# NONLINEAR OPTIMIZATION FOR MANAGING OCCUPATIONAL EXPOSURE RISKS IN THE NANOMATERIAL MANUFACTURING WORKPLACE UNDER UNCERTAINTY

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complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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# ABSTRACT

Critical environmental and human health concerns are associated with the rapidly growing fields of nanotechnology and Engineered nanomaterials (ENMs). The main risk arises from occupational exposure via chronic inhalation of nanoparticles. This research presents a fuzzy chance-constrained nonlinear programming (FCCNLP) optimization approach, which is developed to maximize the nanomaterial production and minimize the risks of workplace exposure to ENMs. The FCCNLP method integrates fuzzy mathematical programming (FMP) and chance-constrained programming (CCP) into nonlinear programming (NLP) optimization framework, and could be used to deal with uncertainties expressed as not only probability distributions and fuzzy values associated with components of constraints but ambiguity of the objective function as well.

The FCCNLP method was examined through a single-walled carbon nanotube (SWNT) manufacturing process. Solutions of the compromise decision alternatives associated with different risk levels of relaxed constraint violations were obtained. This study confirmed that a high level control strategy through strict occupational exposure limits (OELs) combined with a high enforcement of OELs would lower the nanomaterial exposure risks to workers. The related cost and nanomaterial production have also been optimized for different operational scenarios under multi-layer system uncertainties. The results were helpful for decision makers to identify desirable schemes under uncertainties to maximize the economic benefits and ensure workplace safety through minimizing the nanomaterial-related health risks. The developed technology has technical novelty to help finding cost-effective measures for the sustainable development of nanotechnology.

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# LIST OF SYMBOLS

| | |
|---|---|
| $X$ | a fuzzy set |
| $L_\alpha(x)$ | a fuzzy membership function |
| $A$ | right-side coefficients of constraints |
| $\tilde{b}$ | left-side coefficients of constraints |
| $\tilde{c}_i$ | objective-function constraints |
| $\alpha$ | predetermined confidence levels of the constraint |
| $\lambda$ | the degree of objective function constraint-satisfaction |
| $f^+$ | upper bound of objective's aspiration level |
| $f^-$ | lower bound of objective's aspiration level |
| $b_i^+$ | the permissible maximal values of constraints |
| $b_i^-$ | the permissible minimal values of constraints |
| $x_1$ | the feed rate of $Fe(CO)_5$ (g/hr) |
| $x_2$ | the feed rate of CO (g/hr) |
| $x_3$ | the SWNT material production rate (g/hr) |
| P | the revenue from each gram of SWNT manufactured ($/g) |
| $q_1$ | the cost of $Fe(CO)_5$ for each gram of SWCNT produced ($/g) |
| $q_2$ | the cost of CO for each gram of SWCNT produced ($/g) |
| F | the total costs of SWCNT except for the raw materials ($/g) |
| $C_i$ | the exposure control cost |

| | |
|---|---|
| N | the number of production lines |
| Hr | the working hours per day (hours/day) |
| SPY | the synthesized product (carbon nanotube) yield (%) |
| PY | the SWCNT purification yield (%) |
| D | the working days per year (days/year) |
| $a_{11}$ | the percentages of $Fe(CO)_5$ used to synthesize SWCNTs (%) |
| $a_{12}$ | the percentages of CO used to synthesize SWCNTs (%) |
| $PV_1$ | the minimum production volume of SWCNTS per year (g/yr) |
| $PV_2$ | the maximum production volume of SWCNTS per year (g/yr) |
| $\eta_i$ | the removal efficiency of MNMs emissions (%) |
| $e_1$ | the emission coefficients of nano-sized Fe |
| $e_2$ | the emission coefficients of CO |
| $e_3$ | the emission coefficients of SWCNTs |
| V | the volume of the workplace ($m^3$) |
| Con | the estimated concentration of pollutant ($\mu g/m^3 \cdot h$ or $mg/m^3 \cdot h$) |
| Tr | the transformation factor |

# LIST OF ACRONYMS

| | |
|---|---|
| CCP | chance-constrained programming |
| CVP | chemical vapor process |
| ENMs | Engineered nanomaterials |
| EPA | Environmental Protection Agency |
| FMP | fuzzy mathematical programming |
| FCCNLP | fuzzy chance-constrained nonlinear programming |
| HiPco | high-pressure carbon monoxide |
| LCA | Life cycle assessment |
| LP | linear programming |
| NELs | no-effect levels |
| NIOSH | National Institute for Occupational Safety and Health |
| NLP | nonlinear programming |
| NOAEL | no observed adverse effect level |
| REL | recommended exposure limit |
| SWNT | single-wall carbon nanotube |
| OELs | occupational exposure limits |

