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Exergy Analysis of Plastic Waste Management

A Master's Thesis submitted for the degree of
"Master of Science"

supervised by
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Affidavit

I, **ADITI RAMOLA**, hereby declare

1. that I am the sole author of the present Master's Thesis, "EXERGY ANALYSIS OF PLASTIC WASTE MANAGEMENT", 63 pages, bound, and that I have not used any source or tool other than those referenced or any other illicit aid or tool, and
2. that I have not prior to this date submitted this Master's Thesis as an examination paper in any form in Austria or abroad.

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Abstract

Using material flow analysis (MFA) and exergy analysis, two competing scenarios for the management of municipal plastic waste arising from private households are evaluated. In Scenario A there is no source-separation of plastics, and the mixed waste stream is sent for incineration to a waste-to-energy plant (energy recovery). In Scenario B plastics are source-separated and sent to a material recycling facility (MRF) for the production of recyclates that substitute virgin plastics from primary sources (material recovery). The "systems expansion" approach is applied to make the basket of products (electricity, heat, plastics) in Scenario A comparable to that in Scenario B. This step depends on the substitution factor α, defined as the ratio of quantity of primary plastic that can be replaced to the amount of recyclate needed to substitute it to achieve equivalent performance, of the recyclates. The total cumulative exergy demand (CExD) of the expanded systems are computed. It is found that for $\alpha > 0.16$ natural resource depletion in Scenario B is less than that in Scenario A, as measured by the CExD indicator and material recycling of the plastic fraction is favored. When $\alpha < 0.16$, Scenario A, incineration of the plastic fraction, is exergetically favored.

Contents

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Chapter 1

Introduction

The industrial revolution marked the beginning of an era in human civilization during which the consumption and degradation of natural resources grew at an unprecedented exponential rate. During the 20th century there was a fourfold increase in the world population, a twenty-two-fold increase in the economic output, and a fourteen-fold increase in the worlds fossil fuel consumption (UNEP, 2011). The concomitant leaps in science, technology and medicine, coupled with economic growth brought greater welfare to many. However, by the middle of the century, the impact of human activity on the biosphere was apparent. By the 1970s scientists had begun to warn of the dangers of unabated pollution of the environment, and overuse of natural resources (Meadows, Meadows, Randers, & Behrens, 1974). It was in this milieu that the importance of a *sustainable* industrial metabolism came to prominence, and the term sustainable development, defined to be development that *"meets the needs of the present without sacrificing the ability of the future to meet its needs"* (Holdgate, 1987) was coined and became such an indispensable part of contemporary vocabulary.

Plastics are the quintessential product of industrial society: they are derived from a non-renewable and limited resource, namely crude oil and natural gas, and typically require inputs of energy on an industrial scale for their production, and if not properly disposed the end product is potentially toxic to the ecosphere. Despite a short history of the plastics industry, since the 1940s plastics have found their way into a myriad of aspects of modern life and have found use in a wide range of applications (Hopewell, Dvorak, & Kosior, 2009). With increased use of plastics in consumer applications the fraction of plastics in the municipal solid waste streams keeps growing, with the growth being primarily attributable to packaging waste.

The ubiquity of plastic underscores the urgency of finding ways to optimize the industrial metabolism of plastic. There are several levels at which industrial metabolism can be optimized, ranging from the optimization of the efficiency of individual plants (e.g. a waste-to-energy plant), to the optimization of the *overall* industrial metabolism of plastic. It is the latter question that is the subject of this thesis. It is becoming increasingly important to figure out a way to extract these resources from an extremely complex waste stream. The management and utilization of plastic wastes is often debated due to diverse and competing options available for resource recovery. The use of end-of-life plastics can contribute to resource conservation by substituting fuel, reductive agents and/or primary raw materials.

The goal of this study is to optimize plastic waste management for a defined system from a thermodynamic perspective. Furthermore, this study aims to resolve the debate on which plastic waste management path is exergetically more beneficial in the context of sustainable use of resources. To this end, two different plastic waste management scenarios/options are described using material flow analysis (MFA) which is a method to describe, investigate, and evaluate the flow of materials through a system defined within a temporal and spatial boundary. Subsequently, plastic waste utilization is evaluated by means of exergy analysis. The study considers both, the benefits from energy recovery (incineration) and recycling of plastics to substitute virgin materials.

The functional unit of the analysis is 1000 kg of mixed waste generated at the private household. In the baseline case, all the residual waste including the plastic fraction is collected together and directed to a waste to energy (W-t-E) plant. In the alternative case mixed plastic wastes are collected separately and directed to a materials recovery facility (MRF). Two different downstream utilization options are investigated: a) thermal recovery of the energy content, b) material recycling of selected fractions combined with thermal recovery for low-quality fractions. The evaluation takes place within the framework of life-cycle assessment, where exergy consumption data is available for a large number of resources.

Tasks that were completed in the course of this study were:

1. Literature review about exergy analysis, evaluation of waste and resource systems (especially plastics).
2. Material flow analysis of the plastic waste management scenarios.
3. Using the equal basket of benefits approach, cumulative exergy demand (CExD) calculations of a basket of equal goods for both scenarios.
4. Interpretation and discussion of the results in view of optimizing plastic waste utilization based on the second law of thermodynamics (exergy) analysis.

1.1 Goals

If plastic is the quintessential industrial product, then perhaps thermodynamics, and especially the second law, is the quintessential science spawned by the industrial revolution. While energy is conserved in any process, the second law implies that the amount of energy available for useful work - exergy - is consumed in any natural process. The second law has come to be a cornerstone of industrial ecology which has it's roots in the sustainable development movement of the 1970s. Since then there has been a long tradition of analysis of industrial metabolism using exergy and the second law (R. Ayres & Ayres, 2002; J. Dewulf et al., 2008a). However, there do not appear to be many studies applying these concepts, and in particular the notion of cumulative exergy demand, to the metabolism of plastics at a systems level. Such studies have been initiated in (J. P. Dewulf & Van Langenhove, 2004, 2002). This thesis aims to explore and take the ideas a step further and to begin to fill this gap in the existing literature.

This thesis focuses on plastic waste flows through municipal waste generated by private households. The following research questions were identified to help accomplish the goals of this study:

- What are the main processes and what does the system of interest look like?
- What are the flows of plastics and other materials through the defined system in the two scenarios?
- What are the energy consumption requirements for the different processes?
- What are the electricity and heat outputs of the waste-to-energy plant in each scenario?
- How much virgin material does the plastic recyclate substitute?
- What are the exergy flows through the system in both cases - does one scenario perform better than the other exergetically?
- How well is the exergy concept suited to providing guidance on the preferable option to manage plastic wastes?

1.2 Outline of the thesis

This document is structured as follows: Chapter 2 gives a brief overview of what plastics are, their various types and applications, their production and recycling processes, the value of plastics as a resource, and their importance in waste management. Chapter 3 is a quick introduction to the exergy concept, its origins, and its relation to the second law of Thermodynamics. This chapter concludes with a brief discussion of the role of exergy in the context of resource and waste management.

Chapters 4 and 5 constitute the heart of this thesis. Chapter 4 opens with a discussion of the two main methodologies – material flow analysis and cumulative exergy demand analysis – that have been used to conduct this study. Section 4.3 of this chapter is devoted to a detailed description of scenarios A and B within the paradigm of material flow analysis. Material and energy flows in both scenarios are carefully documented. The data values that will be used in the comparison of the scenarios are documented together with their sources. The assumptions made about both scenarios are clearly stated.

In Chapter 5 the data for material flows described in Chapter 4 is fed into the STAN MFA software, allowing a comparison of mass and energy flows. System expansion is carried out, and the cumulative exergy demand for both scenarios is computed. Chapter 6 concludes the paper with a summary of the main results, and a short discussion of the implications of this study.

Chapter 2

Plastics

Plastics is a general term for a wide range of synthetic or semi-synthetic materials used in a vast, and growing, range of applications. Owing to their properties such as durability, inexpensiveness, high strength-to-weight ratio, bio-inertness, high thermal/electrical insulation, and the fact that they can be molded into a vast variety of products, the production and use of plastics has markedly increased over the last 60 years. Worldwide production of plastics reached 288 million tonnes in 2012 and with increasing use in applications is predicted to grow every year (PlasticsEurope, 2014).

The history of modern plastics goes back a couple of centuries, with the most revolutionary developments happening at the beginning of the 20th century. Plastics are increasingly used and find application in packaging, building and construction, transportation, medical and health products, electrical and electronic equipment, agriculture, and sports and leisure equipment. The demand for plastics has grown steadily - plastics are now accepted by engineers and designers as basic materials along with the more traditional materials. The aviation industry, for instance, relies on plastics to reduce weight of airplanes and thus increase energy efficiency.

As reported by PlasticsEurope (2014), plastics are derived from organic products, i.e. from feedstock containing carbon and hydrogen. Currently, fossil fuels (non-renewable resources) are the preferred raw material, but plastics are also made from renewable resources such as sugar and corn. Around 4% of global oil and gas production is used as the raw material for plastics production and a further 3-4% is used as energy in the manufacturing process. However, plastics by their very nature store carbon, and this energy is retained by reusing and recycling plastics (Andrady & Neal, 2009; Hopewell et al., 2009).

2.1 Types

Based on their thermal processing behavior plastic materials can be divided into two main categories: thermoplastics and thermosetting plastics. Figure 2.1 provides a list of different types of plastics, their short name and typical use in products.

Thermoplastics which account for the largest amount of plastics produced (80%) have a structure with long chains of polymers and melt and become mechanically workable when heated up. The items retain their form after cooling, but can be reshaped after re-heating them. Thermoplastics are chemically stable over a large temperature range thus making them suitable for use and also for recycling. Examples of common types of thermoplastics are: polyethylene (PE), polyvinylchloride (PVC), expanded polystyrene (EPS), polystyrene (PS), and polypropylene (PP) (Christensen & Fruergaard, 2011; PlasticsEurope, 2014).

Thermosetting plastics which account for a much smaller amount of plastics produced are polymers in a grid structure. These plastics can be melted and shaped, but once they take form after they have been molded and solidified, they remain solid and, unlike thermoplastics cannot be remelted again. Thermosetting plastics are very resistant to wear, heat, mechanical force, and chemicals - this makes them very hard to recycle. Examples of common types of thermosetting plastics are: phenoplasts, unsaturated polyester (UP), epoxide (EP), polyurethane (PUR), and aminoplasts (Christensen & Fruergaard, 2011; PlasticsEurope, 2014).

Plastic type	Abbreviation	Use
Thermoplastics		
High density polyethylene	HDPE	Containers, toys, house wares, industrial wrappings, gas pipes
Low density polyethylene	LDPE	Pallets, agricultural films, bags, toys, coatings, containers, pipes, wrappings, films
Polypropylene	PP	Film, electrical components, battery cases, containers, crates
Polyethylene terephthalate	PET	Bottles for carbonated soft drinks, textile fibers, film food packaging
Polystyrene	PS	Thermal insulation, tape cassettes, cups, electrical appliances, plates, toys
Expanded polystyrene	EPS	Foam insulation, building material, cycle helmets, packaging of food stuff, medical supplies, electrical consumer goods
Polyamide	PA	Films for packaging of food waste, textile fibers
Polyvinyl-chloride	PVC	Window frames, pipes, flooring, wallpaper, bottles, guttering, cable insulation, toys, credit cards, medical appliances
Polymethyl-methacrylate	PMMA	Transparent all-weather sheet, electrical insulators, bathroom units
Thermosetting plastics		
Epoxide	EP	Protective coatings, composite matrices, adhesives
Unsaturated polyester	UP	Construction and marine applications, e.g. filler for glass fibers in sailing boats
Polyurethane	PUR	Mattresses, vehicle seats, cushions, finishes, coatings
Phenoplasts		Plywood manufacture, insulation, lacquers, varnishes, molding, laminates

Figure 2.1: Types and Uses of Plastics. (Source: Author, adapted from Christensen & Fruergaard, 2011)

2.2 Production

The production of plastics begins by distilling heavy crude oil into lighter groups called fractions. Each of the fractions is a mixture of hydrocarbon chains (chemical compounds made up of carbon and hydrogen), which differ from each other in terms of the structure and size of their molecules. One such fraction, naphtha, is the crucial/necessary element for the production of plastics (PlasticsEurope, 2014). Figure 2.2 illustrates the production of plastics starting from crude oil in a refinery.

