PP powder in a "Vee" blender for 60 hours. The weight ratio of PE powder to PP powder in this mixture was the same as that in the MSW stream. The process condition that yielded highest ethylene concentration from the PE depolymerization study and the process condition that yielded highest

propylene concentration from the PP depolymerization were two of the conditions used to study the depolymerization characteristics of this mixture.

The product distributions for both these experimental conditions are listed in Table 6.10. The product distributions of depolymerization of pure PE and PP at the same conditions as listed in Table 6.10 are presented in Tables 6.11 and 6.12, respectively. Assuming that both of these polymers, even when present in the mixture, would depolymerize as if they were individual polymers, the product compositions were predicted and are listed in Table 6.12. Comparing monomer concentrations it can be seen that the predicted values were similar to those of the experimental values. Hence, instead of doing the whole experimental matrix, four other process conditions [Table 6.10: Runs # A, C, E and F] involving variations in other process parameters such as quench gas flow rate and powder feed rates were carried out and the results are presented in Tables 6.10 and 6.13.

Comparing Tables 6.10 and 6.13 it can be seen that at high power conditions [D, E, F] the depolymerization products of the mixture runs were very similar to those predicted according to the depolymerization of pure polymers [$< 5\%$ difference]. At low power conditions, however, the difference between the experimental and predicted values varied by 3-15 %. The difference was on the higher side when depolymerization was studied at higher powder feed rates.

Table 6.10: PE + PP mixture depolymerization: run parameters and product distributions.

Run Condition Notation		A	B	C	D	E	F
Conditions	Power (kVA)	10	10	10	20	20	20
	Sheath Gas (slm)	40	40	40	40	40	40
	Central Gas (slm)	15	15	40	15	15	40
	Quench Gas (slm)	155	0	0	0	155	0
	Powder Feed Rate (g/min)	5	1.5	5	1.5	5	1.5
Product Distribution	Methane	3.7	3.3	4.2	2.6	4.0	3.1
	Ethylene	3.8	5.3	12.6	2.5	8.5	3.7
	Propylene	88.3	88.5	66.3	92.9	82.7	90.6
	Acetylene	0	0	6.7	0	0.4	0
	Butadiene	0.4	0.5	1.3	0.1	0.7	0.9
	C4's	2.0	2.2	8.6	1.9	3.2	1.2

Table 6.11: PE Depolymerization: run parameters and product distributions.

Run Condition Notation		A	B	C	D	E	F
Product Distribution	Methane	5.4	3.4	5.5	2.5	4.8	2.5
	Ethylene	8.9	8.1	19.4	3.4	13.9	2.7
	Propylene	83.1	84.6	63.9	92.1	74.8	92.0
	Acetylene	0	0	4.5	0	0.5	0
	Butadiene	0.8	0.9	2.0	0.2	1.4	0.2
	C4's	2.1	2.5	4.2	1.4	3.5	1.5

Table 6.12: PP Depolymerization: run parameters and product distributions.

Run Condition Notation		A*	B	C*	D	E	F
Conditions	Power (kVA)	10	10	10	20	20	20
	Sheath Gas (slm)	60	40	60	40	40	40
	Central Gas (slm)	15	15	40	15	15	40
	Quench Gas (slm)	155	0	0	0	155	0
	Powder Feed Rate (g/min)	5	1.5	5	1.5	5	1.5
Product Distribution	Methane	5.3	4.0	5.6	2.9	4.8	2.8
	Ethylene	8.0	3.9	9.0	1.9	5.2	1.9
	Propylene	58.5	86.5	62.9	93.8	82.6	93.2
	Acetylene	10.8	0	11.1	0	0.8	0
	Butadiene	2.0	1.6	1.6	0.1	0.7	0.1
	C4's	10.0	4.1	8.0	1.4	5.0	1.3

Table 6.13: PE + PP mixture depolymerization: product distribution as predicted according to the depolymerization of the individual pure polymers.

Run Condition Notation		A*	B	C*	D	E	F
Product Distribution	Methane	5.6	3.5	5.5	2.6	4.8	2.6
	Ethylene	8.7	7.1	17.0	3.1	11.9	2.5
	Propylene	77.5	85.0	63.6	92.5	76.6	92.3
	Acetylene	2.5	0	6.0	0	0.5	0
	Butadiene	1.0	1.0	1.9	0.2	1.2	0.1
	C4's	3.9	2.8	5.1	1.4	3.9	1.5

At higher power levels the plasma jet with temperatures greater than 9000 K would be larger and the velocity of the gas stream would be higher than at low power level as predicted by Wei, et al. [1988], hence, most of the particles would be processed at high temperatures. Also the products formed at the high power levels would have shorter residence times in the plasma zone and would not have enough time to participate in secondary reactions.

At low power level [10 kVA] the formation of higher amounts of C4's would indicate that polymer particles were undergoing unzipping in lower temperature zones [see Section 4] and also increased residence time would increase the probability of secondary reactions occurring. At lower power levels the mismatch between the predicted and experimental values could also have been due to significant interaction between the polymer particles due to the presence of more methyl radicals generated by scission of branches of the polypropylene. Further systematic studies, including the measurement of species concentrations in different zones of the reactor, would be needed to determine the reaction mechanism completely.

The PE + PP mixture was fed into the clean ICP reactor for 30 minutes at run conditions B & D [Table 6.10]. At run conditions as in D, the highest amount of propylene [92.5 vol.%] was achieved. Run condition B used the same gas flow rates and powder feed rates as run condition D but was run at a low power level and the concentration of propylene [88.5 vol.%] was only 4

% less than at run condition D. Mass balance runs were carried out at both conditions B and D. The total mass of polymer fed into the reactor and the total mass of solid residues collected from different parts of the reactor and downstream filters were measured. This mass balance analysis indicated that 75 wt.% of the total PE + PP mixture fed into the reactor was converted into gaseous products at both the low and high power conditions. The slight decrease in the conversion as compared to pure PP depolymerization could have been due to the larger mean particle diameter of the PE than of the PP. An increase in the power input from 10 to 20 kVA did not affect the solids to gas conversion percentage. This could have been because: [1] the particle loading was too low or [2] the increase in the conversion at the higher power level was compensated by an increase in the secondary reactions to form pure carbon.

7. CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The technical feasibility of using an atmospheric pressure induction-coupled plasma [ICP] heated reactor for the pyrolytic conversion of polymers back to monomers or other useful compounds has been demonstrated. Powdered PE, PP, PET and a mixture of PE and PP were successfully and efficiently converted into monomers or other low molecular weight gaseous hydrocarbons by injecting the polymers as powders axially into the center of an argon plasma jet generated by an RF/ICP plasma torch. Experimental matrices were designed using a commercial software package [Design-EaseTM] to determine the effects of various process parameters on the yields of monomers. This factorial analysis of the key process parameters showed that plasma plate power input, central gas flow rate, probe gas flow rate, powder feed rate and the interaction between the quench gas flow rate and power input were the most important factors affecting the concentrations of ethylene and propylene in the product gas stream.

During PE depolymerization the gaseous products obtained were mainly mixtures of propylene and ethylene, together with smaller amounts of other hydrocarbons. Over the range of conditions investigated, ethylene concentration in the gaseous products ranged from 2.5 to 24 %, propylene concentration ranged from 52 to 92 % and the amount of solid residues collected ranged from 15 to 50 % by weight of the total hydrocarbon powder fed into the reactor. Optimum conditions, within the equipment limitations, for the highest ethylene yield were determined and a mass balance run at these conditions showed that 68 %, by weight, of the total polymer fed into the reactor was converted into gaseous products. The amount of propylene formed was much higher than expected and was believed to be due to a β -scission reaction mechanism occurring at the higher plasma temperatures. Elemental analysis of the residues indicated that they were mostly carbon. The detection of carbon nanotubes in the carbonaceous residue collected from the bottom of the reactor indicated additional potential applications of this plasma process.

During PP depolymerization the gaseous product at optimum conditions, within the equipment limitations, was 94 % propylene along with small percentages of methane, ethylene and C₄'s [on an Argon-free basis]. The actual product concentrations were less than 1 % [vol.]. Over the range of conditions evaluated, propylene yields ranged from 77 % to 94 %. Optimum conditions for the highest propylene yield were determined and a mass balance run at these conditions showed that 78 % by weight of the total polymer fed into the reactor was converted into monomer. Elemental analysis of the carbon residues indicated that they were mostly carbon. SEM analysis of these residues showed that they were agglomerates of submicron-sized spherical particles. Carbon nanotubes were also detected in these residues by TEM analysis.

Depolymerization of PET did not, as expected, yield monomers because PET is not an addition polymer like PE and PP. Acetylene was the major component of the gaseous products, together with small quantities of carbon monoxide and carbon dioxide. Complete analysis of the gaseous products could not be carried out, because the GC columns used and available, could not detect all of the oxygenated hydrocarbons present. Mass balance analysis showed that 75 % by weight of the total polymer fed into the reactor was converted into gaseous products.

A mixture of polyethylene and polypropylene powders in a weight ratio similar to that of a typical MSW stream was successfully depolymerized and, as predicted, from the results of the depolymerization of the individual polymers, the gaseous products were mainly propylene and ethylene together with small amounts of methane, acetylene and butanes. Since depolymerization of mixture of PE and PP resulted in mainly propylene as the products the process would be very

economical in recycling PE and PP as a mixture. Mass balance analysis showed that 75 wt.% of the total polymer fed into the reactor was converted into gaseous products at both high and low power levels. The particle loading did not affect the solids to gas conversion and could have been due to the decrease in conversion being compensated by a decrease in the solid carbon formation from secondary reactions at low power.

Analysis of these four polymer systems demonstrated that plasma depolymerization of polymers yielded low molecular weight gaseous products which could be used either in the production of new polymers or as the raw materials for the synthesis of other valuable chemicals. Chain scission at multiple positions of the polymer backbone followed by unzipping of the radicals seems to be the predominant reaction mechanism occurring during the plasma pyrolysis of polymers. Secondary reactions occurring in the downstream sections of the reactor change the equilibrium concentrations of the products. Quenching of the reactions either due to natural temperature gradients within the reactor or due to a cold jet of argon directed counter to the flow of the plasma gases up to a threshold flow rate yielded high monomer concentrations by suppressing any secondary reactions.

The potential annual production of monomers by treating waste polymers using a thermal plasma process such as has been studied here would be much less than the annual bulk production of these monomers in the petrochemical industry. The specific energy required for heating the polymer particles to the decomposition temperature and then to break the polymer bonds would be of the order of 1 kW/kg. The specific energy input in the laboratory scale reactor used was ~200 kW/kg of polymer treated, i.e. very high relative the specific energy input of commercial polymer manufacturing processes. However, the present study was to demonstrate the technical feasibility of the plasma process to depolymerize waste polymers into recyclable monomers and was not aimed at optimizing the process with respect to energy efficiency. The plasma process, however, would provide a means of recycling those waste polymers which would otherwise be either landfilled or incinerated. One possibility would be the "in-plant" recycling of waste polymers during the manufacturing process.

Economic projections of the depolymerization of pure polypropylene on an industrial scale indicated that a 600 kW system processing ~270 kg/hr of pure polypropylene would be profitable at current market values of these commodities. Process economics would be improved if landfill costs increase, if torch efficiencies improve and/or at lower electricity costs, and also if the value-added carbon found in the solid residues could be utilized.

7.2 Recommendations for Future Work

Results from the present work have successfully demonstrated the potential of recycling model single polymers into their monomers or other useful compounds at yields of 80-90 % using an atmospheric pressure, induction-coupled plasma [ICP] reactor. The present study also demonstrated that varying process conditions can dramatically influence the conversion and selectivity to monomers, but a systematic study linking the detailed reaction mechanisms with the process conditions is necessary in order to fully optimize the process for specific products. Developing a mechanistic model of the physical and chemical steps involved in the plasma pyrolysis of polymers would be the next step needed for the growth of this technology. This would include identification of the chemical species in the plasma and quench zones by *in-situ* Fourier Transform Infrared [FTIR] analysis.

Commercial software packages such as CHEMKIN [Kee, et al., 1996] could be used to model a thermal plasma reactor. However, these would provide little in the way of understanding

the species generated and reactions occurring during the depolymerization, as required to fully understand the process, because they are only applicable to *equilibrium* processes. Another limitation of these packages is the lack of thermodynamic property data and transport properties such as thermal conductivity, heat transfer coefficients etc., of materials, especially hydrocarbon compounds, at temperatures above 1500 K.

As polymer particles pass through the high temperature regions of an ICP reactor [8,000-10,000 K], they will rapidly degrade in several steps: [1] melting of the particles, [2] condensed phase degradation through scission reactions, [3] evaporation of the resulting low molecular weight species, and [4] continued gas-phase pyrolysis of evaporated hydrocarbons. A model should be developed including all these physical and chemical processes.