# Chapter 1 INTRODUCTION

## 1.1. Overview

Engineered nanomaterials (ENMs) are man-made particles having at least one dimension of rougly 1-100 nm (EPA, 2007). ENMs have been employed in a wide spectrum of industrial sectors during recent years, including energy, medicine, electronics, environmental protection, cosmetics, food, agriculture and many other areas. This is due to their unique properties, such as small size and associated large surface area to mass ratio, increased surface reactivity, and altered physic-chemical properties (Savolainen et al., 2010; Bhatt and Tripathi, 2011; Biskos and Schmidt, 2012). The unique chemical and physical properties of ENMs have raised issues regarding occupational health and safety (EHS) in manufacturing facilities (Derk, 2010), particularly when handled in large amounts (Maynard and Aitken, 2007). ENMs can be released to the occupational atmosphere during industries producing processes, where ENMs are synthesized, purified, and packaged, thereby becoming commercial products. As a result, ENMs can enter worker‘s body through inhalation, skin contact and ingestion during manufacturing (Aschberger et al., 2011). Recent publications indicate that chronic occupational exposure to ENPs may lead to a number of negative health and reproductive problems, including hepatic injury (Kobayashi et al., 2009; Myojo et al., 2010; Paur et al., 2011), genotoxicity (Kumar et al., 2011; Hackenberg et al., 2011), carcinogenicity (Ress et al., 2003; Roller, 2009), cytotoxicity (apoptosis) and risks of cardiovascular diseases (Wilson et al., 2007; Shvedova et al., 2012), and reproduction damage (Zhu et al., 2010; Lapresta-Fernandez et al., 2010).

So far, relatively few publications approach directly modelling ENMs occupational exposure risks, which include Monte Carlo models that compare various levels of environmental health and safety (EHS) standards for single wall carbon nanotube (SWCNT) manufacturing (Ok et al., 2008), and expert opinions on development of exposure-response functions for nanomaterials (Kandlkar et al., 2007). To minimize the risks of ENM to workers‘ health as well as to maximize their economic benefits, optimization models are effective tools to model ENMs manufacturing processes. Usually, optimization algorithms involve geometric programming, dynamic programming, linear programming methods (Zuperl et al., 2004). However, most ENMs-producing processes are complex systems with inherent nonlinearities, where the systems are best described by nonlinear optimization method (Slotine and Li, 1991).

Previously, nonlinear programming (NLP) has been widely employed to technological optimization of various processes, such as agriculture (Ostafiev et al., 1984; Kalampoukas and Dervakos, 1996), electronic-industry (Chen and Wang, 2009; Liu et al., 2011), and construction (Kravanja and Silik, 2003). NLP is one of the most frequently applied algorithms for real world problems as its fundamental theories have been well studied and as a result, a wide spectrum of user-friendly software with powerful computational capabilities have been developed. One limitation of NLP is that it relies heavily on the inherent assumption that all relevant variables have deterministic values (Luhandjula, 2006).

Unfortunately most real-life problems involve a certain uncertainties making the implementation of NLP a difficult task (Liu, 2010). For instance, work-related exposures to ENMs are associated with a number of uncertainties in relation to control options and risk quantification. Uncertain variables for a nonlinear $ENM_s$ manufacturing system analysis may include: (1) $ENM_s$ workplace release data. Previous studies indicated a pressing need to distinguish background nanoparticles' concentrations, process-generated nanoparticles' concentrations and $ENM_s$ in workplace risk assessment (Maynard and Aitken, 2007). (2) Occupational exposure limits: it may take several years to establish human no-effect levels (NELs) for each kind of MNM, so in many cases no nano-specific occupational health and safety standards are available (Van Broekhuizen et al., 2012); and (3) $ENM_s$ occupational exposure control efficiency. Data on efficiency and cost of $ENM_s$ control methods are vague (Ok et al., 2008). It is seen that the above-mentioned uncertainties have not been well quantified in the previous studies.

Considering uncertainties in the optimization, incorporation of fuzzy mathematical programming (FMP) and chance-constrained programming (CCP) has been reported to environmental management problem (Xu and Qin, 2010). FMP can deal with vagueness and ambiguity based on fuzzy set theory. CCP is an effective way to deal with numerous uncertainties, where uncertain parameters are considered random variables and described using probability density functions. CCP can be used to convert a stochastic programming model into an equivalent deterministic model, and also to incorporate other uncertain optimization methods, such as FMP, within the nonlineare programming general framework (Xie et al., 2011). Therefore, combining FMP and CCP with NLP is an approach that could be used to deal with various uncertainties pertaining to ENM and workplace exposure control.