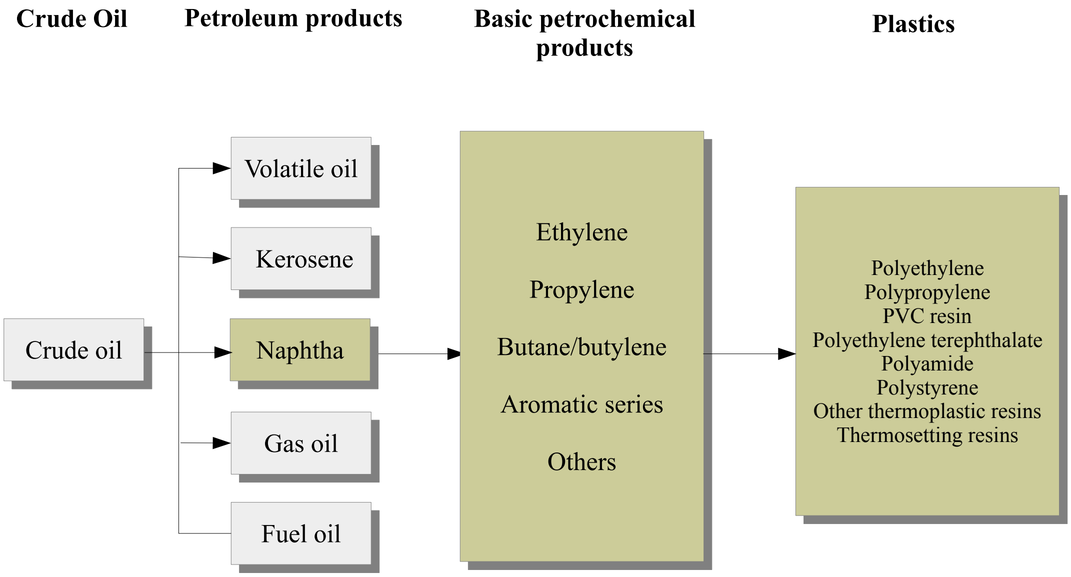

Figure 2.2: Production of plastics from crude oil. (Source: Author, adapted from Plastic Waste Management Institute (PWMI), 2014)

Naphtha is first heated and cracked into monomers to extract substances with a simpler structure (i.e. compounds with a low molecular weight) such as ethylene, propylene, and butylene. The two major processes used to produce plastics are called polymerization and polycondensation. In a polymerization reaction, monomers like ethylene and propylene are linked together to form macro-molecules (i.e. compounds with high molecular weight) with long polymers chains. Each of the polymers produced has its own properties, structure and size depending on the different types of basic monomers used. The molecules obtained are then chemically coupled (polymerized) to form substances with new properties, such as polyethylene (PE) and polypropylene (PP), which are called synthetic resins and polymers. Additives are added to the newly formed polyethylene and other such substances to alter and improve basic mechanical, physical and chemical properties. They are then made into granules and it is from this stage on that they are normally referred to as plastics. Plastic granules (granulates) are the basic product from which plastic products are made. New plastics are usually supplied to processors and molding plants in the form of granules to be turned into plastic products by heating, extruding, and molding. (PlasticsEurope, 2014; Plastic Waste Management Institute (PWMI), 2014; Christensen & Fruergaard, 2011)

2.3 As a resource

Much of what we use and consume in modern society constitutes of plastic in some form, including but not limited to - clothing, footwear, food packaging, and electrical appliances. Millions of tonnes of plastics are converted into textile fiber (mainly nylon, polyester and acrylics) worldwide for use in apparel manufacture. High strength-to-weight ratio gives plastics the advantage of using minimal material in packaging design, and a large portion of plastic produced each year is used to make disposable packaging items or other short-lived products that are discarded and enter the waste stream within a year of manufacture (Andrady & Neal, 2009). High-performance clothing is almost exclusively plastics – polyesters, fluoropolymers and nylons; fleece clothing is 100 per cent plastic (PET) and can be made from recycled PET (Andrady & Neal, 2009). Mattresses, vehicle seats, coating, and cushions are made from polyurethane; protective coatings, adhesives, and composite matrices are all made of plastic materials mostly epoxide (EP) (Christensen & Fruergaard, 2011). It is hence evident that plastics constitute an important component and a large volume of the range of materials used in modern society.

The properties of plastics that deliver unparalleled design versatility also make plastic waste remain in the environment for a very long time unless treated and recovered. At the end of their first use, recovery of plastics can be handled in one of two broad ways: energy recovery and material recovery.

Energy recovery: All plastics being variations of hydrocarbons, have high intrinsic heating (calorific) values and the incineration of plastic waste can recapture the energy resource in plastics and substitute for primary fuels in industrial processes, or electricity and heat generation.

Material recovery: On the other hand, material recovery involves recycling plastic waste into new products by means of mechanical recycling and chemical/feedstock recycling.

- *Mechanical recycling* involves processes where the chemical structure of plastic remains unchanged such as shredding, melting or granulation of plastic waste.
- *Feedstock recycling* refers to techniques that break plastic down into monomers (chemical structure of plastic is not maintained) for use in chemical production and refineries (Christensen & Fruergaard, 2011).

Feedstock or chemical recycling goes one step back in the production/recycling process, and is not of interest for this study and hence is not discussed in this paper.

Many types of plastics are recycled today but recycling into high-quality plastic products requires that material is free of contaminants and foreign items. Additionally, recycling of post-consumer plastics is faced with the problem of keeping different resin or plastic types in separate streams so as to maintain the most significant feature of plastic: great strength and flexibility at very small weights and dimensions. If the recycled plastic waste is source-separated, clean and consists of only one type of resin/plastic, then the recycled waste substitutes use of virgin plastics. If the different types are not carefully separated, then the recycled plastic waste substitutes materials such as wood or concrete, and can only be used to produce low-strength items of secondary importance such as garden furniture, pots, fences, and so on. (Astrup, Fruergaard, & Christensen, 2009; Christensen & Fruergaard, 2011)

Mechanical recycling of plastic waste takes place at a material recovery facility (MRF). This study focuses on a MRF that delivers granulates for the production of new products (material recycling) as opposed to pellets for industry as a fuel, from source-separated plastic waste. Such a MRF receives high-quality plastic waste limited to bottles and containers for liquids. Source-separation of plastics limits the amount of contaminants such as organic waste and dirty plastic films, etc. in the input. In such a case the waste is likely to be dominated by PET, since most bottles are made from plastic resin of this type. Usually the recovered material is received in the receiving area and transported by a conveyor to a manual sorting area, which is commonly done as negative sorting of a plastic waste stream dominated by one type of resin, where large foreign objects are removed. Then mechanical treatment involves automatic sorting primarily using infrared spectroscopic identification, screens, magnetic and eddy-current separation, granulation (i.e. size reduction), washing and drying, finally extrusion and then cutting of extruded plastics into granulates that are typically cooled in water. The granulates are then bagged and stored until sold to a reprocessing plant. The cleaner and purer the fraction of plastic waste received, the lesser the mechanical treatment needed. (Christensen & Fruergaard, 2011; Astrup et al., 2009) The residues from the sorting and recycling processes are sent back to the waste-to-energy plant for incineration.

Recyclates are recycled plastics that come from post-consumer waste, i.e. plastics that have already passed through one complete ‘life cycle’ (been disposed of with household waste at least once after being used), whereas regranulates come from waste recycled during the production process of plastics. It is important not to confuse the two. Recyclates, or secondary raw materials, can be used to make high-quality new products and convert plastic waste into products they once were. (Ecoplast, 2014)

Chapter 3

Exergy

The thermodynamic concept of *exergy* constitutes the conceptual and theoretical foundation of the analysis of plastic waste management carried out in this thesis. This concept has as its basis the first and second laws of thermodynamics - these laws are recalled in Section 3.1, following (Feynman, Leighton, Sands, & Gottlieb, 1963; Waser, Trueblood, & Knobler, 1976; Castellan, 1983). Section 3.2 introduces the notion of exergy following the discussion in (R. U. Ayres, Ayres, & Martinás, 1996; Szargut, 2005). Finally, the role of exergy in the management of natural resources and waste is discussed in Section 3.3.

3.1 The laws of thermodynamics

The modern science of thermodynamics originated in the seminal work of the French engineer Sadi Carnot (Carnot, 1824) titled “Reflections on the Motive Power of Fire”. Carnot was concerned with the efficiency of heat engines - devices that extract work from heat that is flowing from a hotter body to a cooler body. In particular, he posed the following question: what is the maximum amount of mechanical work W that can be extracted from a certain quantity of heat Q flowing from a source at temperature T_1 to a sink at temperature $T_2 < T_1$? Starting from a single assumption, Carnot deduced the remarkable fact that W *is independent of the specific substances* *participating in the process* and that, *regardless of how cleverly the machine or process is designed, there is an upper bound for* W *that depends only on the temperatures* T_1 *and* T_2. Thermodynamics is the subject that is concerned with those aspects of macroscopic processes and phenomena that are independent of the detailed microscopic structure of the materials participating in them. Thermodynamic reasoning is thus a powerful tool in the analysis of complex systems.

The quantity W is given by:

$$W = Q\left(1 - \frac{T_2}{T_1}\right)$$

In modern language, this can be formulated as the assertion that the *exergy* content (see (Szargut, 2005; R. U. Ayres et al., 1996)) of the given amount of thermal energy Q at temperature T_1, with respect to an environment at temperature T_2 is given by $Q(1 - T_2/T_1)$.

The point of departure of Carnot's analysis was the simple premise that *it is impossible to design a reproducible cyclic process whose net result is to extract heat from a reservoir at a single temperature* T *and convert it to work.* In other words, to extract work from heat, Carnot assumed that we must use bodies at *two* distinct temperatures, allowing the heat to "fall" from the hotter to the cooler body. This assumption, and its numerous consequences, has withstood every experimental test; it is now enshrined as the *second law of thermodynamics.*

Formally, a thermodynamic system is specified by a set of *states* that the system can occupy, and a collection of *state variables* - functions that assign a number to each state. Examples of state variables are temperature and pressure. For non-isolated systems, one must specify in addition differentials such a δQ (heat transferred) and δW (work done), which describe the ways in which a system interacts with its environment.

A process is a path from an initial state to a final state. Among the set of all possible processes, there is a subclass consisting of those processes that are realizable in nature. The *laws of thermodynamics* are constraints that processes realizable in nature are required to satisfy. These laws have been abstracted from countless empirical observations.

THE FIRST LAW: *There exists a state variable U, called internal energy, with the property that U remains constant along any realizable process γ of an isolated system.*

Thus, the first law of thermodynamics is the law of conservation of energy. It states that there is an abstract quantity called energy, not necessarily directly measurable or perceivable to the senses, which remains unchanged in an isolated system.

What if the system is not isolated? In this case, the first law becomes the assertion that any change in U during a process should be attributable to a measurable quantity that can interpreted as "the transfer of a form of energy" to/from the system. For many systems of practical interest, these quantities turn out to be of three types: (i) the transfer of an amount δQ of heat ("thermal energy") from the environment to the system, (ii) δW, the work done by the environment on the system and (iii) the transfer of N_i moles of a substance with chemical potential μ_i to the system. For such non-isolated systems, the first law becomes:

THE FIRST LAW (NON-ISOLATED SYSTEMS): *There is a state variable U, such that $dU = \delta Q + \delta W + \sum_i \mu_i N_i$ along any infinitesimal process occuring in nature.*

The second law of thermodynamics has a form very similar to the first law: the only difference is that the term "constant" is replaced by "non-decreasing".

THE SECOND LAW: *There exists a state variable S, called entropy, with the property that S is nondecreasing along any process γ realizable in an isolated system. For a materially isolated but thermally non-isolated system, the infinitesimal change in entropy along an infinitesimal reversible path is given by $dS = \delta Q/T$, where T is the temperature.*

While the statement of this law, due in this form to Clausius and Carathéodory, may seem obscure at first, its physical content is in fact more intuitively easy to grasp than the first law, and it chronologically preceded the first law. In fact, (see, e.g., (Feynman et al., 1963) for an excellent discussion), the second law is equivalent to the following intuitive statement: *It is impossible to construct a reproducible process where heat flows spontaneously from a cooler body to a warmer body.*

With the advent of statistical mechanics, thermodynamic variables acquired an interpretation in terms of the microscopic constituents of matter (molecules). In particular, Boltzmann (see (Feynman et al., 1963)) showed that entropy could be interpreted as the "disorder of a system" in a certain precise sense. To the extent that disorder is palpable to the human consciousness, entropy is perceivable to the senses. However, it is usually not possible to directly measure entropy.

