A Comparative Life-Cycle Analysis of Proton Exchange Membrane Fuel Cells and Internal Combustion Engines

by

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We accept this thesis as conforming to the required standard

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Abstract

The 1989 California legislation requiring that 2% of total vehicle sales in 1998 be zero emission vehicles is the single most important environmental factor that accelerated fuel cell research and development for transportation worldwide. More importantly, the California legislation is increasingly becoming the regulatory beacon for combatting local air quality problems in many jurisdictions[1]. The combination of fuel cells and hydrogen have been advanced as an environmentally 'clean' remedy to transport related air pollution because they produce no in-use emissions other than water and heat. Notable among many reports is the assumption that the life-cycle (manufacture to disposal) of fuel cells will also be inherently 'clean.' This thesis critically examines the cleanliness assumption by developing comparative inventories of life-cycle effects associated with the materials in proton exchange membrane fuel cells (PEMFC) and internal combustion engines (ICE).

If the allocation of resource use to platinum is low, the PEMFC life-cycle will require proportionate material inputs, but produce less pollution outputs than the ICE. PEMFC materials will also demand less energy inputs producing fewer greenhouse gas emissions than will the life-cycle of materials in the ICE. Additionally, the PEMFC vehicle life-cycle will likely emit fewer greenhouse gases than will the ICE vehicle. However, if the allocation of resource use to platinum is high, the balance of life-cycle resource use and emissions could shift to favour the ICE over the PEMFC vehicle.

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Table Of Contents

List of Tables

List of Figures

Nomenclature

AFV	Alternate Fuel Vehicle
Al_2O_3	Alumina
BAM	Ballard Advanced Materials
BC	British Columbia
BTU	British Thermal Units
CaF_2	Calcium Fluoride (Fluorspar)
$CaSO_4$	Calcium Sulphate
CH_4	Methane
$CHCl_3$	Chloroform
$CHClF_2$	Chlorodifluoromethane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DTI	Department of Trade and Industry (UK)
EEV	Emit Elsewhere Vehicle
EIA	Energy Information Administration
EPA	Environmental Protection Agency
FC	Fuel Cell
g	gram
GHG	Greenhouse Gas
h	hour
H_2SO_4	Sulphuric Acid
HCl	Hydrogen Chloride
HF	Hydrogen Fluoride
ICE	Internal Combustion Engine
ICEV	Internal Combustion Engine Vehicle
IPCC	Intergovernmental Panel on Climate Change
kg	kilogram
km	kilometre
kW	kilowatt
kWh	kilowatt hour

LCA	Life-Cycle Analysis
LCI	Life-Cycle Inventory
LEV	Low Emission Vehicle
M	Million
MEA	Membrane Electrode Assembly
MIPS	Material Intensity per unit of Service
Na_3AlF_6	Cryolite
NG	Natural Gas
NMVOC	Non Methane Volatile Organic Compounds
N_2O	Nitrous Oxide
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Nitrogen Oxides
O_2	Oxygen
O_3	Ozone
OECD	Organization for Economic Co-operation and Development
PAH	Polycyclic Aromatic Hydrocarbons
PEMFC	Polymer Electrolyte Membrane Fuel Cell
pgm	platinum group metals
Pt	Platinum
PTFE	Polytetrafluoroethylene
Pd	Palladium
Rh	Rhodium
RTK	Right-To-Know
SETAC	Society for Environmental Toxicology and Chemistry
SIC	Standard Industrial Classification
SO_2	Sulphur Dioxide
SPEFC	Solid Polymer Electrolyte Fuel Cell
TFE	Tetrafluoroethylene
TRI	Toxics Release Inventory
TSCA	Toxic Substances Control Act
Tonne	Metric Ton equivalent to 1000 kg.
ZEV	Zero Emission Vehicle

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CHAPTER 1 - Introduction

1.1 Rationale

Due to combined factors of population density, climatic conditions, and geography certain regions experience higher levels of air pollution than do others. For these regions, air pollution is a high priority environmental and health issue [1]. The leader in addressing these local air quality issues has been California, and its zero emission vehicle (ZEV) legislation. Forty-eight other U.S. States have joined California in discussing a national low emission vehicle (LEV) program. Canadian governments have pursued similar initiatives, such as the task force commissioned in 1994 by Canadian Ministers of the Environment, whose recommendations included adopting the "U.S. 49-State LEV program" or developing a Canadian version should the U.S. Program not proceed [1]. In June of 1994, the British Columbia (BC) government passed The Clean Air Amendment to the Waste Management Act, which "provides a framework for regulations dealing with a number of issues relating to vehicle emissions, including ... pollution control equipment installation and testing ... emission standards and zero-emission vehicles" [2].

With the exception of the BC government Clean Air Amendment, the California and proposed Canadian legislations place a higher priority on in-use emissions than on those resulting from the life-cycle of the fuel, or the vehicle production, assembly, and disposal life-cycle stages. A phrase which properly reflects the intent of these legislations is 'emit-elsewhere vehicle' (EEV). This phrase acknowledges that emissions occur throughout the vehicle and fuel life-cycles.

The priority of EEV legislation is well placed when applied to internal combustion engine vehicles, since in-use greenhouse gas (GHG) emissions for a gasoline or diesel vehicle are estimated to account for 70-80% of its total life-cycle GHG emissions [3]. However, in the case of the alternative vehicles, emissions from electricity generation or material production and disposal become more significant. For example, the same study estimated that a battery powered vehicle using natural gas sourced electricity would have no in-use emissions, but rather that 70% of its life-cycle GHG emissions would come from the production and use of natural gas (NG) [3]. Hence, it is not sufficient to merely control in-use emissions. Before alternatives can be considered less environmentally damaging than internal combustion engine (ICE) vehicles, their full life-cycle environmental impacts must be examined.

Electric vehicles such as those powered by fuel cells and rechargeable batteries are currently proposed as the only option meeting the requirements of the California ZEV legislation [4] [5]. Fuel cells have several inherent advantages over rechargeable batteries, including faster refuelling versus recharging time and longer mileage between refuellings than rechargings. To match the driving range of a gasoline powered vehicle, the recharging time of a technically realistic battery would be several hours [5]. A fuel cell vehicle fuelled with liquid methane or hydrogen should take fractionally less time to refuel. Moreover, the performance of a battery powered vehicle would decrease with battery power, whereas the performance of a fuel cell powered vehicle should be insensitive to fuel level.

If fuelled with hydrogen and oxygen from atmospheric air, fuel cell powered vehicles would produce practically no in-use emissions other than water and heat. It is this characteristic of fuel cells which has led them to be hailed as the environmentally preferred alternative to internal combustion engines. This report critically examines the real life-cycle costs of proton exchange membrane fuel cells compared to internal combustion engines.

A full life-cycle cost analysis would include valuing the total environmental burden of a technology using a common measure such as dollars. Included in total environmental burden, however, are effects such as damage to human health and the environment which are not taken into consideration in a standard economic accounting framework. There is no one accepted methodology for the valuation of these effects. As a result few valuation studies have been performed, and those that do exist show a strong disparity between their results. In addition, ecologists, economists and ethicists are debating whether the monetary valuation of environmental and health effects ought to even be performed [6]. For these reasons, this thesis focuses on identifying life-cycle environmental releases and developing a framework for future full cost analysis.

1.2 Fuel Cells

Fuel cells are electrochemical devices which convert the chemical energy of a fuel (hydrogen) together with an oxidant (oxygen from air) into electrical energy through chemical reactions. As Kartha and Grimes explain, much like batteries, "the key components of fuel cells are an anode, to which the fuel is supplied, a cathode, to which the oxidant is supplied, and an electrolyte, which permits the flow of ions (but not electrons or reactants) between the anode and the cathode" [7]. The proton exchange membrane fuel cell (PEMFC), also known as Solid Polymer Electrolyte fuel cell (SPEFC), is the closest to commercial production for vehicle use and it is believed to be the prime choice for transportation purposes [8][1] [9] . In the case of a PEM fuel cell, the fuel and oxidant spontaneously disassociate, the hydrogen into two H^+ ions which migrate through the electrolyte to react with the 1/2 O_2^- ions to form the waste product, water. The stream of electrons which flow spontaneously from the fuel as a result of these reactions are diverted through an external circuit, thereby ensuring the generation of electrical energy. The fuel and oxidant are stored in external tanks and supplied to the reaction sites as needed.

1.3 Focus Of This Study

Although fuel cells are currently being designed and marketed for urban mass transit vehicles and fleet vehicles, their largest transportation market will ultimately be personal automobiles. This study therefore focuses on mid-sized sedans. This vehicle contains a 70 - 100 hp ICE, which would be replaced by a 50 kW fuel cell [10]. The fuel cells considered here represent a best estimate of two commercially viable 25 kW proton exchange membrane stacks.

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[1] In tabulated comparisons of the relative advantages and disadvantages of different types of fuel cells [6], SPE fuel cells are shown with higher present and predicted efficiencies and power density, greater range of projected power level, and longer projected lifetime at equivalent cost to the alkaline systems. It seems likely that if the cost of SPE systems are reduced they will win-over those who prefer alkaline systems.

1.4 Externalities

The production and use of technologies often involves external costs for which an unambiguous cause-effect relationship is difficult to determine, let alone to quantify in monetary terms. These are costs such as health effects, noise pollution, habitat damage, change in animal migratory patterns, or the loss of an aesthetic view. A result of the difficulty in quantifying these effects is that they are either ignored or valued at zero. These become externalities when the activity of one agent causes a change in welfare to another agent, and that change in welfare is not accounted for [11]. Significant among these externalities are health effects, environmental effects, and social costs and benefits. By externalizing what can represent a significant portion of the real costs of a technology, the wrong pricing message is sent to consumers, corporations, and policy makers, leading them to make decisions between competing technologies based on incomplete information.

Real costs account for all the positive and negative effects of a technology. They are the sum total of costs traditionally internalized (accounted for) by product manufacturers through means such as prices, taxes, or fees, as well as those which remain external to the traditional pricing mechanism (externalities.) When examining the externalities of technologies for transportation applications, it is reasonable to consider principally those externalities which are associated with costs rather than benefits. "While there are some external benefits associated with transport, these tend to be quite limited in the long run. The reason for this is that there is a natural incentive for people to seek out benefits and to internalize them in a way which does not exist with external costs" [12] .

The increasing public concern with environmental issues is creating an incentive to at least identify and possibly internalize the external costs of technologies. The purpose of this research is to identify external costs associated with the manufacture of fuel cells and ICEs, thereby enabling policy makers and individuals to make "more informed judgment[s] about the costs and benefits of the[se] alternatives ..." [12].

1.5 Environmental Effects Identification and Valuation

"The valuation of environmental and health [effects] is a complex process that requires integration of work from a number of disciplines", varying from the sciences to public health and economics [1]. According to Ottinger (et. al.), this process can be described in five steps [13]. The first step identifies the sources of pollution, quantifies the harmful emissions from these sources, and describes the "constituents of the emissions that can cause environmental damages." The second, third, and fourth steps statistically determine the population[2] exposure effects, including the spread of the pollutant into the environment, the size and profile of the exposed population, and the effects of exposure on this population. The final step calculates the costs of these effects.

There are additional considerations outside of the five-steps, including the natural background level of the pollution material, the duration of exposure, the characteristic residence times of the emission in the environment, and the stability of the environment into which the pollutant is emitted [13] [14]. Beyond this there are concerns of mixing average and marginal effects, of using site and technology specific data to represent national and/or global emissions, and of the synergistic outcome of the mix of pollutants involved.

1.5.1 Determination of Emissions

The challenge of understanding environmental and health effects begins with the first of Ottinger's five steps, specifically the determination of emissions from a life-cycle stage. As stated by Ottinger in his report, *Environmental Costs of Electricity*, 1990 [13]:

> *"It is difficult to estimate a 'typical' set of emissions [from electric power plants] for any resource type. Emissions depend on several factors other than simply the plant type, including the ... fuel type, grade and sulphur content; installed emissions control technology; plant operations ... and steam or limestone injection. Finally, the estimate of emissions per unit of energy output can be further complicated by the allocation of emissions to joint products such as steam and electricity."*

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[2] In Ottinger's five steps, "population includes people (including subsets of human populations by age, health and vulnerability, of ethnic background or otherwise), flora, fauna and materials...."

As Ottinger described, it is difficult to have a complete knowledge of the particular plant from which the electric power is sourced as this information is typically unavailable. If the purpose is to determine the emissions from the life-cycle of a product containing aluminum, steel, plastics, and chemicals, it may be unrealistic to determine the exact plants from which the suppliers of all of the raw materials obtain their electricity. Likewise, one would like to "estimate a 'typical' set of emissions" from the production of each of the raw materials [13]. The production processes may be proprietary, or variable depending on the ingredients for each raw material, the manufacturing processes used, and the particular operating conditions of each facility. Thus a complete inventory of the pollution sources is obviously infeasible. However, the fact that the inventory cannot be complete, does not mean that it is useless. An inventory can present a qualitatively, if not quantitatively comprehensive picture of the emissions.

1.5.2 Determination of Population Exposure Effects

Ottinger's middle three steps of determining population exposure effects form an on-going challenge facing analysts today. Pollutants are released into the atmosphere, the earth, water, and living systems, however they do not necessarily remain in the 'sphere' to which they have been released. Rather, they are often interchanged between the spheres, as illustrated by Manahan in Figure 1.1 [15]. The challenges of determining population exposure are additionally compounded by the lack of historical data. As a result, "for many long term effects, such as global warming and the security of nuclear waste repositories, the impacts are [by necessity] very scenario dependent" [17].

In reviewing valuation studies, Ottinger found that his fourth step's dose-response relationship required the greatest amount of research. A significant aspect complicating this step is the fact that pollutants, while they may be identified and measured individually, do not exist in isolation. "Many air pollutants [when mixed together,] have a synergistic environmental effects, inflicting damage greater than the sum of their separate damages. Synergistic effects are incompletely understood, and no studies valuing their effects are available" [13]. The mixing of pollutants can in fact result in one of four types of environmental outcomes: synergism, antagonism, addition or domination [16]. Antagonism is the opposite effect to synergism, such that overall damages are less than the sum of individual damages. Addition outcomes result in total damages equal to the sum of individual ones, while domination effects occur when the damages from one emission override those from any other pollutant in the mixture. Evidently, a complete characterization of the environmental impacts of pollutants must account not only for how that pollutant behaves on its own, but also for how it interacts with every other pollutant already existing in, and being released into the environment. An accounting of this type is well beyond the scope of this thesis.

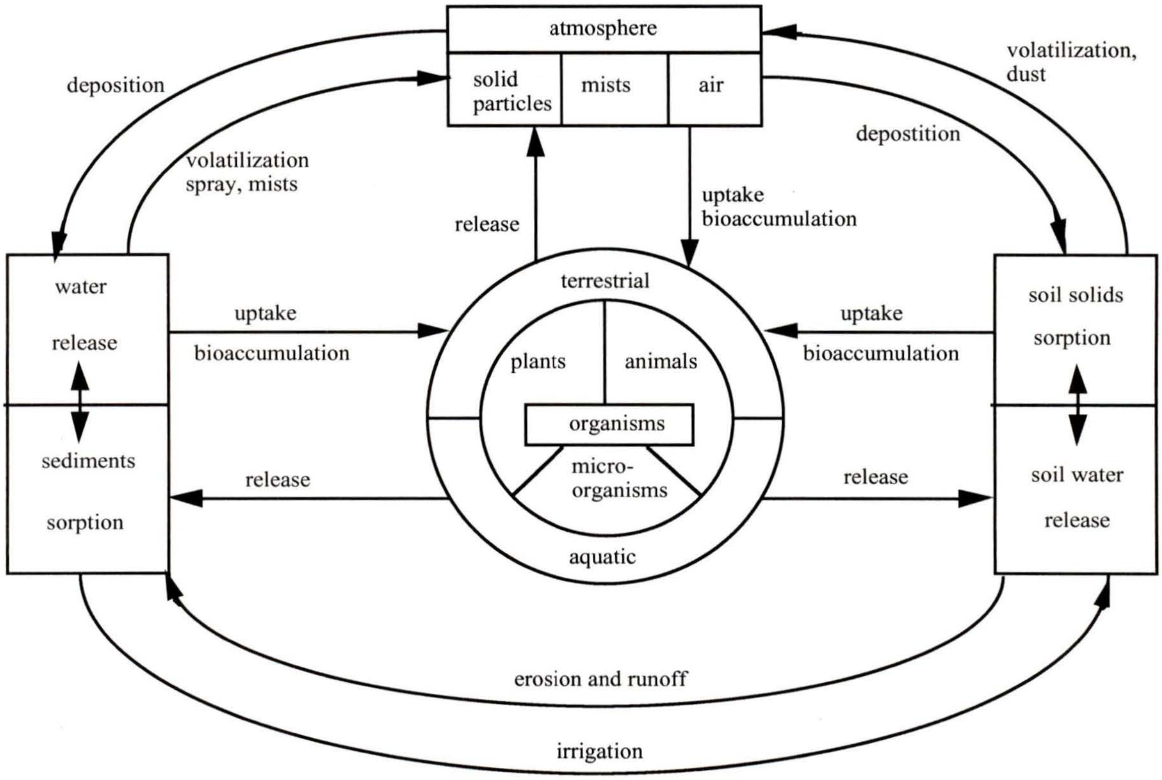

Figure 1.1 Interchange of Pollutant Species Among the Atmosphere, Hydrosphere, Geosphere, and Biosphere.

Figure 3.1 in Manahan, 1990 [13]

Typically, compliance with government-imposed standards and environmental regulations has been used as the basis for determining environmental impact. By this method, if compliance is met, the impact is deemed to be minimal, or zero. However, as Ottinger points out, "standards and regulations do not purport to eliminate pollution", rather they "limit emissions to levels established by a combination of legislative compromise and regulatory feasibility. ... Not all emissions are regulated, and even those emissions that are regulated are not eliminated." [13] Hence, the determination of impact would be better captured as a scientific study of all factors affected by the emission, using government standards only as a basis for understanding the current level of concern with the emitted substance.

1.5.3 The Assignment of Costs

Finally, the assignment of costs to statistically expected outcomes is difficult at best. An acceptable methodology for the calculation and inclusion of external costs in economic analysis has yet to be established [17]. Two methods have been proposed for valuing environmental burden; damage assessment and abatement cost assessment. Damage assessment involves estimating the cost of repairing or reimbursing for damage occurred. Abatement cost assessment refers to the costs of preventing or reducing the damage. Ideally, both costs would be known, and the point at which they balance would be the cost assigned to the environmental effect. However, in many cases only one of damage cost or abatement cost can be determined from available information. Hence many studies pursue only one approach.

Nick Eyre, in his study of external costs, outlined some major difficulties with quantifying externalities. Three of these difficulties are dependence on technology, dependence on location, and a lack of suitable economic valuation studies [17]. Dependence on technology is a problem in situations such as fossil fuel burning power generation stations. Newer, environmentally controlled coal burning stations will have significantly lower associated externalities than will older ones [17]. The difficulty arises in determining or predicting the state of the technology used to provide the energy in any given situation. Incorrect assumptions about the state can misjudge the externalities by one or two orders of magnitude [17]. Similarly, dependence on location can cause problems for quantifying the externalities associated with technologies such as wind, solar, and hydro-generation of power. Large wind farms can cause noise pollution which will have a greater effect on human quality of life if the farm is located near a densely populated area.

Even if the state of a technology and its location are fixed, the lack of studies valuing the effects of these technologies remains a problem. Few valuation studies have quantified the costs from the increased need for health care as a result of pollutant effects, for "damage to artistic and historic properties" and for "infrastructure repairs to public facilities", for the "environmental effects of changes in the energy and nutrient cycles associated with ambient air pollution, and [for] the environmental effects of the loss of ecosystems and habitat diversity" [13].

1.6 Life-Cycle Inventory

Life-Cycle Inventory (LCI) is a tool used to accomplish the first of Ottinger's five steps: identifying and quantifying emissions of pollution. LCI uses the engineering concept of control system analysis to study the mass and energy flows at stages in the life cycle of a technology. At each stage in every material life cycle, a black-box control volume structure is used to identify potential externalities. This approach can be visualized graphically as in Figure 1.2.

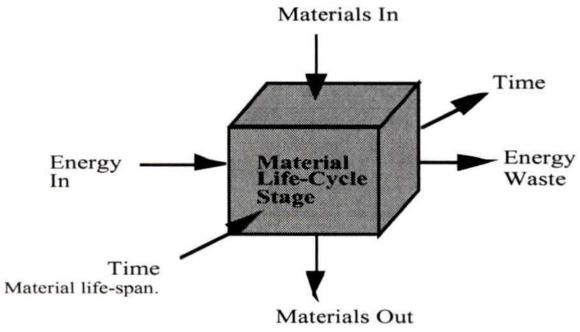

Figure 1.2 Control System Approach for Life-Cycle Inventory

This research uses a control volume approach to create a life-cycle inventory of externalities associated with PEM fuel cells and ICEs. The methodology follows what can be called a "use-out" style in that it begins at the mid-life stage of the technology (product as assembled), and moves back to pre-production and forward to post-production and disposal, as shown in Figure 1.3. At each life-cycle stage, the inventory allows for inputs of raw materials and energy, and outputs of air, water, and solid releases, heat, and other externalities.

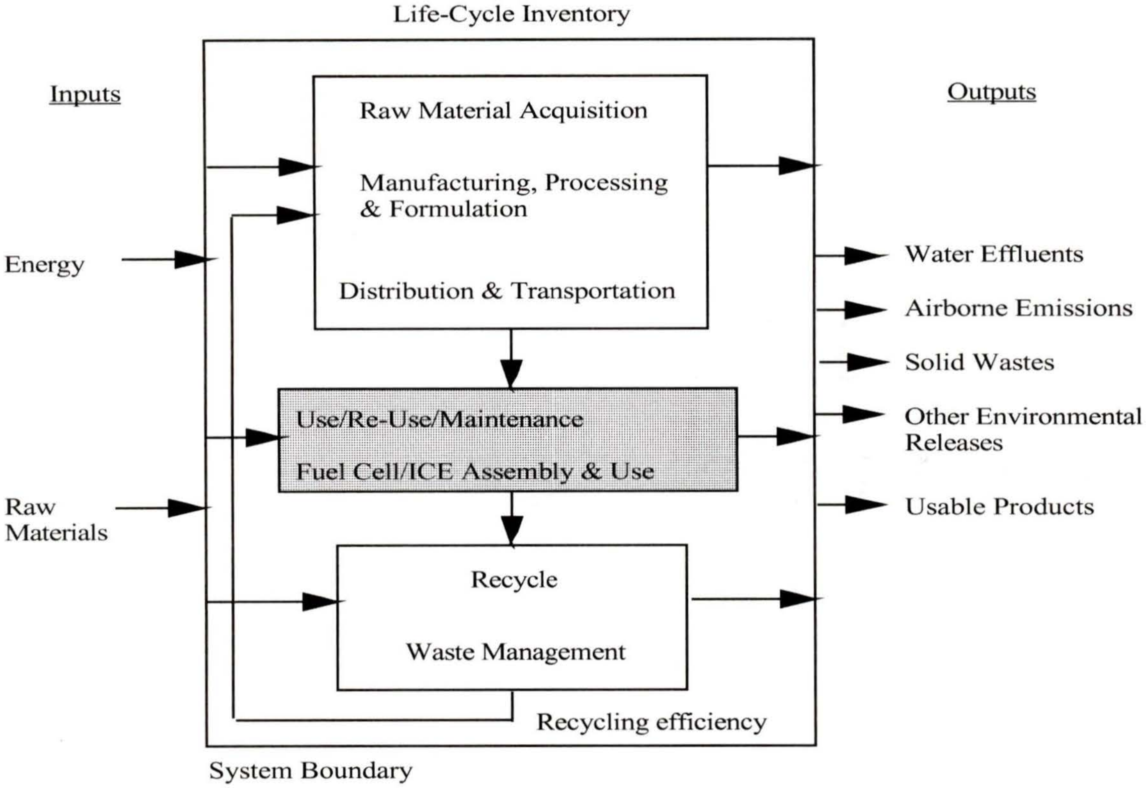

Figure 1.3 Schematic of Life-Cycle Inventory Process Showing Inputs, Outputs, and Life-Cycle Stages

Adapted from [18]

The externalities identification process should ideally follow a bottom-up approach. For environmental externalities, this would involve using specific, local emissions data resulting from each material, and using environment models to predict pollution impacts at the source level. However, the lack of available data necessitated a top-down approach in this study. In this approach, aggregate, annual, and world-wide data is used, sacrificing the finesse associated with specific, local emissions data.

It is appropriate at this point to note that life-cycle inventories are but one component of an overall life-cycle assessment (LCA) as defined by the Society of Environmental Toxicology and Chemistry (SETAC).

SETAC defines an environmental assessment as:

> *an objective process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment, to assess the impact of those energy and materials uses and releases on the environment, and to evaluate and implement opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process, or activity .... [18]*

This assessment process consists of three components: Inventory, Impact Analysis, and Improvement Analysis [18]. Impact analysis characterizes and assesses the effects of the environmental emissions identified in the inventory. Improvement analysis evaluates the needs and opportunities to reduce the impacts. In combination, the three assessment components provide the information necessary to completely evaluate the "environmental consequences associated with the cradle-to-grave life cycle of a process or product" [18]. Limitations on the availability of data and time have restricted this research primarily to the inventory component, with a commentary on impact analysis. Environmental benefits can be achieved from these two components, even though they do not constitute a full life-cycle assessment. The inventory can be used to identify opportunities for reducing emissions, energy, and material use, while the impact analysis communicates the relative importance of the various materials and processes in terms of their environmental impacts.

1.7 Life-Cycle Analysis as Design Tool

Beyond an analysis or comparison of existing technologies, life-cycle environmental impact analysis is increasingly being adopted by engineers as an up-front design tool. LCA and Design for Environment take a proactive approach to environmental impact reduction. They provide designers with the impetus to include environmental considerations among their design constraints, rather than after the design has been finalised. National and international organisations are developing technologies to assist designers in this process[3]. The use of these instruments requires a detailed knowledge of materials and the

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[3] For example, the University of California at Berkeley's "Green Manufacturing Shell" and "Green Machining Planner" which focus on machining processes, and the international standard ISO 14000.

manufacturing processes used to produce them. As is evident in this thesis, the application of LCA is additionally hampered by the need to make assumptions, and to apply questions of strategy and priority which are not fully understood or resolved [19]. The tools and concepts of LCA may not be perfectly applicable to engineering design, but "some things can't be absolute" [14]. We should not let this prevent us from trying to use them. It is only through proposing questions and proactive seeking to answer them that we will raise our collective awareness of environmental issues.