## 1.2. Objectives

The study aims to develop a fuzzy chance-constrained nonlinear programming (FCCNLP) approach to (1) maximize the economic benefits of nanomanufacturing and minimize the nano-related health impacts to workers; and (2) handle uncertainties associated with both the nanomaterial production and workplace exposure control. Moreover, the development of FCCNLP method will be performed in details as the following steps:

(1) to develop a nonlinear optimization approach for modeling the ENMs manufacturing process towards a maximum nanomaterial production at a minimum cost of workplace exposure control under a number of constraints;

(2) to develop a fuzzy chance-constrained nonlinear programming (FCCNLP) method through an integration of FMP and CCP into NLP to address the system uncertainties including the randomness of exposure data and fuzziness of economic return objective, occupational exposure limits and exposure control efficiency;

(3) to apply the FCCNLP model to a typical single-wall carbon nanotube (SWNT) manufacturing process and obtain alternative solutions for economic benefit under different EHS control strategies, different probability levels of system failure and appropriate net return and occupational exposure limits;

(4) to evaluate trade-offs between nanomanufacturing economic benefits and human health risks and provide feasible suggestions to decision makers through a holistic view span.

## 1.3. Organization of the Thesis

This thesis is organized in seven chapters:

Chapter 1 introduces the research background, addresses the research problems, briefly introduces the research methodologies, and states the research objectives and significance.

Chapter 2 provides a general review of the literatures on the concept of engineered nanomaterials (ENMs), typical nanotechnology manufacturing processes, adverse effects of ENMs to environment and human health, nano-related standards, previous optimization studies of manufacturing process and uncertainty analysis techniques used in the optimization in the industry section.

Chapter 3 describes the theories and methodologies about nonlinear programming (NLP), fuzzy nonlinear programming (FNLP), chance-constrained nonlinear programming (CCNLP) and fuzzy chance-constrained nonlinear programming (FCCNLP) approach. In this part, the required knowledge for developing these methods is explained. Moreover, the differences of these four approaches are examined.

After this general description, Chapter 4 presents a specific overview of a case study and then applied the NLP, FNLP, CCNLP and FCCNLP techniques to a realistic example in Houston, Texas, USA to maximize the nanomaterial production and minimize the related occupational exposure risks.

Chapter 5 presents detailed exposure concentrations, production volumes and economic results generated by the NLP, FNLP, CCNLP and FCCNLP methods and results analyses of the four approaches.

Chapter 6 contains the validation of the FNLP results, comparisons of four methods, advantages and limitations of these methods, respectively.

Chapter 7 presents conclusions, research contributions and recommendations to future study.

# Chapter 2 LITERATURE REVIEW

This chapter presents an overview of the concept and classification of engineered nanomaterials (ENMs), typical ENMs manufacturing processes, health effects of ENMs and nano-related occupational exposure limits. In addition, previous researches about optimization of manufacturing process are reviewed and summarized in this section. And nonlinear programming optimization method is selected to manage ENMs production process.

## 2.1. Engineered Nanomaterials

Engineered nanomaterials (ENMs) are man-made particles having at least one dimension of rougly 1-100 nm (EPA, 2007). A nanometre is a billionth of a metre, that is, $10^{-9}$ m. The nanoscale dimension in comparison to microscopic objects is described in Figure 1. Engineered nanomaterials (ENMs) can be classified in different ways according to their origin, state and physicochemical properties, such as size, shape, chemistry, surface area, surface charge, etc. The most common method of classifying nanomaterials is by the chemistry of the core material, that is, organic and inorganic (Figure 2). Organic nanomaterials can be further defined as fullerenes ($C_{60}$ and $C_{70}$ and derivatives), carbon nanotubes (multi-walled or single walled carbon nanotubes) and nanopolymers (dendrimers), while inorganic nanomaterials can be divided into metal oxides (i.e. dioxide, titanium dioxide), metals (i.e. silver, gold) and quantum dots (i.e. cadmium selenides) (Stone et al., 2010). Due to unique properties of ENMs such as small size and large surface area to mass ratio, increased surface reactivity, and altered physic-chemical properties (Savolainen et al., 2010; Bhatt and Tripathi, 2011; Biskos and Schmidt, 2012), ENMs have been employed in a wide spectrum of industrial sectors during recent years, including structural engineering, energy, electronics, environmental protection, cosmetics, food, agriculture, medicine for diagnostic or therapeutic purposes and many other areas.

