5-2012

Towards Sustainable Development of Nanomanufacturing

Sasikumar Ramdas Naidu
University of Tennessee - Knoxville, snaidu1@utk.edu

Recommended Citation

Naidu, Sasikumar Ramdas, "Towards Sustainable Development of Nanomanufacturing. " PhD diss., University of Tennessee, 2012.
https://trace.tennessee.edu/utk_graddiss/1330

To the Graduate Council:

I am submitting herewith a dissertation written by Sasikumar Ramdas Naidu entitled "Towards Sustainable Development of Nanomanufacturing." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Industrial Engineering.

Rapinder S. Sawhney, Major Professor

We have read this dissertation and recommend its acceptance:

Xueping Li, Joesph H. Wilck IV, Frank M. Guess

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Towards Sustainable Development of Nanomanufacturing

A Thesis Presented for
The Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Sasikumar Ramdas Naidu
May 2012

I dedicate this thesis to my parents, Ramdas V. Naidu and Kasthuri R. Naidu

Acknowledgements

I would like to thank my advisor Dr. Rapinder Sawhney for believing in me and being patient with me throughout my time as a doctoral student in his research group. I would also like to thank Dr. Rajive Dhingra for his collaboration, constant support and guidance. I sincerely appreciate Dr. Pedro Balestrassi for his suggestions and help with the development of neural network models.

I would like to thank members of my dissertation committee, Dr. Xueping Li, Dr. Joseph Wilck IV and Dr. Frank Guess, for their support, suggestions and help with the research. I would like to thank Ms. Cary Springer with the office of information technology at UT-Knoxville for all the help with survey development and data collection.

I also thankful for the members of Dr. Sawhney's research group who made my graduate school stay an enjoyable experience. I would like to thank one person in particular, Karthik Subburaman, for all the help when times were tough and helping me during challenging situations in my life.

Above all, I would like to thank my awesome wife, Priya, my "genie" who has been a constant support and for all the help with typesetting this thesis in LaTeX.

"The highest reward for a man's toil is not what he gets for it but what he becomes by it."

– John Ruskin

Abstract

"Sustainability" is a buzz word these days not just among regulatory agencies but even with corporations, as evident by the release of annual sustainability report by a large number of firms. Companies are starting to portray profit making along with corporate environmental responsibility.

Nanotechnology and nanomanufacturing which holds a lot of promise for development in a multitude of science and engineering fields is the "new kid on the block." This carries a lot of apprehension due to public concern about their potential unwanted side effects that may result in a case of an untoward incident or lack of oversight.

This thesis covers the following aspects of nanomanufacturing in light of sustainable development

- Identify regulatory needs
- Use of Life cycle thinking in evaluating products and use of "green" methods for nanomanufacturing
- Methods for selection of manufacturing processes that cause least harm to the environment
- Use of industrial engineering tools for evaluating manufacturing processes at an process step level to identify areas of environmental performance improvement
- Provide guidance to nanomanufacturing facilities in the form of expert opinion to help implement workplace controls

Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Organization of the Thesis and Contribution to Nanomanufacturing

Nanotechnology has resulted in more than 1000 consumer products that have some nanomaterial added to the product to improve its performance or provide new capability to the product (PEN, 2010). While these applications and enhancements are beneficial, the size range, large surface area and the potential unknown physicochemical properties of these nanomaterials is a source of concern. Nanomanufacturing is a term used to describe the production of nanomaterials or nanoenabled products using nanomaterials as intermediates. Nanotechnology and nanomanufacturing places responsibility on governmental organizations, regulatory agencies, manufacturers, public interest groups and environmentalists. These entities are working independently and in collaboration to ensure safe and sustainable development of the new materials and the associated processes.

This research proposes a unique approach in the drive towards a safe and sustainable development of nanotechnology from a combined prospective of a chemist(interested in the manufacture and environmental, health and safety aspects) and an industrial engineer (interested in the application of engineering tools and methods to nanomanufacturing). This culmination of interests utilizes the developments in the field in the form of current research and non-profit organizational efforts, as a basis for the proposed solution for a safer and sustainable manufacture and processing of nanomaterials.

Nanomaterials, in a majority of the products, are usually embedded and bound to the base material. The possibility of exposure and environmental contamination from products during their use is far less as compared to exposure to nanomaterials during their production or use as intermediates to manufacture nanoenabled products.

The literature review performed has identified the issues listed below as key to manufacturing of nanomaterials,

1. Identifying regulatory issues, regulatory options, capability of the current regulatory framework and the need for models for effective regulation.
2. Potential applicability of tools that deal with problems at the source such as green chemistry based methods of manufacturing and Life Cycle Analysis (LCA) that provide a big picture of the cost benefit type of analysis of potential benefits of nanomaterials.
3. Often there are a number of methods reported in literature to manufacture / synthesize nanomaterials and there is a need for a decision tool that compares manufacturing processes on profitability, environmental performance with the ability to incorporate multiple stakeholder input.
4. Conventional manufacturing tools and methods can be modified and applied to nanomanufacturing processes to help identify and reduce nanomaterial based wastes.
5. There is a need for generation and effective dissemination of workplace practices and good manufacturing practices to nanomanufacturing facilities.

This thesis addresses the five key issues listed above in the chapters that follow. Regulation and oversight are tools to ensure development and introduction of products which are safe for consumers and the environment. Chapter 2 provides a regulatory mechanism view needed to ensure sustainable development. It highlights the importance of public perception towards nanotechnology through generation and transparent release of information about the safety of nanomaterials. It follows recent policy initiatives and the possibility of nanotechnology regulation as an extension of chemical regulation. A customized approach of regulation which is a combination of command and control and voluntary methods is proposed given the dearth of information and the need for tools like Life Cycle Assessment (LCA) and green methods in ensuring sustainable development. LCA involves viewing the environmental impact of a product from cradle-to-grave i.e. from manufacture using raw materials to disposal or recycling. Green methods are manufacturing methods that strive to use environmentally benign chemicals for manufacturing.

Chapter 3 builds on the need for the use of LCA and green methods for evaluating the benefits of nano-enabled products as compared to conventional materials through a case study of carbon nanofiber reinforced polymer composites in automotive body panels. Nano-enabled products, while having considerable benefits in their use stage as compared to conventional materials, can carry considerable environmental burden in their manufacturing stage of their life cycle due to low process yields. The proposed solution is to use life cycle thinking while considering the benefits of nano-enabled products and reducing the environmental impact through the use of green methods for synthesis and manufacture of nanomaterials.

The rest of the chapters in the thesis address the issues dealing with the manufacture of nanomaterials and are a part of a three step methodology as depicted in figure 1.1 and is intended to be used as a Decision Support System (DSS). Chapter 4 addresses step 1 of the methodology / DSS, which is a decision support tool for manufacturing process selection. Chapter 5 deals with step 2 of the methodology / DSS dealing with nano-related wastes and concerns and chapter 6 covers step 3 of the methodology / DSS dealing with implementing workplace controls and best practices in handling nanomaterials.

Step 1 of DSS: Selection of a nanomaterial manufacturing method

With rapid development in nanomaterial synthesis, a given nanomaterial can be manufactured using different starting materials and manufacturing methods, some of which are in public domain while others are proprietary and patented. We believe that mathematical tools are available for comparison of manufacturing methods on process metrics and environmental impact metrics and haven't been utilized yet. In Chapter 4, we develop a methodology to select a nanomanufacturing

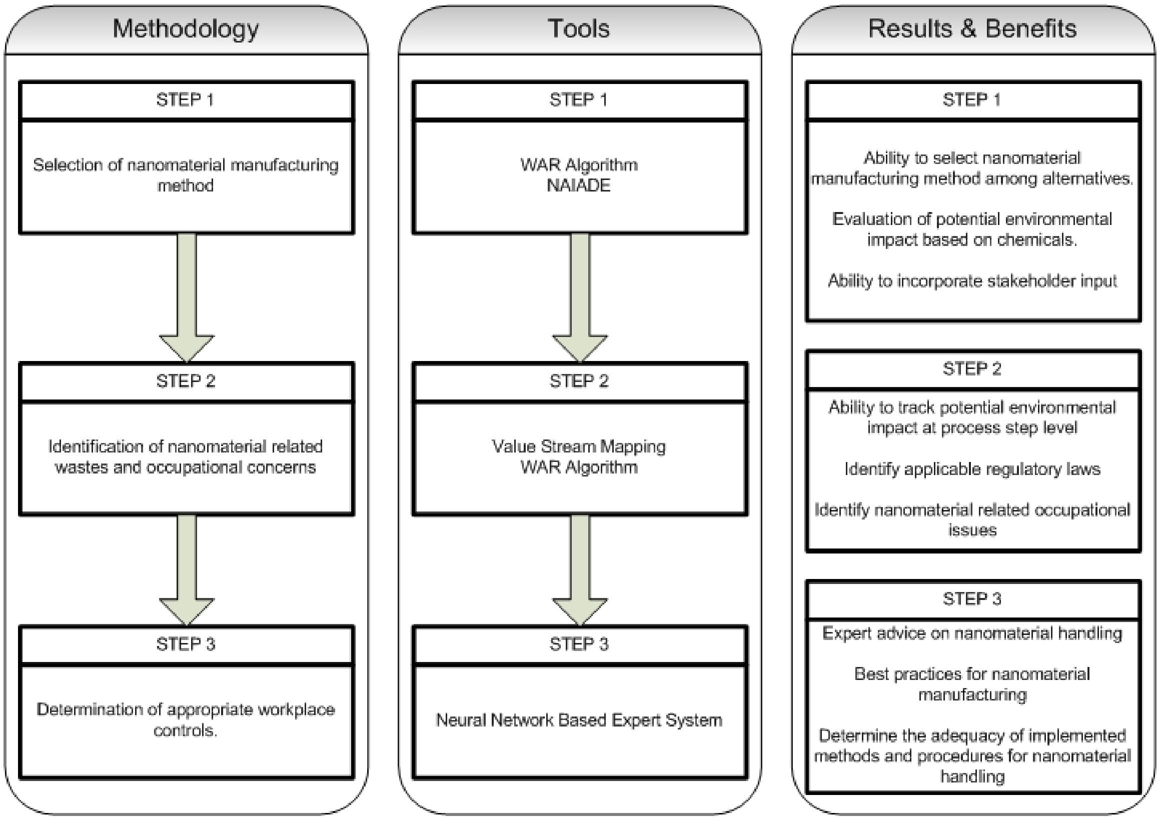


Figure 1.1: Decision Support System (DSS)

process using a set of green metrics that evaluates potential environmental impact of the manufacturing process using the Waste Reduction Algorithm developed by the Environmental Protection Agency (EPA) and performing process selection using a multi criteria decision tool, Novel Approach to Imprecise Assessment and Decision Environments (NAIADE), developed by the European Communities. This methodology is explained in detail using a case study of silica nanoparticle manufacturing process selection based on environmental impact of the chemical wastes generated during manufacturing.

Step 2 of DSS: Identification of nanomaterial related wastes and occupational concerns

A manufacturing process, when implemented in practice, can result in a unique set of characteristics that arise due to the manufacturing procedures and techniques utilized. In simple terms, two firms using the same underlying chemical method for synthesis may differ in their manufacturing steps, equipment and scale of manufacturing used. Step 1 of the methodology provided us with the potential environmental impact of a nanomanufacturing process for chemical wastes. Chapter 5 demonstrates the use of an industrial engineering tool, Value Stream Mapping (VSM), to evaluate a process to identify specific process steps and chemicals that result in the maximum potential environmental impact during the manufacture of nanomaterials using a case study of Carbon Nanofibers. In addition to that, in this step we identify the nano-related wastes that are produced in the process. Environmental impact of a majority of nanorelated wastes are currently not available and hence prevention or containment is the only option for controlling environmental and occupational exposure to nanomaterial wastes. This step tabulates the regulatory framework that addresses the byproducts and wastes of the process. This helps in identifying shortcomings of current regulatory framework and areas of new regulatory requirements that have resulted due to the unique manufacturing characteristics.

Step 3 of DSS: Determining the most likely workplace controls required based on nanomaterial and nanomanufacturing characteristics

Nanomanufacturing is a rapidly growing field and most of the developments are cutting edge research. It is very difficult for regulatory agencies like EPA and OSHA to provide customized procedures and protocols for preventing environmental and occupational exposure to specific nanomaterials and nanomaterial related wastes. The companies involved in nanomanufacturing are the source of new information regarding potential occupational concerns and there is a need to provide a channel for collecting information from these companies and disseminating information as regulatory mechanisms catch up with the rapid development of nanotechnology. Chapter 6 focuses on the need to identify and suggest workplace controls for facilities and laboratories manufacturing nanomaterials and / or using them as intermediates. A neural network based "expert system" is developed that suggests workplace controls for various plausible manufacturing conditions and scenarios. The expert system was built using responses from online and in person interviews of researchers and scientists familiar with the handling of nanomaterials and who have published nanotechnology related articles in journals. This tool can then be used by nanomanufacturing facilities to evaluate their current procedures and methods for prevention and / or mitigation of occupational exposure to nanomaterials with what is suggested by experts familiar with the handling of nanomaterials. This expert system based tool is a stop-gap measure to provide the best possible regulatory guidance till customized regulations are formulated.

Results and benefits of the methodology

The methodology / DSS described is aimed at providing guidance and tools for manufacturers and researchers in their journey towards achieving sustainable development of nanomanufacturing. The outputs from each of the three steps provide the following benefits,

Step 1 of DSS:

1. A procedure to select a nanomanufacturing method from a list of available alternative nanomanufacturing methods.
2. Evaluation of potential environmental impact of a nanomanufacturing method.
3. Ability to incorporate stakeholder input on manufacturing alternatives.

Step 2 of DSS:

1. If process selection is already made, as would be for an existing nanomanufacturing facility, Value Stream Mapping quantifies waste streams and occupational concerns that may arise providing the ability to track the potential environmental impact to a processing step level.
2. Identify the regulatory framework that govern chemical wastes produced.
3. Identify and document any voluntary regulation implemented.
4. Identify nanomaterial related occupational issues.

Step 3 of DSS:

1. Expert opinion for handling nanomaterials.
2. Current best practices for manufacturing nanomaterials.
3. Ability to assess the adequacy of current methods and need to implement new methods / practices to control occupational exposure.

This chapter provides an overview and outline of the thesis. Chapters 2 and 3 provide the “why” for the research and chapters 4, 5 and 6 provide the “how.” In an ideal scenario the above mentioned three step methodology could be applied to a process or a facility manufacturing a given nanomaterial say, carbon nanofibers but due to the nature of research and time period over which this methodology was developed, it was applied in steps to silicia nanomanufacturing process selection and carbon nanofiber manufacturing respectively. This does not, however, in any way impact the validity or applicability of the methodology.

Chapter 2

Origins of Sustainability: Regulatory Issues

2.1 Introduction

Physicist Richard Feynman is credited with being the first to envision nanotechnology in his talk "There's Plenty of Room at the Bottom" given on December 29, 1959 at the annual meeting of the American Physical Society at California Institute of Technology (Drexler, 2006). Nanotechnology is not one type of technology with a defined use; rather, it is an enabling technology that promises to contribute at many frontiers of current science and technology. Nanotechnology has generated a certain degree of hype about the potential technological and economical advantages resulting in a race for discovering new applications and rapid commercialization of discoveries. In the United States (U.S.), the National Nanotechnology Initiative (NNI) was launched to promote and develop nanotechnology to ensure U.S. competitiveness in this leading edge of technology. At the heart of nanotechnology is the synthesis/manufacture of nanomaterials, which possess many unique chemical, physical and mechanical properties. The unique properties are a result of large surface area and small size, resulting in a significantly higher number of surface atoms. Properties of nanomaterials are due to their exposed surface features that have high surface energy, spatial confinement and lesser imperfections as compared to bulk materials. Due to their unique properties, they are considered for a variety of structural, non-structural, biomedical and microelectronic applications. Representative examples include nano-silver, gold, platinum and carbon based nanotubes, nanofibres, fullerenes and metal oxide nanoparticles of zinc and titanium. The nanotechnology value chain involves the synthesis of nanomaterials and their transformation into nanointermediates and nanoenabled products. The general population today is concerned about the effects of anthropogenic activities on the environment for example global warming due to greenhouse gases (Nisbet and Myers, 2007). Advanced technologies like genetically modified foods and stem cell research have been areas of hot debate in recent times and with political ramifications, this leads to skepticism and anxiety towards other new technologies. Nanotechnology, therefore, was bound to be scrutinized in a similar fashion (Nisbet, 2004, Scheufele and Lewenstein, 2005, Whatmore, 2006). The fundamental concern in the minds of the general population about nanomaterials is the size of these materials and the possibility of absorption through the skin or through inhalation (Bergamaschi, 2009). Reports from experts have caused concern in a greater part of the society. For example, toxicology research on nanotechnology is in the initial stages of development and the body of toxicological knowledge of chemicals cannot be extrapolated to nanomaterials made up of the very same chemicals, as they are most likely to be different (Oberdorster et al., 2005). A recent survey of 177 U.S. nanotechnology researchers that was carried out on the risks, benefits and regulation of nanotechnology in the U.S. found that, on average, public health and environmental issues are the areas where risks and regulatory requirements are of greatest concern along with optimism for the technological benefits (Besley et al., 2008). A report published by the International Risk Governance Council (IRGC) indicates that a majority of applications of nanomaterials are in the cosmetics and the food industry (Figure 2.1) (IRGC, 2006). Little et al. (2007)in a report have listed a number of commercial applications of nanomaterials in the cosmetic industry and discuss the issues with their use and the potential risks that they might pose. Chris Toumey, a nanotechnology Research Scientist involved with the South Carolina Citizen's School of Nanotechnology, believes that the future of nanotechnology depends on public acceptance, so the nanotechnology community needs to listen to public opinion, and that there is serious interest in involving non-experts in the decision process (Toumey, 2006). The scientific community thus needs to reach out with new forms of public engagement (Wilsdon and Willis, 2004). NGO's and public interest groups are the most influential stakeholders that can steer public opinion and perception in favor of or against a particular nanotechnology application, for example, stain resistant clothing containing nanofibers caused significant public concern (Moyer, 2005). The Project on Emerging Nanotechnologies (PEN) is one such stakeholder which is a collaborative effort between the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts. PEN has its stated mission to "provide independent,

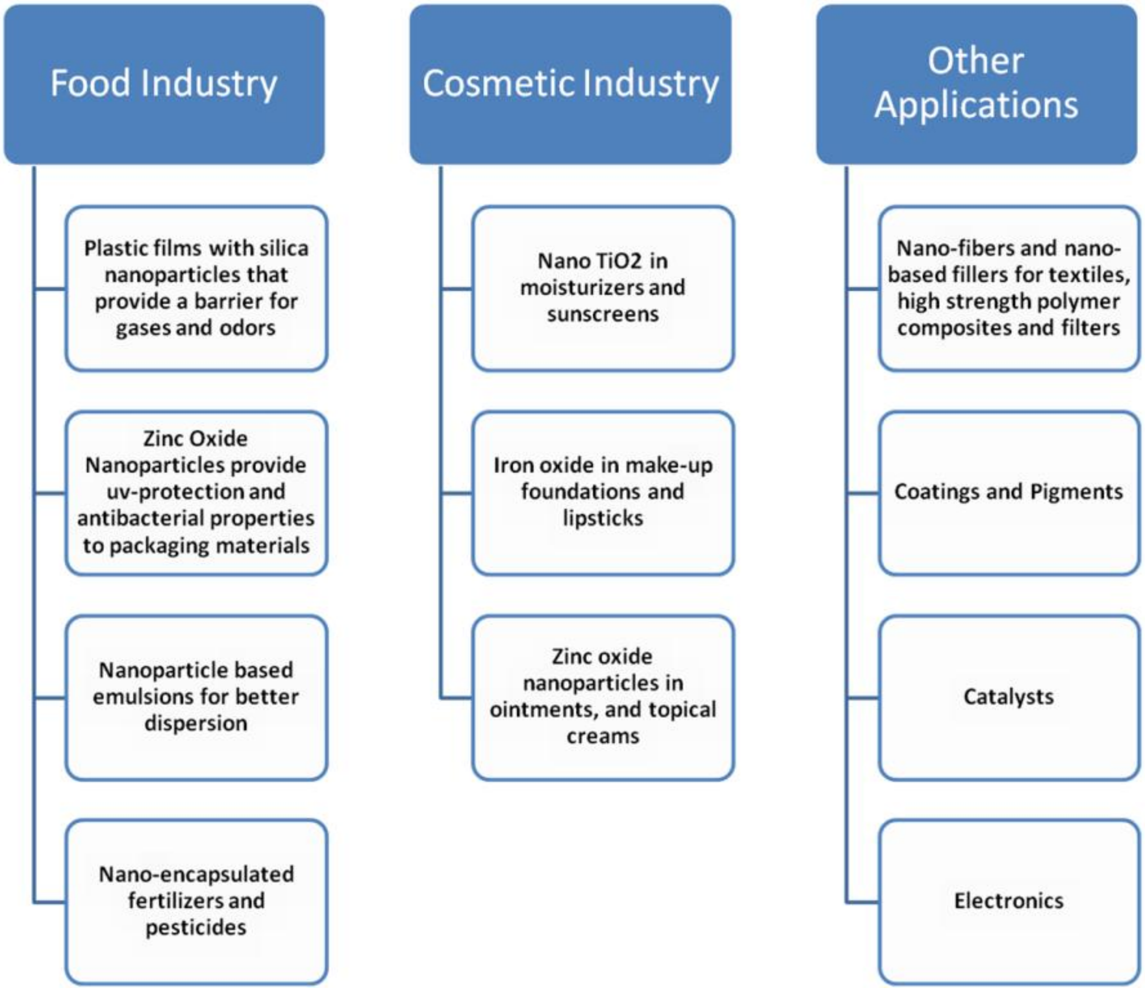


Figure 2.1: Nanotechnology Applications (Adapted from Little et al)

objective knowledge and analysis that can inform critical decisions affecting the development and commercialization of nanotechnologies." PEN also engages to inform and initiate an active public and policy dialogue to ensure sustainable development of nanotechnology by ensuring that human health and environmental impacts are addressed while remaining neutral and not advocating for or against nanotechnology. David Rejeski, Director of PEN, believes that policy makers need to ensure the safe development and applications of Nanotechnology. Rajeski envisions four plausible near-term scenarios that might make nanotechnology an asset or a liability (Goldman and Coussens, 2005).

Scenario 1: "Tipping Scales" Nanotechnology promises to offer technological prowess and subsequent military strength that result from such technological advantage. This has resulted in a rush for nanotech development across the world, not only in the industrialized countries but also in the developing world. The rush for product commercialization can lead to "cutting corners" in the development process, possibly resulting in mistakes that can tip the scales of public opinion against nanotechnology.

Scenario 2: "Nano Bhopal" There is also a possibility of accidental exposure or release, and it need not be of the scale of the Bhopal gas leak disaster of 1984 in India to generate a public backlash against nanotechnology. Accidents involving environmental spills and subsequent clean-up may be a new predicament both financially and technologically. The Kingston Power Plant located in Tennessee USA had a coal ash spill in 2008, which is another example of an accidental release into the environment (Chatterjee, 2009).

Scenario 3: "Hollywood Wins" In this scenario, one has to deal with nanotechnology gone out-of-control. Scientists tend to dismiss these media representations as nonsense, but the general population does not have access to intricate details of science that are needed to arrive at a conclusion.

Scenario 4: "Old Europe" Much of the negative feedback against genetically modified organisms (GMO's) came from Europe, and Rejeski believes that a movement against the ill effects of nanotechnology may also originate there. The European Union (EU) has developed and refined the precautionary principle of "learn and act" over a number of years, as opposed to the U.S. approach of "act and then learn." Public acceptance and regulatory mechanisms may be adversely affected with such a reactive approach.

In the above scenarios some of the key issues of sustainable development can be identified namely,

- Potential economic development benefits that lead to rapid commercialization of technologies without ample risk analysis.
- Environmental resources being harmed due to accidents
- Public and media perceptions that may be a result of lack of information and skepticism that may stunt development of novel applications of nanotechnology beneficial to humankind, for example, environmental remediation applications of iron nanoparticles(Zhang, 2003).
- The state and method of regulation has an impact on the sustainable development of new technologies that may involve the possibility of unforeseeable harm.

There is a relationship between the acceptance of nanomaterials by the public and the comprehensive review and transparent release of information regarding the impact to the general population. The Organization for Economic Co-operation and Development (OECD), funded by 30 countries, is engaged in the development of data and risk assessment of a number of nanomaterials that promise significant applications (OECD, 2009). Unless society is convinced through science that benefits from enabling technology significantly outweigh the risks, the technology will not sustain. The sustainability of nanotechnology is therefore based on evidence that the benefits of nanomaterials outweigh the disadvantages over the entire life-cycle of the material. Risk Assessment data generated from production to disposal of a nanoenabled product is paramount for public perception as well as sustainability assessment. A number of sustainability assessment tools have been developed over the years and these can be classified as tools based on indicators and indices, product related assessment, and risk analysis and multi-criteria decision analysis tools (Ness et al., 2007) (Figure 2.2). Life Cycle Assessment (LCA) is a tool of choice for product related sustainability assessment and can be applied to nanoenabled products for communicating environmental impact information for decision analysis purposes (Curran, 1993). The advantage of LCA is that it covers both the human health and environmental impacts of products (Curran, 1993, Meyer et al., 2009). The drawback of LCA is that it is time consuming and rigorous tool and the process of generating toxicological and environmental fate of the variety of nanomaterials is in itself a challenging process but a proactive approach is needed to ensure sustainable development and to formulate at the least a precautionary policy (Colvin, 2003, Holsapple et al., 2005).

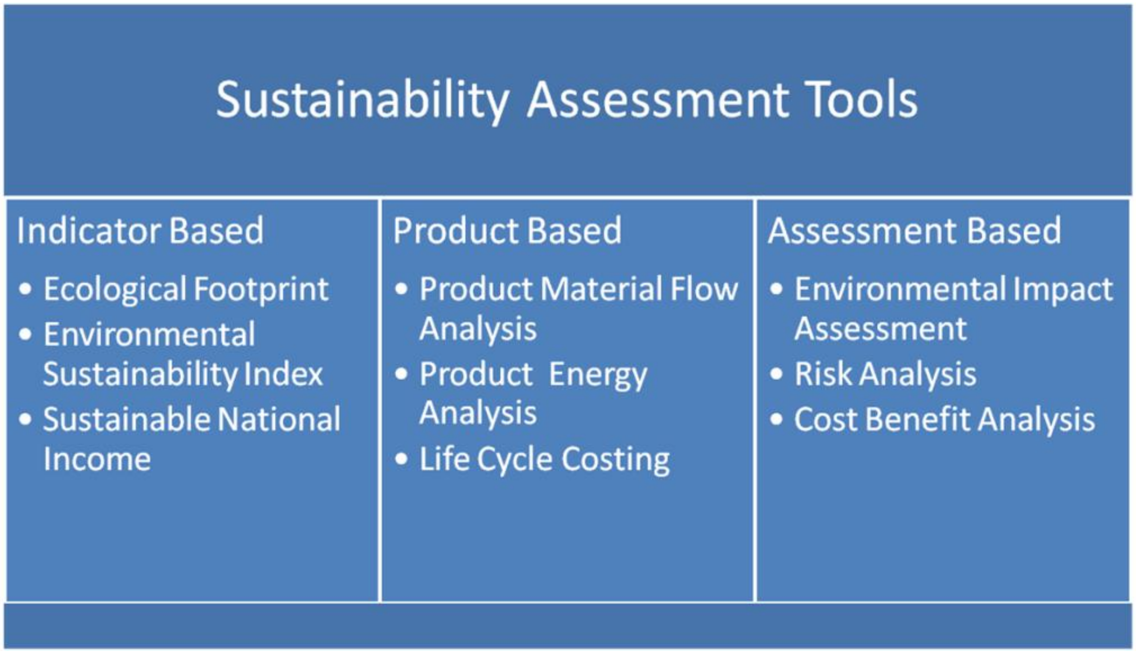


Figure 2.2: Sustainability Assessment Tools (Adapted from Ness et al)

Among the current challenges are the lack of available data for manufacturing and the release, transport and fate of these materials in the environment. Another issue associated with LCA of nanotechnology is the rapidly evolving nature of this fast emerging technology and the difficulties associated with predicting the future course of emerging nanotechnologies. As a result only a limited number of LCAs have been conducted so far. Some of these LCAs deal with the application of nanotechnology to stabilize platinum group metals used as automotive catalysts, and the use of nanocomposites in automotive body panels (Lloyd and Lave, 2003, Lloyd et al., 2005, Roes et al., 2007).Khanna and Bakshi (2009), Khanna et al. (2008) have done studies that bring to light the high energy, resource and environmental impacts that are often associated with the production of nanomaterials, to the extent that they sometimes outweigh the seemingly large benefits of nanomaterials in the use stage of the products life cycle especially production of carbon nanofibers and their use in polymer composites. Another LCA study that compares three different Single-Walled Carbon Nanotube (SWNT) production processes concludes that energy use again dominates the life cycle impact results (Healy et al., 2008). High energy requirements have also been reported in the synthesis of oxide nanoparticles (Osterwalder et al., 2006). Pietrini et al. (2007) have performed LCA analysis to demonstrate the benefits of using bio-based nanocomposites as potential replacement for conventional petrochemical based plastics in terms of lesser environmental impact of production process and biodegradable properties of the product. LCA evaluates the environmental impacts of a product or service on various metrics like ecotoxicity, ozone depletion, eutrophication etc., and is usually referred to as a ‘cradle-to-grave’ analysis of a product or service. Raw materials and chemicals are difficult to analyze from cradle-to-grave as a particular chemical may be used in a large number of products. It is only recently that LCAs of chemicals have been attempted, and they are limited to ‘cradle-to-factory gate’ analyses (Klopffer, 2005). Nanomaterials are used as intermediates and active components of nano-enabled products and need to be considered as chemicals. Life-cycle thinking with respect to nanomaterials is in its infancy, facing issues like identifying the functions of nanomaterials related to applications, need for modeling of nanomaterials if the classical function of the material is not clearly defined, need for evaluating the interactions of these materials with the environment, and data gaps for the manufacturing processes involved (Bauer et al., 2008, Shatkin, 2008b). Having said that, there have been attempts to use LCA in combination with multi-criteria decision techniques and risk analysis tools to make sustainable environmental decisions (Seager and Linkov, 2008, Shatkin, 2008a). LCA studies clearly point out the highly resource intensive nature of nanomanufacturing processes because of stricter purity requirements, low process yields, less tolerance for defects and hence large amount of wastes (Sengül et al., 2008). Nanomaterials have been used for environmental remediation purposes because of their properties but in light of LCA of these materials it is important to evaluate if the benefits outweigh the environmental impact of the production of nanomaterials (Fryxell and Cao, 2007). This is a significant challenge that faces the nanomanufacturing and R&D community to ensure that nanotechnology applications are sustainable in terms of their potential uses and environmental impacts. This article presents the government framework and funding allocated for nanotechnology research and development in the United States. Recent significant regulatory policy initiatives adopted at the state and federal level are listed. We discuss whether chemical policy options can be used as a basis for establishing future regulatory requirements for nanotechnology. We conclude with issues of concern in this ongoing policy journey.

2.2 U.S. Nanotechnology Infrastructure Development and Funding

The involvement of the United States government in the area of nanotechnology began in November 1996, when several federal agencies came together to develop programs in the area of nanoscale science and technology, and led to the formation of the Interagency Working Group on Nanotechnology (IWGN) under the National Science and Technology Council's (NSTC) Committee on Technology. The IWGN in 1999 proposed a nanotechnology initiative with a budget of half a billion dollars for Fiscal Year 2001. In August 2000, the IWGN was replaced by the Nanoscale Science, Engineering and Technology (NSET) subcommittee. NSET was given the task of implementing the NNI by coordinating with federal agencies and R&D programs, along with the White House Office of Science and Technology Policy (OSTP) and the White House Office of Management and Budget (OMB). In January 2001, the National Nanotechnology Coordination Office (NNCO) was established to provide daily technical and administrative support to the NSET subcommittee and to assist in planning, budgeting and program assessment. The 21st Century Nanotechnology Research and Development Act (NRDA) was signed as a law in December 2003. The advisory panel of the NRDA was to be designated by the President, and the responsibilities were assessing the following:

(a) Trends and developments in nanotechnology science and engineering;

(b) Progress made in implementing the NNI;

(c) Need for revision of the NNI;

(d) Balance among the components of the NNI, including funding levels for the program component areas;

(e) Whether the program component areas, priorities, and technical goals developed by the NSET Subcommittee were helping to maintain U.S. leadership in nanotechnology;

(f) Management, coordination, implementation, and activities of the NNI; and

(g) Whether societal, ethical, legal, environmental, and workforce concerns were being adequately addressed.

In response to the NRDA, in July 2004, President George W. Bush announced the formation of the President's Committee of Advisors on Science and Technology (PCAST) to serve as the National Nanotechnology Advisory Panel (NNAP). PCAST then created a Technology Advisory Group (TAG) of about 50 government and private sector scientists for implementing the NNAP duties. The organization chart for the NNI is depicted in Figure 2.3.

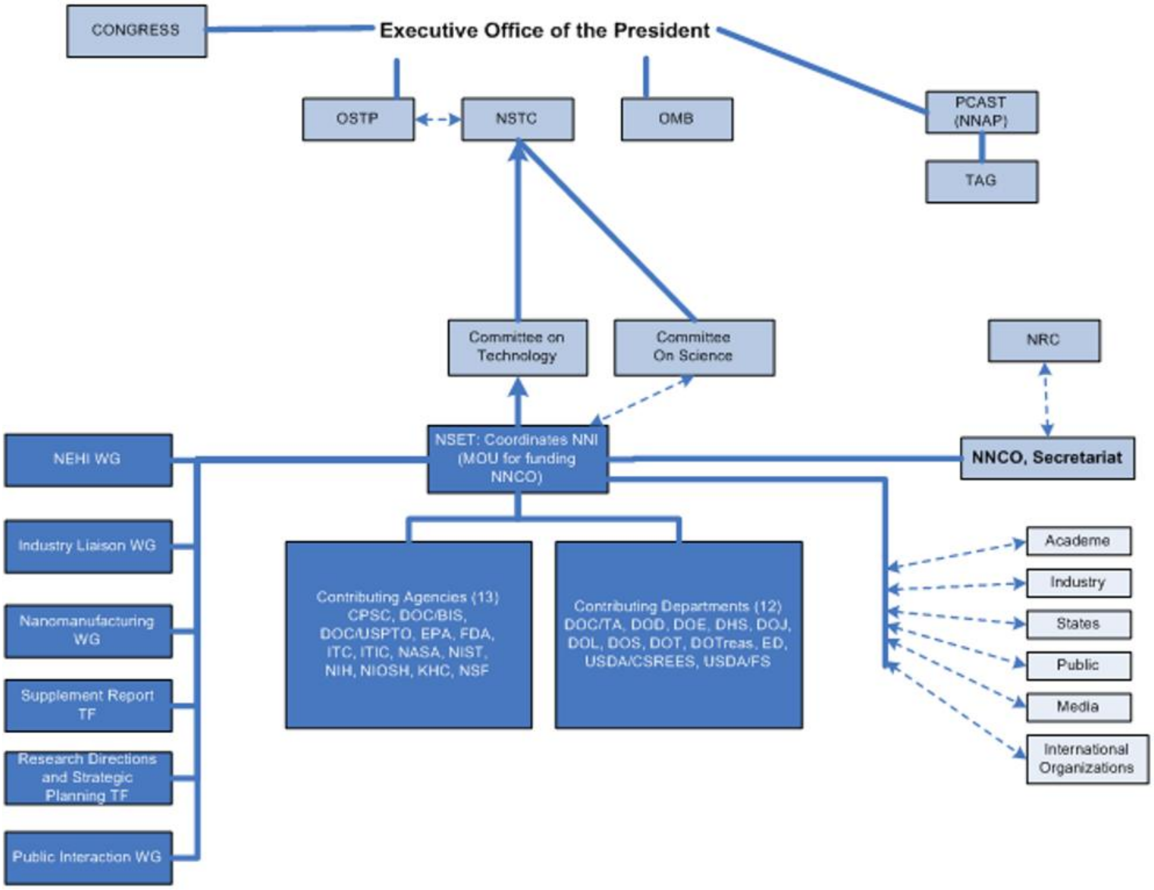


Figure 2.3: Organization of the NNI. Light shading, supervising organizations; dark shading, implementing organizations; PCAST, TAG, and NRC, organizations evaluating the NNI; dashed lines, lines of information exchange. (Source: NSET/NSF)

In its May 2005 report, the PCAST acknowledged that current knowledge and data to assess the actual risks posed by nanotechnology products are incomplete. As a result in 2005, the Nanotechnology Environmental and Health Implications

(NEHI) working group was formed. The Food and Drug Administration (FDA) is co-chair of the NEHI working group and its objective is to develop new test methods and procedures to identify and prioritize risk analysis research. PCAST also concluded that since exposure to nanomaterials is most likely to occur during the manufacturing process, research on potential hazards associated with workplace exposure must be given the highest priority (Committee to Review the National Nanotechnology Initiative, 2006). Table 2.1 lists the funding for nanotechnology for various federal agencies since 2001. It is easy to see the lag in efforts for implementing research efforts in the areas of regulation of nanotechnology by comparing the funding provided to the EPA over the years 2001 through 2006 as compared with other federal agencies. Attention was drawn to the fact that nanotechnology environmental implication funding till 2004 was $< 1\%$ of the NNI budget based on awards made by the NSF and the EPA to research proposals covering environmental implications assessment (Dunphy Guzmán et al., 2006). This probably has led to increased funding for EPA after 2006 with more emphasis being placed on Environmental Health and Safety (EHS) effects. An evaluation of percent funding of total NNI budget allocated to the EPA, the lead regulatory organization, per year is about 1 %. The NSF does provide funding for EHS research but the point being made is that the EPA is held responsible for regulation and policy development for nanotechnology. The level of funding needed to evaluate the transport, fate and environmental impacts in terms of toxicology and reactivity is not sufficient. Data generated from this research is the basis for developing at least a precautionary framework for regulating the potentially large number of nanomaterials being commercialized.

Table 2.1: NNI Budget Overview by Agency (in millions of US dollars) (Source: NSET/NSF)

Agency	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011 Proposed
DOD	125	224	322	291	352	424	450	460	459	439	415
NSF	150	204	221	256	335	360	389	409	408	428	412
DOE	88	89	134	202	208	231	236	245	332	373	380
DHHS (NIH)	40	59	78	106	165	192	215	305	342	464	464
DOC (NIST)	33	77	64	77	79	78	88	86	93	114	95
NASA	22	35	36	47	45	50	20	17	13	19	20
EPA	5	6	5	5	7	5	8	12	11	17	17
USDA			1	2	3	4	7	7	10	13	13
DHHS (NIOSH)					3	4	3	5	6	8	9
USDA (FS)						2	4	6	5	7	5
DOJ	1	1	1	2	2	0.3	2	0	1	0.2	0
DHS		2	1	1	1	2	2	3	9	21	12
DOT (FHWA)						1	1	1	0.9	3	2
Total	464	697	863	989	1200	1351	1425	1554	1690	1906	1844

2.3 Recent Policy Initiatives

The biggest issue with policy initiatives at the state and federal level is the so-called "knowledge gap" that exists in the potential risks and environmental impacts of nanomaterials due to methodological inconsistencies, inconsistencies among various studies and lack of regulatory infrastructure to pursue data generation at a rapid pace (Powell et al., 2008). However, a lack of timely regulation may result in state and federal agencies dealing with "end of pipe" environmental pollution problems similar to the polychlorinated biphenyls (PCBs) scenario.

2.3.1 Regulation and Oversight of Individual States

In many regulatory policy scenarios, the federal government sets up the broad policy objectives, but it is the individual states that act as key drivers of implementation amidst variable political, economic and demographic conditions (Gerber and Teske, 2000). The slow progress and bureaucratic procedures at the federal level have led to individual states initiating oversight that will protect the safety of workers who are handling or manufacturing nanomaterials. The Occupational Safety and Health Administration (OSHA) has approved plans for 21 states that apply federal safety standards to workers in private industry to adopt requirements for ensuring the safety of workers in the nanobusinesses. The Occupational Health and Safety Act gives them the authority to take action in the absence of federal regulation regarding workplace exposures to nanomaterials. California, Michigan, Minnesota and Washington may be the most likely to initiate such oversight (Keiner, 2008). In January 2007, The Council of the City of Berkeley amended sections of the Berkeley Municipal Code to include the manufactured nanoparticle health and safety disclosure requirements (Keiner, 2008), stating that "All facilities that manufacture or use manufactured nanoparticles shall submit a separate written disclosure of the current toxicology of the materials reported to the extent known, and how the facility will safely handle, monitor, contain, dispose, track inventory, prevent releases and mitigate such materials". The City of

Cambridge, Massachusetts, has implemented a reporting statute on the lines of the Berkeley ordinance.