1.8 Project Methodology

Inventories of the component materials in both a 50 kW PEMFC stack and ICE are developed in a format similar to that shown in Table 1.1. Prior works, outlined in Section 2.2, provide a complete inventory of air pollutants and greenhouse gas emissions resulting from the life-cycle of fuels, fuel storage systems, and generic[4] fuel cell and internal combustion engine vehicles. This research takes the prior works a step further, by examining the material differences between the power system components of the FC and ICE vehicles. As a first order simplification, this model assumes that the ancillary systems supporting the fuel cell stack and the internal combustion engine are identical in material composition and weights. It is recommended that future work verify this assumption by examining the actual differences between ancillary component systems.

From the life-cycle of each material, sources of emissions are determined and where possible, the emissions are listed and quantified. This examination focuses on life-cycle stages of raw material production, vehicle use, and recycling (stages I, IV, and V in Table 1.1). From these stages, an inventory is developed of the emissions resulting from the life-cycle use of energy and the raw material production processes. The life-cycle use of energy includes that which is required to extract, produce, and assemble the materials and their component ingredients.

In order to compare the levels of emissions from the various materials and technologies, the inventories of component materials are normalized on a weight of material per system

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[4] That is, ICE and FC vehicles whose composition, except for the fuel storage systems, are considered to be identical.

energy output basis (i.e. g/kWh). The system energy output is 50 kW gross maximum delivered power divided by expected system lifetime hours of operation (3400 hours for an ICE and 6800 hours for the PEM stack, for a first assumption as explained in Section 3.1.1). The normalized weights of materials thus form the foundation of the externalities identification process.

		Inputs per __________			Outputs per ______					
					Releases					
	Life-Cycle Stage	Raw Mat (kg)	Energy Renew (MJ)	Energy Non-Renew (MJ)	Air (kg)	Water (kg)	Solids (kg)	Energy	Other Outputs	Ref. Appendix No.
I.	Raw Material Acquisition (for each raw material from mining/harvesting to delivery at manufacturer's door)									
II.	Manufacturing, Processing, Formulation (for each processing step for all ingredients and packaging up to the point of wholesale/retail sale)									
III.	Distribution and Transportation (from manufacturer to point of use)									
IV.	Use/Re-Use/Maintenance (including storage and repair)									
V.	Recycle/Compost (including collection)									

Table 1.1 Sample Inventory Format Sheet

Adapted from [18]

The emissions model is based primarily on ICE and FC "base-case" models, described in Sections 3.2.1 and 3.3.1. The base-case represents a conservative estimate of the average values and assumptions made. Sensitivity analysis is conducted in order to understand the significance of the major assumptions.

1.8.1 Energy Emissions

Best available estimates are made of the life-cycle energy required to produce a unit mass (kg) of each material. Where possible, these estimates are taken from Delucchi's [3] interpretations of Hudson's work [20]. Where a particular material is not included in Delucchi's report, the life-cycle production energy is calculated either directly from Hudson's values, or from an understanding of the raw material extraction and material production processes. These cases are discussed in more detail in Chapter 5. The normalized energy required to produce the materials in a PEM stack and an ICE engine are calculated from the life-cycle energy required to produce a unit mass of each material multiplied by the normalized weights of each material.

The emissions resulting from the use of the normalized energy are calculated as the emissions resulting from the use of fossil fuels to generate the energy. As such, the energy input is split into its fossil fuel and electricity component mix, and emissions factors for greenhouse gas emissions are applied. This process is described in detail in Chapter 4.

1.8.2 Production Emissions

The complete determination of the energy use and process emissions directly resulting from the manufacturing, processing, and formation of ICE and FC components beyond material semifabrication is not possible at this time. It is recommended, however, that should more complete and public information become available about the processes used to manufacture the various component materials, this data should be used to update and verify the results presented herein.

1.9 Qualification Of Results

"There is more to be said for rough estimates of the precise concept than precise estimates of ... irrelevant concepts" [21]. This thesis is undertaken according to the preceding sentiment. As the field of environmental analysis is still so much younger than manufacturing and energy utilization, no complete characterization of the environmental and health impacts of all technologies examined here has been performed. There remain also considerable shortcomings in the availability of social cost data. To allow the research to proceed and to be immediately useful, the author makes best possible estimates of data where necessary. By its very nature this work is highly assumption driven, and it is recognised that the assumptions used may not match those another person would chose. However every effort has been made to ensure that the work is consistent with the assumptions used, and that these assumptions are transparent.

Because many of the assumptions are based on highly aggregate or averaged data, the performance of a detailed statistical sensitivity analysis would amount to nothing more than a mathematical exercise. This thesis has performed a broad stroke sensitivity analysis on those assumptions which were quickly identified as being the most significant. The structure of the model is intended to be sufficiently rigorous to allow the input of more precise estimates when and if they should become available.

Finally, it should be noted that while the author strives for objectivity, this work is undertaken with an underlying positive bias towards fuel cells and fuel cell research. Evidence of this bias shows in the choice of an optimistic base-case for the fuel cell model.

CHAPTER 2 - Prior Work

To date, most research has assumed the life-cycle environmental impacts of fuel cells to be determined by the "cleanliness" of the fuel source and the on-board emissions. However, recent studies have seen the importance of going beyond the obvious scope and have addressed the full life-cycle of fuel cell vehicles, (ie production, use and disposal.) This chapter provides an introduction to these prior works and identifies their key assumptions and limitations in addressing the requirements of this thesis.

2.1 Delucchi's Work

One example of the prior work in this area is Delucchi's[5] study determining the fuel-cycle emissions of greenhouse gases from the use of transportation fuels and electricity [22]. Delucchi found that in general alternate fuel vehicles (AFV) using fuel cells and hydrogen would have lower total[6] CO_2-equivalent emissions[7] than light duty ICE vehicles (ICEV) .

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[5] Between 1992 and 1994 the spelling of Mark Delucchi's last name changed from DeLuchi to Delucchi. This thesis uses the most recent spelling in the written text, but uses the earlier spelling to cite the pre-1994 reports in the Bibliography: DeLuchi (1991) versus Delucchi (1994).

[6] In Delucchi's study, total emissions encompasses vehicle end use, compression or liquefaction of fuel, fuel distribution, fuel production, feedstock transport, feedstock recovery, CH_4 leaks and flares, car assembly and manufacture of materials in cars.

[7] Delucchi calculated emissions of carbon monoxide (CO), methane (CH_4), nitrous oxide (N_2O), nonmethane organic compounds (NMOCs), nitrogen oxides (NO_x), and carbon dioxide (CO_2). He normalized all of the gas emissions into a single CO_2-equivalent emissions index and expressed his results per mile of travel by the vehicle. The CO_2-equivalent emissions index was calculated by Delucchi as the mass amount of carbon dioxide emissions with the same global warming temperature effect as the mass of the other

(This finding is dependent upon the source for hydrogen used as the fuel for the AFV. If the hydrogen were produced from coal reforming, Delucchi found that the AFV would have higher total emissions than ICEVs.) Breaking down the total emissions, Delucchi found that AFV using hydrogen would have higher CO_2-equivalent emissions in the material production and assembly stages of the vehicle life-cycle than either diesel or reformulated gasoline fuelled ICEV. These results are shown in Tables 2.2 and 2.2A.

Delucchi determined the CO_2-equivalent emissions from the manufacture and assembly of materials in cars according to the following procedure:

1) performing a materials breakdown of the vehicles
2) determining the weight of materials in vehicles
3) calculating the energy used to produce the weights of materials
4) determining the emissions resulting from the above energy use
5) converting the above emissions to CO_2-equivalent emissions.

The results are presented in grams of carbon dioxide equivalent emissions per mile (gCO_2-equivalent/mi) of vehicle travel. This was converted to grams per kilowatt hour (g/kWh) for Tables 2.2 and 2.2A, using the assumptions of 50 kW power output for the FC and ICE, and average driving speeds of 50 km/h. The exact conversion is shown in Appendix A.

Delucchi's work on fuel cell life-cycles is limited in its applicability to PEM fuel cells in two critical ways. First, Delucchi's work focuses exclusively on an identification of life-cycle greenhouse gas emissions. In doing so, Delucchi's report mixes local and global pollution effects, combining them into a single global warming factor. As a result, the author misses the opportunity to examine in detail the impacts of each technology on that which is the current driver of alternative vehicle research: local air quality. The second limitation of Delucchi's work is that he assumed the "materials breakdown in an FCV [fuel cell vehicle], excluding the fuel storage system, would be the *same* as the breakdown in an

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gasses. Delucchi defined the "temperature effect" in terms of the "degree-years over a period of time, where one degree-year is an increased surface temperature of 1°C for one year" [3].

ICEV" (my emphasis) [3]. Delucchi made this assumption because of the lack of available information on the composition and weights of component materials in PEM fuel cell stacks. This thesis has attempted to inventory the potential materials in a PEM fuel cell, thus allowing it to move beyond the limitations of Delucchi's assumption.

ICE Vehicles

Source or fuel-Cycle Stage	Reform Gas ICE	Diesel ICE	Methanol from NG ICE	Methanol from Coal ICE*	Methanol from Wood ICE	H2 From Solar ICE	U.S.National Power Mix EV*	Solar Power EV*
Vehicle end use	207	202	172	172	32	14	0	0
Compression or liquefaction	0	0	0	0	0	0	-	-
Fuel Distribution	4	3	18	9	11	1	5	0
Fuel Production	42	15	52	250	15	0†	250	0.8
Feedstock transport	7	7	6	1	6	0	4	0
Feedstock recovery	7	7	11	6	28	0	5	0
CH4 leaks/flares	3	3	7	23	0	0	12	0
First total	270.6	237.3	266.6	461.2	92.5	15.1	276	0.8
Change (%)	_	-12.3	-1.5	66.8	-65.8	-94.4	-14.5	-99.7
Car assembly	8.7	6.5	8.7	8.7	8.7	9.0	8.9	8.9
Materials in cars	26.0	19.6	26.0	26.0	26.0	28.1	28.9	28.9
Second total	34.7	26.2	34.7	34.7	34.7	37.1	37.8	37.8
Change (%)	_	-24.7	0	0	0	6.8	8.9	8.9
Total	305.3	263.5	301.4	496.0	127.2	52.2	313.8	38.6
Change (%)		-13.7	-1.3	62.4	-58.3	-82.9	-12.2	-89.2

Table 2.2 CO_2 Equivalent Emissions (g/kWh) by Fuel Type for Internal Combustion Engine Vehicles and Battery Powered Electric Vehicles

Based on Table 9a *Base-Case, Total Fuel-Cycle, CO2-Equivalent Emissions from the Use of Transportation Fuels, by Fuel-Cycle Stage* [22] (Reform. Gas refers to U.S. reformulated gasoline.) ICE - Internal Combustion Engine, EV - Battery Powered Electric Vehicle. Change % is measured relative to the Reform Gas ICE.

* - Delucchi compared battery powered vehicles to a reform-gas fuelled ICE in a city driving cycle only. This ICE has lower fuel mileage and thus higher emissions/mile. Other vehicles are compared to the reform-gas fuelled ICE in city/highway driving cycle.

† - Delucchi assumed that emissions from the production of photovoltaic materials are negligible.

FC Vehicles Source or Fuel-Cycle Stage	Methanol from NG	Methanol from Coal	Methanol from Wood	H2 from Solar
Vehicle end use	90.4	90.4	0.6	0
Compression or liquefaction	0	0	0	0
Fuel Distribution	11.6	6.0	7.3	0.6
Fuel Production	33.4	159.4	9.5	0†
Feedstock transport	3.7	0.6	4.0	0
Feedstock recovery	7	3.7	17.8	0
CH4 leaks/flares	4.5	14.8	0	0
First total	150.5	274.9	39.2	0.6
Change (%)	-44.4	-0.6	-85.5	-99.8
Car assembly	9.1	9.1	9.1	9.1
Materials in cars	27.2	27.2	27.2	31.4
Second total	36.3	36.3	36.3	40.5
Change (%)	4.5	4.5	4.5	16.8
Total	186.8	311.2	75.5	41.2
Change (%)	-38.8	1.9	-75.3	-86.5

Table 2.2A CO_2 Equivalent Emissions (g/kWh) by Fuel Type for Fuel Cell Vehicles

Extracted from Table 9c *Base-Case, Total Fuel-Cycle, CO2-Equivalent Emissions from the Use of Transportation Fuels, by Fuel-Cycle Stage, for 100-Year Time Horizon* [22]. Change % is measured relative to the Reform Gas ICE, shown in Table 2.2. NG - Natural Gas, H2 - Hydrogen. Numbers have been converted to g/kWh from g/mi based on the assumption of 50 kW power output and an average driving speed of 50 km/h.

† - Delucchi assumed that emissions from the production of photovoltaic materials are negligible.

2.2 DTI Study

In the U.K. Department of Trade and Industry (DTI) study, life-cycle analysis was carried out to compare the environmental impacts of conventional forms of transport (ICEs) with alternative systems based on batteries and fuel cells [23]. The study concluded that the "energy required during production, along with the ... greenhouse gas emissions, are insignificant in comparison with the respective values during the use stage" [23]. This conclusion mirrors that of Delucchi, however it too has limitations. The design and configuration assumptions for the PEM cell used in the DTI model are unclear.

This makes the results challenging to replicate, and difficult to justify using as a basis for comparison with other reports. Additionally, the measures of environmental impact in the DTI report are presented as single point numbers, with no indication of the sources of their data or the uncertainties surrounding their numbers. This again hinders replication, and provides the results with an illusory precision. In an effort to avoid these pitfalls this thesis intends to provide more reproducible results, with consistent assumptions, clearly indicating the estimated maximum and minimum values of the data.

2.3 University Of London Master's Thesis

Hormandinger, in a more recent study developed through a techno-economic model, included a social cost analysis of an urban fuel cell bus fleet [24]. Hormandinger's purpose was to provide an "understand[ing of] the economics of fuel cells in the transport field" and to highlight areas in need of further research [24]. Using the highest values from a survey of external cost valuation studies, the author found that the life-cycle costs of fuel cell and diesel buses were nearly on par.

Hormandinger's study grouped environmental effects of road traffic into four categories; fuel-cycle air pollution, greenhouse gas emissions, noise, and "danger to others, congestion, [and] landscape consumption" [24]. The author covers only the first two of these categories in his report, citing the scarcity of data on the social cost of noise and the relative balance in impact between current ICE and FC technologies on accident rates, congestion, and road distribution as the basis for ignoring the final two categories.

Similar to the DTI study, Hormandinger's used single number estimates for emissions, took values from a variety of sources without regard for their differing assumptions, and double counted. The use of varied sources was most likely unavoidable, and is repeated in this thesis. Hormandinger's double counting, however, was particularly significant. As emissions parameters he cited Delucchi's GHG equivalent emissions together with more specific gas emissions taken from other sources (carbon monoxide (CO), nitrogen oxides (NO_x), non methane volatile organic compounds (NMVOC), particulate matter or sulphur dioxide.) This amounted to double counting the CO, NO_x, and NMVOC as they were already included in Delucchi's GHG equivalent emissions values.

2.4 Victor Adams' Life Cycle Analysis

Another recent paper presented some preliminary results of an investigation into the "environmental life cycle [impacts] of transport systems" [25]. This paper's results include listing the environmental impacts of fuels used by transport systems, from fuel manufacture to use, as measured in CO_2 emissions per unit of energy developed by the transport systems' power units. The final report is expected to estimate impacts in the form of energy used and emissions resulting from energy use. The methodology in this way appears to mirror that of this thesis, however it limits itself to a study of the fuel cycle, ignoring the materials inherent in the transport systems themselves.

2.5 Typical Flaws in Externality Identification

Six pitfalls are typically associated with externality identification: inconsistent boundaries, double counting, mixing average and marginal effects, averaging of stochastic events, illusory precision, and confusing "things that are countable with things that count" [26]. An awareness of these pitfalls has helped in a critical examination of the prior work, and will provide a valuable guide to this research.

1) Inconsistent Boundaries - External cost analysis is useful for comparing two competing technologies, or for comparing alternatives in a technology's life-cycle. In order for these comparisons to be valid the boundaries defining both systems must be consistent, if not identical.

2) Double Counting - Any particular externality should only be counted as having one effect. An example of double counting is the listing of traffic accidents among externalities to vehicular transportation when insurance is included in the overall cost of owning and operating a vehicle. This insurance compensates for the results of any accidents, and thus the costs of accidents are internalised. Only the portion of accident costs that may not be covered by insurance settlements, or any other means, can be considered an externality.

3) Mixing Average and Marginal Effects - The significance of externalities such as health and environmental effects caused by pollution often increases non-proportionally with emissions. Over any given period of time, the average effect of a pollutant may be insignificant (ie. within the capacity of the environment to assimilate it.) The marginal effect, however, of any one unit of emissions over the previous unit may at some point in the time period tip the scale into considerable environmental damage without raising the average above an environmental threshold level. While it is preferable to use marginal effects of pollution, this is not always possible. Lack of data collection resources and industry security often mean that emission levels are reported only on annual, national, and/or industry wide bases. This has been the case with the data used in this thesis.

4) Averaging of Stochastic Events - Taking the average effect of past or current events can be misleading measures of external costs. The average can either overestimate the cost of low probability events, or can underestimate the cost of events which cause damage "only under extreme circumstances" [26]. This is a difficult pitfall to avoid since most data is only available as annual past totals which must then be converted to averages. In the case of this thesis averaging was performed, but with the acknowledgment that the resulting data can be used only as a guideline. In addition, this thesis provides an inventory of effects, and leaves to the reader the task of assigning value to those effects. The reader should therefore take into consideration the possibility that actual future effects may be higher or lower than those indicated.

5) Illusory Precision - As externalities tend to be difficult to quantify and explicitly identify, the data used to calculate externalities is by nature uncertain. Care must be taken not to present external cost data as "single point estimate[s]" [26]. This is one of the principal weaknesses of the DTI report which listed the environmental life-cycle effects of PEM fuel cells as single point numbers, with no indication of the sources of data, the assumptions made in the report, or the uncertainties surrounding the results [23].

6) Confusing "things that are countable with things that count" - A natural reaction when faced with the task of identifying and quantifying costs is to chose those costs which are easily measured, while ignoring those which are not. It is this reaction which often leads to the existence of externalities in the first place, and it is therefore especially important to overcome this tendency when performing external cost analyses.

This pitfall can become significant during the first stage of research when the focus is on a search for raw data. For this study, a macro approach was used to set up a framework for the analysis. Once environmental understanding has advanced to the point where reliable data is available for those effects which "count", the framework can be filled and decisions can be made on the suitability of these technologies.

2.6 Summary

Prior work has, for the most part, focussed on fuel-cycle impacts. They have quantitatively estimated CO_2-equivalent emissions, and qualitatively estimated other environmental and social effects . The CO_2-equivalent emissions address the growing environmental concern of global warming, they provide a basis for comparing competing technologies and for updating prior work, and they are a good starting point for a life-cycle analysis. A complete analysis must go further than this however, and works are showing a move in this direction [27] [28] [29] [30]. Additionally, many scientists are working to develop a better understanding of emissions from isolated life-cycle stages and their effects on individual organisms. Gradually, all of this work must be brought together. This thesis does not pretend to reach that far, however by listing inputs and outputs of materials and energy together with CO_2-equivalent emissions, it makes a new step towards a full life-cycle inventory and analysis.

CHAPTER 3 - ASSUMPTIONS

3.1 Power Plant Lifetimes

As stated, the vehicle modelled for this research is a mid-sized passenger vehicle with an engine power output of 50 kW. Assuming a standard passenger vehicle ICE engine vehicle has a lifetime mileage of approximately 170,000 km, with an average driving speed of 50 km/hour gives a vehicle operation lifetime of 3400 hours [8]. FC lifetimes could exceed those of ICE by 40 - 100% [9] due to the greater mechanical simplicity of FC systems and electric motors over internal combustion engines [31]. This assumption results in a FC operation lifetime range of approximately 4760 - 6800 hours.

3.2 ICE Assumptions

The internal combustion engine weight-to-power ratio is assumed to be between 2-3 kg/kW for passenger cars [10]. For 50 kW engines, this translates to an engine weight range of 100 - 150 kg. Automotive engine blocks are constructed principally of either aluminum or cast iron. The 100 kg weight is considered representative of an aluminum-block engine

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[8] Delucchi estimated a light duty vehicle lifetime as 173 772 km [22]. Ogden (et. al.) estimate the ICE lifetime to be 193 080 km [8]. I've chosen the low number for simplicity, since the actual figure is not as important as the difference between the ICE and FC lifetimes. This difference is discussed in the following footnote.

[9] Delucchi estimated a 42% longer lifetime for electric vehicles than for ICE vehicles [2]. Ballard Power Systems Inc. of Vancouver BC (Ballard) have proven PEM cell lifetimes of 5000 - 11 000 hours [30]. This thesis examines FCs with the same, 40% longer, and 100% longer lifetimes than the ICE. These limits are reasonable given the data from Ballard.

similar to a Ford Duratec™ which uses about 45 kg of aluminum parts per engine [32]. The 150 kg weight is representative of a cast-iron-block engine which weighs about 45 kg more than the aluminum engine block [32].

3.2.1 Internal Combustion Engine Composition

The engine parts included in the ICE models are shown in Table 3.4 [33]. Not all materials present in an ICE have been included in this table, but it is assumed that any materials not listed are present in minor quantities only (< 0.5% of the engine weight.) The engine components are grouped according to their primary material composition; aluminum, cast iron, steel, lead, copper, rubber, and plastics. The weights of each material group are estimated for the 100 kg and the 150 kg engines. Beyond aluminum and cast iron, the two engines are assumed to have the same weight composition of other materials.

ICE Base Case Model

ICE engine block construction appears to be moving away from cast iron towards aluminum for reasons of weight savings [32]. The ICE base case model is therefore taken to be the 100 kg engine with a cast-aluminum engine block. As previously mentioned, the ICE is assumed to have a lifetime of 3400 hours. Other ICE material assumptions are described in Chapter 5.

100 kg engine		Object		150 kg engine
Material weight (kg)	Material		Material	Material Weight (kg)
	Aluminum	pistons	Aluminum	
	|	valves and valve sets	|	
	|	plain bearings	|	Aluminum....3.5
	|	barrels	Cast Iron	
	|	cylinder heads	|	
	|	crank-cases	|	
Aluminum......48	|	gear cases	|	
	Cast Iron	piston rings	|	
	|	camshafts	|	
Cast Iron........25	|	cam followers	|	Cast Iron......80
	Steel 4140, 4340	piston pins	Steel 4140, 4340	
	|	connecting rods	|	
	|	bolts, studs, nuts	|	
	|	crankshafts	|	
	|	anti-friction bearings	|	
	|	rocker arms	|	
	|	valve springs	|	
	|	push rods	|	
Steel.............23	|	gears	|	Steel............23
Lead.............0.5	Other Materials-Lead	rod bearings	Other Materials - Lead	Lead...........0.5
Copper............2	Copper-Asbestos	cylinder head gaskets & spark-plug gaskets	Copper-Asbestos	Copper..........2
Rubber..........0.5	Rubber O-Ring	water seals	Rubber O-Ring	Rubber........0.5
	Cork/vellum/fibre	water seals	Cork/vellum/fibre	
Plastics.........0.5	|	low-pressure gaskets	|	Plastics.......0.5
Total...........100				Total..........150

Table 3.4 Internal Combustion Engine Component Materials (without ancillaries)

From Taylor [33] and Ward's [32]

3.3 Fuel Cell Assumptions

3.3.1 Fuel Cell Stack Composition

State of the art PEM fuel cell stacks consists of a series of two or more connected fuel cells. A single PEM cell, or membrane electrode assembly (MEA), consists of a solid polymer membrane (SPE) electrolyte "sandwiched between two platinum-catalyzed porous electrodes" one acting as the cathode, and the other as the anode [8]. In a fuel cell stack, the MEAs are supported and separated by electrically conductive plates, typically made of graphite. Flow channels are machined into these moulded graphite plates to allow the supply of reactants (humidified hydrogen and oxygen from atmospheric air), and the removal of products (heat, water, and nitrogen rich air.) In a simplified model of a series connected fuel cell stack, one side of each plate supplies the hydrogen for one cell and the other side provides the air for the neighbouring cell [34]. Hence a stack requires one additional graphite plate than the number of MEAs. The entire stack is held together under pressure: the Mark IV fuel cell from Ballard Power Systems Inc. of Vancouver BC (Ballard) uses metal tie rods running the length of the stack, with metal end plates bolted in place to contain the system. Each individual cell is capable of producing a small voltage (to a maximum theoretical voltage of approximately 1.23 V), as long as the reactants are provided and the products are removed.

The cell membrane has two functions; first to conduct ions between the anode and cathode, and second to physically separate the two reactant gases [35]. Since the late 1960s, membranes of similar composition to DuPont's Nafion® have been used in PEM fuel cells. The electrodes consist of carbon backing (cloth or paper) catalyzed with platinum or platinum supported on carbon. The catalyst can be bound[10] using Teflon® or, recently, an ionomer emulsion [36] [37].

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[10] Wilson et al. describe using ionomer instead of polytetrafluoroethylene (PTFE) to "bind the structure together." Ticianelli et al. referred to the PTFE as a "diffusion layer" in the electrode.

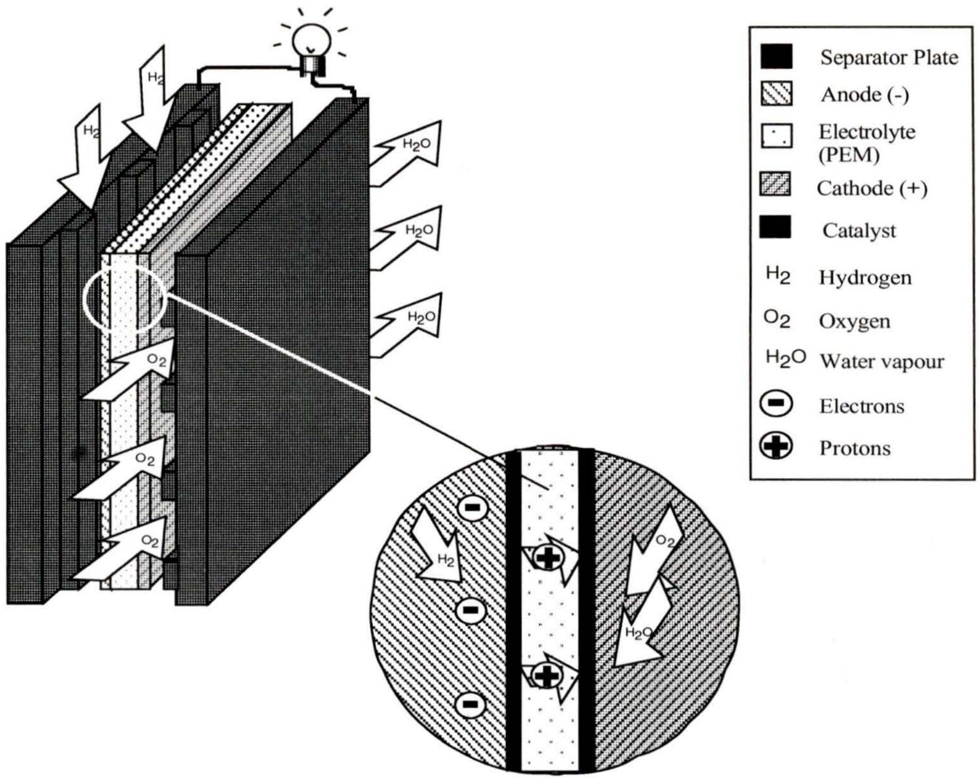

Figure 3.4 Schematic of a Single Proton Exchange Membrane Fuel Cell.

