AN ABSTRACT OF THE THESIS OF

Malcolm O. Brown for the degree of Masters of Science in Industrial Engineering presented on June 3, 2011.

Title: A Process Based Modeling Approach For Economic And Environmental Assessment Of Nano-Assisted Manufacturing

Abstract approved:

Karl R. Haapala

Micro- and nanotechnologies are promising advancements across many industrial sectors, including alternative energy, chemical processing, and healthcare. In particular, a focus of research has been in manufacturing process development aimed at microdevice cost reduction and quality improvement. Microdevices take advantage of enhanced heat and mass transfer to improve energy and material efficiencies, yet device production uncertainties inhibit broad commercialization. Nickel nanoparticle (NiNP) assisted diffusion brazing has been shown to improve bond qualities and reduce processing time in microlaminated stainless steel devices. However, environmental impacts and cost differentials in comparison to conventional techniques remain largely uncertain. A prior life cycle assessment study compared this novel process to a more traditional diffusion brazing approach using nickel phosphorus electroplated laminae. The study found the former to be less environmentally impactful. A major limitation was in

the modeling of the NiNPs, which were assumed to be an equivalent mass of bulk nickel. To extend the prior work, this research develops life cycle inventories for NiNP synthesis and undertakes process-based cost modeling encompassing capital investment and cost-of-goods-sold as a function of annual production volume. Several manufacturing process scenarios are explored and compared on both an environmental and economic cost basis for the production of a microchannel air preheater.

A PROCESS BASED MODELING APPROACH FOR ECONOMIC AND ENVIRONMENTAL ASSESSMENT OF NANO-ASSISTED MANUFACTURING

by
Malcolm O. Brown

A THESIS

Submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented June 3, 2011
Commencement June 2012

Master of Science thesis of Malcolm O. Brown
presented on June 3, 2011

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Malcolm O. Brown, Author

ACKNOWLEDGEMENTS

I would first like to express my gratitude to my advisor, Dr. Karl Haapala, for his unwavering support, patience, and encouragement throughout my graduate studies. His technical and editorial advice was essential to the completion of this thesis and has taught me innumerable lessons and insights which have and will help me throughout my career and life. I would not be where I am today without his constant support, influence, and hard work he has invested within me. He has helped me succeed in my studies as well as prepare me for success in my future career.

This research would not have been as complete without the valuable input from the other members of my graduate advisory committee – Dr. Brian Paul, Dr. Denise Lach, and Dr. Goran Jovanovic– to whom I am very grateful.

I would like to thank Oregon State University and the United States Army (Contract Number: W909MY - 1- C – 0073) for the financial support which enabled the completion of this research.

I would also like to thank my colleagues Misha Sahakian and Babak Lajevardi for their valuable input and support during the completion of my studies.

I must express sincere gratitude for the support and understanding of my family and friends since I began my educational journey that has reached this waypoint. Special mention must go to my mother, step-father, and my brothers. Most of all, I am thankful for the support and sacrifices made by my wife, Elissa. Her always present love and words of encouragement have made this possible. To her, I am forever grateful.

CONTRIBUTION OF AUTHORS

I would like to recognize the contributions of the following coauthors on each of the manuscripts that comprise this thesis.

Manuscript 1.
Challenges Facing Engineers in Evaluating Life Cycle Impacts of Emerging Technologies

Karl R. Haapala,
School of Mechanical, Industrial, and Manufacturing Engineering
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Manuscript 2.
Addressing Uncertainty in the Environmental Analysis of Nickel Nanoparticle Production

Karl R. Haapala and Brian K. Paul,
School of Mechanical, Industrial, and Manufacturing Engineering,
Oregon State University

Richard D. Glover and James E. Hutchison,
Department of Chemistry,
University of Oregon

Manuscript 3.
Combined Cost Modeling and Environmental Assessment of Microfluidic Device Manufacturing

Karl R. Haapala, Babak Lajevardi, and Brian K. Paul,
School of Mechanical, Industrial, and Manufacturing Engineering,
Oregon State University

Steven D. Leith and Dale A. King,
Pacific Northwest National Laboratory

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SUMMARY OF RELEVANT WORK

PEER-REVIEWED PUBLICATIONS

Brown, M. O., K. R. Haapala, R. T. Eluri, B. K. Paul, S. D. Leith, D. A. King, 2011, "Environmental Impacts of Microchannel Air Preheater Manufacturing Under Different Scenarios," 2011 IIE Industrial Engineering Research Conference, Reno, Nevada, May 21-25.

Brown, M. O., K. R. Haapala, B. K. Paul, R. D. Glover, and J. E. Hutchison, 2010, "Addressing Uncertainty in the Environmental Analysis of Nickel Nanoparticle Production," Proc. 2010 ASME International Manufacturing Science and Engineering Conference (MSEC), Paper MSEC2009-34251, October 12-15, Erie, PA.

Brown, M. O. and K. R. Haapala, 2010, "Challenges Facing Engineers in Evaluating Life Cycle Impacts of Emerging Technologies," 2010 CIRP Life Cycle Engineering Conference, Hefei, China, May 19-21.

CONFERENCE AND WORKSHOP PRESENTATIONS

"Environmental Impacts of Microchannel Air Preheater Manufacturing Under Different Scenarios," 2011 IIE Industrial Engineering Research Conference, Reno, NV, May 21-25. (Paper presentation)

"Addressing Uncertainty in The Environmental Analysis Of Nickel Nanoparticle Production," 2010 ASME International Manufacturing Science and Engineering Conference (MSEC), Erie, PA. October 12-15, 2010. (Paper presentation)

"Environmental Analysis of Nanoparticle-Assisted Diffusion Brazing," Oregon Nanoscience and Microtechnologies Institute (ONAMI) MegaMixer 2010, Corvallis, OR, August 27, 2010. (Poster presentation)

“Environmental Analysis of Nanoparticle-Assisted Diffusion Brazing,” Greener Nano 2010: Reducing Principles to Practice. Portland, OR. June 16-18, 2010. (Poster presentation)

LISTS OF ACRONYMS AND ABBREVIATION

AISI	American Iron and Steel Institute
CO	Carbon Monoxide
CO_2	Carbon Dioxide
$CoCl_2$	Cobalt (III) Chloride
COGS	Cost of Goods Sold
C_p	Specific Heat
CTAB	Cetyltrimethylammonium Bromide
DDT	Dichlorodiphenyltrichloroethane
DfE	Design for the Environment
FCC	Face-Centered Cubic
F_n	Family of Nanomaterials
HCl	Hydrochloric Acid
IA	Impact Assessment
ISO	International Organization for Standards
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
$LiBH(C_2H_5)_3$	Lithium hydrotriethylborate
LPSP	Low Pressure Spray Pyrolysis

LISTS OF ACRONYMS AND ABBREVIATION (CONTINUED)

Micro-HX	Microchannel Heat Exchanger
MPT	Microchannel Process Technology
N_2H_4	Hydrazine
N_2H_5OH	Hydrazinium Hydroxide
$NaBH_4$	Sodium Borohydride
NaOH	Sodium Hydroxide
Ni	Nickel
$Ni(CO)_4$	Nickel Carbonyl
$Ni(NO_3)_2{\cdot}6H_2O$	Nickel Nitrate Hexahydrate
$NiCl_2$	Nickel Chloride
NiNP	Nickel Nanoparticles
NiP	Nickel Phosphorus
PCM	Photochemical Machining
PNNL	Pacific Northwest National Laboratory
PVP	Poly-vinylpyrrolidone
R&D	Research and Development
RA	Risk Assessment
SEM	Scanning Electron Microscope
$TC_{12}AB$	Tetradodecylammonium Bromide

LISTS OF ACRONYMS AND ABBREVIATION (CONTINUED)

THF	Tetrahydrofuran
TLP	Transient Liquid Phase
T_{ref}	Reference Temperature, assumed 20 °C (293 K).
Y	Process Yield

A Process Based Modeling Approach for Economic and Environmental Assessment of Nano-Assisted Manufacturing

CHAPTER 1

INTRODUCTION

This chapter gives a background and motivation for the research undertaken. It will be shown there is a need for coupling environmental and economic evaluation techniques to achieve a more sustainable state for emerging technologies, such as micro- and nano-assisted manufacturing.

MOTIVATION

Micro- and nanotechnologies, which take advantage of materials and products with geometries ranging from a few nanometers to tens of micrometers, have benefited many applications including highly efficient and portable kidney dialysis micro-filtering systems [52], production of engineered nanomaterials [53], and nano-assisted manufacturing processes [29]. With 2011 National Nanotechnology Initiative budgets surpassing 1.85 billion dollars [54] and industry and consumers demanding more advanced products and processes, many more innovations can be expected to be developed and commercialized. An emerging area of development is energy recuperation enabled by microchannel process technology (MPT).

Such energy recuperators take advantage of the reduced diffusional distances characteristic of microchannels in extracting heat from the hot fluid. Aggressive weight and volume constraints associated with mobile vehicle platforms make MPT devices particularly suited to these applications due to the size and weight savings achievable through the use of micro- and nano-scale features and materials.

With rising populations driving increasing demands on already-limited resources, the need for dematerialization, e.g., through the MPT device applications, in conjunction with other efforts for sustainable industrial practices, is becoming more evident. No longer are the days where only the bottom-line is to be considered in business decision making. Economic decisions must be coupled with those based in environmental responsibility. By either adhering to the requests of society or realizing the long term benefits, corporations have begun to include the pursuit of sustainability (economic, environmental, and social) principles into their business plans.

To assist in achieving corporate environmental goals, through waste reduction/elimination and resource/energy efficiency improvements, there are but a few concepts and tools currently available. Life Cycle Assessment (LCA), Design for the Environment (DfE), and Life Cycle Impact Assessment (LCIA) can assist in estimating and mitigating the impacts that a product or process may have on the environment and surrounding society and ecosystems [1]. However, in order to ensure longevity, environmental performance alone is not enough. Equally important, economic feasibility must also be incorporated within sustainability decision making.

No matter how diligent companies may be in their quest for sustainability, without the proper tools their efforts can be futile. The research herein examines the unique issues which engineers face when attempting to analyze the sustainability of emerging technologies, such as the aforementioned micro- and nano-technologies.

The need for a framework and development of a modeling approach that accounts for both environmental impacts and economic costs is apparent. The results of such an approach could be used to assess and compare alternative scenarios for creating and manufacturing products and devices being developed on the forefront of technological advancement.

BACKGROUND AND PROBLEM DESCRIPTION

Faced with unique challenges, micro- and nano-technologies lack the methods and tools necessary to assess sustainability on the basis of coupled environmental impacts and economic costs. In the area of microfluidics, specifically, there lies much potential for promising advancements across many sectors in society (e.g., economic, defense, healthcare) [2]. However, due to the relative novelty and complexity of these devices, many of the current manufacturing practices are burdened with inefficiencies and unknowns concerning process yields, quality, costs, and environmental impacts. The work to follow aims to addresses these needs.

THESIS OBJECTIVES

An objective of this research is to examine the unique issues that researchers and engineers face when attempting to assess an emerging technology through coupled economic and environmental assessment of nano-assisted manufacturing. Using a microfluidic air preheater device for demonstration, this work has an additional objective of revealing the issues that are specific to assessing micro- and nanotechnologies. These concerns will be examined and addressed using various tools and approaches. Finally, these approaches will be applied for the case of a microfluidic air preheater. This will demonstrate the process in which an environmental assessment is undertaken in conjunction with process-based cost modeling. This type of analysis for microchannel device manufacturing has not been reported in the literature to date.

THESIS OUTLINE

The research is reported in this thesis in the form of several manuscripts, which begins by identifying the need for assessing new technologies and their respective environmental impacts. Chapter 2, the first manuscript, focuses on the unique differences and challenges that newly introduced technologies pose versus those of more established industries and practices. Several options for examining the environmental impact of nano-technologies are then presented.

Chapter 3, the second manuscript, examines a specific area of emerging technologies, nanomaterials, and addresses issues that arise when attempting to assess products and processes that utilize nanoparticles. The research reported is a continuation of a prior life cycle analysis study that assessed the environmental impacts of manufacturing a micro-heat exchanger using nano-assisted diffusion brazing, but discovered a lack in inventory data for nanomaterial production [3]. This study addressed some uncertainties in how nanomaterials are synthesized by working in collaboration with chemists from the University of Oregon. Through modeling and analysis of several synthesis routes for nickel nanoparticles, life cycle inventories were created to assist in more accurately accounting for the energy and material requirements for producing the nanomaterials.

Chapter 4, the final manuscript, examines the issues unveiled within the first and second studies from an environmental perspective. It also introduces the concept of process-based cost modeling. A representative device, a microchannel air preheater, is examined to assess and compare alternative manufacturing routes using a combined environmental impact and economic cost assessment approach. The microchannel air preheater encompasses the use of both micro- and nanotechnologies.

In Chapter 5, the research from this thesis is reviewed and summarized. The environmental assessment and cost model results of the arrayed microchannel air preheater device and then discussed. Following this, contributions from this study are identified and recommendations for future work are outlined

The common theme throughout the thesis comprises the process, challenges, and methods for the assessment of manufacturing emerging micro- and nano-technologies on the basis of environmental impacts and costs. The ultimate aim of the research reported herein is to demonstrate an approach for combined environmental impact and cost assessment to directly improve the sustainability of nano-assisted manufacturing.

CHAPTER 2

CHALLENGES FACING ENGINEERS IN EVALUATING LIFE CYCLE IMPACTS OF EMERGING TECHNOLOGIES

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Appeared in the Proceedings of the 17th CIRP International Conference on Life Cycle Engineering 2010, Hefei University of Technology. Anhui, China.

ABSTRACT

Life cycle analysis has been used to inform the design of existing technologies, but it is not well equipped to support environmental analysis of emerging technologies (e.g., nanomaterials and molecular medicine). Thus, many of the problems associated with conducting life cycle analyses for existing technologies (e.g., inventory data availability and unknown health effects) are accentuated when attempting to evaluate technologies that are currently under development and do not have a definite application or known lifetime. The issues and challenges associated with the use of life cycle analysis are explored. Approaches to evaluating the impacts of emerging technologies are also discussed.

KEYWORDS

Life Cycle Analysis, Emerging Technologies, Nanomaterials

INTRODUCTION

Engineers are confronted with the challenge of designing and producing transformative technologies that offer the prospect of paradigm shifts in the provision of basic needs (e.g., water and energy) to a growing global society, but which have the potential to cause uncertain effects to people and the environment. One such example is the development of fuel cells and the potential environmental impacts they may have at their end of life [4].