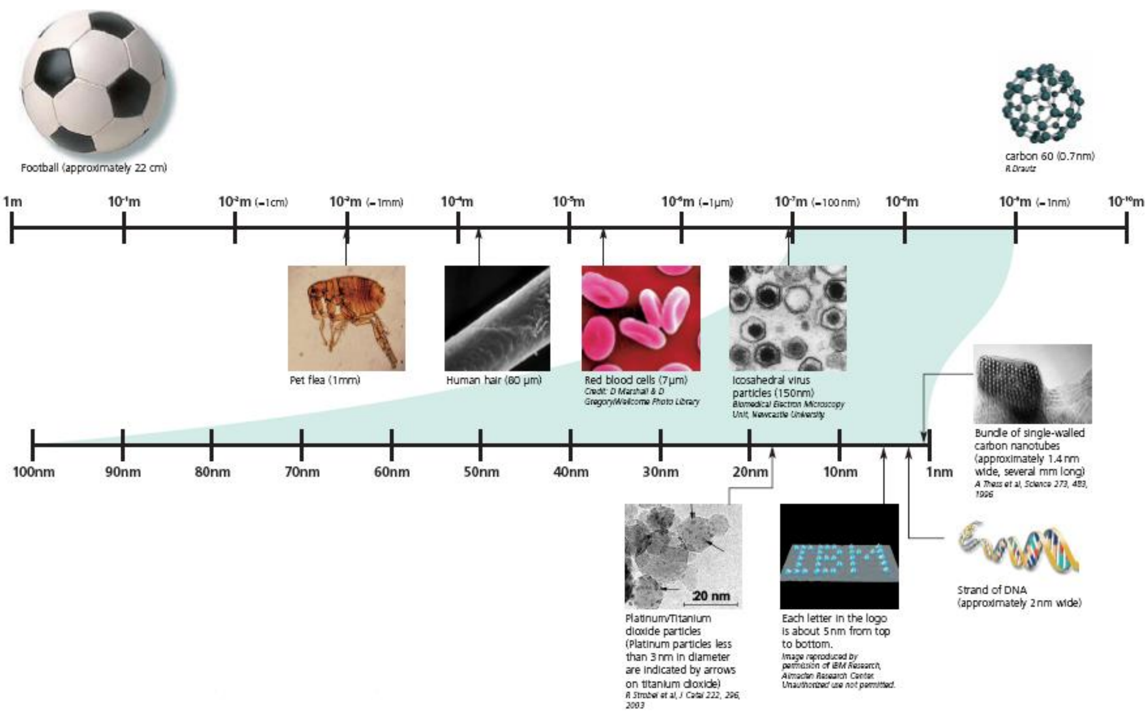


Figure 1 Length scale showing the nanometer in context (Royal society and Royal Academy of Engineering, 2004)

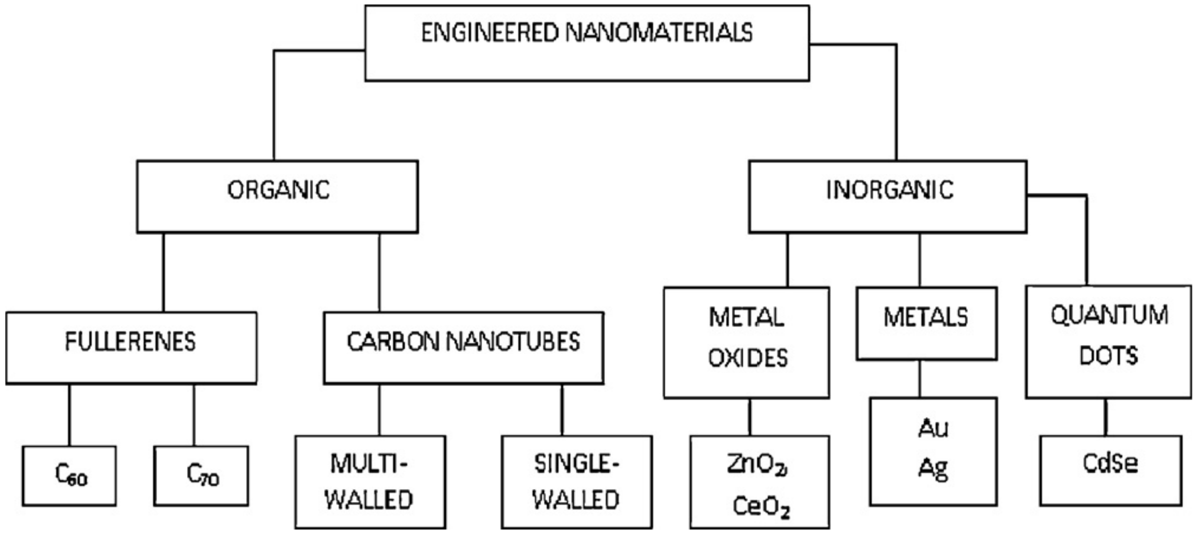


Figure 2 Engineered nanomaterials classification according to the chemistry of their core material (Peralta-Videa et al., 2011)