Since high-energy neutral and ionized particles are present in thermal plasmas other reaction mechanisms are possible. Chain scission, for example, could be initiated by bombardment of dissociating polymer particles by Ar^+ to form metastable compounds of Ar. This could be verified by analyzing the solid residues for the presence of Ar molecules. At 10,000 K and 100 kPa, however, the concentration of Ar^+ in the plasma is on the order of only 1 % and at a feed rate of 5 g/min, assuming no back-mixing, the polymer concentration would only be of the order of 0.1 %, hence, at these concentrations the probability of collisions between the Ar^+ and the polymer molecules would be very low.

Figure 7.1 shows a schematic of a possible commercial thermal plasma recycling process. In order to reach the commercial recycling stage shown in Figure 7.1, process units including recycling of the argon gas, separation of monomers from other gaseous products, etc. need to be designed.

Effects of several input parameters such as the molecular weight of the polymer, particle size distribution of the feed material, positioning of the injection probe, branching on the polymer chain, degree of cross-linking, etc. were not addressed in the present study. Using smaller [$<30 \mu\text{m}$] particles should yield higher solids to gas conversion, but obtaining a smaller particle could be uneconomical, as cryogenic grinding of polymers may be needed. However, in larger commercial systems using larger injection probe diameters and higher power inputs, larger particle sizes [1-5 mm] could possibly be used. A narrower range particle size distribution could narrow the range of distribution of the product gases and could considerably decrease the cost of separation of the products, although feedstock cost may increase.

Figure 7.1: Schematic of a thermal plasma recycling process.

In the present study, the injection probe was located such that the feed material was injected into the center of the plasma zone. Moving the probe up or down from this position could lead to treatment of the polymer particles in different temperature and flow regimes yielding different products. This parameter could be used to further optimize the process for a specific product. The polymers could also be fed directly into the tail flame region of the plasma using one of the side arms of the reactor as feed port. This would not lead to complete decomposition of the polymer, as it would be present in the hot plasma zone for only short period of time. However, this method of injection could be used to produce a specific product.

The present study has successfully shown that natural or forced gas quenching of the reacting species is necessary to prevent complete decomposition of the polymers so that high yields of the respective monomers are obtained in the gas phase. The efficiency of quenching could be improved by incorporating special quench nozzles, such as a radial array of multiple nozzles located at the exit of the torch, designed to interact more uniformly and symmetrically with the plasma jet. The angle of the quench gas flows relative to the plasma jet could also be varied between parallel and counter-flow conditions.

The thermal conductivity and thermal diffusivity of the quench gas used could be increased by using He rather than Ar. Steam, which would be cheaper than either He or Ar, could also be used as the quench gas and would be more easily separated from the resulting monomers than Ar, however, the product composition might vary since steam may react to yield different products. Steam plasmas could also be used, especially in commercial systems, again lowering operating costs, however, the nature of the product stream formed would need to be studied.

The reaction mechanisms could be better understood by systematically studying the depolymerization of PE with varied degrees of branching. As the degree of branching increases [HDPE to LDPE] the PE depolymerization mechanism should shift more towards the PP depolymerization mechanism [Section 4]. However, if the chain lengths of the branches were

longer than a single carbon atom then these branches after separation from the polymer backbone would undergo further depolymerization like an un-branched polymer yielding simple monomers, such as ethylene and propylene. Lower molecular weight polymers would reach the gaseous phase sooner than higher molecular weight polymers, since scission at only two or three locations would be necessary for entire particles to be gasified. Similar studies involving polymers with varying molecular weights would help in understanding the reaction mechanisms.

The residence time of the probe gas was estimated using an RGA. The values measured were a crude estimate because the RGA detector was sensitive to pressure inside the reactor and the step change in the oxygen concentration was timed manually. The residence time of particles were not measured. Modeling of the temperature and flow fields in the plasma would provide a greater understanding of the residence times of the gases, which could then be used to estimate the residence times of the particles injected into the plasma.

The analysis of gaseous products and the liquids extracted from the solid residues produced during PET depolymerization study was not extensive due to the lack of appropriate instrumentation. A GC/FTIR or a GC/MS which could separate the product mixture and identify the species more accurately should be used in future studies involving the depolymerization of oxygen-containing polymers such as PET. A cold finger was used to freeze condensable products and no significant condensation was achieved. This could be because of lack of better heat transfer between the dry ice and the cold finger made of glass. Using a copper-jacketed condenser instead of a cold finger made of glass and liquid nitrogen as the coolant could increase heat transfer.

Using either H_2 or CH_4 as plasma gas could have a significant effect on the product composition. A hydrogen plasma would provide higher enthalpy and hence would lead to higher solids to gas conversions and also higher throughputs and thus a more economical process. This would also decrease the amount of carbon deposited on the walls of the reactor and, hence, would result in a longer cycle time for the process. The presence of so many hydrogen radicals, however, could hydrogenate more valuable olefins into alkanes. The process chemistry becomes more complex due to the presence of abundant hydrogen radicals. Also, a pure hydrogen plasma would require a higher power input to sustain it and would not be possible with the existing power supply. The thermal conductivity of the plasmas could be increased significantly by using an Ar/He mixture as plasma gas. This would likely increase the polymer solids to gas conversion rate. From a commercial viewpoint the use of N_2 as plasma gas would be attractive, due to its low cost and ready availability, however, at plasma temperatures N_2 would be dissociated into excited N atoms and N^+ and N^{++} which could react with hydrocarbon species or fragments to form undesired, or even harmful, compounds, such as cyanides, NO_x etc.

The present study focused on the study of selected pure polymers only. Only one polymer mixture system, consisting of pure polyethylene and pure polypropylene, was evaluated. In order for the process to be successfully commercialized for the recycling of polymers from municipal solid waste, the present study should be extended to evaluate the depolymerization of more complex polymer mixtures as well as polymers containing additives such as plasticizers, antioxidants and dyes. Since the plasma pyrolysis of PET yielded simple gaseous products including acetylene, carbon monoxide and carbon dioxide, the process should be easily extended to the treatment of mixed plastic waste from the MSW streams. Also, further studies would be needed to recycle polymers containing halides such as polyvinyl chloride [PVC], polytetrafluoroethylene [PTFE], etc. since depolymerization of these polymers could yield some highly corrosive acids such as HF and HCl.