Nanotechnology, according to the United States Food and Drug Administration, is defined as a research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nanometers [5]. This emerging technology represents a relatively new area and is still largely underdeveloped. The push to promote continued development of nanotechnology is evident, with the U.S. government allocating more than $1.5 billion to nanotech-related research in 2009 [6]. As shown in Figure 2.1, predictions project a global market of around $3.6 trillion by 2015 [7], which is growth of over 2000%. Currently, there are thousands of applications for many nanomaterials in electronics, medicine and tissue engineering, purification and filtration systems, composite materials, and energy production. As with any new and emerging technology, however, attention is focused toward the new possibilities that it will open up to consumers. The potentially dangerous effects of the production, use, and disposal of nanomaterials, however, remain unknown and largely unexplored.

The scientific community and broader society has learned that new inventions and technologies need to be holistically analyzed with a systems perspective prior to wide distribution even if there are many initial benefits. The invention and advocacy for use of DDT (dichlorodiphenyltrichloroethane), for example, brought to the fore potential effects of a poorly evaluated technology, as it led to devastating human and environmental impacts. DDT was not used as a pesticide until 1939, but it was not until over 30 years later, in 1972, that it was banned for use on crops [8]. Attacking the central nervous system, it is known today that DDT can cause tremors and seizures to humans as well as disruptions in environmental ecosystems [9]. The effectiveness in pest control of DDT was so great that adequate testing was not carried out to determine the presence of adverse effects. This dramatic case provides a historical backdrop to the need for comprehensive examination of new technologies being developed today that may provide society with immeasurable benefits while causing uncertain harm.

Over the decades, the demands and priorities of society tend to change. Technological demands are no exception to this rule, which continue to change along with the societal environment. Amenities often thought of as limitless in the past, such as fossil fuels and old growth timber, have proven to have limits. As the world population continues to grow exponentially, scientists and engineers strive to develop technologies that meet the vital needs of society. These needs include clean water, food, and energy. Emerging technologies have the potential to decrease the difficulty with which these needs can be met by either increasing production capacity or decreasing the overall cost of production for that product.

Today, technologies exist to solve many issues face by society. To provide abundant energy, science has discovered alternative sources of energy and continues to promote research to further develop energy technologies. Emerging alternative technologies include solar power and bioreactors, as well as harnessing wind and wave energy. Advances in nanotechnology have improved the ability to purify water. In fact, the use of nanosorbents and nanocatalysts has allowed for the effective purification of oceanic water, which is the most plentiful source of water in the world [10].

As past experience has shown, emerging technologies require in-depth analysis of the entire life cycle, from cradle to grave, to address potentially harmful effects on people or the environment. Approaches for more holistic assessment of the emerging field of nanotechnology are explored in this paper. In particular, the method, benefits, and limitations of Life Cycle Assessment (LCA) as applied to environmental analysis of nanomaterials are discussed. An LCA study for the production of nickel nanoparticles is reported and used as a basis for discussion of common challenges faced by scientists and engineers in evaluating emerging technologies from a sustainability perspective. Ideas for future improvement of impact assessment of nanomaterials are introduced

LIFE CYCLE ANALYSIS AND ITS CHALLENGES

Life Cycle Assessment (LCA) is the most widely used and accepted method for predicting comprehensive environmental and social effects caused by products, processes, and systems. LCA facilitates the comparison of design alternatives and can assist engineers and other decision makers in identifying the least burdensome, or most environmentally sustainable, solution. With the impacts of nanotechnology vastly unknown, it is imperative that methods and tools be developed to assist in the assessment of emerging technologies. The LCA methodology offers a starting point for such evaluation, and has the following four distinct phases [11]:

Goal and scope definition: Boundaries are established for the study specifying the level of detail the assessment will encompass. In this phase the purpose of the LCA study should be clearly stated (e.g. new product analysis, comparison of alternatives) as well as identifying a product system, functional units, allocation methods, and impact categories.

Life cycle inventory: Material and energy flows (inputs and outputs) of the system are defined, collected, and quantified.

Life cycle impact assessment: Life cycle inventory data, which was previously collected, is converted into environmental impact estimates through an ISO defined classification and characterization process.

Interpretation: Final step in LCA where assessments are completed of previous phases, conclusions are drawn, and recommendations are made.

Although Life Cycle Analysis is a highly beneficial tool in assessing environmental impacts of materials, products, or processes, there are limitations to the procedures and methodology. A later section, General Limitations of LCA, discusses those limitations are discussed in detail below.

GENERAL LIMITATIONS OF LCA

Each of the phases of the life cycle assessment methodology is faced with its own specific problems and limitations as summarized below.

Goal and Scope Definition

The problems that have been identified in defining the goals and scope of LCA studies include assigning a functional unit, boundary selection, environmental versus social and economic impact trade-offs, and alternative scenario consideration problems [11].

Defining a functional unit, a performance measurement unit that is used as a basis of comparison for alternatives, can lead to potential errors when 1) multiple functions (main and sub-functions) are in question, 2) functional equivalents are being compared, and 3) when inventory data is not easily quantifiable [11]. The problem in selecting the boundary of an LCA study is in deciding how much of the processes, activities, and energy flows to include. The scope needs to be justified to support, with confidence, the results of the study given time and resource constraints [8]. The underlying dilemma is in defining objective and scientifically suitable boundaries which will allow for repeatability and provide integrity to the study [12]. Researchers may be tempted to narrow the scope of the study to reduce the amount of data collection required, but this can produce inaccurate or skewed results [13]. Although time and resource constraints play vital roles in scope and boundary selections, researchers are still held accountable to justify their choices. Failure to select appropriate boundaries, resulting in misrepresentations of the actual study environment, can lead to misinterpreted results and lowered confidence levels of the decision maker [14]. Also, when conducting LCA studies, ISO guidelines recommend the impact analysis be focused on strictly environmental issues and the impacts to social and economic systems need not be considered. As always, cost and resource availability are limiting factors, but integration of LCA with social and economics could prove very valuable, especially in the private sector of industry and business [14].

Inventory Analysis

Mapping the flow of materials, resources, wastes, and processes are a few of the key components in this stage of the LCA study. Problems in this phase arise in determining the breadth of data to include and identifying the appropriate cutoff points for unimportant or insignificant contributions [11]. ISO standards allow for resources and waste streams that provide negligible impacts to be excluded from the study. Suh [12], however, discusses that while a single source may be negligible, the sum of many minor sources could have very noticeable impacts to the study.

Impact Assessment

The conversion of life cycle inventory data to environmental impact estimates can prove to be difficult and leaves opportunities for errors and challenges to ensue [11]. Many of the challenges and limitations associated with the impact assessment stage of LCA are linked to data accuracy and availability. Further investigation into this can be seen in the following sections.

Interpretation

Limitations faced in performing life cycle assessments leave room for error and uncertainties. Funtowicz and Ravetz [15] organize these LCA uncertainties into three categories: data uncertainty, model uncertainty, and completeness uncertainty. The exact reasons for these sources of uncertainty can be complex and difficult to agree upon, but they all have a general underlying root cause resulting from information that is unobtainable, incorrect, contains variability, or is simply inaccurate. LCAs require extensive knowledge of a product or process and most limitations are data related. Without a holistic understanding, significant details may be unintentionally excluded and resulting in inaccurate or skewed conclusions.

The amount of subjectivity allowed in the LCA methodology constructed by ISO 14040 standards have been questioned by researchers [11]. Suh [12] states, "…[T]here is no theoretical or empirical basis that guarantees that a small mass or energy contribution will always result in negligible environmental impacts." Allowing such subjective interpretations and analysis could lead to reduced confidence in LCA study results. As with most scientific studies, funds and resources are limited. Accurately conducted LCAs require significant amounts of time and resources to gather the appropriate input and output inventory data [16].

LIMITATIONS OF LCA FOR NANOTECHNOLOGY

In attempts to perform a Life Cycle Assessment of emerging technologies, such as nanotechnology, researchers are faced with even more barriers than attendant to conventional LCA. LCA was created to be used as a comparison tool of conventional, established, and widely understood industries and technologies [17], which are unlike nanotechnology.

Due to nanotechnology's wide variety of products and materials, unknown toxicological effects, and uncertainties behind the final application of nanomaterials, LCA becomes difficult to conduct [18]. Advancing rates of emergent technologies make it difficult to obtain good quality, up-to-date, representative inventory data suitable for accurate life cycle assessments. Combining this with the lack of standardized testing for data quality brings rise to yet another difficulty for nanotechnology LCA [19].

Prepopulated inventory databases have been developed to assist in the LCA background data collection process [20]. These databases, however, lack many of the less-common materials and energy sources that nanomaterials utilize in their early stages of production and synthesis. For studies dealing with nanomaterials, the use of these databases can be difficult if not infeasible, and thus make them relatively crude LCA support tools.

Variations in nanomaterials, processing techniques, and applications of nanotechnology have led to innovation in many different areas of industry. To ensure an organization a competitive advantage, companies may withhold this data from public knowledge, consequently making it more difficult to conduct parallel LCA studies if the material or process under question is confidential or contains proprietary data. Also adding to the complexity, nanomaterials are typically used as additives rather than in the pure phase [17], making it difficult to track and allocate use and disposal impacts. Problems such as these may lead to skewed, incomplete, or inaccurate LCA conclusions, which is a cause for concern when potential risks to human health and the environment are high.

APPLICATION OF LCA FOR NANOTECHNOLOGY

A previous cradle to gate LCA for a microchannel heat exchanger (Micro-HX) explored the use of nickel nanoparticles (NiNPs) within a braze paste to diffusion bond stainless steel laminae [3]. The study showed promising results in the potential to reduce impacts of the NiNP Micro-HX over one produced using an electroplating-diffusion bonding cycle. The study concluded that impacts may not be adequately addressed due to deficiencies in modelling of nanoparticle production. To address this, several synthesis methods were explored in terms of their relative environmental impacts for the production of the same device evaluated in the previous study (Table 2.1).

(mass in kg)	A	B	C	D	E	LCA Process
Nickel ($NiCl_2$ production)	1	1	1	1		Nickel 1
Water ($NiCl_2$ production)	1.842		1.842	1.842		Water, deionized, at plant/CH U
HCl ($NiCl_2$ production)	1.242		1.242	1.242		HCL (100%) B250
Cobalt					1	Cobalt, at plant/GLO U
Sodium hydroxide	0.120					NaOH ETU U
Ethylene glycol	497.0		94837	15638		Ethylene glycol, at plant/RER U
Hydrazine	1.706					Ammonia ETH U
Carbon monoxide		52.31				Carbon monoxide, CO, at plant/RER S
Toluene		0.292				Toluene, liquid, at plant/RER S
Helium		7.225				Helium, gaseous, at plant/RER S
Sulphur hexafluoride		24.94				Sulphur hexafluoride, liquid, at plant/RER S
Hydrogen		.0022				Hydrogen, liquid, at plant/RER S
Sodium tetrahydroborate			766.7	126.5		Sodium tetrahydroborate, at plant/GLO S
PVP			0.022	0.022		Acrylic binder, 34% in H2O, at plant/TER U
Chlorine					1.2	Chlorine ETH U
Superhydride/SB_{12}					57.70	Chemicals organic, at plant/GLO U
$LiBH(C2H_5)_3$					1.798	Chemicals organic, at plant/GLO U
Tetrahydrofuran					15638	Tetrahydrofuran, at plant/RER U
Electricity (MJ)		10.04			Electricity, medium voltage, production UCTE, at grid/UCTE S	
Process heat (MJ)	47.89		27412	4520	Electricity, medium voltage, production UCTE, at grid/UCTE S	

Table 2.1 Materials and energy for each nanoparticle synthesis alternative

Method A involved the production of NiNPs through the reduction of $NiCl_2$ in ethylene glycol using hydrazine at slightly raised temperature (60°C)

[21]. $NiCl_2$ was assumed to be produced as described in [3], using H_2O, Ni, and HCl.

Method B utilized a laser to decompose $Ni(CO)_4$, which was produced as needed from Ni powder and CO gas [22]. Sulfur hexafluoride was used as a photosensitizer and helium as a purge gas. Hydrogen was used as a shielding gas. The NiNPs were collected on a filter, and assumed to be deagglomerated via ball milling in toluene.

Method C was based on a polyol process, as was Method A, but used poly(N-vinilpyrrolidone) (PVP) as a protective agent, and had a lower concentration of $NiCl_2$ solution, resulting in increased use of ethylene glycol [23]. $NaBH_4$ was used as the reducing agent. It should be noted that the case chosen for Method A was at the highest concentration of $NiCl_2$ reported in the study.

Method D assumed the synthesis of NiNPs via the polyol process route is possible using a microreactor, rather than batch processing. Microreactor NP synthesis has been demonstrated for cobalt [24]. The process involved the reduction of $CoCl_2$ in tetrahydrofuran (THF). Lithium hydrotriethylborate ($LiBH(C_2H_5)_3$) was the reducing agent and the stabilizer was 3-(N,N-dimethyldodecylammonia) propanesulfonate (SB_{12}). Although cobalt would likely not be used in this device, it is reported for comparison as Method E in this study. Method D assumed the same quantity of solvent used as in Method E to elucidate the potential reduction in impacts for microreactor synthesis.

The manufacturing processes to produce the Micro-HX device have been previously reported [3] and remain the same in this study with the exception of NiNPs produced using the modified polyol process. It is assumed that these materials will not require a binder material as they are protected with PVP. Energy use in Method B was attributed to the laser and ball milling. Method A considered energy needed to heat the fluid to 60°C, and C and D assumed heating to 140°C. Material and energy inventory data are reported in Table 2.1, and process wastes and emissions are shown in Table 2.2.

(mass in kg)	A	B	C	D	E	LCA Process
Helium		7.225				Helium
Sulphur hexafluoride		24.94				Sulfur hexafluoride (emissions to air)
Carbon monoxide		52.31				Carbon monoxide
Toluene		0.292				Toluene (emissions to air)
Nitrogen gas	0.477					Nitrogen (emissions to air)
Ethylene glycol	497.0 3					Disposal, antifreezer liquid, 51.8% water, to hazardous waste incinerator/CH U
Process wastes (L)	0.120		796.8	129.5	15699	Treatment, black chrome coating effluent, to wastewater treatment, class 2/CH U

Table 2.2 Wastes and emissions for each nanoparticle synthesis alternative

To analyze the environmental impacts associated with production of the Micro-HX device using the different nanoparticle synthesis methods, a commercially available life cycle analysis software is used (SimaPro 7, Pré Consultants). The names of process models used in this study are also reported in Table 2.1 and Table 2.2.