2.3.2 Regulation and Oversight at the Federal Level

In his testimony to the Committee on Science and Technology, Dr Andrew Maynard, Chief Science Advisor for the Project on Emerging Nanotechnologies at the Woodrow Wilson Center, highlighted the shortfalls in the current U.S. Government strategy and stated that without clear leadership and more transparency in federal risk research investment, the emergence of safe nanotechnologies will be a happy accident, rather than a foregone conclusion. After the Berkeley ordinance, the federal government increased its efforts to enact and amend earlier laws passed at the national level, with the most significant being The National Nanotechnology Initiative Amendments Act of 2008. The 2008 NNI Amendments Act addresses five areas to establish a sound framework for enabling safe, sustainable and successful nanotechnologies:

(a) Risk research

(b) Funding for EHS research

(c) Leadership for risk research

(d) Transparency

(e) Public-Private Partnerships

The federal agencies still have to work primarily under the already existing laws, such as the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, etc., as illustrated in Table 2.2.

Table 2.2: Chemical Regulatory Model (C: command and control, V: voluntary, M: market based)

Regulation	**Existing Laws**	**Type of Regulation**	**Regulation of Nanomaterials**
Chemical Use and Assessment Laws	1)Toxic Substances Control Act (TSCA).	C,V	C,V
	2)Federal Insecticide,Fungicide and Rodenticide Act (FIFRA).	C,V	C,V
	3)Federal Food, Drug and Cosmetic Act(FFDCA)	C,V	C
	4)Occupational Safety and Health Act (OSH Act).	C,V	V
Chemical by-Products Laws	1)Clean Air Act(CAA).	C,V,M	C,V
	2)Clean Water Act(CWA).	C,V,M	C,V
	3)Safe Drinking Water Act (SDWA).	C	V
Chemical Waste and Disposal Laws	1)Resource Conservation and Recovery Act (RCRA).	C,V	V
	2)Comprehensive Environmental Response Compensation and Liability Act (CERCLA).	C,V	C
Chemical Transport Laws	1)Hazardous Materials Transportation Act (HMTA).	C	V
Other laws affecting Chemicals	1)Consumer Products Safety Act (CPSA).	C,V	C,V
	2)Federal Hazardous Substances Act (FHSA).	C,V	C,V
	3)Flammable Fabrics Act (FFA).	C	C
	4)Poison Prevention Packaging Act (PPPA).	C	
	5)Ports and Waterway Safety Act (PWSA).	C	

2.4 Can Chemical Policy Options be applied to Nanomaterials?

Regulation of chemicals has always been a tough task, and there are several recent studies on the development of an effective framework even after years of experience of regulatory policy (Cunningham, 2008). Table 2.2 summarizes the types of chemical regulation and the corresponding laws that govern them (Worobec and Hogue, 1992). The regulation of chemicals involves a mix of command and control policies, as well as an expectation of voluntary environmental regulation by the firms involved (Bennear and Stavins, 2007). Regulation of chemicals is by no means complete as the existing laws for example the Toxic Substances Control Act (TSCA), Clean Air Act and the Clean Water Act were formulated in the 1970's and are currently the primary tool for chemical regulation. Most of these laws were supposed to be preventative in nature and historical evidence of shortcomings of existing laws are evident by instances such as lapses in regulation of polychlorinated biphenyls, mercury, phthalates, Teflon, Bisphenol A (BPA), etc. This has led to a call for reform of the TSCA in the research community as well as by the EPA (Applegate, 2008, Sissell, 2009). There is also a need for market-based approaches with a majority of the companies looking to enhance their image and market perception in the use and development of green technology. The current regulation of nanomaterials is an extension of the chemical policy (Table 2.2) and with the issues facing the current regulatory laws; this is a good starting point at best for regulation of nanomaterials. At present, the multiple policy options available at our disposal are:

(a) Relying on current regulatory framework to cover emerging technologies.

(b) Relying on voluntary environmental programs to ensure that human health and the environment are protected, and that Environmental Health and Safety (EHS) information is generated.

(c) Relying on market forces to regulate the technology.

(d) Developing a new framework for public policy custom-designed for nanotechnology.

2.4.1 Current Regulatory Framework

The EPA is a major player in the regulation of the chemical industry. The EPA recently fined California technology company IOGEAR, which sells wireless mice and keyboards with stated antimicrobial or antibacterial claims, due to incorporated nanopesticides. In this case, the EPA held that the company failed to register the chemical as a pesticide, under an age-old law, the Toxic Substances Control Act (TSCA) of 1976. The TSCA of 1976 authorized the EPA to secure information on all existing and new chemical substances, with the objective of controlling the substances that were determined to cause unreasonable risk to public health and /or the environment (Wardak et al., 2007). The TSCA maintains a list of substances, called the TSCA chemical substance inventory. A substance / chemical not already on the inventory is considered to be a new substance or chemical. Under the TSCA, a pre-manufacture notice (PMN) must be obtained from the EPA before manufacturing or importing a chemical substance for commercial use, if the chemical is not listed in the inventory. After review of the PMN, the EPA grants a Commencement of Manufacture or Import Notice, and adds the chemical substance to the inventory. The dilemma here is that most nanoscale substances will not qualify as new substances, and the EPA intends to pursue such nanoscale substances on a case by case approach of determining the inventory status of nanomaterials. The EPA does not distinguish nanomaterials from bulk materials as it does not consider physical aggregates of atoms and molecules based on particle size as new substances with different identities and properties. Some nanomaterials like carbon nanotubes and fullerenes can easily be seen as separate materials from carbon in its allotropic forms of graphite and diamond. The current form of the inventory listing is not robust enough to distinguish nanomaterials from non-nanoscale substances with the same molecular identities, and the EPA is striving to provide assistance to manufacturers and importers by offering consultation regarding inventory search for nanomaterials. Similarly, the Clean Air Act of 1970 and the Clean Water Act of 1972 do provide the EPA with the statutory framework and the authority for regulation of nanomaterials. However, there is lack of tools to identify, measure, and monitor nanomaterials in the environment. The currently available tools were developed to monitor pollution due to aerosols, and are not readily applicable to nanomaterials. The efficiency of the current regulatory framework isn't where one would like to see it and this may be due to loop-holes which are sometimes technical. For example, according to analysis done by the Environmental Working Group (EWG), the chemical industry has placed a "confidential business information (CBI)" tag on 13,596 new chemicals produced since 1976 and this is almost two-thirds of the total number of new chemicals added to the inventory listing over the same period(Andrews and Wiles, 2009). Nanomaterials are obvious candidates for such industry practices. The TSCA reform is eminent and, hopefully, the shortcomings of the TSCA will be addressed, and ways and means to accommodate nanomaterials will be found. Funding for chemical screening programs has to be increased to cope with rapid developments as highlighted in the previous section.

2.4.2 Relying on voluntary environmental programs

The environmental policy outlined for organizations can be described as consisting of three steps, namely: compliance, improvement and prevention. It is practically impossible for the EPA to outline a generalized environmental management program that covers diverse types of organizations with the available limited resources. The process of developing mandatory industry-wide laws and getting them approved through Congress amid probable resistance from the industry is a challenge in itself e.g. greenhouse gas regulations. Such measures need significant research and impact assessment studies which are time consuming and have high costs associated with them. There are currently more than 200 products on the market using nano-silver as the key ingredient, among the PEN inventory list of 800+ nano-based consumer products (PEN, 2010). The best possible solution, therefore, was to have the industry voluntarily implement an Environmental Management System (EMS) which is subject to audits by the EPA for example the ISO 14001 which is a non-governmental program with significant brand reputation (Potoski and Prakash, 2005). The EPA is selling the EMS as a complement to the implementation of Total Quality Management (TQM), which is deemed essential to profitability and competitiveness of an organization, and not as a separate activity. The "compliance" step falls under the domain of the EPA, which is already inundated with a long list of chemicals that need to be studied for Environment Health and Safety (EHS) effects (Rosenbaum, 2008). The addition of nanomaterials to the list has increased the dimensionality of the problem. In January 2008, the EPA launched the Nanoscale Materials Stewardship Program (NMSP) that encourages the development and dissemination of information, including risk management practices for nanoscale materials. The program objectives listed are to:

1) Help the Agency assemble existing data and information from manufacturers and processors of existing chemical nanoscale materials;

2) Identify and encourage use of risk management practices in developing and commercializing nanoscale materials; and

3) Encourage the development of test data needed to provide a firmer scientific foundation for future work and regulatory/policy decisions.

NMSP participants are persons or entities that do, or intend to do, any of the following, with the intent to offer a commercially available product:

(a) Manufacture or import engineered nanoscale materials

(b) Physically or chemically modify an engineered nanoscale material

(c) Physically or chemically modify a non-nanoscale material to create an engineered nanoscale material

(d) Use engineered nanoscale materials in the manufacture of a product

Thirty seven companies have enlisted into the program and the EPA plans to publish a report in 2010 in order to determine the future directions of the program and the development of regulatory authorities under TSCA. DuPont and the non-profit group Environmental Defense have started to put together a framework for responsible development of nanotechnology, and this represents a rare coalition of a corporation and an environmentalist group working together for development of voluntary regulation. The framework developed by these organizations consists of developing information about these materials and their applications, followed by evaluation of life cycles, risk assessment, risk management and continuous improvement, based on review and feedback from research (Walsh and Medley, 2008). Such corporate and environmental group partnerships have always been viewed with skepticism, and the major reason for a corporation's willingness to be involved in such a partnership was due to the risk of litigation for accidental exposure or product liability (Wetmore and Posner, 2009). Voluntary programs are beneficial in principle, and do lead organizations towards sustainable behavior, but the extent of benefits may not be significant and studies have estimated them to be at a 5% level (Borck and Coglianese, 2009, Morgenstern and Pizer, 2007). The need for voluntary programs has been justified by the prohibitively high cost of development and enforcement of mandatory regulation. The question then becomes, are we expecting too much from such voluntary programs and it is clear from studies that these programs cannot be the principal means of regulation. Nanomanufacturing facilities and research labs that process and develop new materials are ideally positioned in terms of know-how and tools for developing voluntary regulation as opposed to traditional regulation by an agency. So even though the extent of benefits from voluntary programs may be less appealing, these programs need to be sustained. The information generated from such programs may be useful as we move towards developing a comprehensive regulatory framework for nanomaterials.

2.4.3 Relying on market forces for regulation

Policy instruments, which include tradable permits and pollution charges, are often described as market forces that encourage behavior through market signals rather than traditional command and control regulation of pollution control levels or methods. The Clean Air Act and Clean Water Act are examples of conventional “command and control” approaches for regulating the environment. This approach tends to force firms to share equally in pollution control activities by applying uniform standards, regardless of the associated costs. The disadvantage of this approach is that holding all firms to the same standards can be expensive, because of differences in production design, age of the assets, and similar unique attributes of the firm. This type of regulation also has the drawback of hindering the development of technologies that might result in lowering pollution levels, to begin with. The advantages that market-based instruments offer over traditional command-and-control approaches are cost-effectiveness and incentives for technology innovation and knowledge dissemination. Market-based instruments provide greater incentives to reduce pollution to firms that can achieve those reductions most cheaply. Market based instruments can be divided into the following four categories (Stavins, 2000),

1) Pollution Charges: In this scenario, a pollution fee or tax is assessed on the amount of pollution that is generated. A variant of this system is implementing a front-end tax on waste precursors as this might force manufacturers to consider safer substitutes, depending on costs and available technology. This approach is sometimes combined with a deposit refund system that helps to keep track of the amount of material that enters the production process and the amount that is recycled. The deposit amount is usually set to the cost of cleanup of illegally disposed wastes. An example of this type of system is refund on beverage containers.

2) Tradable Permits: This is the most common type of market-based instrument applied in the United States. The Tradable Permits system sets an overall

pollution level for firms in the form of permits. Firms are free to sell their permits to other firms if their pollution is well below their permitted quantity. The most common example of this is the EPA's Emission Trading for air quality.

3) Market Barrier Reduction: Creating an environment conducive to new business opportunities and increased competition, and promoting laws that increase sharing of resources that place less burden on the environment, if coupled with liability rules for the firms involved, can result in profitable and responsible business behavior. Example: deregulation of electricity generation and distribution. Mandatory information programs, such as the Toxic Release Inventory (TRI), is grouped under this category, and can serve as a set of liability rules that firms need to comply with by submitting information about the use, storage and release of hazardous chemicals.

4) Government Subsidy Reduction: Incentives are offered to companies in the form of subsidies for implementing efforts to address environmental problems. This method appears to send the right signal to corporations to implement environmentally sound practices. Regulation through the use of discriminatory taxes may increase total pollution, whereas discriminatory subsidies may be the best market-based alternative for pollution reduction as subsidy rewards the environment friendly firm and a tax may result in equating the marginal benefit with the cost of cleanup (Bansal and Gangopadhyay, 2003).

2.4.4 Develop a new framework for public policy custom-designed for nanotechnology

This option may seem daunting at first, because a new paradigm and associated framework (infrastructure) is difficult to conceive and implement and given the pace of development of nanotechnology and nanoenabled products finding their way into consumer goods. A framework can be derived as a blend of the earlier approaches where case studies of previous efforts in the formulation of environmental policy and implementation along with results of regulation can serve as guidelines for a policy on nanomaterials. There may be a need to amend some of the earlier regulation to include nanomaterials. This approach will also have to be different from previous approaches and should involve various consumer interest groups, corporations, policy experts, and international organizations that can chart a course for the responsible development of nanotechnology. The current regulation of nanomaterials is shared to a large extent by corporations as voluntary (Table 2.2) and this can be used as a leverage point for better and more effective policy development. The current government framework includes industry participation by means of the Industry Liaison Working Group (ILWG) of the NSET, with the EPA and the National Institute for Occupational Safety and Health (NIOSH) as contributing members. There is a need for widening the scope of the ILWG to include corporations in the deliberations on the development of policy and regulatory methods, along with the development of risk assessment tools, originating primarily from such voluntarily regulated firms.

The nanotechnology value chain can be depicted as shown in Figure 2.4. We have raw materials in the form of chemicals as “input” to the research and nanomanufacturing infrastructure labeled as “suppliers and manufacturers”. The suppliers can be research labs and or upstream suppliers of nanomaterials, which are then used by manufacturers to produce nano-enabled products (consumer products) generating “environmental waste” in the process. The consumer products have EHS impacts during their life cycle and at the end of their “use cycle” they are either recycled back to the manufacturing infrastructure or end up as environmental waste. The regulatory framework and applicable laws are built to provide oversight on the entire process to ensure sustainable development by limiting pollution levels and EHS impacts. The various regulatory methods and laws that are used in the three policy options and their applicability to the nanotechnology value chain are depicted by color coding the flow diagram. For example the TSCA impacts the raw material inputs to the manufacturing infrastructure and the type of materials ending up in consumer

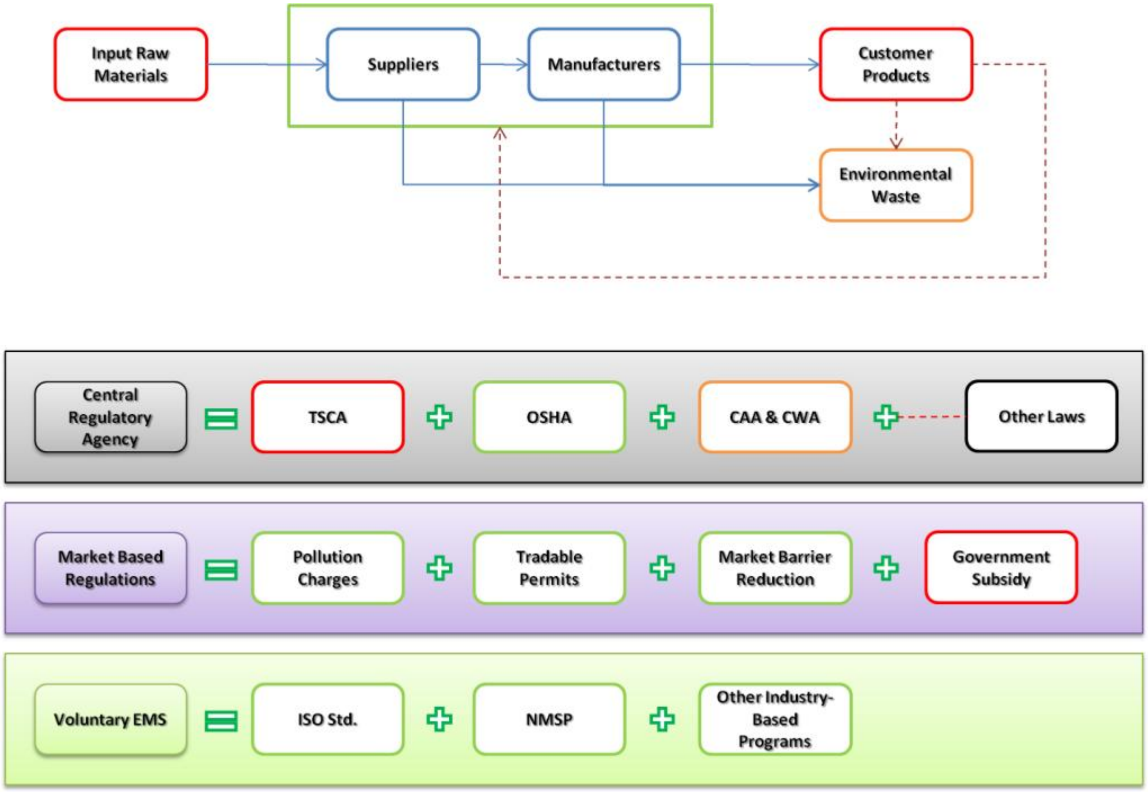


Figure 2.4: Nanotechnology Value Chain and Regulatory Framework

products. Government subsidies impact the materials in consumer products and hence the choices of input raw materials. The CAA and CWA laws are designed to monitor waste streams and minimize environmental impacts. OSHA laws are primarily focused on regulating the incidental and occupational exposure, both short term and long term, in the manufacturing infrastructure. Market based regulatory tools and voluntary regulations are usually focused on the manufacturing infrastructure. There are a number of other regulatory tools developed to be enforced by a central regulatory agency such as HMTA, FFA, FIFRA, FFDCA, etc. as listed in Table 2, and these deal with the supply chain and consumer products or nano-intermediates, and have been classified as “Other Laws”. Based on this structural view of the nanotech sector and the applicable regulatory framework, the nanotechnology value chain can be broadly divided into “Input” raw materials to manufacturing, the manufacturing “Processes”, and the “Output” in the form of nano-enabled products and wastes. The regulatory structure can be viewed as hierarchical with the central regulatory laws forming the backbone, followed by market based regulation and voluntary regulation at the top of the hierarchy (Figure 2.5).

The central regulatory agency forms the laws that lay the groundwork and determine the minimum EHS standards for the inputs, processes and output of the nanotech sector. These laws are then enhanced based on market based initiatives for firms to evaluate their input raw materials, their processes so as to exceed the minimum standards to take advantage of financial incentives. Voluntary measures mainly represent a means of protection against liability of financial risk. The central regulatory agency does create a feedback loop of information flow and results of regulatory actions upon which it can evaluate its policies and develop continuous improvements. In the case of nanomaterials the central regulatory agency may need to depend on voluntary program data to develop an initial policy for some nanomaterials. The proposed goal of such an approach would be to promote the use of greener inputs and processes to manufacture nano-materials. The EPA does have the tools for such an approach developed for chemical processes and these need

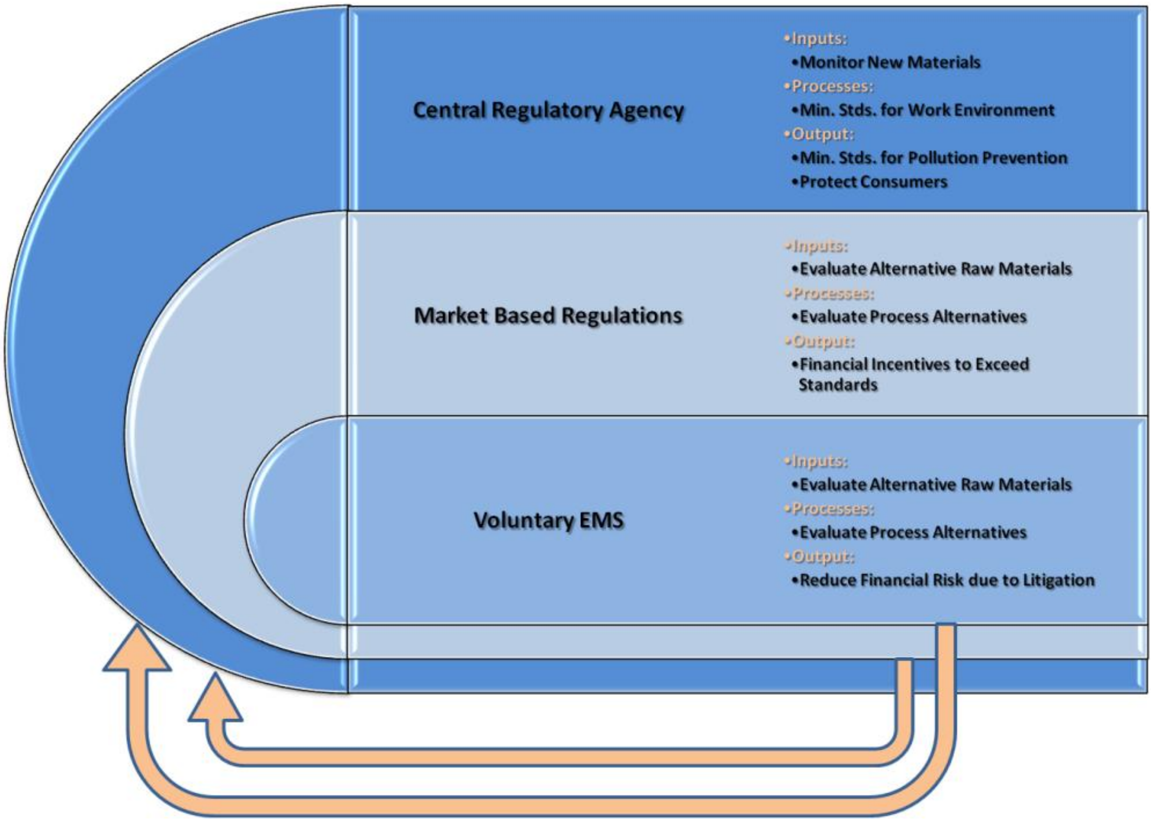


Figure 2.5: Hierarchical Regulatory Structure

to be applied to nanomanufacturing methods. Risk Analysis of nanomaterials and nanomanufacturing processes forms the basis of any regulatory framework and EPA is a key player for generation and evaluation of risk analysis data. The minimum standards for work environment and pollution prevention have to be developed. These standards have to include detailed toxicological studies. The properties of nanomaterials in terms of size and surface area cause their toxicity to be different from the bulk materials they are made of. The rapid commercialization of nano-enabled products has resulted in an acute situation, where the EPA has to depend on firms to provide risk information. The NNI funding for EHS research to evaluate the environmental implications of nanomaterials has been increasing over the years but the growth in nanotechnology applications has been at an overwhelming rate. The proposed hierarchical structure that involves participation of nanomanufacturing firms to develop and provide EHS information may alleviate the burden on the EPA to a certain extent. The use of market based techniques may help firms to adopt environmentally sound manufacturing processes. But the problems of risk assessment to determine minimum EHS standards in the absence of detailed toxicological studies remain. In a white paper in 2005 the EPA acknowledges the need for models to estimate the environmental fate and exposure information of engineered nanomaterials (EPA, 2005a). The models developed for chemicals do not extend to cover nanomaterials. Robichaud et al. (2005) have developed a risk analysis framework to evaluate the risk from an insurance industry perspective of nanomanufacturing processes vis-à-vis chemical manufacturing processes like alumoxane production, polyolefin production etc. Their methodology involves the development of qualitative latent risk scores on several environmental impact metrics of the chemicals used in the manufacturing process. Other recent approaches for risk identification and estimation based on expert opinion in the face of lack of detailed EHS data have been proposed (Wardak et al., 2008). von Gleich et al. (2008) have suggested Technology Assessment as a tool to ensure sustainable development of nanotechnology. A three tier approach is proposed involving,

(a) Technology characterization to identify potential hazards

(b) Eco-efficiency evaluation using LCA

(c) Orientation through Leitbilder (vision statements for EHS goals)

There have been suggestions for the extension of green principles to nanomanufacturing to deal with problems at the source (Berger, 2008). Methods for green synthesis of nanomaterials have been pursued and their scaling and acceptance in large scale processes is needed (Dahl et al., 2007). Decision support tools that enable evaluation and selection of nanomanufacturing processes based on sustainability metrics have also been reported but the lack of EHS data is major drawback (Naidu et al., 2008). Hutchison (2008), director of the Safer Nanomaterials and Nanomanufacturing Initiative (SNNI), which is the leading green nanotechnology effort in the world, suggests an evolving approach towards nanotechnology Environmental Health and Safety (EHS) research in three phases.

Phase 1 Studies of nanomaterial implications

Phase 2 Coordinated applications and implications research

Phase 3 A green nanoscience approach to material and process design to eliminate hazards throughout the material's life cycle.

While research activities are presently being carried out in each of the above 3 phases, the bulk of the research currently being done is transitioning from Phase 1 to Phase 2, with activities in Phases 2 and 3 each just beginning.

2.5 Conclusions

Regulation of nanotechnology with its inherent challenges has the potential to be the benchmark for other related and new technologies developed in the future. Nanotechnology regulation offers a case study for environmental, legal, societal, risk perception and sustainability dimensions of technology. The sustainable development of nanotechnology requires a systems approach that incorporates the interdependencies of the players comprising of business, government and society, factors that are drivers and mediators of development and regulation (Wiek et al., 2008). Public perception of the technology and confidence in the regulatory framework plays a significant role in development of new technologies. The science needed to develop EHS data and transparency of information is also key to public acceptance. Nanotechnology regulation also highlights a traditional "feet dragging" approach of the policy framework in terms of environmental regulation, and the increasing pressure on federal agencies to rapidly act and enforce regulation on such issues, because the ability to develop new and novel nanoscale materials and applications is far ahead of our policy generation and regulatory mechanisms (Fairbrother and Fairbrother, 2009). This may be due to the lack of funding for the principal regulatory agencies for infrastructure development and lack of ample funding for generating EHS data. The laws under the regulatory framework are in need of overhaul to accommodate developments since their inception in the 1970's. The regulation framework still has to derive from chemical regulation but enhanced with other approaches such as market based techniques and voluntary methods because the regulatory agencies depend on these firms to provide EHS data. Another challenge facing regulation of nanotechnology is the implementation phase and, as Erwin Hargrove pointed out, is the "missing link" in policy analysis (Hargrove, 1975). The Clean Air Act (CAA) and its implementation, especially the reduction of Green House Gases (GHG), is an excellent case study of the delay in policy implementation. It is usually believed that in national or cross-national policy scenarios, the implementation phase is a collective bargaining process where policy goals are negotiated rather than enforced (Durant, 1984).

Chapter 3

Sustainable Nanotechnology: Through Green Methods and Life Cycle Thinking

This chapter is revised based on a paper published by Rajive Dhingra, Sasikumar Naidu, Girish Upreti and Rapinder Sawhney:

Dhingra R., Naidu S., Upreti G., Sawhney R. Sustainable Nanotechnology: Through Green Methods and Life-Cycle Thinking. Sustainability. 2010; 2(10):3323-3338.

My primary contributions to this paper include (i) gathering and reviewing literature, (ii) part of the writing covering the application of green methods for sustainable nanotechnology

Abstract

Citing the myriad applications of nanotechnology, this paper emphasizes the need to conduct "life cycle" based assessments as early in the new product development process as possible, for a better understanding of the potential environmental and human health consequences of nanomaterials over the entire life cycle of a nano-enabled product. The importance of this reasoning is further reinforced through an illustrative case study on automotive exterior body panels, which shows that the perceived environmental benefits of nano-based products in the Use stage may not adequately represent the complete picture, without examining the impacts in the other life cycle stages, particularly Materials Processing and Manufacturing. Nanomanufacturing methods often have associated environmental and human health impacts, which must be kept in perspective when evaluating nanoproducts for their "greenness." Incorporating life-cycle thinking for making informed decisions at the product design stage, combining life cycle and risk analysis, using sustainable manufacturing practices, and employing green chemistry alternatives are seen as possible solutions.

3.1 Introduction

Sustainability and futures studies are linked to each other; the time scales involved may be different from the individual viewpoints of stakeholders, depending on whether they are futurists or environmentalists (Tonn, 2007). Futures thinking calls for planning in the time scale of hundreds of years whereas the environmental research community may think in terms of a few decades at the most (Tonn et al., 2006). Sustainability of new technology is a key issue these days, be it genetically modified foods, stem cell research or nanotechnology. The burgeoning field of nanotech applications has left us with no doubt that nano-enabled products will play a dominant role in global manufacturing in the not-so-distant future. With new applications being discovered every day in areas as diverse as medicine, automotive, energy, agriculture, and entertainment, we are becoming increasingly aware of the benefits of nanotechnology in terms of cost and energy savings, increased productivity, increased efficiency, as well as reduced environmental impacts. According to Lux Research, the total revenue from products incorporating nanotechnology is expected to be $2.5 trillion in 2015, even though this estimate is down 21% from their previous projections Research (2009), the downward revision being made considering the global economic downturn, as a result of which the rate of nanotech adoption was expected to be somewhat slower than originally anticipated. A nanometer is one-billionth of a meter. According to the National Nanotechnology Initiative, a program established in 2001 to coordinate federal nanotechnology research and development, nanotechnology is “the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.” Nanotechnology is considered an all-pervasive “enabling” technology (Fleischer and Grunwald, 2008) that transcends sectoral boundaries, resulting in novel applications of nanomaterials that promise radical improvements in various spheres of life. Examples include paper-thin, high-energy, nanoengineered batteries. Capable of being folded and cut like paper and infused with carbon nanotubes, these sheets of nanocomposite paper serve as ultra-thin, flexible batteries and energy storage devices for next-generation electronics and implantable medical equipment (Mullaney). Nano-enabled miniaturized diagnostic devices can be implanted in the human body for early diagnosis of illnesses, and the use of nanotechnology for in-vivo drug delivery and imaging systems is expanding rapidly (Koo et al., 2005). Nano-based coatings can improve the bioactivity and biocompatibility of implants (Commission, 2004), while nanocoatings are also finding use in corrosion-resistance, dirt repellency, water repellency, thermal insulation, and anti-microbial applications. Applications of nanotechnology that directly benefit the environment are nanotechnologies for site remediation and wastewater treatment (Watlington, 2005), nanomaterial-based solar cells for improved energy efficiency, the use of nanocatalysts for air purification (Sinha et al., 2007), and nanostructured filters or nanoreactive membranes for water purification (Theron et al., 2008). Despite the seemingly obvious benefits of nanotechnology, there could be unintended health and environmental risks associated with the widespread use of nanomaterials which might not have yet been fully understood. As discussed in the following sections, there is a need to use a life-cycle based approach, possibly combined with risk assessment, in order to better understand the potential problems, and to adopt green nanomanufacturing methods that are less burdensome to the environment and human health.

3.2 Nanomanufacturing Methods and Environmental Concerns

Nanoscale manufacturing involves one of two approaches: top-down or bottom-up. The top-down approach starts with micro-systems and miniaturizes them, through carving or grinding methods, such as lithography, etching, or milling. Bottom-up methods mimic nature by starting at the atomic or molecular level and building "up" through nucleation and/or growth from liquid, solid, or gas precursors by chemical reactions or physical processes. Examples of techniques include sol-gel or epitaxy (Commission, 2004, Sengül et al., 2008). It is generally believed that top-down methods generate a lot more waste. Though the bottom-up approach is in its early development phase, it promises sweeping changes to current methods of production. Nanostructured materials can be classified as one-dimensional (1D), two-dimensional (2D), or 3-dimensional (3D). Examples of 1-D nanoproducts are thin films and coatings, while 2-D include nanotubes and nanorods, and 3-D nanoproducts include fullerenes and nanoparticles. The production of 2-D and 3-D nanoproducts, generally, has stricter purity requirements. Many of the processes required to manufacture them have low process yields and, therefore, low material efficiencies, resulting in excessive waste. Moreover, these processes usually consume large quantities of energy, water, and solvents. In addition to being excessively resource and energy intensive, some of these processes have the potential to cause unintended acute and chronic human health impacts, from accidental exposure to nanomaterials. Sengül et al. (2008) have discussed various nanomanufacturing methods and have summarized the characteristics of nanomanufacturing processes that make them energy and resource intensive as follows:

- Stricter purity requirements
- Lower process yields
- Repeated processing, post processing or reprocessing steps of a single process or batch
- Use of toxic, acidic or basic chemicals and organic solvents
- Need for moderate to high vacuum
- Use of or generation of greenhouse gases

The authors would like to refer the reader to the Sengul et al. article for an in-depth analysis of the issues pertaining to nanomanufacturing methods for 1-D, 2-D and 3-D nanostructured materials. The manufactured quantities of nanomaterials are expected to increase as the technology becomes pervasive and starts displacing conventional materials in products. The starting materials used in manufacturing processes are usually rare and involve resource intensive extraction or processing that puts additional strain on natural resources and increases the overall life cycle environmental impact of the product they are ultimately used in, as demonstrated in a case study that follows. This raises the issue of finding suitable starting materials for nanomanufacturing methods.

3.3 Industrial Ecology and LCA

Industrial Ecology is a systems approach that provides a holistic view of environmental problems, and helps us understand the way humans use natural resources in the production of goods and services. It emphasizes the need to study the interactions of industrial systems with the environment, and to design products and manufacturing processes in a way that optimizes the use of by-products, maximizes recycling, and minimizes waste (Garner and Keoleian, 1995). This approach strives to ensure that industrial growth in the future is sustainable and in harmony with the environment. The foregoing discussion leads us right to the definition of Sustainable Development which, according to a World Commission on Environment and Development (WCED) report of 1987, is “Development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (Brundtland Commission, 1987.). The wide-ranging applications of nanotechnology have an equally widespread potential to adversely affect human health and the environment, through various exposure routes of nanoparticles (Curran, 1993), including occupational exposure (Boccuni et al., 2008). Despite early calls to adopt measures that would ensure the sustained growth of nanotechnology, little has been done so far, in the unrelenting quest to rapidly introduce more and more novel nano-applications (Allenby and Rejeski, 2008). Life-Cycle Assessment (LCA) is an invaluable tool for assessing the environmental impacts associated with the entire life cycle of a product. In fact, it would be premature to make any claims on the environmental benefits of a product or manufacturing process without first considering its environmental consequences in a "life-cycle" context. The steps typically involved in an LCA are (1) defining the goals and scope of the assessment, (2) quantifying the material and energy inputs, as well as the environmental releases for each unit process that forms part of the assessment (known as Life-Cycle Inventory or LCI), (3) evaluating the potential human health and environmental impacts associated with the inputs and outputs identified in the LCI data collection step, and (4) interpreting the results, highlighting significant issues, drawing conclusions and making recommendations [18]. The life cycle stages usually considered are Material Extraction, Processing, Manufacturing, Use, Transportation, and End-of-Life (Recycling/Disposal). Conducting a life-cycle assessment of conventional products is in itself a daunting task, with boundaries often having to be drawn to limit the scope of the assessment, in order to complete it within a reasonable amount of time, with the finite resources available. Some of the methods available for curtailing the scope of the assessment (also known as LCA streamlining) include (i) restricting it to certain life-cycle stages of interest, for example, the Use stage, (ii) identifying certain environmental impact categories of particular relevance, such as Global Warming, or (iii) just conducting a comparative study of two different manufacturing processes that result in the creation of otherwise identical products. With nanomaterials, the task of conducting a life-cycle assessment becomes even more difficult because of lack of available inventory data on these materials, since their manufacturing processes are new and often subject to confidentiality constraints (Meyer et al., 2009). Another reason for not being able to use inventory data the same way as in the case of conventional materials is that cutoffs based on mass alone do not make sense for nanoparticles (Curran, 1993). Also, current impact assessment methodologies do not incorporate formulas for computing the health and environmental effects of nanomaterials, simply because these effects are not yet fully known. Moreover, manufacturing processes for the production of nanomaterials are not yet standardized, but are in an evolutionary stage, changing constantly. For this reason, the environmental impacts associated with Production Method A for a given product could vary considerably from those associated with Production Method B. In the case of new technologies such as these, which are in their developmental phase, it might be beneficial to conduct scenario analyses when performing LCAs, for addressing uncertainties in possible future outcomes. In spite of the challenges faced in conducting LCAs of nanomaterials, a number of LCAs have been attempted (Khanna et al., 2008, Krishnan et al., 2008, Lloyd and Lave, 2003, Lloyd et al., 2005, Osterwalder et al., 2006, Roes et al., 2007), and even if complete LCAs cannot be performed, it is important to take a life-cycle view of new technologies such as these, to help bring to light any issues or concerns in any of the upstream or downstream stages that may be elusive at first. This "life-cycle thinking" approach needs to be applied at an early stage in the product development process, in order to better understand the environmental implications of new technologies and to be able to make informed decisions on the benefits or drawbacks of one alternative over another. There have been several suggestions to apply the life cycle thinking approach to nanotechnology development (Curran, 1993, von Gleich et al., 2008, Bauer et al., 2008, Köhler et al., 2008). Recognizing the drawbacks of LCA in being inadequate for analyzing the health effects and exposure routes of nanoparticles, this paper later describes more appropriate frameworks that combine the LCA approach with Risk Assessment (RA). The two frameworks discussed are nanoLCRA (Life Cycle Risk Assessment) and Comprehensive Environmental Assessment (CEA). Likely environmental impacts during each life-cycle stage of nano-enabled products are presented in Figure 3.1.

The apparent benefits of nano-enabled products, usually in the "Use" stage, often take center stage, while the environmental problems associated with the remaining upstream and downstream life-cycle stages tend to get overlooked (Bauer

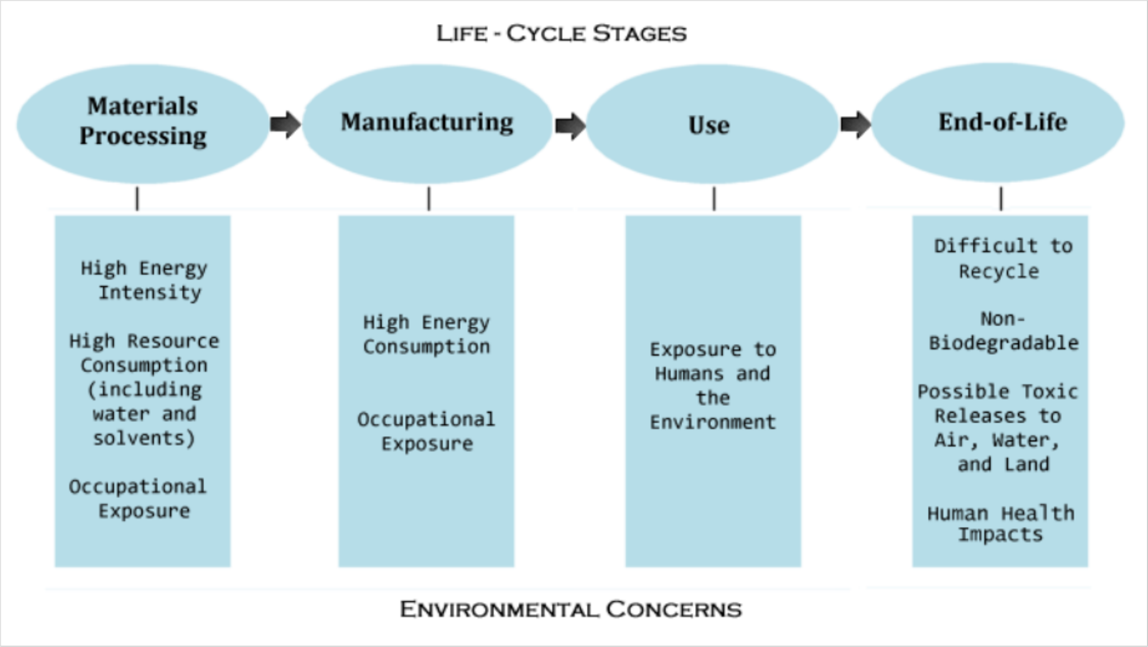


Figure 3.1: Life Cycle of Nanomaterials (Simplified)

et al., 2008). Of particular concern are the Materials Processing and End-of-Life (Recycling/Disposal) stages. The creation of nanomaterials can often be highly energy and resource intensive, as discussed earlier in Section 2. At the End-of-Life stage, we are confronted with the problem of disposing of the nano-enabled product, if it is not fully recyclable and/or reusable. Manufactured nanomaterials have the potential to be released to the environment at each stage of the product life cycle (Oberdorster et al., 2005).