Drawing not to scale

Stack Dimensions and Parameters

As a simplification, this model considers only the most well documented materials in a FC stack: the carbon graphite plates, electrodes, catalyst, membrane, Teflon®, aluminum and steel. Estimation of the amount of these material in a fuel cell requires the determination of stack dimensions, the number of cells per stack, and the cell active area. The fuel cell base case models are "optimistic" scenarios which assume low material usage.

The PEM fuel cell passenger vehicles closest to commercialisation are powered by Ballard fuel cells, as demonstrated by the Daimler-Benz NeCar-II vehicle [38]. The fuel cell stacks in the Daimler-Benz demonstration vehicle are reported to measure about 25 by 25 by 50 cm [38]. These dimensions are assumed to include the end plates and the tie rods, which run through the NeCar-II FC stack. Estimating and subtracting the total space occupied by the tie rod holes gives a base case graphite plate surface area of approximately

576 cm^2 (or 24 cm by 24 cm) [39]. The membrane and electrodes have the same surface area as the graphite plates, whereas the catalyst layer and Teflon® binder are applied only to a smaller, 'active' area. Ballard recently reported active cell areas of 225.5 cm^2 (about 15 by 15 cm) for a "MK5E" cell[11] and 464.5 cm^2 (about 21.6 by 21.6 cm) for an "automotive experimental cell" [35]. The higher of these two areas is chosen as the base case active area for this model, as it seems reasonable that the active area should represent about 80±10% of the plate surface area.

The Daimler-Benz demonstration vehicle fuel cell stacks consists of two stacks of 150 individual cells (or MEAs), each stack capable of producing 25 kW at nominal 0.7V [38]. This corresponds to 166.6 W/cell, or for the base case, 0.36 W/cm^2 active area. As a check, using either the Ballard Advanced Materials (BAM) model '3G' membrane or a Dow experimental one, Figure 3.1 plots power density against cell voltage for both the "automotive experimental" and the MK5E cells from Steck's polarization data [35].

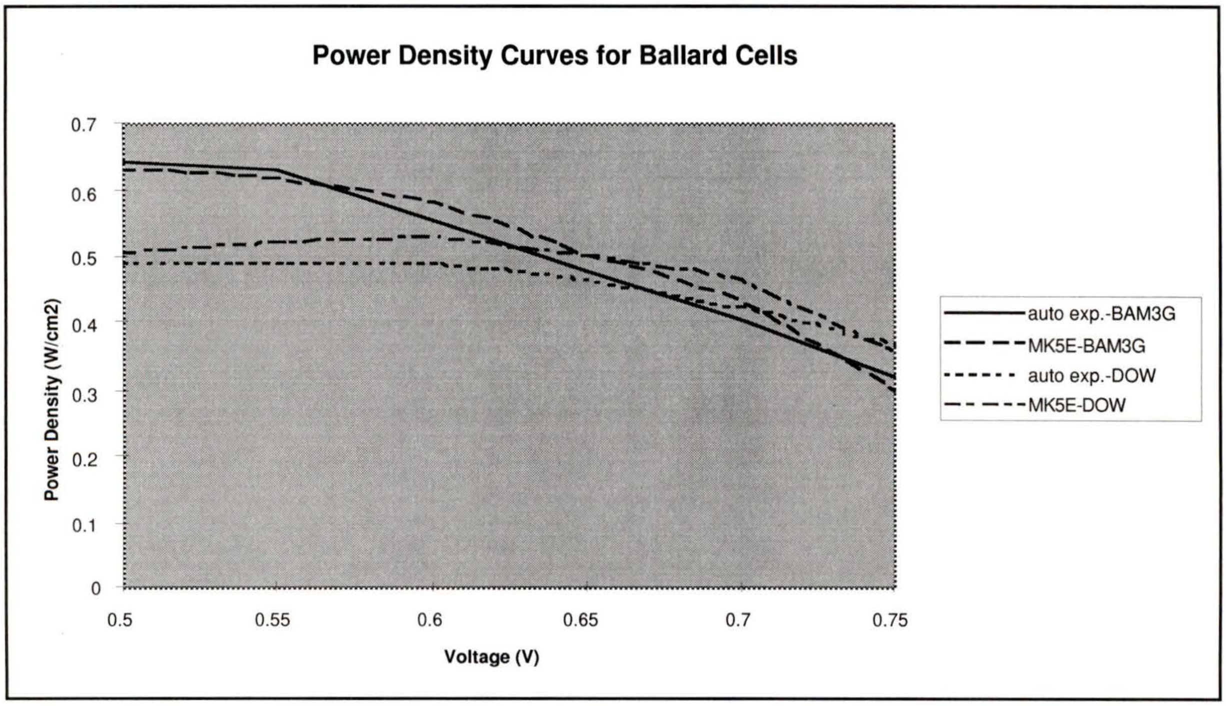

Figure 3.1 Power Density Curves for BAM3G and Dow Membranes in Ballard "MK5E" and "Automotive Experimental" Cells. From Polarisations curves in Steck [35]

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[11] Acronym not defined in article .

The resulting curves for both the BAM membrane and a Dow membrane show power densities in the range of 0.4-0.5 W/cm^2 at 0.7V. Thus, the base case active area assumption seems reasonable. The base case stack model is therefore taken to have 150 cells/stack, 465 cm^2 active area, and 576 cm^2 surface area for the graphite plates, membrane, and electrodes. These values are used below to estimate the amount of each material in the fuel cell stack.

Fuel Cell Base Case Models

This study explores two FC models, each using a different catalyst. The MEA can use either a supported catalyst or a platinum black catalyst. In the case of the supported catalyst, carbon black together with platinum are included among the FC material components. In the case of the platinum black catalyst, the carbon black and platinum numbers do not apply.

The base case fuel cell is composed of two 25 kW stacks. Energy usage and emissions from the fuel cell lifetime may be normalised to either the individual 25 kW, or the combined 50 kW power output, depending on the situation. Individual materials and material weights for the base case model are derived and explained in the following section, and shown in Table 3.5.

3.3.2 Base Case Material Weights

Graphite Plates

The density of carbon graphite is approximately 1.76 - 1.78 g/cm^3 for high purity grade and extruded dense graphite [40]. The base case density is therefore assumed to be 1.77 ± 0.01 g/cm^3. Allowing for the thickness of the end plates (1.5-2.5 cm), the length of the Daimler Benz stack is about 45-47 cm. Since the stack consists of 150 cells, and requires one more graphite plate than the number of MEAs, the stack would need 151 plates. Assuming negligible thickness for the MEA's, each plate would be approximately 0.3 cm thick (±0.1 cm). Using the base case surface area of 576 cm^2, the weight of graphite used in one plate is 306 g. For 25 kW power output per stack, the normalised weight of graphite would be approximately 1848 g/kW.

Carbon Fibre Cloth

Electrodes suitable for use in PEM fuel cells are sold by E-Tek, Inc. and others, or can be assembled using a carbon fibre cloth or paper backing [8] [41]. The E-Tek carbon cloth supports weigh 0.0116 g/cm^2 [41]. Using this weight with the base-case electrode surface area of 567 cm^2, gives an electrode weight of 6.7 g. Two electrodes are used per MEA, thus the normalised weight of carbon fibre cloth is approximately 80 g/kW.

Platinum

This study assumes that the cathode and anode electrodes are identical, and that each electrode is catalyzed on one side only. The standard E-Tek catalyst layer is supported platinum (20%) on Vulcan XC-72 carbon black. The platinum (Pt) loading in these electrodes ranges from 0.35 - 0.50 ± 0.05 mg/cm^2 Pt. This range coincides with the supported platinum loadings of 0.4 mg/cm^2, 10% or 20% Pt on carbon given in another reference [8]. As a base case therefore, the supported platinum loading is assumed to be 0.42 ± 0.13 mg/cm^2. Using the base-case active area, the total platinum weight per electrode is about 195 ± 60 mg. The base case normalised weight of platinum is therefore approximately 2.3 g/kW.

Carbon Black

As with the platinum, this study assumes that the carbon black catalyst support is applied over the active cell area on one side of each electrode. The E-Tek electrode carbon only loading is 2-4 mg/cm^2 [41]. Using as a base case assumption a carbon loading of 3.0 ± 1 mg/cm^2, the weight of carbon black per electrode is 1.4 ± 0.5 g. The base case normalised weight of carbon black is 17 g/kW.

Platinum Black

Unsupported platinum catalysts (platinum black) loadings are in the range of 1.0-5.0 mg/cm^2 [41], or 2.0-10.0 mg/cm^2 [8]. This study assumes a loading of 5.5 ± 4.5 mg/cm^2 over the base case active area of 465 cm^2. The total platinum black weight per electrode is therefore 2.6 ± 2.1 g. The base case normalised weight of platinum black is 31 g/kW.

Teflon®

Teflon® emulsion can be used to bind the catalyst structure, to act as a diffusion layer, and to render portions of the electrode hydrophobic [37][36] [42]. Since the platinum and carbon black loadings are small, only a few drops of the emulsion should be necessary as a binder. The base case assumes that 2/10 cm^3 of 50% Teflon® emulsion are used per cell. If the specific gravity of polymer Teflon® is on the order of 2.15 [43], then the weight of Teflon® per electrode is calculated to be 0.215 g. Assuming the Teflon® is applied to the active cell area, this implies a loading of approximately 0.5 mg/cm^2 which seems reasonably thin. Assume finally that the same loading is applied as a diffusion layer and again to impregnate the electrode. The total Teflon® loading is therefore about 0.65 g per electrode. The normalised weight of Teflon® is near 7.8 g/kW.

Membrane

DuPont membranes range in thickness from 0.254 mm to as low as 0.127 mm (for Nafion® 115) [35]. The Dow membranes are thinner than the Nafion® ones [35]. Assuming they could be as little as 1/2 the thickness of Nafion®, a reasonable range for the membrane thickness is 0.064-0.254 mm. The midway point in this range, 0.159 mm, is used as the base case. Assuming that the surface area of the membrane is equal to that of the carbon fibre electrodes (567 cm^2), the base case membrane volume is approximately 9 ± 5.4 cm^3. Since the density of Nafion® is on the order of that of Teflon® (2.15 g/cm^3) the weight of each membrane is approximately 19.4 g. The base case normalised weight of the membrane is therefore around 116 ± 70 g/kW. The range indicates possible weights if the membrane thickness varies from the base case by ± 0.095 mm.

Aluminum/Steel

The primary use of aluminum and/or steel in a PEM fuel cell stack is in the tie rods, end plates, and collector plates [8]. Each stack requires from 6-16 tie rods[12] [39][34][8]. Using 6 tie rods as the optimistic case, the base model estimates that they are each 50 cm long (from the dimensions for the Daimler Benz stack given at the beginning of this section) and 2 ± 0.25 cm^2 across. The total material usage for tie rods is estimated to be approximately 600 ± 75 cm^3.

The end plates and collector plates are assumed to have approximately the same cross section as the graphite plates, with additional material in the end plates to anchor the tie rods. The collector plates are therefore assumed to have the 576 cm^2 surface area, and the end plates to have a surface area of approximately 625 cm^2. Assuming plate thicknesses of 0.3 ± 0.1 cm, the total material use for two current collector plates is calculated to be 346 cm^3. The material use for two end plates is 375 cm^2.

Using a mild steel density of 7.83 g/cm^3, the amount of steel contained in the tie rods is estimated to be 4.7 ± 0.6 kg (188 ± 24 g/kW). The amount of steel in the end plates or collector plates could be about 2.7 - 2.9 kg (108 kg/kW). If the tie rods are instead assumed to be aluminum, they would contain 1.6 ± 0.2 kg of Al (64 ± 8 g/kW) using an aluminum alloy density of 2.74 g/cm^3. Likewise, the end plates would contain about 1.03 kg of aluminum (41 g/kW). To allow for a mix of materials, but still keep the low material use base case, it is assumed that the tie rods and collector plates are steel and that the end plates are aluminum.

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[12] In Blomen & Mugerwa, the Ballard stack (Figure 11.24) shows sixteen tie rods while the GE stack (Figure 11.9) shows twelve [8]. The newer, NeCar-II stack is assumed to have six [34][38].

Material	Unit	Weight (g)	Range (g)	Weight (g/kW)	25 kW Stack Weight (g)
Graphite	One Plate	306	[base thickness ± 0.1 cm] [density ± 0.01 g/cm^3]	1848	46 206
Carbon Fibre	One Electrode	6.7		80	2 000
Platinum	One Electrode	0.195	[base loading ± 0.13 mg/cm^2]	2.3	58
Carbon Black	One Electrode	1.4	[base loading ± 1 mg/cm^2]	17	425
Platinum Black	One Electrode	2.6	[base loading ± 4.5 mg/cm^2]	31	780
Teflon®	One Electrode	0.65		7.8	195
Membrane	One Cell	19.4	[thickness ± 0.095 mm]	116	2 900
Aluminum	one stack	1030	[number of rods + 10] [rod cross-sectional area ± 0.25 cm^2] [plate thickness ± 0.1 cm]	41	1 030
Steel	one stack	7400	[number of rods + 10] [rod cross-sectional area ± 0.25 cm^2] [plate thickness ± 0.1 cm]	290	7 400
Total (supported catalyst)					68.7 kg
Total (Pt black catalyst)					69.2 kg

Table 3.5 Base Case Material Weights for Proton Exchange Membrane Fuel Cell

CHAPTER 4 - Pollution

This chapter defines and explains the critical pollutants released during the total life-cycle of PEMFCs and ICEs. In addition to outlining the methods used to identify toxic chemicals released during material production, it explains the quantification of greenhouse gases released during the production and use of energy.

Pollution can be defined as

> *the introduction by man into the environment of substances liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity, or interference with legitimate use of the environment" [44] .*

Alternatively, pollution is waste, the level of which exceeds the assimilative capacity of the environment, and which causes a human reaction such as a loss of welfare [11]. Pollution can be released into air, land, and water. Since fuel cells are advanced as a solution to local air quality problems, this chapter focuses primarily on air pollution.

4.1 Local Air Pollution

Air pollution usually refers to pollution of the troposphere, or the lower atmosphere. It is here that pollutants are broken down by chemical reaction, or washed out by rain and deposited on to the earth. Air pollution causes local air quality problems which in turn impact upon all the earth's systems and inhabitants. The transportation industry is a major contributor to local air pollution, emitting 30-75% of all urban air pollutants [9][2].

The dominant transportation fuels (gasoline, diesel) are chemically "mixtures of many compounds with different carbon contents" [3]. These chemical compounds are broken down upon combustion with air, forming products such as carbon dioxide, carbon monoxide, volatile organic compounds, nitrogen oxides, sulphur oxides, water vapour, and very fine particulates [2]. Additionally, unburned hydrocarbons are given off to the environment through leaks and emissions during production, storage and distribution of fuels [3]. Each of these products has the potential to negatively affect the environment should they reach quantities above the environment's capacity to assimilate them. These negative effects can be produced in two ways; the first is through the emission of the pollutant itself to the atmosphere. The second is through the increased requirement for fuel to replace that portion lost from combustion.

4.1.1 Hydrocarbons, Smog and Ozone

Photochemical smog is the most visible local air pollution problem. It is composed of particulate matter, oxidants such as ozone, and noxious organic species such as aldehydes [15]. Smog formation is initiated by photodissociation of nitrogen dioxide, which reacts with hydrocarbons and oxygen to produce smog under conditions of low humidity, sunlight, and temperature inversion [15]. The reactants causing smog are available in large part because of fossil fuel burning motor vehicles. Releases of unburnt gasoline from motor vehicles are responsible for half of the hydrocarbons in the air, and nitrogen dioxide is formed by chemical reaction of nitric oxide emitted during fossil fuel combustion. Each of these releases can be controlled, but not prevented, through the use of catalytic converters.

Smog contributes to human respiratory diseases, reduces visibility, causes eye irritation and often has an unpleasant odour [45]. The oxidants in smog are "toxic to animals and plants and cause damage to rubber and other materials" [15]. One by-product of smog formation is ground level ozone. High quantities of ozone can have toxic effects by oxidizing biological compounds, weakening the immune system, and destroying lung tissue [45]. Ozone may also be responsible for the deaths of forests around the world [45].

4.1.2 Nitrogen Oxides

The formation of ozone through reactions with nitrogen oxides poses severe health and environmental hazards. Three forms of nitrogen oxides (NO_x) are emitted as waste gases from combustion: nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). In addition to playing a role in the formation of ozone, NO_x pose urban air problems of their own. Nitric oxide is the most common form of NO_x emitted from fossil fuel combustion, and is converted to NO_2 in the atmosphere [45]. Nitrogen dioxide is released in much lower levels, but it is the most toxic of the nitrogen oxides and can cause death from pulmonary edema at exposure levels of 115 parts per million (ppm) or greater [45]. The greenhouse gas nitrous oxide is approximately 150-230 times more effective than carbon dioxide at trapping heat, and makes up 6% of the anthropogenic emissions of greenhouse gases [46] [47]. Nitrogen oxides can also form nitric acid, which has been estimated to be responsible for 30-40% of acid rain.

4.1.3 Particulate Matter

Particulates can be released directly from tailpipes into the air, or they can form through physical and chemical reactions with nitrogen oxides, sulphur oxides and volatile organic compounds [2]. Fine particles remain in the air, causing visibility problems associated with smog, and being inhaled and deposited deep in respiratory systems [1][2]. Inhalation of particulates has been linked to impaired lung function and premature death due to cardiopulomonary disease and lung cancer [2].

4.1.4 Sulphur Dioxide and Sulphuric Acid

Sulphur dioxide (SO_2) is released naturally through volcanic eruptions and forest fires, and industrially in the combustion of fossil fuels, the manufacture of sulphur trioxide, and the smelting of copper and nickel [45][45]. Anthropogenic sources are responsible for the same level of global SO_2 emissions as are natural sources. Among industrial sources, the burning of coal is alone responsible for about half of all SO_2 emissions [45].

Sulphur dioxide emissions in urban areas contribute to smog formation and are directly linked to the aggravation of human respiratory disease [47]. Additionally, sulphur dioxide released to the atmosphere may be oxidized to sulphuric acid (H_2SO_4). "The sulphuric acid is washed from the atmosphere as 'acid rain,' which may harm plants or fish or dissolve limestone from building walls" [15]. Acidic precipitation is linked to declining fish stocks, and is blamed for widespread damage to forests and unmanaged biospheres[45].

4.2 Air Pollution Causing Health Hazards

In 1990, the EPA rated ambient air pollutants, including sulphur and nitrogen oxides, carbon monoxide, ozone, and other components of smog, as a high risk to human health. The EPA also rated the depletion of the stratospheric ozone and global climate change high risks to natural ecology and human welfare. Airborne toxics were rated as medium risks. This section presents a few of the these medium risk offenders, while the next section covers pollutants which contribute to global climate change.

4.2.1 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAH) refers to:

> *the compounds made up of carbon and hydrogen atoms grouped into rings containing five or six carbon atoms. They are called ... 'heterocyclic aromatic compounds' (HACs) when any one carbon atom in a ring is replaced by a nitrogen, oxygen, or sulphur atom .* [48]

Forest fires are the most important natural source of PAHs. The greatest anthropogenic sources of atmospheric PAH emissions are aluminum smelters [48]. Sources of water and soil emissions include metallurgical and coking plants, as well as spills of petroleum products [48].

PAHs are relatively non-volatile and have low solubility in water. They are mostly adsorbed by and transported on particulate matter. Degradation of PAHs is very slow in sediments, hence soil becomes a major environmental PAH sink [48]. PAH do not contribute to global warming or ground level ozone formation and they are not associated with depletion of stratospheric ozone, therefore the principal effects of PAH emissions are health effects [48]. These health effects are significant, and at least five PAHs have been listed as "probably carcinogenic to humans" [48].

4.2.2 Fluorides

"Fluorine derivatives are the most aggressive among toxic compounds polluting the atmosphere" [16]. The first member of the halogen family, fluorine is the most reactive of all elements and "combines readily with most organic and inorganic materials at or below room temperature" [49]. Elemental fluorine is not freely occurring in nature, but is found combined with other elements. In particular, the mineral fluorspar (CaF_2) is the "most important natural source of fluorine for industrial purposes" [49].

The most common atmospheric form of fluoride is hydrogen fluoride [16]. "Hydrogen fluoride (HF) is emitted into the atmosphere mainly during production of aluminum, superphosphate ceramics, glass, fluoroplastics and freon, as well as during decomposition of other fluoride compounds" [16]. Acute effects of HF exposure include respiratory problems in people, and metabolism problems in plants. "Fluorine and its volatile compounds and water-soluble salts have the highest phytotoxicity among acid pollutants" [16]. Additionally, chronic fluorine poisoning, or "fluorosis" has been identified in cattle grazing near aluminum production facilities, and in cryolite miners. Fluorosis occurs when the calcium in bones is fixated by the fluoride causing sclerosis. Additional effects of fluorosis include weight loss and anemia [50].

It has been estimated that 20-30 kg of fluorine are leaked per ton of smelted aluminum, split evenly between gaseous and solid emissions [16]. Most (30-75%) of these emissions are trapped by scrubbers at the stack, however wastes from ventilation systems are not cleaned. These ventilation emissions contain more fluorine than those from chimneys or aspiration systems [16]. The background level of fluorine in soil varies from 0.003-0.032%, and is present at approximately 1.3 mg/litre in the hydrosphere.

4.3 Global Air Pollution

4.3.1 Stratospheric Ozone

Oxygen (O_2) in the stratosphere absorbs ultra violet radiation (in the 135-176 nm and 240-260 nm wavelength ranges) to produce oxygen atoms [45]. These atoms react with oxygen molecules to produce ozone (O_3). Stratospheric ozone acts as a protective shield by absorbing ultra-violet radiation in 220-330 nm range, radiation that would otherwise cause skin cancer and other damage to organisms on earth [45][47]. Emissions of chlorofluorocarbons (CFCs) and halocarbons interfere with the ozone forming process, eventually leading to increases in the amount of ultra-violet radiation reaching the earth. Once they reach the stratosphere, CFCs breakdown under the influence of high energy UV radiation to release chlorine atoms [47]. These chlorine atoms accelerate the decomposition of ozone into O_2 and O. Over its lifetime, a single chlorine atom can convert up to 100,000 O_3 molecules to O_2 [47].

4.3.2 Greenhouse Gases

"Society faces potentially rapid changes in future climate because of human activities that alter the atmosphere's composition and change the Earth's radiation balance" [51]. Greenhouse gases is an umbrella term for a group of gaseous compounds including carbon dioxide (CO_2), methane (CH_4), nitrous oxide, and stratospheric ozone. These gases tend to warm the atmosphere by intercepting and absorbing some of the "infrared radiation by which the earth's surface re-radiates energy absorbed from the sun" [15]. Such warming of the earth's surface is known as the 'Greenhouse effect.' Since the start of the industrial era, anthropogenic emissions of greenhouse gases, in large part originating from the energy system, have increased rapidly [51].

"The predominant greenhouse gas is CO_2, which [is responsible for] more than half of the increase in radiative forcing from anthropogenic greenhouse gas sources. The majority of this CO_2 arises from the use of fossil fuels" [51]. One way to measure and compare the environmental impact of competing technologies is to compare the level of greenhouse gases emitted as a result of energy used during their life-cycle. This concept is elaborated in the next section.

4.3.3 CO_2-Equivalent Emissions

CO_2 equivalent GHG emissions resulting from the production and use of energy necessary to make materials can be released at several stages in the energy production and use life-cycle. The total energy input to material manufacture can be divided into its process energy and electricity components, as illustrated in Figure 4.1. Process energy represents the combustion of primary energy sources (coal, natural gas, oil) to provide energy and process heat. Electricity is the electrical input (in kWh) required to run material manufacturing equipment, lighting, and ventilation systems. Each of these energy components is supplied with primary energy: coal, oil, NG, and nuclear as energy sources for process energy; coal, oil, NG, nuclear, and others (hydro, solar, wind, biomass, geothermal) as energy sources for electricity generations.

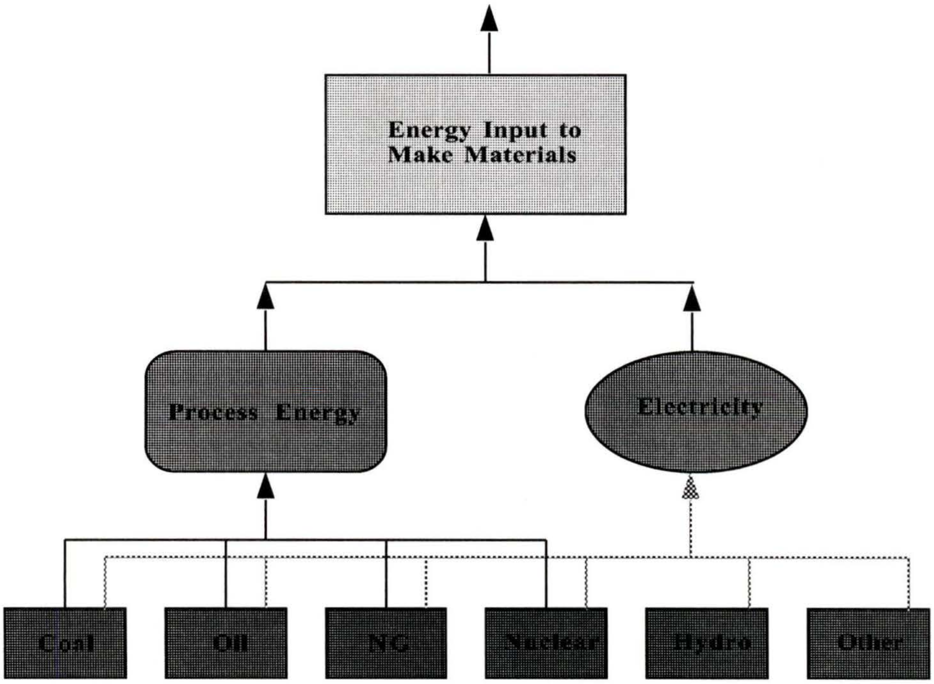

Figure 4.1 Energy Mix for Energy Input to Material Manufacture

CO_2-equivalent Emissions - Determination

CO_2-equivalent emissions resulting from the life-cycle of manufactured materials are estimated from the energy use of fossil fuels during that life-cycle. The Intergovernmental Panel on Climate Change (IPCC) [51] has estimated that "more than half of the anthropogenic greenhouse gas emissions originate from the energy system" and that fossil fuels make up "about 75% of the total energy use". In addition, the IPCC has also estimated that 95% of the carbon content of fossil fuels is emitted either "by the energy sector during conversion to fuels and electricity and distribution to final use... [or] at the point of end use." The remaining 5% can be considered "embodied in durable hydrocarbon-based materials such as plastics" [51]. This material use of fossil fuels would eventually lead to emissions of its embodied carbon, but these emissions are small compared to those from fossil fuel use in the energy system. The most significant source of greenhouse gas emissions from the manufacture of materials can therefore be assumed to come from the use of fossil fuels as energy sources for material conversion processes.