The impact results for producing the Micro-HX device using each nanoparticle synthesis method are shown in Figure 2.2. As mentioned above, the process modeled for Method A assumed the highest concentration of solvent. This may account for its wide variation from other impact results. Looking at the other alternatives, a decision maker is not able to draw a conclusion with high confidence about the most appropriate approach for manufacturing the device.

Figure 2.3 displays the predicted level of environmental impact associated with the production of the necessary amount of nanoparticles for the device using each synthesis method. It can be seen that there is wide variation in impacts among the processing techniques, while this same variation was largely masked when evaluating the methods in the context of their application in the braze paste for the microchannel heat exchanger.

The impact assessment method used is the recently released ReCiPe 2008 [25]. ReCiPe 2008 is the result of an effort that had a goal to harmonize the two main approaches to impact assessment – the first based on characterization of impact categories (midpoint indicators) and the second based on damage types (endpoint indicators). The method consists of eighteen midpoint indicators and three endpoint indicators (damage to human health, to ecosystem diversity, and to resource availability). It allows for valuation similar to the Eco-indicator 99 method, with the default approach using the Hierarchist perspective and an average weighting set (H/A) for Europe (Europe ReCiPe H/A). The World ReCiPe H/A method available in the LCA software was used in conducting the impact assessment in this study.

DISCUSSION

The introduction of new tools and practices for improving the accuracy and applicability of current life cycle assessment techniques to emerging technologies, such as nanotechnology, is vital to engineering decision making. This is especially important when products (or applications) and the necessary production processes are developed simultaneously. Several possible methods to improve decision making in the development and selection of nanomaterials are briefly introduced below.

Life Cycle Assessment and Risk Assessment

To reduce the limitations presented by using LCA alone in capturing human health (toxicity) impacts of nanomaterials, researchers have suggested coupling life cycle assessment with risk assessment (RA) or other impact assessment (IA) methodologies [18][26]. Risk assessment entails a detailed background where all assumptions and uncertainties, along with their encompassed risks, are clearly defined and integrated throughout the entire life cycle of a technology. The process of quantitatively defining the elements of a risk accurately and in a precise manner and detail is the main objective of RA, as well as its underlying challenge. Although it has long been accepted as a decision making support tool, the standardization in RA methods, procedures, and definitions has been hindered due to disagreements upon definitions and the principle characteristics of risk [26]. Thus, a broadly applicable, formalized method for RA does not exist.

Combining the broader applicability of LCA methods with the specific focus of RA could prove valuable in discerning impacts of emerging technologies. A general approach for doing so has been presented for assessing toxicological effects of nanomaterials [18]. It was suggested that toxicology data from specific tests of nanomaterials, for example, could supplement an LCA approach through their inclusion in terms of environmental implications.

Material Property Charts

Another approach that could facilitate impact and risk assessment would require the creation of a nanomaterial selection tool. The tool would allow selection on a basis of physicochemical properties, including toxicity. This approach follows previously developed material selection methods, which utilize material property charts [27]. *Families* of nanomaterials (denoted by F_n in Figure 2.4, which would presumably be based on their core and/or functional group composition, could thus be defined and compared. The tool would be applicable in nanomaterial research and development to direct scientists and engineers in the design and selection of more benign materials based on the set of physicochemical properties (e.g., size, chemical composition, surface structure, solubility, shape, and aggregation) [28]. The guide would be comprised of a series of material property charts that would denote the measure of toxicity versus each physiochemical attribute, as shown in Figure 2.4.

In addition to providing a decision maker with information about known materials, it may be possible to predict the relative toxicity of a new material based on its physicochemical attributes using this visual guide.

Nanomaterial Impact Matrix

A related method for improving the environmental and toxicological assessment of nanomaterials would correlate qualitative and/or quantitative information of environmental and toxicological effects to physicochemical attributes. Impact ratings for each of the physicochemical attributes would be presented in a 1-by-n matrix (A). A separate n-by-1 matrix (B) would contain the value for each physicochemical attribute. Conceptually, these matrices would be multiplied and the result would provide a numerical measure of the potential toxicological impact (I) of the nanomaterial (Equation 2.1).

$$I = A \cdot B = [a_1 \;\; a_2 \cdots a_n] \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{bmatrix} \tag{2.1}$$

This impact measure could then be used as an indicator of the toxicity of the material or as a basis to compare to potential alternatives. Thus, the nanomaterial impact matrix would provide scientists and engineers with a single score quantitative decision making tool, while material property charts would present the same impact versus physicochemical attribute information graphically.

SUMMARY AND CONCLUSIONS

Nanotechnology is an emerging technology with applications in breakthrough materials, products, and processes. The variety of materials and applications that can potentially benefit from nanotechnology present barriers to the application of conventional LCA methods in engineering analysis. Combinations of LCA and other engineering approaches, methods, or tools may need to be applied to accurately assess the true impacts nanomaterials and other nanotechnologies [18]. Although emerging technologies present challenges in data availability and transparency due to proprietary and patent rights, implementation of LCA in the early stages of development of emerging technologies is critical. Focused fundamental and applied research into environmental and health impacts of emerging technologies and their relation to processing parameters will facilitate technology development and implementation in a manner that mitigates harm to human health and the environment, while ensuring the needs of society are adequately met.

FIGURES

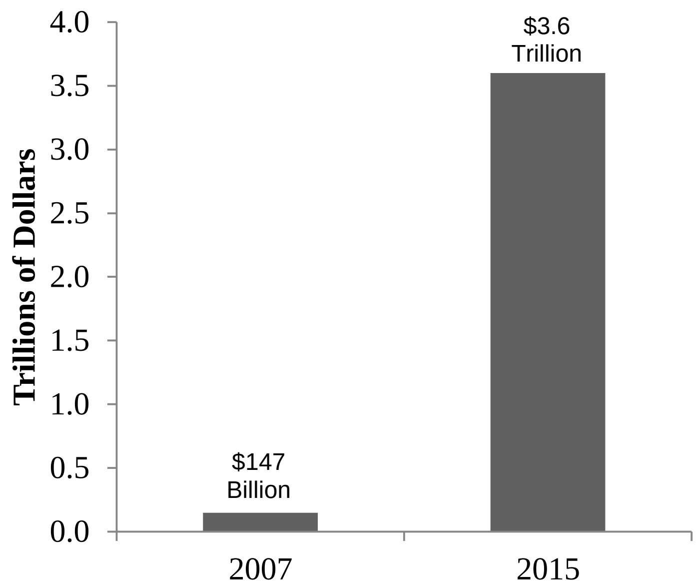

Figure 2.1 Projected global nanotechnology market [7]

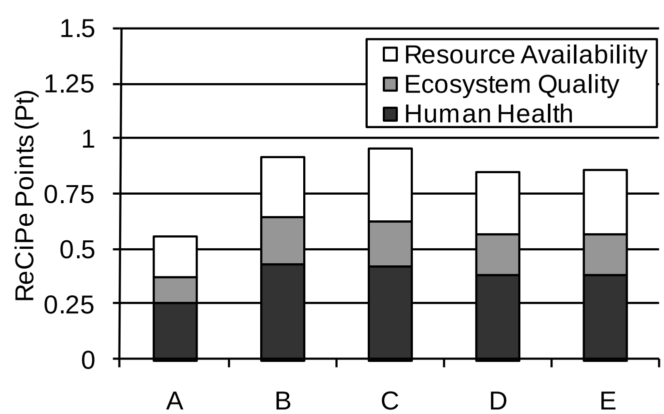

Figure 2.2 Effect of NP synthesis on device

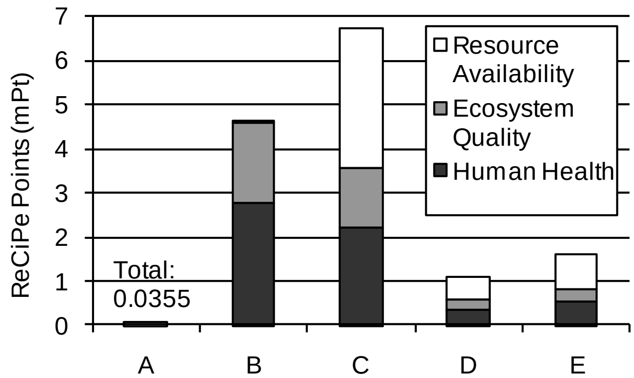

Figure 2.3 Impacts of NP synthesis methods

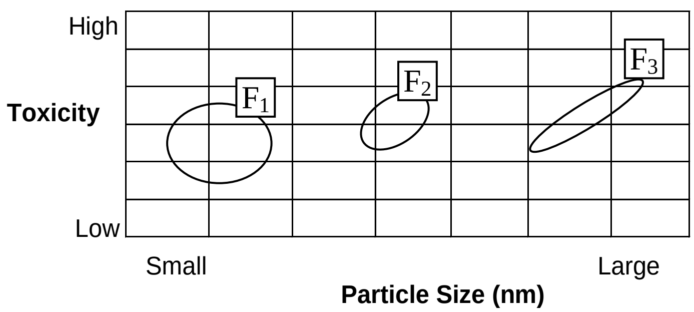

Figure 2.4 Representative nanomaterial property [27]

CHAPTER 3

ADDRESSING UNCERTAINTY IN THE ENVIRONMENTAL ANALYSIS OF NICKEL NANOPARTICLE PRODUCTION

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Appeared in the Proceedings of the 2010 ASME Manufacturing Science and Engineering Conference (MSEC), Erie, PA.

KEYWORDS

Nanomanufacturing, Life Cycle Assessment, Sustainability

ABSTRACT

In spite of the many potential benefits and applications of nanoparticles, concerns have been raised regarding their production, use, and ultimate fate due to poor process yields and uncertain health and environmental impacts. Production of commercial nanoparticles is growing as increasing use in industrial and consumer products is found. Nickel nanoparticles (NiNPs) have shown promise as a single element braze material, but the energy and material efficiencies of NiNP production remain uncertain. In this study, life cycle assessment (LCA) is employed to compare three different NiNP synthesis methods in terms of environmental impact. The study reveals challenges in using LCA to assess nanomanufacturing processes. Sensitivity analysis is performed across several process parameters to demonstrate an approach for addressing data uncertainties. The relative performance of the NiNP synthesis processes are discussed, and potential environmental implications for other NiNP synthesis processes are introduced. Policy change may be necessary to provide adequate transparency in assessing nanotechnologies for engineering applications.

INTRODUCTION

Modern scientific research has led to greater control over engineered materials. An example is the industrial production of nanoscale materials, or nanoparticles, many of which have been produced and existed naturally for eons. Only recently has there been such tight control over size, shape, and functionality of nanoparticles. Along with fundamental research, there has been a dramatic increase in industrial and consumer applications of nanoparticles. One such application under development is nanoparticle-assisted diffusion brazing [29]. Diffusion brazing is a transient liquid phase joining process utilizing a filler material that melts and diffuses into the parent material to form the joint. Diffusion brazing has been used to join many types of metals (e.g., steels, Ni superalloys, aluminum, copper and titanium) [30][31][32][33][34][35][36] and is useful for micro-energy and chemical systems packaging [37]. The use of nanopowders in diffusion brazing has been previously reported by Mohankumar, et al. [38] and Philip, et al. [39]. Tiwari et al. [29] reported a technique for diffusion brazing stainless steel using nickel nanoparticles mixed with a commercial binder and water for microfluidic device packaging.

While metallic nanoparticles are a focus of research due to unique properties and potential applications in areas such as electronics, catalysts, and health care, little is known about their long term health and environmental effects. Particle reactivity can differ from the bulk material, altering toxicity and transport mechanisms [40]. The relatively high levels of energy, waste, and materials needed to manufacture nanomaterials, compared to traditional materials, are also of concern. Production can require multiple times the energy per unit mass and material requirements can be as much as five orders of magnitude greater than bulk material processing [41] [42]. It is important that engineering analyses investigate the possible exposures faced across the life cycle when using nanomaterials, while nanomaterial production process energy use and material efficiencies must be carefully evaluated.

A technique particularly well-suited for comparison among alternatives on an environmental impact basis, including health effects, is life cycle assessment (LCA). A recent study revealed that life cycle analysis of nanotechnology is faced with many challenges, including additional barriers than those presented by conventional manufacturing technologies [43]. These difficulties stem from the ever-developing and often proprietary nature of nanotechnology. Production processes, flows, and energy and material input and outputs may be untraceable due to deficiencies in reporting. Upstream processes, downstream applications, and the ultimate fate of nanoparticles are unknown or highly uncertain. The toxicological effects of nanomaterials are largely unknown. One major challenge that can be addressed through LCA from a manufacturing process perspective is the inadequacy of models for the production of nanomaterials. The authors determined, although LCA methods need to be improved, they are nonetheless able to provide valuable information about the impacts of emerging technologies [43].

In the work presented herein, life cycle assessment (LCA) is applied to the production of nickel nanoparticles (NiNP) using three similar techniques reported in the literature. Examining similar production routes (i.e., nickel chloride reduction with hydrazine) allows several variables to be controlled, while facilitating both comparisons across the three methods and sensitivity analysis. The results of the LCA study are examined and relative impacts of the techniques are discussed. Sources of uncertainty in the analysis are explored and discussed.

BACKGROUND

The effect of NiNPs interlayer application to transient liquid-phase diffusion brazing was investigated for application to microfluidic device production and previously reported [29]. This study examined the use of NiNPs in a braze paste for bonding stainless steel 316L laminae as a part of a microchannel device. NiNPs offered several process benefits, including lower melting point, increased diffusion rate, and improved bond strength, resulting in lower process energy and processing time. Voids along the bondline were reduced, which are sources of crack propagation (Figure 3.1). Due to sustainability concerns, the need for understanding of potential environmental impacts was apparent, and has been a focus over the last year.

The research herein builds upon a prior study exploring the effects of diffusion brazing of a micro heat exchanger using a NiNP braze paste in comparison to conventional NiP (nickel phosphorus) electroplating [3]. The cradle-to-gate environmental analysis found the NiNP deposition method to be superior to NiP electroplating, primarily due to lower bonding energy requirements and reduced usage of nickel. Particles exhibit significantly lower melting temperatures and more rapid diffusion rates as size decreases [44], resulting in lower processing temperature and time. It was concluded that further research and analysis of the environmental and toxicological effects of NiNPs is required due to uncertain impacts and risks [3]. Deficiencies in modeling of nanoparticle production were revealed due to a lack of data transparency and availability in constructing life cycle inventories for processes used.