3.4 Energy Intensity of Carbon Nanofibers and Nanoparticles

Although aluminum is thought to be one of the most energy intensive materials to produce, it has highly desirable properties, namely, light weight and higher strength as compared to steel, the material it usually competes with. Another drawback of aluminum is its higher price, but both the price and higher energy intensity do not usually come in the way of its use in certain critical aerospace, automotive and other applications. Because of its high energy intensity, aluminum has become a kind of yardstick by which some other, newer, materials are evaluated for their energy intensities. Carbon nanoparticles and nanofibers are examples of such materials that are much more energy intensive to produce than aluminum. Two recent studies, one on nanofibers and the other on nanoparticles, show that carbon nanofibers produced from a range of feedstock materials require 13 to 50 times the energy required for the production of primary aluminum on an equal mass basis (Khanna et al., 2008), while the carbon nanoparticles study finds their energy intensity to be 2 to 100 times that of aluminum (Kushnir and Sandén, 2008). When selecting conventional (non-nano) materials for use in a new product or application, product designers have traditionally been confronted with issues like strength, performance, cost and aesthetics. More recently, keeping the principles of Design for the Environment (DfE) in mind, additional environmental considerations like energy intensity, toxicity, recyclability, and ease of disassembly have made their way into their list of design criteria. The advent of nanomaterials, however, has necessitated a change in the traditional material selection process, because now product designers will not only have to keep the above issues in consideration but will also have to think about the health and safety of those who might be exposed to these nanoscale materials that have the potential to be inhaled or to penetrate the skin, and possibly affect vital organs.

3.5 Automotive Body Panels: A Case Study

The results from one of the author's previous studies have been used to show how nano-based products that seem environmentally preferable over other alternatives in the Use stage may not actually turn out to be so when the whole life cycle is considered. The original study compared lightweight alternatives to exterior body panels in vehicles of the future (Overly et al., 2002, Schexnayder et al., 2001).

Aluminum, carbon fiber reinforced polymer (CFRP) composite, and glass fiber reinforced polymer (GFRP) composite were considered as alternatives to steel closure panels (consisting of the 4 doors, hood, and deck lid) in a baseline vehicle (nrc, 2000). The data for that study (which we will refer to as the "exterior body panels" study) were based on carbon fiber produced from polyacrylonitrile (PAN) precursor fiber, which is oxidized and carbonized into carbon fiber by exposing it to progressively higher temperatures in the presence of nitrogen. We have substituted the energy required to produce the PAN-based carbon fiber with the energy required to produce carbon nanofiber, the data for which have been taken from a recent study on carbon nanofiber production (Khanna et al., 2008), performed by Khanna et. al., based on vapor grown fibers synthesized from three different hydrocarbon feedstocks - methane, ethylene, and benzene, using the average energy of the range provided in the study (2,872 - 10,925 Mega Joules/kg). Thus, the carbon fiber reinforced polymer (CFRP) composite in the exterior body panels study has been replaced with carbon nanofiber reinforced polymer (CNFRP) composite material, focusing only on the life-cycle energy requirements. The major assumptions of the previous study are stated in Table 3.1.

Table 3.1: Exterior Body Panels Study - Major Assumptions.

Mass of the baseline (1994 Taurus class) vehicle	3,248 lbs
Useful life of vehicle	120,000 miles
Life of body panels	Equal to life of vehicle
Baseline vehicle fuel efficiency	26.6 mpg
Mass of steel closure panels	220 lbs
Material substitution factor for CFRP	0.4
CFRP composition	30% CF in epoxy resin
Secondary weight savings factor	1.5
Fuel efficiency improvement factor	0.7*
Gasoline density	6.154 lbs/gallon
Gasoline heat content	115,400 BTUs/gallon

Based on the above assumptions, using a material substitution factor of 0.4 for CFRP (Sullivan and Hu, 1995), it was estimated that the weight of CFRP panels would be 88 lbs if they were to replace 220 lbs of steel, resulting in overall weight savings of 132 lbs. However, any major weight reduction in vehicle weight provides opportunities for additional weight reductions in other components (known as secondary weight savings). Taking the secondary weight savings into account, the overall weight savings go up to 198 lbs, bringing the CFRP vehicle weight down to 3,050 lbs. Applying the fuel efficiency improvement factor of 0.7 to the baseline vehicle fuel efficiency of 26.6 mpg, the fuel efficiency of the CFRP vehicle was calculated to be 27.74 mpg. This works out to 4,327 gallons of gasoline used by the CFRP vehicle over its lifetime, as against 4,511 gallons by the baseline vehicle. Since the functional unit for the exterior body panels study was not the whole vehicle, but only the closure panels driven over the lifetime of the vehicle, the quantity of gasoline consumed on account of the body panels alone is the fractional ratio of the mass of CFRP closure panels to the whole car, or 124.8 gallons. This translates to 768 lbs, embodying an energy content of 14.40 million BTUs (MMBTUs). The Energy use results from the exterior body panels study, as well as the modifications incorporating carbon nanofibers in place of bulk carbon fibers, are presented in Table 3.2. It has been assumed that the CNFRP composite will require only half the mass of carbon fibers, as compared to the CFRP composite material in the original study, because of the much higher strength of nanofibers. The 70/30 epoxy/carbon fiber mix in the original study, therefore, has been replaced with an 85/15 epoxy/carbon nanofiber mix, requiring only 13.2 lbs of nanofiber in 88 lbs of CNFRP panels. In estimating the energy requirements of CNFRP panels, the additional energy required to produce nanofibers has been taken into account, based on an average value of 6,899 MegaJoules / kg (taken from the study by Khanna et. al., as described above), as well as the energy required to produce the additional quantity of epoxy resin in the mix.

Table 2 shows the results of the previous study, along with an additional row representing the new CNFRP analysis (in bold). It is observed that the only change in energy numbers for CNFRP over CFRP is in the Extraction & Materials Processing (E&MP) stage, on account of the additional energy required to produce carbon

Table 3.2: Energy Use for Exterior Body Panels by Life-Cycle Stages.

Energy Use (MMBTUs)	E&MP	Use - Fuel Use	Use - Fuel Prod.	EOL	Total
Steel	1.19	35.25	7.78	0.01	44.24
Aluminum	12.97	19.69	4.35	0.02	37.02
GFRP	2.00	24.58	5.43	0.01	32.02
CFRP	4.53	14.40	3.18	0.00	22.11
CNFRP	43.67	14.40	3.18	0.00	61.26

nanofibers, with everything else remaining the same. In the previous study, CFRP turned out to be the material of choice, not only on account of its lowest total life-cycle energy requirement, but also because it was less environmentally burdensome in 8 other environmental impact categories (not shown here), out of a total of 14 impact categories evaluated (Overly et al., 2002, Schexnayder et al., 2001). It is noteworthy that, while the Use (driving) stage typically dominates the environmental life cycle of the automobile, accounting for about 80 % of the environmental impacts, substituting the body panels with nanofiber-based material, albeit in a small quantity, makes the Use stage seem insignificant compared to the Extraction and Materials Processing stage. In the previous assessment, aluminum was the most energy intensive material to produce, with its E&MP stage accounting for 35 % of the life-cycle energy impacts. However, the introduction of CNFRP makes the E&MP stage for this material the biggest contributor to total life-cycle energy, as depicted in Figure 3.2. In fact, the use of nanofibers totally turns the results of the study around, to make this choice of material the worst, at least on the energy front.

The above study clearly indicates that newer materials that are being chosen have numerous advantages, by way of their high strength, light weight, etc., but are also likely to have a relatively higher energy and material resource intensity in the upstream processing stages. In order to derive maximum benefit from the use of these materials in an environmentally responsible manner, we need to look at ways in which we can reduce their environmental burden in the life-cycle stages prior to the Use stage. Since the above results are based on the assumption that half the

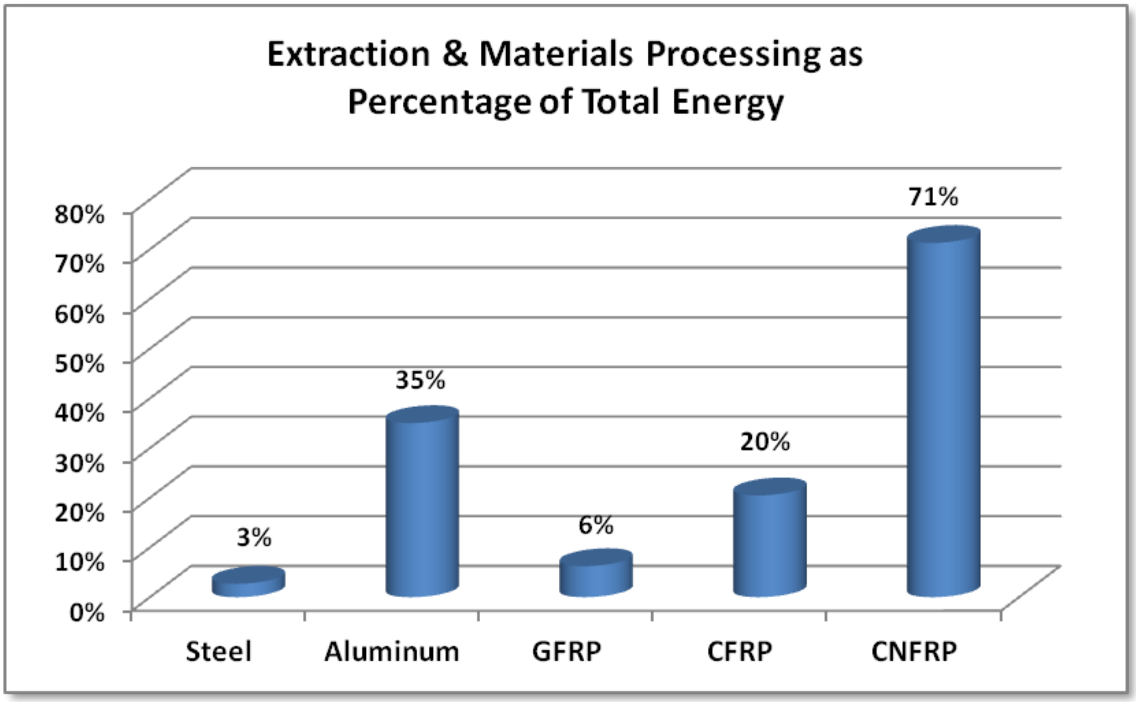


Figure 3.2: Contribution of the Extraction & Materials Processing Stage to Total Life-Cycle Energy.

quantity of carbon nanofibers will be needed in the CNFRP composite as compared to the CFRP material, a sensitivity analysis was conducted using higher and lower percentages of carbon nanofiber in the epoxy resin mix. Values of 10 % and 20 % by mass of carbon nanofibers were utilized to calculate the changes in the energy consumption. The energy required by the 3 different compositions of CNFRP in the Extraction and Materials Processing stage is graphically depicted in Figure 3.3, which also shows comparisons with the energy requirements of the other competing materials.

It is observed that in spite of varying the quantity of carbon nanofibers in the epoxy composite mix, the E&MP energy of the nanocomposites is still much higher than that of the other materials, with the nanofibers continuing to play a dominant role in the total energy requirement. Noting that the purpose of vehicle weight reduction is to maximize fuel economy, with a corresponding decrease in fuel use, it is seen

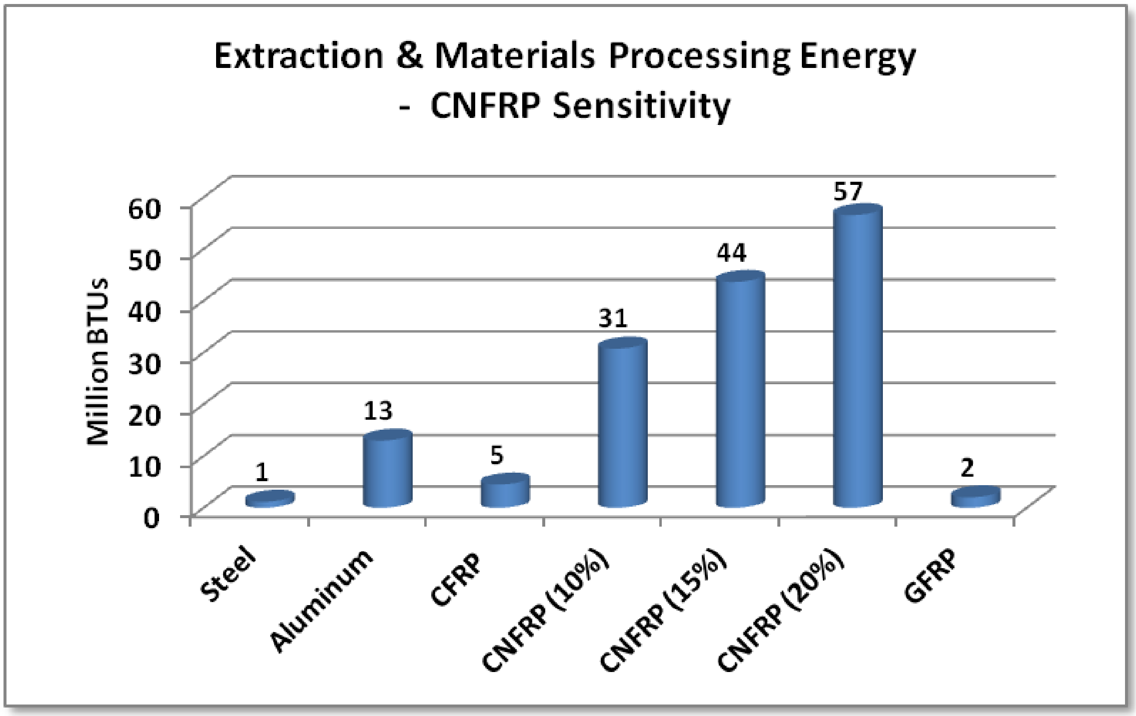


Figure 3.3: Comparison of Extraction & Materials Processing Energy

that in the case of all three CNFRP compositions, the benefit of reduced fuel use is negated by the high energy required for the production of these materials. This is clearly understood by taking a look at the total energy results for the various CNFRP compositions compared to the four competing materials, steel, aluminum, GFRP, and CFRP, as shown in Table 3.3.

Table 3.3: Energy Use Sensitivity to CNFRP Composition.

Energy Use (MMBTUs)	E&MP	Total
Steel	1.19	44.24
Aluminum	12.97	37.02
GFRP	2.00	32.02
CFRP	4.53	22.11
CNFRP (10%)	30.78	48.36
CNFRP (15%)	43.67	61.26
CNFRP (20%)	56.57	74.15

In the case of the 10 % CNFRP material, the total energy approaches the baseline vehicle energy of 44 MMBTUs. However, it is the strength of carbon nanofibers and the mechanics of the nanofiber-matrix interface that ultimately determine the quantity of nanofibers in the epoxy resin mix. For comparison, aluminum has a tensile strength of 110 MegaPascals (MPa), with carbon nanofiber being approximately 50 times stronger, having a tensile strength of 5000 MPa, or 5 GigaPascals (GPa). Carbon nanofiber is also about 10-15 times stronger than the grade of steel used for automotive body panels (which has a tensile strength of about 400 MPa) (Manoharan et al., 2009). A study conducted on the strength of carbon nanofiber-epoxy composites estimates the minimum interfacial strength of the nanofiber-epoxy composite system to be 170 MPa (Manoharan et al., 2009). Carbon Nanotubes (CNTs), on the other hand, are much stronger than even carbon nanofiber, with a tensile strength in the range of 30 - 200 GPa (Sun et al., 2007). In addition to being highly energy-intensive, nanomanufacturing processes can be highly resource-intensive, too. Certain nanomaterials require a practically contaminant-free environment, such as clean rooms and ultrapure water. Nanomanufacturing methods and the environmental concerns associated with them are discussed earlier in Section 2.

3.6 Proposed Solutions

Considering that the production of nanomaterials could be environmentally burdensome, and that there are potential health and safety concerns associated with their production, it is important for us to study the tradeoffs involved by weighing the prospective benefits of nano-based products against their unintended negative impacts. Compounding the problem is the fact existing policies regulate only conventional chemical substances, and there is no obligation on the part of manufacturing companies to label nanomaterials on their products (Som et al., 2010). Potential solutions are seen in the form of greener nanosynthesis methods, which we call “Green Alternatives,” and assessment frameworks that combine life cycle and risk assessment, such as Comprehensive Environmental Assessment (CEA) and Life Cycle Risk Assessment (LCRA). These are discussed in the following sub-sections.

3.6.1 Green Alternatives

Michael Berger of Nanowerk LLC has suggested a potential solution by applying the following principles of green chemistry (Berger, 2008), as outlined by the US Environmental Protection Agency (EPA) on their “Green Chemistry” website, to nanomanufacturing processes.

1. Design chemical syntheses to prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use raw materials and feedstocks that are renewable
5. Minimize waste by using catalytic reactions
6. Avoid chemical derivatives
7. Maximize atom economy
8. Use safer solvents and reaction conditions
9. Increase energy efficiency
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

The application and acceptance of such methods in manufacturing can only be achieved if all the stakeholders are involved in the decision-making process, and the benefits and drawbacks of manufacturing alternatives are evaluated both from process metrics and green chemistry metrics (Naidu et al., 2008). James Hutchison, director of the Safer Nanomaterials and Nanomanufacturing Initiative (SNNI), which is the leading green nanotechnology effort in the world, suggests an evolving approach towards nanotechnology Environmental Health and Safety (EHS) research in three phases (Hutchison, 2008).

1. Studies of nanomaterial implications
2. Coordinated applications and implications research
3. A green nanoscience approach to material and process design to eliminate hazards throughout the material's life cycle.

While research activities are presently being carried out in each of the above 3 phases, the bulk of the research currently being done is transitioning from Phase 1 to Phase 2, with activities in Phases 2 and 3 each just beginning. The maximum benefit can be achieved by focusing on the development of Phase 3, which is a more proactive approach, as it attacks the problem at the source. This leads to reduced potential environmental and human health impacts from the manufacturing process itself and helps us focus on the environmental impacts of nanomaterials and nanoenabled products because most of the syntheses of nanomaterials begin with known toxic materials as raw materials or solvents, which impose additional environmental burdens associated with nanomaterials and nanoenabled products. If there are health and/or safety concerns in handling materials used in the production of nanomaterials, we should study the tradeoffs involved and then see if alternative methods of production can be used to manufacture them. Examples of alternative processes based on green chemistry (Dahl et al., 2007) are:

1. Electrochemical methods and Microcapillary and Integrated Microchannel reactors that minimize the use of solvents, reactants and process times.

2. Sonochemistry and Microwave based techniques as sources of energy which shorten process times and energy consumption.

3. Alternate solvents like Supercritical Fluids (SCF), Ionic Liquids, mixture of SCF and organic solvents that are environmentally benign.

4. Bio-based approaches using biomimetic synthesis or biosynthetic approaches that use microorganisms to grow nanomaterials.

Though efforts to make nanomanufacturing processes greener are currently underway, they need to be coordinated with the efforts of LCA practitioners and product designers who are actually concerned with studying the impact of the use of these materials in nano-enabled products.

3.6.2 Combining Life Cycle and Risk Assessment

There is definitely a need for adequately addressing the human health consequences of the use of nanomaterials. However, current LCA methodology does have its limitations, as pointed out earlier. For instance, current LCA methodology has no means of distinguishing nanoparticles from bulk materials. Moreover in Step 3 of LCA methodology (Impact Assessment), the effects on human health and the environment are characterized based on environmental loadings. In other words, human health and environmental impacts are calculated using formulas based upon quantities of pollutants discharged to air, water, and land. Life-Cycle Assessment, therefore, can essentially only conclude that less is better but not whether one particular impact is more significant than another, when tradeoffs are involved (Matthews et al., 2002). Risk Assessment addresses that issue, by helping us better understand the nature and probability of adverse human health effects from exposure to toxic substances and other contaminants (US-EPA, 2009). Risk Assessment goes from quantities of pollutants discharged to analyzing their effects under ambient conditions, through various exposure pathways. In the case of nanomaterials where, in addition to quantity, additional parameters such as particle size and surface area play a significant role in affecting human health, an approach that combines LCA and Risk Assessment is likely to work well even though they are faced with similar challenges in terms of data gaps for nanomaterials they complement each other (Savolainen et al., 2010, Olsen et al., 2001). One such approach that combines LCA and Risk Assessment is the ten-step Nano LCRA (Life Cycle Risk Assessment) framework for nanomaterials, an iterative process that involves the following (Shatkin, 2008b):

1. Describe the life cycle of the product.
2. Identify the materials and assess potential hazards in each life cycle stage.
3. Conduct a qualitative exposure assessment for materials at each life cycle stage
4. Identify stages of life cycle when exposure may occur.
5. Evaluate potential human and non-human toxicity at key life cycle stages.
6. Analyze risk potential for selected life cycle stages.
7. Identify key uncertainties and data gaps.
8. Develop mitigation/risk management strategies and next steps.
9. Gather additional information.
10. Iterate process, revisit assumptions, adjust evaluation and management steps.

Another approach that combines the "environmental impact" focus of LCA with the "exposure" focus of Risk Assessment (RA) and includes toxicological effects of nanomaterials is Comprehensive Risk Assessment (CEA). A basic structure to summarize the CEA approach is proposed by Davis (Davis, 2007). It begins with a qualitative description of the life cycle of the product, thus providing a framework for systematically characterizing the potential multimedia impacts associated with the nanomaterials. Primary and secondary contaminants are then identified as entering various exposure pathways. The process ends with the evaluation of their effects on human health and ecosystems. No instances could be found of studies that have been conducted using any of the above "combined approach" frameworks. This is because of lack of inventory data and the fact that impact and risk characterization methods have not yet been developed for nanomaterials. In the future, when more data become available on these materials, using a combined LCA-RA approach would be immensely useful in evaluating the environmental and human health consequences of nanomaterials. This process can be expedited if practitioners in the areas of LCA and RA work more closely together in the future, specifically in the area of nanomaterials.

3.7 Conclusions

Considering that nanotechnology is estimated to be a multi-trillion dollar industry in the next decade, it is important to take a life-cycle approach to evaluate the environmental as well as human health (both occupational and end-use) impacts at each stage of a nano-enabled product's life cycle before arriving at any conclusions regarding the product's potential environmental benefits or drawbacks. However, current Life-Cycle Assessment methodology, developed for use with conventional bulk materials, needs to be reconsidered and modified, if necessary, to make it suitable for evaluating nanomaterials. Two frameworks that combine LCA and Risk Assessment, Nano LCRA as well as Comprehensive Environmental Assessment, seem particularly useful for adequately assessing the human health impacts of nanomaterials. In addition, the application of green chemistry principles to nanomanufacturing methods, the use of green chemistry metrics for assessing the greenness of nanomaterials and nanomanufacturing processes, and taking a more proactive approach when designing new nano-based products, are some of the recommended solutions to ensure that nanomaterials make an overall "positive" impact in future applications of this pervasive technology.

Chapter 4

A methodology for evaluation and selection of nanoparticle manufacturing processes based on sustainability metrics.

This chapter is revised based on a paper published by Sasikumar Naidu, Rapinder Sawhney and Xueping Li:

Naidu, S., Sawhney, R., Li, X., A methodology for evaluation and selection of nanoparticle manufacturing processes based on sustainability metrics.Environ Sci Technol. 2008;42(17):6697-6702

My primary contributions to this paper include (i) development of the problem into research, (ii) identification of the study areas and objectives, (iii) gathering and reviewing literature, (iv) processing,analyzing and interpretation of data, (v) pulling various contributions into a single paper, (vi) most of the writing.

Abstract

A set of sustainability metrics covering the economic, environmental and sociological dimensions of sustainability for evaluation of nanomanufacturing processes is developed. The metrics are divided into two categories namely industrial engineering metrics (process & safety metrics) and green chemistry metrics (environmental impact). The Waste Reduction Algorithm (WAR) is used to determine the environmental impact of the processes and NAIADE (Novel Approach to Imprecise Assessment and Decision Environments) software is used for evaluation and decision analysis. The methodology is applied to three processes used for silica nanoparticle synthesis based on sol-gel and flame methods.

4.1 Introduction

Recently, the world community is paying close attention to climate change and has become more concerned about the effects of human activity on the environment. This has brought the concept of sustainable development to the forefront because economic sustainability has an environmental cost. Another important development in recent years is green chemistry, which arose from the need for environmental responsibility.

Sustainability of existing technologies are being evaluated and new technologies have to be developed under the framework of sustainable development as these technologies promise potential for considerable economic benefits and maintaining a competitive advantage in an age of globalization. Such potential gains may lead to a rush for rapid commercialization of technology without looking into sustainability aspects. For example, Nanotechnology, touted as the next big phenomenon to happen to mankind after computers, is the study at the nano-scale ($10^{-9}m$) involving a few hundred atoms and is also referred to as 21st century manufacturing; based on predictions of how it might revolutionize the manufacturing industry. Nanomaterials possess many unique chemical, physical and mechanical properties. Due to their unique properties, they are considered for a variety of structural, non-structural, biomedical and microelectronic applications. Federal funding for nanotechnology has considerably increased in the past few years. Actual spending on nanotechnology by U.S government agencies for the fiscal year 2006 was 1,351 million dollars and the estimated budget for 2007 is 1,392 million dollars (Thayer, 2007). New applications are found for nanomaterials on a regular basis and there is a race to gain first movers advantage for new materials to gain control over new markets for such products. Such fervor has potential to overlook some of the problems that might emerge. There is already tremendous effort from National Nanotechnology Initiative (NNI) to allay concerns in the general public and to promote the potential for this technology and the associated economic development. Research on the application of green chemistry to nanoparticle synthesis is also underway (Albrecht et al., 2006). The Environmental Protection Agency (EPA) has developed a “Performance Track” program for the chemical industry which promotes voluntary implementation of an Environmental Management System (EMS) and subsequent reporting (EPA, 2005b). This EMS facilitates, audits and inspection of facilities and helps industries avoid fines and legal action and self regulates the chemical industry’s impact on the environment. There is a need for standard procedures for successful implementation of similar measures in nanomanufacturing while taking into consideration new parameters and metrics that address sustainability issues. Process selection and design decisions have to reflect economic and environmental sustainability.

4.2 Problem Description

The Nanotechnology value chain involves the synthesis of nanomaterials and their transformation into nanointermediates and nanoenabled products. Nanomaterial synthesis is at the core of the application and development of Nanotechnology. The current challenges and needs facing nanomaterial synthesis can be summarized as follows:

- Skepticism about the effects of nanomaterials on humans and the environment.
- Need for an industry standard similar to chemical process engineering for evaluation and rating of nanomanufacturing processes based on sustainability metrics (Gani et al., 2005).

Robichaud et al have done a risk assessment study of manufacturing nanomaterials vis-à-vis other processes like Alumoxane production, polyolefin production, Lead-Acid battery production etc. in a qualitative fashion from an insurance industry perspective (Robichaud et al., 2005). They have developed qualitative risk rankings for evaluating processes on metrics like toxicity, water solubility, bioaccumulation, flammability and emissions. The metrics are derived from latent risk scores of the chemicals involved and the temperature and pressures used in the processes. The Robichaud et al methodology evaluates processes that manufacture different nanomaterials but it could have also been applied to nanomanufacturing processes that use different synthetic methods to obtain the same nanomaterial. Additional metrics that quantitatively represent environmental, economic and ecological domains of sustainability need to be considered. Multi Criteria Decision Analysis (MCDA) methods can be applied for evaluating various manufacturing processes on sustainability metrics. Stakeholders that include the general public and environmentalists need to be accommodated in the decision process (Gregory et al., 2005).

4.3 Methodology

The present study uses silica nanoparticles as a model nanomaterial, which has traveled the entire value chain and is currently being used in finished products. For example, silica nanoparticles are used to provide scratch resistance to automotive coatings (Presting and König, 2003). The research methodology involves two components as illustrated in Figure 4.1.

1. Developing a set of sustainability metrics.
2. Using a decision support system (model) that uses these metrics to evaluate and rate processes.

4.3.1 Metrics

The sustainability metrics defined are process and safety metrics grouped under the name Industrial Engineering (I.E) metrics and Green Chemistry (environmental impact) metrics. These metrics conform to standards for manufacturing and eco-friendliness as recommended by the American Institute of Chemical Engineers (AIChE). Some of the parameters listed are from the Environment Performance Table (EPT) as recommended by the Performance Track program of the EPA. For nanomaterials, new parameters like particle size and/or surface area are needed that represent their special properties.

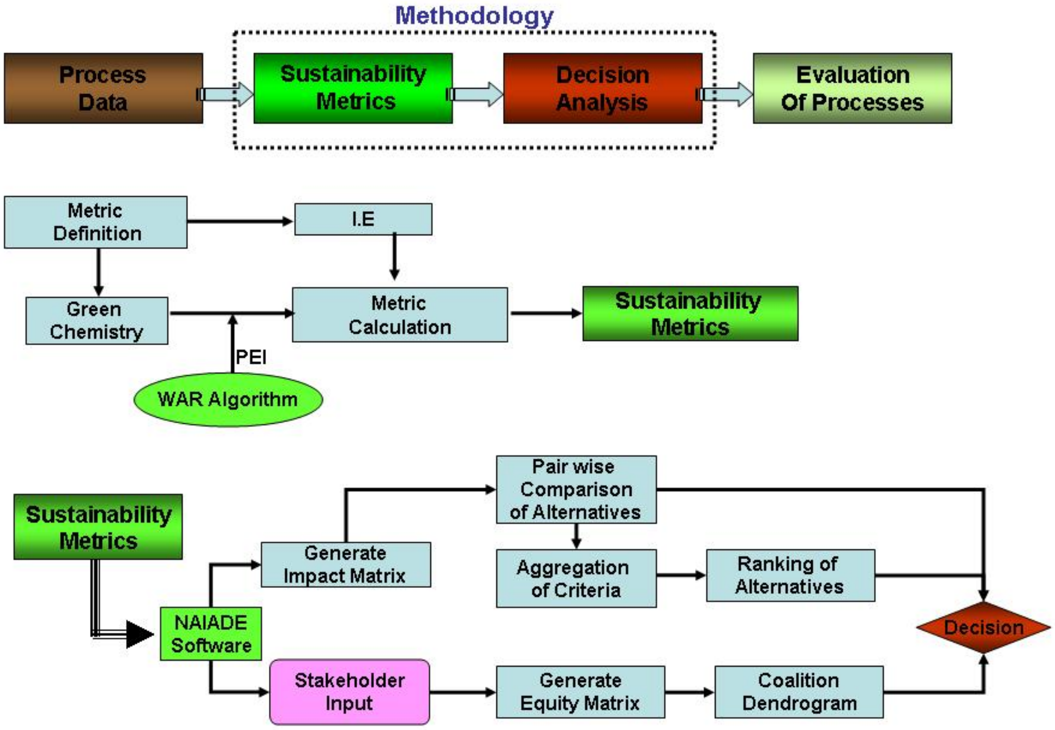


Figure 4.1: Flow Chart of the Methodology

Metric Definition and Calculation

Industrial Engineering:

1. Yield: Amount of product produced per batch or per hour.

2. Particle Size: The average size of the nanoparticles produced in nm.

3. Cost per unit (C_t): Cost of producing a unit of product involving all process related costs, including raw materials and cost for waste treatment and disposal.

$$C_t = (C_{process} + C_{raw-mat} + C_{waste}) / \ Product\ in\ Kg \tag{4.1}$$

4. Work Environment Index: This determines the exposure levels at the workplace which would include chemicals and nanomaterials. Studies where air samples are taken for Mass Spectrometry analysis are needed to evaluate the levels of exposure. Current Mass Spectroscopy techniques make this a trivial job. The exposure to nanoparticles can be determined using aerosol detectors such as Condensed Nucleus Counters (CNC's) which are quite cost effective as compared to Mass Spectrometry (Kulmala et al., 2007). CNC equipments provide rapid and accurate data about particle counts, but are rarely used for continuous monitoring because of need for regular maintenance after a couple of hundred hours of operation. Exposure assessment studies also require the size distribution data of the nanoparticles. The Work environment Index includes calculating the Time-Weighted Average (TWA) for an 8 hour shift and Short-Term Exposure Limit (STEL) for 15 minutes.

$$STEL\ or\ TWA\ = \sum_i (C_i * t_i) / \sum_i t_i \tag{4.2}$$

Where, t_i is the period of time during which one sample is taken, and C_i is the average concentration over time period t_i.

5. Chemical Safety Index and 6. Process Safety Index: Rafiqul Gani et al have described inherent safety indices that comprise of both chemical and process sub-indices (Jensen et al., 2003), and the details of assigning these scores are provided as supplementary information (Heikkilä, 1999). The actual score for the chemical safety sub-indices are the highest scoring chemical involved in the process for each individual criterion.

Green Chemistry :

1. Material Procurement (M_p): Raw materials used per unit mass of product.
2. Generation of Waste (G_w): Waste generated per unit mass of product.
3. Hazardous Materials: List of hazardous materials used or produced as by products.
4. % Atom Economy:

$$\%\,Atom\ Economy = \frac{Mass\,of\ Desired\ Product}{Total\ Mass\,of\ all\ Reagents} \times 100 \tag{4.3}$$

Solvents are not included as they are recycled in most manufacturing processes. Solvents are considered as a separate metric (solvent index) Table 4.1.

Table 4.1: Chemical Safety and Process Safety Index

Chemical inherent safety sub-indices	Score	Process inherent safety sub-indices	Score
Heat of the main reaction, I_{rm}	0 - 4	Inventory, I_i	0 - 5
Heat of the side reaction, I_{rs}	0 - 4	Temperature, I_t	0 - 4
Chemical interactions, I_{int}	0 - 4	Pressure, I_p	0 - 4
Flammability, I_{fl}	0 - 4	Equipment, I_{eq}	
Explosiveness, Iex	0 - 4	I_{Isbl}	0 - 4
Toxicity, I_{tox}	0 - 6	I_{Osbl}	0 - 3
Corrosivity, I_{cor}	0 - 2	Process structure, I_{st}	0 - 5
Maximum chemical inherent safety index, I_{csi}	28	Maximum process safety index score, I_{psi}	25

5. Energy Efficiency: This would include utilities such as water, electricity and natural gas and is defined as the energy used to produce a kg of product.

6. Potential Environment Impact(PEI): This index is generated by the Waste Reduction(WAR) Algorithm as developed by Douglas Young and Heriberto Cabezas at the US-EPA (Young and Cabezas, 1999, Young et al., 2000, Cabezas et al., 1999). The algorithm presently comes bundled within the ChemCAD software and evaluates the following eight environmental impact categories.

    (a) Human toxicity potential by ingestion (HTPI),
    (b) Human toxicity potential by exposure both dermal and inhalation (HTPE),
    (c) Terrestrial toxicity potential (TTP),
    (d) Aquatic toxicity potential (ATP),
    (e) Global warming potential (GWP),
    (f) Ozone depletion potential (ODP),
    (g) Photochemical oxidation potential (PCOP) and
    (h) Acidification potential (AP).

    The WAR algorithm uses a database of chemicals to evaluate the above metrics for products and non-products. A detailed explanation of the WAR algorithm and the calculation of its parameters are provided as supplementary information.

7. Solvent Index: The solvent index is the environment impact scores for the solvent as calculated by the WAR algorithm.

8. Recovery of nanomaterials from products: Finally, we need to make sure that there is a system in place that designs ways and means of recovering nanomaterials from waste streams if they are not biodegradable.

Many of the above parameters have sub-parameters and the net score of these sub-parameters would be the actual score.

Martins et al. (2007) have elegantly divided sustainability metrics into various dimensions of sustainability namely economic, ecological and societal and have given priorities to variables that overlap in the following order 3D, 2D and 1D. Table 4.2 shows the classification of the I.E. and Green Chemistry metrics into various dimensions of sustainability.

4.3.2 Decision support model

The WAR algorithm itself is a decision support model where the user can assign weights to various PEI criteria and evaluate processes but we need to consider other metrics as well that look into process chemistry, design and costs. When evaluating processes, one process may not be the clear choice and decisions have to be made considering process metrics that may be qualitative or fuzzy. We decided to use NAIADE (Novel Approach to Imprecise Assessment and Decision Environments) method as developed by Giuseppe Munda and available as a software application (Munda, 1995). Input data for NAIADE can include qualitative data which are expressed by means of linguistic evaluations and quantitative data expressed in the form of crisp, stochastic or fuzzy numbers and hence, data can be used under uncertainty. Linguistic variables are treated as fuzzy sets. No weighting of criteria is done.

Table 4.2: Dimensions of Sustainability Metrics

Dimension	Category	Industrial Engineering Metrics	Green Chemistry Metrics
1-D	Economic	Yield, Particle Size	
	Environmental		Potential Environment Impact
	Sociological		
2-D	Eco-efficiency		Solvent index Generation of Waste
	Socio-economic	Cost per unit	
	Socio-ecological		Hazardous Waste
3-D	Sustainability	Chemical Safety Index	Material Procurement
		Process Safety Index	% Atom Economy.
		Work Environment Index	Energy Efficiency
			Recovery of Nanomaterials

Implementation of NAIADE involves generating an Impact Matrix that consists of the alternatives being compared versus the metrics used for the comparison and an Equity Matrix based on stakeholder input of their preference towards the alternatives by means of linguistic variables. The ranking of the alternatives is arrived by applying the following three steps to the Impact Matrix.

i. Pair wise comparison of alternatives

ii. Aggregation of all criteria

iii. Ranking of alternatives

Pair wise comparison of alternatives: This is done by calculating the distance between the alternatives (i.e. difference of their values) if they are crisp (numeric) and is denoted by the semantic distance, which is the distance between the probability density functions or fuzzy membership functions. For a criterion j and a pair of alternatives i and i' , we can define six membership functions to denote the comparison namely,

$$\mu_{\gg}(i,i')_j(i \text{ much better than } i'),$$

$$\mu_{>}(i,i')_j(i \text{ better than } i'),$$

$$\mu_{\cong}(i,i')_j(i \text{ approximately equal to } i'),$$

$$\mu_{=}(i,i')_j(i \text{ very equal to } i'),$$

$$\mu_{<}(i,i')_j(i \text{ worse than } i') \textit{ and}$$

$$\mu_{\ll}(i,i')_j(i \text{ much worse than } i').$$

These comparisons are scaled from 0 to 1, where 0 is much worse than and 1 is much better than. The membership functions are defined in Table 4.3 where C_*($*$ stands for $\gg$,$>$,$\cong$, $=$, $\ll$ and $\leq$) is the crossover value i.e. the point at which the function equals 0.5 and d is the distance.

Table 4.3: Preference relation functions

$\mu_{\gg}(d) = \frac{1}{(1+\frac{C^2_{\gg}(\sqrt{2-1})}{d^2})^2}$ for $d \geq 0$ and $\mu_{\gg}(d) = 0$ for $d < 0$	$\mu_{>}(d) = \frac{1}{(1+\frac{C^2_{>}}{d^2})}$ for $d \geq 0$ and $\mu_{>}(d) = 0$ for $d < 0$
$\mu_{\cong}(d) \;=\; exp - (\frac{log2}{C_{\cong}}\lvert d\rvert) \;\forall\; d$	$\mu_{=}(d) \;=\; exp - (\frac{log2}{C^2_{=}}d^2) \;\forall\; d$
$\mu_{\ll}(d) = \frac{1}{(1+\frac{C^2_{\ll}(\sqrt{2-1})}{d^2})^2}$ for $d \leq 0$ and $\mu_{\ll}(d) = 0$ for $d > 0$	$\mu_{<}(d) = \frac{1}{(1+\frac{C^2_{<}}{d^2})}$ for $d \leq 0$ and $\mu_{<}(d) = 0$ for $d > 0$

Aggregation of all criteria: This is done so that all pair wise performance of alternatives can be combined into a single criterion and can be taken into account simultaneously. A preference intensity index $\mu_*(i,i')_j$ of one alternative with respect to another is calculated.

$$\mu_*(i,i') = \frac{\sum\limits_{j-1}^{m} max(\mu_*(i,i')_j - \alpha, 0)}{\sum\limits_{j-1}^{m} |\mu_*(i,i')_j - \alpha|}, \tag{4.5}$$

Where $*$ stands for $\gg$,$>$,$\cong$, $=$,$\ll$ and $\leq$. And α is a parameter used to express the minimum requirements of the credibility indexes and only those that are greater than α are considered.