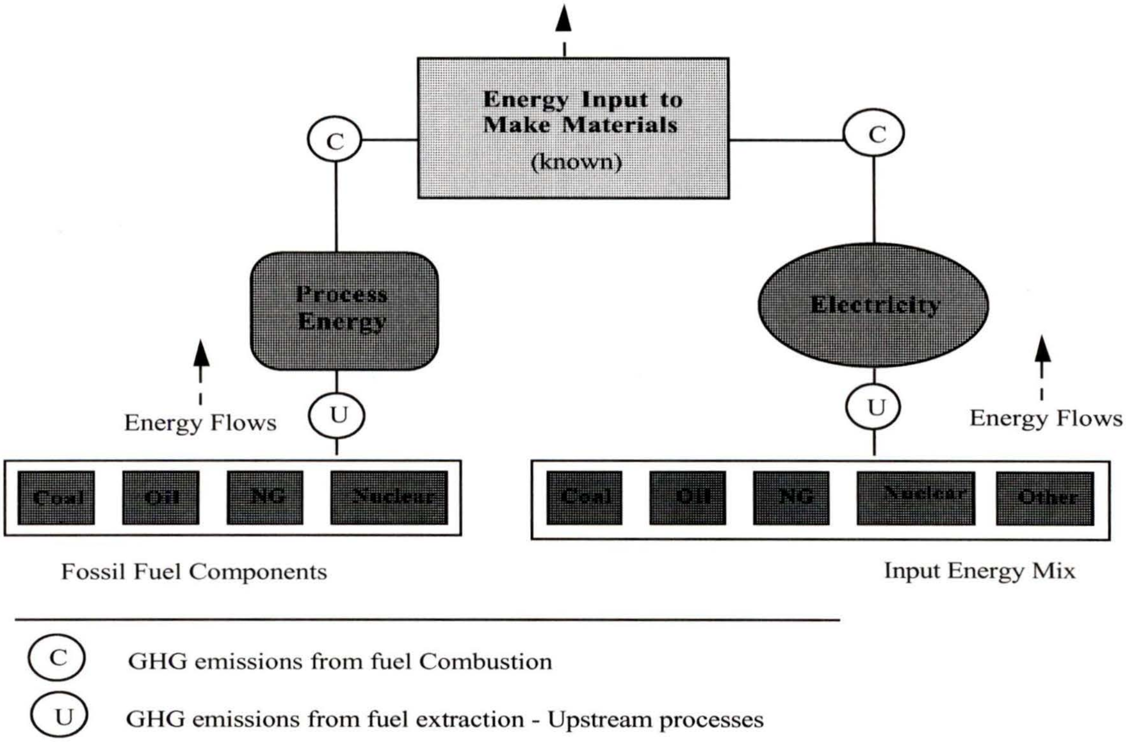

Figure 4.2 Schematic Representation of Method for Determining CO_2 Equivalent Emissions From the Use of Energy to Make Materials

Figure 4.2 illustrates the process for determining CO_2 equivalent emissions released by the use of energy to make materials. The energy input required to make or assemble materials is initially divided into its fossil fuel and electricity components. The electricity input is further divided into its fossil fuel and other primary energy sources, identified as the input energy mix. For process energy uses, CO_2 equivalent emissions are produced in two stages: upstream of the process and during combustion. Upstream includes feedstock recovery, transport, fuel production and fuel delivery to the processor. Combustion is taken to be combustion at a power plant.

Delucchi [3] estimated CO_2-equivalent emissions from four sources for electrical energy delivered to consumers (coal, oil, natural gas, and nuclear), and from the life-cycle, including recovery, processing, and delivery, of fuel available to consumers. He estimated the latter emissions for both the energy used to produce the materials in ICEV and alternate fuel vehicles (AFV), and for the energy used in the production of fuels for the ICEV or AFV.

With this in mind, the energy required to produce each material is determined and normalized (kJ/kWh of power plant output). This energy requirement is divided into its primary energy source components (coal, crude oil, natural gas, nuclear, others) and Delucchi's carbon-emissions factors for each energy source are applied. For process energy emissions, the IPCC's factors for carbon released during fuel combustion are added to Delucchi's upstream emission factors. For electric energy, Delucchi assumed that any CO_2-equivalent emissions from the use of the "other" energy sources are negligibly small compared to those from the four main sources [3]. In the short term, this assumption seems reasonable and has been carried through this thesis.

Calculation of greenhouse gas emissions from process energy used to manufacture materials is made according to the following formula:

$$T_{CO_2-equivalent\ emissions} = \sum_f T_{fuel_f} + \sum_f T_{electric_s} \qquad (4.3.1)$$

$$T_{fuel_f} = \sum_f fuelshare_f * energy_T * \left(DL_f + IPCC_f\right) \qquad (4.3.2)$$

T_{fuel_f} – total $CO_{2\,equivalent}$ emissions from use of fuel f for material $(gCO_{2\,equivalent}/kg)$

$fuelshare_f$ – portion of $energy_T$ supplied by fuel f

$energy_T$ – total energy required to produce material(kJ/kg)

DL_f – Delucchi's $CO_{2\,equivalent}$ emissions factor to fuel f $(gCO_{2\,equivalent}/kJ)$

$IPCC_f$ – The IPCC's CO_2 emissions factor in $(gC/kJ * 3.67\ gCO_2/gC)$

$$T_{electric_s} = \sum_f share_s * energy_e * DL_s \qquad (4.3.2)$$

$T_{electric_s}$ – total CO_2 emissions from electricity use for material $(gCO_{2\,equivalent}/kg)$

s – electricity source

$share_s$ – portion of power supplied to electricity generation by source s

$energy_e$ – total electrical energy required to make material T

DL_s – Delucchi's $CO_{2\,equivalent}$ emissions factor for source s $(gCO_{2\,equivalent}/kJ)$

Delucchi's emissions factors have been converted to S.I. units, and are listed in Table 4.6 along with the IPCC fuel combustion emissions factors.

CO_2-equivalent Emission Factors

Fuel (f)		IPCC	Electricity Source[a] (s)		
	Upstream[a]	Combustion[b]			
	g/kJ	g/kJ		g/kWh	g/kJ
Coal	0.0087	0.09	Coal	1296.9	0.360
Oil	0.015	0.07	Oil	1138.5	0.316
Natural Gas	0.011	0.05	Natural Gas	776.5	0.216
Nuclear	0.014	0	Nuclear	69.0	0.019
			Other[c]	0.0	0.0

Table 4.6 CO_2-equivalent Emissions Factors for Various Fuel Types and Electricity Source Types.

Values have been converted from g/10^6 BTU and g/kWh to g/kJ.

(a) Emissions factors include fuel compression or liquefaction, fuel distribution , fuel production, feedstock transport, and feedstock recovery. See Delucchi's text for more details [22].

(b) Combustion factors from reference [50].

(c) Emissions from the use of Hydro, Geothermal, Wind, Biomass, and Solar Power from U.S. National Power Mixes in 2000 are assumed negligible by Delucchi. [22].

Energy Source Breakdown

Unless otherwise stated, this thesis uses the primary energy source breakdown from the Energy Information Administration (EIA) projected U.S. average electricity mix for the year 2000 (EIA, Annual Outlook for U.S. Electric Power 1989, 1989) [3]. This average mix, shown in Table 4.7, is used for those cases where the energy users are located all over the country, and thus the "fuel input to the electricity they use is not likely to be significantly different than the national average mix" [3]. For those cases where the material is produced in a limited number of known cities, the average electricity mix determined by Delucchi for those cities has been used. An example of this would be the Dow membrane. It is known that this membrane was manufactured in Texas. Delucchi listed the energy mix supplied to electricity for two cities in Texas, and I have used the average mix of these two cities as representative of a closer approximation to the energy supply mix for all of Texas than would be the national average mix.

U.S. City	Coal	Nuclear	NG	Oil	Other
Houston, TX	0.314	0.117	0.564	0.005	0.0
Dallas, TX	0.515	0	0.48	0.005	0.0
Average	0.415	0.059	0.522	0.005	0.0
U.S. Average	0.570	0.195	0.094	0.055	0.086
Percent Diff.	37	230	82	1000	∞

Table 4.7 Electricity Generation Mix in 1988 by Type of Fuel in Selected U.S. Cities

Adapted from [3].

4.4 Non-Energy Related Material Production Emissions

4.4.1 TRI Database

The information in this section and all quotations are from the Executive Summary of the US Environmental Protection Agency (EPA) *Public Data Release Report: 1993 Toxics Release Inventory* [52]. The EPA requires that all facilities with manufacturing operations within Standard Industrial Classification (SIC) codes 20-39, that have at least ten employees, report releases of those chemicals listed in the EPA's Toxics Release Inventory (TRI) that they manufacture or process in excess of 25,000 pounds, or use in excess of 10,000 pounds. The 1993 TRI listed 316 chemicals and 20 chemical categories for which reporting was required. For the purposes of TRI reporting, a release is "an on-site discharge of a toxic chemical to the environment" [52]. Included in these discharges are air releases, surface water releases, releases to land within the boundaries of the facility, and contained releases into underground injection wells.

Air releases are divided into stack and fugitive emissions. Stack releases account for those that occur "through confined air streams," while fugitive emissions cover all remaining releases including "equipment leaks, evaporative losses from spills, and releases from building ventilation systems" [52]. Surface water releases include discharges to any body of water from both contained sources, such as "industrial process outflow pipes," and from runoff. Releases to land within the boundaries of the facility are reported for disposal of chemicals in on-site landfills, land treatment, and surface impounding, along with other accidental release methods such as spills and leaks. Finally, contained releases into underground injection wells are reported for injection into both Class I and Class V wells. Class I wells are located below the "lowermost underground source of drinking water" and are designed for injections of liquid hazardous wastes. Class V wells are located above or within "underground sources of drinking water." The potential environmental and health impacts of these two types of wells obviously differs, however TRI reporting as of 1995 does not differentiate the two. The primary external costs associated with these emissions will come from leaks, spills, and other 'non-controlled' [13] releases. [52]

4.4.2 TRI Chemicals Released During Material Production

The process used in this thesis to determine the TRI controlled chemicals released during the production of the component materials in the ICE engine block and PEM stack follows a three step process. Releases are normalized on the basis of the power generation system's output (ie g chemical released per kWh of energy produced.) During the time of this research, TRI data was available up to reporting year 1992.

> STEP 1. The Right-To-Know (RTK) Network's copy of the US EPA's TRI database is used to develop a list of the quantity of TRI chemicals released annually to the environment during the production of materials classified under Standard Industrial Classification (SIC) codes [53]. This study includes stack and fugitive air releases, water releases, and land releases. Underground storage and off-site transfers are not included as these represent a direct cost to the manufacturing facility and are therefore assumed to be internalized in their cost structure.

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[13] This is as opposed to what I chose to call 'semi-controlled' releases such as those through confined air or water streams. Pollutants released in a semi-controlled manner are more likely to be trapped and properly disposed of than are those released in a non-controlled manner. The costs of pollutants which are released in a semi-controlled manner are therefore more likely to be internalised.

STEP 2. Total U.S. production quantities for the FC and ICE component materials during the year of interest are determined, and this information is used together with the TRI release data to estimate the quantity of each TRI controlled chemical released to the environment per unit (kg) of material produced.

STEP 3. This estimate is normalized on the basis of FC or ICE system output (kWh). The amount of chemical released per kg of material produced is multiplied by the total mass of material in the FC or ICE according to the following formula.

$$\frac{m_{TRI}}{m_{material}} * \left(\frac{m_{material}}{kWh_{output}}\right) = \left(\frac{m_{TRI}}{kWh_{output}}\right) \tag{4.4.1}$$

Where: m_{TRI} - total mass of chemicals released

$m_{material}$ - total mass of material produced

$\left(\frac{m_{material}}{kWh_{output}}\right)$ - normalized mass of materials in ICE or FC (4.4.2)

$\left(\frac{m_{TRI}}{kWh_{output}}\right)$ - normalized mass of chemical released during production (4.4.3)

CHAPTER 5 - MATERIALS

The determination of life-cycle energy and emissions impacts associated with the materials in PEMFCs or ICEs requires knowledge of the material production processes and energy requirements, together with raw material inputs and outputs. This chapter provides this background information for each of the primary raw materials in the PEM fuel cell and the ICE: FC membrane, Teflon®, carbon graphite, platinum, carbon black, carbon fibre, aluminum, steel, cast iron, copper, lead, rubber and plastics. Chapter sub-sections briefly overview the material manufacturing processes together with the assumptions and estimations used to determine the energy required to produce both 'new' (virgin and pre-consumer recycled materials) and post-consumer recycled materials (the 'recycle' option.) Additional sections summarize the material inputs and outputs for the production processes. This research is limited to an examination of primary raw materials only. For example, sulphur trioxide (SO_3) is an ingredient in Nafion®. The SO_3 represents a secondary raw material to the fuel cell and as a result its life-cycle impacts are not examined. An ideal analysis would include and even extend beyond secondary raw materials, and it is recommended that this process be undertaken in the future.

5.1 Membrane

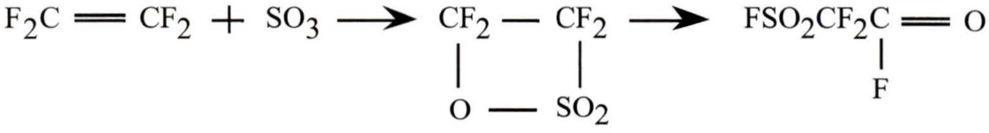
The membrane in a PEM fuel cell acts as both a separator for the reactant gases and as the electrolyte, or ionic conductor between the anode and cathode. The first few versions of PEM fuel cells used styrene based copolymers for the membrane. These were replaced in the late sixties with perfluorinated sulphonic acid membranes developed under the tradename Nafion® by E.I. DuPont de Nemours & Co. [8]. In 1988 the Dow Chemical

Company produced a perfluorinated membrane similar to Nafion®. The Dow membrane is more complicated and thus more expensive to manufacture than Nafion®, however Ballard Power Systems has reported higher power densities in test PEM fuel cells using the Dow membrane than Nafion® 115 and 117 [35]. This same source reports that Ballard Advanced Materials Corp. (BAM) are developing lower cost, low or non-fluorinated polymers for use in PEM cells. As will be shown in this report, the removal of fluorine from membranes has the potential to represent an environmentally responsible step. Non-fluorinated membranes represent current state-of-the-art, therefore the specific details of their construction and production are trade secrets. Thus, this study focuses on the more established fluorinated membranes from DuPont and Dow.

5.1.1 Membrane Material Production

The Dow and Nafion® families of membranes have similar chemical structures. This section focuses on Nafion® because more detailed information was available on the production of these membranes than of the Dow membranes. The opposite is true for the identification of TRI chemicals released during membrane production.

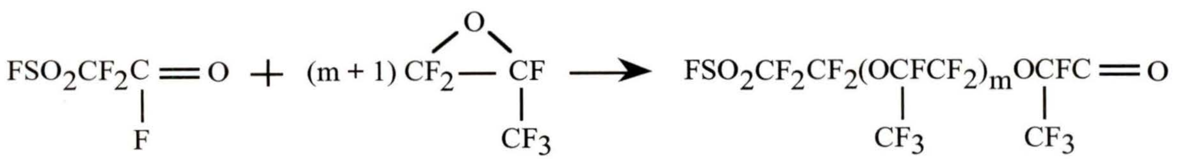
Nafion® is produced in a sequence of steps [35] [54][58]. Commercially available tetrafluoroethylene (TFE) is initially reacted with SO_3 to produce a 'cyclic sultone' according to Equation 5.1.1.



Adapted from Appleby & Foulkes (1993)

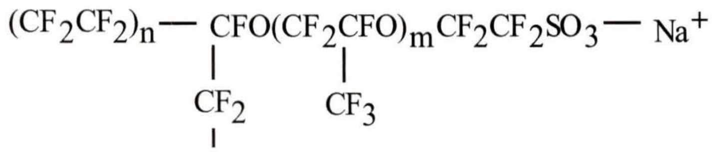
(5.1.1)

The rearranged product is reacted with (m+1) molecules of commercially available hexafluoropropylene epoxide according to Equation 5.1.2.



Adapted from Encyclopedia of Polymer Science and Engineering (1989) (5.1.2)

The reaction product is heated in the presence of sodium carbonate and the resultant is copolymerized with additional tetrafluoroethylene to form a melt-fabricable resin. The resin is formed into the desired shape and reacted with a solution of sodium or potassium hydroxide to yield Nafion®, the structure of which is shown in Equation 5.1.3.



$$(CF_2CF_2)_n-\underset{\underset{|}{CF_2}}{\underset{|}{C}}FO(CF_2\underset{CF_3}{\underset{|}{C}}FO)_mCF_2CF_2SO_3-Na^+$$

From Appleby & Foulkes (1993) m = 1, n = 1-6
For the Dow membranes, m = 0 (Nafion®) (5.1.3)

5.1.2 Membrane Raw Materials

Raw materials for the membrane include tetrafluoroethylene, SO_3, hexafluoropropylene epoxide, sodium carbonate, and sodium or potassium hydroxide. It is not possible to determine the quantities of these ingredients based on public information.

5.1.3 Energy Input to Membrane Production

The energy required to produce the membrane and membrane materials is approximated by the energy required to produce generic 'plastics', 100 MJ/kg [3]. The model assumes that the energy required to recycle membranes is 20% of that required to produce new material, or 20 MJ/kg. This fraction represents the author's engineering estimate.

5.1.4 Recycling/Reuse

The 'recycle' option assumes that 70-80% (80% base case) of the membrane in a fuel cell will be recovered and ultimately recycled and refined at 20 MJ/kg [55]. The remaining 20-30% of the membrane will be disposed of as solid waste. The amount of material input to the FC manufacturing process that is not provided by membrane recycled from the FC will come from "standard" production and is produced at about 100 MJ/kg. In this case, "standard" refers to the production of the membrane as described in Section 5.1.1.

5.1.5 Emissions from Membrane Production

Dow's perfluorosulfonate membrane (hereafter referred to as "membrane") is considered representative of Nafion® for the purposes of determining emissions. This assumption is reasonable since future membranes are more likely to follow the Dow structure than the previous Nafion® ones, evidenced by the fact that Dow is licensing its membrane technology to DuPont as of fall 1995 [56].

Dow's membrane was produced in Texas. The EPA's TRI database identifies all TRI chemicals released from the Dow Chemical Company Texas Operations facility in 1990 [53]. The Toxic Substances Control Act (TSCA) database gives the minimum 1990 total annual production quantities from the same facility, which manufactures primarily in the area of SIC code 2812 (alkalies and chlorine)[14] [57]. Production quantities of many of this facility's TSCA registered chemicals (for example ethylene and methanol) were withheld from the TSCA database due to confidentiality, therefore the total production volume used in this research represents a minimum plant production only [57]. Actual production volumes would most likely be an order of magnitude larger [15].

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[14] This facility also manufactures in the areas of SIC codes 2813 (industrial gases), 2819 (industrial inorganic chemicals), 2821 (plastics materials and resins), 2822 (synthetic rubber), and 2865 (cyclic crudes and intermediates) [52]. SIC code 2821 is considered significant for the manufacture of ionomer membranes.

[15] From Standard & Poor's Industry Surveys for January 1995, the US annual production of ethylene for 1992 was on the order of 40 billion pounds, and for methanol it was 8.7 billion pounds. These figures represent at a minimum, two times the total chemical production volume for Dow's Texas Operations facility. By the fact that their

The above data allows a determination of the maximum average release of each TRI chemical per kilogram of total production at Dow's Texas facility. This number estimates the amount of each chemical that may be released during the manufacture of a unit mass of membrane produced at the same facility. The chemicals list is highly aggregated and includes chemicals which are not related to the manufacture of the membrane. It is therefore edited to include only those chemicals known to be involved in the Nafion® membrane production process, as described in Section 5.1.1. In the absence of more accurate data, this provides a measure of the potential level of environmental releases caused by the manufacture of the membrane.

5.2 *Teflon®*

Teflon® is DuPont's trade name for polytetrafluoroethylene (PTFE). Other manufacturers of PTFE include Hoechst (Holtaflon) and Daikin Kogyo (Polyflon) [58]. PTFE is a perfluorinated straight-chain high polymer $-(-CF_2-CF_2-)_n-$ made by polymerizing tetrafluoroethylene. PTFE is described as being difficult to polymerize and process, and thus more expensive to produce than other thermoplastics. [60]

5.2.1 Tetrafluoroethylene Manufacture

Tetrafluoroethylene is the principal raw material in Nafion®. It is manufactured in stages, beginning with the manufacture of hydrogen fluoride (HF) from calcium fluoride (CaF_2) and sulphuric acid (H_2SO_4), with calcium sulphate ($CaSO_4$) as a resultant by-product [58]:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF \tag{5.2.4}$$

From Encyclopedia of Polymer Science and Engineering (1989)

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production quantities are being withheld due to maintain confidentiality, it seems reasonable to assume that Dow's Texas Operations may produce a large share of these chemicals.

Next, methane (CH_4) is reacted with chlorine to produce chloroform ($CHCl_3$) and by-product hydrogen chloride (HCl):

$$CH_4 + 3\,Cl_2 \rightarrow CHCl_3 + 3\,HCl \tag{5.2.5}$$

From Encyclopedia of Polymer Science and Engineering (1989)

The chloroform is partially fluorinated with the hydrogen fluoride to produce chlorodifluoromethane ($CHClF_2$) together with more by-product hydrogen chloride:

$$CHCl_3 + 2\,HF \rightarrow CHClF_2 + 2\,HCl \tag{5.2.6}$$

From Encyclopedia of Polymer Science and Engineering (1989)

Antimony chloride is used as a catalyst in this fluorination process. The final stage involves the "pyrolysis" of the chlorodifluoromethane to tetrafluoroethylene, with the associated production of still further hydrogen chloride waste:

$$2\,CHClF_2 \rightarrow CF_2{=}CF_2 + 2\,HCl \tag{5.2.7}$$

From Encyclopedia of Polymer Science and Engineering (1989)

In addition to the $CaSO_4$ and HCl wastes, a large number of trace by-products are formed in the TFE manufacturing process, including "small amounts of highly toxic perfluoroisobutylene, $CF_2{=}C(CF_3)_2$" and "significant quantities ... of hexafluoropropylene [$CF_2{=}CFCF_3$], perfluorocyclobutane, 1-chloro-1,1,2,2-tetrafluoroethane, and 2-chloro-1,1,1,2,3,3-hexafluoropropane." [58]

5.2.2 TFE Raw Materials

Raw materials for tetrafluoroethylene include CaF_2, H_2SO_4, CH_4, Cl_2, and antimony chloride. As with the membrane materials, there is insufficient information to determine the quantities of these raw materials, as some, like antimony chloride do not appear in the process 'equations.'

5.2.3 Health and Safety Issues

There are no major health issues associated with TFE. It has no irritating effect on the skin and test animals showed no adverse reactions to ingestion or inhalation of TFE dust [60]. Safety concerns centre around the decomposition products formed when TFE burns in air: carbon tetrafluoride, carbonyl fluoride, and carbon dioxide. TFE can also form explosive mixtures with air and oxygen. TFE itself is non-toxic, but may be contaminated by highly toxic compounds. [60]

5.3 Carbon-Graphite

5.3.1 Carbon-Graphite Production

A rough description of the process used to manufacture the graphite bus plates for Ballard's PEM fuel cells led to the conclusion that the moulded carbon-graphite is not mined, but rather is manufactured, or synthetic [59]. The Encyclopedia of Chemical Technology is the principal reference for this section [60]. Carbon products are made by first mixing a ratio of coke filler with a pitch binder and then moulding or extruding the mix to a given form. The binder is set and the shape controlled by heating the formed mix in a packed container.

The carbon graphite used in PEM fuel cells is similar to that used in furnace electrodes. The primary raw materials (in terms of total weight) in artificial graphite furnace electrodes are petroleum coke and coal tar pitch. The calcined petroleum coke is initially crushed, sized and milled in preparation for processing. Calcinating is a process of "heating raw coke to [1200 - 1400°C], removing volatiles [primarily methane and hydrogen] and shrinking the coke to produce a strong, dense particle" [60]. After calcinating, less than 0.5% of volatile matter, in the form of hydrocarbons, remains in the raw coke [55]. Burning the extracted volatiles during the calcinating process provides the necessary heat. For coarse grained products (particles ≤ 25 mm diameter) such as furnace electrodes, the pitch and coke are proportioned in approximately a 1:4 ratio [60].

The first processing step is the mixing and blending of the coke filler and the pitch binder to evenly distribute the binder over the grains. Mixing is followed by a 15-30 minute cooling cycle. After mixing and cooling, the carbon is formed as nearly as possible to the finished electrode shape and cooled in air. Forming not only serves to reduce scrap, but it compresses the mix into a dense mass, ensuring that the "pitch-coated filler particles and flour are in intimate contact" [60].

After forming, the carbon electrodes are baked to convert the thermoplastic pitch binder to solid coke and to shrink the product by evolving volatiles. Weight loss of 30-40% occurs during baking, resulting in a loss of "approximately 150 cm^3 of volatiles at standard condition ... per gram of pitch binder" [60]. Impregnation of the product with additional pitch can be performed at this point in order to adjust the properties of the finished graphite product. The final stage in the graphite production is the graphitization which consists of electrical heat treatment to 3000°C, in order to "cause the carbon atoms in the petroleum coke filler and pitch coke binder to orient into the graphite lattice configuration" [60].

5.3.2 Raw Materials

The base case raw materials are shown in Table 5.8. Calculations are shown in Appendix A.