The goal of the present study is to assess the relative environmental impacts for the production of NiNPs using several synthesis methods. Completing the impact assessment for specific synthesis methods would allow for a more complete environmental analysis of microfluidic device manufacturing methods to be initiated. Several production routes for nickel nanoparticles are described below.

NICKEL NANOPARTICLE PRODUCTION

Due to desirable material properties and compatibility with stainless steel for diffusion bonding, nickel nanoparticles (NiNPs) have been investigated for the use in diffusion bonding of the microfluidic devices as discussed above. Specifically, NiNPs particles ranging from 1-100 nm exhibit benefits in diffusion rates and melting temperatures to reduce processing time, energy use, and bond quality. NiNPs are being produced in batch processing through chemical synthesis methods. These routes primarily utilize basic ingredients, such as a nickel compounds (e.g., nickel powder, nickel carbonyl, and nickel chloride), a reducing agent, and a solvent such as acetone. Additives and alterations in chemistries may be used to produce particles of varied shapes, sizes, and structure.

NiNP synthesis techniques as described above have been reported in the literature, and several are shown in Table 3.1 (Methods 1-6). These are illustrative of the breadth (e.g., laser, spray pyrolysis, and solution phase synthesis) of the methods reported. Method 1 utilized a CO_2 laser to assist in the decomposition of a diluted mixture of nickel carbonyl using sulfur hexafluoride as a photosensitizer with a helium purge gas and hydrogen as a shielding gas. This process allowed, through varying a multitude of production parameters, the controlled production of NiNPs of sizes ranging from 5 to 50 nanometers (nm) in diameter [45].

Method	Description
1	Laser-assisted synthesis [45]
2	Synthesis aided by spray pyrolysis [46]
3	Modified polyol process synthesis [47]
4	Synthesis in ethylene glycol [48]
5	Synthesis in aqueous surfactant solution [49]
6	Synthesis in Microemulsions [50]

Table 3.1 Methods used for NiNP synthesis

Method 2 produced NiNPs with the assistance of a low pressure spray pyrolysis (LPSP) using nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$). This process reduce nickel nitrate using formic acid, ethanol, and hydrogen gas. Particles of 20-30 nm were produced [46]. The synthesis of NiNPs was examined in Method 3 by using nickel chloride ($NiCl_2$) as a precursor and sodium borohydride as a reducing agent. Poly-vinilpyrrolidone (PVP) was employed as a protective agent. This process yielded face-centered cubic (FCC) NiNPs with a median diameter of 3.8 nm [47].

Method 4 produced NiNPs from nickel chloride ($NiCl_2$) in ethylene glycol using a hydrazine (N_2H_4) reduction technique. This route produced monodispersed particles with a mean diameter of 9.2 nm [48]. In Method 5, NiNPs were synthesized from nickel chloride ($NiCl_2$) in an aqueous solution of cationic surfactants, i.e., CTAB (cetyltrimethylammonium bromide) and $TC_{12}AB$ (tetradodecylammonium bromide), using hydrazine (N_2H_4) as a reducing agent. The mean diameter of the produced particles was 10-36 nm [49][48]. Method 6 formed NiNPs from $NiCl_2$ using hydrazine in water-in-oil microemulsions of water, CTAB, and hexyl alcohol (n-hexanol). This method produced particles with an average diameter of 4.6 nm. [50]

Methods 4, 5, and 6 were examined using LCA. These routes were chosen for comparison due to their similarities in processing procedures and materials and energy use. In addition, the methods rely on solution-phase reactions, which have the potential to be adapted for production using microfluidic devices.

ANALYSIS METHODOLOGY

LCA follows four basic steps [43]: (1) Goal and scope definition, (2) Inventory analysis, (3) Impact assessment, and (4) Interpretation of results and improvement opportunities. This approach was followed for the analysis of the three NiNP production methods introduced briefly above; details of the LCA study are provided below.

Goal and Scope Definition

The scope of the study was defined to be cradle-to-gate for the production of the nickel nanoparticles. This scope allowed for a more focused assessment of a portion of the life cycle impacts of a diffusion brazed microfluidic device using NiNPs in the braze paste. The life cycle phases included materials and manufacturing processes required to produce the nanoparticles, as well as several precursor chemicals described below. The particles are assumed to experience the same handling methods, method of application, and ultimate fate, thus the use and disposal phases were not examined.

A functional unit of 1 kilogram of nickel nanoparticles was selected, which allowed the processes to be equally compared in terms of energy, waste, and material usage. It should be noted that variations in the methods lead to different particle sizes, which ultimately impact the functional characteristics of the NiNPs in their intended application within a braze paste, as shown by Tiwari and Paul [44].

Life Cycle Inventory

The three selected methods for NiNP production each utilize nickel chloride ($NiCl_2$), hydrazinium hydroxide (N_2H_5OH), and sodium hydroxide (NaOH). The chemical types which vary include ethylene glycol, cetyltrimethylammonium bromide (CTAB), tetradodecylammonium bromide ($TC_{12}AB$), and ammonia. Water is used as a solvent in Methods 5 and 6. The reduction reaction was consistent for each method as shown below [49][50].

$$2Ni_{2+} + N_2H_4 + 4OH_{-} \rightarrow 2Ni + N_2 + 4H_2 \qquad (3.1)$$

NiNP production in Method 4 was initiated with $NiCl_2$ solution (2.5-45 mM) being dissolved directly into ethylene glycol. Hydrazine (0.05-0.9 M) and NaOH solution (0.1 M) were then added in sequence [48]. NaOH was added at a ratio of 10-72 mL/L of solution. In this LCA study, 72 mL NaOH solution per liter of 45 mM $NiCl_2$/0.1 M hydrazine solution was considered. The temperature was elevated to 60 °C, and after stirring for 1 hour, NiNPs formed. In Method 5, NiNPs were synthesized from $NiCl_2$ using a solution of CTAB and $TC_{12}AB$ [49]. CTAB (0.025 M), $TC_{12}AB$ (0.5 mg/mL), $NiCl_2$ (0.005-0.1 M), and acetone (10 μL/mL) were dissolved in water to form a 10 mL aqueous solution. Hydrazine (0.05-1.25 M) and 1.0 M sodium hydroxide solution (20 μL/mL) were then added. As in Method 4, temperature was elevated to 60 °C, and NiNPs formed after stirring for 1 hour.

The third synthesis route analyzed, Method 6, used two microemulsion solutions by solubilizing aqueous solutions of $NiCl_2$ and hydrazine into a CTAB/n-hexanol mixture [50]. Equal volumes of the two microemulsions were rapidly mixed at 73 °C for an hour to produce NiNPs. Conditions were varied in the experiments, with the following considered in this LCA study: 0.05 M NiCl2, 1.0 M hydrazine, and a weight fractions of water, CTAB, n-hexanol of 22/33/45.

For the conditions considered in the LCA study, mean particle sizes were 9.2, 12, and 4.2 nm for Methods 4, 5, and 6, respectively. The calculated material and energy inputs and outputs using the above conditions to produce 1 kg of NiNPs are shown in Table 3.2. A yield of 50% is assumed based on the efficiency of converting $NiCl_2$ to pure nickel. Remaining nickel is assumed to remain in solution as $NiCl_2$. For each method, $NiCl_2$ was assumed to be produced as described in [44], using water, nickel, and hydrochloric acid.

Material (kg) Energy (MJ)	Method 4		Method 5		Method 6		SimaPro Processes for Input Materials and Energy
	In	Out	In	Out	In	Out	
Nickel chloride	4.42		4.42		4.42		*Unavailable, modeled after* [3]
Hydrazine	3.41		68.2		34.1		Ammonia, liquid, at regional storehouse/RER with US electricity U
Sodium hydroxide	0.24		1.09				NaOH ETH U
Water			1363		682		Water, deionized, at plant/CH with US electricity U
Ethylene glycol	994						Ethylene glycol, at plant/RER with US electricity U
CTAB			12.4		1022		*Unavailable, see Table 3.3*
n-Hexanol					1394		Cyclohexanol, at plant/RER with US electricity U
$TC_{12}AB$			0.68				*Unavailable, see 3.3*
Acetone			10.8				Acetone, liquid, at plant/RER with US electricity U
Waste chemicals		4.15		1.24		1.82	Chemical waste, unspecific
Process liquid waste				1363		2452	Treatment, black chrome coating effluent, to wastewater treatment, class 2/CH with US electricity U
Waste ethylene glycol		994		93.7			Disposal, antifreezer liquid, 51.8% water, to hazardous waste incineration/CH U
Heat (MJ)	95.8		228		687		Electricity, medium voltage, production UCTE, at grid/UCTE

Table 3.2 Material and energy inputs/outputs for several NiNP production methods (50% Yield)

As noted in Table 3.2, CTAB and $TC_{12}AB$ were not available in the life cycle inventory (LCI) databases of the software. CTAB ($C_{19}H_{42}BrN$) and

$TC_{12}AB$ ($C_{48}H_{100}BrN$) are surfactants comprised of an ammonium head and alkyl chains with a bromide counter ion [51]. As fatty acids are the only polar, long chain substances in the databases, surfactants are modelled as ammonium chloride and fatty alcohol, which are available in the software LCI databases, as shown in Table 3.3. Since the molar mass of ammonium chloride (53.56 g/mol) and ammonium bromide (97.94 g/mol) differ, two levels were selected for representative CTAB and $TC_{12}AB$ production. One level was for an equivalent mass, while the other was for an equivalent number of moles. This variation allowed the sensitivity of impact results to the assumption to be evaluated. Process energy to produce the two chemicals was assumed to the same as for general organic chemicals (8.7 MJ/kg), using the SimaPro process of *Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity U*, which assumes they were made in the US.

Nickel chloride was also absent from the LCA software databases, and modeled using the material components required in its production as described in [3]. Chemical processing waste types are remarkably absent in LCI databases. Thus, process outputs are modeled as three different types of waste. These inventories are detailed in Table 3.2. Process heating energy, Q (J), is assumed to be supplied by electricity, and depends on the mass of liquid heated, m (kg), its specific heat, c_p (J/kg K), and the temperature change required,

$$Q=m\times c_p(T-T_{ref}) \tag{3.2}$$

where T_{ref} is assumed to be 20 °C (293 K).

Life Cycle Impact Assessment

The third step in completing the LCA study of NiNP production was to perform an impact assessment based on the inventory data gathered for the three production methods. Impact assessment was conducted using SimaPro 7.1 (PRé Consultants), one of the most widely used LCA software packages.

CTAB 1 (kg)	CTAB 2 (kg)	$TC_{12}AB$ 1 (kg)	$TC_{12}AB$ 2 (kg)	SimaPro Process
0.2687	0.1469	0.1269	0.0694	Ammonium chloride, at plant/GLO U
0.7312	0.7312	0.8729	0.8729	Fatty alcohol, petrochem., at plant/RER U

Table 3.3 Modeled CTAB and $TC_{12}AB$ variations

Several impact assessment methods are available in the software. The most recently released method is ReCiPe 2008, which is replacing the Eco-indicator 99 method [25]. ReCiPe 2008 analyzes impact by harmonizing the previous two main approaches. The first approach is based on the characterization of an impact category and the second based on the type of damage. ReCiPe 2008 characterizes impact categories using eighteen midpoint indicators (e.g., climate change, ozone depletion, and human toxicity) and characterizes damage types using three endpoint indicators (Resource Availability, Ecosystem Quality, and Human Health). As with Eco-indicator 99, three cultural perspectives can be applied to account for subjectivity (e.g., chosen time horizon), which have been termed Individualist, Hierarchist, and Egalitarian archetypes. In this study, world normalization, Hierarchist perspective, and an average weighting set were applied, or World ReCiPe (H/A).

Interpretation

The final step of the LCA for NiNP production was to inspect the analysis results and to perform a sensitivity analysis for the three methods to identify critical factors effecting process environmental impacts. As noted above, there are several sources of uncertainty in this study, which can be termed *procedural gaps* and *data gaps*. During the study it was discovered that description of NiNP synthesis procedures were not comprehensively reported in the literature, thus LCA errors could result. To account for these procedural gaps, including unclearly reported or unavailable of procedural data, baseline conditions were established for each of the three methods. To demonstrate the effect of procedural gaps, varying levels of process yield were selected. Process yield can have a significant impact on environmental impact results, and while it is notoriously low for nanoparticle synthesis, yields are not reported in any of the studies examined. It should be noted that the method of NiNP production is a procedural gap of the prior LCA study, which necessitated the study reported here.

The second type of uncertainty, resulting from data gaps, is related to known material and energy types and quantities for each method studied. Though specific information may be known about the process, it may not be well-represented by existing process models in the LCA software database. This was particularly true for the two surfactants used in Methods 5 and 6 (CTAB and $TC_{12}AB$). Thus, the sensitivity of impact assessment results were investigated for two representative models of the surfactants, which were described above.

	Yield (%)	CTAB (1, 2)	$TC_{12}AB$
5A	50	CTAB 1	$TC_{12}AB$ 1
5B	90	CTAB 1	$TC_{12}AB$ 1
5C	50	CTAB 1	$TC_{12}AB$ 2
5D	90	CTAB 1	$TC_{12}AB$ 2
5E	50	CTAB 2	$TC_{12}AB$ 1
5F	90	CTAB 2	$TC_{12}AB$ 1
5G	50	CTAB 2	$TC_{12}AB$ 2
5H	90	CTAB 2	$TC_{12}AB$ 2

Table 3.4 Method 5 parameter variations

Thus, for all three NiNP production methods considered, trial process yields were established as 50% and 90%, which are noted as trials A and B, i.e. trial 4A represents Method 4 assuming a 50% process yield on a basis of the amount of nickel chloride reacted. Thus, Method 4A requires twice the level of input materials than if 100% yield were assumed.

In the analysis of Method 5, where a solution of cationic surfactants (CTAB and $TC_{12}AB$) was used for NiNP synthesis, uncertainties were due to both procedural (yield) and data (surfactant) gaps. Thus, parameter variations were applied for CTAB and $TC_{12}AB$, as well as yield, as shown in Table 3.4. Similarly, Method 6 involved procedural and data gaps due to uncertainties in process yield and surfactant type. However, this NiNP synthesis method did not incorporate the use of $TC_{12}AB$. The variations for method 6 are shown in 3.5

.

	Yield (%)	CTAB
6A	50	CTAB 1
6B	90	CTAB 1
6C	50	CTAB 2
6D	90	CTAB 2

Table 3.5 Method 6 parameter variations

The results of the environmental impact assessment are reported and discussed below.