SEM and TEM analysis of the solid residues produced during the present study showed novel carbon structures including carbon nanotubes. Further characterization of these solid residues with better instruments such as High Resolution Transmission Electron Microscope [HRTEM] would be needed. This would add more value to the thermal plasma recycling of polymers and would make the process more economical. Also, the process parameters could be optimized to increase the yield of carbon residues and hence could be used as means of converting waste polymers into high value carbon.

8. PUBLICATIONS AND PRESENTATIONS FROM THIS PROJECT

- 1] Guddeti, R. R., Knight, R. and Grossmann, E. D., "Depolymerization of Waste Polymers Using Induction Coupled Plasma [ICP] Reactor," Presentation at American Chemical Society [ACS] National Meeting, Anaheim, CA, March 20-25, 1999.
- 2] Knight, R., Grossmann, E. D. and Guddeti, R. R., "Thermal Plasma Process for Recovering Monomers and High Value Carbons from Polymeric Materials, U.S. Provisional Patent Application, June 1999.
- 3] Hager, J.W., Knight, R., Guddeti, R. R., Grossmann, E. D. and Lafdi, K., "Nanotube Synthesis Using Hydrocarbon Precursors and Induction-Coupled Plasma Technology," Presentation at American Carbon Society Meeting "Carbon '99", Charleston, SC. July 11-16, 1999.
- 4] Knight, R., Guddeti, R. R. and Grossmann, E. D., "Recycling of Waste Polymers via Induction Coupled Plasma [ICP] Technology," Presentation at EPRI Center for Materials Production [CMP] Meeting, Philadelphia, PA, October 26, 1999.
- 5] Guddeti, R. R., Knight, R. and Grossmann, E. D., "Depolymerization of Polyethylene Using Induction-Coupled Plasma Technology," *Plasma Chemistry and Plasma Processing*, Vol. 20, No. 1, pp. 37-63, 2000.
- 6] Guddeti, R. R., Knight, R., and Grossmann, E. D., "Depolymerization of Polypropylene in an Induction-Coupled [ICP] Reactor," *Industrial & Engineering Chemistry Research*, Vol. 39, No. 5, pp. 1171-1176, May 2000.
- 7] Guddeti, R. R., "Depolymerization of The Waste Polymers in Municipal Solid Waste Streams Using Induction-Coupled Plasma Technology," Ph.D. Thesis, Drexel University, June 2000.

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APPENDIX A: Feed Particle Size Distribution and Feed Rate Calibration Charts

Particle size distributions of the polymer feedstocks and the solid residues were determined using a laser scattering particle size analyzer [Horiba Ltd., Model LA-910]. Distilled water mixed with a drop of Tween[®] 80, a surfactant, was used as the medium of dispersion. The dispersion medium was stirred [@ 4 rpm], circulated [@ 4 rpm] and sonicated for 2 minutes and then a blank reading was taken. Polymer powder was then added to the stirred and circulated medium until the percentage transmission of light through the measuring cell at two different wavelengths was between 50 and 90 %. The particle size distribution was measured after two minutes of sonication. Relative refractive indices of 1.15, 1.15 and 1.28 were used for the PE, PP and PET powders, respectively.

Figure A.1: PE powder particle size distribution.

Figure A.2: PP powder particle size distribution.

Figure A.3: PET powder particle size distribution.

Figure A.4: Particle size distribution of PE + PP mixture.

Figure A.5: PE powder feed rate calibration.

Figure A.6: PP powder feed rate calibration.

Figure A.7: PET powder feed rate calibration.

Figure A.8: Feed rate calibration of PE + PP mixture.

APPENDIX B: DESIGN-EASE™ - Experimental Matrix and Statistical Analysis Description

A large number of variables can be varied during the thermal plasma processing of materials. Six [6] variables were considered during the depolymerization of polymers. To study the process response due to variations of all the variables over the entire range [say 4 points for each variable] would require $4^6 = 4096$ experiments. A full 2-level factorial design would still require $2^6 = 64$ experiments. Thus, a factorial design of experiments would, although unable to explore the entire span of the variables, allow major trends to be determined and eliminate the insignificant parameters and give a positive direction for further experimentation.

In a 2-level factorial design, the experimental matrix is built using a simple sequential strategy at the two levels of each variable. The *response* [product conc.] was measured at each condition of the matrix. The *effect* [the change in the mean value when a variable goes from its low level to high level] is calculated. The effects caused by individual variables are called *main effects*, and the effects resulting from a combined change in two or more variables producing an effect greater or lesser than that of the sum of effects expected from each variable alone. In a full 2^6 factorial design there would be 1 average effect, 6 main effects, 15 2-variable interaction effects, 20 3-variable interaction effects, 15 4-variable interaction effects, 6 5-variable interaction effects and 1 6-variable interaction effect. In terms of absolute magnitude main effects tend to be larger than interaction effects. By assuming that higher interaction effects are negligible, fractional factorial designs can be built. For 6 variables only 8 experiments would be needed. The first 8 experiments shown in Table B.1 would represent such a matrix. The main effects can be deconfounded from interactions by building a "foldover design" consisting of an additional 8 experiments, as shown in Table B.1. This was achieved by confounding the higher interactions as shown below:

A	BD=CE=BEF=CDF
B	AD=CF=AEF=CDE
C	AE=BF=ADF=BDE
D	AB=EF=ACF=BCE
E	AC=DF=ABF=BCD
F	BC=DE=ABE=ACD
AF	BE=CD=ABC=ADE=BDF=CEF

The higher order confounding of interactions can be obtained by substituting the factors $D=AB$, $E=BC$ and $F=CD$.

Once the responses have been experimentally determined, the variable coefficients are calculated using a least squares estimation. The effects are calculated and plotted on a normal probability graph as shown in Figure 6.1. Effects which represent a sample from a normal distribution will fall on the normal probability line while a few effects which are important show up as outliers. These outliers are selected to finish the statistical analysis by constructing an analysis of variance [ANOVA] table [Table B.2] and evaluating the diagnostic table [Table B.3].

Table B.1: PE Depolymerization: experimental matrix.