There are two other important fundamental laws of thermodynamics - the zeroth and third laws. These will not be discussed in this thesis.

3.2 The concept of exergy

The exergy Ex of a system $\mathcal{S}$, with respect to a given environment $\mathcal{S}_{env}$, is defined to be the maximum amount of useful work that can be extracted from the system in a process that brings the system into equilibrium with its environment (R. U. Ayres et al., 1996; Szargut, 2005). Here we assume that the environment is an infinite reservoir, whose temperature, pressure, etc. do not change appreciably during the equilibration process. The availability of energy for conversion to useful work is constrained by both the first and second laws of thermodynamics. Indeed, applying the first law to $\mathcal{S}$, the second law to the combined system $\mathcal{S}_{tot} = \mathcal{S} + \mathcal{S}_{env}$, and the second law to $\mathcal{S}_{env}$, respectively, we have

$$dU = \delta Q + \delta W + \sum_i \mu_i N_i$$

$$dS_{tot} = dS + dS_{env} \geq 0$$

$$\delta Q = -T_{env} dS_{env}$$

Now part of the work $-\delta W$ done by the system $\mathcal{S}$ goes into expanding against the environmental pressure P_{env}, and is not useful in the sense that it cannot be converted into mechanical potential or kinetic energy. Therefore, the useful work δW_{useful} done by the system satisfies $\delta W_{\text{useful}} \leq -\delta W - P_{env} dV$. Combining this with the three equations above, one sees immediately that

$$\delta W_{\text{useful}} \leq -dEx$$

where the *exergy* Ex is given by

$$Ex = U - T_{env} S + P_{env} V - \sum_i \mu_i N_i$$

The essential points to note here are

- The exergy of a system $\mathcal{S}$ with respect to the environment $\mathcal{S}_{env}$ is a function of the state of the combined system $\mathcal{S} + \mathcal{S}_{env}$, and not a function of the state of $\mathcal{S}$ alone.

- The second law of thermodynamics applied to $\mathcal{S}_{tot}$ manifests above as the statement that in any process where the system $\mathcal{S}$ performs a certain amount of useful work, there must be an equal or greater loss of exergy from $\mathcal{S}$.

The concept of exergy, or "available energy" dates back to Gibbs (Gibbs, 1871, 1957), (Duhem, 1886), and other works in the 1800s. Duhem and Gibbs introduced the notion of a thermodynamic potential, which is the thermodynamic analogue of the concept of potential energy associated to a mechanical system. Examples of thermodynamic potentials commonly used in thermodynamics include enthalpy ($H = U + PV$), the Gibbs free energy ($G = H - TS$) and the Helmholtz free energy ($F = U - TS$). These thermodynamic potentials provide a description, for *materially closed* systems in internal equilibrium subject to various constraints, of the evolution toward equilibrium with the environment. See (Castellan, 1983) for a detailed discussion, and (R. U. Ayres et al., 1996) for an excellent overview. The concept of exergy can be regarded as a generalization of the notion of thermodynamic potential to open systems that are not subject to any constraints. The term exergy was coined in (Rant, 1956), but the precursors of the concept goes back to (Gibbs, 1871), as noted above.

3.3 Exergy in resource and waste management

In common parlance, as well as in much of the scientific literature on environmental science and sustainability, the term "energy consumption" is ubiquitous. However, according to the first law of thermodynamics, energy is conserved - it can neither be created nor destroyed. As explained above, the quantity that *is* consumed, when useful work is done, is the exergy of the system.

Since thermodynamic analyses are, by their very nature, independent of the detailed microscopic structure of the systems being considered, they are well adapted to the methods of systems analysis (Meadows et al., 1974). Although the precursors of the exergy concept were discovered in the 1800s, it was only in the 1970s that exergy started to be applied systematically to the analysis of complex industrial, economic, biological and economic systems (R. U. Ayres et al., 1996). During this decade, publication of "Limits to Growth" (Meadows et al., 1974) drew greater attention to the issue of resource depletion. The landmark studies (United States. Congress. Joint Committee on Atomic Energy, 1973; Carnahan, W. and American Physical Society and National Science Foundation (U.S.) and United States. Federal Energy Administration and Electric Power Research Institute, 1975), commissioned by the Joint Committee on Atomic Energy of the U.S. Congress and the American Physical Society respectively, marked the beginning of what is now a long tradition of the application of exergy and the second law of thermodynamics in the study of resource use and conservation, a practice which is a cornerstone of the thriving field of industrial ecology (R. Ayres & Ayres, 2002).

Complex systems - whether single organisms, entire ecosystems, economies, or industrial systems - sustain themselves by performing useful work. The idea that the second law should play a central role in the description of how “living systems” sustain themselves was proposed in (Schrödinger, 1955), where it was argued that such systems sustain themselves by feeding on “negative entropy”, and “excreting” entropy into their environment. In the language of this thesis, one might formulate this by saying that these systems sustain themselves by consuming exergy. These ideas have been developed further by several authors (Murphy & O’Neill, 1997; Schneider & Kay, 1994) using the exergy concept, and it has been argued that (i) the exergy content an ecosystem and (ii) its ability to effectively dissipate exergy are strong indicators of the integrity and health of the ecosystem (Bendoricchio & Jørgensen, 1997; Fath, Patten, & Choi, 2001). Considerable evidence in favor of this hypothesis has been found: see (J. Dewulf et al., 2008b) and the references therein.

In as much as the “value” of a resource to a given system (biological, ecological, industrial, etc) is determined by its utility in maintaining or “improving the integrity/stability of” the system, it is clear then that the exergy content of the resource is a good indicator of its value. It provides a universal currency, measured in units of energy, with which to measure and compare materials and processes of disparate origins and types. This observation lies at the foundation of the subject of thermo-economics, an approach to economics based on entropy and exergy, introduced in (Georgescu-Roegen, 1971). The subject is now very well-developed; see (R. Ayres & Warr, 2010) for an overview of the literature, and a discussion of how various traditional economic indicators, such as GDP, are strongly correlated with exergy flows.

Exergy can also be used to assess the impact of a given product on the environment. To evaluate the resource depletion brought about by a given product, it is necessary to take into account the exergies of all the resources participating in the process that leads from raw materials occuring in the environment to the given product (the supply chain in a manufacturing process from cradle to grave). The *cumulative exergy consumption* (CExC) (Szargut, Morris, & Steward, 1987; Szargut, 2005) of a product, also known as the *cumulative exergy demand* (CExD) (Bösch, Hellweg, Huijbregts, & Frischknecht, 2007), is a measure of the total amount of exergy depleted from the environment in the production of the product. It is not an attribute of the product itself, but of the process that the leads to the product from its naturally occuring components. This notion will be discussed in detail in Section 4.2; it forms the basis for the analysis in this paper of the environmental impacts of different plastic waste management scenarios.

Chapter 4

Material and Methods

A number of steps/tasks were completed in carrying out this study. First, a literature review about exergy analysis and evaluation of waste and resource systems (especially plastics) was conducted.

The second step involved defining the system of interest and it's processes and flows, within temporal and geographical boundaries. Two scenarios were elaborated for the material flow analysis: Scenario A, the baseline case, assumed no source-separation for plastic waste generated at private households and where mixed solid waste (residual waste) with the plastic fraction was sent for incineration to a waste-to-energy plant with energy (heat and electricity) recovery capability. Scenario B, differed from Scenario A in that the plastic fraction was source-separated at households and was sent instead to a material recycling facility for production of recyclates to substitute plastic production from virgin sources. Next an inventory of the material and energy flows for the two plastic waste management scenarios was conducted.

The third step included conducting an impact assessment of the two scenarios using cumulative exergy demand (CExD) indicators.

Finally, the fourth step involved interpretation and discussion of the results in view of optimizing plastic waste utilization based on the second law of thermodynamic analysis.

The two methodologies applied to reach the goals of this thesis – material flow analysis (MFA) and exergy analysis – are briefly described below, followed by the description of the two scenarios and the sources from which material and energy flow data was gathered.

4.1 Material Flow Analysis (MFA)

As defined by Brunner and Rechberger (2004), material flow analysis (MFA) *"is a systematic assessment of the flows and stocks of materials within a system defined in space and time. It connects the sources, the pathways, and the intermediate and final sinks of a material."* Based on the principle of conservation of matter, MFA is a simple yet powerful tool that can analyze a process by comparing and balancing it's input, stock, and output material flows. It is this property of MFA that makes it a useful decision-making tool in resource and waste management. An MFA of a system or process provides an accurate picture of all the flows and stocks of a particular substance/material within it, and it becomes easier to identify the loadings and sources of the substance/material. This can lead to early identification of depletion or accumulation of particular materials and allow for the implementation of appropriate policy measures - either to allow accumulation for future use or to counteract the depletion. Also, changes that would otherwise take a long time to measure become evident by conducting a MFA of a system or process. (Brunner & Rechberger, 2004)

It should be noted that anthropogenic systems are intricately linked to space, information, energy, society - and though an MFA can be performed with a simple mass-balance analysis, these aspects have to be taken into consideration while interpreting the results of an MFA. Applying MFA to a system involves conducting an **inventory analysis** for the material flows and stocks of the system.

Listed are key terms and procedures used in MFA methodology as developed by Baccini and Brunner in the 1980s:

- ***Material***: The term material encompasses both, substances and goods. Substances are defined as a particular form of matter consisting of uniform properties or units. Goods are substances or a mixture of substances that have an assigned economic value which can be either positive or negative.

- ***Process***: A process can be defined as a transport, transformation, or storage of materials. A process on the whole can be examined as a closed system or black box, meaning that only the inputs and outputs are of interest and not the details within the box. When the processes within the black box are of relevance or interest then they can be subdivided into two or more processes. Processes are linked together by flows and fluxes.

- ***Flows and Fluxes***: Flow is defined as the rate of flow mass through a conductor, and a flux is defined as the flow per cross section.

- ***Transfer Coefficients (TC)***: These describe the partitioning of a substance within a process and are defined for each output good of a process. Transfer coefficients are a substance specific value and when multiplied by 100, give the percentage of the total throughput of a substance that is transferred to a specific output good (also called partitioning). Furthermore, transfer coefficients depend on the characteristics of a process and need not always be constant.

- ***System and System Boundary***: The system is the object that is investigated by an MFA. It consists of a set of material flows, stocks, and processes within a defined spatial and temporal boundary (system boundary). The temporal boundary is the time span over which the system of interest needs to be studied and balanced. It is defined by the system and the problem to be investigated, for instance it could range from seconds for a combustion process to a 1000 years for a landfill. The spatial boundary is generally the geographical region in which the processes are located but can also be an abstract area. For example, a city, region, country, the whole planet, or even a virtual limit such as a waste-management system of a town. A system can be represented by a single process or a collection of processes.

Material flow analysis for this study was performed using the free software STAN (short for subSTance flow ANalysis) that can graphically model arbitrarily complex systems using predefined components (flows, processes, subsystems, system boundaries, and text fields) and allows known data (mass flows, volume flows, stocks, and transfer coefficients) with corresponding physical units to be either entered or imported for different time periods and hierarchical layers (goods/substances and energy).

4.2 Exergy Analysis - Cumulative Exergy Demand

Having introduced the concept of exergy and it's origins in the second law of thermodynamics in Chapter 3 above, this section describes the notion of cumulative exergy demand (CExD) and why it will be used in this study.

The CExD indicator is introduced by Bösch et. al. (2007) to mean the sum of exergies of all the resources required to provide a particular product. This depicts the total exergy removed from nature to provide that product. "*CExD assesses the quality of energy demand and includes the exergy of energy carriers as well as of non-energetic materials*" (Bösch et al., 2007). From the laws of thermodynamics we know that energy and mass are conserved in an (materially and energetically) isolated system – for all practical purposes the Earth can be considered to be a materially isolated system. What *is* consumed and eventually depleted is 'usable matter and usable energy', and exergy is a measure of such useful and available energy (Bösch et al., 2007). Hence, the cumulative exergy demand (CExD) is a suitable useful energy based indicator for the quality of resources that are removed from nature to provide a particular good or product. CExD is equivalent to the concept of *cumulative consumption of exergy*(CExC) introduced by Szargut (1987, 2005) and Morris (1987) (Bösch et al., 2007; Szargut & Morris, 1987; Szargut et al., 1987).