RESULTS AND DISCUSSION

From the environmental impact results shown in Figure 3.3, it appears that Method 5 is the most environmentally friendly approach. As this method involves aqueous solutions as a basis for reactions, environmental impacts due to solvent usage is greatly reduced, since it is merely water. The other two approaches require ethylene glycol, organic surfactants (CTAB and $TC_{12}AB$), and n-hexanol to facilitate NiNP production, which significantly increases the level of impact of these processes.

In each method, solvent volumes make up the major of the input chemical mass, ranging from nearly 1000 to almost 2500 kg per kg of NiNPs. This analysis does not account for solvent and other chemical use in subsequent purification steps, which would increase the amount of chemicals required for overall NiNP production. Method 6, which requires large volumes of water, CTAB, and n-hexonal, is shown to be the least environmentally responsible option. This method also requires heating of a larger volume of fluid to a higher temperature.

Impact assessment results reveal that variation in input chemicals other than solvents would be expected to have less of an effect on environmental performance than either variations in process yield or the actual method of production. This point is demonstrated when examining the impact scores across the different synthesis routes for Method 6. Varying the CTAB material input had little effect (1.1%) on the predicted environmental impact, while increasing yield from 50% to 90% reduced predicted impacts by nearly half (44%). Similarly, for Method 5, varying surfactant composition has an insignificant effect on predicted environmental impact (0.005% for $TC_{12}AB$ and 0.22% for CTAB), while increasing yield from 50% to 90% results in a 44% decrease in predicted impacts.

Comparing among the methods used, Method 5A (baseline) is predicted to have 12% of the impact as Method 4A and 4.2% of the impacts of Method 6A. It should be noted that Method 5A requires about 45% more inputs by mass than Method 4A. While Method 6A requires more than three times the input material of Method 4A and more than twice the material inputs of Method 5A, it also requires significantly more energy. Method 6A is three times as energy intensive as Method 5A and more than 7 times as energy intensive as Method 4A.

To investigate the influence of process yield on environmental impacts over a range of values, several levels were chosen for Method 4 (i.e., 40%, 50%, 70%, 90%, and 100% yield), as shown in Figure 3.2. These are noted as 4A-Yield %, below. Impact assessment results for 4A and 4B relate to yields of

50% and 90%, respectively. Figure 3.2 indicates that environmental impacts greatly decrease with process yield improvements, when poor process yields are exhibited. In fact, a 10% yield improvement from 40% to 50% results in a 20% decrease in environmental impacts. However, the 10% increase in yield from 90% to 100% results in a 10% decrease in environmental impacts. On a ReCiPe point basis, this difference becomes more starkly evident. The increase in yield at lower process yields results in an improvement of 127 points, while at higher yields the decrease is 28 points. Thus, there are diminishing returns on environmental impact improvements as process yields increase. The relationship exhibited by Figure 3.2 is characteristic of changes in process input requirements with varying process yield. In this case, environmental impact (I) results are directly correlated with process yield (Y) as;

$$I=256\ Y^{-1} \tag{3.3}$$

This trend shows that for Method 4, environmental impacts can be directly estimated at any process yield, by assuming the process is scalable and knowing the predicted environmental impact for a process exhibiting 100% process yield (256 Pts).

SUMMARY AND CONCLUSIONS

Despite the many potential benefits and applications of nanoparticles, the need for an analysis of environmental impacts has become apparent with uncertain health effects and the implications of poor process yields and associated material and energy inefficiencies. The study herein examined the environmental impacts of three production routes for nickel nanoparticles (NiNPs) using life cycle assessment (LCA) methods. LCA software was used to complete environmental impact assessments and a sensitivity analysis to investigate the effects of procedural and data gaps. Procedural gaps have been defined as unknown data or information regarding the synthesis procedure reported in literature. Data gaps were defined as the unknown relevance of existing process models to the materials and processes under consideration.

In order to account for these uncertainties in process procedures and data, the three different routes were subjected to a sensitivity analysis which varied process yields and the material inputs. From the sensitivity analysis, it was found that improvements to process yield could greatly reduce environmental impacts. The synthesis method also has a significant effect, while other chemical and energy inputs appeared to have a minor effect for the routes investigated.

In cases where solvent usage is more equivalent to actual production volumes of nanoparticles, which may be possible with microfluidic devices, other chemicals would be expected to have a more significant effect on overall environmental impacts. In current practice, focusing on yield improvements may prove more beneficial than to focus on selections of material inputs in synthesis production methods.

The development of synthesis methods that utilize water rather than ethylene glycol, surfactants, and other chemicals can potentially reduce processing environmental impacts. In addition, localized production with improved process yields has the potential to reduce environmental impacts of nanoparticle production. These advancements can directly improve the sustainability of nano-assisted manufacturing.

FIGURES

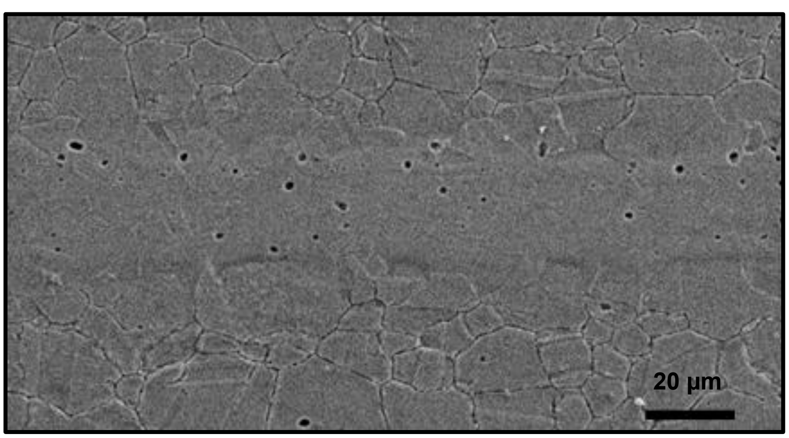

Figure 3.1 SEM of NiNP brazed bondline

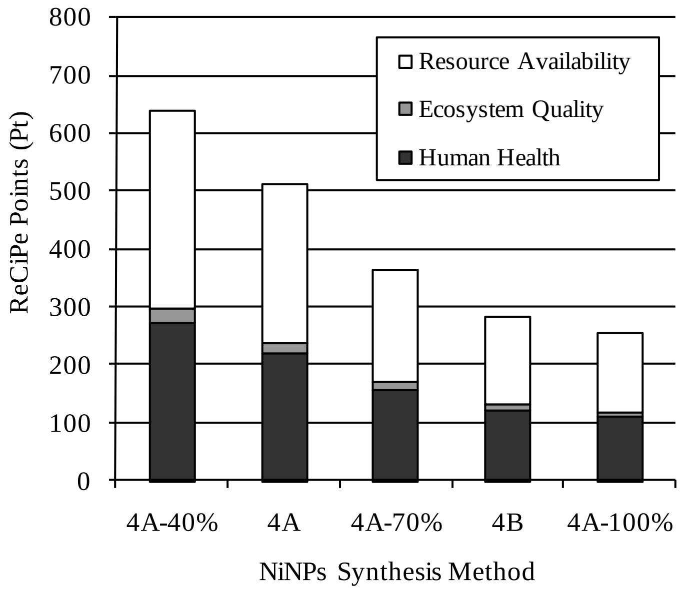

Figure 3.2 Effect of process yield on environmental impact

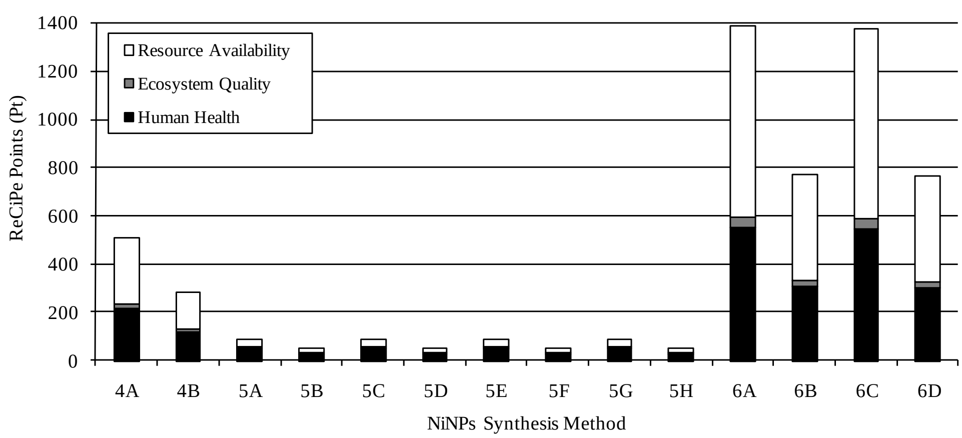

Figure 3.3 Predicted environmental impact of NiNP synthesis under several scenarios

CHAPTER 4

COMBINED COST MODELING AND ENVIRONMENTAL ASSESSMENT OF MICROFLUIDIC DEVICE MANUFACTURING

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ABSTRACT

Micro- and nanotechnologies are promising advancements across many industrial sectors including alternative energy, chemical processing, and healthcare. In particular, a focus of research has been in manufacturing process development aimed at microdevice cost reduction and quality improvement. Microdevices take advantage of enhanced heat and mass transfer to improve energy and material efficiencies, yet device production uncertainties inhibit broad commercialization. Nickel nanoparticle (NiNP) assisted diffusion brazing has been shown to improve bond qualities and reduce processing time in microlaminated stainless steel devices. However, environmental impacts and cost differentials in comparison to conventional techniques remain largely uncertain. A prior life cycle analysis study compared this novel process to a more traditional diffusion brazing approach using nickel phosphorus electroplated laminae. The study found the former to be less environmentally impactful, however, a major limitation was in modeling of the NiNPs, which were assumed to be an equivalent mass of bulk nickel. To extend the prior work, this study takes advantage of research that developed life cycle inventories for NiNP synthesis and combines it with a process-based cost model encompassing capital investment and cost-of-goods-sold as a function of annual production volume. Several manufacturing process scenarios are then

explored and compared on an environmental impact and economic cost basis for the production of a microchannel air preheater.

INTRODUCTION

Micro- and nanotechnologies, which take advantage of materials and products with geometries ranging from a few nanometers to tens of micrometers, have benefited many applications including highly efficient and portable kidney dialysis micro-filtering systems [52], production of engineered nanomaterials [53], and nano-assisted manufacturing processes [29]. With 2011 National Nanotechnology Initiative budgets surpassing 1.85 billion dollars [54] and industry and consumers demanding more advanced products and processes, many more innovations can be expected to be developed and commercialized in the near future. An emerging area of development is energy recuperation enabled by microchannel process technology (MPT). Such energy recuperators take advantage of the reduced diffusional distances characteristic of microchannels in extracting heat from the hot fluid. Aggressive weight and volume constraints associated with mobile vehicle platforms make MPT devices particularly suited to these platforms due to the size and weight savings achievable through the use of micro- and nano-scale features and materials.

MPT production via microlamination is attendant with manufacturing challenges, including inconsistent patterning of features and distortion of internal features during bonding. Thus, novel materials and processing are being pursued, which introduces additional, and often uncertain, costs and environmental impacts. To support the goals of sustainable manufacturing, the production of MPT devices must be examined in light of economic, environmental, and social impacts. This study focuses on economic and environmental performance.

The research herein examines the fabrication of a stainless steel microchannel air preheater device under several representative manufacturing scenarios, and estimates the concomitant environmental impacts and economic costs associated with their manufacture. Patterning and bonding processes investigated include photochemical machining (PCM), laser cutting, nano-assisted diffusion brazing (with nickel nanoparticles), and diffusion bonding (with no interlayer).

BACKGROUND

The construction approach used for the air preheater, shown in Figure 4.1, is the same as previously reported for MPT devices [29]. The architecture of MPT devices is based on a stacked-shim fabrication process, termed microlamination. For this study, the device is assumed to be fabricated of

150 shims. The individual shims are first patterned from a sheet of AISI 316 stainless steel and then aligned (registered) and bonded into a single-celled stack under heat and pressure. During stack bonding, two end-plates are joined to the ends of the device to allow for the addition of interconnects for fluidic communication between the device channels and the overall system [2]. Several techniques can be used for patterning the shims, or laminae, for MPT devices. The first process commonly used, photochemical machining (PCM), is based on chemical etching through the use of a photoresist stencil to remove material to a prescribed depth over specific and precise areas [55]. The second technique examined in this study is laser cutting. A production-representative CO_2 laser cutting system is assumed to pattern stainless steel shims for the air preheater assembly. The general process of CO_2 laser cutting utilizes a beam of laser energy focused onto the surface of the material, where it forms a locally melted capillary through the depth of the substrate. An oxygen or nitrogen gas jet assists in ejecting the molten material from the base of the capillary. In some cases, the gas can further aid the process by assisting chemical reactions, as well as material removal [56].

After the laminae have been patterned, they are aligned and bonded. Solid-state diffusion bonding and nano-assisted diffusion brazing are two common methods for bonding the laminae of MPT devices are. In solid state diffusion bonding, joining occurs under a combination of high temperature, time, and pressure where the two parent materials melt (without the aid of an interlayer) and diffuse into a single bonded material. A vacuum hot press, capable of a 10^{-5} torr vacuum and temperatures reaching 1350°C, was modeled to facilitate the diffusion bonding processes. From a prior study [29], the diffusion bonding process was assumed to require a furnace ramp-up rate of 0.5 °C/min. to 400°C, then a 5°C/min. ramp to 980°C, where it is held for 2 hours.

The nano-assisted diffusion brazing process is similar to the previously discussed diffusion bonding process, but employs nickel nanoparticles (NiNPs) within a braze paste as an interlayer between the parent material substrates. This paste is applied to the stainless steel shims where it melts during process heating, leading to transient liquid-phase (TLP) diffusion bonding of the device. NiNP-assisted diffusion brazing offers several benefits over conventional processes, including lower processing times and temperatures, increased diffusion rate, and improved bond strength [29]. Nanoparticle-enhanced TLP bonding was previously investigated for joining stainless steel laminae and demonstrated in bonding of microfluidic device stacks [29]. In the current study, the process is identified as NiNP diffusion brazing or nano-assisted diffusion brazing.

The goal of the present work, through needs identified in a previous study [57], is to assess different microchannel air preheater device manufacturing scenarios with respect to both the relative environmental impacts and economic costs. To do so, life cycle assessment (LCA) was employed to determine the environmental impacts, and a process-based cost model was used to assess the economics of device manufacturing. In combining these methods, a more comprehensive decision-making approach for sustainable nano-assisted microchannel device manufacturing is demonstrated.