Nanotechnologies utilizing ENMs have envisaged to become a highly promising industry. Currently, the commercialization of ENMs is at an early but rapid-growth stage. The worldwide investment in nanotechnology has increased from \$432 million in 1997 to \$147 billion in 2007. And, by the year 2015, the global nanotechnology market value is expected to grow to approximately \$3.1 trillion and millions of jobs opportunities will be created in this domain (Delgado, 2010; Mirabile et al., 2014).

## 2.2. The Nanotechnology Manufacturing Process

### 2.2.1. Engineered nanomaterials (ENMs) manufacturing processes

There are two main engineering design methods for preparing nanoparticles, top-down and bottom-up. The top-down approach works on the basis of breaking down a large piece of material into smaller pieces, and in the case of nanostructures these dimensions are in the nanometer range:

1 to100 nm. This is a conventional engineering using lathes or millers to machine structures with sizes of a few nanometers. For example, in top down method, lithographic techniques are used to cut a larger piece of a material into ENMs. Particles with sizes lesser than 30 nm can be produced by using electron beam lithography. In other cases, grinding of a micro-material in a ball mill can further be used for the production of ENMs with sizes lesser than 30 nm (Colson et al., 2013). The bottom-up approach is a more conventional method for producing ENMs. The bottom-up fabrication relies on increasing the size of small molecules or atoms up to the size of MNMs via techniques such as gas-phase synthesis, liquid-phase synthesis and self-assembly techniques. The type of production method is very important for ENMs exposure to workers. Generally, bottom-up techniques are less waste-producing than top-down techniques. It is often suggested that bottom-up techniques should be the ultimate tools for sustainable manufacturing, as they allow for customized design of reactions and processes at the molecular level, thereby minimizing waste (Sengul, 2008).

The principle of the bottom up approach for the formation of ENMs relies on supersaturation. It is a state of a homogeneous solution that contains more of the solute than could be dissolved by the solvent under normal circumstances (Lead and Smith, 2009). At some point the supersaturation of the solution is relieved by the formation of the precipitated particles. These particles which usually consist of two or three atoms or molecules are the smallest stable units in this solution. They will be the first nuclei for further condensation of atoms or molecules. Condensation is a stochastic process. The nucleus grows and forms clusters and later a particle. Colliding clusters or small particles may coagulate. During coagulation by exchange of surface energy, a new particle is formed. Having reached a certain size, the difference in surface energy will be so small that further coagulation of particles is impossible. Therefore, nucleation, condensation and coagulation are the three major steps of the process of nanomaterials formation (Vollath, 2008). Different ENM gas-phase production processes are categorized by various condensation methods. In the following section, some of the well-established industrial ENM production processes using gas-phase technique will be described.