CExD is an ***impact assessment*** indicator, that is, it measures the *total resource* *depletion* and assesses the impact of producing a product on the environment. To highlight that CExD is not an inventory of elementary flow but an impact assessment indicator, it is specified in MJ-equivalents (Bösch et al., 2007). CExD can be calculated as:

$$CExD = \sum_i m_i * Ex_{(ch),i} + \sum_j n_j * r_{ex-e(k,p,n,r,t),j}$$

where

$CExD =$ cumulative exergy demand per unit of product or process (MJ-eq)

$m_i =$ mass of material resource i (kg)

$Ex_{(ch),i} =$ exergy per kg of substance i (MJ-eq/kg)

$n_j =$ amount of energy from energy carrier j (MJ)

$r_{ex-e(k,p,n,r,t),j} =$ exergy to energy ratio of energy carrier j (MJ)

$ch =$ chemical

$k =$ kinetic

$p =$ potential

$n =$ nuclear

$r =$ radiative

$t =$ thermal exergy

Exergy is stored in resources in the form of chemical, kinetic, potential, nuclear, thermal and radiative energy, and the assignment of the adequate type of exergy depends on the kind of resources used (Bösch et al., 2007). CExD values may comprise the sum of values of primary exergy. The analysis of a cumulative exergy indicator can be considered similar to the definition of cumulative consumption of primary energy (CED). However, when using the latter the quality or usefulness of the energy is not taken into account while it is accounted for by CExD. Furthermore, CExD "*accounts for the exergy captured in non-energetically used materials*", thus making

CExD indicator a more comprehensive energy-based resource demand indicator than CED (Bösch et al., 2007). The ecoinvent database contains CExD values that were calculated for a large number of ecoinvent product and process systems and provides life cycle resource demands of various products. CExD values for electricity and plastics used in this study are taken from the ecoinvent database.

4.3 Description and Data

The goal of this study is to evaluate competing waste management options for plastic wastes generated at private households by identifying whether one option is exergetically significantly more beneficial than the other. Two scenarios, A and B, are developed and analyzed to enable comparison to be made between competing disposal options for plastic waste.

Functional unit: The basis for the two scenarios described is the recycling, reprocessing, or incineration of 1 tonne – 1000 kg – of residual waste (mixed solid waste) generated by private households.

System/Study boundaries: This study only analyzes energy or material recovery options for mixed plastics and does not evaluate the management of the plastics within the mixed or residual waste stream.

- *Temporal boundary*: The temporal boundary is taken to be one year.
- *Geographical boundary*: For the sake of representative data from waste streams, waste-to-energy plants, and material recycling facilities, the geographical boundary is set to be a town/city in a developed nation with an established waste management system. Though a majority of data used in this study is from the city of Vienna in Austria, it is not a study of the Viennese waste management system, but could equally well be applied to other regions with equivalent processes in place for the management of resources and waste. It is expected that

the direct performance of the processes (energy consumption, recycling efficiency, energy recovery efficiency, etc.) would not be affected by location and are representative of a town/city with a similar municipal waste management system as analyzed/described in this study.

Data uncertainties: Data uncertainties are ignored for the purpose of this study.

Assumptions: The large number of different waste streams and the potential for cross-contamination of a recycled stream makes the scenarios complex to model. As such, a number of assumptions have been made to simplify the assessment. Where and when made every assumption has been clearly stated.

Data for the evaluation and inventory of municipal waste collection and composition is obtained primarily from MA48 for Vienna in the year 2011. Other data for heating values, plastic production processes, efficiencies etc. are taken from a variety of published literature, including scientific publications and governmental statistics and reports. CExD values for various fuels, electricity sources, and plastic fractions are taken from the Ecoinvent database. In the case where data for a particular process was not available generic figures for other cities in Europe from peer-reviewed literature was used.

Once the boundary of the system was defined and the individual processes were elaborated, data was gathered for conducting material balances on each individual process, this included input data for mass flows and transfer coefficients. A materials' balance helped in determining the appropriate weight factor used for calculating the energy requirements and outputs of each process.

After completing the data inventory, the STAN software was used to build a graphical model for each of the two scenarios. Material flow analysis was conducted on the goods level and additionally energy inputs and outputs were calculated for the processes. Subsequently, cumulative exergy demand (CExD) calculations were conducted for processes in both scenarios.

The accuracy of this study is directly related to the quality of the input data and the assumptions made. Data necessary for this study were process-related data and fuel-related data.

4.3.1 Scenario A - Energy recovery

In this baseline scenario, it is assumed that there is no source-separation of the plastic fraction and that all mixed solid waste (residual waste) from private households is sent to an incineration plant with energy and heat recovery capability. For the purpose of this study the incineration (waste-to-energy) plant is modelled very simply, meaning that no pre-processing or sorting of mixed solid wastes prior to incineration is required. The system boundary was set starting at the collection and transport of municipal waste from private households to when it was incinerated at a waste-to-energy plant. Figure 4.1 graphically depicts Scenario A which consists of 3 processes – Private Households, Waste Collection and Transport, and the Waste-to-energy plant – and the various input and output flows into the system.

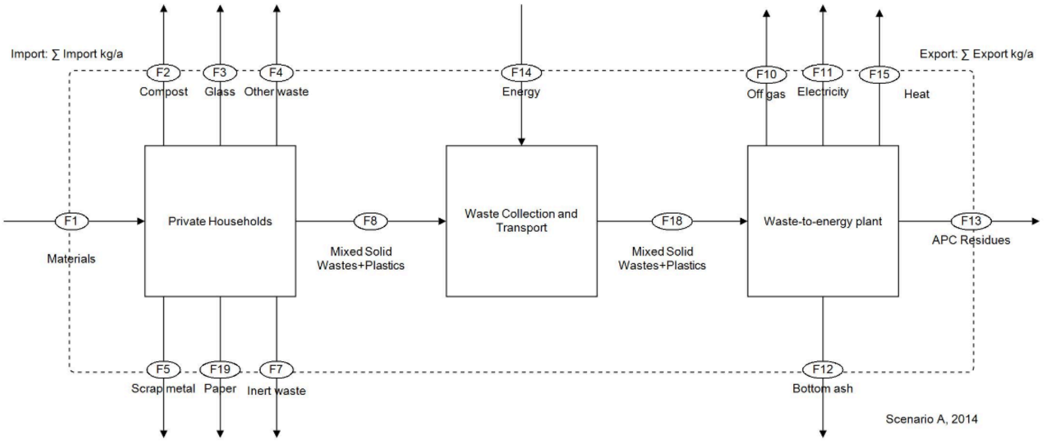

Figure 4.1: STAN system - Scenario A.

PROCESSES

Private Households:

Material imports (1) - the municipal waste generated by private households.

Material exports (7) - Compost, Glass, Other waste, Scrap metal, Paper, Inert waste, and Mixed Solid Wastes + Plastics.

Data for yearly waste collection was obtained from MA48 and is given in Table 4.1.(MA48, 2011)

Table 4.1: From collection activity, MA 48, Leistungsbericht 2011, p. 69

Collection system	Amount [Tons]
Mixed solid waste (MSW)	626,281
Plastic	8,686
Compost	115,797
Glass	27,260
Scrap metal	13,863
Paper	125,855
Inert waste	69,831
Other waste	57,211
TOTAL	1,044,784

The municipal waste collection data given in Table 4.1 was then analyzed to calculate the percentage fractions of mixed waste, plastic, compost, glass, paper, scrap metal, inert waste, and other waste streams, these are represented in Figure 4.2. Material flows of plastic and other wastes through the system are calculated based on these percentages and it is shown that an input of 1640 kg of municipal solid waste partitions into 1000 kg of mixed solid wastes + plastics. The rest of the waste streams are not of interest for this study.

Waste Collection and Transport:

Material imports (1) - Mixed Solid Wastes + Plastics.

Material exports (1) - Mixed Solid Wastes + Plastics.

Energy imports (1) - Energy for waste collection and transportation.

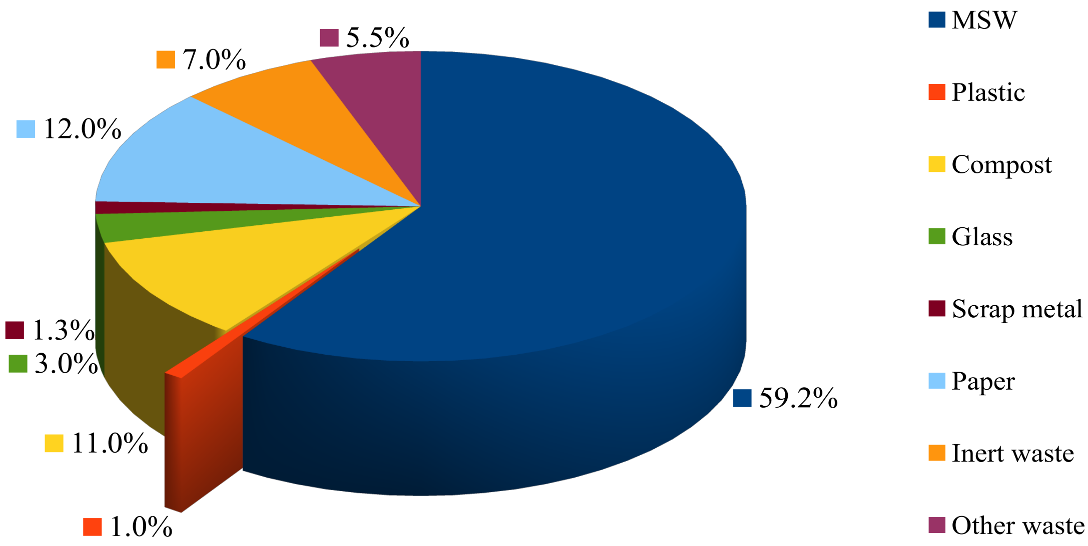

Figure 4.2: Waste composition of private households. (Source: Author, adapted to data from MA48, 2011)

The 1000 kg of waste coming in is sent directly for incineration to a waste-to-energy plant with electricity and heat generation capability.

Data on fuel requirements for the collection and transportation of waste materials from households to the waste facility, was gathered from MA48 and is shown in Table 4.2. Figures for densities and lower heating values (LHV) of fuels shown in Table 4.2 were acquired from the Tank-to-Wheels report (Edwards, Larivé, Mahieu, & Rouveirolles, 2007).

The transportation of mixed wastes and plastics takes place with other fractions of waste. A mass based allocation is used in order to account for solely the fractions

Table 4.2: Energy Input for Waste Collection and Transport

Vehicle Fuels	Amount	Density [kg/L]	LHV [MJ/kg]	Energy [MJ/ton]
Diesel	1403926 L	0.832	43.1	79.2
Gasoline	13704 L	0.747	42.3	0.7
Natural Gas	4831 kg		45.1	0.3
Biodiesel	19467 L	0.835	42.8	1
Total				**81.2**

of inputs/outputs of mixed and plastic waste streams. In reality vehicle fuel consumption (diesel, gasoline, natural gas, and biodiesel) for each separated fraction will depend on the size of the bins, frequency of collection etc.However, for our analysis it is assumed that the fuel consumed by the collection vehicles is in proportion to the weight of waste transported. By this simplification energy requirement for the Waste Collection and Transport process is calculated to be 81.2 MJ/tonne of waste transported.

Hence, the energy requirement for the import of 1000 kg of mixed solid wastes + plastics into the Waste Collection and Transport process is:

$$1000\,\mathrm{kg} * 81.2\,\mathrm{MJ}/1000\,\mathrm{kg} = \mathbf{81.2\ MJ}.$$

Waste-to-energy plant:
Material imports (1) - Mixed Solid Wastes + Plastics.
Material exports (3) - Offgas, APC residues, and Bottom ash.
Energy exports (2) - Electricity and heat.

As has been mentioned above, for the purpose of our study the waste-to-energy plant is modelled very simply with no pre-processing or sorting of waste required. The mass balances of outputs for mixed solid wastes (MSW) fed into the incinerator is taken to be an average but in reality will vary depending on the composition of the MSW and the specific waste-to-energy facility. Figure 4.3 shows the average mass balance for incineration of MSW used in this study. The energy produced by the incineration of MSW at the waste-to-energy plant is used to produce electricity and heat and is assumed to displace electricity and heat generation from primary fuel sources.