ENVIRONMENTAL ASSESSMENT

A *cradle-to-gate* life cycle assessment (LCA) approach is used to determine the environmental impacts of the four manufacturing processes (i.e., PCM, laser cutting, diffusion bonding, and diffusion brazing), and combinations of the two patterning and two bonding methods are examined. A commonly used and commercially available LCA software package, SimaPro7™, is used to assist in completing the life cycle inventory and environmental impact assessment. LCA can assist engineers in making decisions regarding the device design and materials and manufacturing processes used on an environmental sustainability basis. [11]

PROCESS-BASED COST MODELING

Process-based cost models are used to estimate manufacturing costs. Using this approach, the total manufacturing cost is broken down into a number of cost elements associated with each step in the production process. Each cost element is estimated separately and then all are summed to establish an overall manufacturing cost. Typical cost elements include capital equipment, labor, direct materials, indirect materials, energy/utilities, facilities and maintenance. Variation in each cost element is estimated through functional relationships that quantify the impact of manufacturing variables (e.g., production volume, equipment throughput, labor and loading rates, and electricity cost) on each cost element. The output from the process-based model is an estimate of cost of goods sold (COGS); typical overhead cost contributors such as sales and marketing, R&D, administration, management, profit and taxes are not considered. [2]

Application of the process-based cost modeling methodology to the manufacturing of the air preheater can be used to illustrate the relative contribution of design, materials, and fabrication process choice on the final device cost. Identification of these cost drivers is a critical enabler in effectively prioritizing the fabrication processes that give the highest probability for commercial success. Cost model sensitivity analyses can be used to determine areas of technical and/or financial risk and are useful in developing more sophisticated economic assessments; for example supporting make vs. buy decisions in production. The process-based cost model is used here to identify primary cost drivers in the manufacture of the air preheater device across a range of production volumes and to determine a range of COGS in an effort to determine the feasibility for military markets.

ENVIRONMENTAL ASSESSMENT METHODOLOGY

LCA follows four basic steps [58]: (1) Goal and scope definition, (2) Inventory analysis, (3) Impact assessment, and (4) Interpretation of results and identification of improvement opportunities. Goal and scope definition is the phase where the purpose and method for the study are defined. Items to be addressed include the type of information needed to perform the study, how sensitive the results need to be (accuracy), and the interpretation method to be used to assess the results. A careful definition of the goal and scope is important to ensure an adequate amount of time and resources will be allocated to conduct the study. This phase will ultimately determine the relevance of the final results [59].

Next, in the inventory analysis step, all the relevant data is collected. In the case of this study, inventory analysis is limited to energy and material inputs/outputs. The results from this phase can then be segregated by life cycle stage, process type, or a combination. During the next step, environmental impact assessment, the data gathered from the inventory analysis is evaluated. The goal of environmental impact assessment is to evaluate the potential environmental impacts for a given process, product, or system. In the final step of LCA, interpretation, the results from the two previous steps are quantified, evaluated, and justified. When comparing impact results, it is important to understand that assumptions and decisions must be made based upon the constraints of various stakeholders. In this phase, it is also important to identify potential areas for improvement in the product or process, in addition to improvements to the LCA study itself. Details of the LCA study for the MPT air preheater are provided below.

Goal and Scope Definition

The goals of the environmental life cycle assessment are to identify the least impactful patterning and joining processes for the microchannel air preheater and to understand the drivers of environmental impacts for the various processes. The scope is cradle-to-gate, and encompasses the energy and material inputs/outputs associated with the patterning and joining processes, as well as upstream material processing. Environmental impacts of other processing steps, use, and disposal are assumed to be equivalent for each scenario and out of the boundaries of the study. A representative annual production volume of 10,000 devices was chosen as the functional unit for the study based on the cost modeling work described below. This allowed for an equivalent comparison of the production scenarios in terms of environmental impacts.

Life Cycle Inventory

Materials and energy data were inventoried for each manufacturing process. For the processes requiring chemicals, all chemical densities were assumed at 20°C to calculate mass. Depending upon the process, different concentrations of specific chemicals were required. Due to the lack of availability in inventory databases, certain substances were substituted with similar compounds contained in the LCA software databases, as reported in Table 4.1. Information from *ecoinvent* databases was relied upon when possible, with unit processes used, as denoted by “U” in the process name. An “E” designator denotes a process from the Industry Data 2.0 library.

Material (kg) Energy (kW-hr)	Process 1 PCM	Process 2 Laser Cutting	Process 3 Diffusion Brazing	Process 4 Diffusion Bonding	Assumed Equivalent SimaPro Substance or Process
Sodium chlorate (45%)	0.025				Sodium chlorate, powder, at plant/RER with US electricity U
Sodium carbonate resist developer (1%)	0.025				Sodium carbonate from ammonium chloride production, at plant/GLO with US electricity U
Sodium hydroxide photoresist stripper (3%, 4%, 25%)	10.91				Sodium hydroxide (concentrated) E
Ferric chloride (40%)	0.283				Iron (III) chloride, 40% in H2O, at plant/CH with US electricity U
Hydrochloric acid (10%, 15%, 30%)	35.01				Hydrochloric acid, 30% in H2O, at plant/RER with US electricity U
3000W CO_2 laser * in min./part		*25			Laser machining, metal, with CO2-laser, 3200W power/RER with US electricity U
Nitrogen cutting gas		2.913		2160	Nitrogen, liquid, at plant/RER with US electricity U
Nickel nanoparticles			0.04		NiNP by hydrazine reduction (previously modeled in [29])
Braze paste binder			0.21		Acrylic binder, 34% in H2O, at plant/RER U
Deionized water	1150	615	3.75		Water, deionized, at plant/CH with US electricity U
Electricity	86.5	19	6.17	6.116	Electricity, medium voltage, production UCTE, at grid/UCTE U

Table 4.1 Material and energy inputs for several air preheater device manufacturing processes

The processing parameters for environmental impact assessment of diffusion bonding were identical to those used for cost modeling. To calculate the electrical energy required to maintain the furnace at the processing temperature, it was modeled as described in [3], which enabled six parts per batch to be processed. Parameters needed to estimate the energy required to heat the parts and furnace atmosphere (nitrogen), as well as heat losses are reported in Table 4.2

.

	AISI 316 Stainless Steel	Nitrogen	Firebrick
Density (kg/m^3)	8238		1790
Specific heat (J/kg·K)	468	1056	829
Conductivity (W/m·K)	21.5		1
Emissivity			0.9

Table 4.2 Material data at 500°C [60]

The environmental impacts due to diffusion bonding were represented by the use of electrical energy and nitrogen used for operating the furnace. In a prior study [29], the energy required for the operation of the vacuum hot press pumps was found to be negligible and thus not considered in the present study. A sensitivity analysis on nitrogen flow rates was conducted, and it was found that the overall environmental impact is not significantly affected by varying levels; a nitrogen flow rate of 1 L/min. was assumed.

Life Cycle Environmental Impact Assessment

The third step in completing the LCA study for the air preheater was to perform an environmental impact assessment based on the inventory data gathered for the manufacturing scenarios. A myriad of impact assessment methods have been devised to compare environmental impacts of alternatives. The ReCiPe 2008 method was chosen for this particular study, which is available in the LCA software, and replaces the commonly used Eco-indicator 99 method [25]. Impacts are categorized using eighteen midpoint indicators (e.g., climate change, ozone depletion, and human toxicity), and three endpoint indicators, or damage types (i.e., Resource Availability, Ecosystem Quality, and Human Health). To account for uncertainties in the weighting of environmental impacts, three cultural perspectives can be applied (i.e., Individualist, Hierarchist, and Egalitarian archetypes). A breakdown of these different weighting schemes can be explained better noting that Egalitarian and Individualist archetypes place Resources as the damage type of highest concern, while Human Health was found to be the highest concern using the Hierarchist archetype. The Individualist archetype assigns greater weight to Human Health impacts and a lower level to Ecosystem Resource impacts than the other two archetypes. In this study, the world normalization scheme, Hierarchist perspective, and average weighting set were first applied, identified as *World ReCiPe (H/A)*.

Variability and uncertainties were identified in areas such as the inventory data and processes, the software process modeling approach, and in the transition between the inventory analyses to impact assessments. In order to more accurately account for these uncertainties, environmental assessments performed throughout this study were conducted using the three different weighting schemes (i.e., Individualist I/A, Hierarchist H/A, and Egalitarian E/A archetypes) available in the LCA software. As seen in comparing Figure 4.5A and Figure 4.5B, the final environmental impacts scores were higher with the Individualist archetype (I/A) than with the Hierarchist (H/A). In a similar comparison to the H/A weight, the environmental impact scores appear to be lower when applying the Egalitarian perspective weight (Figure 4.5C, E/A). Following these observations, the Hierarchist average weighting set (World ReCiPe H/A) was chosen to be used throughout the study because it reflected a more balanced weighting. Finally, to better understand the units of environmental impact, it should be noted that the outputs of the impact assessment are given in terms of Points (Pt). One thousand points is equivalent to the annual overall environmental impact generated by a single European citizen [25]. Environmental impact assessment results are discussed in greater detail below.

PROCESS-BASED COST MODELING APPROACH

Process-based cost models for each of the four manufacturing processes were developed and applied in the analysis of COGS of the air preheater. The four manufacturing scenarios devised for the environmental impact study were assessed using the cost models.

The basis for the process-based cost models is bottom-up costing [2]. Bottom-up costing requires discrete analysis of all the required costs for a particular process, and includes raw material costs, labor cost, tool capital cost, facility costs, machine maintenance costs, utilities costs, and supplies costs. The COGS per device is calculated by finding the summed processing and the raw material costs required to fabricate the device. Because of the nature of the microchannel device, which is comprised of multiple identical shims, by finding the manufacturing cost for a single shim, the cost per device and the total manufacturing cost can be estimated. Therefore, for all the cost elements, the model is designed to calculate the cost per shim.

A volume price for the material, AISI 316 stainless steel, was determined through interaction with a vendor. For the patterning technique of photochemical machining (PCM), it was assumed that the etch depth was 250μm into a 610mm x 610mm panel that was 500μm thick. The size of the air preheater was assumed to be 152mm x 152mm allowing for 16 devices per panel stack. The blind cut area for the lamina designs was assumed to be 60sq.cm. The cycle time for making panels was based on the etching rate of stainless steel using ferric chloride. Cycle times for other lithography steps (e.g., photoresist application, cleaning, inspection) were based on input from a PCM equipment vendor.

For the second patterning option, laser cutting, a Prima Platino™ CO_2 laser was modeled. The cycle time of 25 minutes per device (10 seconds per shim) was determined through the consideration of equipment capabilities, processing constraints, and device requirements. The pricing and processing parameters for the laser cutting process were obtained from vendors and subject matter experts at the Pacific Northwest National Laboratory (PNNL).

For both NiNP diffusion brazing and diffusion bonding, it was assumed that a bond area of 400cm^2 per shim was needed and thus, the work envelope of the vacuum hot press was determined to be 1016mm. These assumptions facilitated obtaining equipment pricing from vendors. Further, it was assumed that the bonding hold time was 120 minutes with a furnace load time of 30 minutes. The differences between the two joining processes were in the bonding temperature. For diffusion bonding, the furnace temperature requirement was 980˚C, while NiNP diffusion brazing required 800˚C.

A large number of parameters were identified that directly or indirectly influence the COGS. These parameters were categorized as raw material, device geometry, process based parameters, and operations parameters. Additional details are provided in Leith et al. 2010 [61]. Single variable sensitivity analyses were conducted to isolate key parameters for consideration.

ENVIRONMENTAL IMPACT ASSESSMENT RESULTS

After laying the groundwork for the environmental impact assessment, primarily encompassed by the first steps of the LCA method – definition of the goal and scope, conducting an inventory analysis, and conducting an impact assessment – the remaining task is to interpret the results.

INTERPRETATION

The final step of the LCA was to interpret the results obtained from the environmental impact assessment. From here, the critical factors that affect environmental impacts could be identified, and conclusions and recommendations drawn. Table 4.3 reports the input numbers to corresponding material and energy inputs for each process. However, Process 3, NiNP diffusion brazing, and Process 4, diffusion bonding, involve only minimal inputs which allowed them to be reported directly in their respective graphs. Thus, these two processes are not reported in the table. When examining Process 1, photochemical machining, it can be seen in Figure 4.2 that the largest environmental impact driver appears to be from input 7 (electricity). Process inputs 2 (sodium carbonate) and 5 (hydrochloric acid) appear to be major contributors to the overall environmental impact score, as well. These three inputs appear to be the key drivers of environmental impact for PCM.

Material (kg) Energy (kWh)	Process 1	Process 2
	Input Number	Input Number
Sodium chlorate, powder, at plant/RER with US electricity U	1	
Sodium carbonate from ammonium chloride production, at plant/GLO with US electricity U	2	
Sodium hydroxide (concentrated) E	3	
Iron (III) chloride, 40% in H2O, at plant/CH with US electricity U	4	
10%, 15%, and 30% Hydrochloric Acid	5	
Laser machining, metal, with CO2-laser, 3200W power/RER with US electricity U		1
Nitrogen, liquid, at plant/RER with US electricity U		3
Water, deionized, at plant/CH with US electricity U	6	
Electricity, medium voltage, production UCTE, at grid/UCTE U	7	2

Table 4.4 Device manufacturing processes

Comparing the two patterning techniques, PCM and laser cutting, from Table 4.1 it can be seen that PCM appears to require a greater amount of material and energy inputs than laser cutting, which contributes to greater environmental impacts. The graph on the right in Figure 4.2 shows the breakdown of environmental impact scores for laser cutting. As expected, due to the energy requirements of using an electrically powered laser, the major impact driver stems from electricity. With a power consumption of 19kWh, as shown in Table 4.1, it dwarfs the impacts from the 2.91kg of nitrogen and even the 615kg of water required to operate the laser cutting system. However, the overall impact score of this process is still significantly lower than that of PCM.

The results from the impact assessment for NiNP diffusion brazing (Process 3) can be seen in Figure 4.3. The two impact drivers of this process are derived from the nickel chloride and process electricity, which account for 76% and 14% of the environmental impacts, respectively. These inputs are mainly for the production of NiNPs, which supports the supposition that NiNPs require significantly more energy to produce than bulk nickel [62]. When the manufacturing processes are compared, as seen in Figure 4.5A, it is apparent that nano-assisted diffusion brazing performs more poorly than diffusion bonding. In addition, laser cutting appears to outperform PCM for patterning.

RESULTS AND DISCUSSION

From Figure 4.2, it is apparent that the largest impact driver for patterning is electricity as represented by inputs 7 and 2 for PCM and laser cutting, respectively. With PCM requiring large amounts of processing heat and the laser requiring a large amount of electrical power, it is understandable that these two processing techniques would have a high level of impact due to electricity.