Run #	Power Input [A] (kVA)	Sheath Gas [B] (slm)	Central Gas [C] (slm)	Quench Gas [D] (slm)	Probe Gas [E] (slm)	Powder Feed Rate [F] (g/min)	Ethylene Conc. [Response] (%)
1	10	40	15	155	9	5	8.9
2	20	40	15	0	7	5	5.1
3	10	60	15	0	9	1.5	8.8
4	20	60	15	155	7	1.5	6.7
5	10	40	40	155	7	1.5	6.1
6	20	40	40	0	9	1.5	2.5
7	10	60	40	0	7	5	18.7
8	20	60	40	155	9	5	12.0
9	10	60	40	0	7	1.5	3.4
10	20	60	40	155	9	1.5	8.1
11	10	40	40	155	7	5	11.7
12	20	40	40	0	9	5	22.3
13	10	60	15	0	7	5	9.8
14	20	60	15	155	9	5	6.8
15	10	40	15	155	7	1.5	9.3
16	20	40	15	0	9	1.5	6.2

Table B.2: PE Depolymerization: analysis of variance data.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F Value	Prob > F
Block	6.2	1	6.2		
Model	381.7	7	54.5	36.4	< 0.0001
Residual	10.5	7	1.5		
Corr. Total	398.3	15			
Root MSE	1.2		R-Squared	= 0.97	
Dep. Mean	9.1		Adjusted R-Squared	= 0.95	
C.V. %	13.5		Predicted R-Squared	= 0.85	
Predicted Residual of Sum of Squares [PRESS]				= 54.8	

Model: Terms estimating a factor's effect on response.

Residual: Terms estimating the experimental error within treatment variation.

F Value: Test for comparing the factor variance with the error variance.

Prob > F: Probability of seeing the observed F value if the null hypothesis [H_0] is true. Small probability values call for rejection of the null hypothesis, i.e., the model is a good fit. The probability equals the proportion of the area under the curve of the F-distribution that lies beyond the observed F value.

Predicted R-Squared: A measure of the amount of variation in new data as predicted by the model.

C.V.: Coefficient of variation, the standard deviation as a percentage of the mean.

PRESS: A measure of how the model fits each point in the design.

Table B.3: PE Depolymerization: factorial model estimates.

Factor	Coefficient Estimate	Degrees of Freedom	Standard Error	t for H_0 Coefficient=0	Prob. > t
Intercept	9.05	1	0.31		
Block 1	-0.62				
Block 2	0.62				
A	-1.48	1	0.31	-4.8	0.0019
C	1.50	1	0.31	4.9	0.0018
D	-0.51	1	0.31	-1.7	0.1403
E	0.97	1	0.31	3.2	0.0161
F	2.66	1	0.31	8.7	<0.0001
AC	-1.69	1	0.31	-5.5	0.0009
AD	2.89	1	0.31	9.5	<0.0001

Standard Error: The standard deviation associated with the coefficient estimate.

t for H_0 Coefficient=0: The number of standard deviations that the coefficient is away from zero.

Prob. > |t|: Probability of seeing the absolute value of the observed t value if the null hypothesis [H_0] is true. Small probability calls for rejection of null hypothesis, i.e., the coefficient does not differ from zero. The probability equals the proportion of the curve of the t-distribution that lies beyond plus and minus the observed t value, i.e.; a two tailed test.

Figure B.1: PE Depolymerization: effect of (a) central gas flow rate [C] and (b) probe gas flow rate [E] on ethylene concentration.

Figure B.2: PE Depolymerization: effect of (a) quench gas flow rate [D] and (b) powder feed rate [F] on ethylene concentration.

Figure B.3: PE Depolymerization: effect of interaction between plasma plate power input [A] and central gas flow rate [C] on ethylene concentration.

Table B.4: PP Depolymerization: experimental matrix.

Run #	Power Input [A] (kVA)	Sheath Gas [B] (slm)	Central Gas [C] (slm)	Quench Gas @ A [D] (slm)	Powder Feed Rate [F] (g/min)	Quench Gas @ B [G] (slm)	Propylene Conc. [Response] (%)
1	10	60	15	155	1.5	155	74.7
2	20	60	15	0	1.5	0	91.8
3	10	40	15	0	5	155	83.8
4	20	40	15	155	5	0	82.6
5	10	40	40	155	1.5	0	73.2
6	20	40	40	0	1.5	155	82.3
7	10	60	40	0	5	0	62.9
8	20	60	40	155	5	155	78.0
9	20	40	40	0	5	0	82.2
10	10	40	40	155	5	155	74.1
11	20	60	40	155	1.5	0	84.6
12	10	60	40	0	1.5	155	82.0
13	20	60	15	0	5	155	83.4
14	10	60	15	155	5	0	58.5
15	20	40	15	155	1.5	155	82.6
16	10	40	15	0	1.5	0	88.5

Table B.5: PP Depolymerization: standardized effects and regression coefficients as computed by Design-EaseTM using propylene concentration as the response.

Parameter	Coefficient	Standardized Effect	Sum of Squares
A: Plasma plate power input	4.4	8.8	307.5
B: Sheath gas flow rate	-2.1	-4.2	69.9
C: Central gas flow rate	-1.7	-3.4	44.8
D: Quench gas flow rate [Position A]	-3.1	-6.1	147.9
F: Powder feed rate	-3.4	-6.8	183.2
G: Quench gas flow rate [Position B]	1.1	2.1	17.2
AB	3.1	6.2	153.3
AC	-0.01	-0.02	0.00
AD	1.6	3.1	38.2
AF	1.5	3.0	36.2
FB	-2.9	-5.8	134.8
FC	0.3	0.6	1.3
FD	0.7	1.3	6.7
AFC	-0.1	-0.1	0.1

APPENDIX C: Sample gas chromatograms.

A GC chromatogram obtained during calibration of the GC for retention times is shown in Figure C.1. The retention times were calculated using a standard hydrocarbon mixture. Retention times of other gases were extrapolated from the manufacturer's calibration. A typical GC sample analysis output is shown in Figure C.2. The argon-free volumetric concentrations are proportional to the areas under the peaks. By using a variable baseline any drift in the baseline during the analysis was accounted for in the calculation of the area under the peaks. Methane, ethylene and propylene peaks were the major components and the other small peaks corresponded to butanes and butenes.

Figure C.1: GC calibration chromatogram.

Figure C.2: Sample gas chromatogram.