The intensity index $\mu_*(i,i')$ has the following characteristics

$0 \leq \mu_*(i,i') \leq 1$

$\mu_*(i,i') = 0$ If none of the $\mu_*(i,i')_j$ are more than α.

$\mu_*(i,i') = 1$ If $\mu_*(i,i')_j \geq \alpha \forall$ m and

$\mu_*(i,i')_j > \alpha$ for at least one criterion.

An index $H_*(i,i')$ based on the entropy concept is introduced and gives an indication of the variance in the credibility indexes that are above the threshold value and around 0.5 (maximum fuzziness). An entropy value of 0 means that all criteria give an exact indication (definitely credible or not credible) and an entropy value of 1 means that all criteria give an indication biased by maximum fuzziness (0.5). The information provided by the preference intensity index $\mu_*(i,i')_j$ and the corresponding entropies $H_*(i,i')$ is used to build the degrees of truth (τ) of the following statements.

According to most of the criteria,

1. i is better than i'.

$$\omega_{better}(i,i') = \frac{\mu_{\gg}(i,i')\hat{}C_{\gg}(i,i') + \mu_{>}(i,i')\hat{}C_{>}(i,i')}{C_{\gg}(i,i') + C_{>}(i,i')} \tag{4.6}$$

2. i and i' are indifferent.

$$\omega_{indifferen}(i,i') = \frac{\mu_{==}(i,i')\hat{}C_{==}(i,i') + \mu_{\cong}(i,i')\hat{}C_{\cong}(i,i')}{C_{==}(i,i') + C_{\cong}(i,i')} \tag{4.7}$$

3. i is worse than i'.

$$\omega_{worse}(i,i') = \frac{\mu_{\ll}(i,i')\hat{}C_{\ll}(i,i') + \mu_{<}(i,i')\hat{}C_{<}(i,i')}{C_{\ll}(i,i') + C_{<}(i,i')} \tag{4.8}$$

Where,$C_*(i,i') = 1 - H_*(i,i')$ and,

$$\tau = \begin{cases} 1 \quad \forall \quad \omega \geq 0.8 \\ 0.33 \quad -0.66 \quad \forall \quad 0.5 \leq \omega \leq 0.8 \\ 0 \quad \forall \quad \omega \leq 0.5 \end{cases}$$

The ^ operator can be a minimum operator or the Zimmmermann-Zysno operator which allows for varying degrees of compensation γ which has values from 0 (no compensation) to 1(maximum compensation).

Ranking of alternatives:

Rankings are derived from the preference intensity indexes and their corresponding entropies. The final ranking is derived from two separate rankings. The first one $\phi^{+}(i)$ is based on the *better* and *muchbetter* preference relations ranging from 0 to 1 and indicates how i is better than all other alternatives. The second one $\phi^{-}(i)$ is based on *worse* and *muchworse* preference relations having values from 0 to 1 indicating how i is worse than all other alternatives.

$$\phi^{+}(i) = \frac{\sum_{n=1}^{N-1} (\mu_{\gg}(i,n)^{\wedge}C_{\gg}(i,n) + \mu_{>}(i,n)^{\wedge}C_{>}(i,n))}{\sum_{n=1}^{N-1} C_{\gg}(i,n) + \sum_{n=1}^{N-1} C_{>}(i,n)} \tag{4.10}$$

$$\phi^{-}(i) = \frac{\sum_{n=1}^{N-1} (\mu_{\ll}(i,n)^{\wedge}C_{\ll}(i,n) + \mu_{<}(i,n)^{\wedge}C_{<}(i,n))}{\sum_{n=1}^{N-1} C_{\ll}(i,n) + \sum_{n=1}^{N-1} C_{<}(i,n)} \tag{4.11}$$

Coalition Dendrogram:

NAIADE allows for analysis of conflicts between stakeholders involved in the decision making process as well as the possibility of coalition formation to the proposed alternatives. This is done by constructing an equity matrix which comprises of linguistic evaluations of the alternatives by different groups involved. A mathematical reduction algorithm is used to build a coalition of dendrogram which shows level of conflict and possible coalition formation between different groups (Please refer to the NAIADE manual for a detailed explanation).

4.4 Application/Experiment

The above methodology was applied to the synthesis of silica nanoparticles by three different methods namely, Sol-Gel method and Flame Methods involving Tetraethylorthosilicate (TEOS) and Hexamethyldisiloxane (HMDSO) as precursors. The sustainability metrics were generated from the synthesis procedures reported and are shown in Tables 4.4 and 4.5 respectively (Park et al., 2002, Jang, 2001, Wegner and Pratsinis, 2003, Hshieh et al., 2003). Data for some of the metrics were not available and denoted as NDA (No Data Available). Cost analysis was done using data from Sigma-Aldrich and the cost of commercial gases and waste disposal costs were used as charged to University of Tennessee-Knoxville. Equipment and set up costs were not included in the calculations.

The impact matrix (Figure 4.2) was generated from the metrics. Only the parameters where data was available were used and qualitative data were assigned to show the implementation of the method. The Equity Matrix (Figure 4.3)depicting the involvement of stakeholders was generated without any actual surveys and was included to demonstrate the available features of NAIADE.

4.5 Results and Discussion

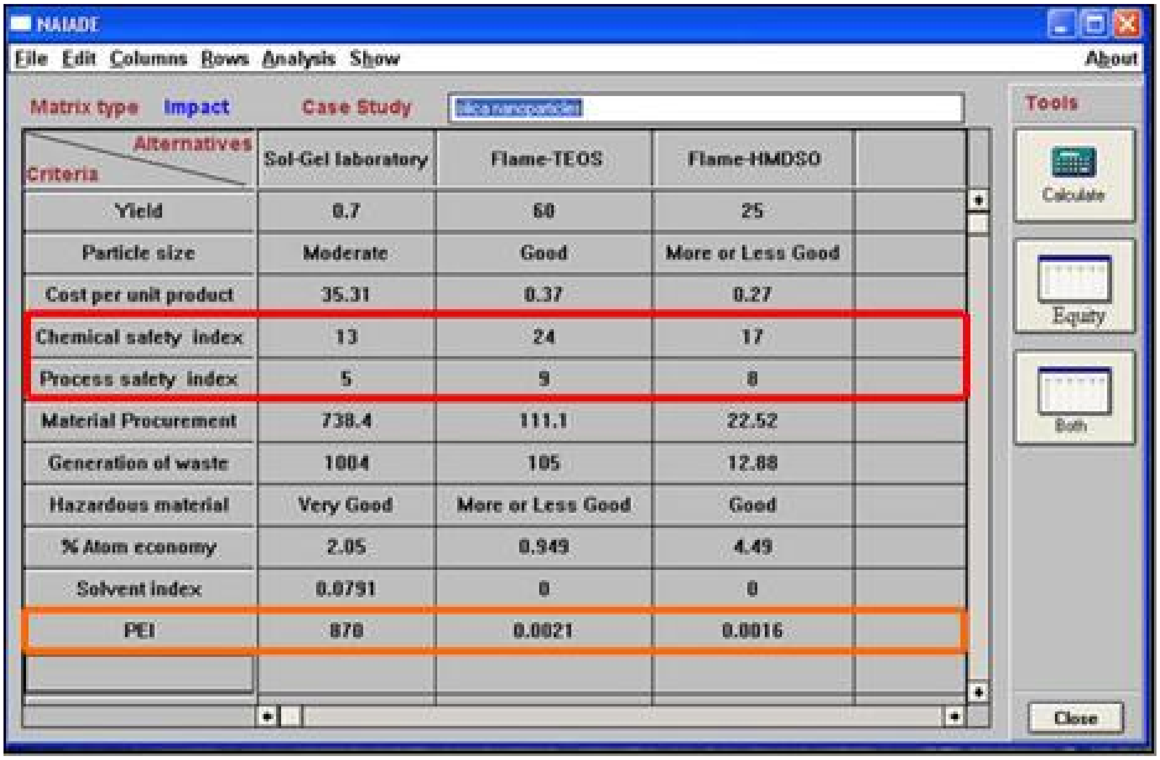
The multicriteria analysis result in Figure 4.4 clearly shows that the processes are ranked as HMDSO>TEOS>Sol-Gel overall. In this simple case, we can deduce that by inspection of the Impact Matrix itself, but most real life scenarios may be difficult to conclude at first glance. Pairwise comparisons between alternatives as depicted in Figure 4.5. Threshold values ($\alpha = 0.4$) can be set for variables so that only those variables greater than the threshold can be compared. The degree of truth (τ) values suggests that the two alternatives flame HMDSO and flame TEOS are almost comparable to each other with HMDSO having a slight advantage. One of the biggest advantages of NAIADE is that it allows stakeholder participation as

Table 4.4: I.E Parameters

I. E Parameter	**Sol-Gel**	**Flame-TEOS**	**Flame-HMDSO**
Yield	0.7 g	60 g/h	25 g/h
Particle Size	150 nm	40 nm	60 nm
Cost/unit of product	35.31 $/g	0.37 $/g	0.27 $/g
Work Environment Index	NDA	NDA	NDA
Chemcial Safety Index			
I_{rm}	1	4	4
I_{rs}	0	4	4
I_{int}	4	4	4
I_{fl}	3	4	4
I_{ex}	1	4	1
I_{tox}	3	3	0
I_{cor}	1	1	0
I_{csi}	13	24	17
Process Safety Index			
I_i	3	1	0
I_T	0	4	4
I_P	0	1	1
I_{eq}			
I_{Osbl}	1	1	1
I_{Isbl}	0	1	1
I_{st}	1	1	1
I_{psi}	5	9	8

Table 4.5: Green Chemistry Parameters

Green Chemistry Parameters	**Sol-Gel**	**Flame-TEOS**	**Flame-HMDSO**
Material Procurement	738 g	111 g	22.5 g
Generation of Waste	1004 g	105 g	12.88 g
Hazardous Material	none	hydrogen	methane
% Atom Economy	2.05	0.95	4.49
Solvent Index	0.079	none	none
Energy Efficiency	NDA	NDA	NDA
PEI / kg of product	8.70 E+2	2.08 E-3	1.61 E-3
PEI / hr	6.09 E-1	1.25 E-4	4.04 E-5
Recovery of Nanomaterials	NDA	NDA	NDA

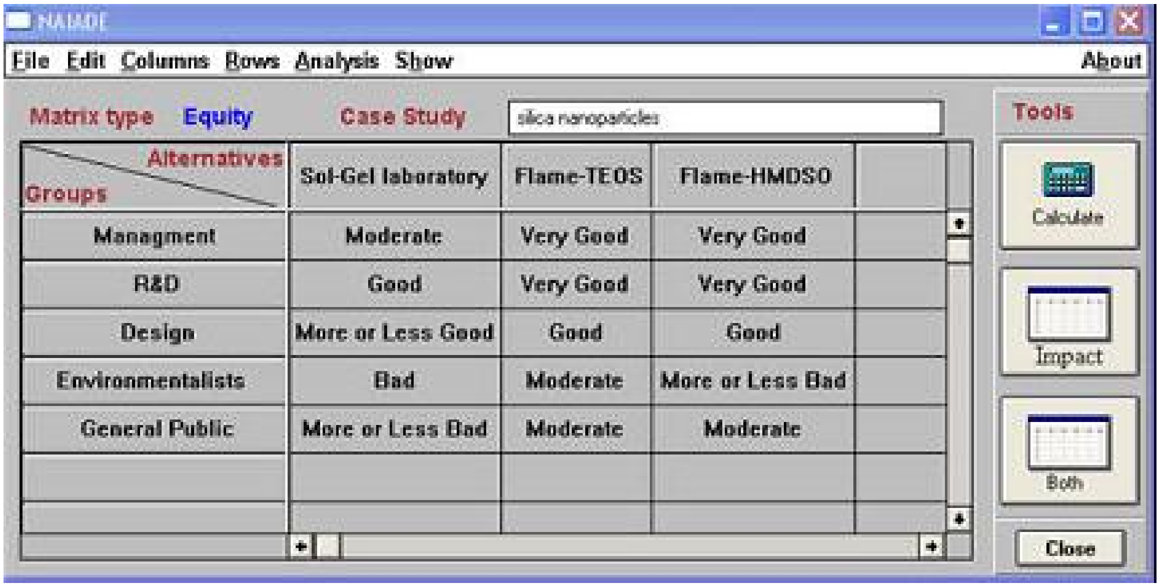


Matrix type Impact

Case Study silica nanoparticles

Alternatives / Criteria	Sol-Gel laboratory	Flame-TEOS	Flame-HMDSO
Yield	0.7	60	25
Particle size	Moderate	Good	More or Less Good
Cost per unit product	35.31	0.37	0.27
Chemical safety index	13	24	17
Process safety index	5	9	8
Material Procurement	738.4	111.1	22.52
Generation of waste	1004	105	12.88
Hazardous material	Very Good	More or Less Good	Good
% Atom economy	2.05	0.949	4.49
Solvent index	0.0791	0	0
PEI	870	0.0021	0.0016

Figure 4.2: Impact Matrix

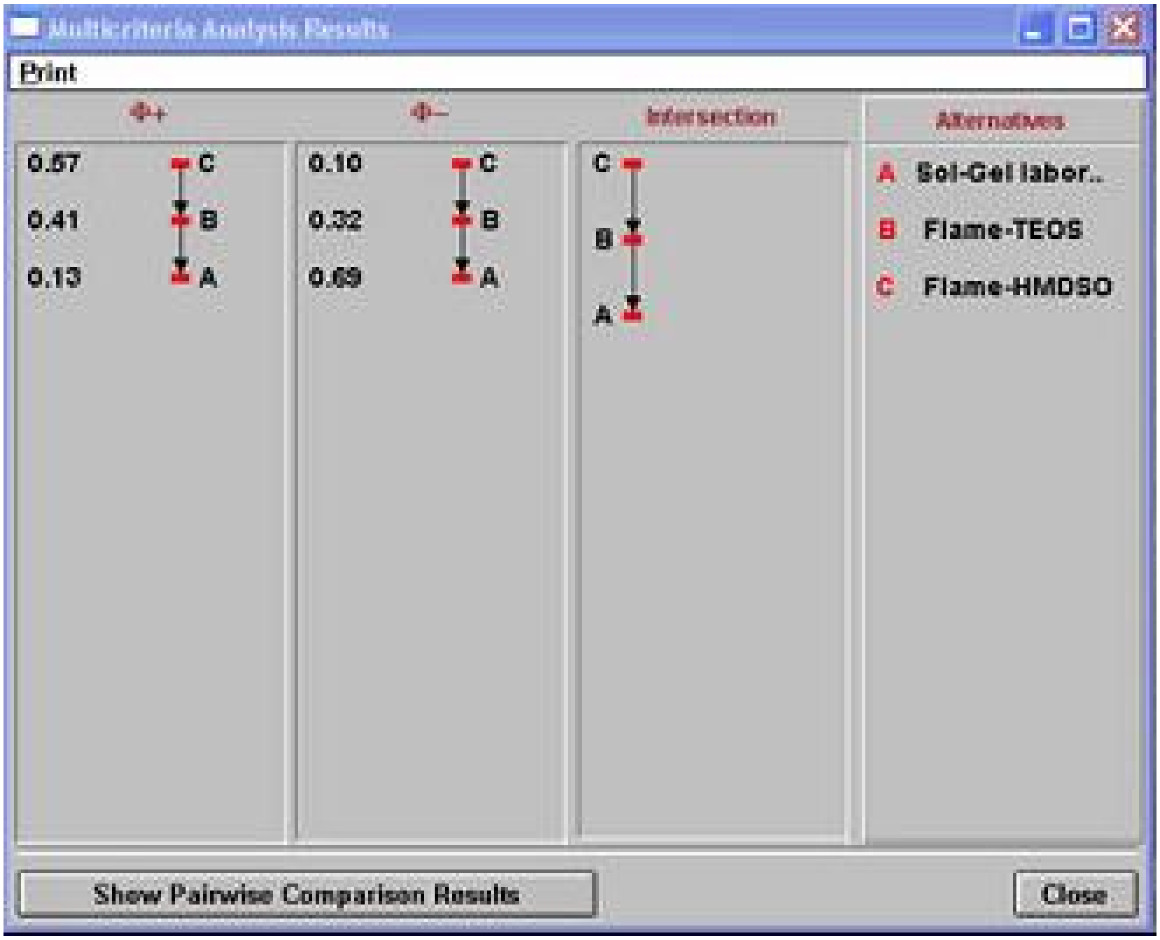


Matrix type Equity

Case Study silica nanoparticles

Alternatives / Groups	Sol-Gel laboratory	Flame-TEOS	Flame-HMDSO
Managment	Moderate	Very Good	Very Good
R&D	Good	Very Good	Very Good
Design	More or Less Good	Good	Good
Environmentalists	Bad	Moderate	More or Less Bad
General Public	More or Less Bad	Moderate	Moderate

Figure 4.3: Equity Matrix



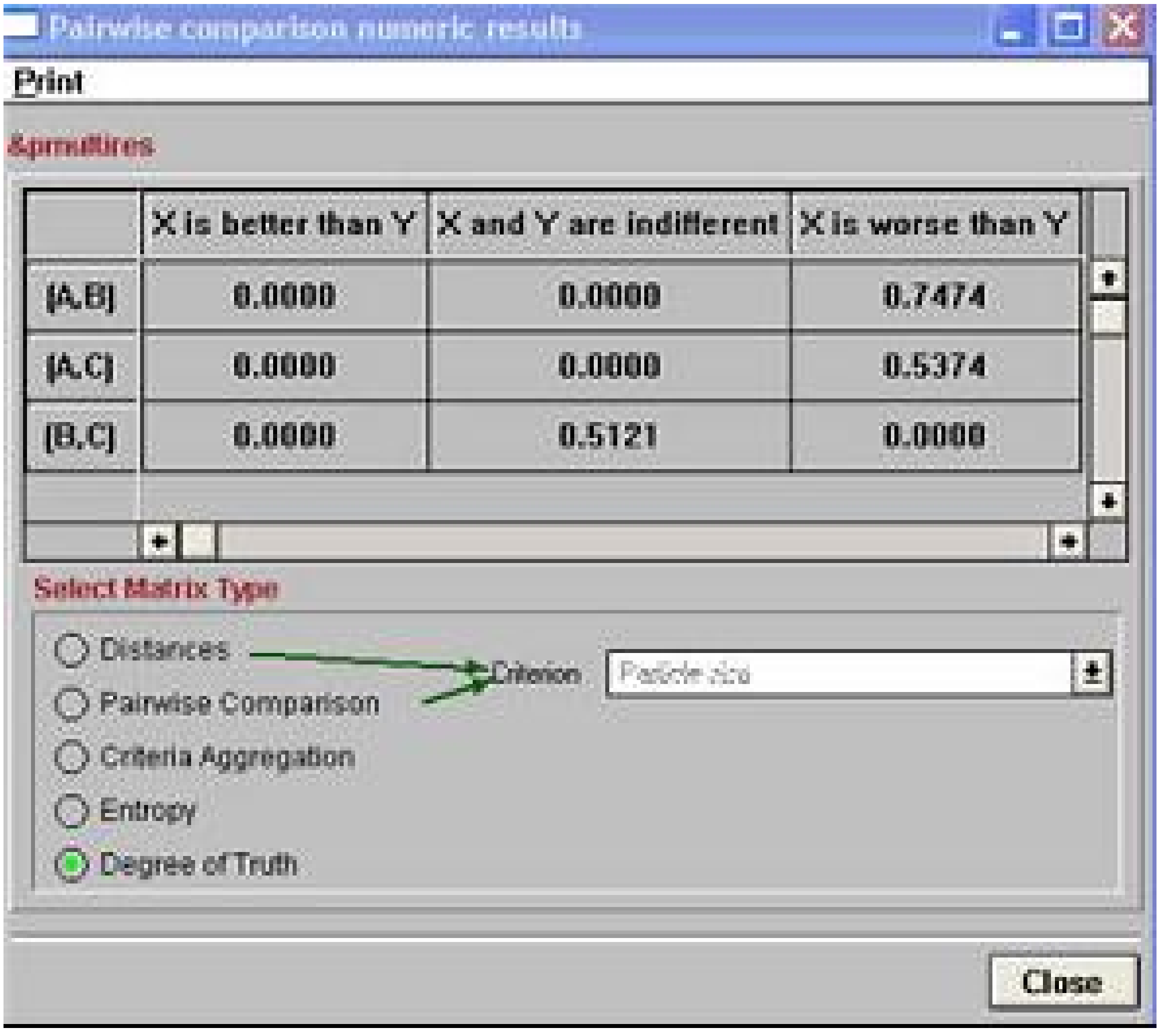
Φ+
0.57 C
0.41 B
0.13 A

Φ−
0.10 C
0.32 B
0.69 A

Intersection
C
B
A

Alternatives
A Sol-Gel labor..
B Flame-TEOS
C Flame-HMDSO

Figure 4.4: Multicriteria Analysis Results and Ranking of Alternatives.



	X is better than Y	X and Y are indifferent	X is worse than Y
{A,B}	0.0000	0.0000	0.7474
{A,C}	0.0000	0.0000	0.5374
{B,C}	0.0000	0.5121	0.0000

○ Distances

○ Pairwise Comparison

○ Criteria Aggregation

○ Entropy

● Degree of Truth

Criterion: Particle size

Figure 4.5: Pairwise Comparison of the Three Methods

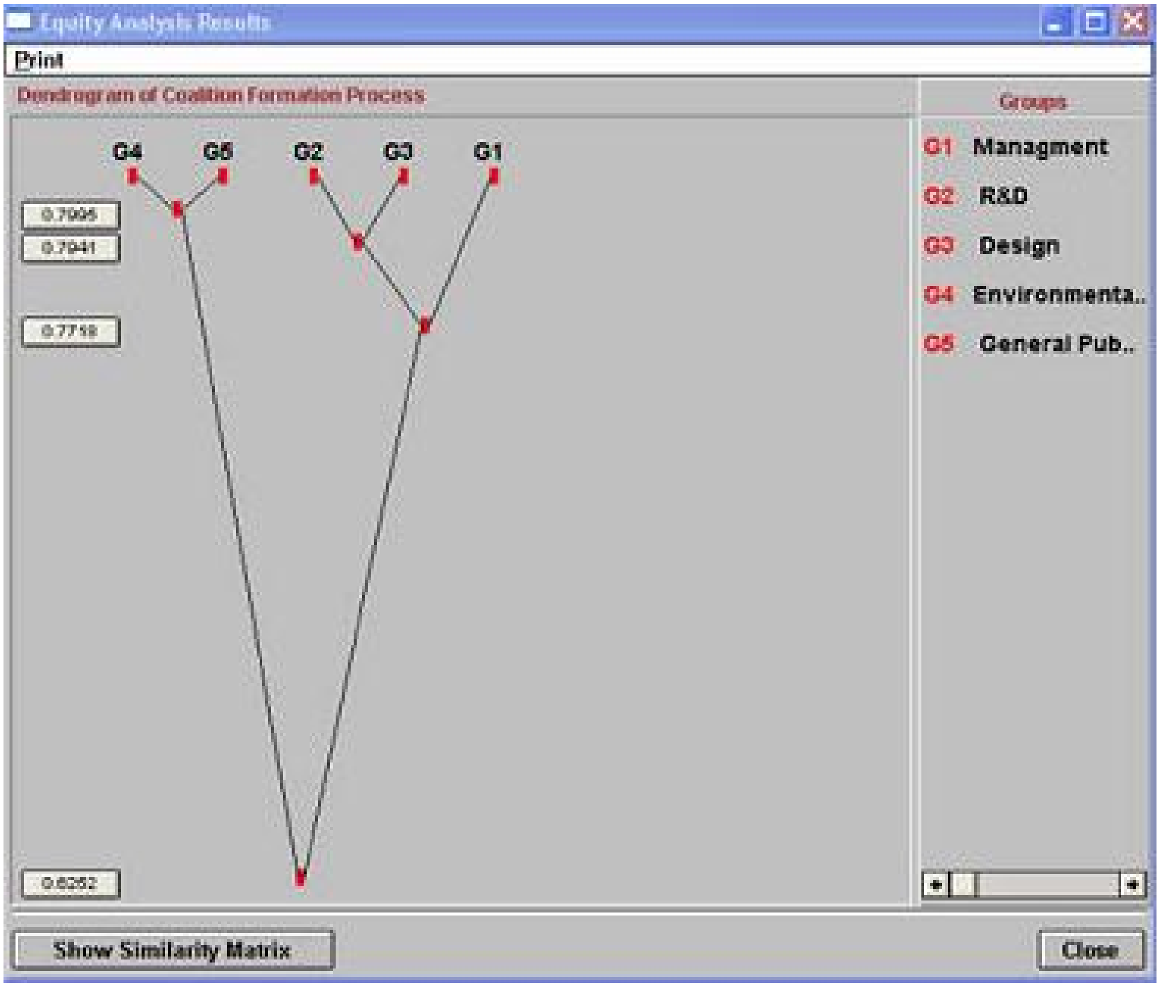


Figure 4.6: Equity Analysis Results

depicted in the equity matrix. Since the equity analysis matrix was generated just as a proof of concept for the application and not based on actual surveys, we shall refrain from making inferences from the equity analysis. The Equity matrix results in a dendrogram (Figure 4.6) which shows where each group stands and the potential for coalition formation among various groups or to find an amicable solution that is acceptable to the various groups involved. A method like NAIADE can streamline the decision making for process selection for nanomanufacturing or help retrofit better designs to currently used processes. The methodology can thus be used to evaluate processes based on sustainability metrics and involving different stakeholders in the decision analysis. This has advantages over comparing processes based on process and safety metrics (Gani et al., 2005) or the environmental impact metrics (Young et al., 2000) individually as highlighted in Figure 4.4. Although in this particular case, the rankings based on PEI and sustainability metrics are the same Table 4.6, the use of combined process safety metrics and PEI as well as other sustainability metrics leads to an exhaustive analysis of the process under consideration.

Table 4.6: Comparison with individual methods

Process	**Rank**		
	Process & Safety Metrics	Potential Environmental Impact	Sustainability Metrics (combined along with additional metrics)
Sol-Gel	1	3	3
TEOS	3	2	2
HMDSO	2	1	1

The WAR algorithm does not calculate the PEI of the products from the processes being evaluated. PEI of most nanomaterials is yet to be determined. The fate of nano-materials and their behavior toward other chemical species (pollutants and regulated materials) and the effects of the generated byproducts need to be considered as well.Research efforts are also needed in determining the occupational exposure of nanomaterials as this is an important sustainability metric.

Our methodology can be applied to evaluate processes that may not be related to nanomaterials but involve the application of green principles for e.g. chemical synthesis using ionic liquids or using microwave based methods. In principle the methodology with appropriate selection of metrics can be used for evaluation of new technologies on sustainable metrics.

4.6 Additional Information Available in Appendix

In order to understand and follow our methodology, the following information is provided in Appendix A, 1. Reference tables used for assigning the Chemical and Process Safety Index scores. 2. The input data for the WAR algorithm; used to evaluate the Potential Environmental Impact for the three processes in consideration. 3. The intermediate steps of NAIADE leading to the ranking of alternatives.

Chapter 5

Sustainable Nanomanufacturing under Current Chemical Regulation: Case Study of Carbon Nanofibers

This chapter is revised based on a paper published by Sasikumar Naidu, Rapinder Sawhney and Rajive Dhingra:

Naidu, S., Sawhney, R., Dhingra, R., Upreti, G., Sustainable Nanomanufacturing under Current Chemical Regulation: Case Study of Carbon Nanofibers. Proceedings of the Industrial Engineering Research Conference, Institute of Industrial Engineers Annual Meeting. May 2011; Reno, Nevada.

My primary contributions to this paper include (i) development of the problem into research, (ii) identification of the study areas and objectives, (iii) gathering and reviewing literature, (v) processing,analyzing and interpretation of data, (vi) pulling various contributions into a single paper, (vii) most of the writing.

Abstract

Regulation plays a key role in the sustainable development of technology. Unique properties of nanomaterials along with delay in the development of extensive and comprehensive research on the Environmental Health and Safety (EHS) of nanomaterials have lead to a predicament for regulatory agencies. The current solution to the problem may be to extend the chemical regulatory framework to accommodate nanomaterials and is highly dependent on voluntary regulatory mechanisms by the firms that are developing the technology and applications of nanomaterials. This paper proposes a methodology to evaluate the regulatory structure for nano-materials and manufacturing processes. Manufacture of vapor grown carbon nanofibers is analyzed as a case study. Value Stream Mapping (VSM) is used to identify waste generated throughout the manufacturing processes and potential occupational exposure. These wastes are then classified into components of an EHS System with the types of regulation governing them. This results in the identification of significant areas and gaps in carbon nanofiber regulation.

5.1 Introduction

Nanotechnology and manufacturing of nanomaterials labeled as “Nanomanufacturing” provides new opportunities and challenges in terms of potential benefits and unseen hazards. A recent article in Industrial Engineer magazine highlights this issue by discussing the potential benefits, applications and their rapid commercialization into everyday products along with the associated environmental and occupational concerns (King and Gibbs, 2010). The issue of regulation at the federal level as opposed to regulation by individual states like California and Massachusetts shows the trailing nature of federal regulation for manufacturing and use of nano-enabled products (Keiner, 2008). Some of the laws like the Toxic Substance Control Act (TSCA) were developed in the 1970’s and are scheduled for an update to cover current manufacturing and environmental issues (Sissell, 2009). The regulatory agencies also understand the fact that the manufacturing firms are ideally placed at the frontline of regulation in terms of EHS data generation. Most firms regulate themselves voluntarily as specific regulations are yet to be developed for nanomaterial manufacture and handling. The EPA has established the nanomaterial stewardship program that includes thirty seven firms that collect and provide valuable EHS data to the EPA which can be used to formulate new regulatory requirements (EPA, 2009). The EPA has also advocated the use of Lean and Green methods for the chemical industry using tools like VSM and 5S as a toolkit (EPA, 2007). In this paper we propose to extend the use of tools familiar to Industrial Engineers (IE’s) to nanomanufacturing with the goal of developing a systematic methodology to evaluate a nanomanufacturing process on environmental metrics and to identify regulatory gaps and establish priority areas of regulation.

5.2 Methodology

We propose a methodology that systematically analyzes the nanomanufacturing process, its environmental performance, the current regulatory structure that impacts the process and regulatory gaps that may exist. For this we plan to use some of the tools and concepts familiar to IE's. Figure 5.1 depicts a four step methodology to evaluate a manufacturing process for a nano-material and list the applicable laws and regulation that currently govern so as to identify gaps in regulatory framework.

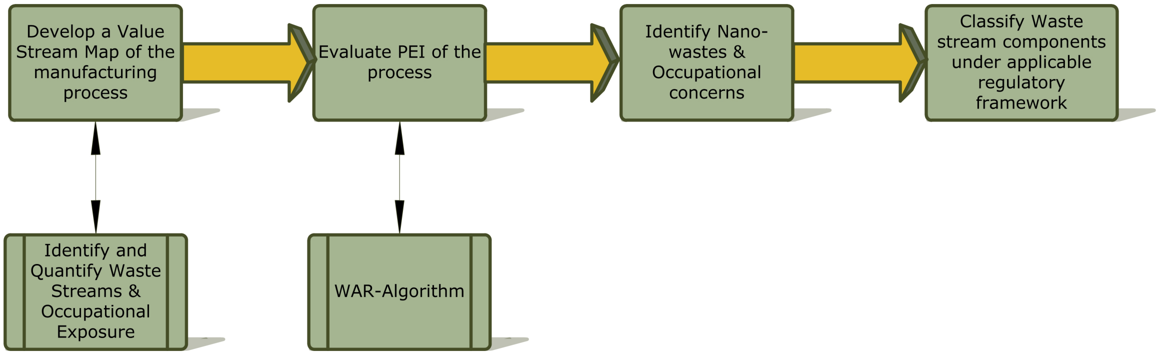


Figure 5.1: Proposed Methodology

The first step in process improvement is to Value Stream Map the process in consideration. This step is in line with the recommendations of the EPA for the chemical industry. But the new VSM is designed to identify and quantify different types of wastes that are generated at each stage of the manufacturing process along with material usage efficiency. This is then coupled to an Environmental Management System (EMS) that exists in the manufacturing facility depicting any process recycles and waste treatment. The waste streams are then identified and their compositions determined. The waste streams from individual process steps may be combined or remain as a unique stream. A template of the enhanced VSM is depicted in Figure 5.2. The waste streams are labeled so as to identify the type of waste stream and the number indicating the process step where it originated. After it is processed by the EMS of the facility, the waste streams may combine for e.g. A12 denoted that streams A1 and A2 were combined for treatment whereas A3 still remained separate waste stream. The process time line of a conventional VSM can be utilized here to evaluate material usage efficiency instead of measuring process times. The second step is to evaluate the environmental performance of the process in consideration. For this, we use software developed at the EPA, called the Waste Reduction Algorithm (WAR-algorithm). This software evaluates a chemical process on eight potential environmental impact (PEI) categories namely,

- Human toxicity potential by ingestion (HTPI),
- Human toxicity potential by exposure both dermal and inhalation (HTPE),
- Terrestrial toxicity potential (TTP),
- Aquatic toxicity potential (ATP),
- Global warming potential (GWP),
- Ozone depletion potential (ODP),
- Photochemical oxidation potential (PCOP) and
- Acidification potential (AP).

The WAR algorithm requires the user to provide process details in the forms of input streams and output streams of the process in consideration. The user can pick a list of chemicals from a built in database. Suing the principle of mass balance and the potential environmental impact of the chemicals used and generated during the process, PEI of the process is evaluated. The detailed theory of WAR algorithm and evaluation of PEI are explained in Young et al. (2000). Once we have evaluated these metrics, these then can serve as metrics for continuous improvement. The PEI metrics can be evaluated on the basis of PEI / kg of product or PEI / hr or PEI / functional equivalent of the product. Functional equivalent is a concept borrowed from Life Cycle thinking and represents the amount of nano-material that would replace the conventional material to provide the same intended function. WAR algorithm can be

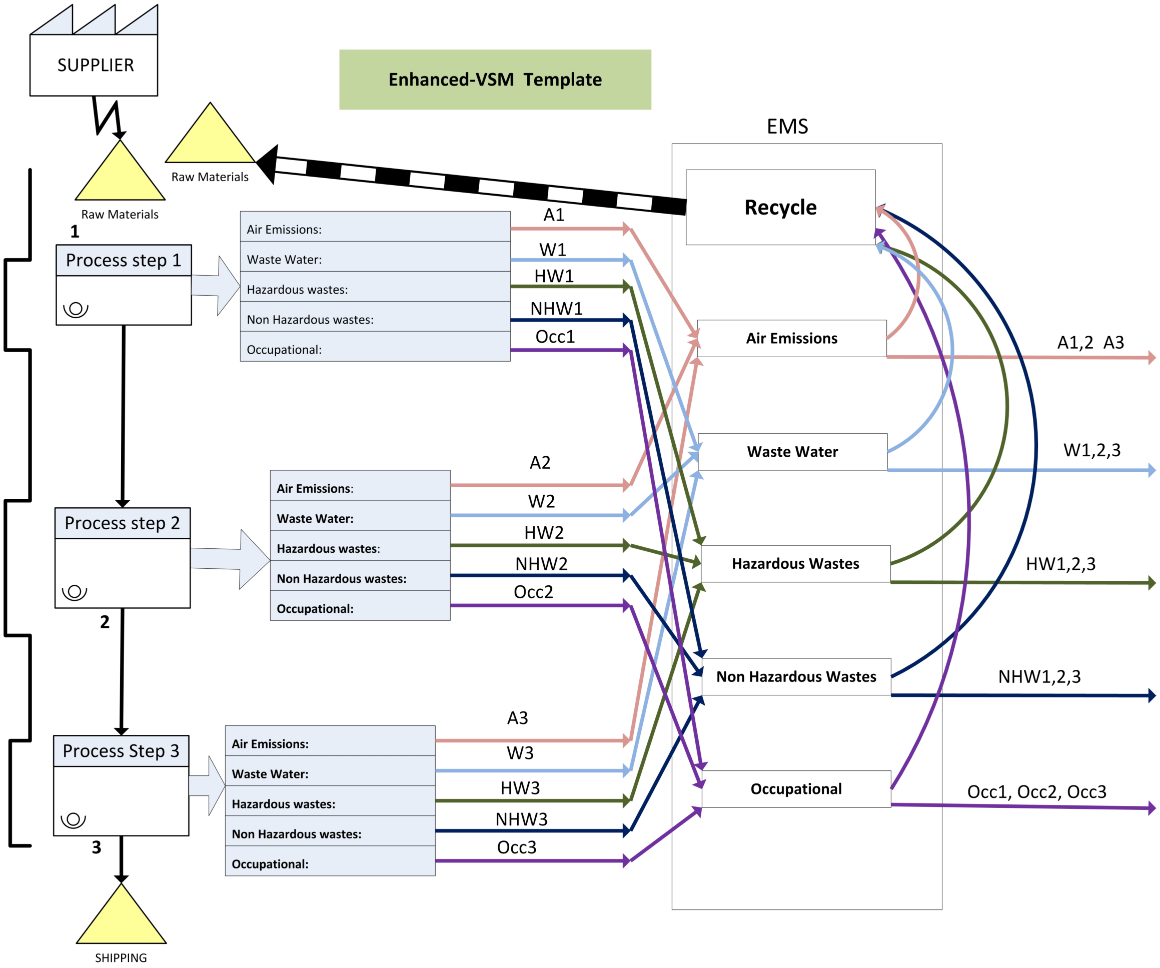


Figure 5.2: Enhanced-VSM Template

used to compare processes on environmental metrics, evaluate the effect of process changes, raw material substitution etc. WAR algorithm has been used to evaluate various alternatives of silica nanomanufacturing processes (Naidu et al., 2008).

The third step is to identify the nano-related wastes and occupational concerns during manufacturing and processing. This step though listed third should basically contain information collected in the first step during the process of developing a VSM. The separation of nano-related wastes into a separate step is to highlight the nano-related concerns. These are not dealt with in the second step in the WAR algorithm because of lack of data on the occupational and environmental effects of nano-materials and nano-based wastes.

The fourth step would be to classify the waste streams and their components according to the disposal methods used namely, waste treatment, secure disposal and direct release to the environment. We then also list the various applicable laws that regulate the wastes concerned namely Clean Air Act (CAA), Clean Water Act (CWA), Toxic Substances Control Act (TSCA), Occupational Safety and Health Administration (OSHA) Laws and finally any voluntarily regulated materials and wastes by the firm involved. This step will highlight the gaps in regulating nano-materials under current regulatory framework. This step also identifies and prioritizes the areas for new regulation or modification of existing regulation to cover nano-material and their manufacturing processes.

5.3 Case Study: Carbon Nano-Fiber (CNF) Manufacturing

As a case study we analyze a gas phase CNF manufacturing process outlined in Genaidy et al. (2009). The process describes a small manufacturing facility located in the United States producing 70,000 lbs of CNF per year. It utilizes a patented gas phase CNF production method using methane as source of Carbon and Iron pentacarbonyl as nucleation site and hydrogen sulfide as catalyst (Genaidy et al., 2009). The manufacturing process is depicted in Figure 5.3 .