From the environmental impact results shown in Figure 4.3, diffusion bonding is predicted to be the more environmentally benign bonding approach. With an impact score of 4,800 ReCiPe points (Pt), it is dwarfed by the 102,000 Pt for NiNP diffusion brazing. As for impact drivers, diffusion bonding does not require the harsh chemicals to synthesize the nickel nanoparticles as used in the diffusion brazing technique, thus it significantly decreases the overall level of impact. In comparison to laser cutting, diffusion bonding still produces less of an impact due to the environmental unfriendliness of the laser energy use as depicted in Figure 4.5A.

In comparing both patterning and bonding processes, the impact scores differ greatly. Diffusion bonding boasts the lowest score, 4,800 ReCiPe points, while PCM claims the highest with 167,000. As described above, combinations of patterning and bonding processes are represented as four scenarios for manufacturing the air preheater for comparison of impacts due to production, as shown in Figure 4.5A. The scenarios are comprised of processes as shown in Table 4.4.

Scenario	Patterning Process	Bonding Process
1	Photochemical Machining	NiNP Diffusion Brazing
2	Photochemical Machining	Diffusion Bonding
3	Laser Cutting	NiNP Diffusion Brazing
4	Laser Cutting	Diffusion Bonding

Table 4.4 Patterning and bonding components of the different manufacturing scenarios

From Figure 4.5A, it appears that Scenario 4, laser cutting and diffusion bonding, is the most environmentally benign. As gathered from Figure 4.2 and Figure 4.3 in conjunction with Table 4.1, the major drivers for PCM impacts are electricity and volume of chemicals as used. Specifically, 28% of the total environmental impacts of PCM are due to the hydrochloric acid, while 41% was from electricity use. The major driver stemmed from nanoparticle synthesis, resulting in 94% of the nano-assisted diffusion brazing process environmental impact.

COST MODELING RESULTS

The total costs of each of the four individual processes were examined and aggregated into four patterning and bonding scenarios. Scenario 4, which consisted of the laser cutting patterning and diffusion bonding, was found to be the most economically attractive. As seen in Figure 4.6, Scenario 4 outperformed Scenarios 1, 2, and 3 with their total costs of 513, 499, and 358 USD, respectively.

COST OF GOODS SOLD

A key assumption for the model is that the entire market demand is satisfied by the production volume of a single factory. Figure 4.7 illustrates how the key cost drivers for COGS vary as a function of market size, in terms of annual production volume. Upon applying the cost model to Scenario 4 under different market sizes, the result shows the total COGS significantly decreasing from almost 2,000 USD, for a demand of 200 devices/year, to less than 350 USD for 10,000-20,000 devices/year. At this level of production, the results suggest that an increase in production by a factor of 100 will lead to more than 10 times reduction in cost. Compared with contract manufacturing services used to prototype the air preheater device, this represents a cost reduction of well over 30 times. As suggested in Figure 4.8, this reduction is largely due to an improvement in the utilization of labor and capital. Expendable supplies and raw material are the major cost drivers above 10,000 units per year.

The curve from the trend depicted in Figure 4.7 suggests that for the particular product and production line specified (e.g., 1016mm work envelope), production volumes beyond 10,000 units per year would yield minimal reductions in COGS. For example, doubling the production volume from 10,000 to 20,000 devices/year would only provide total cost reduction of less than 6%. Thus, the product and production lines investigated here are aimed to suit market sizes on the order of 10,000 units per year.

For a market size of 200 devices/year, as seen in Figure 4.7, the dominant cost drivers are labor and tools. In this context, the tool parameter represents the depreciated expense of the necessary capital equipment investment. These labor and tool costs are the drivers because of the relatively low cycle times for most of the tools used in the patterning and bonding processes. Thus, in high production volume, number of tools required in a few process steps is increased to meet the market demand. As the increase of tool cost is not proportional to the escalation of production volume, there is a considerable decline in tool and labor cost per device at high manufacturing volumes and as a result the total cost of the device is substantially reduced. This trend is evident across all manufacturing scenarios, as seen below in Figure 4.8 and was studied more closely for Scenario 4, since it was the best-performing scenario on a cost basis.

POTENTIAL CONSIDERATIONS

Although economic and environmental assessments appear to point to particular processes or scenarios as being more favorable, certain manufacturing constraints do apply for this device and warrant discussion. The laser cutting process for patterning has certain operational restrictions that ultimately do not allow it to pattern shims for the air preheater device. The shims that make up the air preheater utilize raised-features, known as islands or ribs, to assist in flow and pressure deflection. To create these blind-cut features, precise etching depths are required, which the laser cutting system, only capable of through-hole material removal, cannot perform. Therefore, due to these dimensional and processing constraints specific to the microchannel air preheater device, laser patterning is not truly feasible.

Similarly, the diffusion bonding approach has constraints that should be taken into consideration. The microchannels within the device periodically buckle and fail due to the higher pressures required for diffusion bonding. Through lab based tests and small scale manufacturing, this diffusion bonding process has historically produced poor yields. When a device is scrapped in this stage of the process the importance of yield is magnified. Due to the makeup of the device, which consists of 150 patterned laminae, the work and resources invested are compounded and, therefore, losses are higher in this stage compared to patterning. The diffusion brazing process, which has shown higher yields over diffusion bonding, has been more likely to be used in low volume manufacturing of this type of device. However, since no high volume industrial manufacturing lines currently exist, it should be noted that the true yields from these two processes are unknown and should be investigated in the application of the arrayed microchannel air preheater.

SUMMARY

The study herein examined the environmental impacts and economic costs of four unit manufacturing processes, encompassing patterning and bonding techniques for microchannel processing technologies (MPT), and four production scenarios for a microchannel air preheater. Life cycle assessment (LCA) methods were employed to assess relative environmental impacts. A process-based cost model was utilized to determine the likely cost of goods sold (COGS) and capital investment needed. In both assessments a demand of 10,000 units/year was assumed. This demand was determined through projected MPT market studies and application of the cost model to different annual production volumes. It was determined that this volume is not only an accurate projection of demand, but correlates to an ideal production level, i.e., efficient equipment and labor utilization rates.

An LCA software package (SimaPro 7) was used to assist inventory analysis and complete environmental impact assessments to facilitate conclusions about the relative environmental impacts of each processing type and each manufacturing scenario. After conducting a cradle-to-gate inventory analysis and impact assessment utilizing the ReCiPe 2008 method, it is evident that the four different microchannel device manufacturing process explored, i.e., photochemical machining (PCM), laser cutting, nickel nanoparticle-assisted diffusion brazing, and diffusion bonding significantly vary in process parameters and the resulting environmental impacts. Differences were further accentuated with the results from the economic cost model.

Of the several processes investigated, the most environmentally friendly patterning approach was found to be laser cutting. Similarly, the most environmentally friendly bonding approach appeared to be diffusion bonding. Combining these two processes gave a total environmental impact score of 163,000 ReCiPe points. This level of impact was the lowest of the four manufacturing scenarios, predicting a performance improvement of 39%, 5%, and 37% over Scenario 1, 2, and 3, respectively. The cost modeling results supported those of the environmental impact analysis. With a total cost of 344 USD per device, scenario 4 has a cost reduction of 33%, 31%, and 4% over Scenario 1, 2, and 3 respectively. Thus, environmental impact reductions appear to be driven by changes to bonding, while costs reductions are driven by patterning process changes.

Although the results show a promising differentiation among the alternative scenarios, it should be noted that uncertainties do exist and under different assumptions for modeling parameters the results may change. For example, in this case, the diffusion bonding process requires a projected 10% increase in utilities usage over NiNP diffusion brazing, so facility location will affect both utilities costs and concomitant environmental impacts. Future research can apply the approach and concepts from this work to estimate and evaluate costs and environmental impacts of manufacturing by taking product and process design variations into consideration.

FIGURES

Figure 4.1 Air preheater microchannel device

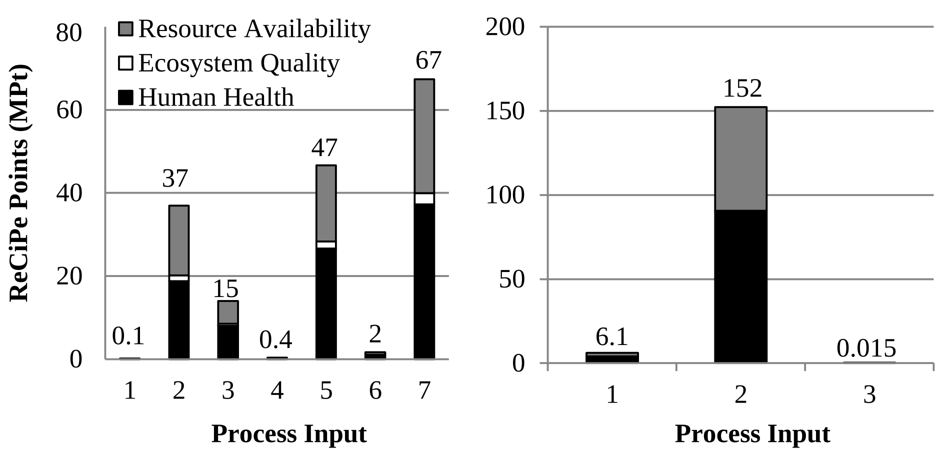

Figure 4.2 Environmental impacts for PCM (left) and Laser Cutting (right)

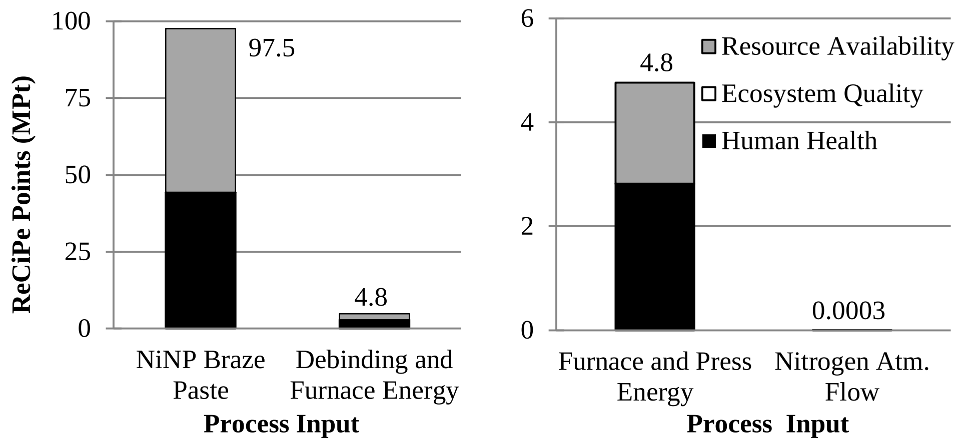

Figure 4.3 Environmental impacts for diffusion brazing (left) and diffusion bonding (right)

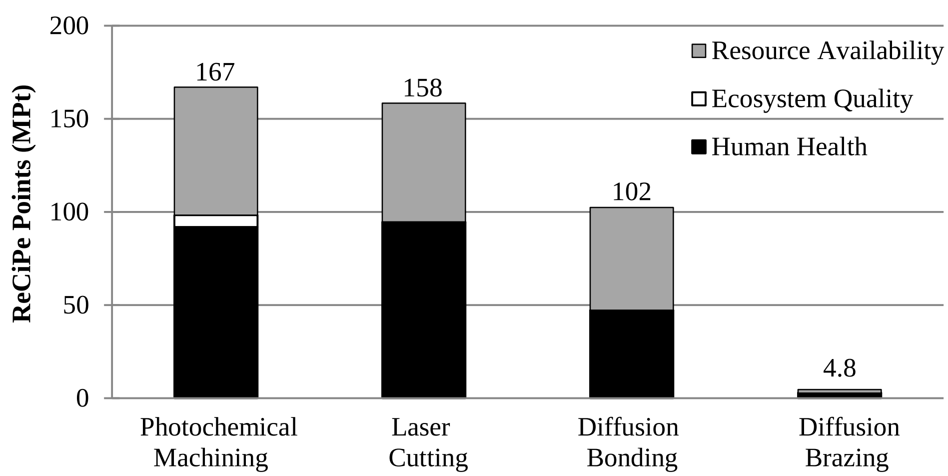

Figure 4.4 Environmental impact comparison of three air preheater device manufacturing techniques

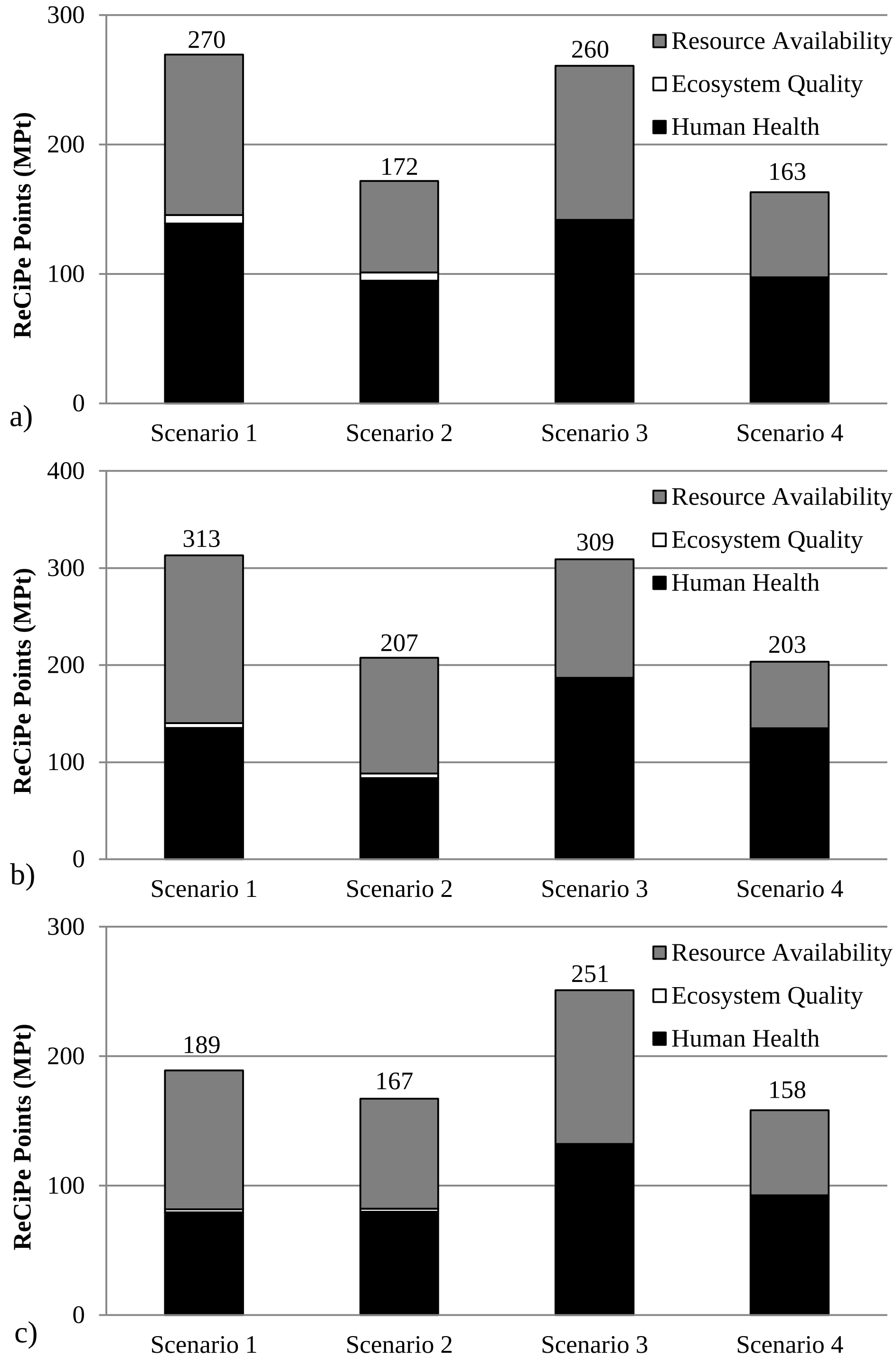

Figure 4.5 Environmental impact comparison of different manufacturing scenarios for a) Heirarchist, b) Individualist, and c) Egalitarian archetypes