Material	Approximate Quantity (g/kWh)
Graphite input to FC manufacturing process	0.3
Raw material coke	0.294
Raw material pitch	0.044

Table 5.8 Base Case Raw Materials for Graphite in Proton Exchange Membrane Fuel Cell

5.3.3 Energy Input to Carbon-Graphite Production

The total electric energy inputs to the carbon production process are estimated to average a minimum of 4.5 kWh/kg carbon graphite [16] [60]. Hudson estimates an energy mix for graphite production of 19.6% oil, 39.6% natural gas, and 40.8% electric[17] [20]. From this it is determined that the total normalised energy input is 42 MJ/kWh (MJ/kWh fuel cell output). The numerical values for the energy inputs of oil and NG follow from this total using Hudson's fuel mix fractions. The energy required to recycle carbon-graphite is assumed to be 20% of that required to produce new material, or 8.4 MJ/kg. This figure is based on an engineering estimate.

5.3.4 Recycling/Reuse

The 'recycle' option assumes that 70-80% (80% base case) of the carbon graphite in a fuel cell can be recovered and ultimately recycled. The remaining 20-30% of the graphite will be disposed of as solid waste. The amount of material input to the FC manufacturing process that is not provided by graphite recycled from the FC will come from 'standard' production, as described in the Section 5.3.1, and is produced at about 42 MJ/kg.

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[16] From [23], Vol 4, page 971. It is not clear if this energy input value represents the total energy input to the entire production process, or to the graphitization stage only. I have assumed that the value applies to the entire process, but represents the electrical energy input only.

[17] It should be noted that Hudson qualifies these figures by writing that "too little is known of the process to make reasonable assumptions."

5.3.5 Emissions From Carbon-Graphite Production

TRI Emissions from Carbon-Graphite Production

TRI emissions are estimated following the procedure outlined in Section 4.4.2, as no TRI listings were found for individual firms known to be producing furnace electrodes. SIC code 3624 (Carbon and Graphite Products) is assumed to be representative of the carbon-graphite manufacturing industry. The estimation of the total US production volume of carbon and graphite products assumes that all of the coal carbonized [18] in the U.S. is subsequently used in carbon and graphite products, with no exports or imports of coke. Further assuming that all carbon and graphite products produced in the U.S. are prepared as furnace electrodes allows an estimation of the total carbon and graphite products produced. (These are first order assumptions that give an upper limit to the U.S. production, and thus a lower limit to the TRI emissions produced per unit of production.) In 1992, approximately 29 million (M) tonnes of coal were carbonized in the U.S. [61]. This allows the calculation of the production of carbon and graphite products to be a maximum 19-22 million tonnes. This calculation is based as follows:

> The carbonized coal is first calcinated, where it is reduced in weight by 10-14%, from 29 M tonnes to 25-26 M tonnes. The calcined coke is combined with pitch in a ratio of 4:1, increasing the total material weight to approximately 31-32 M tonnes. The combined materials are baked, further reducing the weight by 30-40%, leaving in the range of 19-22 M tonnes of finished product.

5.3.6 Environmental and Health Issues

Environmental Issues

Sulphur is released as one of the volatile compounds during graphitization. These releases can be reduced by choosing low-sulphur cokes as the raw material.

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[18] Carbonization refers to the process of reducing to carbon or coke. Fowler, H. W. and F. G. Fowler. The Concise Oxford Dictionary. 5th Edition, Clarendon Press, Oxford, UK, 1964.

Health Issues

The main human health concern from coal tar waste sites is the carcinogenic potential of polycyclic aromatic hydrocarbons [48][60]. The health risk this poses to workers can be minimized through the use of protective clothing and respirators, however these protective devices do not guard against accidental releases of fumes or dust to the environment.

5.4 Platinum

The platinum group metals (pgm) include platinum (Pt) palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir), and ruthenium (Ru). These metals are found together in differing proportions in the world's major pgm deposits. Platinum is the most abundant of the pgm metals, and composes from 19-59% of the pgm deposits [62]. Available new platinum (not recycled) supplies were estimated at 141 tonnes/year in 1994 [64] and world resources in 1985 were estimated at 99.5 thousand tonnes [63].

5.4.1 Platinum Production

Over 98 per cent of the world's platinum comes from South Africa, Canada and the former Soviet Union (FSU) [62]. In Canada, China, and Russia, platinum is produced primarily as a by-product of nickel (in Russia, copper-nickel) mining. Canada has one primary platinum group metals mine, North American Palladium, while the United States Stillwater mine supplies the bulk of US internal platinum supplies. In South Africa and Russia, platinum is mined in both open pit and underground mines. South African mines exploit various pgm-containing reefs, which may or may not also contain economic concentrations of copper, nickel and/or cobalt [64]. These latter metals would be mined as by-products, or revenue supplements to the pgm-mining operations [64].

In the world's pgm mines, metal grades range from 0.9-27 g pgm/tonne ore, with the average being around 8 g/tonne [62]. Mine ore is crushed and ground to liberate the minerals, which are separated from the waste rock by froth flotation [65]. The resulting concentrate contains pgm together with copper, nickel and other precious metals. This is dried, pelletized, and then smelted at high heat in electric arc furnaces [65][62]. The product matte is converted with the addition of oxygen, slow cooled, and sent to base metal refineries. Sulphur dioxide is generated during conversion [65]. The slag waste from the smelters is milled to retrieve any matte which can be collected by froth flotation and returned to the smelter. The final slag waste is either dumped or sold as road construction material.

Precious metal refineries use a chloride technology (chlorine and HCl) to separate pgm from other precious metals [65].

5.4.2 Platinum Raw Materials

Materials input to the platinum production process include ore, water, and oxygen. This is a partial list only, however complete information is unavailable. Since the average ore grade is about 8 g pgm/tonne of ore, the ore input must be at least 125 kg ore/g pgm output. Since 19-59% of pgm output is platinum, the ore input must be at least 212-658 kg ore/g Pt. The majority of platinum deposits will fall within the lower end of this range, since the proportion of Pt in pgm is high (25-59%) in South African, Canadian, and Russian deposits.

5.4.3 Energy Input to Platinum Production

The largest pgm producing country (South Africa) produces nickel as a by-product of pgm mining, while the next two largest producers (Canada and the USSR) recover pgm as a by-product of nickel mining. Nickel and platinum are therefore linked at the raw material extraction stage and an examination of one process should give insight into the other. As is the case with all co-production, however, this linkage complicates the task of allocating energy usage among the co-products. In particular, the complication arises when determining the percentage of total energy input that should be attributed to platinum production. Possible assumptions range from assigning all of the production energy to platinum group metals, for example in the case of South African mines where nickel and copper are produced as by-products only, to assigning all of the production energy to nickel, for example in the case of Canadian mines where platinum group metals are the by-products. In the latter case, the production of platinum would require only the relatively minor energy needed to refine the pgm from concentrate (estimated to cost approximately CAN$ 6.00/ounce Pt [66]). The former assumption requires a more complicated approach outlined in Appendix A, resulting in an energy requirement to produce platinum that is on the order of 0.11-0.26 GJ/kg.

In conclusion, the energy required to produce platinum can range from 0 - 0.26 GJ/kg. This study focuses on the impacts of these two extremes, however any intermediate value could also be used given different assumptions about the allocation of energy use. In either case, the energy required to recycle platinum would be significantly less (at the most 20%) than that required to mine and smelt it. This assumption represents an engineering estimate.

5.4.4 Fuel Cell Catalyst and Platinum Black Production

Most of the steps in the preparation of the catalyst layer in PEM fuel cells are proprietary, but "there is 100% platinum usage" [67]. If platinum black is chosen for the catalyst, "the only significant energy usage is in heating the platinum salt solution to boiling during preparation of the platinum black. Other steps are done at room temperature with no emissions or significant waste or effluent, apart from those from washing the platinum black" [67].

5.4.5 Recycling/Reuse

PEM Fuel Cell

The 'recycle' option assumes that 80-95% (95% base case) of the platinum or platinum black in a fuel cell can be recovered and ultimately recycled. This range represents the author's engineering estimate. The remaining 5-20% of the platinum will be disposed of as solid waste. The amount of material input to the FC manufacturing process that is not provided by platinum recycled from the FC will come from 'standard' production, as described in the Section 5.4.1.

5.4.6 Emissions from Platinum Production

Following the same logic as that was used to determine the energy input to platinum production, the emissions from platinum production should be similar to emissions from the mining and smelting of other non-ferrous metals. The IPCC estimates that the major GHG emission from the production of copper and other nonferrous metals is CO_2 associated with the energy needed to smelt from ore [51], although they did not provide an estimate on the levels of those emissions.

Other waste products include mine tailings, water, dust, sulphur dioxide, slag, toxic organics, toxic metals, cyanide, phenols, ammonia, oil and grease, and fluorides [63]. The water is treated prior to discharge into the environment [63]. In older plants sulphur dioxide was vented to the atmosphere. In newer ones it is mostly trapped by sulphur scrubbers [65]. Impacts of past SO_2 releases are visible in and around Sudbury, Ontario as dead lakes and black rocks. The waste slag can be sold as road construction material.

5.4.7 Health and Environmental Effects

Health Effects

Potential health problems associated with the refining of platinum and the preparation of platinum black are restricted to worker sensitization to certain platinum compounds. Sensitization can occur in workers during the later stages of the refining process, however proper industrial hygiene procedures should minimize if not eliminate the risk of this occurring [68]. In a worse case scenario platinum sensitized workers would have to be transferred to a position not requiring contact with platinum. This would ensure no long term effects of the sensitization.

There are no known health effects associated with the metallic form of platinum, including platinum black (apart from the safety aspect of keeping it away from flammable organics to prevent catalytic ignition) [68].

Environmental Effects

There is no evidence of "harmful environmental effects as the result of emissions of platinum during the mining and refining of this metal. The value of the metal ensures that great care is taken to avoid significant losses" [68].

5.4.8 ICE Use of Platinum

Platinum is used in several stages of the automobile manufacturing processes for both ICE and FC vehicles [64]. The catalyst also has uses unique to each of the vehicles examined in this thesis. In ICE vehicles, the largest and most well known use of platinum is in emissions controlling autocatalysts (catalytic converters) [62]. The platinum can be used on its own, in a platinum-rhodium (Pt-Rh) combination, or in combination with rhodium and palladium as in a three-way automobile catalyst [62][68]. Three-way catalysts or a combination of catalyst systems (a palladium-rhodium catalyst used in conjunction with another containing platinum) provide the broadest on-board vehicular emissions controls [69]. Autocatalysts control exhaust emissions by oxidizing carbon monoxide and unburnt hydrocarbons, as well as reducing nitrogen oxides and the emissions of carcinogenic polyaromatic hydrocarbons [68].

Three-way catalysts for a typical mid-sized sedan contain 1.5-2.2 g of platinum, 0.31-1.05 g of palladium, and 0.15-0.31 g of rhodium ([63] 1.5g Pt, 0.62g Pd, 0.15g Rh; [69] 2.18g Pt, 0.31g Pd, 0.31g Rh; [70] 1.4-2.2 g Pt, 0.7-1.1g Pd) [19]. Platinum in ICE vehicles is also used in oxygen sensors and, more recently, in spark plugs [69][64]. Oxygen sensors (lambda probes) are equipped with a platinum tip to detect minute changes in the amount of oxygen in exhaust gases. To ensure the efficient operation of autocatalysts, the engine must receive an air-fuel mixture close to stoichiometric. The

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[19] The big three automotive manufacturers are studying a move towards higher palladium loadings due to its lower cost and lower sensitivity to heat compared to platinum. Depending on the engines and vehicles, an option under investigation would be an all-palladium converter [70].

number of oxygen sensors used in vehicles is expected to increase due to US legislation requiring monitoring of emissions control components in North American vehicles manufactured from 1996 [64].

Platinum tipped spark plugs are gaining use in European and Japanese vehicles, and have been widely used in new North American vehicles since 1993. These plugs are estimated to contain 0.01 - 0.02 g of platinum each [69] and the loading is expected to increase as manufacturers seek to extend the electrode life span [64].

In 1994, total world wide platinum demand for oxygen sensors and spark plugs was 20% of the Pt demand for autocatalysts [64]. This percentage is expected to increase. The use of palladium and rhodium in autocatalysts has been growing rapidly in the 1990s (total Pd use for autocatalysts increased 35% from 1993 to 1994, and total world wide rhodium demand for autocatalysts rose 7% in the same period [64]) and is expected to continue rising over the next few years, led by one of the Big Three US auto makers and by European auto makers.

5.4.8.1 Recycling/Reuse of Platinum from Autocatalysts

World wide recovery of platinum from autocatalysts reached an estimated 9950 kg in 1994 [64]. At a platinum loading of 1.5 - 2.0 g per autocatalyst [63][69] and a 100% recovery rate, this represents approximately 6.6 - 5.0 million autocatalysts recovered. Assuming that approximately 40 million automobiles and light trucks are scrapped every year [71] the current platinum recycling rate from autocatalysts would be approximately 12-16%. This recycling rate represents a world wide average and the actual recycling rate for individual parts of the world is expected to vary from this average by as much as +15 to -10% [20].

Platinum recovery levels rose 16% from 1993 to 1994 and are expected to keep rising through 2000, in part due to the increasing number of scrapped vehicles containing high pgm loadings, and in part due to efforts to increase the overall recycling rate of automotive

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[20] This comes from looking at 1994 usage to recovery ratios for Pt in autocatalysts [64]. The world wide ratio stands at 17%. The ratio for North America, however, is approximately 35% and for the "Rest of the World" (Johnson Matthey's term - excluding North America, Japan, and Europe) it is approximately 2%. I have estimated that platinum recovery to vehicles scrapped ratios would follow a similar trend.

parts [64]. Oxidation catalysts have been in use in North America since the 1970s, and since 1983 most North American cars have been equipped with the higher pgm loaded three-way catalysts. More of these later model vehicles were scrapped in 1994 than in 1993, and this accounts for the higher recovery of platinum in 1994 than in 1993. Johnson Matthey explain that autocatalysts did not come into widespread use in Western Europe until the late 1980s, and thus only a small proportion of vehicles scrapped in Europe in 1994 contained pgm [64]. As the later model vehicles begin to be scrapped in greater numbers, the pgm recovery rate from Europe should increase. Similar arguments can be made for Japanese and "Rest of the World" vehicles.

The European Union set an objective of recycling 85% of the materials in a vehicle by early next century [64]. It is likely that similar objectives will be attempted by North American auto makers if Europe proves successful. Thus an ultimate average recycling recovery rate of pgm from autocatalysts of 85% is not unlikely in the next century.

5.4.8.2 Emissions from ICE Use of Platinum

A small amount of platinum and palladium, estimated to be less than 0.8-1.9 micro-grams per km [21] is emitted from the catalytic converter through the vehicle exhaust system during use. A study by Hodge and Stallard (1986) reported Pt concentrations of 0.037 to 0.68 ppm in dust on the leaves of roadside plants at a distance of roughly 60 cm from the road edge [72]. These observations were taken in conditions of light to heavy traffic (14,000 - 156,000 average daily vehicle count) in San Diego California in 1986. Hodge and Stallard found these concentrations to be "much higher than the reported natural abundance of platinum group metals ... of 0.005 ppm". The authors of this study make no comments on the effects that this possible increase in platinum concentrations from auto emissions may have on the environment, however Seiler reports that the emitted material is "in a chemical form that is physiologically innocuous. Extracts [of emitted platinum] did not elicit a response from platinum sensitized workers" [68].

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[21] Researchers at General Motors reported this rate of emissions in 1977 [67]. Converter technology has advanced since 1977, and thus in-use emissions of Pt should be lower than the value reported in the GM study, to a minimum of zero.

In summary, although platinum is used in both FCV and ICEV, fuel cell vehicles use three orders of magnitude more platinum per kW (one order of magnitude more Pt/kWh) than do internal combustion engine vehicles, with correspondingly increased energy requirements and greenhouse gas emissions.

5.5 Carbon Black

Carbon black is used in PEM fuel cells as a support for the platinum catalyst.

5.5.1 Carbon Black Production

The US is the largest manufacturer of carbon black followed closely by Russia, producing approximately 23% and 19% of the world's capacity respectively [60].

The Encyclopedia of Chemical Technology describes five methods for manufacturing carbon black: the oil-furnace, thermal black, acetylene black, lampblack, and impingement (or channel, roller) processes [60]. Popular catalyst support materials for use in acid fuel cells have been Cabot Corporation's Vulcan XC-72R, Monarch 1300, Regal 660R, and Black Pearls 2000 (all furnace blacks), and Gulf Corporation's Shawinigan acetylene black (a thermal black) [13][42]. Since most carbon blacks (95%) are manufactured using the oil-furnace process, this method is chosen as the base case for this thesis [60]. The oil-furnace method produces blacks containing greater than 97% elemental carbon along with trace amounts of hydrogen, oxygen, sulphur, mineral oxides, salts, and absorbed hydrocarbons. This method is based on the "partial combustion [in air] of liquid aromatic residual hydrocarbons" [60]. Natural gas combustion provides the heat necessary to vaporize the atomized feedstock and decompose it into carbon black and hydrogen. Products of the combustion reactions are carbon dioxide, water and tail gases consisting mainly of water, nitrogen, CO, CO_2, and hydrogen. Feedstocks in the US are primarily (95%) the decant oils from petroleum refining operations. The remaining feedstock are tars obtained as by-products from ethylene production.

5.5.2 Raw Materials for Carbon Black Production

The production of carbon black requires material inputs of decant oils from petroleum refining operations and/or air.

5.5.3 Energy Input to Carbon Black Production

The energy input to oil-furnace carbon black is in the range of 93 - 160 MJ/kg [60]. The base case energy utilization is 126.5 ± 33.5 MJ/kg. The production of 100% recycled carbon black requires approximately 20% of the energy required to produce new material. This fraction represents the author's engineering estimate.

Input Energy Mix for Furnace Black Production

This thesis assumes an input energy mix for the production of thermal blacks to be:

Oil Fraction = 67.5 ± 11.5 %
NG Fraction = 22 ± 21 %
and Electricity Fraction = 10.5 ± 9.5 %

The derivation of these base case values is shown in Appendix A.

Electricity Fuel Supply Mix

Carbon black manufacturing facilities in the US are centred in the south-central and south-eastern states [60]. The average mix of fuels supplied to electricity generation in this region is significantly different from the US national average mix, as shown in Table 5.9. It is therefore worthwhile using the adjusted average.

	Fuel Share			
U.S. City	Coal	Nuclear	NG	Oil
New Orleans, LA	0.071	0.305	0.617	0.007
Houston, TX	0.314	0.117	0.564	0.005
Dallas TX	0.515	0	0.48	0.005
Virginia	0.518	0.43	0.002	0.058
Kansas	0.793	0.179	0.024	0.004
Ohio	0.784	0.138	0.065	0.005
Oklahoma	0.502	0	0.498	0
Average	0.500	0.167	0.321	0.012
St. Dev.	0.235	0.145	0.256	0.019
U.S. Average	0.570	0.195	0.094	0.055
Percent Diff.	14	14	241	78

Table 5.9 Calculation of Average Fuel Mix Supplied to Carbon Black Electricity Generation in Selected South-Central and South-Eastern States.

Adapted from [3], Table D.1

5.5.4 Recycling/Reuse

The ‘recycle’ option assumes that 80-90% (90% base case) of the carbon black in a fuel cell can be recovered and ultimately recycled. This range represents the author’s engineering estimate. Thus, 80-90% of the carbon black in use in the FC will be recycled and refined at 30 MJ/kg. The remaining 10-20% of the carbon black will be disposed of as solid waste. The amount of material input to the FC manufacturing process that is not provided by carbon black recycled from the FC will come from ‘standard’ production, as described in the Section 5.5.1, and is produced at about 127 MJ/kg.

5.5.5 Emissions from Carbon Black Production

Material outputs from the production of carbon black include carbon dioxide, water, and tail gases (water, nitrogen, carbon monoxide, carbon dioxide, hydrogen).

TRI Emissions

TRI emissions are estimated following the procedure outlined in Section 4.4.1. Emissions in 1992 from U.S. industries in SIC code 2895 (Carbon Black) are normalised with respect to the 1992 U.S. production of carbon black. This production value is estimated to be 1.23 M tonnes of carbon black [73].

5.5.6 Health Hazards

Statistical studies on the frequency, over a 17 year period, of cancer in long-term employees in a carbon black plant showed no evidence of increased cancer risk from exposure to industrial carbon black [60]. Similar results have been found in studies on carbon black dust inhalation and intratracheal administration with animals. The OSHA regulations limit the average exposure level to carbon black dust at not more than 3.5 mg/m^3 air.

The manufacture of carbon black produces impurities such as the salts of toxic metals and adsorbed polynuclear hydrocarbons (PNAs), a few of which are known to be mutagens and/or animal carcinogens [60].

5.5.7 Environmental Hazards

Carbon black manufacturing produces gases consisting of nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, and small amounts of hydrogen sulphide, along with other sulphur- and nitrogen-containing gases. These process gases are burned for process energy, either in the form of heat, steam, or electricity [60]. No mention is made of the disposal of combustion products.

5.5.8 Other Carbon Black Uses

Rubber industries consume approximately 90% of the carbon black produced world wide (70% by the rubber tire industry, and 20% by other rubber products) [60]. The remaining 10% of production is consumed by special non-rubber applications such as plastics and printing inks. A very minor amount of carbon black production is used for catalyst support purposes.

Putting Things in Context

The fuel cell modelled in this thesis uses 0.017 kg/kW carbon black. At a power rating of 50 kW, an average passenger vehicle would require 0.85 kg carbon black. As shown in Table 5.10, recent carbon black production is estimated to have been greater than 6 M metric tonnes for the world, and approximately 1.6 M metric tonnes for the US [60].

	Carbon Black Production (a)	Rubber tire consumption of carbon black (a)	Tire Production (b)	Carbon black use per rubber tire	Tires per vehicle (c)	Carbon black use per vehicle
(1988)	(kg)	(kg)	(tires)	(kg/tire)		(kg/vehicle)
World	6.00E+09	4.20E+09	8.67E+08	4.85	5	24.2
US	1.60E+09	1.12E+09	2.11E+08	5.30	5	26.5

Table 5.10 Data for Calculation of Carbon Black Usage per Passenger Vehicle

a) From Encyclopedia of Chemical Technology [60]
b) From UN Statistical Yearbook [74]
c) Assuming four tires plus one spare per vehicle

The rubber tire industry consumes 70% of carbon black production, therefore the world wide rubber tire industry would have consumed an estimated 4.2 M tonnes, and the US rubber tire industry 1.12 M tonnes of carbon black in 1988. In the same year, the minimum "total"[22] world production of tires was approximately 866 M, and for the US was 211 M tires [74]. The average carbon black consumption per tire is therefore calculated to be about 4.8 kg/tire for the world and 5.3 kg/tire for the US. At a minimum, each vehicle requires the associated production of five tires (four plus a spare), therefore

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[22] From the United Nations *Statistical Yearbook* 40th Issue, NY (1995). This reference lists the tire production for individual countries and provides a "Total" production for those countries listed. In the case of tire production, the "Total" is not considered comprehensive for the world. In this thesis the "Total" value is assumed to be a minimum production level for the world.

the average carbon black consumption for rubber tires per vehicle would be 24.23 kg for the world total, and 26.50 kg for the US. At an average power rating of 50 kW per vehicle, this equates to about 48 kg/kW, an order of magnitude more carbon black than the amount used in the PEM cells.

The US tire production figure is for passenger cars [23] only, whereas the world total includes bicycles and/or motorcycles in some countries (Australia, Yugoslavia, Brazil), and all tires in others (China, Malaysia). Since the world tire consumption of carbon black accounts for nearly all tire uses (including passenger vehicles, bicycles, and farm equipment) the world total tire production figure is better representative of an average value. This thesis uses the world total value, but with the acknowledgement that the carbon black consumption per tire could be higher or lower depending on the actual world tire production and the actual use of carbon black in passenger tires.

5.6 Carbon Fibre

5.6.1 Carbon Fibre Production

This study assumes that the manufacture of carbon fibre is similar to that of graphite. This assumption is undoubtedly farfetched, however information and time constraints have limited further refinement of these assumptions.

5.6.2 Energy Input to Carbon Fibre Manufacture

The amount and mix of energy required to manufacture carbon fibre is also assumed to be the same as that required to make carbon graphite.

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[23] The U.N. Statistical Yearbook, 38th issue defines passenger cars as including "three-and four-wheeled road motor vehicles other than motor-cycle combinations intended for the transport of passengers and seating not more than nine persons (including the driver), which are manufactured wholly or mainly from domestically-produced parts and passenger cars shipped in "knocked-down" form for assembly abroad. Not included are busses with greater than 9 passengers, tractors, tractor-trailers" Department of Economic and Social Information and Policy Analysis Statistical Division. NY, 1993.

5.6.3 Recycling/Reuse

The 'recycle' option assumes a 70-80% recovery rate, recycled at 20% of the energy required to produce virgin materials.

5.7 Aluminum

5.7.1 Aluminum Production

The Encyclopedia of Chemical Technology is the principal reference for the following section [75]. Aluminum production starts with the mining of bauxite minerals which are mostly composed of oxides of aluminum, iron, and silicon [76]. Alumina (Al_2O_3) is extracted from the mined bauxite and is electrolysed to form aluminum.

Bauxite is usually strip mined, and the ores ground and prepared for digestion. Bauxite preparation may include washing or drying the ores in order to control their clay or moisture contents. The washed-off silicates can represent large quantities of polluted waste [76]. The next step, digestion, serves to extract the aluminum minerals from the prepared bauxite through a reaction of "hot spent liquor" with the "aluminum minerals in the bauxite to form soluble sodium aluminate. Virtually all other constituents [of the bauxite] are rejected as undissolved solids" [75]. The 'hot spent liquor' is a sodium hydroxide solution containing low levels of dissolved sodium aluminate. It is recycled through the digestion cycle until the level of sodium aluminate dissolved in solution becomes sufficiently high and the solution is termed "green."

Bauxite solids separated and recovered from the saturated green liquors, are calcined under high heat (1100 °C) to metallurgical grade alumina [75]. If fossil fuel combustion provides this heat, emissions of sulphur dioxide, carbon monoxide, methane, carbon dioxide, non-methane volatile organic compounds, and possibly NO_x (if natural gas is used as the fuel source) are produced [76]. Prior to calcination, water and process liquor are removed and the liquor is recycled.

Metallurgical grade alumina contains oxides of sodium (Na), iron (Fe), silicon (Si), calcium (Ca), titanium (Ti), copper (Cu), phosphorous (P), magnesium (Mg), potassium (K), and chromium (Cr), all present at less than 1% chemical composition. The alumina is electrolysed to produce aluminum. The primary material in the cell electrolyte is cryolite (Na_3AlF_6). Cryolite is generally produced synthetically by reacting hydrofluoric acid (HF) with the sodium aluminate from the green liquor, producing cryolite, water and alumina. The hydrofluoric acid is made by reacting fluorspar (CaF_2) with sulphuric acid according to equation 5.6.1.