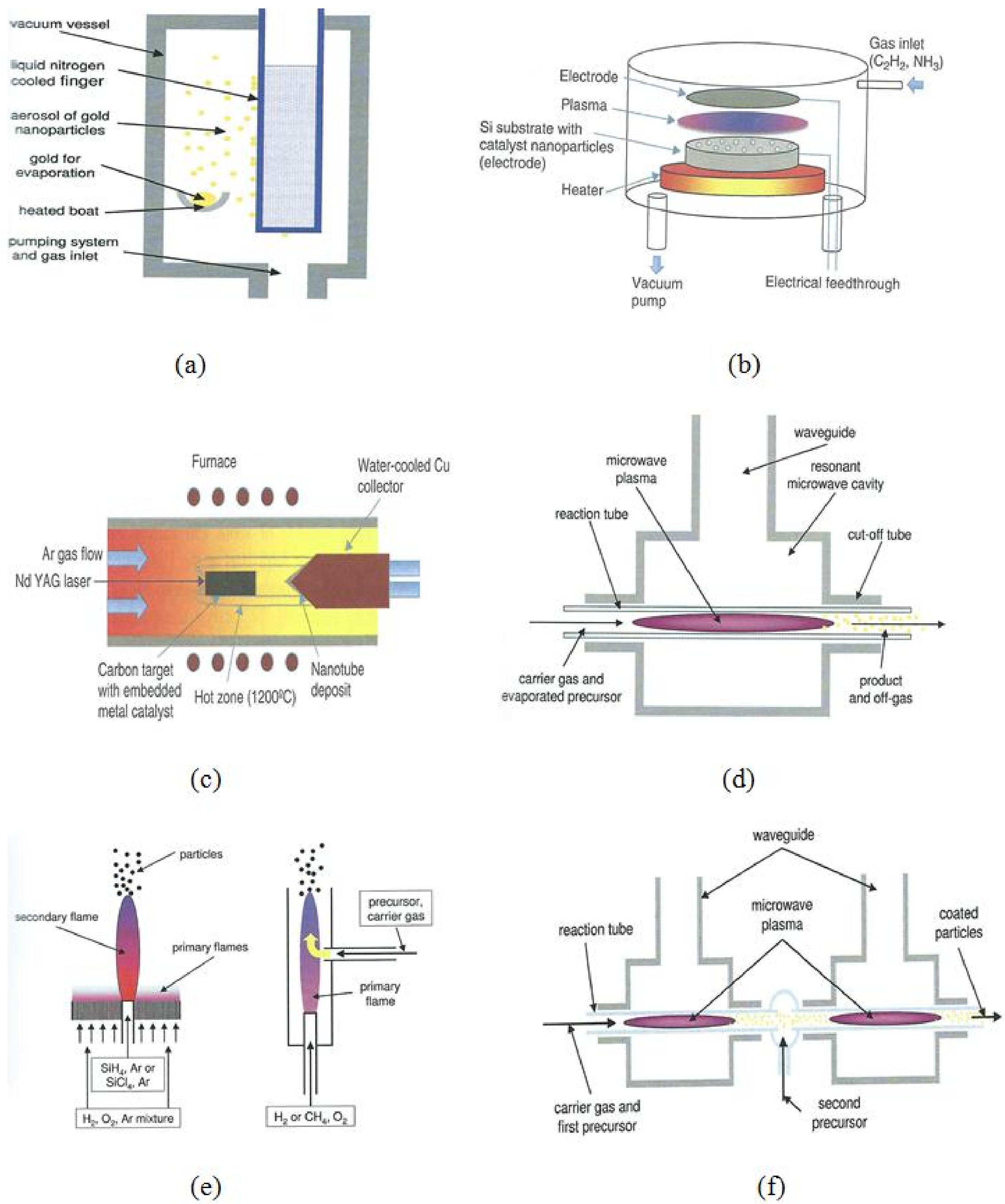


Figure 3 Schematics of the typical gas-phase processes for ENMs production. (a) Inert gas process. (b) Chemical vapor process. (c) Laser ablation process. (d) Microwave plasma process. (e) Flame aerosol process. (f) Synthesis of coated particles. (Binns, 2010).

#### 2.2.1.1 Inert gas condensation process

Inert gas condensation process is the most important process for synthesizing ENMs in the gas phase. This process applies thermal evaporation to a metal within a vacuum chamber filled with a small amount of inert gas. As figure 3(a) shows, a metal (i.e. gold) is evaporated in a vacuum vessel, filled at reduced pressure with an inert gas. The metal vapor loses thermal energy by colliding with the inert gas atoms, leading to nucleation, and then forms nano-sized gold particles. The products move to a liquid nitrogen-cooled finger and are collected from the surface. Because the synthesizing of the ENMs is a purely random process, the inert gas evaporation process leads to products with a broad particle size distribution.

#### 2.2.1.2 Chemical vapor process

To control the particle size distribution, chemical vapor process (CVP) is using chemical compounds with a relatively high vapor pressure as precursor to reduce the reaction time. Take SWNTs production for example, as shows in Figure 3. (b), the evaporated precursor ($C_2H_2$) was generated by glow discharge plasma. A carrier gas ($NH_3$) transports the evaporated precursor through the heated reaction zone, that is, the electrodes supporting catalyst on which the SWNTs grow. To limit particle agglomeration, the gas carrying the articles is quenched. Finally, the SWNTs are collected. Due to its simplicity and relatively low synthesis temperatures, CVP is rapidly becoming one of the methods for the commercial manufacturing SWNTs.

#### 2.2.1.3 Laser ablation process

The laser ablation process has the advantage of allowing not only the use of metals but also oxides as precursors, which makes it more popular in its application. A system for powder production using the laser ablation process generally consists of two important elements: the pulsed high-power laser, and with the optical focusing system and feeding device for the precursor. Figure 3 (c) presents a set-up for SWNTs synthesis according to the laser ablation process. The laser beam is focused at the surface of a carbon target, which is vaporized under the laser spot. The hot plume of carbon is generated in the furnace. Within the plume, there is a supersaturated vapor succeeding the formation of SWNTs which are condensed in the gas space and transported with the carrier gas to the powder collector.