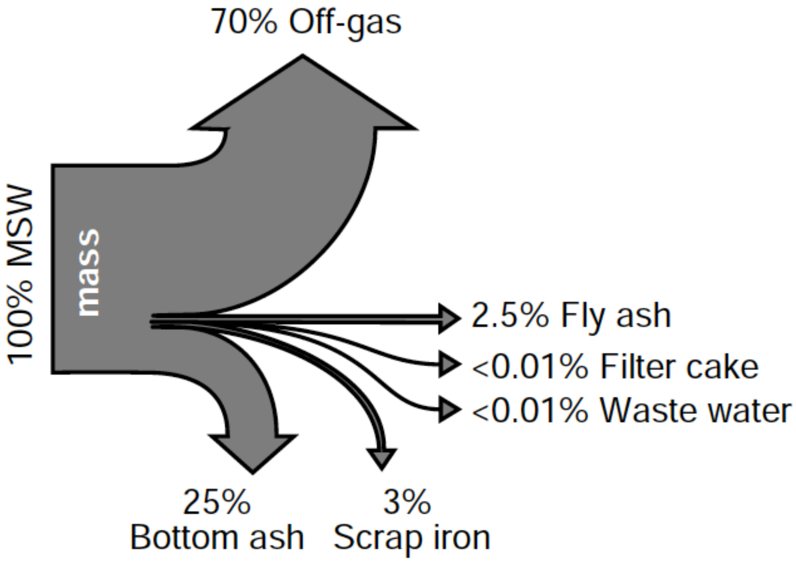

Figure 4.3: Mass balance for MSW incineration. (Source: Brunner & Rechberger, 2004)

Using the transfer coefficients from Figure 4.3, it is calculated that 250 kg bottom ash, 50 kg air pollution control residues, and 700 kg off-gas is produced. It should be noted, however, that the transfer coefficients used are representative of an average plant, whereas in reality they would differ from plant to plant.

The energy produced by incinerating 1000 kg of mixed solid waste + plastics is calculated as follows. As no source-separation of the plastic waste stream is taking place in this scenario, a fraction of the waste sent for incineration is mixed solid waste and the rest is mixed plastics waste. This partitioning is of interest for energy recovery as the different waste streams have very different heating values which affect energy generation.

From Figure 4.2 the percentages of mixed solid wastes and plastic wastes in municipal waste are known to be 60% and 1% respectively. Based on these values it is calculated that in a waste stream of 1000 kg with no source-separation of plastics, 984 kg is mixed solid waste and 16 kg is plastic waste.

Using calorific value of mixed waste to be 10 MJ/kg (Spliethoff, 2010), and of mixed plastic waste to be 40 MJ/kg (Astrup et al., 2009), energy generated at the incineration plant is calculated as follows. Let E_{tot} be the total energy generation, E_{MSW} the energy generation from mixed waste, and E_{Plastics} be the energy generation from mixed plastics. Then:

$$\begin{aligned} E_{\mathrm{tot}} &= E_{\mathrm{MSW}} + E_{\mathrm{Plastics}} \\ &= (984\,\mathrm{kg} * 10\,\mathrm{MJ/kg}) + (16\,\mathrm{kg} * 40\,\mathrm{MJ/kg}) \\ &= 10240\,\mathrm{MJ} \end{aligned}$$

Waste incineration plants with heat and electricity recovery capability (cogeneration) can achieve an optimum energy efficiency of upto 82% in some cases, with thermal energy or heat utilization of upto approximately 70%, and electricity generation efficiency of upto approximately 12% (Austrian Federal Ministry of Agriculture & Management, 2010). Based on the efficiency of the waste-to-energy plant, the heat and electricity generated can be calculated as follows:

$$\begin{aligned} \text{Heat generated} &= 70\% * 10240\,\mathrm{MJ} = 7170\,\mathrm{MJ}. \\ \text{Electricity generated} &= 12\% * 10240 = 1230\,\mathrm{MJ} \end{aligned}$$

The rest of the energy is lost. Hence, the energy outputs of the waste-to-energy process are, **7170 MJ** of electricity and **1230 MJ** of heat.

4.3.2 Scenario B - Material recovery

In this scenario it is assumed that the mixed plastics waste fraction from private households is source separated, collected, and processed through a materials recycling facility (MRF) which models a situation where the major polymer types (PE, PP, PS, PET, and PVC) in the waste stream are sorted/separated and mechanically recycled. It should be noted that the MRF processing the plastic waste and producing the granulates may in some cases be physically co-located with the reprocessing facility using the plastic granulates making it difficult to distinguish between the processes that are related to the MRF and those to the reprocessing facility. (Astrup et al., 2009) For the purpose of clarity, both the facilities are chosen to be separate in this study.

Plastic recyclates leave the MRF facility ready to be made into 'new' products. Non-recycled fractions are sent back to the waste-to-energy plant for incineration where they can substitute primary fuels. It should be noted that the calorific value of the mixed plastic waste from the MRF is much higher than normal residual waste feedstock accepted for incineration.

Though the sorting and shredding and subsequently granulation takes place at the same material recycling facility (MRF), for the sake of clarity they have been defined as separate processes in this MFA. Based on literature data (Astrup et al., 2009), electricity requirement for handling and mechanical treatment, corresponding to sorting and shredding, is around 25 kWh/tonne of plastic waste; electricity requirement for final granulation to obtain a high-quality product is around 600 kWh/tonne of plastic waste. Important assumption: markets exist for the recycled plastics that are produced - PP, PET, PE, PVC and mixed PP/PE blends.

In the case of recovered/recycled products the analysis also includes the avoided production of virgin material and energy from primary sources. This follows a system expansion methodology commonly applied in such studies, which, in this case, is used to take into account the benefits of the recovery process.

Figure 4.4 graphically depicts Scenario B which consists of 5 processes – Private Households, Waste Collection and Transport, Waste-to-Energy Plant, Material Recycling Facility (MRF), and the Granulation Facility – and the various input and output flows into the system.

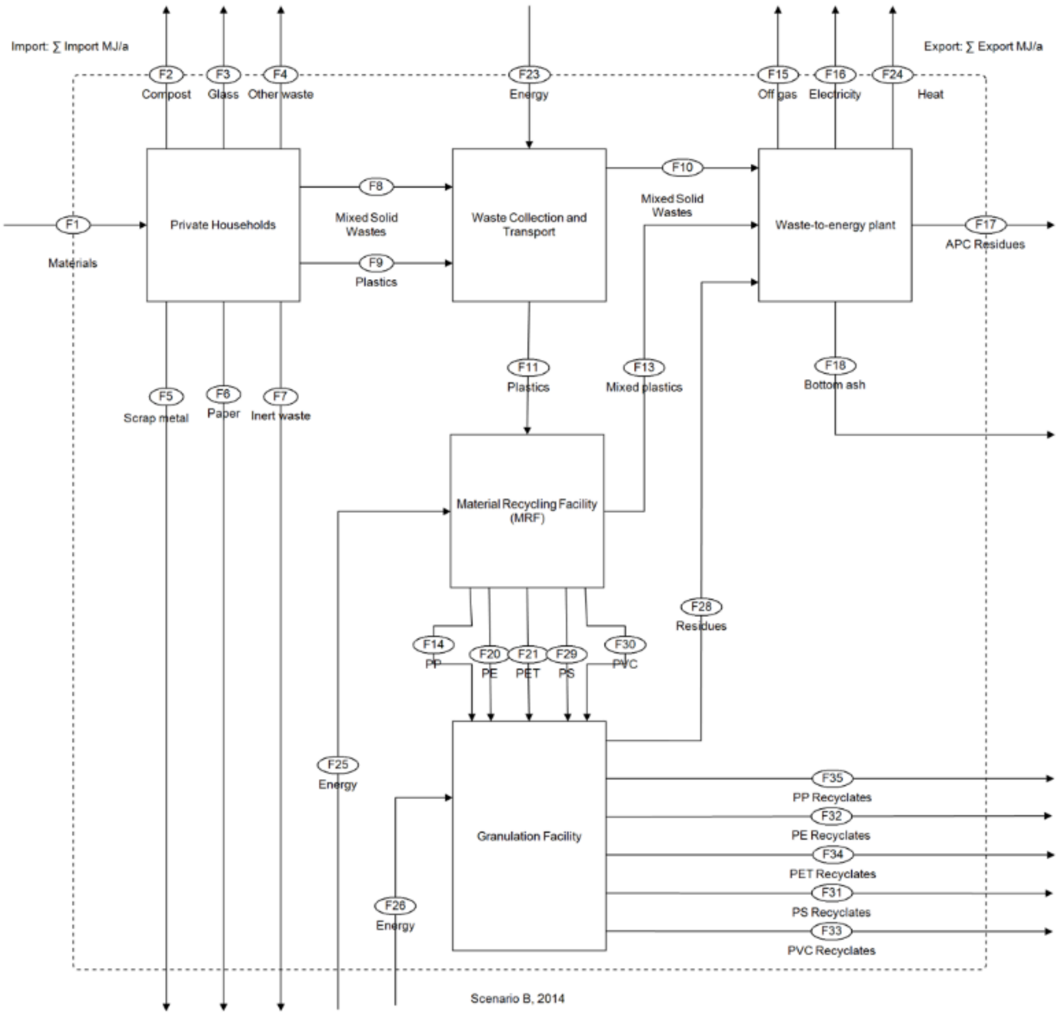

Figure 4.4: STAN system - Scenario B.

Processes

Private Households:

Material imports (1) - the municipal waste generated by private households.

Material exports (8) - Compost, Glass, Other waste, Scrap metal, Paper, Inert waste, Mixed Solid Wastes, and Plastics.

Based on data from Table 4.1 and Figure 4.2, 1640 kg of municipal solid waste partitions into 984 kg of mixed solid wastes and 16 kg of source-separated plastic wastes. The rest of the waste streams are not of interest for this study.

Waste Collection and Transport:
Material imports (2) - Mixed Solid Wastes, and Plastics.
Material exports (2) - Mixed Solid Wastes, and Plastics.
Energy imports (1) - Energy for waste collection and transportation.

Same as in Scenario A, data on fuel requirements for the collection and transportation of waste materials from households to the waste facility, was gathered from MA48 and is shown in Table 4.2. Figures for densities and lower heating values (LHV) of fuels shown in Table 4.2 were acquired from the Tank-to-Wheels report (Edwards et al., 2007).

The transportation of mixed wastes and plastics takes place with other fractions of waste. A mass based allocation is used in order to account for solely the fractions of inputs/outputs of mixed and plastic waste streams. In reality vehicle fuel consumption (diesel, gasoline, natural gas, and biodiesel) for each separated fraction will depend on the size of the bins, frequency of collection etc., however, for our analysis it is assumed that the fuel consumed by the collection vehicles is in proportion to the weight of waste transported. By this simplification energy requirement for the Waste Collection and Transport process is calculated to be 81.2 MJ/tonne of waste transported.

Hence, the energy requirement for the import of 984 kg of mixed solid wastes + 16 kg of plastics into the Waste Collection and Transport process is:

$$(984\,\mathrm{kg} + 16\,\mathrm{kg}) * 81.2\,\mathrm{MJ}/1000\,\mathrm{kg} = \mathbf{81.2\ MJ}.$$

The 984 kg of mixed waste coming in is sent directly for incineration to a waste-to-energy plant with electricity and heat generation capability, while the 16 kg of source-separated plastic waste is sent to a material recycling facility (MRF).

Waste-to-Energy Plant:
Material imports (2) - Mixed Solid Wastes, and Mixed Plastics.
Material exports (3) - Offgas, APC residues, and Bottom ash.
Energy exports (2) - Electricity and heat.

As has been mentioned above, for the purpose of this study the waste-to-energy plant is modelled very simply with no pre-processing or sorting of waste required. Using the transfer coefficients from Figure 4.3, it is calculated that 250 kg bottom ash, 50 kg air pollution control residues, and 690 kg off-gas is produced. It should be noted, however, that the transfer coefficients used are representative of an average plant, whereas in reality they would differ from plant to plant.

The energy produced by incineration (of 984 kg mixed solid waste + residues from MRF + residues from Granulation facility) is calculated as follows. In this scenario mixed plastic wastes are source separated and sent to a material recycling facility for recovery and recycling while only the mixed waste fraction is sent for incineration. As can be seen from the calorific values of the different fractions, it is evident that removing the high calorific plastics fraction will decrease the amount of energy produced. The change in composition compared to scenario A leads to a lower heating value of the incoming waste to the waste-to-energy plant.