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4 \tag{5.6.1}$$

Once smelting of the alumina begins, the cryolite can be replenished within the cells by neutralizing the Na_2O contained in the alumina with aluminum fluoride. In the electrolytic cell, molten aluminum is deposited onto the carbon cathode while oxygen consumes the carbon anode(s). Melting occurs at between 920-980 °C which allows melting of the alumina together with additives of calcium fluoride, aluminum fluoride, lithium fluoride, and magnesium fluoride. Oxidation of the electrodes releases CO_2 [51].

5.7.2 Raw Materials

In the literature, the production of 1 kg of aluminum required an estimated 1.9 kg alumina, 0.4-0.6 kg carbon, 0.1-0.2 kg pitch, 0.02-0.05 kg cryolite, 0.01-0.03 kg aluminum fluoride, and 14-20 kWh electrical energy [76]. Other raw materials include bauxite ore, calcium fluoride, lithium fluoride, magnesium fluoride, and water.

5.7.3 Energy Input to Aluminum Manufacture

The energy required to mine, refine, and produce aluminum is approximately 100 MJ/kg [3]. This energy input is composed of about 4% coal, 5% oil, 60% NG and 31% electric [20]. This estimate for electrical energy input (approximately 31 MJ/kg) is low compared to estimates from the EIA (46-61 MJ/kg) and IPCC (46-56 MJ/kg) [51]. However, increasing the electricity share to 46 or 61% results in no significant change ($\leq$1%) in the total CO_2-equivalent emissions resulting from the use of energy to produce all materials in the ICE or FC. Thus, this model uses Hudson's energy splits. In addition, it assumes that the energy required to refine scrap (or recycled) aluminum is 20% of that required to produce new material from ore, or 20 MJ/kg. This figure is based on Hudson's estimate of the energy required to produce 100% recycled cast aluminum [20].

5.7.4 Recycling/Reuse

The 'recycle' option assumes that 30-100% (100% base case) of the aluminum in either an ICE or PEM fuel cell can be recovered and ultimately recycled. The low value is the IPCC's estimate for aluminum recycling rate in all OECD countries [51] and the high value is from Hudson [20]. The remaining 70-0% of the aluminum will be disposed of as solid waste. The amount of material input to the ICE or FC manufacturing process that is not provided by aluminum recycled from the ICE or FC will come from 'standard' production, as described in the section 5.5.1.

5.7.5 Outputs and Environmental Hazards

Disposal of the bauxite residue containing sodium, iron, silicon, and aluminum is the major environmental problem resulting from the production of alumina [75, 76]. The newest disposal method is semidry disposal which involves drying out, or concentrating the residue to high percent solids. Residue disposal sites have been returned to productive use either by landscaping the semidry sites or by "dewatering" lakes and lagoons into which the residue was deposited.

Other emissions include gaseous and solid fluorides, along with gaseous carbon monoxide, carbon dioxide, sulphur dioxide, carbon tetrafluoride, hexafluoroethylene, and water vapour [76]. From the IPCC report, estimated total releases of carbon in the form of CO and CO_2 are 0.45 kgC/kg aluminum, released during anode oxidation [51]. The IPCC also estimates releases of carbon tetrafluoride to be between 0.6-2.5 kg/tonne of aluminum, and releases of hexafluoroethylene to be between 0.06-0.25 kg/tonne of aluminum.

Fluorides

Aluminum industries have historically been the greatest industrial producers of fluorine-containing emissions [76]. The Encyclopedia of Chemical Technology reports that "the aluminum industry in the United States uses about 15 kg of fluoride ion per tonne of aluminum, 10-25% of which is lost" through releases to the environment or absorption into the lining of the electrolytic cell [75]. These linings must be stored or disposed of in landfill. Other researchers have reported amounts of fluorine released (and therefore used) to be much greater, from 20-30 kg per tonne of aluminum smelted [16] to as high as 350-400 kg per tonne of aluminum if the alumina content in the electrolytic cell is allowed to fall below a critical level [76].

Hydrogen fluoride from the molten electrolyte may be emitted during the electrolysis process. As a result of the fluoride pollution, cattle grazing near the smelting site can be subject to fluorosis, an ultimately fatal bone damage condition [45]. Hydrogen fluoride emissions have recently been trapped by "highly (over 99%) efficient dry scrubbers that catch particulates and sorb HF on alumina .... Hence, nearly all the fluoride evolved is fed back into the [electrolytic] cell" [75]. Older plants are not as efficient in trapping emissions, and effective purification rates have been reported at between 25-70% [16]. Hydrogen fluoride is the most abundant form of fluorine emitted from aluminum smelters, however gaseous emissions of carbon tetrafluoride (CF_4), silicon tetrafluoride (SiF_4) and solid emissions of sodium fluoride (NaF), aluminum fluoride (AlF_3), and calcium fluoride (CaF_2) have also been reported [16].

TRI Emissions

The procedure outlined in Section 4.4.2 estimates the 1992 TRI emissions from U.S. industries in SIC code 3334 (Primary Aluminum). The 1992 U.S. production of primary aluminum is estimated to be 4.04 Million tonnes [77]. A first order estimate assumes that the emissions resulting from the production of primary aluminum are representative of the emissions from the entire mining-finished product production process

5.8 Steel

The Encyclopedia of Chemical Technology is the principal reference for the following section [78]. The primary ingredients in steel are iron (>98 weight %) and carbon (<2%). Since the 1970s, most steel (about 75% in the U.S.) has been made by processes using oxygen to refine pig iron. Alternate steelmaking methods include the melting of steel scrap in electric-arc furnaces. "On average, the steel industry consumes one-fifth more pig iron ... than scrap" [78]. In the U.S., this equates to 0.672 tonnes of pig iron and 0.56 tonnes of iron and steel scrap being consumed for the production of one tonne of raw steel [78].

5.8.1 Pig Iron Production

'Pig iron' refers to the molten product of blast furnaces. Blast furnaces are described as essentially large chemical reactors [80]. Iron ore (Fe_2O_3 or Fe_3O_4), coke (mostly carbon with volatile matter, ash, sulphur, and water), and fluxes (usually either limestone or dolomite) are charged into the furnace. These raw materials are combined under pressure with preheated air, during which the oxygen in the air reacts with the coke to produce hot carbon monoxide gas. The hot product gas heats the raw materials to "reaction temperature", providing the heat necessary to melt the iron ore and reducing the iron ore to iron [80]. After passing through the furnace, the gases are "cleaned, cooled, and used as fuel to preheat the air for the hot blast" [80]. The products of the chemical reactions are pig iron, heat, and slag, which consists of molten oxides of sodium, potassium, phosphorus, magnesium, and titanium.

Each kilogram of pig iron produced requires the input of approximately 1.6 kg of iron-bearing materials (in the form of pellets, steelmaking slag, and fluxed sinter), 0.46 kg of coke, 1.4 kg of dry air, 0.005 kg of pure oxygen, 0.1 kg of moisture, and 0.035 kg of tar [80]. Outputs include the pig iron, 0.27 kg of slag, 2.2 kg of gas (recycled), 0.084 kg of moisture, and 0.44 kg of dust and sludge [80]. Dusts recovered from cleaning the hot gases are recycled or disposed of in landfill. The product slag is generally sold and used in road or driveway construction.

Pig iron is composed of iron together with other elements including carbon (3-4.5%), manganese (0.5-2.5%), phosphorous (0.025-2.5%), sulphur (≤0.2%), and silicon (0.5-4.0%) [78]. The quantity of these elements is reduced by refining the pig iron before converting it to steel.

5.8.2 Steelmaking

Oxygen Furnaces

The basic oxygen furnace operates by blowing oxygen onto the surface of the molten pig iron, reacting iron oxide with carbon to form carbon monoxide. The formation and bubbling up of the carbon monoxide accelerates the metal refining by violently stirring the metal bath. Gases and "dense reddish-brown fume" are emitted by the furnace during oxygen blowing. These by-products are caught by a water cooled hood and conducted to a cleaning system where solids are removed and the remaining effluent gas, containing carbon monoxide and carbon dioxide is discharged to atmosphere. If the solids contain no contaminants they are added to the sintering machines "used to agglomerate fine ore, blast-furnace dust, and so on" [78]. If they contain contaminants, the solids are disposed of by dumping.

Electric-arc Furnaces

Electric-arc furnaces use scrap steel together with small quantities of pig iron or direct-reduced iron as raw materials. In the furnace, the scrap is melted to reduce its carbon, phosphorus, and sulphur contents. Reduced carbon is released as carbon monoxide which serves to stir the molten metal bath as the gas bubbles rise to the surface. Other materials such as ferromanganese and ferrosilicon may be added to deoxidize the steel and control its composition.

5.8.3 Energy Input to Steelmaking

The ICE model uses the energy required to mine, refine, and produce high strength steel, which is assumed to be about 50 MJ/kg [3]. The fuel cell model uses the energy requirement for stainless steel, which is about 53 MJ/kg. Both high strength and stainless steel energy inputs are composed of 59% coal, 6% oil, 23% NG and 13% electric [3]. The energy required to refine scrap (or recycle) steel is 19% of that required to produce new material from ore, or about 10 MJ/kg. This figure is based on the average of Hudson's scenario I and III values for the energy required to collect and recycle stainless steel [20].

5.8.4 Recycling/Reuse

The 'recycle' option assumes that 43-57% (57% base) of the steel in either an ICE or PEM fuel cell can be recovered and ultimately recycled. The low figure represents the average recycling rate of steel in OECD countries [51] and the higher figure is an estimate of the amount of recycled steel contained in ICE vehicles [79]. The remaining 43-57% will be disposed of as solid waste. The amount of material input to the ICE or FC manufacturing process that is not provided by steel recycled from the ICE or FC will come from 'standard' production, as described in section 5.8.2, and is produced at about 50 MJ/kg.

5.8.5 Material Inputs and Outputs

Table 5.11 lists the inputs required to produce 1 kg of steel.

The outputs from the production of 1 kg of steel include carbon dioxide, methane [51], carbon monoxide, "brown fume", pig iron, 0.27 kg of slag, 2.2 kg of gas (recycled), 0.084 kg of moisture, and 0.44 kg of dust and sludge [80].

TRI Emissions

The procedure outlined in Section 4.4.2 estimates the 1991 TRI emissions from U.S. industries in SIC code 3312 (Blast Furnace and Steel Mills). The 1991 U.S. production of pig iron for steelmaking is estimated to be 48 M tonnes [80]. This model assumes that the quantity of pig iron produced in blast furnaces and converted to steel is approximately equal to the quantity of steel produced.

Material	kg material/ kg steel	Composition	kg component/ kg material	Source
iron ore	1.25			(a)
pig iron	0.672	iron bearing material	1.588	(b)
		coke	0.46	
		dry air	1.4	
		oxygen	0.005	
		moisture	0.1	
		tar	0.035	
iron and steel scrap	0.56			(b)
coal	0.5			(a)
carbon	0.002-0.005			(c)
air	ND			(b)
fluxes	0.2	limestone (or dolomite)		(a)

Table 5.11 Material Inputs to Steelmaking

ND - No Data
Source: (a) Jost, 1995 [79]
(b) Encyclopedia of Chemical Technology, Vol. 14, 1995 [80].
(c) Encyclopedia of Chemical Technology, Vol. 4, 1992 [60].

5.8.6 Environmental and Health Issues

Health and Safety Issues

Health issues associated with steel are concentrated about the steelmaking process. Potential sources of hazard include radiant heat from the furnaces and hot-rolling mills, exposure to carbon monoxide from the furnaces, and exposure to excessive levels of noise [80]. The risks to workers from these hazards are addressed and reduced through the use of heat shields, self-contained breathing apparatus, carbon monoxide monitors and alarms, mufflers, sound-proofing, and the provision of hearing protection [80].

Environmental Issues

Emissions of concern include dusts, sulphur dioxide and carbon dioxide. Control of dusts and sulphur dioxide, along with the reclamation of areas where open pit mining has occurred have been receiving increasing industry attention since the 1980s. The Encyclopedia of Chemical Technology lists the most significant environmental concern with ironmaking to be the emissions of CO_2, and its subsequent impact on global warming [80].

5.9 *Cast Iron*

5.9.1 Cast Iron Production

The Encyclopedia of Chemical Technology is the principal reference for the following section [80]. Primary raw materials for cast iron are ferrous scrap and pig iron. ‘Pig iron’ refers to the molten iron product of blast furnaces, less than 1% of which is used in cast iron production. Iron for casting is most often produced by melting the raw materials in a device resembling a small blast furnace. The combustion of coal coke in air provides the heat for melting. The cast iron composition can be adjusted during the melting process through the addition of silicon and carbon, possibly together with manganese, phosphorus, chromium, nickel, molybdenum, and/or copper.

5.9.2 Raw Materials for Cast Iron Production

In 1991, the US produced about 50 M tonnes of pig iron and 3.9 M tonnes of cast iron [80]. Cast iron production therefore requires about 0.128 tonnes of pig iron per tonne of cast iron, since less than 1% of pig iron produced is used in cast iron manufacturing. The primary raw materials in cast iron production are pig iron and ferrous scrap, therefore at a minimum, cast iron production also requires (1-0.128) = 0.872 kg ferrous scrap/kg cast iron. Additional raw materials include coal coke, air, silicon, carbon, and other metallic elements as outlined in section 5.9.1.

5.9.3 Energy Input to Cast Iron Production

The energy required to produce cast iron is assumed to be 20 MJ/kg [3]. This energy input is composed of about 65% coal, 6% oil, 25% natural gas and 4% electric [80]. The energy required to make 100% recycled cast iron is assumed to be 8% of that required to produce new material from pig iron and ferrous scrap. This fraction is the average of Hudson's scenario I and III values for the fraction of total energy required to produce cast iron, from mining ore to semi-fabricated mill end product, that is consumed in the collection and processing of recycled materials [20].

5.9.4 Recycling/Reuse

The 'recycle' option assumes that 57% of the cast iron in an ICE can be recovered and ultimately recycled [79]. Thus, 57% of the material in use in the ICE or FC will be recycled and refined at 4.6 MJ/kg. The remaining 43% of the cast iron will be disposed of as solid waste. The amount of material input to the ICE or FC manufacturing process that is not provided by cast iron recycled from the ICE or FC will come from 'standard' production as described in section 5.9.1.

5.9.5 Emissions from Cast Iron Production

TRI Emissions

An estimated 3.9×10^7 tonnes of cast iron were produced world-wide in 1991, about 10% of which was produced by the U.S. [80]. The US production figure (3.9 M tonnes) is used together with the 1991 TRI emissions from U.S. industries in SIC Code 3321 (Gray and Ductile Iron Foundries) for the estimation of TRI emissions per kilogram of cast iron production.

5.9.6 Health and Safety and Environmental Issues

Health and safety and environmental issues are presumed the same for both steelmaking iron and cast iron.

Health and Safety

Iron does not represent a significant health risk. In large quantities, the inhalation or ingestion of iron dusts can be expected to cause eye irritation or gastrointestinal problems. The LD_{50} toxicity rating for oral ingestion is 30 g/kg [80], although it is not clear that this represents the toxic dose for humans.

5.10 Copper

5.10.1 Copper Production

The Encyclopedia of Chemical Technology is the principal reference for the following section [81]. Copper is produced by mining, concentration, smelting and refining.

Copper-iron sulfides or copper oxides (copper ore) are principally mined in open pits. Energy is required to separate the ores, which contain less than 1% copper along with iron, sulphur and other impurities, from waste rock. The concentration (or milling) process serves to separate copper minerals in the ores from non-copper ones. The non-copper minerals are rejected as tailings and impounded in "large ponds behind dams" [81]. Concentration consumes 40% of the total mining-to-refining process energy, and involves first crushing and grinding the ores with water to make a slurry. The slurry is sent to flotation cells where copper minerals are separated from the tailings and "collected as a froth known as concentrate" [81]. The concentrate contains between 25-35% copper by weight [81]. The minerals are filtered from the froth and shipped to the smelter, while nearly 100% of the recovered water is recycled to the grinding stage.

In the smelting furnace, the copper concentrate reacts with air and oxygen and is melted to produce a matte containing mixed sulfides of copper and iron, sulphur dioxide gas, and "a slag containing much of the iron and all of the silicates in the concentrates" [81]. The passage of air through the matte separates out impure copper (99% Cu) from more SO_2 gas and further slag. In total, about 2.7 times more sulphur dioxide and 2.3 times more slag are produced than impure copper. The impure copper is sent to the refinery to adjust the oxygen and sulphur levels in the metal, which is usually purified by electroplating.

By-product SO_2 from the smelter can often be recovered and sold to sulphuric acid producers. The recovery process produces calcium sulphate, which in turn can be sold to wallboard producers [81]. This SO_2 scrubbing results in only minor releases of the gas to the environment. Other environmental releases include heat equivalent to about 30% of the fuel energy input to the smelter, and slag, which is disposed of as solid waste. Releases from the refinery include arsenic and antimony compounds, as shown by the TRI releases. By-products of the refining process include gold, silver, platinum, and other precious metals.

5.10.2 Raw Materials for Copper Production

The production of refined copper requires material inputs of copper ore, water, air, and oxygen. Other inputs are most likely required, but this list should account for the major materials.

5.10.3 Energy Input to Copper Production

The energy required to produce copper is approximately 100 MJ/kg [3]. This input energy is composed of about 56% coal, 19% oil, 13% natural gas and 11% electric [3]. The energy required to make 100% recycled copper is 5% of that required to produce new material from ore. This fraction comes from averaging Hudson's scenario I and III values for the fraction of the total energy required to produce copper from mining ore to semi-fabricated mill end product that is consumed in the collection and processing of recycled materials [20].

5.10.4 Recycling/Reuse

The 'recycle' option assumes that 15-35% of the copper in an ICE can be recovered and ultimately recycled. The low value is the average of Hudson's scenario I and III values for the fraction of semifabricated material originating from recycled material [20], and the high value is the IPCC's estimate for the copper recycling rate in all OECD countries [51]. Thus, 15-35% of the copper in use in the ICE will be recycled and refined at 5 MJ/kg. The remaining 65-85% of the copper will be disposed of as solid waste. The amount of material input to the ICE manufacturing process that is not provided by copper recycled from the ICE will come from 'standard' production, as described in the section 5.9.1, and is produced at 100 MJ/kg.

5.10.5 Emissions from Copper Production

Again from Section 5.9.1, material outputs from the production of copper include waste rock (containing non-copper minerals), tailings (also containing non-copper minerals), water (which is nearly 100% recycled), sulphur dioxide gas (the release of which is being reduced due to scrubbing and sale to sulphuric acid producers), slag, calcium sulphate (most sold to wallboard production), arsenic and antimony compounds, and gold, silver, platinum, and other precious metals (recovered and sold). Heat energy is also produced, approximately equal to 26 MJ/kg (representing 30% of the fuel energy input.)

TRI Emissions

The procedure outlined in Section 4.4.2 estimates the 1991 TRI emissions U.S. industries in SIC code 3331 (Primary Copper). The 1991 U.S. production of refined copper is estimated to be 2 M metric tonnes [77]. This model assumes that the quantity of copper refined is approximately equal to the quantity of primary copper produced.

5.10.6 Health and Safety Issues

"No chronic copper poisoning has been reported", however copper can cause gastrointestinal problems if its salts from copper contaminated foods are ingested, and "metal fume fever" if it is inhaled as copper fumes [81]. Copper concentrations of less than 0.025 mg/l in fresh water do not present toxicological problems to fish [81].

5.11 Lead, Rubber, and Plastics/Composites

These materials represent a small fraction of the ICE engine weight. As a result this model only considers their production energy inputs and their CO_2 equivalent emissions produced as a result of that energy use. It is recommended that in the future, however, these materials should be examined more closely. In particular, if examinations are to consider battery powered vehicles, the production and disposal of lead should be closely examined.

5.11.1 Energy Input to Production

Table 5.12 shows the production energy and energy mixes used.

Material	Production Energy MJ/kg	Coal Fraction %	Oil Fraction %	NG Fraction %	Electricity Fraction %
Lead	15	37	3	30	30
Rubber	90	20	30	41	10
Plastics	140	0	28	70	2

Table 5.12 Energy and Energy Mix Required to Produce Lead, Rubber, and Plastics.

Source: [3]

CHAPTER 6 - RESULTS

This chapter compares the quantities of material use, energy use, and CO_2-equivalent emissions from the life-cycles of FC and ICE components and vehicles. *Component life-cycle* refers to the production, use, and disposal of *component materials* in the vehicles. *Vehicle life-cycle* refers to the combined total of *component life-cycle, vehicle use, and fuel-cycle.*

6.1 Material Use - MIPS

One method for examining the material impacts of a technology is to look at its Material Intensity per Unit of Service (MIPS). This zero-order indicator assumes that the quantity of a material alone has the potential to directly determine its environmental and health impacts. Three limiting assumptions underlie the approach. First, all materials are equivalent in terms of impacts, such that a kilogram of any material X has the same environmental and health implications as a kilogram of any other material Y. Second, heavier materials require more resources and energy inputs, and their use produces greater impacts than lighter materials. Third, greater quantities of materials use more resources and energy, and produce more impacts than smaller quantities of materials. These limitations are discussed in Section 6.2. However, for a zero-order analysis, Tables 6.13 and 6.14 use this technique to compare the component life-cycle inputs and outputs of raw materials for the FC and ICE.

Table 6.13 shows that the FC as modelled requires more component life-cycle raw material inputs than the ICE, but fewer inputs of the materials common to both ICEs and FCs. The higher raw material need for the fuel cell is directly attributable to the use of platinum and the extraction and subsequent disposal of the ore from platinum mining. The bottom line in Table 6.13 shows that the production of the FC vehicle uses 31 to 287 times more platinum than the production of the ICE vehicle. In the base case model all of the ore extracted during the mining of this platinum (together with platinum's co-product, nickel) has been attributed to platinum. If the ore were instead attributed entirely to nickel, the material life-cycle input requirement for fuel cells with either catalyst option would drop to 0.2 with respect to that of the internal combustion engine.

Raw Material Input	ICE	FC Supported Catalyst	FC Platinum Black Catalyst
Within System[(a)]			
All Materials	1	29	268
Within System[(a)] (common materials)			
Aluminum	1	0.05	0.05
Steel	1	0.2	0.2
Outside System[(b)] (common materials)			
Carbon black	1	0.01	0
Platinum	1	31	287

Table 6.13 Base Case Material Inputs for Raw Material Stage of Component Life-Cycles Assuming 100% of Material Inputs to Platinum/ Nickel Production are Allocated to Platinum, Normalized to Internal Combustion Engine Results

a) Common Materials within systems refers to materials common to both the ICE engine and the PEM stack.

b) Common Materials outside the systems refers to materials in the PEM stack which are also present in an ICE vehicle, but outside the ICE engine and therefore outside the control system under study.

Table 6.14 shows that the life-cycle production of materials in the FC produces one to two orders of magnitude fewer outputs through fugitive air, stack air, and water releases than does the life-cycle production of materials in the ICE. However, the FC component life-cycle is responsible for significantly more total outputs of solids materials than is the ICE system. The high solid waste output for the fuel cell stacks is primarily attributable to the disposal of the ore from platinum mining. If these ores are attributed to nickel rather than platinum mining, the results shift such that the FC life-cycle produces at most the same order of magnitude of solid outputs as the ICE life-cycle.

Base Case Outputs	ICE	FC Supported Catalyst	FC Platinum Black Catalyst
Fugitive Air	1	0.05	0.05
Stack Air	1	0.8	0.8
Water	1	0.2	0.2
Solids (a)	1	65	574.2
Solids without Pt ore (b)	1	2	0.4

Table 6.14 Base Case Total Material Output for all Life-Cycle Stages Assuming that 100% of the Material Outputs from Platinum/ Nickel Production are Allocated to Platinum, Normalized to Internal Combustion Engine Results.

(a) In the fuel cell case, "solids" gives the solid outputs if the ores from platinum mining are 100% assigned to platinum production.
(b) "Solids without Pt ore" gives the normalised outputs if the ores from platinum mining are 100% assigned to nickel production

(These results represents only those outputs identified, and are not to be taken as complete.)

In absolute numbers, the inputs and outputs from each model are very nearly equal (taking into account round-off error.) However total numbers tell a misleading story. Closer examination of the inputs and outputs of individual materials, elements, and compounds reveals that most of the chemicals released are unaccounted for as inputs. More detailed information on each material's production methods are required in order to better understand these input/output relationships. Data limitations also affect the consistency of output detail in the ICE and FC models. Further data would likely alter the above results, however the relative orders of magnitude of total material inputs and outputs are expected to remain consistent.

6.2 Material Use - Beyond MIPS.

The MIPS approach considers that all materials are equivalent, however this equivalency is invalid for environmental and health impacts. Among other factors, materials differ in their toxicity, carcinogenicity, reactivity, and natural abundance. The release of one kilogram of a highly toxic or highly reactive material is likely to have a greater impact than the release of one kilogram of a benign or stable substance. Several measures for evaluating the differences between materials have been proposed and examined, however none have been adopted as a standard [82]. In the absence of such a basis for comparison, this research focuses on the uses and releases of fluorine. The potential environmental and health issues surrounding this material were outlined in Section 4.1.4. Fluorine is used and released during the production of materials for both PEMFCs and ICEs. This section more closely examines the release of fluorine during the production of aluminum and the use of fluorine in the fuel cell membrane.

6.2.1 Fluorides and Aluminum

Hydrogen Fluoride Releases	Fluorine Releases	Source	Notes
(g HF/kg Al)	(g F/kg Al)		
0.7	0.67	TRI	Based on atomic weights, HF contains 95wt% F. TRI assumptions described in Section 5.7.5. This number is the total of fugitive and stack air releases.
	5 - 30	Rozhkov [16]	25-100% of 20-30 kg F released per ton of Al.
	1.5 - 3.75	Kroschwitz, [75]	10-15% of 20-30 kg F released per ton of Al.
	350 - 400	Ibid	If alumina content is not controlled, releases could go as high as this.

Table 6.15 Estimates of the Releases of Hydrogen Fluoride and Fluorine per Unit of Aluminum Produced

Aluminum is used in both the FC and the ICE, however the base case ICE contains an order of magnitude (approximately 46 kg) more aluminum than does the FC. Section 5.7.5

outlined various estimates for the amount of fluorine emitted during the production and smelter of aluminum, shown in Table 6.15.

It is reasonable to assume that environmental regulations will require strict control of the aluminum production process such that releases greater than the tens of grams fluorine per kg of aluminum produced will be unlikely. The range of fluorine released is therefore assumed to be 0.67 - 30 g/kg aluminum.