#### 2.2.1.4 Microwave plasma process

The chemical vapor synthesis and laser ablation are purely random processes. Hence, there are only three means available by which ENMs size and size distribution can be influenced: the concentrations of active species in the gas, the reaction temperature, and the rapid cooling (quenching) of the gas after leaving the reaction zone. This situation is entirely different from that of the microwave plasma process, where the nano-particles originating in the plasma zone carry electric charges. As a consequence, the probability for coagulation and agglomeration is significantly reduced, as the collision parameter decreases with increasing particle size. Figure 3 (d) shows a typical process for nano-particle synthesis using the microwave plasma process. The microwave plasma is ignited in a reaction tube which passes a resonant microwave cavity. A carrier gas containing the reaction gas transports evaporated precursors into the plasma zone. The reaction products (ENMs) are collected after the reaction zone. Microwaves are coupled into the device with the waveguide.

#### 2.2.1.5 Flame aerosol process

Historically, among all of the processes used to produce nanomaterials, the flame aerosol process is the oldest. In this process, the ENMs are synthesized and formed at very high temperatures and over very short times. In the simplest case, a flame reactor set-up is as shown in Figure 3 (e). The flame reactor consists of a primary flame that is fueled with hydrogen, methane, or another hydrocarbon fuel. In the case shows in the Figure 3 (e), many small primary flames surround the secondary flame, in which the products are produced. Figure 3 (e) demonstrate the synthesis of silica, $SiH_4$ or $SiCl_4$ are assumed as the precursor compounds. Reaction of the precursors with excess oxygen forms the secondary flame, while the particle size is adjusted by diluting the precursor with an inert gas such as argon or nitrogen.

#### 2.2.1.5 Synthesis of coated ENMs

Many applications of nanomaterials require the coated nanoparticles. For example, a coating is used as a distance holder to adjust particle interactions; or designing coatings to add additional properties to the ENMs. One of the cases includes magnetic nanoparticles with luminescent coatings. A set-up used to produce ceramic-coated nanomaterials using the microwave plasma process is shown in Figure 3(f). The system consists of two subsequently arranged microwave cavities and a reaction tube passing through both cavities. The reaction is carried out in the microwave plasma at the intersections between the reaction tube and the microwave cavities.

Nanoparticles leave the reaction zone with electrical charges of equal sign. The most advanced examples involve the development of nanoparticles on which two or more functional coatings.

There are many other mechanisms for the formation of nanoparticles and other processes that mass produce them which are not discussed in detail here. Some of the most exciting research arises out of combining the top-down and bottom-up approaches (Song et al., 2011; Colson, 2013).

After synthesized, ENMs will be processed further, e.g., to be purified, inspected, packaged, and then becoming commercial products.

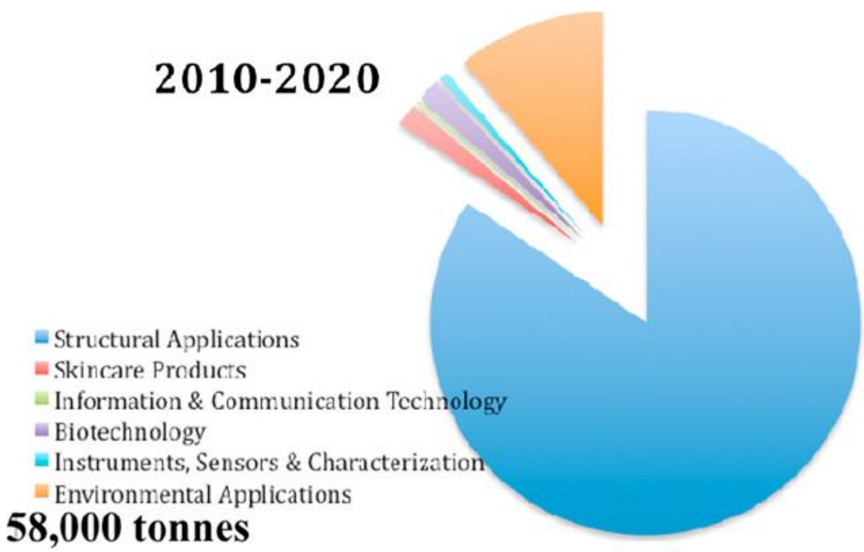


Figure 4 Estimated annual global production for engineered nanomaterials (G.C. Delgado, 2010)

It has been estimated that annual worldwide production of ENMs from 2010 to 2020 is about 58,000 tonnes (G.C. Delgado, 2010) (Figure 4). With the rapid growth of production of engineered nanomaterials, the occupational and public exposure to ENMs is supposed to increase dramatically in the coming years and then cause potential adverse health effects to humans.