Using calorific value of mixed waste to be 10 MJ/kg (Spliethoff, 2010), and that of mixed plastics to be 40 MJ/kg (Astrup et al., 2009) energy generated at the waste-to-energy plant is calculated as follows. Let E_{tot} be the total energy generation, E_{MSW} the energy generation from mixed waste, E_{MRF} be the energy generation from mixed plastics sent by the material recycling facility (MRF), and E_{Res} be the energy generation from residues sent by the granulation facility. Then:

$$\begin{aligned} E_{\text{tot}} &= E_{\text{MSW}} + E_{\text{MRF}} + E_{\text{Res}} \\ &= (984\,\text{kg} * 10\,\text{MJ/kg}) + (1.8\,\text{kg} * 40\,\text{MJ/kg}) + (5.84\,\text{kg} * 40\,\text{MJ/kg}) \\ &= 10104\,\text{MJ} \end{aligned}$$

Based on the efficiency of the waste-to-energy plant, the heat and electricity generated can be calculated as follows:

$$\text{Heat generated} = 70\% * 10104\,\text{MJ} = 7070\,\text{MJ}.$$

$$\text{Electricity generated} = 12\% * 10104 = 1210\,\text{MJ}$$

The rest of the energy is lost. Hence, the energy outputs of the waste-to-energy process are, **7070 MJ** of electricity and **1210 MJ** of heat.

Material Recycling Facility (MRF):
Material imports (1) - Plastics.
Material exports (6) - PP, PE, PET, PS, PVC, and Mixed Plastics.
Energy imports (1) - Energy for material sorting and shredding.

As stated previously, the MRF depicted in this study is the type that produces granules (recyclates) for production of new products (material recovery) as opposed to a MRF that produces fuel pellets for energy recovery. Using data acquired from (WRAP, 2008) a typical mix of materials leaving the MRF is given in Table 4.3 where column 2 depicts a default distribution of plastics and column 3 depicts a high polyolefin alternative.

Since this study uses a calorific value of 40 MJ/kg for mixed plastic waste the high polyolefin distribution is chosen for the MRF. It is calculated from these percentages that 16.8 kg of incoming source-separated plastic waste into the MRF is partitioned

Table 4.3: Composition of materials leaving the MRF (adapted to data from WRAP LCA (2008))

Material type	Default Distribution, %	High Polyolefin Alternative, %
Polypropylene (PP)	40	50
Polyethylene (PE)	15	26
Polyethylene terephthalate (PET)	17	5
Polystyrene (PS)	6	3
Polyvinyl chloride (PVC)	11	5
Others	11	11

into:

$$\text{PP} = 16.4\,\text{kg} * 50\,\% = 8.2\,\text{kg}$$

$$\text{PE} = 16.4\,\text{kg} * 26\,\% = 4.26\,\text{kg}$$

$$\text{PET} = 16.4\,\text{kg} * 5\,\% = 0.82\,\text{kg}$$

$$\text{PS} = 16.4\,\text{kg} * 3\,\% = 0.492\,\text{kg}$$

$$\text{PVC} = 16.4\,\text{kg} * 5\,\% = 0.82\,\text{kg}$$

$$\text{Others} = 16.4\,\text{kg} * 11\,\% = 1.8\,\text{kg}$$

The PP, PE, PET, PS, and PVC streams are then sent on to the granulation facility while ‘others’ is sent for incineration to the waste-to-energy plant.

Column 1 in Table 4.4 gives lower heating values based on data from (Themelis, Castaldi, Bhatti, & Arsova, 2011), and column 2 gives the CExD values of the various plastic fractions based on data from (J. P. Dewulf & Van Langenhove, 2004).

Table 4.4: Polymers - LHV and CExD values

Polymer Type	LHV [MJ/kg]	CExD [MJ-eq]
Polyethylene (PE)	44	86.00
Polypropylene (PP)	44	85.20
Polyethylene terephthalate (PET)	24	86.80
Polystyrene (PS)	41	91.90
Polyvinyl chloride (PVC)	19	67.00

Using data from column 1 of Table 4.4 on the lower heating value of various resin fractions, the calorific value (CV) of mixed plastic waste can be calculated by:

$$\mathrm{CV} = \sum_i \mathrm{P}_{Resin,i} * \mathrm{LHV}_{Resin,i}$$

where

CV = calorific value of mixed plastics waste (MJ/kg)
$\mathrm{P}_{Resin,i}$ = percentage of resin fraction i (%)
$\mathrm{LHV}_{Resin,i}$ = lower heating value of fraction i (MJ-eq/kg)

Using this formula the calorific value of mixed plastics waste is calculated to be 33 MJ/kg. However, the composition of plastic materials entering the mixed plastics waste stream are not consistent and can vary widely. In the literature the calorific value of mixed plastic waste – with large shares of PP and PE, and moderate shares of PET, PVC and PS – is taken to be 30-40 MJ/kg. (Astrup et al., 2009) Calculations in this study are done based on lower heating value of 40 MJ/kg of mixed plastic waste.

Electricity consumption for simple sorting and shredding processes is in the range of 16-32 kWh/tonne of plastic waste (Astrup et al., 2009; WRAP, 2008). An average value of 24 kWh/tonne of plastic waste is used for the calculations in this analysis. Using the conversion $1\,\mathrm{KWh} = 3.6\,\mathrm{MJ}$ this is converted to 0.086 MJ/kg.

For an amount 16.4 kg of source separated mixed plastic waste coming into the MRF, the electricity requirement for the facility is calculated to be:

$$16.4\,\mathrm{kg} * 0.086\,\mathrm{MJ/kg} = 1.41\,\mathrm{MJ}$$

Hence, the energy input for MRF is **1.41 MJ**.

Granulation Facility:

Material imports (5) - PP, PE, PET, PS, and PVC

Material exports (5) - PP, PE, PET, PS, and PVC Recyclates.

Energy imports (1) - Electricity for granulation processes.

From the literature surveyed it is known that plastic material recycling can reach efficiencies of 60% while the remaining 40% of the material is sent for incineration (J. P. Dewulf & Van Langenhove, 2002, 2004; WRAP, 2008). Based on the amount of material coming into the facility which is 14.6 kg of plastics (PP, PE, PET, PS, and PVC), a total of 10.56 kg of recyclate material is produced while 5.84 kg is sent back for incineration to the waste-to-energy plant. An important assumption is that markets exist for the produced recycled plastics – PP, PET, PE, PVC and mixed PP/PE blends – and the 10.56 kg of recycled plastic produced at the granulation facility can substitute production of plastics from virgin sources.

Electricity consumption for the granulation processes is in the range of 240-300 kWh/tonne of plastic waste (Astrup et al., 2009; WRAP, 2008). An average value of 270 kWh/tonne of plastic waste is used for the calculations in this analysis. Using the conversion $1\,\mathrm{KWh} = 3.6\,\mathrm{MJ}$ this is converted to 0.97 MJ/kg.

For an amount of source separated mixed plastic waste coming into the MRF, the electricity requirement is calculated to be:

$$14.6\,\mathrm{kg} * 0.97\,\mathrm{MJ/kg} = 14.2\,\mathrm{MJ}$$

Hence, the energy input for the granulation facility is **14.2 MJ**.

Chapter 5

Results

This chapter assesses and describes the results of the material flow analysis and cumulative exergy demand calculations for scenarios A and B.

5.1 Material & Energy Flows

5.1.1 Scenario A

Figure 5.1 illustrates the material flows and mass balances of Scenario A at the goods level.

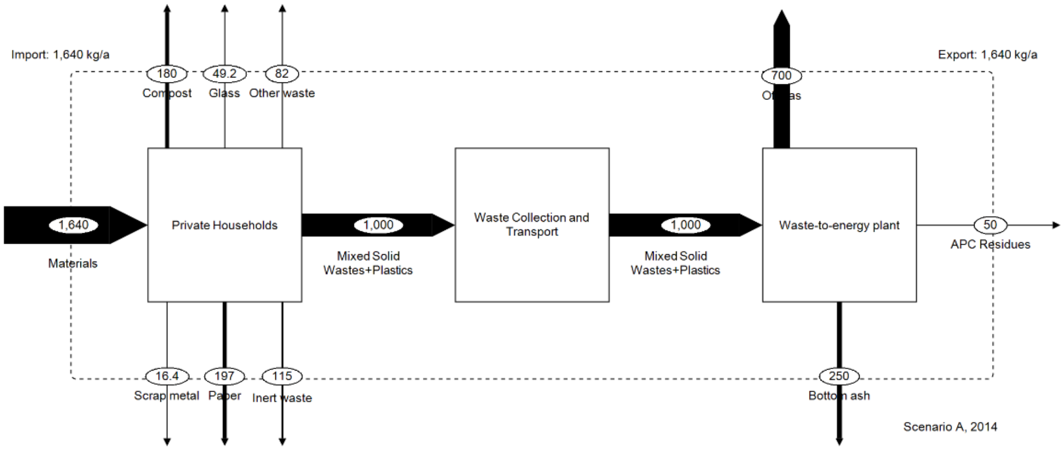

Figure 5.1: STAN system - Scenario A, Goods layer.

1000 kg of mixed solid waste + plastic is collected and transported straight for incineration to a waste-to-energy plant for energy recovery.

Figure 5.2 illustrates the energy input into the waste collection and transportation process and the energy (electricity and heat) outputs from the waste-to-energy process. Note that this study ignored the energy content of the material streams and quantified only those energetic imports and exports that were relevant to the study.

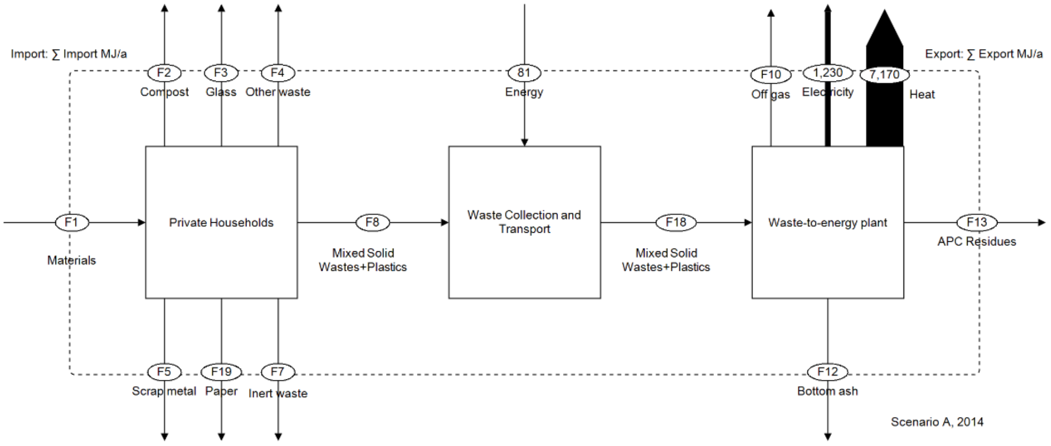

Figure 5.2: STAN system - Scenario A, Energy layer.

5.1.2 Scenario B

Figure 5.3 illustrates the material flows and mass balances of Scenario B at the goods level. 980 kg of input mixed solid wastes are collected and transported to a waste-to-energy plant for energy recovery while 16 kg of source-separated plastic wastes are sent for material recovery to a material recycling facility (MRF) and further to a granulation facility. The mass of plastic streams are depicted on the diagram and it can be seen that 4.92 kg of PP, 2.56 kg of PE, 0.492 kg of PET, 0.295 kg of PS, and 0.492 kg of PVC recyclates are produced after recycling the plastic waste stream.