Fluorides Released During the Production of ICE Aluminum

The base case ICE has a lifetime of 3400 operating hours and weighs about 100 kg, 48.5% of which is aluminum. Subtracting from this the 2.4 kg of aluminum in the PEMFC gives a difference of approximately 46 kg more aluminum in the ICE than the FC. The range of fluorine emitted during the production of this excess aluminum is calculated and shown in Table 6.16. Fluorine releases per unit of ICE power output are in the order of 10^{-1}-10^{1} g/kW, and the fluorine releases per unit of ICE energy output are in the order of 10^{-4}-10^{-3} g/kWh.

Fluorine Emitted Per Unit Al (g F/kg Al)	Fluorine Emitted to Produce ICE (g F/ICE)	Fluorine Emitted per Unit ICE Power Output (g F/kW)	Fluorine Emitted per Unit ICE Energy Output (g F/kWh)
0.7	32	0.6	0.0002
30	1382	27.6	0.0081

Table 6.16 High and Low Estimates of the Increased Fluorine Released as a Result of the Production of the Excess 46 kg of Aluminum in the Internal Combustion Engine over the Proton Exchange Membrane Fuel Cell.

Future ICE engine blocks will most likely be made of cast aluminum, such as the base case one described above. If they are instead made predominantly of cast iron, the ICE aluminum content could drop to as low as 3.5 kg/ICE, representing a difference of less than one kg over the aluminum content of the FC. The fluorine emissions from the production of this ICE would be two orders of magnitude less than those outlined in Table 6.16.

6.2.2 Fluoride Use in Membranes

Fluorides are used in the production of both Teflon® and the membranes for PEM fuel cells, however the following discussion focuses only on the membrane. Since Teflon® is the backbone of both the Dow and Nafion® families of membranes, any examination of these latter materials will automatically deal with Teflon®.

Public information does not provide sufficient detail to determine the amount of fluorine input to or released from the membrane production process. It is possible, however, to determine the amount of fluorine contained within the membrane. The Dow and Nafion® membranes have similar structures, shown in Equation 5.1.3. Based on atomic weights, Nafion® contains 66-69% fluorine, while the Dow membranes may contain slightly less, 62-69% fluorine. Since the Dow membranes have the greatest range of fluorine content, they are chosen for examination. This section describes the base case model, and then looks at the sensitivities of the membrane lifetime and thickness.

Base Case

This section uses the base case membrane developed in Chapter 3. It has a long lifetime (6800 hrs), and a weight per unit FC power output (normalised weight) of 116 g/kW (from Table 3.5.) The model assumes the weight fraction of fluorine in the membrane to be between 62-69%. The weight of fluorine per unit power in the membrane will therefore vary from 72-80 gF/kW and the weight of fluorine per unit FC energy output will vary from 10.6-11.8 gF/kWh, as shown in Table 6.17 .

PEM Lifetime (hours)	Membrane weight per unit power (g/kW)	Membrane weight per unit energy (g/kWh)	Fluorine content (%)	Fluorine weight per unit power (g/kW)	Fluorine weight per unit energy (g/kWh)
6800	116	0.0171	0.62	71.9	0.0106
			0.69	80	0.0118

Table 6.17 Estimates of the Amount of Fluorine Contained in the Base Case Proton Exchange Membrane

Sensitivities - Membrane Lifetime and Thickness

A decrease in membrane lifetime which causes a directly proportional increases in the membrane weight per unit energy, will also cause a corresponding increase in the weight of fluorine per unit energy in the membrane. Thus, decreasing the membrane lifetime by 30% to the lower end of the assumed PEM lifetime range (4760 - 6800 hours, from Section 3.1.1) results in a 30% increase in the normalised weight of fluorine in the membrane. Decreasing the membrane lifetime an additional 30% to the assumed lifetime of the ICE (3400 hours) causes a further 30% increase in the normalised fluorine weight in the membrane, shown in Table 6.18.

PEM Lifetime (hours)	Membrane weight per unit power (g/kW)	Membrane weight per unit energy (g/kWh)	Fluorine content (%)	Fluorine Weight per unit power (g/kW)	Fluorine weight per unit energy (g/kWh)
6800	116	0.0171	62	71.9	0.0106
			69	80	0.0118
4760	116	0.0244	62	71.9	0.0151
			69	80	0.0168
3400	116	0.0341	62	71.9	0.0212
			69	80	0.0235

Table 6.18 Estimate of the Amount of Fluorine Contained in the Base Case Proton Exchange Membrane if the Membrane Lifetime is Decreased to that of the Internal Combustion Engine (3400 hours) and to 40% Greater than that of the Internal Combustion Engine (4760 hours)

A similar argument can be made for variations in membrane thickness. Changing this variable 60% to the high or low end of the possible range developed in Section 3.3.1 (0.064 - 0.254 mm) increases the normalised membrane weight to 47 - 186 g/kW. Thus bringing about a directly proportional change in the normalised fluorine weights, shown in Table 6.19.

PEM Lifetime (hours)	Membrane weight per unit power (g/kW)	Membrane weight per unit energy (g/kWh)	Fluorine content (%)	Fluorine weight per unit power (g/kW)	Fluorine weight per unit energy (g/kWh)
6800	47	0.0068	0.62	28.9	0.0042
	116	0.0171		71.9	0.0106
	186	0.0273		115.2	0.0169

Table 6.19 Estimates of the Amount of Fluorine Contained in the Base Case Proton Exchange Membrane if the Membrane Thickness is Increased or Decreased 60% from the Base Case Value of 0.159 mm, and Thus the Membrane Weight per Unit Power is Varied 60% from 116 g/kW.

The impacts of decreasing the membrane lifetime and varying the membrane thickness give a maximum range in the fluorine weight per unit FC power output of 28.9-128.2 gF/kW, and in the fluorine weight per unit FC energy output of 4.2- 37.7 mg/kWh. Both normalised fluorine weights have the potential to vary from the base case by as much as an order of magnitude. This is shown in Table 6.20.

PEM Lifetime (hours)	Membrane weight per unit power (g/kW)	Membrane weight per unit energy (g/kWh)	Fluorine content (%)	Fluorine weight per unit power (g/kW)	Fluorine weight per unit energy (g/kWh)
6800	47	0.0068	0.62	29	0.0042
3400	186	0.0546	0.69	128	0.0377

Table 6.20 Estimates of the Maximum Range in the Amount of Fluorine Contained in the Proton Exchange Membrane

A key observation from Tables 6.20 and 6.16 is that even at its lowest value (with the longest lifetime, the thinnest membrane, and the lowest fluorine content), the FC membrane will contain the same order of magnitude fluorine per unit energy as is released in the production of aluminum. At worst (with the shortest lifetime, the thickest membrane, and the highest fluorine content) the membrane will contain an order of magnitude more fluorine than is emitted during the production of aluminum for the ICE. The same observations hold for the amount of fluorine per unit power. If the aluminum content in the ICE were to drop, the difference will become even more significant.

6.2.3 Conclusions

Care must be taken in the recovery and disposal of the membrane. If the membranes are not recycled, but rather are disposed of as solid waste, they will eventually be responsible for releases of at least as much, and potentially far more fluorine into the environment than is caused by the manufacture of aluminum engine blocks for ICEs. This is significant when it is recognised that aluminum production is one of the largest industrial users and emitters of fluoride compounds. Additionally, if the disposal and eventual release of the fluorine in membranes occurs, it cannot be claimed that PEM fuel cells are environmentally preferable in their use of fluorine to ICEs. Several options are available to FC manufacturers to reduce the fluoride impacts of membranes relative to ICEs. These options include; maintaining a high membrane lifetime, reducing the membrane thickness, complete recovery and recycling of the fluorinated membrane, and/or reductions in the fluorine content of the membrane by a factor of 10 to bring it in line with the maximum fluorine emissions from the 100 kg ICE .

In evaluating these conclusions it must noted that time constraints have prevented this analysis from examining the fluorine emissions or contents of other materials in either the ICE or FC. While it is expected that these values will be low compared to the emissions from aluminum production and compared to the fluorine content in the PEM membrane, it should not be assumed that they will have no impact on the above results.

6.3 Energy Use

Energy use provides a second basis for comparing the life-cycle impacts of FC and ICEs. The preferred technology is the one requiring the lowest overall life-cycle energy input and/or the lowest inputs of 'high polluting' energy (ie. coal versus natural gas.) This latter comparison is measured by the CO_2-equivalent emissions resulting from energy use in the next section. This section focuses on total energy use.

Two conditions are examined for each scenario in this section, 'standard' and 'recycled' raw material inputs. The 'standard' condition explores a product, FC or ICE, which has no post-consumer recycle (PCR) content and contains only new and post-industrial recycled materials. This product might represent the output from the first few material production runs. In contrast, the 'recycle' condition is more representative of steady-state manufacturing, incorporating post consumer recycling and reuse of FC and ICE materials. The steady-state condition uses less energy and resources than the standard one. The magnitude of this difference depends on the actual recycling rates and energy requirements, but the trends shown here are expected to remain consistent.

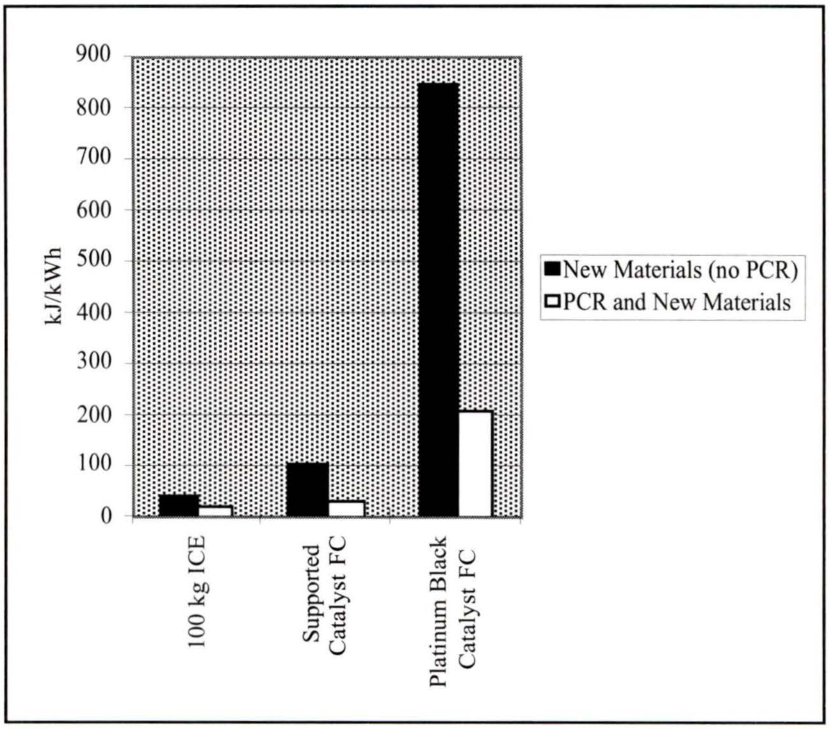

Figure 6.1 Total Energy Required to Produce Either All New Materials or Materials Having a Portion Post Consumer Recycle (PCR), in the Base Case Internal Combustion Engine and for two Catalyst Options in the Fuel Cell, Assuming 100% of the Energy Required to Produce Platinum/Nickel is Allocated to Platinum.

The normalised process energy (kJ/kWh) required to produce the base case materials in a PEM fuel cell stack exceeds the energy required to produce a 100 kg ICE by a minimum of 65% if both the FC and ICE materials are recycled and the FC uses a supported catalyst. If instead, no PCR materials are used and the FC has a platinum black catalyst, the production of materials in the FC will require nearly 1600% more energy than the production of materials in the ICE. This is shown in Figure 6.1. The above base case assumes that all of the production energy for nickel/platinum mining is allocated to platinum production, as discussed in Section 5.4.3. Figures 6.2 and 6.3 show that regardless of whether platinum is used as a supported catalyst or as a black, it is the critical material in terms of energy use for these fuel cells.

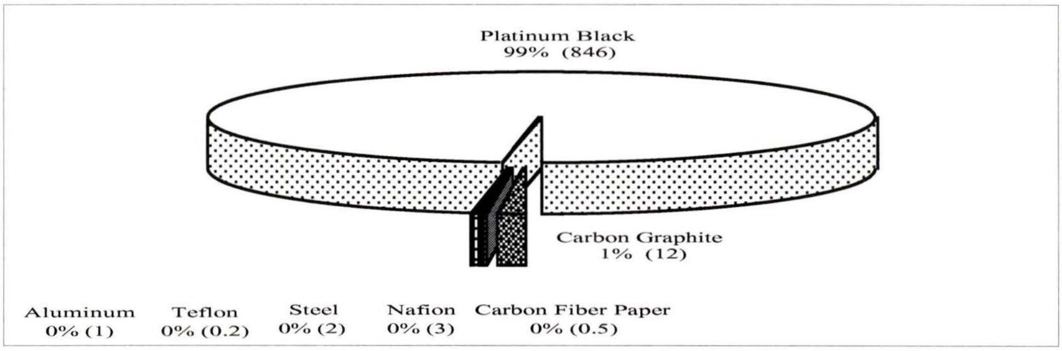

Figure 6.2 Division of Total Energy Required to Produce the New Materials (no PCR) in a Platinum Black Catalyst Fuel Cell, Assuming 100% of the Energy Required to Produce Platinum/Nickel is Allocated to Platinum % (kJ/kWh)

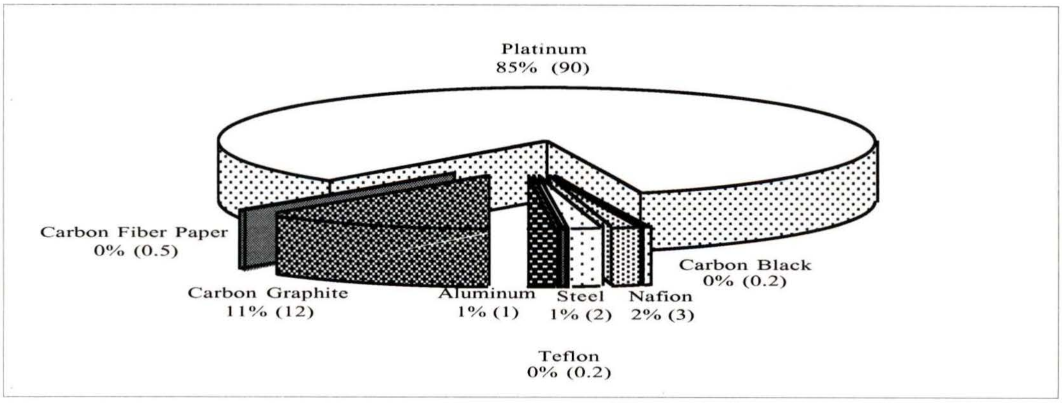

Figure 6.3 Division of Total Energy Required to Produce the New Materials (no PCR) in a Supported Catalyst Fuel Cell, Assuming 100% of the Energy Required to Produce Platinum/Nickel is Allocated to Platinum % (kJ/kWh)

Of all the materials in either a supported or unsupported catalyst fuel cell, the production of platinum (having been allocated 100% of platinum/nickel production energy) requires the largest process energy input of coal (exceeding the next greatest coal energy requirement, from steel, by an order of magnitude), oil (exceeding the next greatest oil energy requirement, from carbon graphite, by 60-100%), natural gas (exceeding the NG requirement from carbon graphite by over 300%) and of electricity (exceeding the electricity requirement from carbon graphite by over 700%).

These results are surprising since at least an order of magnitude less platinum is used over any other material in the supported catalyst FC, and at least 50% less platinum is used over any other material in the case of the platinum black catalyst FC. The high platinum process energy requirement, approximately 0.3 GJ/kg, is the determining factor in the overall FC materials energy demand. This energy requirement is at least five orders of magnitude greater than that of any other material. Obviously, if the energy needed to produce nickel/platinum were instead allocated entirely to nickel, the results would be significantly different. Figure 6.4 shows that in this case, carbon graphite becomes the most energy intensive material in the fuel cell, requiring 65% of the total material production energy. The next greatest energy demands come from the membrane (14%), aluminum, and steel (8% each.)

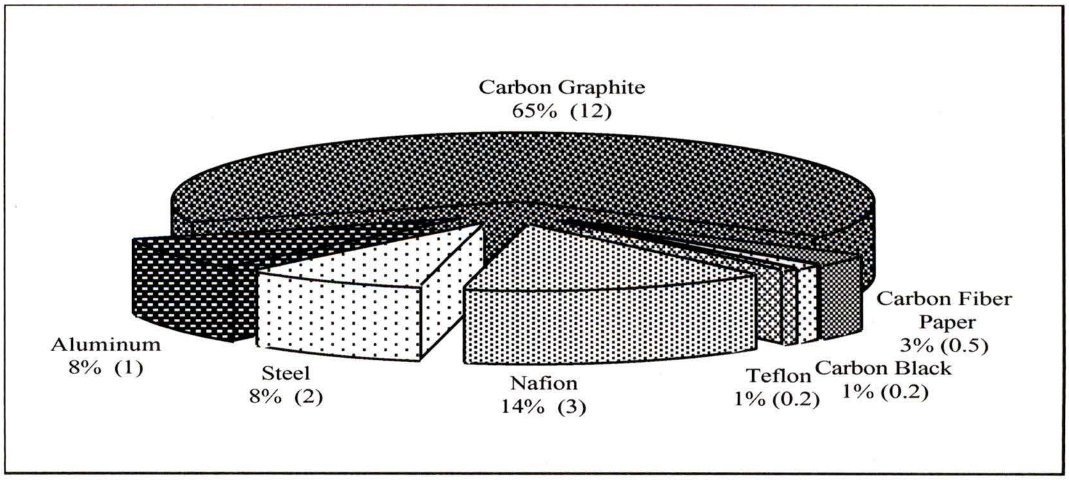

Figure 6.4 Division of Total Energy Required to Produce the New Materials in a Proton Exchange Membrane Fuel Cell, Assuming 0% of the Energy Required to Produce Platinum/Nickel is Allocated to Platinum % (kJ/kWh)

Figure 6.5 shows the comparison between the total energy needed to produce the materials for a cast aluminum engine block (100 kg ICE), a cast iron engine block (150 kg ICE), and a PEM fuel cell, assuming that no energy is required to produce platinum as a by-product of nickel production. The energy needed to produce the ICE materials can exceed the production energy demand of the FC materials by 50-540%. The only exceptions to this are *recycled* ICEs which require 6-10% less production energy than a PEM fuel cell composed of *new materials*. This situation might occur during FC manufacturing start-up stages, but is inconsistent with large-scale, steady state FC production.

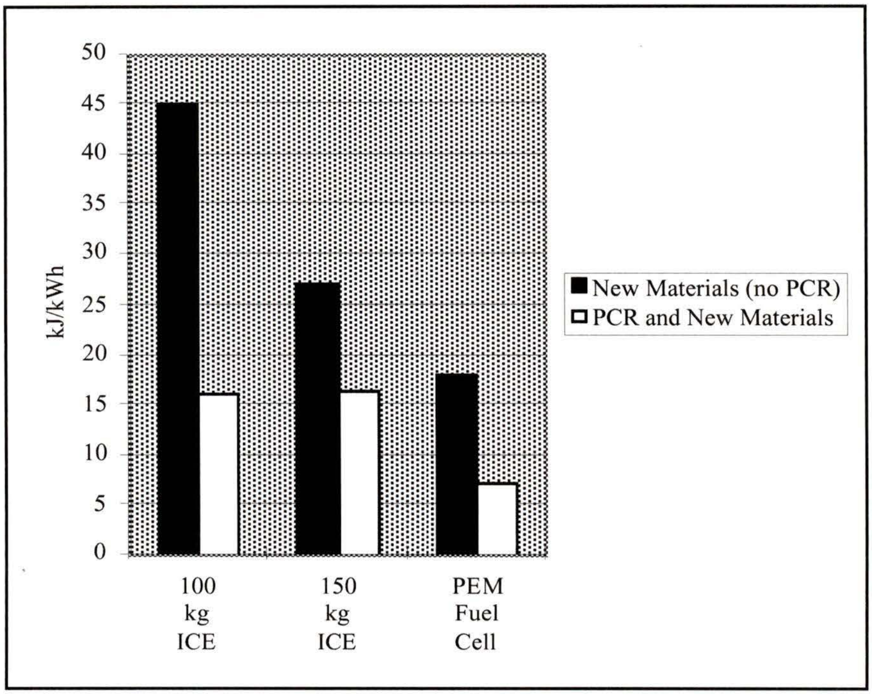

Figure 6.5 Total Energy Required to Produce Materials, Either all new or Having a Portion Post Consumer Recycle (PCR), for the 100 kg and 150 kg Internal Combustion Engine and for a Fuel Cell, Assuming that all of the Energy Required to Produce Nickel/PGM is attributed to Nickel.

If the energy required to produce platinum is assumed to be zero, there is no significant difference between the catalyst options in the fuel cell. The comparison can therefore be made between a generic fuel cell and the two options of ICE. PEM - Proton Exchange Membrane, PGM - Platinum Group Metals

Not surprisingly, the most energy intensive material for the 100 kg ICE is aluminum, demanding 73% of the total energy needed to produce the ICE materials.

6.4 CO_2-equivalent Emissions from Energy Use

The energy related CO_2-equivalent emissions are highest from the use of coal, followed by oil, natural gas, and nuclear. This section presents the component life-cycle CO_2-equivalent emissions arising from the use of energy to produce the materials in an ICE and FC. Additionally, it incorporates these material emissions into a full vehicle life-cycle emissions summation. This section presents results using base case assumptions about energy input components.

6.4.1 Material Production Results

CO_2-equivalent emissions have been calculated following the method described in Chapter 4. Assuming that 100% of the platinum/nickel production energy is allocated to platinum, total CO_2-equivalent emissions from the manufacture of 'standard' materials for the FC are one to two orders of magnitude greater than those resulting from the production of materials for either the cast-aluminum or cast-iron ICE. This difference is reduced when 'recycled' materials are used. The CO_2-equivalent emissions from recycling and manufacturing materials in the FC are on the same-to-one order of magnitude greater than those from recycling and manufacturing materials in the ICEs.

These results are expected since it was determined that, under the above assumptions, the manufacture of materials in the FC requires one-to-two orders of magnitude more energy than the manufacture of materials in the ICE. It is also consistent, under the assumption of high energy allocation to platinum production, that the extraction and production of platinum produces more CO_2-equivalent emissions than does the production of all other materials in the FC and ICE combined. Pt in the supported catalyst would be responsible for 83-88% of all FC production CO_2-equivalent emissions, and the platinum black would be responsible for up to 97-99% of all FC production CO_2-equivalent emissions. If the production of platinum as a by-product of nickel is instead assumed to require little or no energy, then the total CO_2-equivalent emissions from the production of new or recycled materials for the ICE and FC are approximately the same.

It is obvious from the above results that the assumptions surrounding the extraction and production of platinum can significantly affect the component life-cycle impacts of FCV. This study has bracketed the potential impacts of FCV assuming 100% and 0% allocation of energy to platinum production over nickel. It is unlikely that the allocation of energy to platinum production will ever reach 100%, however it seems reasonable that it will move closer to 100% than to zero. This is because large scale production and use of PEM FC vehicles will greatly increase the world wide demand for platinum.

As a case study, imagine a scenario where 10% of all new vehicles produced per year are FC vehicles using the base-case PEM FC model. In 1988 there were approximately 500 M vehicles in use in the world, and it is expected that this number will double early in the next century [83]. This new construction is being produced at a rate of about 50 M per year [74]. The FC vehicle production rate will therefore be 5 M per year. Each FC vehicles produced in this scenario requires about 110 g Pt, therefore the annual Pt demand during this "build-up" period will be 550 Mg for fuel cells alone. The 1994 world Pt supply levels are estimated to have been 141 Mg/year, 40% of which is used by autocatalysts [64]. Accounting for the fact that 10% of this autocatalyst Pt demand will no longer be required due to the FC production, the *available* Pt supply is about 5.6 Mg/year. Subtracting this amount from the FC demand leaves 544 Mg Pt, which exceeds current supply levels by 380%.

The case study can be changed to instead consider steady-state FC vehicle production ten years down the road, where 10% of the ultimate 50 M fuel cell vehicles are scraped and replaced each year. Even allowing for 80-95% recovery of Pt from the scraped fuel cells, this scenario will still require new supplies of 5-20% of 110 g Pt/vehicle. This amounts to an annual Pt demand for FC vehicles on the order of 50 Mg/year which represents an approximately 35% increase over current supplies.

Either case outlined above will likely increase platinum demand to the extend of altering the product-co product relation between platinum and nickel. This in turn will provide impetus to allocate a higher proportion of the total platinum/nickel production energy to platinum. The 100% allocation results presented in this study show extreme, but not unreasonable, potential component life-cycle impacts of fuel cell vehicles.

6.4.2 Vehicle Life-Cycle Results

The production and recycling of materials for the base case PEM fuel cell can have at least the same, if not significantly greater impacts in terms of material use and emissions, energy use, and CO_2-equivalent emissions resulting from energy use, than do the production and recycling of materials for the base case ICE. As this thesis explains, however, it is important to not just look at one stage in a technology's life, but also to examine the relative impacts from the entire vehicle life-cycle. To do this, the CO_2-equivalent emissions calculated above are used to update Delucchi's life-cycle analysis [22].

Delucchi's analysis, described in Section 2.2, and expanded in Ogden, Larson and Delucchi (1994) [9], estimated the greenhouse gas emissions produced during the life-cycle of vehicles and their fuels. He included material production and assembly, vehicle operation, and fuel extraction, production, transportation and use. For the calculation of emissions from material production and assembly, Delucchi examined the differences between FCV and ICEV with the exception of the vehicle power plants, which he assumed to be identical in material composition to the ICE engine. This thesis more closely examines the differences between the FC and ICE vehicle power plants, and its results can thus be added to Delucchi's to provide an updated picture of the CO_2-equivalent emissions from the life-cycles of these two vehicles.

Delucchi assumed that both ICEV's and FCVs had the same engine block. To change this assumption, his FCV results must first be adjusted to remove the emissions resulting from the production of materials in the internal combustion engine block. This is done by first subtracting our study's estimation of the total g/kWh CO_2-equivalent emissions from the production of the base case ICE materials from Delucchi's "Materials in cars" emissions. The amount subtracted is approximately 2-5 g/kWh for the cast-aluminum engine, with the lower value representing the "recycled" materials scenario and the higher value representing "new materials" scenario. Next, our estimates of the greenhouse gas equivalent emissions resulting from the production of materials in the FC are next added to the adjusted "Materials in cars" emissions from Delucchi. Finally, the adjusted material production emissions results are plugged into Delucchi's vehicle life-cycle emissions model, as shown in Tables 6.21 and 6.22.

Table 6.21 allocated 100% of the platinum/nickel production energy to platinum, thus assuming that it takes giga-joules of energy to produce a kilogram of platinum. The "low" values in this table represent the optimistic case scenario, using some PCR materials and a supported catalyst. The "high" values represent the worst case scenario, using all new materials and a platinum black catalyst.