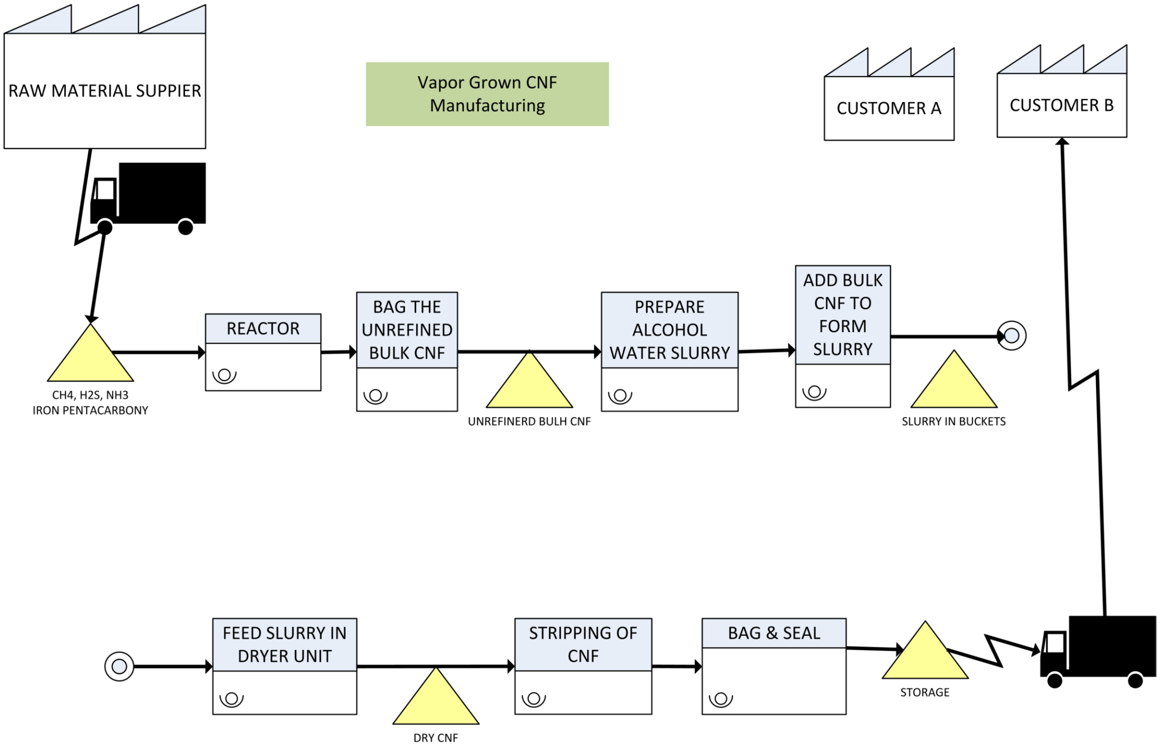


Figure 5.3: Process Map of CNF Manufacturing Process (Adapted from Genaidy et al.)

The raw materials are fed to the reactor through overhead tubes. When the reaction is complete, the operator bags the bulk CNF in 15 lbs bags to a storage area. Further processing involves converting this bulk CNF to individual fibers and this is accomplished by forming slurry of bulk CNF in an alcohol-water mixture. The alcohol-water mixture evaporates in the dryer to yield dry nanofiber powder. A stripping unit is used to remove any impurities and moisture from the CNF. We now apply the proposed methodology to the CNF manufacturing process.

5.3.1 Step 1: Develop an enhanced VSM of the process

The VSM is developed based on information obtained from Genaidy et al. (2009)(Figure 5.4). The raw materials are Ammonia, Methane, Hydrogen Sulfide, Iron

Pentacarbonyl and Oxygen. For the VSM, the production of bulk CNF and bagging of the bulk CNF have been combined to form process 1. Converting the bulk CNF to slurry is designated as process 2. Drying of CNF denotes process 3 and the stripping unit and bagging of refined CNF is designated as process 4. The wastes resulting from each of these process steps are labeled and they enter the EMS of the facility. The information about the EMS system deployed at the facility is not available. The process steps 2, 3 and 4 are located in close proximity and share the same ventilation as outlined in the plant layout (Genaidy et al., 2009). Hence the wastes from these three steps were combined with the exception of occupational related wastes, which are similar for process steps 3 and 4 only.

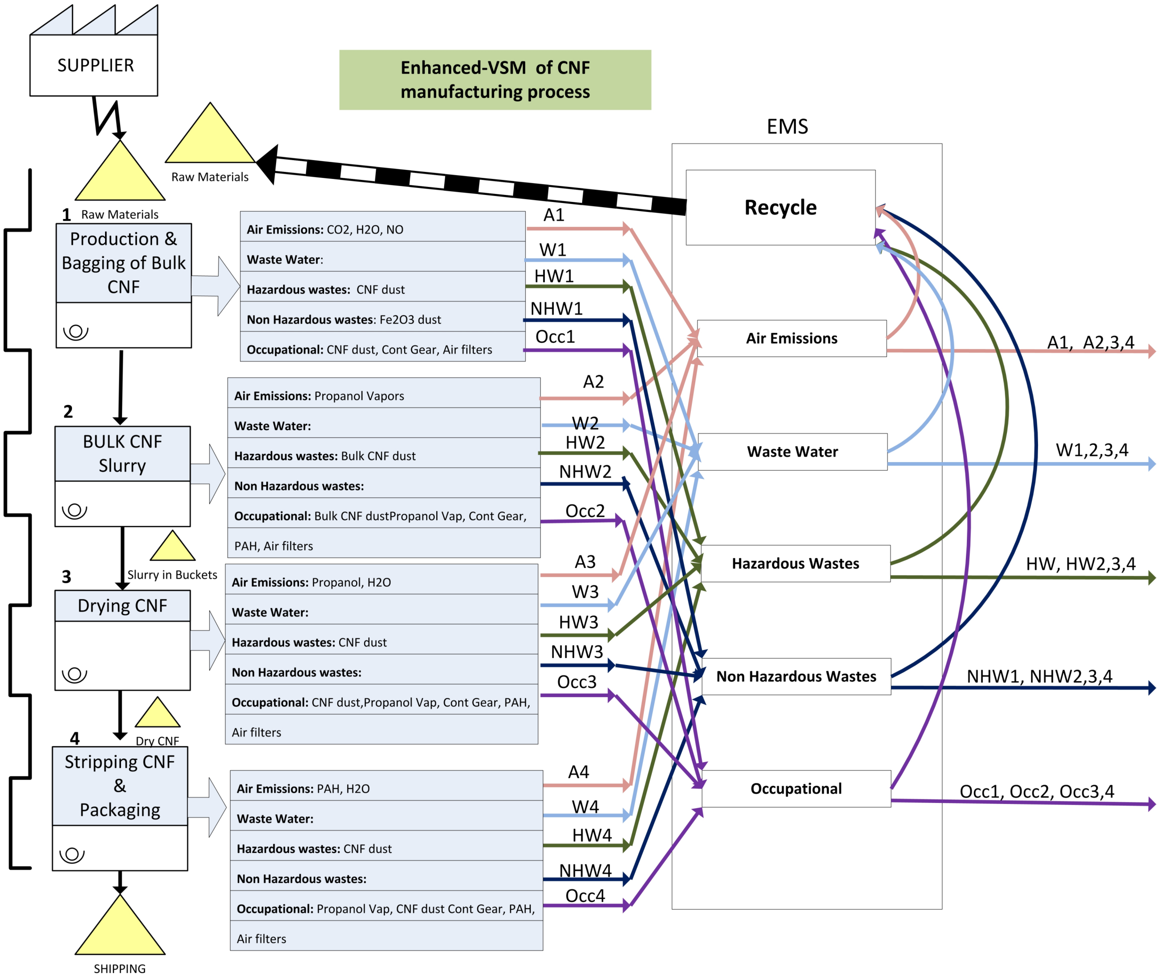
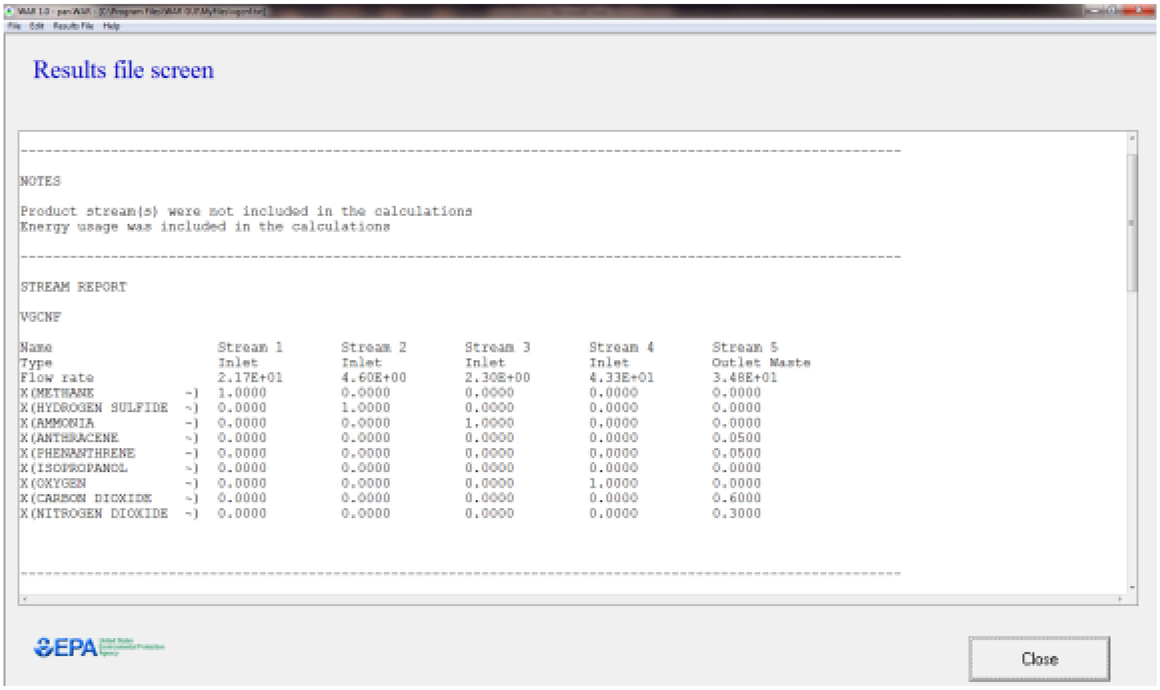


Figure 5.4: Enhanced-VSM of CNF manufacturing process

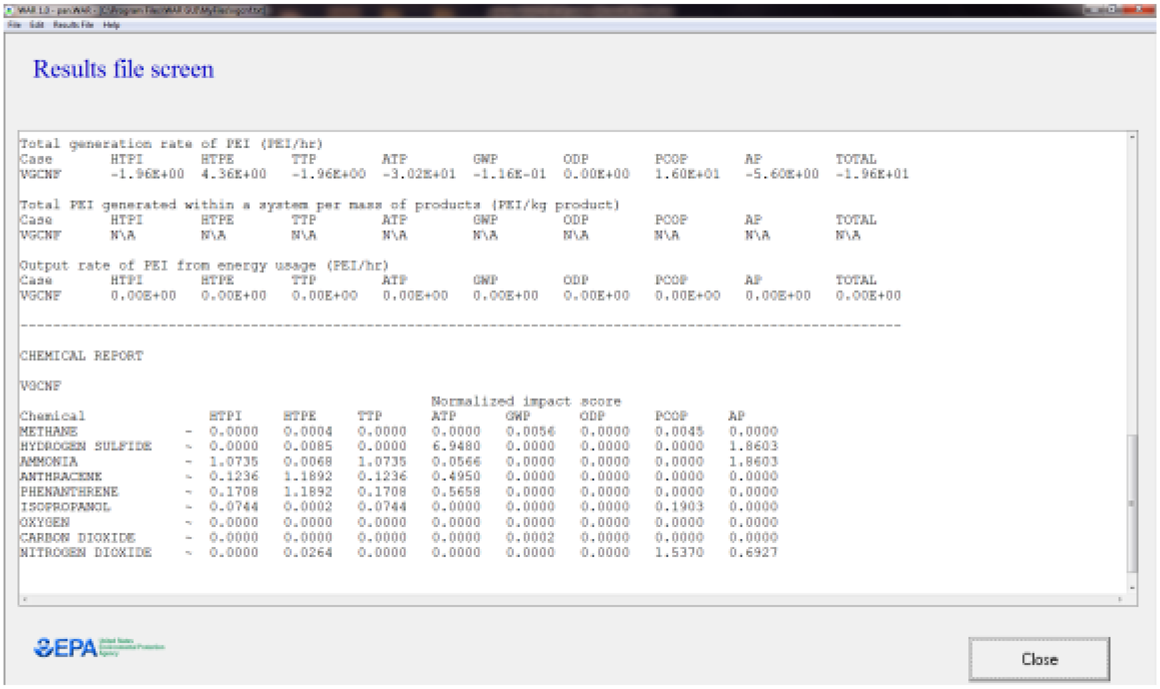
5.3.2 Step 2: Evaluation of PEI using the WAR-algorithm

The waste streams and their composition after they have been through the manufacturing plant's EMS are used as input to the WAR algorithm. This step is a method of evaluating the environmental performance of the manufacturing process. It requires stoichiometric information about the reaction at the industrial scale. The available literature and patent information does not provide this data. The method of determining the PEI of a process using waste stream compositions per unit kg of product has been well documented Naidu et al. (2008). Figures 5.5 and 5.6 show the output for an assumed waste stream composition (PAH is assumed to be composed of anthrancene and phenanthrene). This step highlights the chemicals that have the maximum potential environmental impact and directs appropriate steps for reduction of pollution at source. The normalized impact scores for the chemicals is an indication of chemicals that contribute the most to the PEI. The quantity of these wastes can be reduced or the chemical itself can be substituted if feasible or the PEI needs to be mitigated using an appropriate EMS system.



```
------------------------------------------------------------------------------------------------

NOTES

Product stream(s) were not included in the calculations
Energy usage was included in the calculations

------------------------------------------------------------------------------------------------

STREAM REPORT

VGCNF

Name                        Stream 1      Stream 2      Stream 3      Stream 4      Stream 5
Type                        Inlet         Inlet         Inlet         Inlet         Outlet Waste
Flow rate                   2.17E+01      4.60E+00      2.30E+00      4.33E+01      3.48E+01
X(METHANE              -)   1.0000        0.0000        0.0000        0.0000        0.0000
X(HYDROGEN SULFIDE     -)   0.0000        1.0000        0.0000        0.0000        0.0000
X(AMMONIA              -)   0.0000        0.0000        1.0000        0.0000        0.0000
X(ANTHRACENE           -)   0.0000        0.0000        0.0000        0.0000        0.0500
X(PHENANTHRENE         -)   0.0000        0.0000        0.0000        0.0000        0.0500
X(ISOPROPANOL          -)   0.0000        0.0000        0.0000        0.0000        0.0000
X(OXYGEN               -)   0.0000        0.0000        0.0000        1.0000        0.0000
X(CARBON DIOXIDE       -)   0.0000        0.0000        0.0000        0.0000        0.6000
X(NITROGEN DIOXIDE     -)   0.0000        0.0000        0.0000        0.0000        0.3000



------------------------------------------------------------------------------------------------
```

Figure 5.5: Chemical Streams of the CNF manufacturing process



```
Total generation rate of PEI (PEI/hr)
Case      HTPI       HTPE       TTP        ATP        GWP        ODP        PCOP       AP         TOTAL
VGCNF     -1.96E+00  4.36E+00   -1.96E+00  -3.02E+01  -1.16E-01  0.00E+00   1.60E+01   -5.60E+00  -1.96E+01

Total PEI generated within a system per mass of products (PEI/kg product)
Case      HTPI       HTPE       TTP        ATP        GWP        ODP        PCOP       AP         TOTAL
VGCNF     N\A        N\A        N\A        N\A        N\A        N\A        N\A        N\A        N\A

Output rate of PEI from energy usage (PEI/hr)
Case      HTPI       HTPE       TTP        ATP        GWP        ODP        PCOP       AP         TOTAL
VGCNF     0.00E+00   0.00E+00   0.00E+00   0.00E+00   0.00E+00   0.00E+00   0.00E+00   0.00E+00   0.00E+00

-----------------------------------------------------------------------------------------------------------

CHEMICAL REPORT

VGCNF
                                                   Normalized impact score
Chemical                 HTPI      HTPE      TTP       ATP       GWP       ODP       PCOP      AP
METHANE               -  0.0000    0.0004    0.0000    0.0000    0.0056    0.0000    0.0045    0.0000
HYDROGEN SULFIDE      -  0.0000    0.0085    0.0000    6.9480    0.0000    0.0000    0.0000    1.8603
AMMONIA               -  1.0735    0.0068    1.0735    0.0566    0.0000    0.0000    0.0000    1.8603
ANTHRACENE            -  0.1236    1.1892    0.1236    0.4950    0.0000    0.0000    0.0000    0.0000
PHENANTHRENE          -  0.1708    1.1892    0.1708    0.5658    0.0000    0.0000    0.0000    0.0000
ISOPROPANOL           -  0.0744    0.0002    0.0744    0.0000    0.0000    0.0000    0.1903    0.0000
OXYGEN                -  0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
CARBON DIOXIDE        -  0.0000    0.0000    0.0000    0.0000    0.0002    0.0000    0.0000    0.0000
NITROGEN DIOXIDE      -  0.0000    0.0264    0.0000    0.0000    0.0000    0.0000    1.5370    0.6927
```

Figure 5.6: Chemical PEI scores

5.3.3 Step 3: Identify nano related wastes and occupational issues

The nano related wastes as listed in the enhanced-VSM are,

- Bulk CNF and Bulk CNF dust
- CNF dust and airborne CNF dust
- CNF in slurry
- Contaminated gear

Other wastes are mainly due to contaminated protective gear that includes aprons, gloves, footwear covers and respirators. Since there are airborne CNF, the air filters employed in the facility are contaminated as well.

Occupational issues such as need for defining the type of protective gear, air filters, cleaning and or disposal of contaminated gear are not clearly defined. In case of the manufacturing facility under consideration, the contaminated gear is being stored until treatment and disposal methods are determined.

5.3.4 Step 4: Classify wastes according to regulatory framework

The EMS component of any manufacturing facility results in the manufacturing wastes being treated to convert them to a form that can be directly released to the environment for e.g. waste gases. Some wastes are disposed of securely or they are directly released in to the environment. We have added occupational issues to the EMS components and classified the wastes generated according to the regulatory structure that govern them. Issues that are voluntarily regulated by the facility are also considered. This provides a course for prioritizing the modification of current regulation to accommodate these nano-related wastes and occupational issues. OSHA does regulate CNF-fibers suggesting methods and exposure levels to those of asbestos exposure. It is observed from the Table 5.1 that custom laws regulating the CNF dust, its treatment and secure disposal are needed. Also protective gear and occupational air quality needs to be regulated along with the type of air filters, their use and disposal. Training requirements need to be established for workers handling CNF and associated equipment and providing maintenance.

Table 5.1: Manufacturing wastes classified into regulatory structure and the EMS components

EMS Component	Chemical/Regulatory Substances & Regulatory Tools				
	OSHA	CAA	CWA	TSCA	Voluntary
Waste Treatment		NOx , CO2, Propanol vapors	Propanol - water slurry	Propanol-water slurry	Contaminated gear, Air Filters, CNF in slurry, CNF dust (Bulk and Refined)
Secure Disposal					Contaminated Gear, Air Filters
Direct Release to the Environment		PAH	PAH	PAH, Fe(CO)5, NH3, H2S, CNF dust(Bulk and Refined)	
Occupational Exposure	PAH, Propanol, NH3, H2S, Fe(CO)5, CNF-fibers				HEPA filters, vaccum of shop floor, Contaminated gear, type of protective equipment, OEL limits

5.4 Conclusion

The concerns identified in the proposed methodology can be arrived at using an exploratory investigation. The main goal of the paper was to develop a systematic methodology using concepts and tools familiar to IE's and promoted by the EPA for chemical industry applied to the problem of regulation nano-manufacturing and nano-materials. Future research would be to validate the method in a nano-manufacturing facility and is currently being pursued. Although the case study here describes CNF, it could be easily extended to any other nano-material manufacturing and processing. This paper is a step in the direction of sustainable nanomanufacturing development under very little and sluggish development of regulation specifically targeting the manufacture, handling, use and disposal of nanomaterials. Our methodology attempts at a structured way of analyzing a nano-manufacturing process using existing tools to identify gaps and priority areas of regulatory needs.

Chapter 6

Implementing Workplace Controls: Development of an Artificial Neural Network Based Expert System

This chapter will be revised and submitted as a paper for publication in a journal. My primary contributions to this paper include (i) development of the problem into research, (ii) identification of the study areas and objectives, (iii) gathering and reviewing literature, (iv) collecting data, processing,analyzing and interpretation of data, (v) pulling various contributions into a single paper, (vi) most of the writing.

Abstract

With the rapid development of nanotechnology, a plethora of products now incorporate nanomaterials that improve product performance and durability. However, the possibility of exposure to nanomaterials during the manufacturing stage creates hazards that are not well understood. The existence of effective regulation plays a key role in the safe and sustainable development of technology, while workplace controls and safety procedures are tools for effective regulation. The current state of monitoring nanomaterial based processes is that it is difficult to arrive at a customized set of regulations because of the wide variety in methods, procedures and size of nanomanufacturing facilities. Currently, regulation of nanomaterial exposure is mostly based on methods and tools that have been developed to regulate chemicals and is largely voluntary. We propose an expert system based approach to help identify and implement appropriate workplace controls in nanomanufacturing facilities. A prototype neural-network-based expert system is developed based on responses collected from a set of surveys sent to researchers (experts) familiar with the synthesis, manufacture and handling of nanomaterials.

6.1 Introduction: Need for Guidance in Environmental Health and Safety Issues

The primary regulatory agency in the United States that deals with workplace controls is the Occupational Safety and Health Administration (OSHA). OSHA requires manufacturers to inform workers of any potential hazards associated with the material they handle or produce. When a recognized hazard is present, businesses must implement the following (Sarahan, 2008):

1. Engineering controls, through implementation or modification of design of the facility, equipment, process or job function to remove the hazard if possible or enclose the hazard and establish barriers to reduce exposure.
2. Administrative controls,through communication and implementation of safe work practices and emergency procedures.
3. Personal Protective Equipment (PPE), in the form of gloves, masks etc. when hazards cannot be completely mitigated using engineering and administrative controls.

Nanomanufacturing firms are usually small to medium sized enterprises (SME's) that need a system / tool that guides them in implementing workplace controls for nanomaterials considering that even after years of regulatory experience, most chemical firms still seek guidance in Environmental Health and Safety (EHS) related matters. A new variation of chemical manufacturing such as nanomanufacturing will naturally demand more guidance and regulatory agencies will have to build upon the existing framework for chemical regulation. The above statements are validated in a couple of studies. A 1998 study performed in the United Kingdom (UK) to assist small firms to control health risks from chemicals identified four criteria that would lead to a useful and workable approach to chemical regulation (Russell et al., 1998).

1. Advice should be of practical help to SME's,

2. The best use should be made of any available hazard information,
3. The approach should be easy to use and understand, and
4. Information should be readily accessible to SME's.

The International Council on Nanotechnology, based at Rice University, dedicated to the development and collection of EHS information on nanomaterials conducted a survey of nanomanufacturing facilities to identify and document best-practice guidelines for manufacturing, handling and use of nanomaterials. The significant conclusions of the survey were as follows:

1. The companies surveyed were actively seeking additional information on how to best handle nanomaterials;
2. Actual EHS procedures did not significantly diverge from the safe handling practices customarily used for chemicals;
3. The biggest challenge in implementing nano-specific practices was a lack of information on the toxicological properties of nanomaterials and the nascent state of regulatory guidance in this field;
4. Considerable variances exist in EHS practices amongst organizations of different size.

The above two studies highlight the similarities between chemical and nanomaterial regulation in the workplace and the need for proactive guidance with hazard information and EHS practices targeted towards SME's. There have been calls for OSHA to do more and look at new approaches to generating, sharing and using the information to help manufacturers implement better workplace controls for nanomaterials (Maynard, 2009). While government is trying to provided enough guidance, another source of guidance has emerged, the "GoodNanoGuide"(2011), a collaborative platform that serves as an interactive forum and repository for nanomaterial handling practices in an occupational setting. Registered users qualifying as experts can edit content pertaining to workplace controls and safe handling procedures for nanomaterials similar to Wikipedia but with oversight. GoodNanoGuide does a great job in structuring this information into various categories to make it useful for potential users, mostly nanomanufacturing facilities and research labs, with measures like control banding of materials, packaging, workplace cleaning, spill cleanup, equipment cleaning etc. to name a few. However, so far this is the only existing effort to help create a system to help manufacturers. The challenge in implementing a highly successful system is to collect information from experts and to suggest the best plausible workplace controls for different companies having specific user characteristics and needs. That is the system / tool should consider nanomaterial properties and manufacturing characteristics while providing expert opinion to implement workplace controls and measures.

6.2 Proposed Methodology

Artificial Intelligence in the form of "expert systems" was developed in the 1970's to help accumulate expert opinion and provide an interface through a computer program to the logic of a human expert. By definition, an "expert system" is a computer program that simulates the thought process of a human expert to solve complex decisions problems in a specific domain (Badiru and Cheung, 2002). The advantages of expert systems are that they can help distribute human expertise and that they can facilitate real-time, low-cost, expert-level decisions even by the non-expert.

Neural Networks are ideal candidates for developing expert systems and have found applications in medical diagnosis, nuclear plant operation, financial modeling, etc. Therefore, we initiated efforts to develop a prototype neural-network-based expert system as a potential solution to the problem of predicting specific workplace control information for the myriad types of nanomaterials and manufacturing processes that are appearing in this rapidly changing field. The experts in this process are researchers who are familiar with the manufacture, use and handling of nanomaterials. Their responses / opinion were sought using an online survey developed with the help of the Statistical Consulting Center at the University of Tennessee-Knoxville. Some surveys were conducted by means of in-person interviews.

6.2.1 Survey Development

The logic behind developing an expert system is to present various manufacturing scenarios with a set of properties of the nanomaterial and to obtain feedback on appropriate workplace practices and controls that are needed. We based our survey on the lines of the survey, mentioned in the introduction section of this chapter, administered by the International Council on Nanomaterials (ICON), to identify EHS and product stewardship practices at companies, research labs and university laboratories. The factors that we selected were manufacturing characteristics and nanomaterial properties and were based on the ICON survey and are listed in Table 6.1. The levels selected are broad enough to the cover the range of plausible manufacturing scenarios. For example, the particle size ranges up to $> 1000\ nm$ are considered, which is outside the normal definition of "nanomaterial" to include fine powders and materials like single walled carbon nanotubes (SWNT) having a long axis in the micron size range but a diameter of a couple of nanometers. Some of the characteristics (Factors) such as Toxicity, Airborne Capacity and Detection Limit are qualitative, as for most nanomaterials, such information is not yet available. The exposure limit is selected to be in the range of exposure limits for asbestos, a generally accepted reference material for particulate and fibrous material exposure. Engineering controls like positive pressure (PP) (dilution ventilation) or negative pressure (NP) (exhaust ventilation) are considered in combination with open systems (O) and closed systems (C).

A large number of combinations of variables are possible; however, design of experiments based methods provided an efficient way of collecting information using

Table 6.1: Factors and Levels

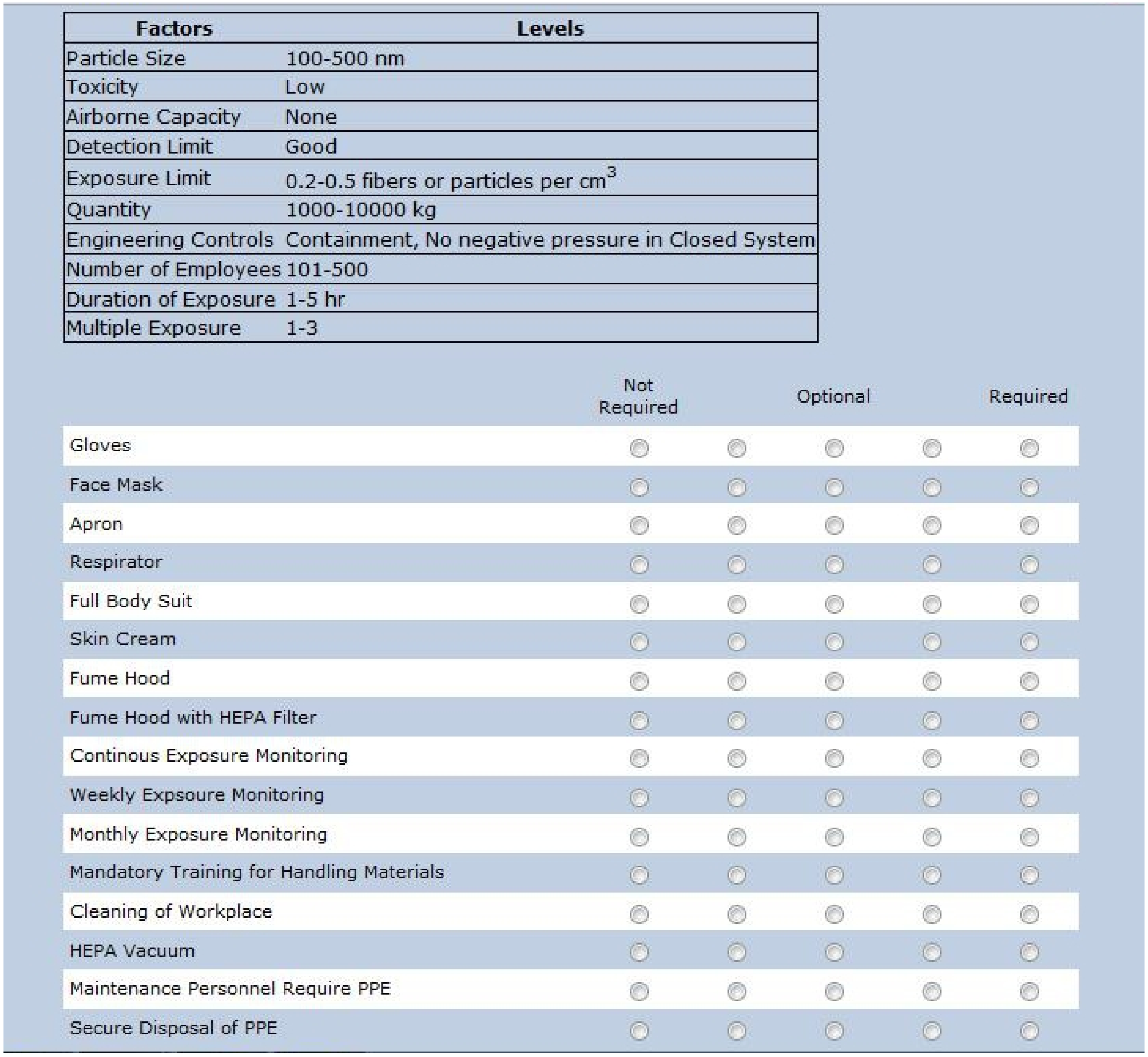
Factors	**Levels**	**Number of Levels**
Particle Size	$< 2nm, 2 - 10nm, 10$ $-100nm, 100 - 500nm,$ $500 - 1000nm, > 1000nm$	6
Toxicity	High, Moderate, Low	3
Airborne Capacity	High, Moderate, Low, None	4
Detection Limit	Good, Moderate, Poor, None	4
Exposure Limit	$< 0.1, 0.1 - 0.2, 02 - 0.5, 0.5$ $-1.0, > 1.0$	5
Quantity	$> 10000, 1000 - 10,000,$ $100 - 1000, 1 - 100, < 1$	5
Engineering Controls	O-PP, O-NP, C, C-NP	4
Number of Employees	$101 - 500, 51 - 100, 11 - 50,$ $3 - 10, 1 - 3$	5
Duration of Exposure	$5 - 8hr, 1 - 5hr, < 1hr,$ $< 15min$, incidental	5
Multiple Exposure	Unknown Number,> 3, $1 - 3$, None	4

a minimum number of combination of variables (survey questions / runs). The experiment design was generated using JMP® statistical software. The factors / nanomanufacturing characteristics listed in Table 6.1 were used as categorical variables with the listed levels. The default design suggested by JMP® had 120 runs and is a D-optimal design and is listed in appendix B as supporting information. The expert was asked to respond to five questions (manufacturing scenarios) by selecting the appropriate workplace controls (Table 6.2) on a 5 point Likert scale (1 being Not Required, 3 being Optional and 5 being Required) for a given combination of nanomanufacturing characteristics. A screen shot of an online survey question is depicted in Figure 6.1.The collected survey responses are listed in appendix B.

Table 6.2: Workplace measures and controls

Personal Protective Equipment(PPE)	**Engineering Controls**	**Work Practices**
○ Gloves (y01)	○ Fume Hood (y07)	○ Mandatory training for Handling Materials (y12)
○ Face Mask (y02)	○ Fume Hood with HEPA Filter (y08)	○ Cleaning Of Workplace (y13)
○ Apron (y03)	○ Continuous Monitoring (y09)	○ HEPA Vaccum Cleaner (y14)
○ Respirator (y04)	○ Weekly Monitoring (y10)	○ Maintenance personnel require PPE (y15)
○ Full Body Suit (y05)	○ Monthly Monitoring (y11)	○ Secure Disposal of PPE (y16)
○ Skin Cream (y06)		

Attribute agreement analysis was performed between two appraisers answering the same set of 5 questions with 16 responses (workplace controls) for each question. The responses matched in 35 cases out of 80. Fleiss' Kappa statistics and Concordance coefficient are listed in Tables 6.3 and 6.4. There is an agreement between the two respondents and especially for Likert response levels 1 and 5.



Factors	Levels
Particle Size	100-500 nm
Toxicity	Low
Airborne Capacity	None
Detection Limit	Good
Exposure Limit	0.2-0.5 fibers or particles per cm^3
Quantity	1000-10000 kg
Engineering Controls	Containment, No negative pressure in Closed System
Number of Employees	101-500
Duration of Exposure	1-5 hr
Multiple Exposure	1-3

	Not Required		Optional		Required
Gloves	○	○	○	○	○
Face Mask	○	○	○	○	○
Apron	○	○	○	○	○
Respirator	○	○	○	○	○
Full Body Suit	○	○	○	○	○
Skin Cream	○	○	○	○	○
Fume Hood	○	○	○	○	○
Fume Hood with HEPA Filter	○	○	○	○	○
Continous Exposure Monitoring	○	○	○	○	○
Weekly Expsoure Monitoring	○	○	○	○	○
Monthly Exposure Monitoring	○	○	○	○	○
Mandatory Training for Handling Materials	○	○	○	○	○
Cleaning of Workplace	○	○	○	○	○
HEPA Vacuum	○	○	○	○	○
Maintenance Personnel Require PPE	○	○	○	○	○
Secure Disposal of PPE	○	○	○	○	○

Figure 6.1: Sample online survey question

Table 6.3: Fleiss' Kappa Statistics

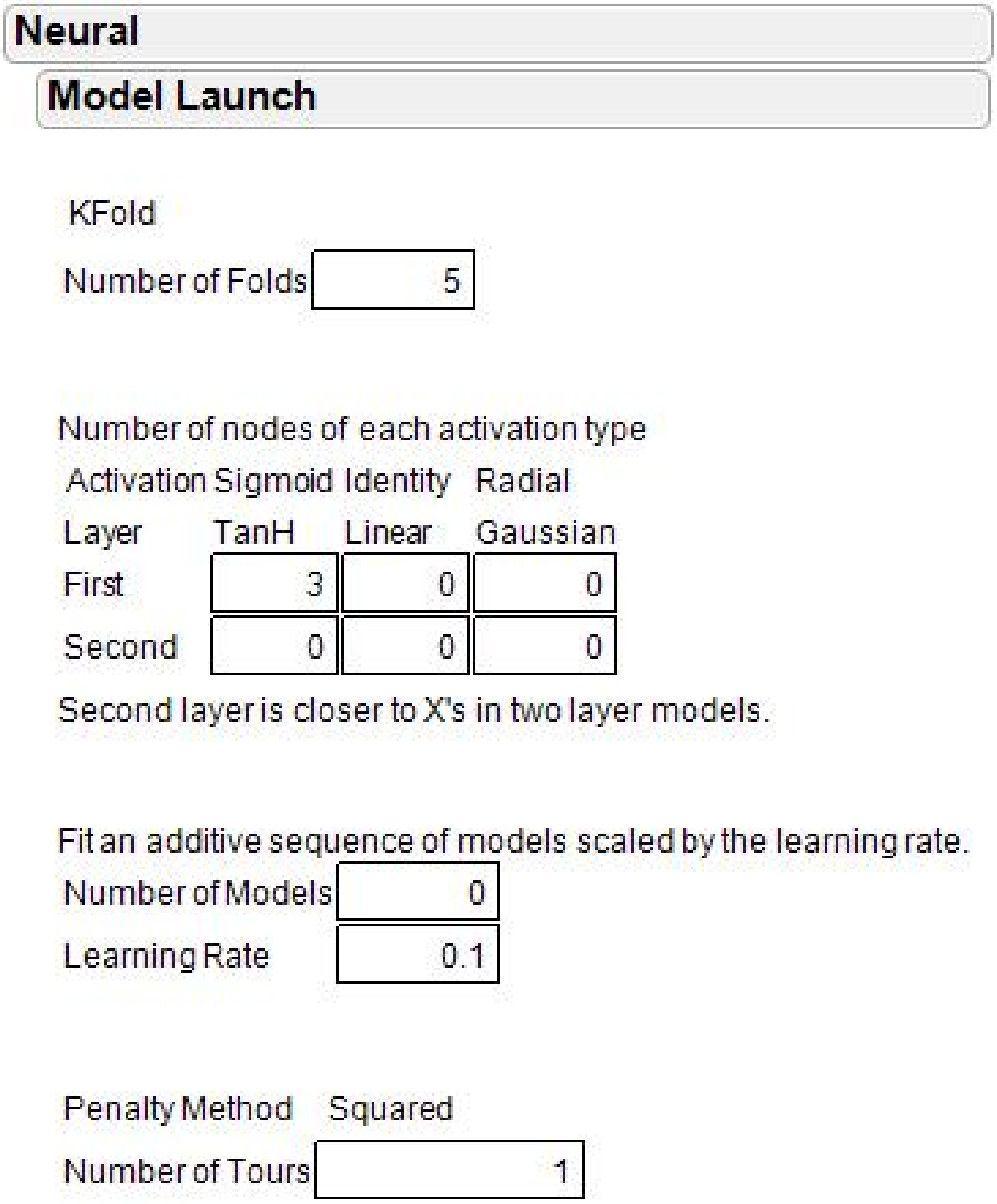
Response	Kappa	SE Kappa	Z	P(vs > 0)
1	0.313725	0.111803	2.80605	0.0025
2	-0.103448	0.111803	-0.92527	0.8226
3	0.079770	0.111803	0.71348	0.2378
4	-0.159420	0.111803	-1.42590	0.9231
5	0.232737	0.111803	2.08166	0.0187
Overall	0.111586	0.060876	1.83299	0.0334

Table 6.4: Kendall's Coefficient of Concordance

Coef	Chi - Sq	DF	P
0.681262	107.639	79	0.0178

6.3 Neural Network Development

The proposed neural network based expert system would learn from the data obtained from the experts and will develop the logic to predict appropriate workplace controls for a particular manufacturing scenario. Modeling the collected data is essentially a classification problem, with the workplace measures and controls as response variables to be classified as one of the following categories required, not required and optional; using data on nanomanufacturing characteristics as independent variables. In principle, a single neural network could be used to classify the workplace-controls categories however; we chose to develop an individual neural network model for each of the workplace measures and controls to maintain model simplicity as the logic required to determine the need of gloves vs. the need for a respirator or other more advanced workplace control would differ. Preliminary neural networks did not perform well and this was attributed to the limited data at our disposal. The solution to the problem of limited amount of data was solved using the method of K-fold validation which is suggested for small datasets and makes the most efficient use of data. The neural network usually contained a single layer of neurons using the hyperbolic tangent activation function. The JMP neural network model platform is depicted in Figure 6.2. A 5-fold validation method was used using penalty method of squared penalty function to prevent over-fitting. Boosting or additive sequence of models were not used.



Neural

Model Launch

KFold

Number of Folds 5

Number of nodes of each activation type

Activation	Sigmoid	Identity	Radial
Layer	TanH	Linear	Gaussian
First	3	0	0
Second	0	0	0

Second layer is closer to X's in two layer models.

Fit an additive sequence of models scaled by the learning rate.