APPENDIX D: Carbon Nanotubes

Charcoal, Carbon black, graphite and diamond are the most common forms of carbon. In 1985 Krato, Smalley and Curl discovered a new form of carbon called *Fullerenes*. Fullerenes are closed cage clusters containing 60 or 70 carbon atoms which have a unique stability and symmetry. In 1990, Krätschmer and Huffman successfully developed a method to produce fullerenes containing 90% C_{60} and 10% C_{70} in bulk quantities [Harris, 1990] by vaporizing graphite using a simple carbon arc in an inert He atmosphere. Since then many researchers have studied these materials and many derivatives of fullerenes have been found. Endohedrals, exohedrals, heterofullerenes, carbon nanotubes, carbolites and nanocarbons are a few of these discoveries [Scharff, 1997].

Carbon nanotubes were first discovered by Sumio Iijima in 1991 while performing TEM analysis of the deposits formed on the cathode during the arc-evaporation of carbon [Iijima, 1991]. Carbon nanotubes are cylindrical graphitic fibers closed or open at each end with caps as shown in Figure D.1 [Harris, 1999]. Most of the nanotubes grown do not have perfect hemispherical caps as shown in Figure D.1. The irregularities are due to the presence of pentagonal and heptagonal carbon rings.

Figure D.1: Drawing of a nanotube capped with a C_{60} hemisphere [Harris, 1999].

Figure D.2: TEM image of multi-walled nanotubes. Scale bar 10 nm [Harris, 1999].

Single-walled and multi-walled nanotubes [Figure D.2] are the two types of nanotubes that have been identified to date. The length of these nanotubes varies between tens of nanometers to a few micrometers. The diameter of multi-walled nanotubes varies between 4 nm to 30 nm. Single-walled nanotubes as small as 1.4 nm have also been found [Iijima, 1993].

Nanotubes can be synthesized by several methods. Arc vaporization of graphite with or without transition metal catalysts, laser evaporation of graphite, catalytic pyrolysis of hydrocarbons, template carbonization, electrochemical synthesis of nanotubes, heat treatment of fullerene soot, catalytic decomposition of carbon monoxide and catalytic decomposition of pitch using thermal plasma are examples of the different ways of generating carbon nanotubes [Benito et al., 1998; Ebbesen, 1997; Hager et al., 1999, Harris, 1999; Scharff, 1998, Setlur et al., 1998].

The arc evaporation method, so far, is considered to be the best technique for producing carbon nanotubes [Harris, 1999, Ebbesen, 1997]. The main problems impeding this research are:

- i. Very low yields [~ 1 gm/day].
- ii. Batch process and difficulties in scale-up.
- iii. Contamination with other forms of carbon such as carbon nanoparticles, semi-crystalline graphitic structures, etc.

Purification of these carbon nanotubes is another vast field of research. Unlike fullerenes, carbon nanotubes are insoluble, which makes their separation and purification very difficult. Selective oxidation of the nanoparticles surrounding the nanotubes was one of the first techniques developed by Ebbesen and co-workers to purify nanotubes [Ebbesen, et al., 1994]. The disadvantage of this technique was the loss of over 99 % of the sample to achieve any measurable purification. Intercalating the open graphitic

structures with copper chloride and then using copper as an oxidation catalyst yielded improved purification of nanotubes [Harris, 1999]. Other methods such as centrifugation, filtration and chromatography have also been used. Carbon nanotubes of specific lengths have been separated using a centrifuge.

Carbon "onions" [Figure D.3] and carbon nanobeads [Figure D.4] are some of the novel nano-structures formed together with the carbon nanotubes [Carbioc'h, et al., 1997; Harris, 1999; Sharon, et al., 1998]. These particles are quasi-spherical and are components of many types of soot formed under controlled conditions. Partial combustion of petrochemical or tar oils and gas phase pyrolysis of hydrocarbons are the two methods used to produce these carbon nano-structures. Due to their high surface area it is predicted that these materials can be used as the anodes in secondary lithium batteries [Ishigaki, et al., 1999], as hydrogen storage materials and as catalyst particles.

Figure D.3: Carbon "onions" prepared by electron irradiation of polymer-derived carbon. Scale bar 5 nm [Harris, 1999].

Figure D.4: SEM picture of carbon nanobead [Sharon et al., 1998].

Carbon nanotubes have a variety of unique properties and, hence, can be used in a number of applications. Due to their high aspect ratio and structural stability together with low mass, carbon nanotubes have twice the elastic modulus [1000 GPa] of any existing carbon fiber and ten times higher flexural modulus [5000 GPa] than iridium [Ebbesen, 1997]. These properties could enable carbon nanotubes to be used as reinforcements in polymer, ceramic and metallic matrix composites. Due to their high electrical conductivity and high mechanical strengths nanotubes could also be used to reinforce battery electrodes, as AFM tips and SEM filaments [Ebbesen, 1997]. Carbon nanotubes have very high specific surface areas and hence could be used as catalysts. Carbon nanotubes being hollow, could be used for the storage of H_2 gas and controlled drug delivery. However, further development of these applications will need bulk production of pure and uniform materials, which would require an understanding of the growth mechanisms, and further characterization of the material properties.

APPENDIX E: Economic Projections of PP Recycling using ICP Technology

The results presented in this report relate only to a lab-scale process, which obviously would not be economically viable or suitable for actual recycling on an industrial scale. Some preliminary economic analysis, however, indicates that a 600 kW system processing 270 kg of PP/hr would be both economical and profitable. The basis for these economic predictions is summarized below.

1. Available Waste [PP]	600	lb/hr
2. Hours/yr On-Stream	7500	hr/yr
3. Plasma Plate Power Level	600	kW
4. Argon Circulation Rate	2000	SCFH
5. Argon Loss [1% of Circulation Rate]	20	SCFH
6. Gaseous Hydrocarbon Yield:	468	lb/hr
[a] Average Molecular Weight	41.95	lb/lbmole
[b] Ethylene Conc.	1.7	mole %
[c] Propylene Conc.	93.7	mole %
[d] % Recovery of C ₂ & C ₃	99	%
7. Commodity Prices:		
[a] Argon	0.02	\$/ft ³
[b] Ethylene	0.2	\$/lb
[c] Propylene	0.18	\$/lb
[d] Waste Polymer	0.00	\$/lb
8. Other Costs & Prices:		
[a] Electricity	0.04	\$/kWh
[b] Landfilling Waste Polymers	50	\$/ton
9. Equipment Costs:		
[a] Feed Preparation Equipment [i]	500,000	\$
[b] Separations Equipment [ii]	500,000	\$
[c] Plasma Reactor & Controls	1,000,000	\$
10. Depreciation [St. Line]	11	years
11. Working Capital	30,000	@ 15% of Investment \$
12. Labor Assoc. Costs [iii]	250,000	\$/yr
13. Power Requirements:		
[a] Plasma	600	kW
[b] Feed Preparation	25	kW
[c] Separations Section	25	kW
14. Lb. of C ₂ /600 lb of Waste PP	5.37	
15. Lb. of C ₃ /600 lb. of Waste PP	438.82	