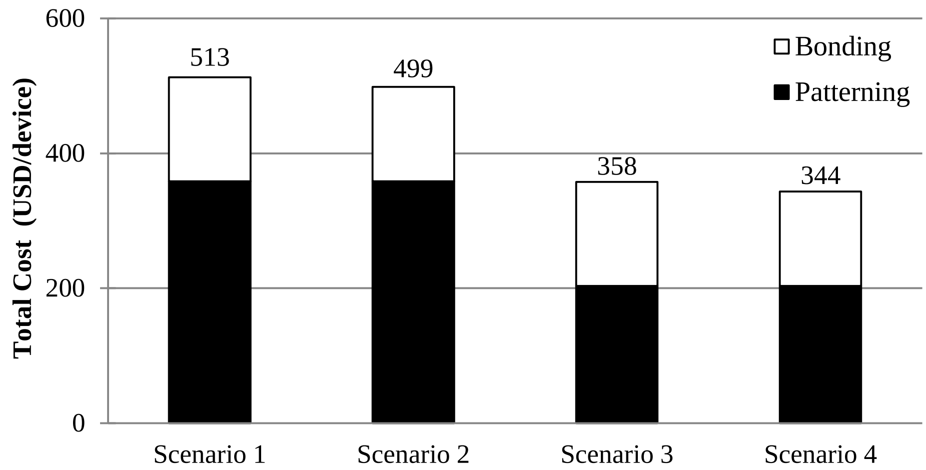

Figure 4.6 Estimated cost (USD/device) under different manufacturing scenarios

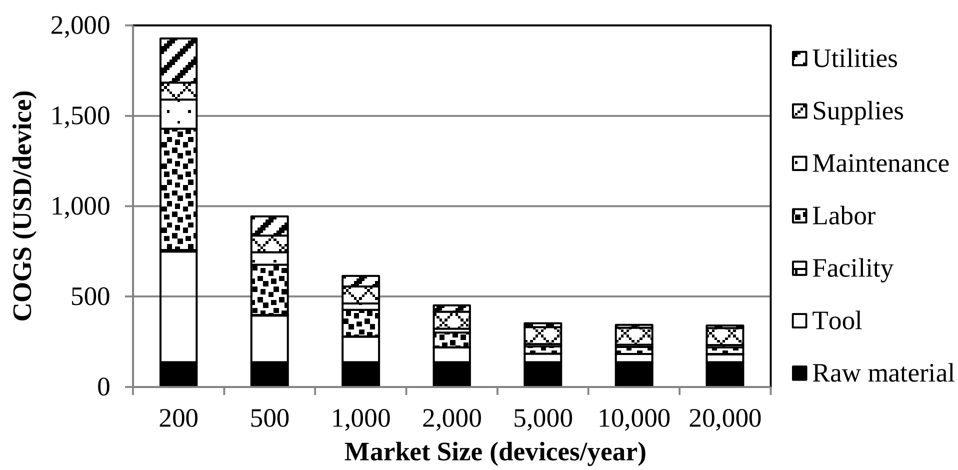

Figure 4.7 Estimated COGS under manufacturing Scenario 4 for different annual market sizes (USD/device)

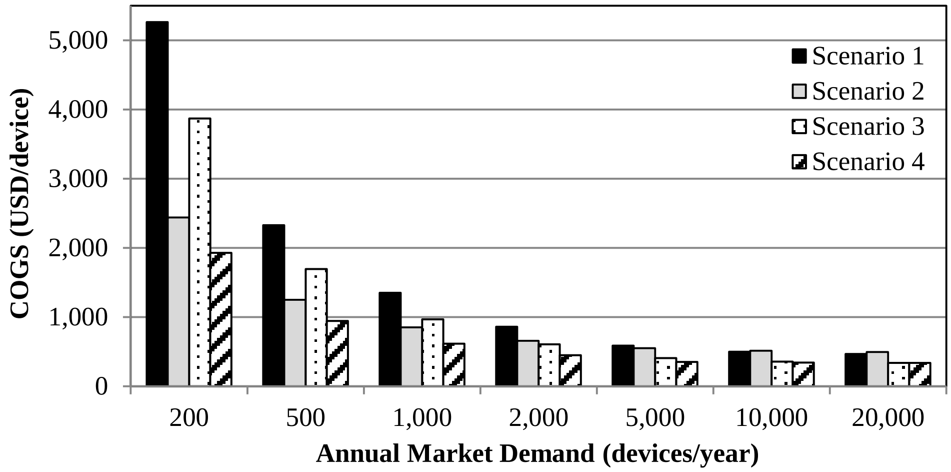

Figure 4.8 Estimated COGS under the manufacturing scenarios as a function of annual market size

CHAPTER 5

SUMMARY AND CONCLUSIONS

In this chapter, the research undertaken as a part of this thesis is reviewed. The results of the nickel nanoparticle synthesis study and of the cost and environmental assessments on the air preheater device are discussed. Contributions from this study are identified and recommendations for future work are outlined.

SUMMARY OF THESIS

Due to an increasing global population and diminishing resources, the need for sustainability initiatives has become starkly evident. Micro- and nanotechnologies have the potential to help move towards a more sustainable future by allowing for material, energy, and waste reductions and improved efficiencies. However, the benefits of these new technologies, are attendant with increasing material- and energy-intensive manufacturing requirements. Consideration of associated environmental impacts of these emerging technologies must be undertaken in concert with technology development.

Tools and methodologies have been developed for assessing environmental impacts of established technologies, but as discussed in Chapter 1, data deficiencies and lack of clear assessment methodologies have hindered attempts at applying life cycle analysis (LCA) to vital micro- and nanotechnologies. The difficulties that arise when applying these methods to emerging technologies were examined in Chapters 2 and 3.

Chapter 3 was motivated by prior work [3] in which the environmental impacts of nano-assisted diffusion brazing were compared to those for bonding of conventionally electroplated shims. Since information was not available for nickel nanoparticle production, a study was initiated to develop process life cycle inventories for several nanomaterial synthesis routes. These inventories enabled more accurate and detailed environmental impact comparisons to be made. Work completed as part of this thesis also addressed the need for coupling environmental assessment with cost modeling to achieve sustainability goals.

From needs regarding alternative manufacturing techniques identified in Chapter 3, diffusion bonding was added to the comparison of the nano-assisted and electroplated diffusion brazing processes in Chapter 4. A micro device was examined by applying a process model based approach for cost and environmental impact assessment. The device, an arrayed microchannel air preheater, was deemed of interest due to the combination of both micro- and nanotechnologies that it utilizes in its design and manufacture. This research compared several manufacturing scenarios in terms of their respective environmental and cost performance. The patterning steps examined were photochemical machining (PCM) and laser cutting. The bonding steps included diffusion bonding and a diffusion brazing process that employs a nanomaterial interlayer, referred to as nickel nanoparticle diffusion brazing.

Assessing the environmental impacts of these manufacturing processes requires extensive investigation into the process inputs and outputs, including raw materials, energy use, and waste/emissions. These parameters were then input into an LCA software tool, SimaPro, and environmental impact scores were generated based on the energy and material amounts. The impact values were then used to compare the environmental performance of the alternative manufacturing scenarios for the microchannel air preheater device.

Similarly, the economic costs were compared by understanding the various costs associated with each process. Many of the same parameters were used for conducting both assessments. However, to determine economic performance, a process-based cost model was designed. As discussed in Chapter 4, this cost modeling approach uses a summation of individual cost elements, each associated with steps in the manufacturing process, to predict the final manufacturing costs. Such cost elements include capital equipment, green-space facility construction, maintenance, raw materials, labor, and energy/utilities. In addition, through the implementation of functional relationships, the cost model incorporates impacts of varying yield efficiencies across process and equipment parameters. In both cases of environmental and cost performance, a functional unit of 10,000 devices/year was examined. As discussed in Chapter 4, this production rate was determined as a demand feasible for projected markets. A decision to use such a process-based model was chosen in order address a current deficiency in sustainability tools and methodologies that support product design, manufacturing, and policy decision making.

CONCLUSIONS

As demonstrated by research completed as part of this thesis, environmental and cost models can be developed and used collaboratively to support goals of sustainable manufacturing. Employing methodically constructed inventory data that accurately depicts material and energy inputs/outputs, life cycle assessment (LCA) can be applied for emerging technologies, such as those on the micro- and nanoscale. Predictions from processed-based cost modeling efforts can be integrated with life cycle assessment efforts, which can enhance industrial application. Decision makers are more apt to use tools such as this which will assist in revealing more potential areas for improvement and, through the combination of cost and environmental impacts, increase confidence levels in findings. The primary reasons confidence in the assessment results increase include 1) the inclusion of cost element sensitivity analyses and 2) enhanced scrutiny of product and process input/output parameters.

Environmental performance greatly varies across manufacturing techniques. As demonstrated in the LCA of the microchannel air preheater device:

- Among the patterning process, laser cutting appeared to have the better environmental performance with an impact score of 158,420 ReCiPe points, while photochemical machining (PCM) appeared to have the higher impact at 167,080 points, or a performance improvement of 5%. Given the assumptions of the analysis and impact assessment results, it is uncertain that laser cutting is clearly the better choice.
- Comparing bonding processes, diffusion bonding appeared more environmentally benign with a performance improvement of 95% over the nickel nanoparticle (NiNP) diffusion brazing. The impact scores for diffusion bonding and NiNP diffusion brazing were 4,760 and 102,400 ReCiPe points, respectively. In this case, nanomaterial

production, rather than brazing process-related impacts drive environmental performance.

- Several scenarios were devised from combinations of patterning and bonding processes. The scenario that appeared to have the best environmental performance consisted of laser cutting and diffusion bonding (Scenario 4). The impact assessment gave a resulting environmental impact score of 163,180 ReCiPe points, and was more environmentally benign by 39%, 5%, and 37% over Scenarios 1 (photochemical machining + nickel nanoparticle diffusion brazing), 2 (photochemical machining + diffusion bonding), and 3 (laser cutting + nickel nanoparticle diffusion brazing).

By applying the process-based cost model to the different manufacturing processes and scenarios the following results were obtained:

- Laser cutting appeared to be the better choice at 203.43 USD per device, as opposed to 358.45 USD per device for PCM, a cost reduction of 43%.
- The cost of diffusion bonding was predicted at 140.19 USD per device, nearly a 10% cost reduction from the 154.47 USD for NiNP diffusion brazing.

- As for environmental performance, Scenario 4 was predicted to have the best cost performance. With an estimated cost of 344.60 USD per device, it was shown to have cost reductions of 33%, 31%, and 4% over Scenarios 1, 2, and 3, respectively.

Thus, given the assumptions described in Chapter 4, manufacturing Scenario 4, as defined above, appears to be the most environmentally benign and cost effective process for the production of the microchannel air preheater of the process scenarios selected.

CONTRIBUTIONS

While the work undertaken within this thesis has focused on the economic cost and environmental impact assessment of nano-assisted manufacturing of microchannel devices, other contributions are as follows:

- A process modeling approach for the prediction of manufacturing environmental impacts and cost performance was developed. Process models were created from information assembled from diverse sources including empirical data and relationships and subject matter experts. Prior modeling efforts were merged to form new process models. The assessment approach undertaken establishes an environmental profile for several key manufacturing processes used in microchannel processing technology (MPT).

- Framework for the use of environmental and cost performance measures for device production was developed. This framework can be adapted to devices of a similar nature and used to assist decisions from a technical or policy perspective. The assessment approach is demonstrated for a particular product design and processing parameters, but can be modified for other products and/or processes. This concept may also be developed to work in conjunction with alternate assessment tools to provide a more accurate and encompassing method for assessing sustainability.

RECOMMENDATIONS FOR FUTURE WORK

The research presented herein has begun to address the critical need within the manufacturing community to evaluate the sustainability of emerging technologies. There is still remaining work to be done to allow for full potential use and integration to other products within industry. However, to better assist in this work, research can still be extended.

Expanding upon the present work of assessing economic performance must be undertaken. In particular, the development of an enhanced user interface would enable the model to be more easily applied to other products and manufacturing scenarios as well as adding an eased level of usability. In adding a user interface, thus expanding the application and usability, the cost modeling tool would be more flexible to assist in sustainable decision making across a multitude of products and devices.

In addition to economics, development must be undertaken to facilitate environmental assessments of other products, processes, and technologies. As discussed in this thesis, problems with performing LCA on emerging technologies arise from deficiencies in inventory data and uncertainties in environmental impact assessment. In order to obtain accurate environmental impact assessments, the development of these databases is critical.

Finally, further resources need to be allotted to facilitate a study of micro- and nanotechnologies' impacts on society. The development of a methodologies and/or tools which encompasses impacts from environmental, economic, and social perspectives would allow for a more holistic assessment of impacts on a sustainability basis.

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