Number of Models 0

Learning Rate 0.1

Penalty Method Squared

Number of Tours 1

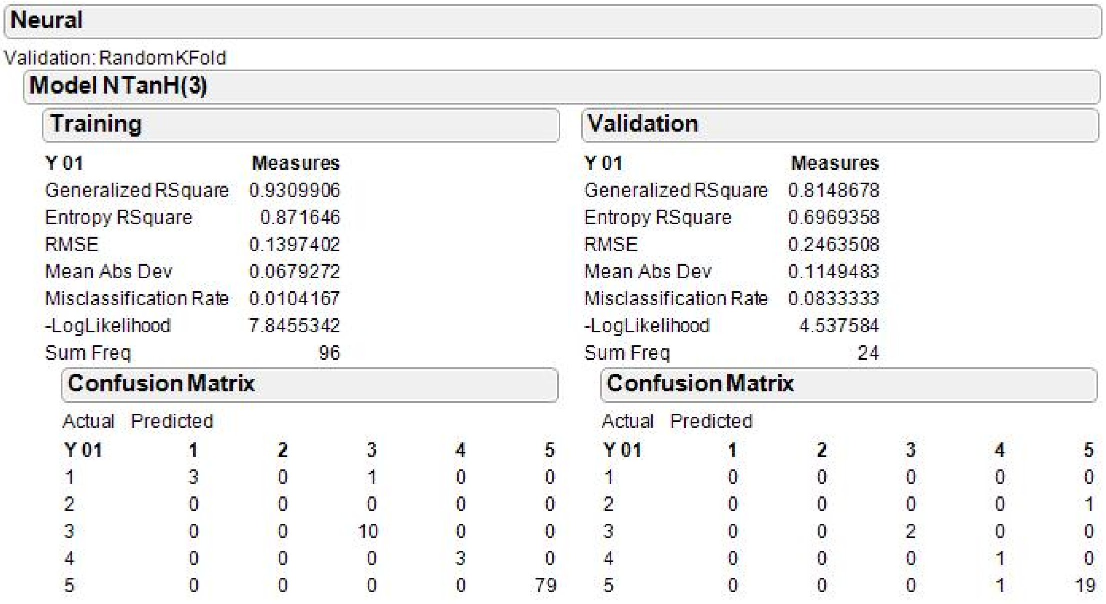
Figure 6.2: Model Parameters

6.4 The Neural Networks Models developed using JMP®

The objective was to select the best performing simplest neural network. The best performing neural network was selected based on the performance on validation data set. The goal of the models were to minimize the misclassification rate of level 5 “Required” to one below level 3 “Optional”. The neural network usually contained a single layer of neurons with at the most 6 nodes using the hyperbolic tangent activation function. A 5-fold validation method was used using squared penalty function to prevent over fitting. Figures 6.3 to 6.18 depict the model performance of the best model (simplest model) selected for each of the sixteen workplace controls. All models selected had very small misclassification rate in the range of 5 % to 13 % for the validation data set as summarized in Table 6.5. As an example, lets analyze the model output for the response variable Respirator (Figure 6.6) generated with a neural network consisting of four nodes using a TanH activation function. The goal of the model was to minimize the misclassification rate of level 5 “Required” to one below level 3 “Optional”. Both the training and validation dataset have very high R-square values. The confusion matrix evaluates the model peformance in correctly classifying the repsonse variable. The diagonal elements of the confusion matrix are responses correctly classified whereas the off-diagonal elements of the confusion matrix are incorrect classifications. In the training dataset there is only one serious misclassification of a level 5 to a level 1. But the validation dataset does not shown any serious misclassifications. This could be attributed to the property of the data point in question. We could build a more complex model to account for such behavior but that will most likely result in overfitting and reduce the performance of the model on the training dataset and any new data that we might want to fit. In developing the models, attention was given to develop the simplest neural network possible. The developed neural network models can be used to suggest (required, optional or not required) workplace controls for various nanomanufacturing characteristics considered.

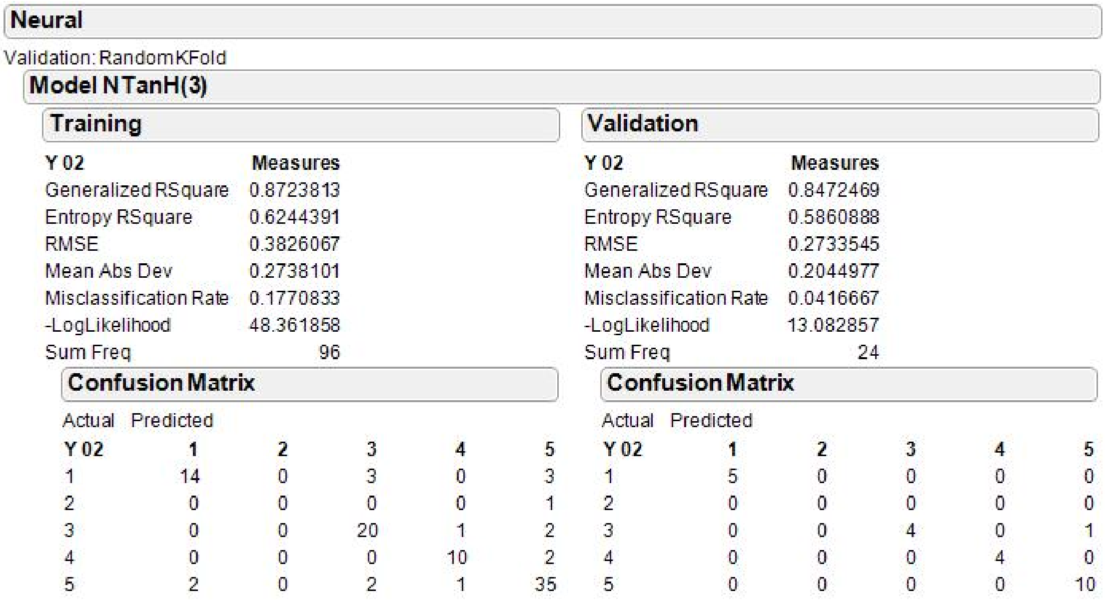
Table 6.5: Neural Network Model Performance

Response Variable	Number of Nodes in the Neural Network	Training Misclassification Rate	Validation Misclassification Rate
Gloves	3	0.01	0.08
Face Mask	3	0.17	0.04
Apron	4	0.14	0.04
Respirator	4	0.10	0.04
Full Body Suit	6	0.08	0.08
Skin Cream	5	0.04	0.04
Fume Hood	5	0.02	0.04
Fume Hood with HEPA filter	5	0.05	0.04
Continuous Monitoring	5	0.09	0.04
Weekly Monitoring	4	0.06	0.08
Monthly Monitoring	5	0.07	0.12
Mandatory Training for Handling Materials	4	0.01	0.00
Cleaning of Workplace	4	0.04	0.04
HEPA Vacuum Cleaner	5	0.09	0.04
Maintenance Personnel require PPE	4	0.02	0.04
Secure Disposal of PPE	4	0.04	0.04



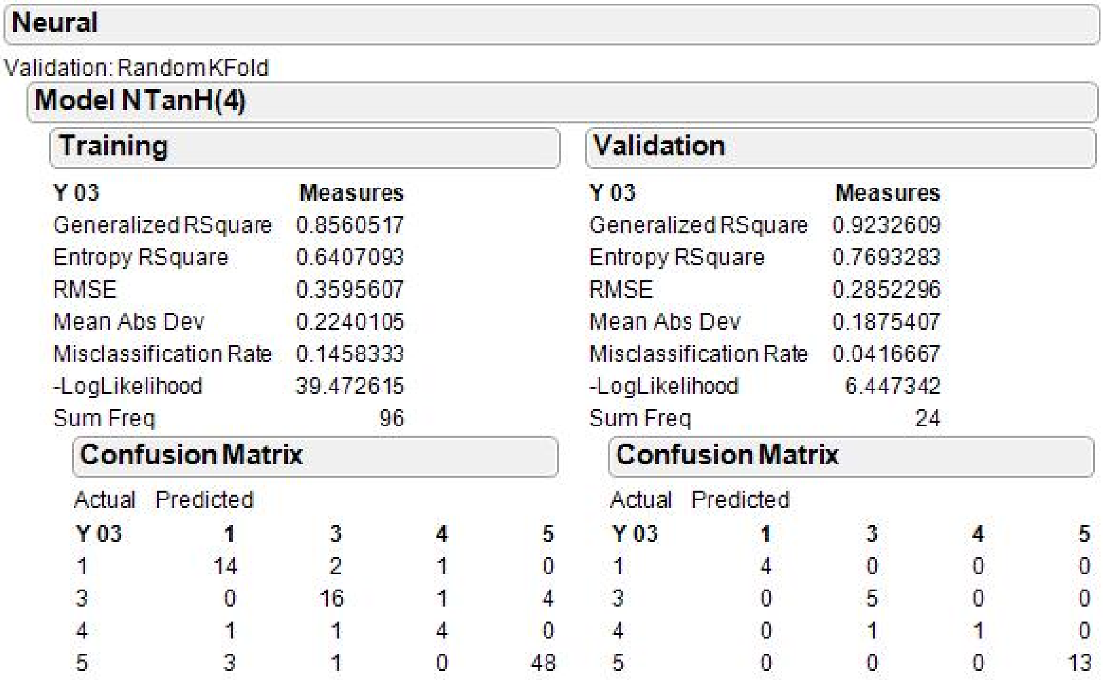
```
Neural
Validation: RandomKFold
Model NTanH(3)
Training                                      Validation
Y 01                 Measures                 Y 01                 Measures
Generalized RSquare  0.9309906                Generalized RSquare  0.8148678
Entropy RSquare       0.871646                Entropy RSquare      0.6969358
RMSE                 0.1397402                RMSE                 0.2463508
Mean Abs Dev         0.0679272                Mean Abs Dev         0.1149483
Misclassification Rate 0.0104167              Misclassification Rate 0.0833333
-LogLikelihood       7.8455342                -LogLikelihood        4.537584
Sum Freq                    96                Sum Freq                    24
  Confusion Matrix                              Confusion Matrix
  Actual  Predicted                             Actual  Predicted
  Y 01    1    2    3    4    5                 Y 01    1    2    3    4    5
  1       3    0    1    0    0                 1       0    0    0    0    0
  2       0    0    0    0    0                 2       0    0    0    0    1
  3       0    0   10    0    0                 3       0    0    2    0    0
  4       0    0    0    3    0                 4       0    0    0    1    0
  5       0    0    0    0   79                 5       0    0    0    1   19
```

Figure 6.3: Model Performance for Gloves (Y01)



```
Neural
Validation: RandomKFold
Model NTanH(3)
Training                                      Validation
Y 02                 Measures                 Y 02                 Measures
Generalized RSquare  0.8723813                Generalized RSquare  0.8472469
Entropy RSquare      0.6244391                Entropy RSquare      0.5860888
RMSE                 0.3826067                RMSE                 0.2733545
Mean Abs Dev         0.2738101                Mean Abs Dev         0.2044977
Misclassification Rate 0.1770833              Misclassification Rate 0.0416667
-LogLikelihood       48.361858                -LogLikelihood       13.082857
Sum Freq                    96                Sum Freq                    24
  Confusion Matrix                              Confusion Matrix
  Actual  Predicted                             Actual  Predicted
  Y 02    1    2    3    4    5                 Y 02    1    2    3    4    5
  1      14    0    3    0    3                 1       5    0    0    0    0
  2       0    0    0    0    1                 2       0    0    0    0    0
  3       0    0   20    1    2                 3       0    0    4    0    1
  4       0    0    0   10    2                 4       0    0    0    4    0
  5       2    0    2    1   35                 5       0    0    0    0   10
```

Figure 6.4: Model Performance for Facemask (Y02)



Neural

Validation: RandomKFold

Model NTanH(4)

Training

Y 03	Measures
Generalized RSquare	0.8560517
Entropy RSquare	0.6407093
RMSE	0.3595607
Mean Abs Dev	0.2240105
Misclassification Rate	0.1458333
-LogLikelihood	39.472615
Sum Freq	96

Confusion Matrix

Actual	Predicted			
Y 03	1	3	4	5
1	14	2	1	0
3	0	16	1	4
4	1	1	4	0
5	3	1	0	48

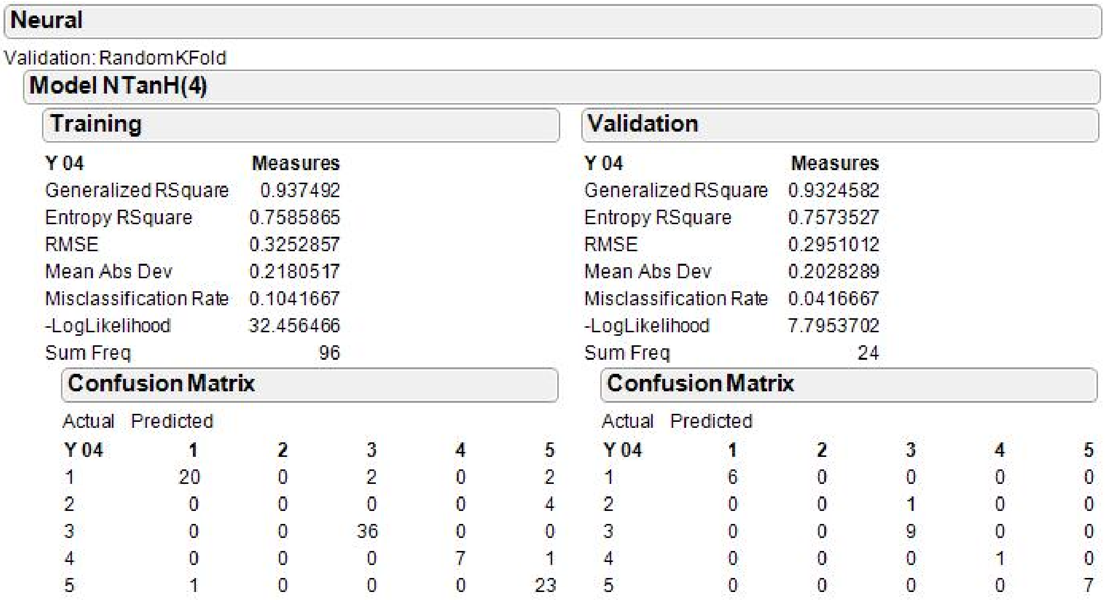
Validation

Y 03	Measures
Generalized RSquare	0.9232609
Entropy RSquare	0.7693283
RMSE	0.2852296
Mean Abs Dev	0.1875407
Misclassification Rate	0.0416667
-LogLikelihood	6.447342
Sum Freq	24

Confusion Matrix

Actual	Predicted			
Y 03	1	3	4	5
1	4	0	0	0
3	0	5	0	0
4	0	1	1	0
5	0	0	0	13

Figure 6.5: Model Performance for Apron (Y03)



Neural

Validation: RandomKFold

Model NTanH(4)

Training

Y 04	Measures
Generalized RSquare	0.937492
Entropy RSquare	0.7585865
RMSE	0.3252857
Mean Abs Dev	0.2180517
Misclassification Rate	0.1041667
-LogLikelihood	32.456466
Sum Freq	96

Confusion Matrix

Actual	Predicted				
Y 04	1	2	3	4	5
1	20	0	2	0	2
2	0	0	0	0	4
3	0	0	36	0	0
4	0	0	0	7	1
5	1	0	0	0	23

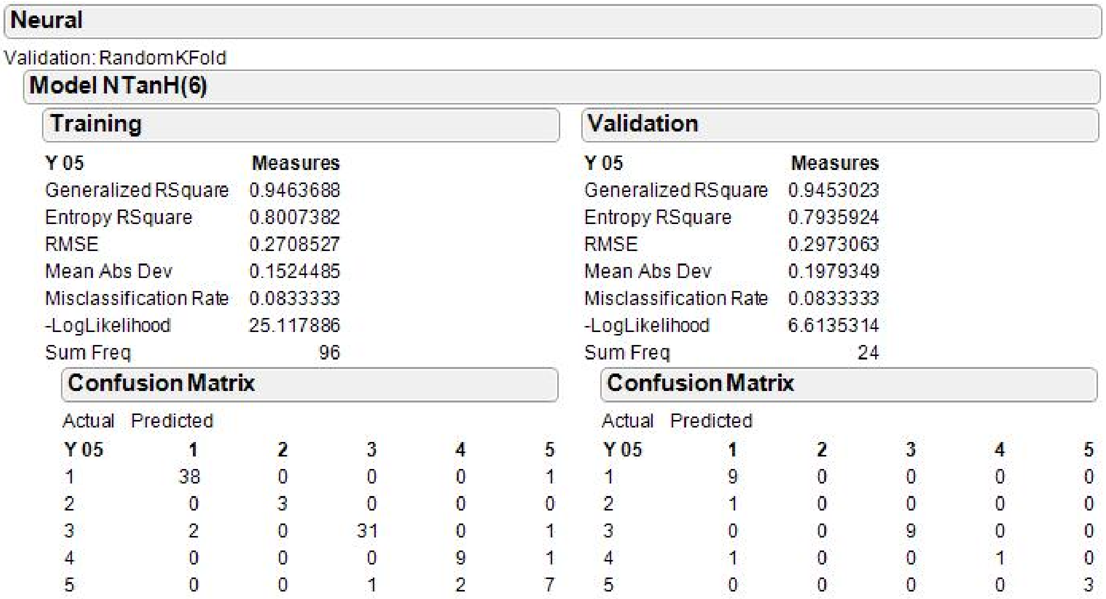
Validation

Y 04	Measures
Generalized RSquare	0.9324582
Entropy RSquare	0.7573527
RMSE	0.2951012
Mean Abs Dev	0.2028289
Misclassification Rate	0.0416667
-LogLikelihood	7.7953702
Sum Freq	24

Confusion Matrix

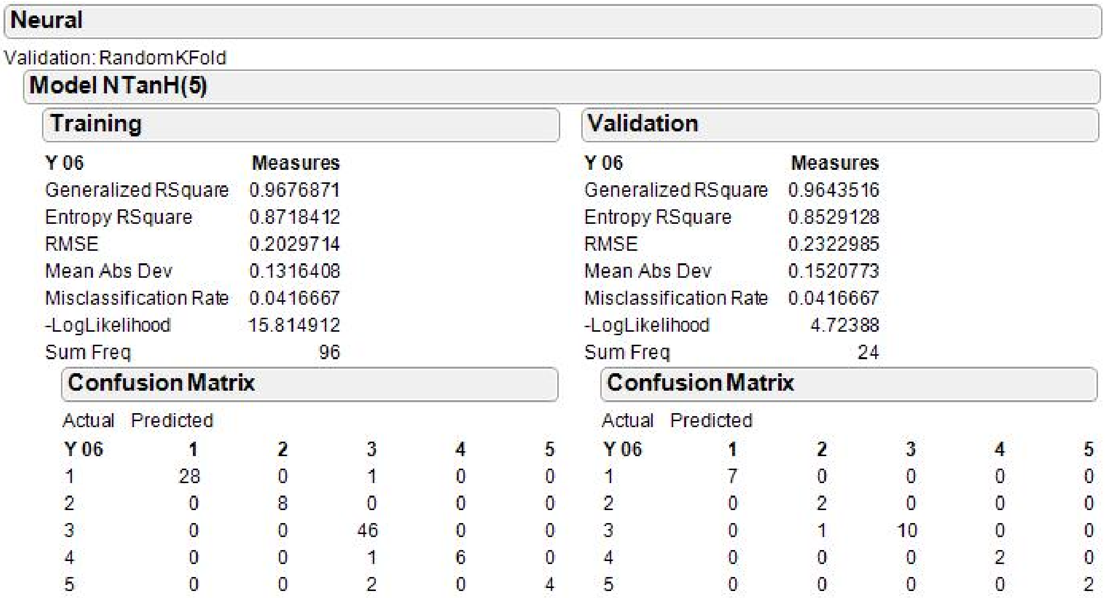
Actual	Predicted				
Y 04	1	2	3	4	5
1	6	0	0	0	0
2	0	0	1	0	0
3	0	0	9	0	0
4	0	0	0	1	0
5	0	0	0	0	7

Figure 6.6: Model Performance for Respirator (Y04)



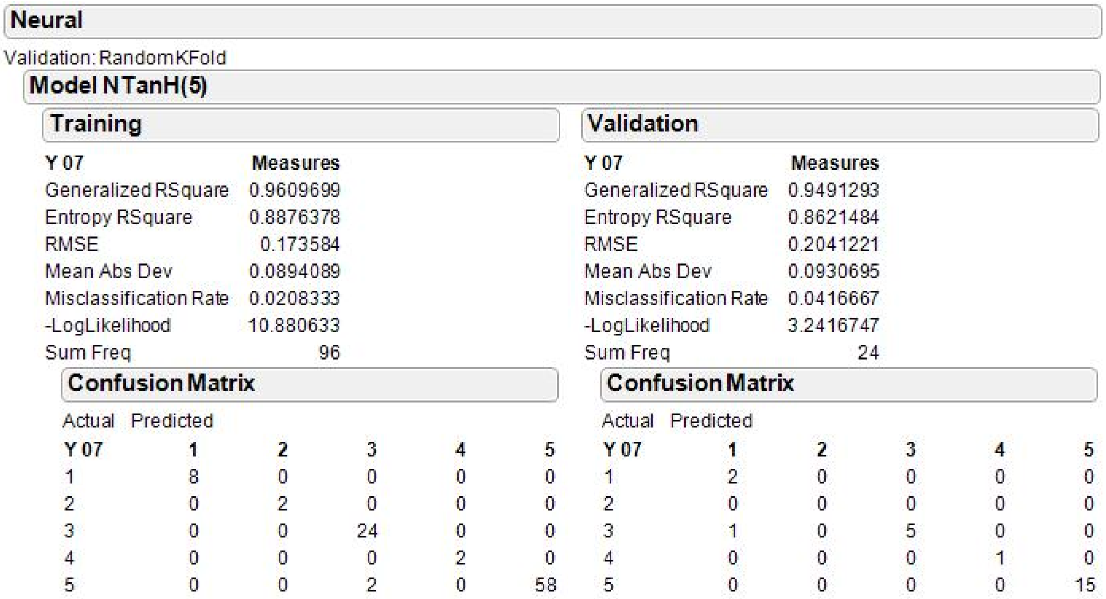
```
Neural
Validation: RandomKFold
Model NTanH(6)
Training                                        Validation
Y 05                      Measures              Y 05                      Measures
Generalized RSquare       0.9463688             Generalized RSquare       0.9453023
Entropy RSquare           0.8007382             Entropy RSquare           0.7935924
RMSE                      0.2708527             RMSE                      0.2973063
Mean Abs Dev              0.1524485             Mean Abs Dev              0.1979349
Misclassification Rate    0.0833333             Misclassification Rate    0.0833333
-LogLikelihood            25.117886             -LogLikelihood            6.6135314
Sum Freq                         96             Sum Freq                         24
  Confusion Matrix                                Confusion Matrix
  Actual  Predicted                               Actual  Predicted
  Y 05       1      2      3      4      5        Y 05       1      2      3      4      5
  1         38      0      0      0      1        1          9      0      0      0      0
  2          0      3      0      0      0        2          1      0      0      0      0
  3          2      0     31      0      1        3          0      0      9      0      0
  4          0      0      0      9      1        4          1      0      0      1      0
  5          0      0      1      2      7        5          0      0      0      0      3
```

Figure 6.7: Model Performance for Full Body Suit (Y05)



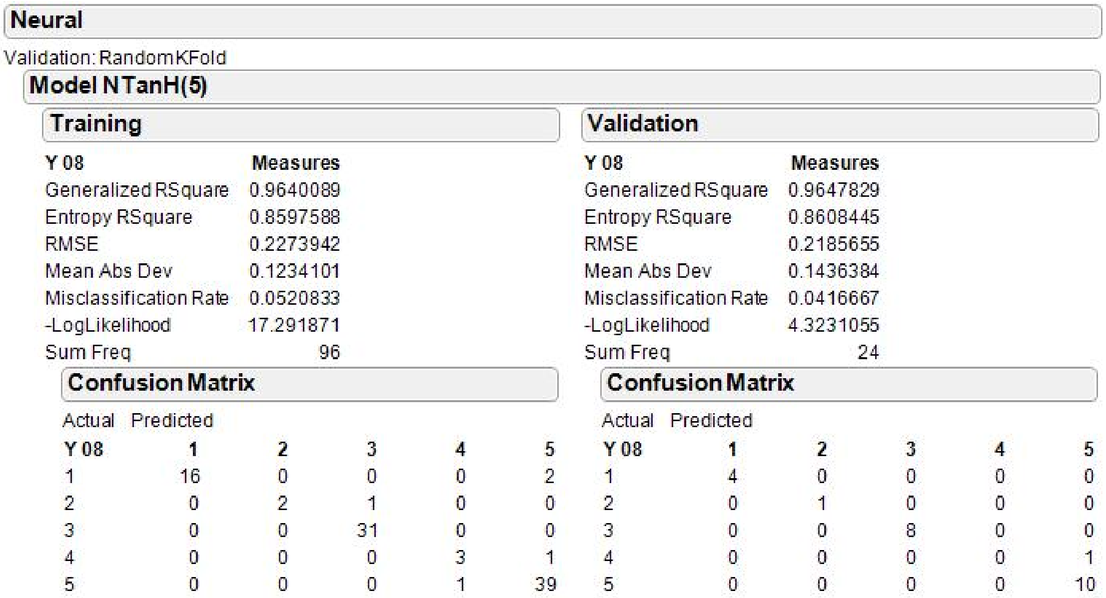
```
Neural
Validation: RandomKFold
Model NTanH(5)
Training                                        Validation
Y 06                      Measures              Y 06                      Measures
Generalized RSquare       0.9676871             Generalized RSquare       0.9643516
Entropy RSquare           0.8718412             Entropy RSquare           0.8529128
RMSE                      0.2029714             RMSE                      0.2322985
Mean Abs Dev              0.1316408             Mean Abs Dev              0.1520773
Misclassification Rate    0.0416667             Misclassification Rate    0.0416667
-LogLikelihood            15.814912             -LogLikelihood              4.72388
Sum Freq                         96             Sum Freq                         24
  Confusion Matrix                                Confusion Matrix
  Actual  Predicted                               Actual  Predicted
  Y 06       1      2      3      4      5        Y 06       1      2      3      4      5
  1         28      0      1      0      0        1          7      0      0      0      0
  2          0      8      0      0      0        2          0      2      0      0      0
  3          0      0     46      0      0        3          0      1     10      0      0
  4          0      0      1      6      0        4          0      0      0      2      0
  5          0      0      2      0      4        5          0      0      0      0      2
```

Figure 6.8: Model Performance for Skin Cream (Y06)



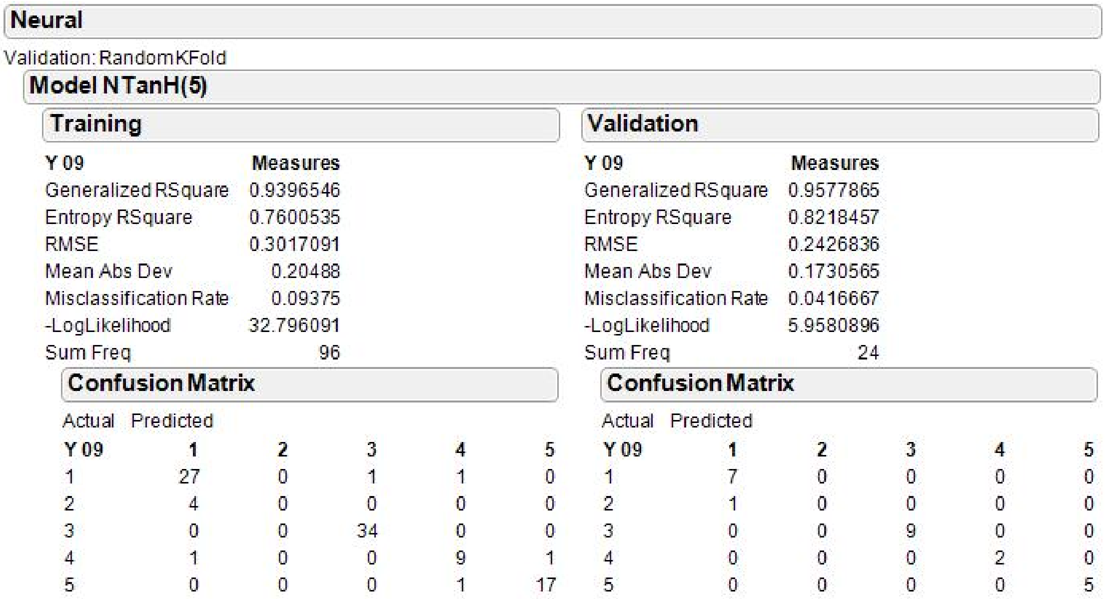
```
Neural
Validation: RandomKFold
 Model NTanH(5)
  Training                                        Validation
  Y 07                   Measures                 Y 07                   Measures
  Generalized RSquare    0.9609699                Generalized RSquare    0.9491293
  Entropy RSquare        0.8876378                Entropy RSquare        0.8621484
  RMSE                    0.173584                RMSE                   0.2041221
  Mean Abs Dev           0.0894089                Mean Abs Dev           0.0930695
  Misclassification Rate 0.0208333                Misclassification Rate 0.0416667
  -LogLikelihood         10.880633                -LogLikelihood         3.2416747
  Sum Freq                      96                Sum Freq                      24
   Confusion Matrix                                Confusion Matrix
   Actual  Predicted                               Actual  Predicted
   Y 07       1     2     3     4     5            Y 07       1     2     3     4     5
   1          8     0     0     0     0            1          2     0     0     0     0
   2          0     2     0     0     0            2          0     0     0     0     0
   3          0     0    24     0     0            3          1     0     5     0     0
   4          0     0     0     2     0            4          0     0     0     1     0
   5          0     0     2     0    58            5          0     0     0     0    15
```

Figure 6.9: Model Performance for Fume Hood (Y07)



```
Neural
Validation: RandomKFold
 Model NTanH(5)
  Training                                        Validation
  Y 08                   Measures                 Y 08                   Measures
  Generalized RSquare    0.9640089                Generalized RSquare    0.9647829
  Entropy RSquare        0.8597588                Entropy RSquare        0.8608445
  RMSE                   0.2273942                RMSE                   0.2185655
  Mean Abs Dev           0.1234101                Mean Abs Dev           0.1436384
  Misclassification Rate 0.0520833                Misclassification Rate 0.0416667
  -LogLikelihood         17.291871                -LogLikelihood         4.3231055
  Sum Freq                      96                Sum Freq                      24
   Confusion Matrix                                Confusion Matrix
   Actual  Predicted                               Actual  Predicted
   Y 08       1     2     3     4     5            Y 08       1     2     3     4     5
   1         16     0     0     0     2            1          4     0     0     0     0
   2          0     2     1     0     0            2          0     1     0     0     0
   3          0     0    31     0     0            3          0     0     8     0     0
   4          0     0     0     3     1            4          0     0     0     0     1
   5          0     0     0     1    39            5          0     0     0     0    10
```

Figure 6.10: Model Performance for Fume Hood with HEPA Filter (Y08)



Neural

Validation: RandomKFold

Model NTanH(5)

Training

Y 09	Measures
Generalized RSquare	0.9396546
Entropy RSquare	0.7600535
RMSE	0.3017091
Mean Abs Dev	0.20488
Misclassification Rate	0.09375
-LogLikelihood	32.796091
Sum Freq	96

Confusion Matrix

Actual	Predicted				
Y 09	1	2	3	4	5
1	27	0	1	1	0
2	4	0	0	0	0
3	0	0	34	0	0
4	1	0	0	9	1
5	0	0	0	1	17

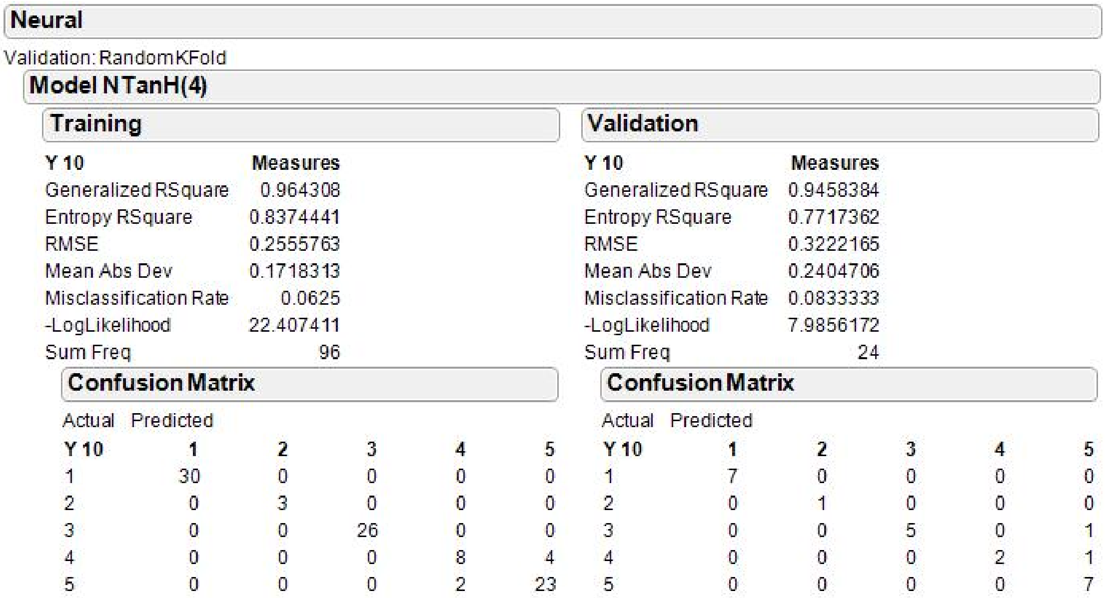
Validation

Y 09	Measures
Generalized RSquare	0.9577865
Entropy RSquare	0.8218457
RMSE	0.2426836
Mean Abs Dev	0.1730565
Misclassification Rate	0.0416667
-LogLikelihood	5.9580896
Sum Freq	24

Confusion Matrix

Actual	Predicted				
Y 09	1	2	3	4	5
1	7	0	0	0	0
2	1	0	0	0	0
3	0	0	9	0	0
4	0	0	0	2	0
5	0	0	0	0	5

Figure 6.11: Model Performance for Continuous Monitoring (Y09)



Neural

Validation: RandomKFold

Model NTanH(4)

Training

Y 10	Measures
Generalized RSquare	0.964308
Entropy RSquare	0.8374441
RMSE	0.2555763
Mean Abs Dev	0.1718313
Misclassification Rate	0.0625
-LogLikelihood	22.407411
Sum Freq	96

Confusion Matrix

Actual	Predicted				
Y 10	1	2	3	4	5
1	30	0	0	0	0
2	0	3	0	0	0
3	0	0	26	0	0
4	0	0	0	8	4
5	0	0	0	2	23

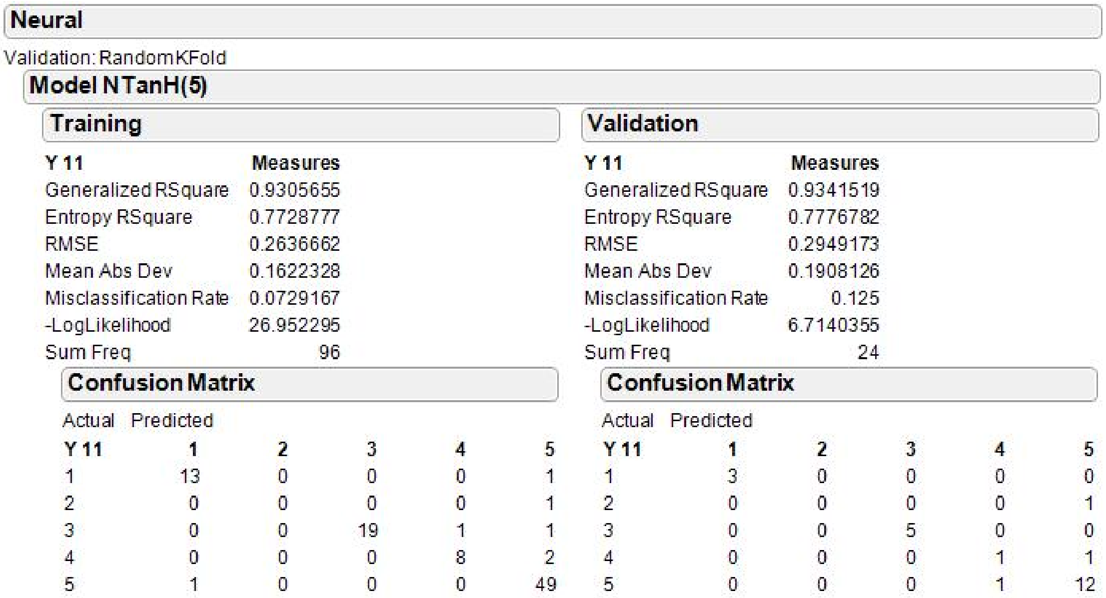
Validation

Y 10	Measures
Generalized RSquare	0.9458384
Entropy RSquare	0.7717362
RMSE	0.3222165
Mean Abs Dev	0.2404706
Misclassification Rate	0.0833333
-LogLikelihood	7.9856172
Sum Freq	24

Confusion Matrix

Actual	Predicted				
Y 10	1	2	3	4	5
1	7	0	0	0	0
2	0	1	0	0	0
3	0	0	5	0	1
4	0	0	0	2	1
5	0	0	0	0	7

Figure 6.12: Model Performance for Weekly Monitoring (Y10)



Neural

Validation: RandomKFold

Model NTanH(5)

Training

Y 11	Measures
Generalized RSquare	0.9305655
Entropy RSquare	0.7728777
RMSE	0.2636662
Mean Abs Dev	0.1622328
Misclassification Rate	0.0729167
-LogLikelihood	26.952295
Sum Freq	96

Confusion Matrix

Actual Predicted

Y 11	1	2	3	4	5
1	13	0	0	0	1
2	0	0	0	0	1
3	0	0	19	1	1
4	0	0	0	8	2
5	1	0	0	0	49

Validation

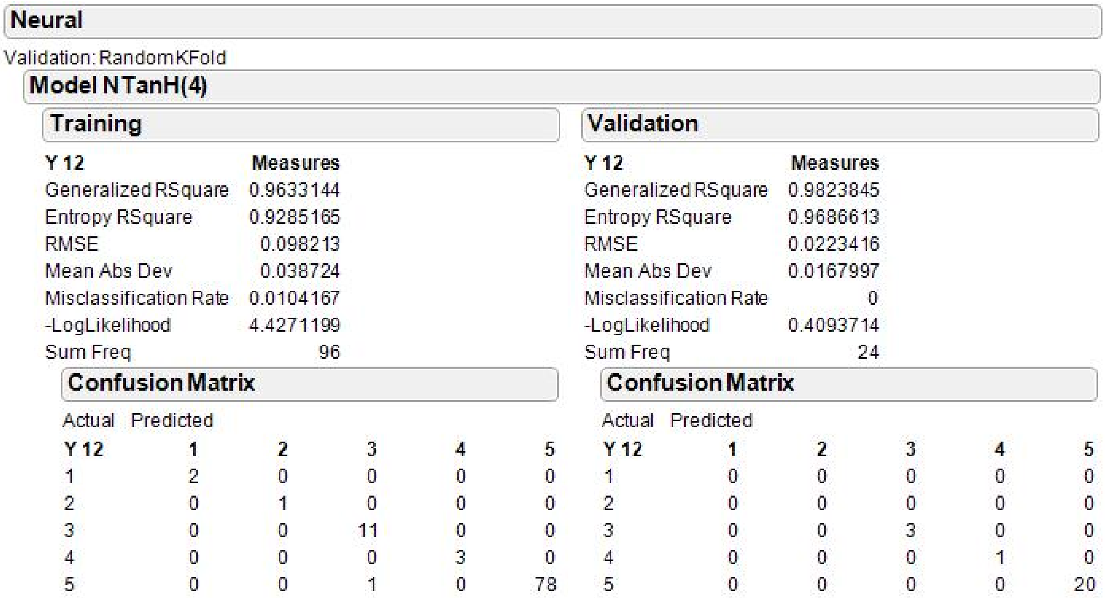
Y 11	Measures
Generalized RSquare	0.9341519
Entropy RSquare	0.7776782
RMSE	0.2949173
Mean Abs Dev	0.1908126
Misclassification Rate	0.125
-LogLikelihood	6.7140355
Sum Freq	24

Confusion Matrix

Actual Predicted

Y 11	1	2	3	4	5
1	3	0	0	0	0
2	0	0	0	0	1
3	0	0	5	0	0
4	0	0	0	1	1
5	0	0	0	1	12

Figure 6.13: Model Performance for Monthly Monitoring (Y11)



Neural

Validation: RandomKFold

Model NTanH(4)

Training

Y 12	Measures
Generalized RSquare	0.9633144
Entropy RSquare	0.9285165
RMSE	0.098213
Mean Abs Dev	0.038724
Misclassification Rate	0.0104167
-LogLikelihood	4.4271199
Sum Freq	96