Notes:

[i] Grinding, classifying, feeding equipment

[ii] Based on 78% conversion of PP waste into light hydrocarbons = 468 lb/hr

[iii] Four shift operation

Capital Costs = $[9(a)+9(b)+9(c)]/11$ + working capital = \$ 211,818 /yr

Operating Costs = Electricity + Labor + Argon Loss =
 $650 \times 7500 \times 0.04 + 250,000 + 20 \times 7500 \times 0.02$
= \$ 448,000 /yr

Total Annual Cost = Capital + Operating Costs = \$ 659,818 /yr

Value of Recovered Monomers = Value of [ethylene + propylene]
 $= 5.37 \times 7500 \times 0.2 + 438.82 \times 7500 \times 0.18$
= \$ 594,457 /yr

Landfill Cost Avoided = $600 \times 7500 \times 50 / 2000$ = \$ 112,500 /yr

Total Potential Income = \$ 706,957 /yr

Net Income = \$ 47,139 /yr

The process economics would be improved if the land-fill costs were to increase, and/or at lower electricity costs and also if the high value added carbon found in the solid residues were utilized.

Appendix F: SEM micrographs of pure polymer powders and carbonaceous residues.

Figure F.1: SEM micrograph of pure polyethylene particles.

Figure F.2: SEM micrograph of pure polypropylene particles.

Figure F.3: SEM micrograph of pure polyethylene terephthalate particles.

Figure F.4: PP Depolymerization: SEM micrograph of solid residue collected in the hood.

APPENDIX G: FTIR Spectrum of gas product from PET depolymerization

Gas samples collected in TedlarTM bags were analyzed using a Bio-Rad FTIR. The gas cell was flushed with pure argon before injecting the sample. The sample cell was maintained at a temperature of 400 K through out the analysis. The spectrum obtained after subtracting the background is shown in Figure G.1. A summary interpretation of the spectrum is listed below:

- i. No peaks were observed between 2840 and 3000 cm^{-1} wave numbers => No Alkanes.
- ii. No strong peaks were observed between 991 and 910 cm^{-1} wave numbers => No Alkenes.
- iii. Peaks were observed between 2260 and 2100 cm^{-1} wave numbers => Alkynes are present.
- iv. Peaks were observed between 900 and 675 cm^{-1} wave numbers => Aromatics with one ring.
- v. No peaks were observed between 1260 and 1000 cm^{-1} wave numbers => No Alcohols and Phenols.
- vi. Peaks were observed between 1740 and 1685 cm^{-1} wave numbers => Aldehydes are possibly present.
- vii. Peaks were observed between 1710 and 1395 cm^{-1} wave numbers => Carboxylic acids are possibly present.
- viii. CO_2 and H_2O are possible. Could be absorbed or desorbed in the cell itself.

It was very difficult to deconvolute the spectrum any further with the existing capabilities. The analysis could be significantly improved by attaching a GC column before the FTIR cell.

Figure G.1: PET Depolymerization: FTIR spectrum of gas sample.

APPENDIX H: Residence Time Estimation

The residence time in the reactor were estimated based on the following assumptions:

- i. The total volume of the reactor up to the sampling port = 11.7 liters.
- ii. All reactions were fully quenched by the time the gas reached the sampling port.
- iii. Simple volumetric expansion of gases was assumed.
- iv. The gases were assumed to be ideal.
- v. No backmixing occurred.
- vi. A uniform mean gas temperature of 2000 K at low power levels and 3000 K at high power levels was assumed.
- vii. Base Case: plasma plate power input = 10 kVA, sheath gas flow rate = 50 slm, central gas flow rate = 20 slm, probe gas flow rate = 9 slm and quench gas flow rate = 0 slm.

Based on these assumptions the residence time of the gas at the base case condition was calculated to be 1.33 s. The residence time of the gas at 20 kVA with other conditions being kept constant at base case was calculated to be 0.89 s.

Determination of the residence time of solid particles would be even more complex as many other factors such as depolymerization of the polymer particle leading to reduction in particle size, drag forces due to viscous plasma gas, variations in the particle size distribution, etc. are involved. The residence time of polymer particles in a thermal plasma is not reported in the literature. For a 100 μm Fe particle, Wei [1987] predicted a residence time of 100 ms in an RF plasma zone. Using Laser Doppler Anemometry Francke et al. [1998] showed that a 125 μm particle could have velocities in the range of 20 to 30 m/s. Residence time of such a particle would be less than 100 ms.

Experimental determination of the gas residence time was attempted using a Residual Gas Analyzer [RGA]. The sampling line was located at the position shown in Figure 4.2. Argon was used as the central, sheath and probe gas. The residence time was measured by rapidly switching the probe gas to oxygen and recording the time interval for the detector of the RGA to observe an oxygen peak. The sampling line lag time and carrier gas line lead times were initially measured separately by placing the sampling probe very close to the injection probe and timing a step change in the oxygen flow rate in the probe. Residence time was calculated by subtracting the sampling line lag time + the carrier gas line lead-time from the time need for the oxygen to reach the RGA through the reactor. This test was repeated 6-8 times.

The method is somewhat inaccurate due to (1) variation of the sampling line lag time with the reactor pressure, especially at high power levels and high gas flow rates and (2) measuring the time manually using a stop watch. The residence times measured by this method at different power levels are shown in Figure H.1. Similar measurements made at different central and sheath gas flow rates are shown in Figure H.2. The measured residence time values were comparable to those predicted using a simple volumetric expansion of gases method.

Figure H.1: Residence time of the reactor at different power levels [RGA measurements].

Figure H.2: Residence time vs. gas flow rates.

APPENDIX I: Mass Balance Calculations

Mass balance runs were carried out at optimum conditions, within the limitations of the equipment, as determined by statistical analysis using Design-EaseTM. Known masses of polymer powder were placed in the powder feeder hopper. The polymer powders were fed into the carefully cleaned reactor for 20 to 45 minutes. After the experiment was completed, the polymer powder left in the feeder hopper was carefully collected and weighed. The difference between the mass of the polymer left in the feeder before and after the run gave the total mass fed into the reactor. The error between the calculated value [using calibration chart] and the experimental value was less than 5 %. The summary of the mass balance analysis for each polymer system is shown in Tables I.1 - I.4.