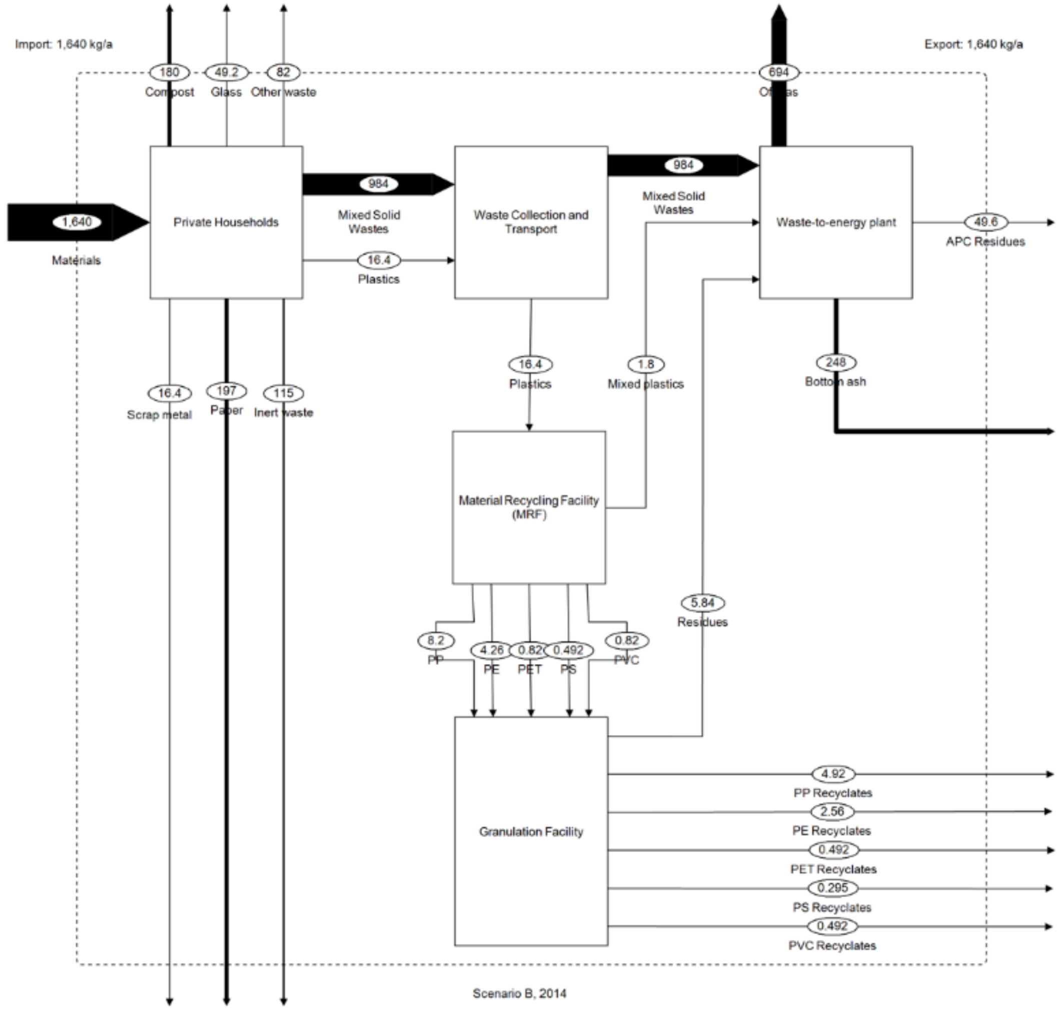

Figure 5.3: STAN system - Scenario B, Goods layer.

Figure 5.4 illustrates the energy input into the waste collection and transportation process, the energy (electricity and heat) outputs from the waste-to-energy process, energy input to the MRF process, and energy input to the granulation process.

As mentioned above, note that this study ignored the energy content of the material streams and quantified only those energetic imports and exports that were relevant to the study.

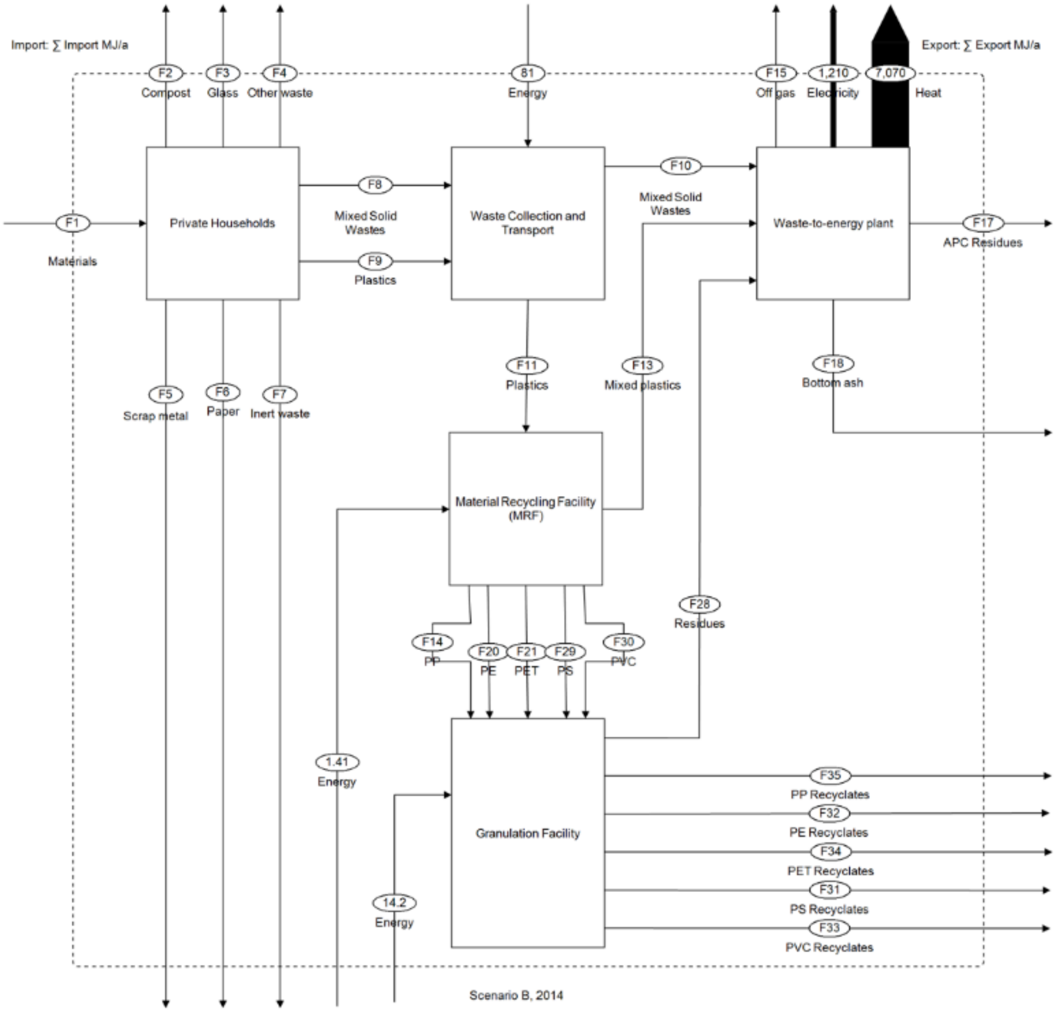

Figure 5.4: STAN system - Scenario B, Energy layer.

5.2 CExD Calculations

A key challenge lay in ensuring that Scenario A and Scenario B were compared on a fair basis. Since the products and energetic inputs of the two cases were different from each other, the “system expansion” technique considering an “equal basket of benefits/outputs” was used to make them comparable (Vandermeersch, Alvarenga, Ragaert, & Dewulf, 2014; Shen, Worrell, & Patel, 2010). To account for the benefits and indirect savings of resources and energy which are achieved by the recycling/recovery process and the subsequent substitution of “virgin” materials by recyclates produced, the equal basket of products/outputs is an appropriate method for this assessment. The basket of equal outputs as applied to the two analyzed scenarios is pictorially illustrated in Figure 5.5.

As depicted in the figure, the outputs of Scenario A that are relevant for comparison are electricity and heat. Following from the equal basket of outputs approach, in order to match the products of Scenario A to those of Scenario B, cumulative exergy demands (CExD) for traditional production of virgin plastics (PE - 2.96 kg, PET - 0.49 kg, PP - 4.92 kg, PS - 0.29 kg, and PVC - 0.49 kg) are also considered as inputs into the system. These flows of virgin plastics are depicted by dotted lines entering and exiting the system.
Similarly, in the case of Scenario B where recyclates were produced from plastics recycling, the assessment also includes the avoided production of plastics from primary sources. This means that in Scenario B in addition to the the energy inputs into Waste Collection and Transport process, Material Recycling Facility (MRF) process, and Granulation Facility process, the amount of extra energy input from traditional sources to the Waste-to-Energy plant required to compensate for the less electricity and heat produced due to change in the incinerated waste stream, is also taken into account. These energy input flows into the system are depicted by dotted lines in Figure 5.5.

The benefits accrued from incineration are based on the avoided requirement to obtain electricity from other sources. The benefits accrued from recycling are based on the avoided production of plastic from virgin resources/materials.

The input of energy from traditional sources into the system processes is assumed to be coming from the Austrian electricity mix, shown in Table 5.1. Column 1 lists the fraction of types of sources in the electricity-mix and column 2 lists their CExD values. Data for column 1 was obtained from (E-Control, 2013; Hydro, 2011) and for column 2 (CExD values for each type) were looked up in the Ecoinvent database.

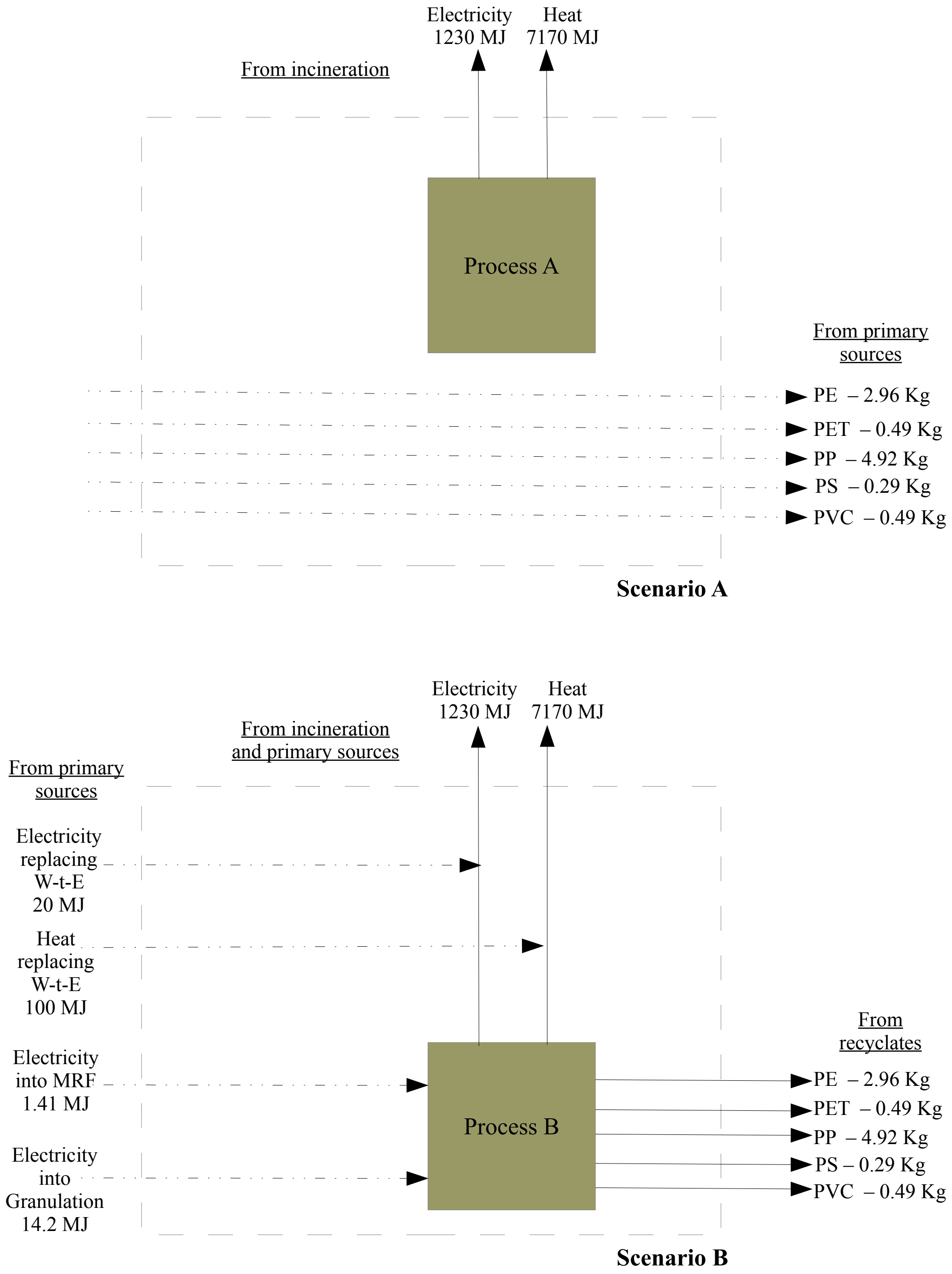

Figure 5.5: System Expansion (basket of equal outputs) - Scenario A and Scenario B. The dotted lines depict energy and material input from primary sources.

Austria's electricity generation is dominated by hydro-power with approximately 65% of the total supply, where base load is covered by run-of-river plants, peak load is covered by hydro-storage plants in the alpine region, and extra energy is stored by using pumped storage power plants.