Confusion Matrix

Actual Predicted

Y 12	1	2	3	4	5
1	2	0	0	0	0
2	0	1	0	0	0
3	0	0	11	0	0
4	0	0	0	3	0
5	0	0	1	0	78

Validation

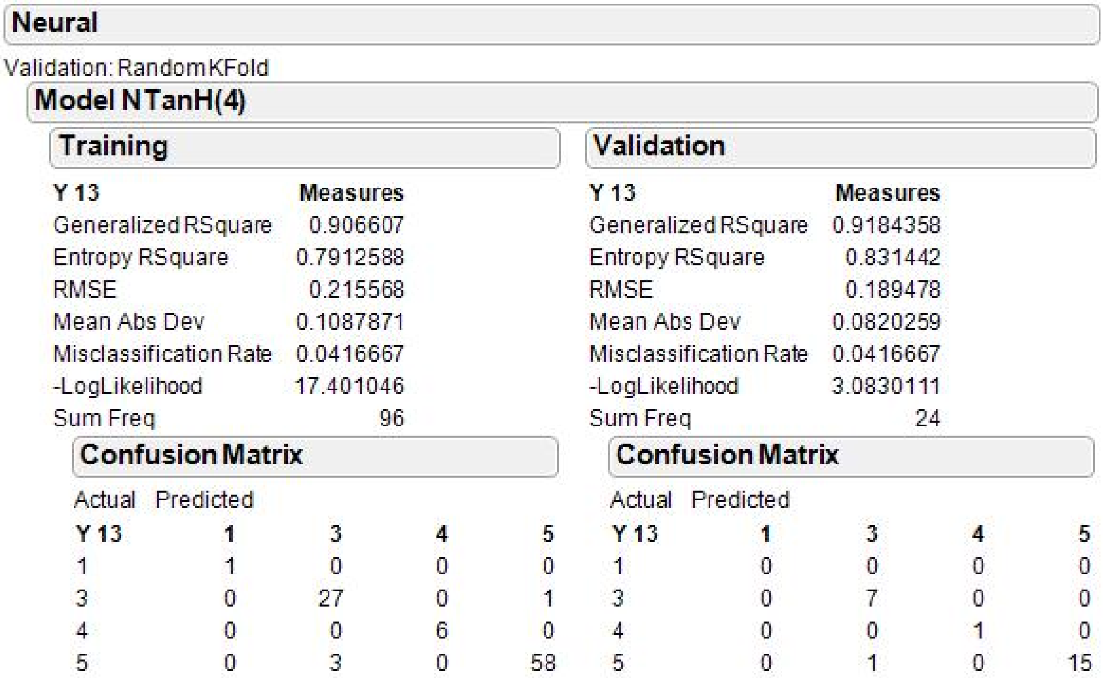
Y 12	Measures
Generalized RSquare	0.9823845
Entropy RSquare	0.9686613
RMSE	0.0223416
Mean Abs Dev	0.0167997
Misclassification Rate	0
-LogLikelihood	0.4093714
Sum Freq	24

Confusion Matrix

Actual Predicted

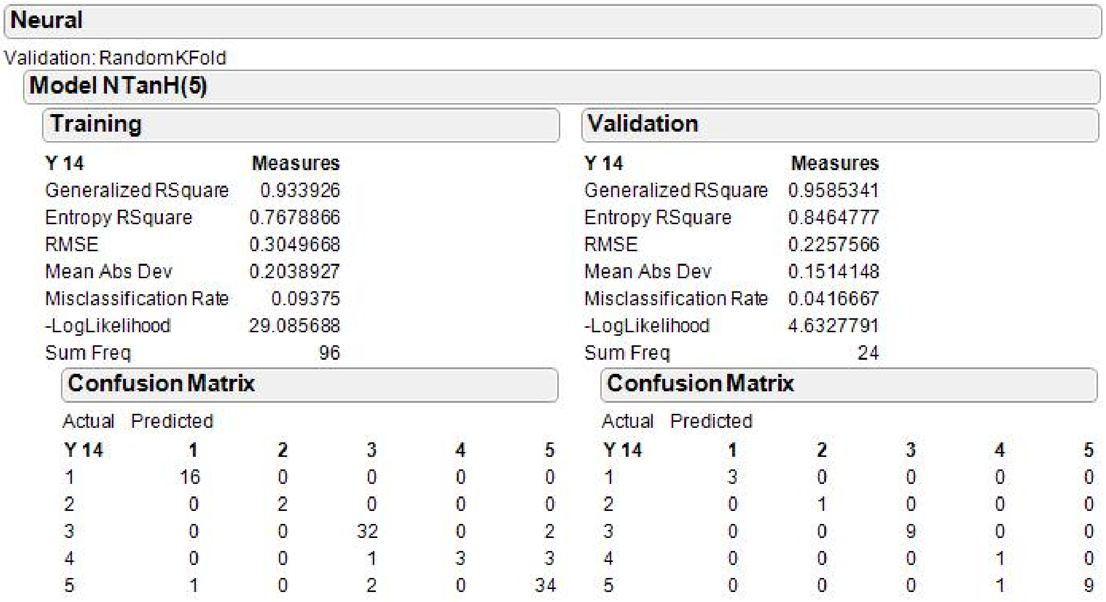
Y 12	1	2	3	4	5
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	3	0	0
4	0	0	0	1	0
5	0	0	0	0	20

Figure 6.14: Model Performance for Mandatory training for Handling Materials (Y12)



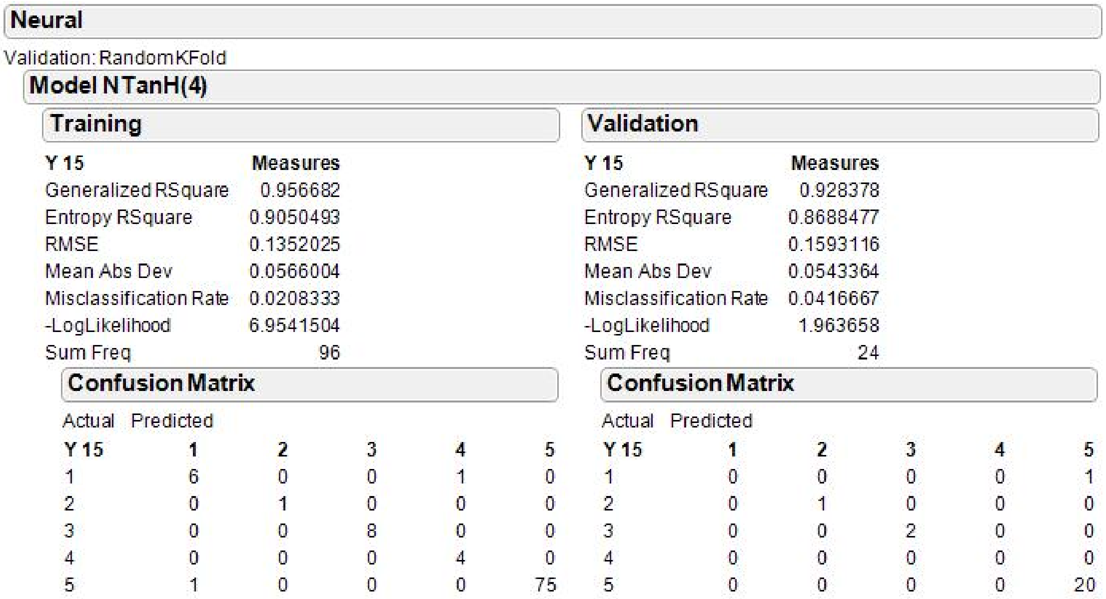
```
Neural
Validation: RandomKFold
  Model NTanH(4)
    Training                                  Validation
    Y 13                    Measures          Y 13                    Measures
    Generalized RSquare     0.906607          Generalized RSquare     0.9184358
    Entropy RSquare         0.7912588         Entropy RSquare          0.831442
    RMSE                    0.215568          RMSE                     0.189478
    Mean Abs Dev            0.1087871         Mean Abs Dev            0.0820259
    Misclassification Rate  0.0416667         Misclassification Rate  0.0416667
    -LogLikelihood          17.401046         -LogLikelihood          3.0830111
    Sum Freq                       96         Sum Freq                       24
      Confusion Matrix                          Confusion Matrix
      Actual  Predicted                         Actual  Predicted
      Y 13        1     3     4     5           Y 13        1     3     4     5
      1           1     0     0     0           1           0     0     0     0
      3           0    27     0     1           3           0     7     0     0
      4           0     0     6     0           4           0     0     1     0
      5           0     3     0    58           5           0     1     0    15
```

Figure 6.15: Model Performance for Cleaning of Workplace (Y13)



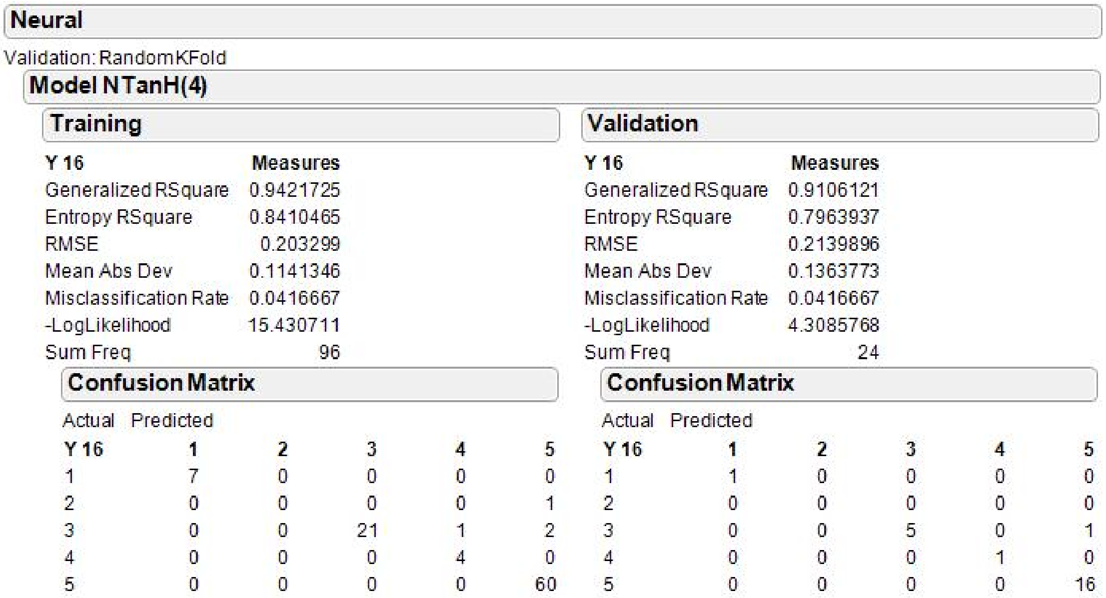
```
Neural
Validation: RandomKFold
  Model NTanH(5)
    Training                                      Validation
    Y 14                    Measures              Y 14                    Measures
    Generalized RSquare     0.933926              Generalized RSquare     0.9585341
    Entropy RSquare         0.7678866             Entropy RSquare         0.8464777
    RMSE                    0.3049668             RMSE                    0.2257566
    Mean Abs Dev            0.2038927             Mean Abs Dev            0.1514148
    Misclassification Rate    0.09375             Misclassification Rate  0.0416667
    -LogLikelihood          29.085688             -LogLikelihood          4.6327791
    Sum Freq                       96             Sum Freq                       24
      Confusion Matrix                              Confusion Matrix
      Actual  Predicted                             Actual  Predicted
      Y 14      1     2     3     4     5           Y 14      1     2     3     4     5
      1        16     0     0     0     0           1         3     0     0     0     0
      2         0     2     0     0     0           2         0     1     0     0     0
      3         0     0    32     0     2           3         0     0     9     0     0
      4         0     0     1     3     3           4         0     0     0     1     0
      5         1     0     2     0    34           5         0     0     0     1     9
```

Figure 6.16: Model Performance for HEPA Vaccum Cleaner (Y14)



```
Neural
Validation: RandomKFold
Model NTanH(4)
Training                                      Validation
Y 15                  Measures                Y 15                  Measures
Generalized RSquare    0.956682               Generalized RSquare    0.928378
Entropy RSquare       0.9050493               Entropy RSquare       0.8688477
RMSE                  0.1352025               RMSE                  0.1593116
Mean Abs Dev          0.0566004               Mean Abs Dev          0.0543364
Misclassification Rate 0.0208333              Misclassification Rate 0.0416667
-LogLikelihood        6.9541504               -LogLikelihood         1.963658
Sum Freq                     96               Sum Freq                     24
  Confusion Matrix                              Confusion Matrix
  Actual  Predicted                             Actual  Predicted
  Y 15      1     2     3     4     5           Y 15      1     2     3     4     5
  1         6     0     0     1     0           1         0     0     0     0     1
  2         0     1     0     0     0           2         0     1     0     0     0
  3         0     0     8     0     0           3         0     0     2     0     0
  4         0     0     0     4     0           4         0     0     0     0     0
  5         1     0     0     0    75           5         0     0     0     0    20
```

Figure 6.17: Model Performance for Maintenance Personnel require PPE (Y15)



```
Neural
Validation: RandomKFold
Model NTanH(4)
Training                                      Validation
Y 16                  Measures                Y 16                  Measures
Generalized RSquare   0.9421725               Generalized RSquare   0.9106121
Entropy RSquare       0.8410465               Entropy RSquare       0.7963937
RMSE                   0.203299               RMSE                  0.2139896
Mean Abs Dev          0.1141346               Mean Abs Dev          0.1363773
Misclassification Rate 0.0416667              Misclassification Rate 0.0416667
-LogLikelihood        15.430711               -LogLikelihood        4.3085768
Sum Freq                     96               Sum Freq                     24
  Confusion Matrix                              Confusion Matrix
  Actual  Predicted                             Actual  Predicted
  Y 16      1     2     3     4     5           Y 16      1     2     3     4     5
  1         7     0     0     0     0           1         1     0     0     0     0
  2         0     0     0     0     1           2         0     0     0     0     0
  3         0     0    21     1     2           3         0     0     5     0     1
  4         0     0     0     4     0           4         0     0     0     1     0
  5         0     0     0     0    60           5         0     0     0     0    16
```

Figure 6.18: Model Performance for Secure Disposal of PPE (Y16)

6.5 Conclusion and Future Work

Our objective was to show a proof of the concept that neural network models could be used for the problem of collecting expert opinion, making it readily available to firms needing guidance with nano-specific EHS implementation. This prototype expert system can be easily developed, modified and deployed as a web-based tool for use by nanomanufacturing facilities. A user can select the appropriate manufacturing characteristics of his facility and the neural-network model will suggest the appropriate workplace measures and controls. As new information about nanomaterials is generated, the neural-network models can be updated / trained to be applicable to specific nanomaterials.

Chapter 7

Conclusion and Future Work

Conclusion

Can sustainability ever be achieved? That is a question to which we currently don't know the answer and that should not stop us to strive towards achieving or getting as close to achieving it as possible, given the fact that the sustainability goal isn't clearly and quantitatively defined. As in many mathematical programming based optimization problems, a solution close to the global optimum should be considered acceptable.

This thesis has delved into some of the challenges faced by nanotechnology development and nanomanufacturing in particular, so that tools and methodologies could be developed for use by researchers and manufacturers. The biggest challenge for nanomanufacturing is to ensure that there is no accidental harm done to the environment or the general population that might result in a public backlash. Public perception of nanotechnology and confidence in regulatory framework is key to sustainable development of nanotechnology. The regulatory framework has to be derived from chemical regulatory options. Nanomanufacturing firms need to be a part of the framework as they are source of information and unique issues arising due to nanomaterial properties.

A life cycle approach with the promotion of green methods to the manufacture of nanomaterials can go a long way in fixing the problem at its source. Evaluation of processes on environmental impact metrics can provide guidance in reducing chemical wastes given the low yields of nanomanufacturing processes. Providing help to companies in implementing appropriate safety procedures and workplace practices can prevent occurrence of untoward incidents and potential liabities to nanomanufacturing companies.

Future Work

It would be great to see the tools developed in this thesis made available as a web-based tool to ensure broader reach and impact. The lack of EHS information on nanomaterials is a significant challenge. EPA, OSHA and various other organizations are striving to develop EHS information. Soon EHS information on a number of nanomaterials should become available and the methods developed in this thesis can be updated with EHS information on nanomaterials to provide wider applicability and better specificity to the problems addressed.

Bibliography

Bibliography

Review of the Research Program of the Partnership for a New Generation of Vehicles: Sixth Report. The National Academies Press, Washington, D.C., 2000. 50

Matthew A. Albrecht, Cameron W. Evans, and Colin L. Raston. Green chemistry and the health implications of nanoparticles. *Green Chemistry*, 8:417–432, 2006. 63

Braden R. Allenby and Dave Rejeski. The industrial ecology of emerging technologies. *Journal of Industrial Ecology*, 12(3):267–269, 2008. 46

David Andrews and Richard Wiles. Off the books: Industry's secret chemicals, December 2009. URL `http://www.ewg.org/files/secret-chemicals.pdf`. 28

John S. Applegate. Synthesizing tsca and reach: Practical principles for chemical regulation reform. *SSRN eLibrary*, 2008. 26

Adedeji B. Badiru and John Y. Cheung. *Fuzzy Engineering Expert Systems with Neural Network Applications*. John Wiley & Sons. Inc, 2002. 102

Sangeeta Bansal and Subhashis Gangopadhyay. Tax/subsidy policies in the presence of environmentally aware consumers. *Journal of Environmental Economics and Management*, 45(2):333–355, 2003. 32

C. Bauer, J. Buchgeister, R. Hischier, W. R. Poganietz, L. Schebek, and J. Warsen. Towards a framework for life cycle thinking in the assesment of nanotechnology. *Journal of Cleaner Production*, 16(8):910–926, 2008. 18, 47

Lori Snyder Bennear and Robert N. Stavins. Second-best theory and the use of multiple policy instruments. *Environmental and Resource Economics*, 37(1):111–129, 2007. 26

Enrico Bergamaschi. Occupational exposure to nanomaterials: Present knowledge and future development. *Nanotoxicology*, 3(3):194–201, 2009. 12

Michael Berger. Nanotechnology-not that green?, 2008. URL `http://www.nanowerk.com/spotlight/spotid=7853.php`. 38, 56

John C. Besley, Victoria L. Kramer, and Susanna H. Priest. Expert opinion on nanotechnology: risks, benefits and regulation. *Journal of Nanoparticle Research*, 10(4):549–558, 2008. 12

Fabio Boccuni, Bruna Rondinone, Carlo Petyx, and Sergio Iavicoli. Potential occupational exposure to manufactured nanoparticles in italy. *Journal of Cleaner Production*, 16(8-9):949 – 956, 2008. 45

Jonathan C. Borck and Cary Coglianese. Voluntary environmental programs: Assessing their effectiveness. *Annual Review of Environment and Resources*, 34 (1):305–324, 2009. 30

Brundtland Commission. *Our common future : The report of the World Commission on Environment and Development*. Oxford University Press,, New York :, 1987. 45

Heriberto Cabezas, Jane C. Bare, and Subir K. Mallick. Pollution prevention with chemical process simulators: the generalized waste reduction (war) algorithm-full version. *Computers & Chemical Engineering*, 23(4-5):623 – 634, 1999. 69

Rhitu Chatterjee. Coal-ash spills highlight ongoing risk to ecosystems. *Environmental Science & Technology*, 43(9):3003–3004, 2009. 14

Vicki L. Colvin. The potential environmental impact of engineered nanomaterials. *Nat Biotech*, 21(10):1166–1170, 2003. 16

European Commission. Towards a european strategy for nanotechnology. Technical report, European Commission, 2004. 43, 44

National Research Council Committee to Review the National Nanotechnology Initiative. *A Matter of Size: Triennial Review of the National Nanotechnology Initiative.* National Academic Press, 2006. 21

Neil Cunningham. Environment, self-regulation, and the chemical industry: Assessing responsible care. *Law & Policy*, 17(1):57–109, 2008. 26

Mary Ann Curran. Broad-based environmental life cycle assesment. *Environmental Science and Technology*, 27(3):430–436, 1993. 16, 45, 46, 47

Jennifer A. Dahl, Bettye L. S. Maddux, and James E. Hutchison. Toward greener nanosynthesis. *Chemical Reviews*, 107(6):2228–2269, 2007. 38, 57

J. Michael Davis. How to assess the risks of nanotechnology: Learning from past experience. *Journal of Nanoscience and Nanotechnology*, 7(2):402–409, 2007. 59

Eric K. Drexler. *Nanotechnology: From Feynman to Funding.* Nanotechnology: Risks, Ethics and Law. Earthscan, London, 2006. 11

Katherine A. Dunphy Guzmán, Margaret R. Taylor, and Jillian F. Banfield. Environmental risks of nanotechnology: National nanotechnology initiative funding, 2000-2004. *Environmental Science & Technology*, 40(5):1401–1407, 2006. 21

Robert F. Durant. Epa, tva and pollution control: Implications for a theory of regulatory policy implementation. *Public Administration Review*, 44(4):305–315, 1984. 39

EPA. Nanotechnology white paper. Electronic, 07/30/2010 2005a. URL `http://www.epa.gov/osa/pdfs/EPA_nanotechnology_white_paper_external_review_draft_12-02-2005.pdf`. 37

EPA. Performance track program guide. Technical report, US-EPA, 2005b. URL `https://grc-pirk.recomply.com/pirk/CGI-EPA_PerformanceTrack_Guide.pdf`. 63

EPA. The lean and environment toolkit, 2007. URL `http://www.epa.gov/lean/environment/toolkits/environment/resources/LeanEnviroToolkit.pdf`. 86

EPA. Nanoscale materials stewardship program. Technical report, US-EPA, 2009. URL `http://www.epa.gov/oppt/nano/stewardship.htm`. 86

Anne Fairbrother and Jennifer R. Fairbrother. Are environmental regulations keeping up with innovation? a case study of the nanotechnology industry. *Ecotoxicology and Environmental Safety*, 72(5):1327–1330, 2009. 39

Torsten Fleischer and Armin Grunwald. Making nanotechnology developments sustainable. a role for technology assessment? *Journal of Cleaner Production*, 16(8-9):889 – 898, 2008. 42

Glen E Fryxell and Guozhong Cao. *Environmental Applications of Nanomaterials: Synthesis, Sorbents and Sensors*. Imperial College Press, London, 2007. 18

Rafiqul Gani, Concepción Jiménez-González, and David J.C. Constable. Method for selection of solvents for promotion of organic reactions. *Computers & Chemical Engineering*, 29(7):1661 – 1676, 2005. 64, 82

Andy Garner and Gregory A. Keoleian. *Industrial Ecology : An Introduction*. National Pollution Prevention Center for Higher Education, 1995. 45

Ash Genaidy, Reynold Sequeira, Magda Rinder, and Amal A-Rehim. Risk analysis and protection measures in a carbon nanofiber manufacturing enterprise: An exploratory investigation. *Science of The Total Environment*, 407(22):5825 – 5838, 2009. 90, 91, 92

Brian J. Gerber and Paul Teske. Regulatory policy making in the american states: A review of theories and evidence. *Political Research Quarterly*, 53(4):849–886, 2000. 23

Lynn Goldman and Christine Coussens. *Preparing for Nanotechnology: Health, Policy, and Emerging Issues.* IMPLICATIONS OF NANOTECHNOLOGY FOR ENVIRONMENTAL HEALTH RESEARCH. National Academic Press, Washington DC, 2005. 14

GoodNanoGuide, 2011. URL `www.GoodNanoGuide.org`. 101

Robin Gregory, Baruch Fischhoff, and Tim McDaniels. Acceptable input: Using decision analysis to guide public policy deliberations. *Decision Analysis*, 2(1):4–16, 2005. 65

Erwin C. Hargrove. *The Missing Link.* Urban Institute, Washington D.C., 1975. 39

Meagan L. Healy, Lindsay J. Dahlben, and Jacqueline A. Isaacs. Environmental assessment of single-walled carbon nanotube processes. *Journal of Industrial Ecology*, 12(3):376–393, 2008. 17

Anna Marie Heikkilä. *Inherent Safety in Process Plant Design: An Index Based Approach.* PhD thesis, Helsinki University of Technology, 1999. 68

Michael P. Holsapple, William H. Farland, Timothy D. Landry, Nancy A. Monteiro-Riviere, Janet M. Carter, Nigel J. Walker, and Karluss V. Thomas. Research strategies for safety evaluation of nanomaterials, part ii: Toxicological and safety evaluation of nanomaterials, current challenges and data needs. *Toxicol. Sci.*, 88 (1):12–17, 2005. 16

Fu-Yu Hshieh, David B. Hirsch, and Harold D. Beeson. Predicted heats of combustion of some important organosilicon intermediates. *Fire and Materials*, 27(1):41–49, 2003. 76

James E. Hutchison. Greener nanoscience: A proactive approach to advancing applications and reducing implications of nanotechnology. *ACS Nano*, 2(3):395–402, 2008. 38, 57

IRGC. Risk governance of nanotechnology applications in food and cosmetics, 2006. URL `http://www.irgc.org/-Nanotechnology-.html`. 12

Hee Dong Jang. Experimental study of synthesis of silica nanoparticles by a bench-scale diffusion flame reactor. *Powder Technology*, 119(2-3):102 – 108, 2001. 76

Niels Jensen, Nuria Coll, and Rafiqul Gani. An integrated computer-aided system for generation and evaluation of sustainable process alternatives. *Clean Technologies and Environmental Policy*, 5:209–225, 2003. 68

Suellen Keiner. *Room at the Bottom? Potential State and Local Strategies for Managing the Risks and Benefits of Nanotechnology*. Woodrow Wilson International Center for Scholars, 2008. 23, 86

Vikas Khanna and Bhavik R. Bakshi. Carbon nanofiber polymer composites: Evaluation of life cycle energy use. *Environmental Science & Technology*, 43(6): 2078–2084, 2009. 17

Vikas Khanna, Bhavik R. Bakshi, and L. James Lee. Carbon nanofiber production. *Journal of Industrial Ecology*, 12(3):394–410, 2008. 17, 47, 49, 50

G. E. King and L Gibbs. The little unknown. *Industrial Engineer*, 42(7):32–37, 2010. 86

Walter Klopffer. Life cycle assesment as part of sustainability assesment of chemicals. *Environmental Science and Pollution Research*, 12(3):173–177, 2005. 17

Andreas R. Köhler, Claudia Som, Aasgeir Helland, and Fadri Gottschalk. Studying the potential release of carbon nanotubes throughout the application life cycle. *Journal of Cleaner Production*, 16(8-9):927 – 937, 2008. 47

Otilia M. Koo, Israel Rubinstein, and Hayat Onyuksel. Role of nanotechnology in targeted drug delivery and imaging: a concise review. *Nanomedicine: Nanotechnology, Biology and Medicine*, 1(3):193 – 212, 2005. 43

Nikhil Krishnan, Sarah Boyd, Ajay Somani, Sebastien Raoux, Daniel Clark, and David Dornfeld. A hybrid life cycle inventory of nano-scale semiconductor manufacturing. *Environmental Science & Technology*, 42(8):3069–3075, 2008. 47

Markku Kulmala, Genrik Mordas, Tuukka Petäjä, Tiia Grönholm, Pasi P. Aalto, Hanna Vehkamäki, Anca I. Hienola, Erik Herrmann, Mikko Sipilä, Ilona Riipinen, Hanna E. Manninen, Kaarle Hämeri, Frank Stratmann, Merete Bilde, Paul M. Winkler, Wolfram Birmili, and Paul E. Wagner. The condensation particle counter battery (CPCB): A new tool to investigate the activation properties of nanoparticles. *Journal of Aerosol Science*, 38(3):289 – 304, 2007. 67

Duncan Kushnir and Björn A. Sandén. Energy requirements of carbon nanoparticle production. *Journal of Industrial Ecology*, 12(3):360–375, 2008. 49

Tim Little, Sanford Lewis, and Pamela Lundquist. Beneath the skin: Hidden liabilities, market risk and drivers of change in the cosmetics and personal care products industry, 2007. URL `http://iehn.org/publications.reports.beneath.02-07.php`. 12

Shannon M. Lloyd and Lester B. Lave. Life cycle economic and environmental implications of using nanocomposites in automobiles. *Environmental Science & Technology*, 37(15):3458–3466, 2003. 17, 47

Shannon M. Lloyd, Lester B. Lave, and H. Scott Matthews. Life cycle benefits of using nanotechnology to stabilize platinum-group metal particles in automotive catalysts. *Environmental Science & Technology*, 39(5):1384–1392, 2005. 17, 47

M. P Manoharan, A Sharma, A. V Desai, M. A Haque, C. E Bakis, and K. W Wang. The interfacial strength of carbon nanofiber epoxy composite using single fiber pullout experiments. *Nanotechnology*, 20:295701, 2009. 55

António A. Martins, Teresa M. Mata, Carlos A. V. Costa, and Subhas K. Sikdar. Framework for sustainability metrics. *Industrial & Engineering Chemistry Research*, 46(10):2962–2973, 2007. 70

H. Scott Matthews, Lester Lave, and Heather MacLean. Life cycle impact assessment: A challenge for risk analysts. *Risk Analysis*, 22(5):853–860, 2002. 58

Andrew D. Maynard. Commentary: Oversight of engineered nanomaterials in the workplace. *The Journal of Law, Medicine & Ethics*, 37(4):651–658, 2009. 101

David E. Meyer, Mary Ann Curran, and Michael A. Gonzalez. An examination of existing data for the industrial manufacture and use of nanocomponents and their role in the life cycle impact of nanoproducts. *Environmental Science & Technology*, 43(5):1256–1263, 2009. 16, 46

Richard D. Morgenstern and William A. Pizer. *Reality Check: The Nature and Performance of Voluntary Environmental Programs in the United States, Europe and Japan*. RFF Press, Washington, DC, 2007. 30

Michael Moyer. Protesting high tech trousers. *Popular Science*, 267(2):98, August 2005. 12

Michael Mullaney. Beyond batteries: Storing power in a sheet of paper. URL `http://www.eurekalert.org/pub_releases/2007-08/rpi-bbs080907.php`. 43

Giuseppe Munda. *Multicriteria Evaluation in a Fuzzy Environment: Theory and Applications in Ecological Economics*. Physica-Verlag, 1995. 70

Sasikumar Naidu, Rapinder Sawhney, and Xueping Li. A methodology for evaluation and selection of nanoparticle manufacturing processes based on sustainability metrics. *Environmental Science & Technology*, 42(17):6697–6702, 2008. 38, 57, 90, 93

Barry Ness, Evelin Urbel-Piirsalu, Stefan Anderberg, and Lennart Olsson. Categorising tools for sustainability assessment. *Ecological Economics*, 60(3):498–508, 2007. 16

Matthew C. Nisbet. Public opinion about stem cell research and human cloning. *Public Opin Q*, 68(1):131–154, 2004. 12

Matthew C. Nisbet and Teresa Myers. The polls trends: Twenty years of public opinion about global warming. *Public Opin Q*, 71(3):444–470, 2007. 11

Gunter Oberdorster, Eva Oberdorster, and Jan Oberdorster. Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. *Environmental Health Perspectives*, 113(7):823–839, 2005. 12, 48

OECD. Safety of manufactured nanomaterials, 2009. URL `http://www.oecd.org/department/0,3355,en_2649_37015404_1_1_1_1_1,00.htm`. 15

Stig Irving Olsen, Frans Møller Christensen, Michael Hauschild, Finn Pedersen, Henrik Fred Larsen, and Jens Tørsløv. Life cycle impact assessment and risk assessment of chemicals- a methodological comparison. *Environmental Impact Assessment Review*, 21(4):385 – 404, 2001. 59

Neil Osterwalder, Christian Capello, Konrad Hungerbühler, and Wendelin Stark. Energy consumption during nanoparticle production: How economic is dry synthesis? *Journal of Nanoparticle Research*, 8(1):1–9, 2006. 17, 47

Jonathan G. Overly, Rajive Dhingra, Gary A. Davis, and Sujit Das. Environmental evaluation of lightweight exterior body panels in new generation vehicles. Proceedings of the Future Car Congress. Society for Automotive Engineers, 2002. 49, 52

Sung Kyoo Park, Ki Do Kim, and Hee Taik Kim. Preparation of silica nanoparticles: determination of the optimal synthesis conditions for small and uniform particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 197(1-3):7 – 17, 2002. 76

PEN. Inventories of nano-enabled products, 2010. URL `http://www.nanotechproject.org/inventories/`. 2, 29

Matteo Pietrini, Lex Roes, Martin K. Patel, and Emo Chiellini. Comparative life cycle studies on poly(3-hydroxybutyrate)-based composites as potential replacement for conventional petrochemical plastics. *Biomacromolecules*, 8(7):2210–2218, 2007. 17

Matthew Potoski and Aseem Prakash. Green clubs and voluntary governance: Iso 14001 and firms' regulatory compliance. *American Journal of Political Science*, 49 (2):235–248, 2005. 29

Maria C. Powell, Martin P.A. Griffin, and Stephen Tai. Bottom-up risk regulation? how nanotechnology risk knowledge gaps challenge federal and state environmental agencies. *Environmental Management*, 42(3):426–443, 2008. 23

Hartmut Presting and Ulf König. Future nanotechnology developments for automotive applications. *Materials Science and Engineering: C*, 23(6-8):737 – 741, 2003. 65

Lux Research. Nanotech in the recession, 2009. URL `http://www.luxresearchinc.com/blog/2009/07/nanotech-in-the-recession/`. 42

Christine Ogilvie Robichaud, Dicksen Tanzil, Ulrich Weilenmann, and Mark R. Wiesner. Relative risk analysis of several manufactured nanomaterials: An insurance industry context. *Environmental Science & Technology*, 39(22):8985–8994, 2005. 37, 64

A. Roes, E. Marsili, E. Nieuwlaar, and M. Patel. Environmental and cost assessment of a polypropylene nanocomposite. *Journal of Polymers and the Environment*, 15 (3):212–226, 2007. 17, 47

Walter A Rosenbaum. *Environmental Politics and Policy*, chapter A Regulatory Thicket: Toxic and Hazardous Substances. Seventh edition, 2008. 29

R. M. Russell, S. C. Maidment, I. Brooke, and M. D. Topping. An introduction to a uk scheme to help small firms control health risks from chemicals. *Annals of Occupational Hygiene*, 42(6):367–376, 1998. 100

Paul C. Sarahan. Nanotechnology safety: A framework for identifying and complying with workplace safety requirements. *Nanotechnology Law & Business*, 5:191–205, 2008. 100

Kai Savolainen, Harri Alenius, Hannu Norppa, Lea Pylkkänen, Timo Tuomi, and Gerhard Kasper. Risk assessment of engineered nanomaterials and nanotechnologies: A review. *Toxicology*, 269(2-3):92 – 104, 2010. 59

Dietram Scheufele and Bruce Lewenstein. The public and nanotechnology: How citizens make sense of emerging technologies. *Journal of Nanoparticle Research*, 7 (6):659–667, 2005. 12

Susan M. Schexnayder, Sujit Das, Rajive Dhingra, Jonathan G. Overly, Bruce E. Tonn, Jean H. Peretz, Greg Waidley, and Gary A. Davis. Environmental evaluation of new generation vehicles and vehicle components. Technical Report ORNL/TM-2001-266, Oak Ridge National Laboratory, December 2001. 49, 52

Thomas P. Seager and Igor Linkov. Coupling multicriteria decision analysis and life cycle assessment for nanomaterials. *Journal of Industrial Ecology*, 12(3):282–285, 2008. 18

Hatice Sengül, Thomas L. Theis, and Siddhartha Ghosh. Toward sustainable nanoproducts: An overview of nanomanufacturing methods. *Journal of Industrial Ecology*, 12(3):329–359, 2008. 18, 44

Jo Anne Shatkin. Informing environmental decision making by combining life cycle assessment and risk analysis. *Journal of Industrial Ecology*, 12(3):278–281, 2008a. 18

Jo Anne Shatkin. *Nanotechnology: Health and Environmental Risks.* CRC Press, Boca Raton FL, 2008b. 18, 59

Anil K. Sinha, Kenichirou Suzuki, Minoru Takahara, Hirozumi Azuma, Takamasa Nonaka, and Kazuhiro Fukumoto. Mesostructured manganese oxide/gold nanoparticle composites for extensive air purification. *Angewandte Chemie International Edition*, 46(16):2891–2894, 2007. 43

Kara Sissell. EPA outlines principles for TSCA reform. *Chemical Week*, 171(24): 12–12, 2009. 26, 86

Claudia Som, Markus Berges, Qasim Chaudhry, Maria Dusinska, Teresa F. Fernandes, Stig I. Olsen, and Bernd Nowack. The importance of life cycle concepts for the development of safe nanoproducts. *Toxicology*, 269(2-3):160 – 169, 2010. 55

Robert N Stavins. *Market Based Environmental Policies.* Public Policies for Environmental Protection. RFF Press, Washington DC, second edition, 2000. 31

John Sullivan and Jenny Hu. Life cycle energy analysis for automobiles. Technical report, 1995. 50

Ying Sun, Jianren Sun, Miao Liu, and Quanfang Chen. Mechanical strength of carbon nanotube-nickel nanocomposites. *Nanotechnology*, 18:505704, 2007. 55

Ann M Thayer. Building up nanotech research. *Chemical & Engineering News*, 85 (15):15–21, April 2007. 63

J. Theron, J. A. Walker, and T. E. Cloete. Nanotechnology and water treatment: Applications and emerging opportunities. *Critical Reviews in Microbiology*, 34(1): 43–69, 2008. 43

Bruce Tonn, Angela Hemrick, and Fred Conrad. Cognitive representations of the future: Survey results. *Futures*, 38(7):810 – 829, 2006. 42

Bruce E. Tonn. Futures sustainability. *Futures*, 39(9):1097 – 1116, 2007. 42

Chris Toumey. Science and democracy. *Nature Nanotechnology*, 1(1):6–7, 2006. 12

US-EPA. Human health risk assessment, 2009. URL `http://www.epa.gov/riskassessment/health-risk.htm`. 58

Arnim von Gleich, Michael Steinfeldt, and Ulrich Petschow. A suggested three-tiered approach to assessing the implications of nanotechnology and influencing its development. *Journal of Cleaner Production*, 16(8-9):899–909, 2008. 37, 47

Scott Walsh and Terry Medley. A framework for responsible nanotechnology. In David H. Guston, editor, *The Year Book of Nanotechnology in Society*, volume vol 1 : Presenting Futures. Springer Netherlands, 2008. 30

Ahson Wardak, Michael E. Gorman, Nathan Swami, and David Rejeski. Environmental regulation of nanotechnology and the tsca. *Technology and Society Magazine, IEEE*, 26(2):48–56, 2007. 27

Ahson Wardak, Michael E. Gorman, Nathan Swami, and Shilpa Deshpande. Identification of risks in the life cycle of nanotechnology-based products. *Journal of Industrial Ecology*, 12(3):435–448, 2008. 37

Katherine Watlington. Emerging nanotechnologies for site remediation and wastewater treatment. Technical report, U.S. Environmental Protection Agency, August 2005. URL `http://clu-in.org/download/studentpapers/K_Watlington_Nanotech.pdf`. 43

Karsten Wegner and Sotiris E. Pratsinis. Scale-up of nanoparticle synthesis in diffusion flame reactors. *Chemical Engineering Science*, 58(20):4581 – 4589, 2003. 76

Jameson M. Wetmore and Jonathan D. Posner. Should corporations contribute to nano-regulation? *Nano Today*, 4(3):217–219, 2009. 30

Roger W. Whatmore. Nanotechnology–what is it? should we be worried? *Occup Med (Lond)*, 56(5):295–299, 2006. 12

Arnim Wiek, Daniel J. Lang, and Michael Siegrist. Qualitative system analysis as a means for sustainable governance of emerging technologies: the case of nanotechnology. *Journal of Cleaner Production*, 16(8-9):988–999, 2008. 39

James Wilsdon and Rebecca Willis. See-through science: why public enagagement needs to move upstream, 2004. 12

Mary Devine Worobec and Cheryl Hogue. *Toxic Substances Controls Guide: Federal Regularion of Chemicals in the Environment*. Bureau of National Affairs, Washington, D.C, 1992. 26

Douglas Young, Richard Scharp, and Heriberto Cabezas. The waste reduction (war) algorithm: environmental impacts, energy consumption, and engineering economics. *Waste Management*, 20(8):605 – 615, 2000. 69, 82, 88

Douglas M. Young and Heriberto Cabezas. Designing sustainable processes with simulation: the waste reduction (war) algorithm. *Computers & Chemical Engineering*, 23(10):1477 – 1491, 1999. 69

Wei-Xian Zhang. Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research*, 5(3):323–332, 2003. 15

Appendix

Appendix A

Supporting Information for Chapter 4

A.1 Assigning Chemical and Process Safety Index scores

Table A.1: Heat of the reaction subindices I_{rm} and I_{rs}

Heat of reaction / total reaction mass/J/g	**Score**
Thermally neutral ≤ 200	0
Mildly exothermic < 600	1
Moderately exothermic < 1200	2
Strongly exothermic < 3000	3
Extremely exothermic ≥ 3000	4

Table A.2: Chemical interaction subindex I_{int}

Chemical Interaction	**Score**
Heat formation	1-3
Fire	4
Formation of harmless nonflammable gas	1
Formation of toxic gas	2-3
Formation of flammable gas	2-3
Explosion	4
Rapid polymerization	2-3
Soluble toxic chemicals	1

Table A.3: Flammability subindex I_{fl}

Flammability	**Score**
Nonflammable	0
Combustible (flash point $> 55°C$)	1
Flammable (flash point $\leq 55°C$)	2
Easily flammable (flash point $< 21°C$)	3
Very flammable (flash point $< 0°C$ & $boilingpoint \leq 35°C$)	4

Table A.4: Explosiveness subindexI_{ex}

Explosiveness (UEL-LEL) $/vol\%$	**Score**
nonexplosive	0
$0 - 20$	1
$20 - 45$	2
$45 - 70$	3
$70 - 100$	4

Table A.5: Toxicity subindex I_{tox}

Toxic limit /ppm	**Score**
TLV > 10000	0
TLV ≤ 10000	1
TLV ≤ 1000	2
TLV ≤ 100	3
TLV ≤ 10	4
TLV ≤ 1	5
TLV ≤ 0.1	6

Table A.6: Corrosivness subindex I_{cor}

Construction material required	**Score**
Carbon steel	0
Stainless steel	1
Better material needed	2

Table A.7: Process Inventory subindexI_i

Inventory		
ISBL /tones or kg	**OSBL /tones or kg**	**Score**
$0 - 1$	$0 - 10$	0
$1 - 10$	$10 - 100$	1
$10 - 50$	$100 - 500$	2
$50 - 200$	$500 - 2000$	3
$200 - 500$	$2000 - 5000$	4
$500 - 1000$	$5000 - 10000$	5

Table A.8: Process Temperature subindexI_t

Process Temperature /$^\circ C$	**Score**
< 0	1
$0 - 70$	0
$70 - 150$	1
$150 - 300$	2
$300 - 600$	3
> 600	4

Table A.9: Process Pressure subindex I_p

Pressure /bar	**Score**
$0.5 - 5$	0
$5 - 25$	1
$25 - 50$	2
$50 - 200$	3
$200 - 1000$	4

Table A.10: Equipment safety index I_{Isbi}

Equipment	**Score** I_{Isbi}
Equipment handling nonflammable, nontoxic materials	0
Heat exchangers, pumps, towers and drums	1
Air coolers, reactors, high hazard pumps	2
Compressors, high hazard reactors	3
Furnaces, fired heaters	4

Table A.11: Equipment safety index I_{Osbi}

Equipment	**Score** I_{Osbi}
Equipment handling nonflammable, nontoxic materials	0
Atmospheric storage tanks, pumps	1
Cooling towers, compressors, blowdown systems	2
Flares, boilers, furnaces	3

Table A.12: Process structure index I_{st}

Safety level of process structure	**Score**
Recommended (safety etc. standard)	0
Sound engineering practice	1
No data or neutral	2
Probably unsafe	3
Minor accidents	4
Major accidents	5

A.2 WAR Algorithm and determination of its parameters

The WAR algorithm calculates the overall potential environmental impact, Ψ_k of chemical k using the following equation.