Source or Fuel-Cycle Stage	Reform Gas ICEV	Methanol from NG FCV (low)	(high)	Methanol from Coal FCV (low)	(high)	Methanol from Wood FCV (low)	(high)	H2 from Solar FCV (low)	(high)
Vehicle	207	90.4	90.4	90.4	90.4	0.6	0.6	0	0
Compression or liquefaction	0	0	0	0	0	0	0	0	0
Fuel Distribution	4	11.6	11.6	6.0	6.0	7.3	7.3	0.6	0.6
Fuel Production	42	33.4	33.4	159.4	159.4	9.5	9.5	0†	0†
Feedstock transport	7	3.7	3.7	0.6	0.6	4.0	4.0	0	0
Feedstock recovery	7	7.0	7.0	3.7	3.7	17.8	17.8	0	0
CH4 leaks/flares	3	4.5	4.5	14.8	14.8	0.0	0.0	0	0
First total	270.6	150.5	150.5	274.9	274.9	39.2	39.2	0.6	0.6
Change (%)	_	-44.4	-44.4	-0.6	-0.6	-85.5	-85.5	-99.8	-99.8
Car assembly	8.7	9.1	9.1	9.1	9.1	9.1	9.1	9.2	9.2
Materials in cars	26.0	29.2	158.2	29.2	158.2	29.2	158.2	33.4	162.4
Second total	34.7	38.3	167.3	38.3	167.3	38.3	167.3	42.6	171.6
Change (%)	_	10.4	382.1	10.4	382.1	10.4	382.3	22.8	394.5
Total	305.3	188.8	317.8	313.2	442.2	77.5	206.5	43.2	172.2
Change (%)		-38.5	4.1	2.6	44.7	-74.9	-32.5	-86.2	-43.8

Table 6.21 Updated CO_2 Equivalent Emissions (g/kWh) by Fuel Type for Fuel Cell Vehicle, Assuming 100% of the Platinum/Nickel Production Energy is Allocated to Platinum

Based on Table 9a, Delucchi [22]. Reform. Gas refers to U.S. reformulated gasoline. ICEV - Internal Combustion Engine Vehicle, FCV - Fuel Cell Vehicle, NG - Natural Gas, H2 - Hydrogen. Change % is measured relative to the Reform Gas ICEV.

"Low" is the best recycled scenario with a supported catalyst fuel cell. "High" is the new-materials scenario with platinum black catalyst fuel cell.

† - Delucchi assumed that emissions from the production of photovoltaic materials are negligible

Table 6.22 allocates 0% of the platinum/nickel production energy to platinum. In this table, the choice of catalyst is irrelevant.

Source or Fuel-Cycle Stage	Reform Gas ICEV	Methanol from NG FCV		Methanol from Coal FCV		Methanol from Wood FCV		H2 from Solar FCV	
		(low)	(high)	(low)	(high)	(low)	(high)	(low)	(high)
Vehicle end use	207	90.4	90.4	90.4	90.4	0.6	0.6	0	0
Compression or liquefaction	0	0	0	0	0	0	0	0	0
Fuel Distribution	4	11.6	11.6	6.0	6.0	7.3	7.3	0.6	0.6
Fuel Production	42	33.4	33.4	159.4	159.4	9.5	9.5	0†	0†
Feedstock transport	7	3.7	3.7	0.6	0.6	4.0	4.0	0	0
Feedstock recovery	7	7.0	7.0	3.7	3.7	17.8	17.8	0	0
CH4 leaks/flares	3	4.5	4.5	14.8	14.8	0.0	0.0	0	0
First total	270.6	150.5	150.5	274.9	274.9	39.2	39.2	0.6	0.6
Change (%)	–	-44.4	-44.4	-0.6	-0.6	-85.5	-85.5	-99.8	-99.8
Car assembly	8.7	9.1	9.1	9.1	9.1	9.1	9.1	9.2	9.2
Materials in cars	26.0	26.1	27.5	26.1	27.5	26.1	27.5	30.3	31.7
Second total	34.7	35.2	36.6	35.2	36.6	35.2	36.6	39.5	40.9
Change (%)	–	0.1	5.5	0.1	5.5	0.1	5.5	13.8	17.9
Total	305.3	185.7	187.1	310.1	311.5	74.4	75.8	40.1	41.5
Change (%)		-39.2	-39.0	1.6	2.0	-75.6	-75.2	-86.9	-86.4

Table 6.22 Updated CO_2 Equivalent Emissions (g/kWh) by Fuel Type for Fuel Cell Vehicle, Assuming 0% of the Platinum/Nickel Production Energy is Allocated to Platinum

Based on Table 9a, Delucchi [22]. Reform. Gas refers to U.S. reformulated gasoline. ICEV - Internal Combustion Engine Vehicle, FCV - Fuel Cell vehicle, NG - Natural Gas, H2 - Hydrogen. Change % is measured relative to the Reform Gas ICEV.

"Low" is the best recycled scenario with either catalyst fuel cell. "High" is the new-materials scenario with either catalyst fuel cell.

† - Delucchi assumed that emissions from the production of photovoltaic materials are negligible

The "Materials in cars" rows in Tables 6.21 and 6.22 show the amount of emissions resulting from the production of materials for various fuel types of fuel cell vehicles, compared to the emissions resulting from the production of materials in a gasoline fuelled ICE. The other values highlighted show the total vehicle life-cycle CO_2-equivalent emissions for the various fuel cell vehicles compared to the ICE.

The results in Table 6.22, with the assumption of 0% platinum production energy requirement, have not changed significantly from Delucchi's original results shown in Table 6.23. The "low" results from Table 6.21, with the assumption of 100% platinum production energy requirement, are also essentially the same as Delucchi's. The "high" case results are significant however, in that the total, vehicle life-cycle CO_2-equivalent emissions from the fuel cell fuelled by methanol produced by natural gas exceeds those resulting from the ICE vehicle life-cycle. In addition, these emissions surpass those estimated by Delucchi for the diesel and liquid natural gas fuelled ICEVs in Table 6.23.

Source or fuel-Cycle Stage	Reform Gas ICE	Diesel ICE	Methanol from NG ICE	Methanol from Coal ICE*	Methanol from Wood ICE	H2 From Solar ICE	U.S.National Power Mix EV*	Solar Power EV*
Vehicle end use	207	202	172	172	32	14	0	0
Compression or liquefaction	0	0	0	0	0	0	-	-
Fuel Distribution	4	3	18	9	11	1	5	0
Fuel Production	42	15	52	250	15	0†	250	0.8
Feedstock transport	7	7	6	1	6	0	4	0
Feedstock recovery	7	7	11	6	28	0	5	0
CH4 leaks/flares	3	3	7	23	0	0	12	0
First total	270.6	237.3	266.6	461.2	92.5	15.1	276	0.8
Change (%)	_	-12.3	-1.5	66.8	-65.8	-94.4	-14.5	-99.7
Car assembly	8.7	6.5	8.7	8.7	8.7	9.0	8.9	8.9
Materials in cars	26.0	19.6	26.0	26.0	26.0	28.1	28.9	28.9
Second total	34.7	26.2	34.7	34.7	34.7	37.1	37.8	37.8
Change (%)	_	-24.7	0	0	0	6.8	8.9	8.9
Total	305.3	263.5	301.4	496.0	127.2	52.2	313.8	38.6
Change (%)		-13.7	-1.3	62.4	-58.3	-82.9	-12.2	-89.2

Table 6.23 CO_2 Equivalent Emissions (g/kWh) by Fuel Type for Internal Combustion Engine Vehicles and Battery Powered Electric Vehicles

Based on Table 9a in Delucchi [22]. Reform. Gas refers to U.S. reformulated gasoline. ICE - Internal Combustion Engine, EV - Battery Powered Electric Vehicle. Change % is measured relative to the Reform Gas ICE.

* - Delucchi compared battery powered vehicles to a reform-gas fuelled ICE in a city driving cycle only. This ICE has lower fuel mileage and thus higher emissions/mile. Other vehicles are compared to the reform-gas fuelled ICE in city/highway driving cycle.

† - Delucchi assumed that emissions from the production of photovoltaic materials are negligible

Another change appears in the FC vehicle fuelled by hydrogen, which could ultimately produce four times the life-cycle CO_2-equivalent emissions of a correspondingly fuelled ICEV, the difference resting entirely in the production of the fuel cell materials. Similarly, the emissions from the vehicle life-cycle of a fuel cell vehicle fuelled by methanol from wood could also exceed those of an ICEV fuelled by methanol from the same source. Finally, while the emissions from the vehicle life-cycle of either a fuel cell or ICE fuelled by methanol from coal were both calculated by Delucchi to exceed those of a gasoline fuelled ICE, the emissions from the worst-case fuel cell could reach approximately the same level as those from the coal sourced methanol ICEV.

Summary results show that the relative rank in terms of emissions of Delucchi's variously fuelled FC vehicles compared to a gasoline fuelled ICEV are not likely to change. They may, however, produce higher CO_2-equivalent emissions during their life-cycle than similarly fuelled ICEV, as a result of the higher emissions from the production of fuel cell materials.

CHAPTER 7 - Conclusions

Life-cycle analysis is a tool for understanding the real costs associated with the production, use, and disposal of a product or technology. A life-cycle inventory forms the critical first step in such an analysis by detailing the inputs and outputs of materials and energy at every stage in the product's life. Prior works have developed inventories of environmental impacts associated with the life-cycles of PEM fuel cell and internal combustion engine vehicles and fuels. These works have concentrated on qualitatively listing social effects and quantitatively estimating the technology or fuel's contributions to global warming through emissions of greenhouse gases.

This study bridges some of the gaps in the prior works by providing a detailed analysis of the life-cycle (including raw material extraction, material production, and recycling) of materials in the fuel cell stack and internal combustion engine. The focus of this analysis is referred to as the 'component life-cycle'. The resulting inventory identifies inputs and outputs of energy and materials, including solids such as ores and slag, liquids such as water, and gases such as greenhouse gases and toxic chemicals released during material production. The inventory is used to compare the impacts of material use, energy use, and CO_2-equivalent emissions released throughout the ICE and FC component life-cycles. The CO_2-equivalent emissions from the production of FC and ICE materials is also used to update existing models of GHG emissions from vehicle production, vehicle use, fuel production and fuel distribution for ICE and FC vehicles. This model provides a full 'vehicle life-cycle' comparison of the GHG emissions from the fuel cell and internal combustion engine vehicles.

7.1 Platinum

The product-co product relation between platinum and nickel is the greatest determining factor in the level of environmental effects examined in this study for both the component life-cycle of a PEM stack and the full life-cycle of a PEM fuel cell vehicle. Unfortunately, this product-co product relation has not been firmly established. To provide the most useful information, this study bracketed, with 0% and 100%, the allocation of energy use and material emissions to platinum. This study also established that the actual energy/material allocation to platinum, given large scale production of PEM fuel cell vehicles, will likely move closer to 100% than 0%.

7.1.1 Zero Percent Allocation of Energy and Materials to Platinum

To understand the impacts of this product-co product allocation, it is important to first examine the results of this research with the assumption of a zero percent allocation of energy and materials to platinum production. The study of the component life-cycles for FC and ICEs shows that the production and use of the fuel cell stack will likely require similar levels of raw materials, but will demand less energy input than will the ICE. Additionally, the FC component life-cycle will produce fewer greenhouse gas emissions from the use of energy, and will emit less pollution into air, water, and solid wastes than will the component life-cycle of materials in the internal combustion engine.

The results of this study also show that the FC vehicle will likely emit fewer greenhouse gases over its entire vehicle life-cycle than will the ICE. Overall, the production and assembly of materials is responsible for 11% of the total vehicle life-cycle CO_2-equivalent emissions from the ICE fuelled by gasoline. For FC vehicles using methane from natural gas, methane from wood, or hydrogen from solar as fuels, the production and assembly of materials is responsible for 20%, 48% and 99% respectively of the total vehicle life-cycle CO_2-equivalent emissions. Individual results will vary with the assumptions about engine or stack lifetime, the amount of post-consumer recycle used in the engine or stack, and whether supported platinum or platinum black is used as the catalyst layer. These variations may bring the FC and ICE life-cycle impacts closer together, however they do not affect a significant change in the overall results presented above.

7.1.2 One Hundred Percent Allocation of Energy and Materials to Platinum

The impacts of changing the product-co product allocation one hundred percent to platinum shows up in the increased requirement for material inputs and outputs. This increased requirement is sufficiently large to shift the balance of solid material use and emissions, energy use, and greenhouse gas emissions to favour the component life-cycle of the materials in an ICE over that of the FC. When the material greenhouse gas emissions are incorporated into a full vehicle life-cycle inventory, the results also have the potential to favour ICE over FC vehicles. In this case, the assumptions about the use of zero post-consumer recycle content and/or low engine lifetime (not shown) can increase the overall FC vehicle life-cycle emissions of GHGs to levels higher than those of an ICE vehicle using the same fuel (methanol from natural gas, wood, or hydrogen.)

When 100% of the platinum/nickel production energy is allocated to platinum, the production and assembly of materials for the FC vehicle using methanol from natural gas could increase from 20% to 48% of the vehicle's life-cycle CO_2-equivalent emissions. Likewise, the production and assembly of materials for the FC vehicles using methanol from wood, and hydrogen from solar could increase to 78%, and 99.5% respectively of the total vehicle life-cycle greenhouse gas emissions. However, steady state, large-scale production FC vehicles having an operating lifetime of at least 4760 hours and making full use (80-95%) of materials recovered and recycled from scrapped FC stacks, are likely to produce lower total vehicle life-cycle greenhouse gas emissions than will ICE vehicles using the same fuels. For these vehicles, the proportion of total life-cycle CO_2-equivalent emissions that result from the production and assembly of materials would be similar to that from the low-platinum material and energy allocation scenario described above. As it has been shown in Chapter 6, however, getting to this steady state poses some material acquisition problems.

7.2 Fluorine

This study has also examined the relative effects of FC stacks and ICEs in terms of the amount of fluorine contained within the FC membrane and emitted during the production of the ICE aluminum. Here, again, the assumptions about the cell operating lifetime, together with assumptions about the membrane thickness and the amount of fluorine emitted during aluminum production become critical. The results indicate that the FC stack can have at least as much of a fluorine effect as the ICE, and potentially much more.

7.3 Areas for Opportunity

Areas for opportunity in FC development identified by this research include reducing the amount of platinum, choosing a supported platinum catalyst over platinum black, ensuring a long FC operating lifetime, reducing the amount of membrane or the fluorine content of the membrane, and developing methods for recycling and re-using fuel cell materials. All of these areas are currently being explored in fuel cell research, and could have been identified using a simple FC cost analysis (more accurately referred to as a *price* analysis, since it would not include the external costs of the technology.) This is somewhat counter-intuitive, since it is often materials which have a low price, for example coal, that have a high environmental burden. However, in the case of the fuel cell, high monetary cost and high environmental burden coincide in the platinum and the membrane.

The benefit arising from doing a longer, more detailed life-cycle cost analysis is in the depth of information which lies behind the above recommendations. The impetus to reduce the amount of platinum, or the thickness of the membrane in a fuel cell in order to reduce the overall manufacturers cost of the device would be reduced or removed if the price of platinum or the membrane should fall. This thesis has identified life-cycle costs, measured by inputs and emissions, most likely not included in the manufacturers cost of FC and ICE materials. It has thus shown that the areas for opportunity should be pursued for environmental reasons, if not for simple cost reasons.

Finally, the overall results of this thesis show that it is not sufficient to make claims of environmental superiority over internal combustion engine vehicles, without making explicit the assumptions used in this claim. This thesis has also shown that the effects of local air pollution, and the relative significance of air, water, and solid emissions, beyond fluorine, need to be determined. Additionally, it is clear that the results from this, and any other life-cycle analysis, must only be used with a complete understanding of the assumptions underlying its development.

7.4 Recommendations for Future Work

- This study has investigated some of the principal inputs and emissions from the life-cycle of PEM fuel cells and internal combustion engines. The next step must be to evaluate the impacts of these emissions in terms of their health, environmental, and social consequences, considering socioeconomic and aesthetic issues along with physical concerns. Further work should extend into a valuation of these effects.

- The CO_2-equivalent emissions factors should be expanded to differentiate local and global pollution problems, as discussed in Chapter 2.

- This work has focused on the primary-level, life-cycle of materials. Each material presented here could have its life-cycle analysis extended to secondary levels and beyond. In the case of Teflon®, for example, this would involve understanding and incorporating the effects of hydrogen fluoride and chloroform production, which in turn lead to chlorine, methane, calcium fluoride, and sulphuric acid production. Ideally, each of these materials should be pursued forward and backward to its ground state in order to identify and completely understand all of their life-cycle impacts.

- This work has by necessity used U.S. National and aggregated data. Where possible, future work should use regional or site-specific data, indicating marginal emissions rather than average ones.

- Life-cycle analysis is a powerful tool that needs to be more widely adopted by the engineering design community. The life-cycle inventory developed in this thesis can be used to identify the environmental costs of potential design changes to PEM fuel cells and internal combustion engines. Similar works are examining the environmental emissions from manufacturing processes [82]. Ultimately, full life-cycle analysis should be incorporated into all engineering design methodologies.

- For the purposes of externalities analysis, corporations must be encouraged to provide complete, accurate information about their production processes, including all inputs, outputs, and process conditions. It is recognised that in many cases this information represents the only competitive advantage a company holds. However, it is only through complete disclosure and analysis that consumers will have sufficient information to make informed, and efficient, decisions between products. One solution to this dilemma may be to form an independent, confidential review group who will have full access to company information but who will release only the results of their analyses.

- Exergy analysis should be added to the life-cycle inventory of inputs and outputs. Energy and material balances are useful bases for measuring environmental effects. The use of energy involves the extraction and transformation of high quality materials together with the release to the environment of lower quality materials and energy. Since the quality of these resources cannot be recovered, products or processes which demand greater amounts of energy and/or materials place a greater burden on the environment. Thus, energy and material balances provide a first order measure of the products of processes which will cause the greatest burden. However, to parallel the criticism of the MIPS approach to material balances, not all energy demands are equivalent. "It is not sufficient to account for energy-in versus energy-out ratios without due regard for the quality difference" [51]. Exergy defines this concept of quality, and "although energy is conserved, exergy is destroyed in all real-life energy conversion processes" [51]. An exergy analysis thus provides a higher order understanding of the extent to which a given use of energy can impact the quality (or usefulness) of material and energy resources. Minimum exergy destruction means a minimum environmental burden, as long as the high exergy products are available to be used.

  Exergy analysis can additionally be used as a measure of the potential external costs of emissions from material and energy conversion processes. If these products are not reduced to the ground state prior to release to the environment, they are not completely internalised. The current limitation of exergy analysis to environmental effects determination is that it requires information not only about the mass of inputs and emissions, but also about their thermodynamic state. This information often represents trade secrets. The limitation to the application of exergy analysis will only fade when more complete information about products and processes is made publicly available. A more detailed discussion of this technique is beyond the scope of this thesis, but interested readers are referred to references [84] [85][51].

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APPENDIX A - Calculations

A.1 Unit Conversions for CO_2 Emissions Factors

Converting g/mi to g/kWh

First, miles are converted to km using 1 mile = 1.609 km. The following equations outline the process for further converting g/km to g/kWh.

CO_2-equivalent emissions X lifetime mileage = lifetime emissions
(g/km) (km) (g)

lifetime emissions ÷ lifetime hours = emissions per lifetime hour
(g) (h) (g/h)

emissions per hour ÷ FC/ICE power output = normalised emissions
(g/h) (kW) (g/kWh)

Thus, for an assumed driving speed of 50 km/h and a FC/ICE power output of 50 kW, the end result is that g/km = g/kWh.

A.2 Calculation of Raw Material Weight of Graphite

The desired output is the weight of graphite used in the fuel cell, ϕ kg. This finished material is for the most part composed of pitch and coke. Assuming that no loss of coke during baking or graphitization, the weight of coke in the finished graphite is equal to the weight of coke input to the baking stage. This, in turn, is approximately equal to 92.4% of the weight of coke input to calcination. Prior to the graphite manufacturing process, calcination evolves the volatiles in the coke [51]. If (α) represents the total weight of raw coke, it is composed of 8 wt% volatiles (0.08α) and 92 wt% other (0.92α) [51]. Less than 5% of the original volatiles remain after calcination ($0.05 \times 0.08\alpha = 0.004\alpha$ remains.) Therefore, calculate the weight of coke after calcination (β), i.e. the weight of coke input to the baking process to be:

$$0.92\alpha + 0.004\alpha = 0.924\alpha = \beta. \tag{A.2.1}$$

The weight of pitch in the graphite is equal to about 65% of the weight of pitch input to baking (from Section 5.3.1, the 35 wt.% lost is evolved as volatiles and burned to provide heat.) The weight of pitch input into baking is in turn equal to 1/4 the weight of coke input to baking, or

$$1/4\ \beta = 1/4(0.924)\alpha = 0.150\ \alpha. \tag{A.2.2}$$

Therefore, the weight of pitch in the graphite is about

$$0.65(0.150)\alpha = 0.098\ \alpha\ . \tag{A.2.3}$$

Assuming the graphite is about 100% coke and pitch, then the total weight of graphite (ϕ) is equal to the combined weights of pitch and coke:

$$\phi = 0.098\,\alpha + 0.924\alpha$$

$$= 1.022\alpha \tag{A.2.4}$$

Since ϕ is known, α, the weight of raw coke input to the graphite manufacturing process, can also be calculated. From this, the weight of raw material pitch (0.150α) can also be calculated.

A.3 Input Energy Mix for Furnace Black Production

The input energy for furnace blacks is split principally between oil, NG, and electricity. The oil provides the process feedstock, the NG provides process energy, and the electricity is used to drive the blowers and rotary dryer. The cost of the feedstock oils is estimated to make up about 60% of the total manufacturing cost for carbon black [60]. This assumption, together with the total energy input and the cost of each "fuel" (including electricity as a "fuel"), is used to calculate the energy mix.

In 1996, North American crude oil was approximately 4 times less expensive than electricity, and 1.3 times more expensive than natural gas.

Given,

I $$T = O + \Gamma + E = 1.265\ x\ 10^{8}\ J/kg \tag{A.3.1}$$

Where T - Total Input Energy

O - Oil Input in J/kg

Γ - NG Input in J/kg

E - Electricity Input in J/kg

II $$Total\ Manufacturing\ Cost = Oil\ Cost + NG\ Cost + Electricity\ Cost \tag{A.3.2}$$

III $$\frac{Oil\ Cost}{Total\ Manufacturing\ Cost} = 0.6 \tag{A.3.3}$$

IV $$\begin{cases} Oil\ Price = \$4.00 / MBTU \\ NG\ Price = \$3.36 / MBTU \cong 0.8 * Oil\ Price \\ Electricity\ Price = \$15.14 / MBUT \cong 2.6 * Oil\ Price \end{cases} \tag{A.3.4}$$

Then,

V $$\begin{cases} Oil\ Cost\ (\$) = O * price / unit\ oil \\ NG\ Cost\ (\$) = \Gamma * 0.8 price / unit\ oil \\ Electricity\ Cost\ (\$) = E * 2.6 price / unit\ oil \end{cases} \tag{A.3.5}$$

Now from III and V

$$\begin{aligned} &\frac{O * \ price / unit\ oil}{(O + .8\Gamma + 2.6E) * \ price / unit\ oil} = 0.6 \\ &\Rightarrow \quad O = 0.6\ (O + .8\Gamma + 2.6E) \\ &\Rightarrow \quad 4O = .48\Gamma + 1.56E \end{aligned} \tag{A.3.6}$$

and rearranging I,

$$\begin{aligned} O &= T - (\Gamma + E) \\ &= 1.265\ x\ 10^8 - \Gamma - E \end{aligned} \tag{A.3.7}$$

all of which are constrained by

$$O, \Gamma, E \geq 0 \tag{A.3.8}$$

Solving Equations (A.3.6) and (A.3.7) for Γ gives

$$\begin{aligned}\Gamma &= \frac{.4T - 1.96E}{.88} \\ &= .454T - 2.227E \\ &= 5.7431 \, x \, 10^7 - 2.227E\end{aligned} \tag{A.3.9}$$

Which, together with Equation (A.3.8) constrains E such that

$$\begin{aligned} & 0.454T - 2.227E \geq 0 \\ \Rightarrow \quad & 0.454T \geq 2.227E \\ \Rightarrow \quad & 0.2039T \geq E \\ \Rightarrow \quad & E \leq 20.39 \ \%\ of\ Total\ Input\ Energy \end{aligned} \tag{A.3.10}$$

Now, making a first guess at E = .20T , gives Γ = .0086T and O = .7914T.

As a second guess, let E = .10T , giving Γ = .2313T and O = .6687T .

Finally, letting E = .01T , gives Γ = .4317T and O = .5583T .

Therefore, approximate ranges for the energy mix are

56% of T $\leq$ Oil Fraction *(O)* $\leq$ 79% of T

.86% of T $\leq$ NG Fraction *(Γ)* $\leq$ 43% of T

1% of T $\leq$ Electricity Fraction *(E)* $\leq$ 20% of T

A.4 Energy Required to Mine Platinum

The richest Canadian mine deposit, which has a pgm grade of about 0.9 g pgm/tonne ore, produces 75 g pgm/tonne of nickel [62]. This allows the calculation of a nickel yield of 12 kg Ni/tonne ore in Canada.

If it takes X kJ of process energy per kg of nickel to mine 12 kg Ni/tonne ore, then it takes 12X kJ/tonne of ore to mine nickel. Assuming that it takes the same amount of energy to mine for ore in Canada as for ore in South Africa, then it must also take 12X kJ/tonne of ore to mine pgm in South Africa. The South African mines produce between 8-27 g pgm/tonne ore, of which 42-59% is platinum[1], giving 4.6-11.3 g Pt/tonne ore. It therefore takes 12X/0.0046 (12X/0.0113) kJ/kg pgm, or about 1060X to 2600X kJ/kg Pt.

The total energy required to produce platinum is calculated from the above, based on Hudson's value for the energy required to mine, process (refine and fabrication of ores) and fabricate materials, accounting for scrap recycling. Hudson's energy value is adjusted for platinum by setting the energy required to fabricate nickel materials to zero, assuming that the energy required to fabricate platinum salts from refined platinum metals is considerably less than the energy required to fabricate finished nickel materials. The resulting X is on the order of 100, giving the energy required to produce platinum to be on the order of 0.11 - 0.26 GJ/kg.

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[1] Pt mines produce 42-59% platinum from pgm, where 59% comes from a mine with grade 8 (8 g pgm/tonne ore) ore and 42% from a mine with grade 7-27 ore [62].

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