Table 5.1: Austria Electricity mix. Source: E-Control, Eurelectric for % distribution, Ecoinvent database for CExD values.

Type	Percentage [%]	CExD value [MJ-eq/Kg]
Hydropower run-of-river	43	0.058
Hydropower alpine storage	19	0.076
Hydropower pumped storage	3	9.61
Wind energy	4.29	0.49
Biomass	3.78	0.77
Natural Gas	13.22	14.20
Coal	4.66	14.63
Other	8.81	Calculated: 3.19
Weigthed value		Calculated: 3.21

Based on weighted fractions given in Table 5.1 the CExD value for the electricity mix is calculated by:

$$\text{CExD}_{E-mix} = \sum_i \text{CExD}_{Type,i} * P_{Type,i}$$

where

CExD_{E-mix} = CExD of Austrian electricity mix (MJ-eq)

$\text{CExD}_{Type,i}$ = CExD of type i (MJ-eq)

$P_{Type,i}$ = percentage fraction of type i (%)

Using the above formula the CExD value of the Austrian electricity mix is calculated to be **3.21 MJ-eq**.

5.2.1 Scenario A

To calculate the cumulative exergy demand for Scenario A, the various inputs into the system need to be considered. To make the basket of outputs of Scenario A equal that of Scenario B, the inputs into the system are energy input for waste collection and transportation and the various fractions of plastic (PE, PET, PP, PS, PVC) from primary sources. The CExD values and input quantities are given in Table 5.2. CExD data for incoming electricity is calculated above and taken to be 3.21 MJ-eq, and CExD values for the plastic fractions from primary sources are obtained from (J. P. Dewulf & Van Langenhove, 2004).

Table 5.2: Scenario A - Cumulative exergy demand (CExD) calculations. Where 'α' = substitution factor of recyclates into primary plastics.

Type	CExD	Input	CExD Total [MJ-eq]
Electricity into Waste Collection and Transport	3.21 MJ-eq/KWh	22.5 KWh	72.22
PE Virgin	86 MJ-eq/kg	2.56 kg * α	220.16 α
PET Virgin	86.8 MJ-eq/kg	0.49 kg * α	42.53 α
PP Virgin	85.2 MJ-eq/kg	4.92 kg * α	419.18 α
PS Virgin	91.9 MJ-eq/kg	0.29 kg * α	26.65 α
PVC Virgin	67 [MJ-eq/kg]	0.49 kg * α	32.83 α
Total			**72.22 + 742.17** α [MJ-eq]

The input or quantity of primary/virgin plastic that is needed to equalize the outputs in both scenarios depends on the quality of the recycled plastics from the Material Recovery Facility and Granulation Facility processes. The basis for substitution of plastics is that the recyclates perform the same function as primary plastics. The ability of recycled plastic to substitute for virgin polymers generally depends on the purity of the recovered plastic feed and the property requirements of the plastic product to be made, and how much primary plastic can be substituted for by recycled plastic is defined by the *'substitution factor'* α. The substitution factor α can be said to be the quantity of virgin or primary material (in kg) that can be substituted by 1 kg of recyclate in the end product in order to achieve **equivalent** performance. For example, if a 500 gm plastic product made from virgin plastic can only be substituted by 1 kg of recyclate, then $\alpha = 0.5$ (Jenseit, Stahl, Wollny, & Wittlinger, 2003)

Depending on the properties and quality of the recyclates and additionally on the markets existing for the type of resin, each plastic fraction will have a different substitution factor for instance, PP = α_1, PE = α_2, PET = α_3, PS = α_4, PVC = α_5.

For the sake of simplicity, in this study it is assumed that:

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = \alpha$$

The value of α can lie anywhere between 0 and 1. An α of 0 means that recyclates do not substitute for any virgin plastics and an α of 1 means that recycled plastic is of very high quality and will directly substitute for virgin plastic on a 1:1 basis.

The substitution factor α which is dependent on the quality of the recyclates is very important in this analysis as the benefits from either Scenario A or Scenario B depend on the products or materials that can be substituted by recyclates.

Taking the substitution factor of the recyclates produced to be α, as shown in Table 5.2 the cumulative exergy demand (CExD) for Scenario A is calculated to be: **72.22 + 742.17 αMJ-eq**.

5.2.2 Scenario B

To calculate the cumulative exergy demand for Scenario B, the various inputs into the system need to be considered. To make the basket of outputs for Scenario B equal that of Scenario A, the inputs into the system are electricity for the Waste Collection and Transport process, for the Material Recycling Facility (MRF) process, and for the Granulation Facility process, as well as, input into the Waste-to-Energy plant to compensate the less heat and electricity being generated in Scenario B. The CExD values and input quantities are given in Table 5.3. CExD data for incoming electricity is calculated above and taken to be 3.21 MJ-eq.

Table 5.3: Scenario B - Cumulative exergy demand (CExD) calculations

Type	CExD [MJ-eq/KWh]	Input [KWh]	CExD Total [MJ-eq]
Electricity into Waste Collection and Transport	3.21	22.5	72.22
Electricity into MRF	3.21	0.4	1.28
Electricity into Granulation	3.21	3.94	12.64
Electricity replacement W-to-E	3.21	5.55	17.81
Heat replacement W-to-E	3.21	27.7	88.91
Total			**192.88** [MJ-eq]

As shown in Table 5.3 the cumulative exergy demand (CExD) for Scenario B is calculated to be: **192.88 MJ-eq**.

5.3 Discussion

The cumulative exergy demand (CExD) for Scenario A as shown in Table 5.2 is **72.22 MJ-eq + 742.17** α **MJ-eq**, and the CExD for Scenario B is **192.88 MJ-eq** as shown in Table 5.3. These are graphically illustrated in Figure 5.6.

The value of α at which both scenarios will be equally beneficial is given by:

$$\begin{aligned} 72.22 + 742.17 * \alpha \,\text{MJ-eq} &= 192.88 \,\text{MJ-eq} \\ \alpha &= (192.88 - 72.22)/742.17 \\ &= \mathbf{0.16} \end{aligned}$$

A substitution factor $\alpha = 0.16$ means that 1 unit of recycled plastic replaces or substitutes 0.16 units of virgin plastics. For values of $\alpha > 0.16$ Scenario B is exergetically more beneficial and material recycling of the plastic waste stream is favored. For values of $\alpha < 0.16$ Scenario A is exergetically more beneficial and energy recovery by incineration of plastic wastes is favored. At $\alpha = 0.16$ both scenarios A and B are equally beneficial. Figure 5.6 graphs the change of CExD values with the change in the substitution factor.

In a free market, the prices of primary plastics and of recyclates can be a good indicator for the quality of the product. That is, it can be assumed that the higher

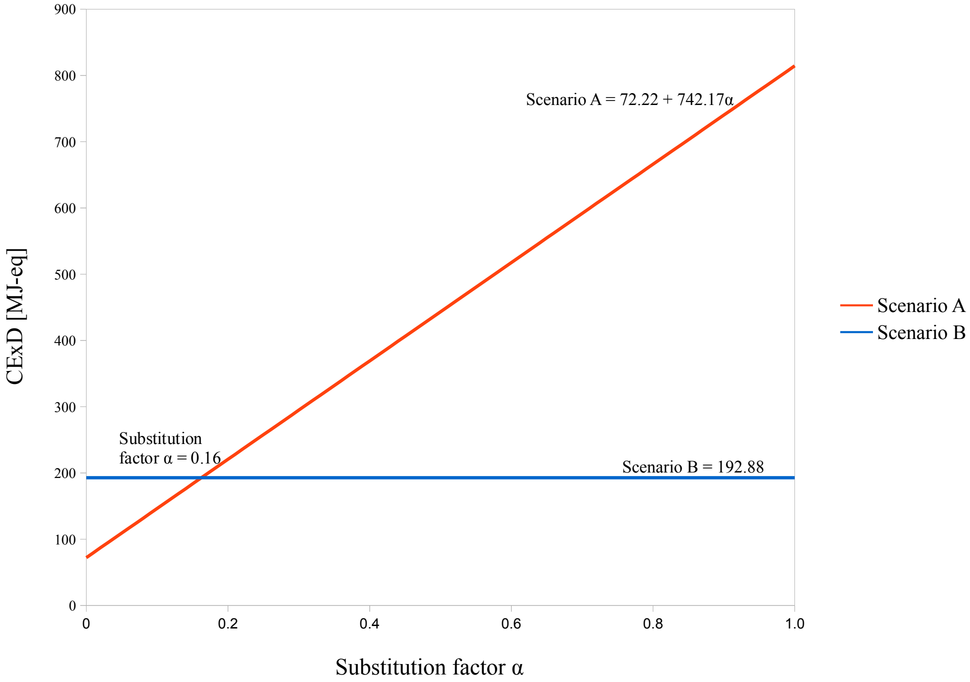

Figure 5.6: Scenario A vs Scenario B - substitution factor α

the price better the quality. Depending on the market conditions and the price of a barrel of crude oil the prices of primary plastics and recylates fluctuate and change constantly over time. For the purpose of illustrating the use of a cost based substitution factor, March 2014 data from WRAP for the prices of virgin and recycled plastics are taken and used for the calculations. Virgin PET plastic prices averaged £1,040 per tonne, and recovered clear PET bottle prices averaged £248 per tonne (WRAP, 2014). Using these values the substitution factor can be calculated to be $248/1040 = 0.23$. Since $0.23 > 0.16$, Scenario B or material recycling of the plastic waste stream is exergetically favored in this particular case. In essence, the greater the substitution factor α, meaning that 1 unit of recyclates substitutes a greater quantity of virgin material, the greater the advantage of plastic material recycling. This is an example of how the substitution factor might be used in policy decisions.

Chapter 6

Conclusion and further considerations

Beginning in the 1970s there has been a long tradition of analysis of industrial metabolism using exergy and the second law of thermodynamics (R. Ayres & Ayres, 2002; J. Dewulf et al., 2008a). However, there do not appear to be many studies applying these concepts, and in particular the notion of cumulative exergy demand, to the metabolism of plastics at a systems level. Such studies have been initiated in (J. P. Dewulf & Van Langenhove, 2004, 2002) and this thesis takes another step in this direction.

Two competing options for the management of plastic wastes generated by private households were analyzed. Scenario A represented the energy recovery option in which plastics were part of the mixed waste stream and were sent for incineration to a waste-to-energy plant. Scenario B, on the other hand represented the material recovery option in which plastics were source separated and sent to a material recycling facility (MRF) and further to a granulation facility to be recycled for use as substitutes for plastics produced from primary sources. Material flow analysis and cumulative exergy demand calculations were used to analyze the material and energy requirements of the two scenarios. System expansion using the equal basket of benefits approach was used to make the two cases comparable.

It is important when comparing the environmental impacts of the two scenarios to note that neither of the options were better than the other in absolute terms. The resource depletion brought about by the scenarios is dependent upon the quality of the recyclates produced and how much plastic from primary production they replaced as indicated by the substitution factor α. It should be noted that the α is closely related to numerous factors including the price of crude oil, quality of plastic recyclates, and the recycling technology.

For values of $\alpha < 0.16$ Scenario A was the better option exergetically, while for $\alpha > 0.16$ scenario B was the favored option. At $\alpha = 0.16$ both options were equally favored. Scenario A seemingly requires more exergy mainly due to the high CExD inputs of plastics from primary production.

This study relates only to waste management options of source separated mixed plastics. An assessment of the potential effect of managing mixed plastics as part of a mixed municipal waste stream was beyond the scope of the system. It would be interesting to study the plastic waste stream within the mixed wastes which accounts for roughly 14% of the total wastes and is much harder to sort and clean due to contamination from organics and other streams in the mixed waste. Additionally, data uncertainties were not taken into account and no consideration has been taken of future changes in the electricity mix, technology improvements, or changes in the waste fractions. A future refinement of this study, that includes these aspects, as well as a sensitivity analysis, would be a valuable addition.

CExD is a robust and powerful indicator with which to study resource and waste management as it takes into account *all* the *useful* energy that was consumed in the creation of a product. Therefore the concept of CExD is a valuable one in assessing degradation of natural resources and systems. It helps account for the consumption of natural resources using a thermodynamic perspective that takes into account the second law and entropy production.

In summary, the results indicated that any value of the substitution factor, α, greater than 0.16 favored the recycling of the plastic waste. The results of the analysis in this thesis can serve as a guide for planners and policy makers with which to make an informed decision for the exergetically optimal management of the mixed plastic waste stream in municipal waste.

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