Table I.1: PE Depolymerization: mass balance analysis.

	Run #1	Run # 2
Polymer Fed into the Reactor [g]	132	115
Residue from the Reactor Walls [g]	24.8	19.7
Residue from the Un-Cooled Bottom Section of the Reactor [g]	9.0	2.6
Residue from the Filter Upstream of the Eductors [g]	10.8	11.2
Residue from the Filter in the Hood [g]	0.4	0.4
Total Amount of Residue Collected [g]	45.0	33.9
% Conversion of Solid PE Particles into Gaseous Products	66	70.5

Table I.2: PP Depolymerization: mass balance analysis.

	Run #1	Run # 2
Polymer Fed into the Reactor [g]	68.3	68
Residue from the Reactor Walls [g]	8.4	8.0
Residue from the Un-Cooled Bottom Section of the Reactor [g]	1.7	1.8
Residue from the Filter Upstream of the Eductors [g]	0.8	4.0
Residue from the Filter in the Hood [g]	4.1	2.4
Total Amount of Residue Collected [g]	15.0	16.2
% Conversion of Solid PP Particles into Gaseous Products	78	76.2

Table I.3: PET Depolymerization: mass balance analysis.

	Run #1	Run #2	Run # 2
Polymer Fed into the Reactor [g]	46.5	45	45
Residue from the Reactor Walls [g]	7.8	5.3	8.7
Residue from the Un-Cooled Bottom Section of the Reactor [g]	3.0	1.9	4.7
Residue from the Filter Upstream of the Eductors [g]	0.8	0.3	0.6
Residue from the Filter in the Hood [g]	0.7	0.5	0.7
Total Amount of Residue Collected [g]	12.3	8.0	14.7
% Conversion of Solid PET Particles into Gaseous Products	73.8	82.3	67.3

Table I.4: PE + PP Mixture Depolymerization: mass balance analysis.

	Run #1 @ High Power	Run # 2 @ Low Power
Polymer Fed into the Reactor [g]	45	45
Residue from the Reactor Walls [g]	7.5	6.1
Residue from the Un-Cooled Bottom Section of the Reactor [g]	1.8	1.1
Residue from the Filter Upstream of the Eductors [g]	1.5	3.0
Residue from the Filter in the Hood [g]	1.0	0.2
Total Amount of Residue Collected [g]	11.8	10.4
% Conversion of Solid PE + PP Mixture into Gaseous Products	74	76.8

APPENDIX J: Bomb Calorimetry Calculations

The calorific values of the solid residues collected during the plasma pyrolysis of polymers were determined using a Parr [Model 1341] plain oxygen bomb calorimeter. Using a pellet maker, the powdery residues were converted into small pellets weighing less than 1 gram. A pellet was placed inside the bomb head and was placed on the stand supported from the bomb lid. Ten [10] cm of nickel alloy wire was attached using the same stand such that the fuse wire was just touching the pellet surface. One [1.0] ml of distilled water was added to the bottom of the bomb as a sequestering agent. The bomb was closed carefully so that the sample was not disturbed. The bomb was then filled with oxygen until the pressure inside the bomb reached 30 atm. The calorimeter bucket was filled with 2000 g of distilled water. The bomb was then placed inside the bucket and closed with a lid. The temperature inside the bucket was kept uniform using a motor-driven stirrer. After 5 minutes the temperature was recorded and then the bomb was ignited. Temperature readings were recorded at intervals of 30 s until the temperature profile leveled [usually about 12-15 minutes]. The temperature corresponding to the 60 % rise in the temperature of the bucket was then calculated. After the last temperature reading, the motor was stopped and the bomb was removed from the bucket. The pressure was released very slowly [~2 min.]. The interior of the bomb was examined for soot formation or other evidence of incomplete combustion. If any such evidence was observed, the result was discarded. The remains of the fuse wire were collected and the sum of its length was recorded. The bomb was washed with distilled water and the solution titrated with a 0.0725 N sodium carbonate solution using methyl orange indicator for acid correction. The solution was not analyzed for sulfur content as the elemental analysis indicated that the solid residues were free of sulfur. The energy equivalent of the calorimeter was determined using a standard benzoic acid pellet.

The temperature rise, t , is given by Eq. [J.1]:

$$t = t_c - t_a - r_1(b-a) - r_2(c-b) \quad [J.1]$$

where a = time of firing.

b = time when the temperature reaches 60 % of the total rise.

c = time at the beginning of the period [after temperature rise] over which the rate of temperature change has been constant.

t_a = temperature at a , corrected for thermometer scale error.

t_c = temperature at c , corrected for thermometer scale error.

r_1 = rate at which the temperature was rising before firing.

r_2 = rate at which the temperature was rising after time c .

The gross heat of combustion, H_g , is given by Eq. [J.2];

$$H_g = [tW - e_1 - e_2]/m \quad [J.2]$$

where W = energy equivalent of the calorimeter, 2426 cal./ $^{\circ}\text{C}$,

e_1 = correction in calories for the heat of formation of nitric acid,

= volume of 0.0725 N alkali in milli-liters,

e_2 = correction in calories for the heat of combustion of the fuse wire,

= (2.3) x length of fuse wire consumed in centimeters,

m = mass of sample in grams.

Sample calculations using a solid pellet made out of residue collected from the filter in the hood during a PE mass balance run are shown below:

$$m = 0.152 \text{ g}$$

$$b - a = 1.4 \text{ min.}$$

$$c - a = 6.0 \text{ min.}$$

$$r_1 = 0$$

$$r_2 = -0.002 \text{ } ^\circ\text{C/min.}$$

$$t_a = 25.60 + 0.004 = 25.604 \text{ } ^\circ\text{C}$$

$$t_c = 26.11 + 0.008 = 26.118 \text{ } ^\circ\text{C}$$

$$t = (26.118 - 25.604) - (-0.002)6 = 0.526 \text{ } ^\circ\text{C}$$

$$e_1 = 0.0$$

$$e_2 = 2.3 \times 4.78 = 11 \text{ cal.}$$

$$H_g = [(0.526 \times 2426) - 11] / 0.152 = 8322.9 \text{ cal./g} = 8322.9 \times 4.192 = 34,890 \text{ kJ/kg.}$$

The calorific value of the solid residue was determined 2-3 times and the mean values are reported in Section 6.