$\Psi_k = \sum_l \alpha_l \psi^s_{kl}$

where,

l is the impact category.

α_l is the relative weighing factor for impact category l .

ψ^s_{kl} is the specific potential environment impact for chemical k for category l .

A. Impact Categories and their scores:

1. Human toxicity potential by ingestion (HTPI): This is determined by using values for lethal-dose that causes death in 50% of rats by oral ingestion (LD_{50}).

$$(score)_{k,HTPI} = \frac{1}{(LD_{50})_k} \tag{A.1}$$

2. Human toxicity potential by exposure both dermal and inhalation (HTPE): This is estimated using time weighted average values of the threshold limit values $(TLV)_{time}$ for exposure to chemicals as published by OSHA, ACGIH and NIOSH.

$$(score)_{k,HTPE} = \frac{1}{(TLV)_{time}} \tag{A.2}$$

3. Terrestrial toxicity potential (TTP): This is determined similar to HTPI using LD_{50} data.

$$(score)_{k,TTP} = \frac{1}{(LD_{50})_k} \tag{A.3}$$

4. Aquatic toxicity potential (ATP): ATP values are derived from LC_{50}(lethal concentration) which causes death in the fish species Pimephales promelas.

$$(score)_{k,ATP} = \frac{1}{(LC_{50})_k} \tag{A.4}$$

5. Global warming potential (GWP): GWP is determined by calculating the amount of infrared radiation a given chemical absorbs over its atmospheric life time as compared to that of a reference compound usually CO_2 as shown in the equation below

$$(score)_{k,GWP} = \frac{\int_0^{TH} a_k.\,[k(t)]\,dt}{\int_0^{TH} a_{ref}.\,[ref(t)]\,dt} \tag{A.5}$$

   where TH is the time horizon taken as 100 years.

   a_k and a_{ref} are radiative efficiencies, the increase in radiation absorption per unit increase in abundance of the chemical species and,

   $[k(t)]$ and $[ref(t)]$ are the time dependent decay in abundance.

6. Ozone depletion potential (ODP): ODP is defined as the ratio of the rate at which a unit mass of chemical reacts with ozone to produce molecular oxygen to the rate at which a unit mass of $CFC-11$(trichlorofluoromethane) reacts with ozone.

$$(score)_{k,ODP} = \frac{rate_k}{rate_{CFC-11}} \tag{A.6}$$

7. Photochemical oxidation potential (PCOP): PCOP, also known as smog formation potential is the ratio of the rate at which a chemical reacts with a hydroxyl radical (OH) to that of the rate of reaction of ethylene with OH .

$$(score)_{k,PCOP} = \frac{rate_k}{rate_{ethylene}} \tag{A.7}$$

8. Acidification potential (AP): AP or acid rain potential is the ratio of rate at which a chemical reacts with moisture to release H^+ in the atmosphere to the rate of at which sulphur dioxide (SO_2) reacts to produce H^+.

$$(score)_{k,AP} = \frac{rate_k}{rate_{SO_2}} \tag{A.8}$$

B. Weighing factor:

The weighing factor α_l gives user defined weights to each of the eight impact potentials and is usually assigned on a scale of 0 to10.

C. Specific potential environment impact ψ^s_{kl} :

The individual scores are normalized within their categories to give the specific PEI for that chemical

$$\psi^s_{kl} = \frac{(score)_{kl}}{\langle (score)_k \rangle_l} \tag{A.9}$$

where $(score)_{kl}$ represents the scores for impacts on their respective scales and,$\langle (score)_k \rangle_l$ is the average value of all chemicals in impact category l .

A.2.1 Input Data for WAR Algorithm

1) Silica Lab

Table A.13: Input Data for Sol Gel synthesis

Stream Name	**Reaction**	**Washing**	**Waste**	**Product**
Type	Inlet	Inlet	Outlet Waste	Product
Flow Rate*	$3.50E-01$	$3.58E-01$	$7.06E-01$	$7.00E-04$
X(Ethanol)	0.9027	0.4400	0.6657	0.0000
X(Ammonia)	0.0873	0.0000	0.0482	0.0000
X(TEOS)	0.0100	0.0000	0.0000	0.0000
X(Water)	0.0000	0.5600	0.2833	0.0000
X(Silicon Dioxide)	0.0000	0.0000	0.0028	1.0000

2) Flame-TEOS

Table A.14: Input Data for Flame Synthesis using TEOS

Stream Name	TEOS-Ar	Argon	Hydrogen	Oxygen	Air	Product	Waste
Type	Inlet	Inlet	Inlet	Inlet	Inlet	Product	Waste
Flow Rate	3.14E-01	1.06E-01	3.21E-02	1.29E+00	4.93E+00	6.00E+00	6.32E+00
X(TEOS)	0.6600	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X(Argon)	0.3400	1.0000	0.0000	0.0000	0.0000	0.0000	0.0340
X(Hydrogen)	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
X(Oxygen)	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.1020
X(Air)	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.7810
X(CarbonDioxide)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0550
X(Water)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0550
X(SiliconDioxide)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000

3) Flame-HMDSO

Table A.15: Input Data for Flame Synthesis using HMDSO

Name	Argon	Methane	Oxygen	Waste Gas	Product
Type	Inlet	Inlet	Inlet	Outlet Waste	Product
Flow Rate	6.30E-02	2.00E-02	4.80E-01	3.22E-01	2.50E-02
X(Silicon Dioxide)	0.0000	0.0000	0.0000	0.0000	1.0000
X(Argon)	0.4700	0.0000	0.0000	0.0928	0.0000
X(Methane)	0.0000	1.0000	0.0000	0.0000	0.0000
X(Oxygen)	0.0000	0.0000	1.0000	0.5582	0.0000
X(Carbon Dioxide)	0.0000	0.0000	0.0000	0.3490	0.0000
X(HMDSO)	0.5300	0.0000	0.0000	0.0000	0.0000

4) Weighting profile: The following weights were used for the three method

Table A.16: Weighting profile:

Category	**HTPI**	**HTPE**	**TTP**	**ATP**	**GWP**	**ODP**	**PCOP**	**AP**
Weight	1	1	1	1	1	1	1	1

5) Product streams and Energy usage were not included in the calculations.

A.3 NAIADE Calculations

Tables S17-S22 depict the steps involved in the NAIADE calculations namely, determining the semantic distance, pairwise comparison of alternatives, preference intensity index and the corresponding entropy.

The three processes are labeled as following,

A. Sol-Gel Synthesis.

B. Flame TEOS

C. Flame HMDSO

Table A.17: Semantic distance from pairwise comparison

Parameters	(A,B)		(A,C)		(B,C)	
	Expected Value Difference	Semantic Distance	Expected Value Difference	Semantic Distance	Expected Value Difference	Semantic Distance
Yield	-59.3	-59.3	-24.3	-24.3	-35.0	-35.0
Particle Size	-0.3000	0.2940	-0.2000	0.2026	0.1000	0.1303
Cost per unit	34.94	34.94	35.04	35.04	0.10	0.10
Chemical Safety Index	-11.0	-11.0	-4.0	-4.0	7.0	7.0
Process Safety Index	-4	-4	-3	-3	1	1
Material Procurement	627.3	627.3	715.88	715.88	88.58	88.58
Generation of Waste	899.0	899.0	991.12	991.12	92.12	92.12
Hazardous Material	0.2537	0.2406	0.1537	0.1550	-0.1000	0.1222
% Atom Economy	-1.1010	-1.1010	-2.4400	-2.4400	-3.5410	-3.5410
Solvent Index	0.0791	0.0791	0.0791	0.0791	0.0000	0.0000
PEI	869.9979	869.9979	869.9984	869.9984	0.0005	0.0005

Table A.18: Preference Relation Functions between Alternatives A and B

(A, B)	$\mu_{\gg}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{\ll}$
Yield	0.0000	0.0000	0.0000	0.0000	0.9974	0.9962
Particle Size	0.0000	0.0000	0.3211	0.0000	0.5902	0.3763
Cost per unit	0.0000	0.0000	0.0000	0.0000	0.9927	0.9892
Chemical Safety Index	0.8988	0.9308	0.0221	0.0000	0.0000	0.0000
Process Safety Index	0.5000	0.6400	0.2500	0.0000	0.0000	0.0000
Material Procurement	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Generation of Waste	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Hazardous Material	0.0000	0.0000	0.3946	0.0009	0.5074	0.2827
%Atom Economy	0.0239	0.1187	0.6828	0.4316	0.0000	0.0000
Solvent Index	0.0000	0.0000	0.9730	0.9957	0.0007	0.0000
PEI	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000

Table A.19: Preference Relation Functions between Alternatives A and C

(A, C)	$\mu_{\gg}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{\ll}$
Yield	0.0000	0.0000	0.0002	0.0000	0.9850	0.9779
Particle Size	0.0000	0.0000	0.4734	0.0106	0.3902	0.1711
Cost per unit	0.0000	0.0000	0.0000	0.0000	0.9927	0.9893
Chemical Safety Index	0.5000	0.6400	0.2500	0.0000	0.0000	0.0000
Process Safety Index	0.3317	0.5000	0.3536	0.0020	0.0000	0.0000
Material Procurement	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Generation of Waste	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Hazardous Material	0.0000	0.0000	0.5862	0.0981	0.2744	0.0866
% AtomEconomy	0.0000	0.0000	0.4293	0.0161	0.3981	0.2239
Solvent Index	0.0000	0.0000	0.9730	0.9957	0.0007	0.0000
PEI	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000

Table A.20: Preference Relation Functions between Alternatives B and C

(B, C)	$\mu_{\gg}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{\ll}$
Yield	0.9893	0.9927	0.0000	0.0000	0.0000	0.0000
Particle Size	0.0225	0.1379	0.6256	0.1668	0.0000	0.0000
Cost per unit	0.0000	0.0000	0.9659	0.9931	0.0011	0.0000
Chemical Safety Index	0.0000	0.0000	0.0884	0.0000	0.8448	0.7759
Process Safety Index	0.0000	0.0000	0.7071	0.5000	0.1000	0.0172
Material Procurement	0.0000	0.0000	0.0000	0.0000	0.9989	0.9983
Generation of Waste	0.0000	0.0000	0.0000	0.0000	0.9989	0.9984
Hazardous Material	0.0225	0.1379	0.6119	0.1403	0.0000	0.0000
% Atom Economy	0.0000	0.0000	0.2931	0.0002	0.5821	0.4280
Solvent Index	0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
PEI	0.0000	0.0000	0.9998	1.0000	0.0000	0.0000

Table A.21: Preference Intensity Indices between Alternatives after Aggregation.

Aggregation of Criteria	$\mu_{\gg}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{\ll}$
(A,B)	0.1434	0.1813	0.2468	0.1484	0.6727	0.6317
(A,C)	0.0265	0.0863	0.2818	0.1333	0.6902	0.6073
(B,C)	0.1297	0.1373	0.6080	0.4316	0.4034	0.3652

Table A.22: Entropy Level Associated with the Preference Intensity Indices.

Entropy	$H_{\gg}$	$H_{>}$	$H_{\cong}$	$H_{==}$	$H_{<}$	$H_{\ll}$
(A,B)	0.1339	0.1187	0.0982	0.0933	0.1877	0.0112
(A,C)	0.0909	0.1766	0.2856	0.0037	0.0159	0.0218
(B,C)	0.0078	0.0057	0.2733	0.0963	0.1480	0.1625

Appendix B

Supporting Information for Chapter 6

Table B.1: Experimental Design

Size	Toxicity	Airborne Capacity	Detection Limit	Exposure Limit	Quantity	Engineering Controls	No of Employees	Duration of Exposure	Multiple Exposure
100-500 nm	Low	None	Good	0.2-0.5	1000-10000	Closed	101-500	1-5 hr	1-3
2-10 nm	Moderate	Low	Poor	0.2-0.5	1-100	Open-PP	11-50	< 15 min	1-3
2-10 nm	Low	Moderate	Moderate	0.1-0.2	< 1	Closed-NP	1-3	< 1 hr	> 3
500-1000	Moderate	None	None	0.1-0.2	1000-10000	Open-PP	3-10	< 1 hr	1-3
500-1000	Moderate	High	Moderate	0.5-1.0	< 1	Open-NP	101-500	5-8 hr	None
100-500 nm	Low	High	Moderate	0.2-0.5	1000-10000	Open-NP	51-100	< 1 hr	> 3
100-500 nm	Moderate	Moderate	Good	> 1.0	100-1000	Closed-NP	101-500	5-8 hr	None
< 2nm	High	High	None	0.2-0.5	< 1	Open-NP	3-10	1-5 hr	Unknown Number
< 2nm	High	Low	None	> 1.0	1-100	Closed	101-500	< 15 min	> 3
>1000	Low	High	None	> 1.0	1-100	Closed	3-10	5-8 hr	Unknown Number
2-10 nm	High	None	Good	< 0.1	< 1	Open-PP	3-10	incidental	Unknown Number
10-100 nm	Low	Low	None	0.5-1.0	>10,000	Open-PP	51-100	incidental	Unknown Number
500-1000	Moderate	High	None	> 1.0	< 1	Closed	51-100	incidental	Unknown Number
10-100 nm	Low	Low	Poor	0.1-0.2	100-1000	Open-NP	11-50	< 1 hr	Unknown Number
100-500 nm	High	High	Poor	< 0.1	< 1	Closed-NP	11-50	< 1 hr	None
<2nm	Moderate	Low	Good	0.2-0.5	>10,000	Closed	1-3	< 1 hr	> 3
100-500 nm	Moderate	None	Poor	> 1.0	>10,000	Open-PP	1-3	5-8 hr	1-3
< 2nm	High	None	Moderate	0.5-1.0	100-1000	Closed-NP	101-500	< 1 hr	Unknown Number
10-100 nm	Moderate	High	None	0.1-0.2	1-100	Closed	51-100	< 1 hr	Unknown Number
2-10 nm	Low	High	Moderate	< 0.1	>10,000	Open-PP	11-50	1-5 hr	Unknown Number
100-500 nm	High	High	Moderate	0.2-0.5	1-100	Open-PP	11-50	< 15 min	Unknown Number
2-10 nm	Moderate	High	None	< 0.1	100-1000	Open-NP	11-50	5-8 hr	> 3
500-1000	Low	Moderate	Good	< 0.1	1000-10000	Open-NP	1-3	< 15 min	Unknown Number
100-500 nm	Low	High	Good	> 1.0	1000-10000	Closed-NP	1-3	< 1 hr	Unknown Number
10-100 nm	Low	None	Good	< 0.1	100-1000	Closed	3-10	5-8 hr	> 3

Size	Toxicity	Airborne Capacity	Detection Limit	Exposure Limit	Quantity	Engineering Controls	No of Employees	Duration of Exposure	Multiple Exposure
10-100 nm	Low	Low	Poor	0.5-1.0	1000-10000	Closed	3-10	5-8 hr	None
10-100 nm	Low	Moderate	Poor	0.2-0.5	< 1	Open-PP	101-500	incidental	1-3
100-500 nm	High	Low	None	0.5-1.0	< 1	Open-NP	1-3	5-8 hr	Unknown Number
10-100 nm	Moderate	Low	Good	0.5-1.0	1000-10000	Open-NP	101-500	1-5 hr	1-3
2-10 nm	Low	None	Good	0.2-0.5	1-100	Closed-NP	51-100	5-8 hr	1-3
<2nm	Moderate	High	Poor	0.2-0.5	1-100	Closed-NP	101-500	incidental	> 3
100-500 nm	Moderate	Low	Poor	< 0.1	100-1000	Closed-NP	1-3	1-5 hr	Unknown Number
< 2nm	Moderate	Low	None	< 0.1	1000-10000	Closed	11-50	5-8 hr	1-3
>1000	High	High	Moderate	0.5-1.0	1000-10000	Closed-NP	51-100	< 15 min	> 3
< 2nm	Low	High	Good	0.5-1.0	>10,000	Open-PP	3-10	< 15 min	None
>1000	Low	None	Moderate	0.5-1.0	< 1	Closed	11-50	1-5 hr	Unknown Number
2-10 nm	High	None	Poor	0.2-0.5	1000-10000	Closed	1-3	1-5 hr	None
>1000	High	Low	Good	0.2-0.5	< 1	Open-PP	51-100	5-8 hr	None
>1000	Low	None	Moderate	0.1-0.2	1-100	Closed	101-500	1-5 hr	None
< 2nm	Low	High	Moderate	< 0.1	>10,000	Open-PP	101-500	5-8 hr	1-3
>1000	High	Low	Poor	< 0.1	1000-10000	Open-PP	11-50	incidental	Unknown Number
< 2nm	Low	Low	Moderate	0.1-0.2	100-1000	Open-NP	3-10	incidental	None
500-1000	Low	High	None	0.2-0.5	100-1000	Closed	11-50	< 15 min	None
2-10 nm	Moderate	High	Good	> 1.0	< 1	Open-PP	11-50	< 1 hr	None
100-500 nm	Low	Low	Moderate	> 1.0	1-100	Open-NP	101-500	< 15 min	Unknown Number
>1000	Low	Low	None	< 0.1	< 1	Closed-NP	101-500	< 15 min	None
>1000	Low	Moderate	Moderate	0.1-0.2	100-1000	Open-PP	51-100	1-5 hr	1-3
100-500 nm	Low	Moderate	Poor	0.2-0.5	>10,000	Closed-NP	3-10	1-5 hr	1-3
2-10 nm	Moderate	Moderate	Good	0.1-0.2	>10,000	Open-PP	101-500	< 15 min	Unknown Number
10-100 nm	Low	High	Poor	0.2-0.5	100-1000	Open-PP	1-3	5-8 hr	Unknown Number

Size	Toxicity	Airborne Capacity	Detection Limit	Exposure Limit	Quantity	Engineering Controls	No of Employees	Duration of Exposure	Multiple Exposure
>1000	Low	High	None	> 1.0	100-1000	Closed	1-3	< 15 min	1-3
100-500 nm	High	None	Poor	0.1-0.2	100-1000	Closed	101-500	incidental	> 3
500-1000	High	Low	Moderate	< 0.1	>10,000	Open-PP	101-500	< 1 hr	None
100-500 nm	Low	None	Good	0.5-1.0	1-100	Open-PP	1-3	< 1 hr	> 3
>1000	High	Moderate	Poor	> 1.0	>10,000	Open-NP	11-50	5-8 hr	None
10-100 nm	High	None	Good	0.5-1.0	>10,000	Open-NP	11-50	< 15 min	None
100-500 nm	Moderate	Low	Good	< 0.1	1-100	Closed	51-100	1-5 hr	None
500-1000	Moderate	Moderate	None	0.2-0.5	< 1	Open-NP	1-3	5-8 hr	1-3
10-100 nm	Moderate	None	Moderate	0.2-0.5	100-1000	Closed	11-50	< 1 hr	Unknown Number
>1000	Moderate	None	Poor	< 0.1	>10,000	Open-NP	3-10	< 1 hr	Unknown Number
< 2nm	High	Moderate	Good	> 1.0	>10,000	Closed	51-100	1-5 hr	Unknown Number
2-10 nm	Low	Moderate	None	< 0.1	1000-10000	Closed-NP	51-100	< 15 min	None
500-1000	Low	Low	Poor	> 1.0	< 1	Closed	51-100	< 1 hr	1-3
< 2nm	Low	Moderate	Good	0.1-0.2	< 1	Closed	11-50	incidental	None
< 2nm	Low	Moderate	Poor	< 0.1	1-100	Open-NP	3-10	< 1 hr	1-3
>1000	High	High	Good	0.1-0.2	100-1000	Open-NP	101-500	5-8 hr	1-3
500-1000	Moderate	Moderate	Moderate	0.5-1.0	1-100	Closed-NP	3-10	1-5 hr	Unknown Number
>1000	Moderate	Moderate	Moderate	> 1.0	1000-10000	Open-PP	1-3	incidental	> 3
500-1000	Low	Low	Good	0.5-1.0	100-1000	Open-PP	1-3	incidental	1-3
2-10 nm	High	Low	Moderate	> 1.0	1-100	Open-NP	1-3	incidental	1-3
2-10 nm	Moderate	Moderate	Poor	0.5-1.0	100-1000	Closed	51-100	< 15 min	> 3
500-1000	High	Low	Good	> 1.0	>10,000	Closed	101-500	1-5 hr	> 3
>1000	Moderate	Moderate	Moderate	0.2-0.5	100-1000	Closed-NP	3-10	< 15 min	Unknown Number
>1000	Moderate	High	Poor	0.5-1.0	1000-10000	Closed	1-3	incidental	None
100-500 nm	High	None	Moderate	< 0.1	1000-10000	Closed	3-10	< 15 min	1-3

Size	Toxicity	Airborne Capacity	Detection Limit	Exposure Limit	Quantity	Engineering Controls	No of Employees	Duration of Exposure	Multiple Exposure
500-1000	Low	Low	None	0.1-0.2	>10,000	Closed-NP	3-10	incidental	> 3
500-1000	Moderate	None	Moderate	0.2-0.5	1-100	Open-PP	3-10	5-8 hr	None
>1000	Moderate	None	None	< 0.1	1-100	Open-NP	1-3	< 1 hr	None
100-500 nm	High	Moderate	None	0.1-0.2	1-100	Open-PP	11-50	5-8 hr	> 3
2-10 nm	Low	None	None	0.5-1.0	< 1	Open-PP	101-500	1-5 hr	> 3
500-1000	Low	High	Poor	0.1-0.2	1-100	Closed-NP	1-3	1-5 hr	None
10-100 nm	Moderate	High	Good	< 0.1	1-100	Closed-NP	101-500	incidental	> 3
500-1000	Low	None	Poor	0.2-0.5	>10,000	Open-NP	51-100	< 15 min	> 3
< 2nm	High	Low	Moderate	0.2-0.5	100-1000	Open-NP	1-3	1-5 hr	None
< 2nm	Low	None	Poor	> 1.0	1000-10000	Closed-NP	11-50	incidental	None
>1000	Low	Moderate	Good	0.5-1.0	1-100	Open-NP	11-50	< 1 hr	> 3
500-1000	High	Moderate	Poor	0.1-0.2	1000-10000	Closed-NP	101-500	5-8 hr	Unknown Number
< 2nm	High	Moderate	None	0.5-1.0	1000-10000	Open-PP	51-100	< 1 hr	1-3
10-100 nm	Moderate	Low	Moderate	> 1.0	< 1	Closed-NP	11-50	< 15 min	1-3
10-100 nm	Moderate	Moderate	Poor	> 1.0	< 1	Open-NP	3-10	1-5 hr	> 3
2-10 nm	High	Low	Poor	0.5-1.0	1-100	Closed	3-10	5-8 hr	Unknown Number
10-100 nm	High	None	None	0.1-0.2	>10,000	Closed-NP	1-3	< 15 min	None
500-1000	High	Moderate	Good	< 0.1	1-100	Closed	1-3	< 15 min	Unknown Number
500-1000	High	High	Poor	< 0.1	100-1000	Open-NP	51-100	1-5 hr	> 3
100-500 nm	Moderate	High	Good	0.1-0.2	< 1	Open-NP	3-10	< 15 min	1-3
10-100 nm	High	High	Good	> 1.0	1000-10000	Open-PP	3-10	1-5 hr	> 3
10-100 nm	High	Moderate	Poor	> 1.0	1-100	Open-PP	51-100	< 1 hr	None
< 2nm	Low	Low	Good	0.1-0.2	1000-10000	Closed-NP	51-100	5-8 hr	Unknown Number
500-1000	High	None	Good	0.5-1.0	100-1000	Closed-NP	11-50	incidental	1-3
< 2nm	Moderate	None	None	> 1.0	100-1000	Open-PP	51-100	1-5 hr	None

Size	Toxicity	Airborne Capacity	Detection Limit	Exposure Limit	Quantity	Engineering Controls	No of Employees	Duration of Exposure	Multiple Exposure
2-10 nm	High	High	Good	0.1-0.2	1-100	Open-NP	51-100	incidental	1-3
10-100 nm	Low	None	Moderate	< 0.1	< 1	Closed-NP	51-100	5-8 hr	> 3
2-10 nm	Moderate	High	Moderate	0.1-0.2	1000-10000	Closed	3-10	< 1 hr	None
100-500 nm	High	Moderate	None	0.5-1.0	100-1000	Open-PP	3-10	incidental	None
2-10 nm	Low	None	None	> 1.0	1000-10000	Open-NP	101-500	incidental	Unknown Number
10-100 nm	High	High	None	0.1-0.2	>10,000	Closed-NP	1-3	1-5 hr	1-3
>1000	High	Low	Good	0.2-0.5	< 1	Closed-NP	3-10	< 1 hr	> 3
< 2nm	High	None	Poor	0.1-0.2	< 1	Open-PP	1-3	< 15 min	> 3
100-500 nm	Low	Moderate	None	0.2-0.5	>10,000	Closed	11-50	incidental	> 3
< 2nm	Moderate	None	None	0.5-1.0	1-100	Closed-NP	11-50	1-5 hr	1-3
100-500 nm	Moderate	Low	Moderate	0.1-0.2	>10,000	Open-NP	51-100	incidental	None
< 2nm	Moderate	None	Poor	0.1-0.2	< 1	Open-NP	51-100	< 15 min	Unknown Number
2-10 nm	High	Low	None	> 1.0	100-1000	Closed-NP	3-10	< 1 hr	1-3
>1000	Moderate	None	Good	0.2-0.5	>10,000	Closed-NP	51-100	incidental	Unknown Number
>1000	Moderate	Low	None	0.1-0.2	1000-10000	Open-PP	11-50	1-5 hr	> 3
>1000	High	High	Poor	0.5-1.0	>10,000	Closed	101-500	< 1 hr	1-3
500-1000	High	None	Moderate	> 1.0	1000-10000	Open-NP	11-50	5-8 hr	> 3
2-10 nm	Moderate	Moderate	Moderate	0.5-1.0	>10,000	Closed	1-3	5-8 hr	> 3
10-100 nm	High	Moderate	None	0.2-0.5	1000-10000	Open-NP	101-500	< 1 hr	None
10-100 nm	High	Moderate	Moderate	< 0.1	< 1	Closed	1-3	incidental	1-3

Table B.2: Survey Response Data

Y01	Y02	Y03	Y04	Y05	Y06	Y07	Y08	Y09	Y10	Y11	Y12	Y13	Y14	Y15	Y16
5	4	4	3	3	3	4	4	4	4	4	5	4	3	4	4
5	5	5	5	4	4	5	5	5	5	5	5	5	5	5	5
5	4	5	4	4	4	5	5	4	5	5	5	5	4	5	5
5	4	5	4	4	4	5	4	3	5	5	5	4	4	5	4
5	4	5	5	4	4	5	4	4	4	5	5	4	4	5	4
5	5	5	5	1	3	5	5	3	3	5	5	3	3	5	3
5	3	5	3	3	1	3	3	3	3	5	5	3	3	5	3
5	5	5	5	3	5	5	5	3	5	5	5	5	5	5	5
5	5	5	3	3	3	3	5	3	5	5	5	3	3	5	5
5	1	5	3	1	1	3	3	3	3	5	5	3	3	5	5
5	3	5	3	1	1	5	3	3	3	5	5	3	3	5	5
5	1	5	3	1	1	5	3	3	3	5	5	3	3	5	3
5	5	5	3	3	3	3	3	3	5	5	5	3	3	5	3
5	3	5	3	3	3	5	3	3	5	5	5	3	3	5	3
5	3	5	3	3	3	5	3	3	5	5	5	3	3	5	5
5	3	5	3	3	3	3	3	3	5	5	5	3	3	5	5
5	3	5	3	3	3	5	1	3	3	5	5	3	3	5	3
5	5	5	3	3	3	3	3	3	5	5	5	5	3	5	5
5	3	5	3	3	3	3	5	3	5	5	5	3	3	5	5
5	5	5	5	5	3	5	5	5	5	5	5	5	3	5	5
5	3	5	5	3	3	5	5	5	5	5	5	5	3	5	5
5	5	5	5	5	3	5	5	3	5	5	5	5	5	5	5
5	3	5	5	3	1	3	3	3	3	5	5	3	3	5	3
5	5	5	3	3	3	3	5	3	5	5	5	3	3	5	3
5	3	5	3	3	3	3	3	3	3	5	5	3	3	5	3

Y01	Y02	Y03	Y04	Y05	Y06	Y07	Y08	Y09	Y10	Y11	Y12	Y13	Y14	Y15	Y16
5	1	1	1	5	1	5	5	5	1	1	5	5	5	5	3
5	1	1	1	5	1	5	5	5	1	1	5	5	5	5	3
5	3	1	3	5	1	5	5	5	1	1	5	5	5	5	4
5	1	1	1	5	1	5	5	5	1	1	5	5	5	5	3
5	1	1	1	5	1	5	5	5	1	1	5	5	5	5	3
5	5	5	3	3	3	5	5	3	5	3	5	5	5	3	3
3	3	3	1	1	1	1	1	1	3	5	3	3	1	1	3
5	5	5	3	3	5	5	3	3	5	5	5	5	5	3	3
1	1	3	3	1	3	3	3	1	3	5	3	3	3	3	3
5	3	3	1	1	3	5	3	3	5	5	3	5	3	3	1
1	1	1	1	1	1	3	1	1	1	5	3	3	1	1	3
5	3	5	3	3	5	5	3	1	5	5	5	3	3	3	1
3	1	3	1	1	3	3	1	1	3	5	3	3	1	3	1
3	1	3	1	1	1	3	1	1	3	5	3	3	1	1	3
5	5	5	3	3	5	5	3	3	5	5	5	5	3	5	3
3	3	3	1	1	1	3	1	1	3	5	3	3	1	1	1
3	1	1	1	1	3	3	1	1	3	5	3	3	1	1	1
3	1	1	1	1	1	3	1	1	5	5	3	3	1	1	1
5	1	1	1	1	3	3	1	1	3	5	1	3	1	1	1
3	1	1	1	1	1	1	1	1	1	3	1	1	1	1	1
4	3	3	3	1	2	4	4	3	1	2	5	5	4	4	3
4	4	3	3	1	2	4	3	3	1	2	5	5	3	4	3
5	4	4	3	1	2	3	5	4	2	3	5	5	4	5	5
5	4	5	4	4	4	3	5	5	4	5	5	5	5	5	5
5	4	5	4	4	4	3	5	5	4	4	5	5	5	5	5

Y01	Y02	Y03	Y04	Y05	Y06	Y07	Y08	Y09	Y10	Y11	Y12	Y13	Y14	Y15	Y16
5	5	5	5	1	3	5	5	5	5	3	5	5	5	5	5
5	5	5	3	1	3	5	5	1	1	3	5	5	5	5	5
5	5	5	5	1	1	5	5	5	3	3	5	5	5	5	5
5	3	5	3	1	3	5	3	1	1	3	5	5	3	5	5
5	5	5	3	3	3	5	5	1	1	5	5	5	5	5	5
5	5	5	3	1	3	5	5	5	3	3	5	5	5	5	5
5	3	5	3	1	1	5	5	5	3	3	5	5	3	5	5
5	1	5	1	1	3	1	3	1	1	3	5	5	3	5	5
5	5	5	3	3	3	5	3	1	1	5	5	5	3	5	5
5	5	5	1	1	3	5	3	1	1	5	5	5	3	5	5
5	4	1	1	1	1	5	1	1	1	1	5	5	1	5	3
5	1	1	1	1	1	5	1	1	1	1	5	5	1	5	3
5	1	1	1	1	1	5	5	1	1	1	5	5	3	5	5
5	1	1	1	1	1	5	1	1	1	1	5	5	1	5	5
5	1	1	1	1	1	5	1	1	1	1	5	5	1	5	5
2	3	3	2	2	3	3	2	2	4	4	3	3	3	3	3
3	3	3	2	2	2	3	2	2	3	4	3	3	3	3	3
1	1	3	2	1	2	2	2	2	2	4	2	3	2	2	2
1	2	3	2	1	2	2	2	2	2	4	3	3	2	2	3
4	4	3	3	3	3	3	3	3	4	4	3	3	4	4	3
5	1	5	1	1	1	5	5	1	1	1	5	5	5	5	5
5	1	5	1	1	3	5	5	1	1	3	5	5	5	5	5
5	1	5	1	1	1	5	3	1	1	3	5	5	3	5	5
5	1	5	5	3	3	5	5	5	3	3	5	5	5	5	5
5	5	5	5	1	3	5	5	1	1	5	5	5	3	5	5

Y01	Y02	Y03	Y04	Y05	Y06	Y07	Y08	Y09	Y10	Y11	Y12	Y13	Y14	Y15	Y16
3	3	4	1	1	1	1	1	1	1	1	4	4	1	5	5
3	3	3	1	1	1	1	1	1	1	1	4	4	1	5	5
3	3	3	1	1	1	1	1	1	1	4	4	4	1	5	5
3	3	3	1	1	1	1	1	1	1	1	4	4	1	5	5
4	4	3	1	1	1	1	1	1	1	1	5	5	1	5	5
5	5	5	5	3	2	5	3	5	5	5	5	5	5	5	5
5	5	5	4	4	2	5	4	5	5	5	5	5	5	5	5
5	5	5	2	2	2	5	3	5	5	5	5	5	3	5	5
5	5	5	3	3	3	5	3	5	5	5	5	5	3	5	5
5	5	5	3	2	2	5	3	5	5	5	5	5	2	5	5
5	4	3	4	4	1	5	5	4	4	5	5	5	4	5	4
5	4	4	4	4	1	5	5	4	4	5	5	5	4	5	5
5	4	3	5	5	3	5	5	4	4	5	5	5	5	5	5
5	5	3	5	5	3	5	5	4	4	5	5	5	5	5	5
5	4	3	5	5	3	5	5	4	4	5	5	5	5	5	5
5	5	1	5	3	3	5	3	1	1	3	5	3	5	3	5
5	3	1	3	3	1	5	3	3	5	3	5	3	1	5	5
5	1	1	1	3	3	5	3	3	5	3	5	3	3	5	5
5	5	1	3	3	3	5	3	3	5	3	5	3	3	5	5
5	5	1	3	3	3	5	3	3	3	5	5	3	3	5	5
5	5	3	3	3	3	5	5	4	4	4	5	5	5	5	5
5	5	4	4	4	4	5	5	4	4	4	5	5	5	5	5
5	5	4	4	4	4	5	3	4	4	4	5	5	5	5	5
5	3	3	3	3	3	5	5	3	3	3	5	5	5	5	5
5	4	4	3	4	4	5	5	4	4	4	5	5	5	5	5

Y01	Y02	Y03	Y04	Y05	Y06	Y07	Y08	Y09	Y10	Y11	Y12	Y13	Y14	Y15	Y16
5	5	3	5	3	3	5	3	1	1	1	5	5	5	5	5
5	5	3	5	1	3	5	3	3	3	3	5	5	3	5	5
5	5	5	5	3	3	1	1	3	3	3	5	5	5	5	5
5	5	5	5	3	3	3	3	3	3	3	5	5	5	5	5
5	5	5	5	3	3	5	5	3	3	3	5	5	5	5	5
5	5	5	5	3	3	5	5	3	3	3	5	5	5	5	5
5	3	5	3	1	1	5	5	3	3	3	3	5	5	3	3
5	3	3	3	1	1	5	5	3	3	3	5	5	5	5	5
5	5	5	5	3	3	3	1	3	3	3	5	5	5	5	5
5	5	5	3	1	3	5	5	1	1	1	5	5	5	5	5
5	5	4	5	1	5	5	5	2	2	5	5	5	5	5	5
5	5	5	5	5	5	5	5	5	1	5	5	5	5	5	5
5	5	5	5	5	5	5	5	5	1	5	5	5	5	5	5
5	5	1	5	1	1	3	3	1	1	5	5	5	5	5	5
5	5	5	5	5	5	1	5	5	1	5	5	5	5	5	5
5	5	5	5	3	3	3	5	3	5	5	5	5	5	5	5
5	5	5	5	3	3	5	5	3	5	5	5	5	5	5	5
5	5	5	3	3	3	5	3	3	3	5	5	5	3	5	3
5	5	5	3	3	3	3	1	1	1	5	5	5	3	5	5
5	5	5	3	3	3	3	3	3	3	5	5	5	3	5	5

Vita

Sasikumar Naidu was born in Madras (Chennai), Tamil Nadu, India and grew up in Kalina, Bombay(Mumbai), India. He completed his schooling from St. Mary's High School, Kalina, Mumbai. He earned his bachelor's degree in chemistry from the University of Mumbai and master's degree in chemistry from the Indian Institute of Technology(IIT), Bombay in 2001. He came to United States of America for his doctoral studies and completed his doctoral degree in industrial engineering and simultaneously a master's degree in statistics at the University of Tennessee, Knoxville.