### 2.2.2. High pressure carbon monoxide (HiPco) process for manufacturing single-walled nanotubes (SWNTs)

As Figure 5 shows, single-walled nanotubes (SWNTs) are cylindrical molecules of graphite with diameters of 1 to 2 nm that have attracted considerable interest due to their superior electrical, mechanical, and thermal properties, and particularly, their fascinating ability to withstand high current density (109 Amps/$cm^2$) (Hwang et al., 2009). The use of SWNTs has raised concerns because of their resemblance to asbestos in terms of dimensions, rigidity and solubility, as these factors determine fiber toxicity leading to lung fibrosis, so consequently carbon nanotubes known as high aspect ratio nanoparticles have engendered concern about their potential for a similar risk as that from the asbestos. (Maynard, 2004).

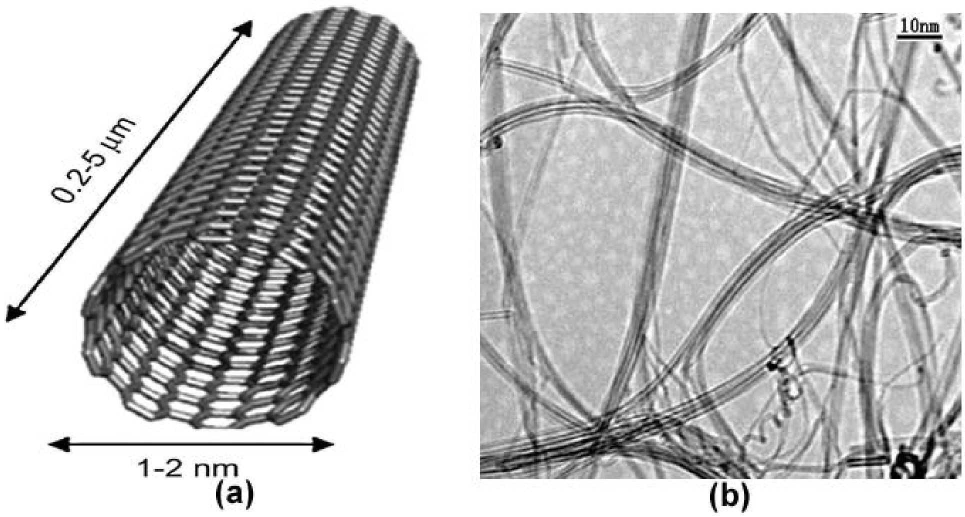


Figure 5 Single-walled carbon nanotube. (a) Schematic of a single-walled carbon nanotube. (b) a TEM image of single-walled nanotubes.

Among the several methods available for producing carbon nanotubes, three technical processes are commonly used: arc ablation (arc), chemical vapor deposition (CVD) (which are briefly introduced in the section 2.2.1.2 and 2.2.1.3) and high-pressure carbon monoxide (HiPco). Because the HiPco process is significantly less costly ($450/g *vs.* $1,830/g and $1,586/g for arc ablation and CVD, respectively) (Kalapoukas and Dervakos, 1996),we focused on the HiPco manufacturing method in the CCNLP model to explore profits under various EHS standards (High, Medium, Low). In the HiPco process, it is proposed that iron clusters form first, then solid carbon nucleates and grows SWNTs. Iron pentacarbonyl ($Fe(CO)_5$) is injected into a stream of CO gas at high temperature (800-1,000 ºC) and pressure (≥10 atm).The iron clusters form by aggregation of iron atoms from the decomposition of $Fe(CO)_5$ via Equation (1) (see below) around 250 °C. There are two main functions for the iron clusters. They act as catalysts for carbon source decomposition as well as SWNT formation sites. The clusters grow by collision with additional metal atoms and other clusters, eventually reaching a diameter comparable to that of a

SWNT, 0.7–1.4 nm, corresponding to 50–200 iron atoms. By the time they reach this size, CO can disproportionate (a specific type of redox reaction) on the surface of such cluster via the Boudouard reaction (Equation (2)) to yield solid carbon, and SWNTs will nucleate and grow from these clusters (Nikolaev et al., 1999).Figure 1 shows the material flows in the manufacturing reactor. The SWNTs and iron particles pass through the reactor propelled by the hot, dense gas flow, and into the product collection apparatus. The CO gas recalculates back through the gas flow system and reactor using a compressor. The product contains Fe particles and other by-products and requires subsequent purification (Healy 2006; Healy et al., 2008).

$$Fe(CO)_5 \rightarrow\rightarrow Fe + 5CO \quad (1)$$

$$2CO(g) \rightarrow\rightarrow C(s) + CO_2(g) \quad (2)$$

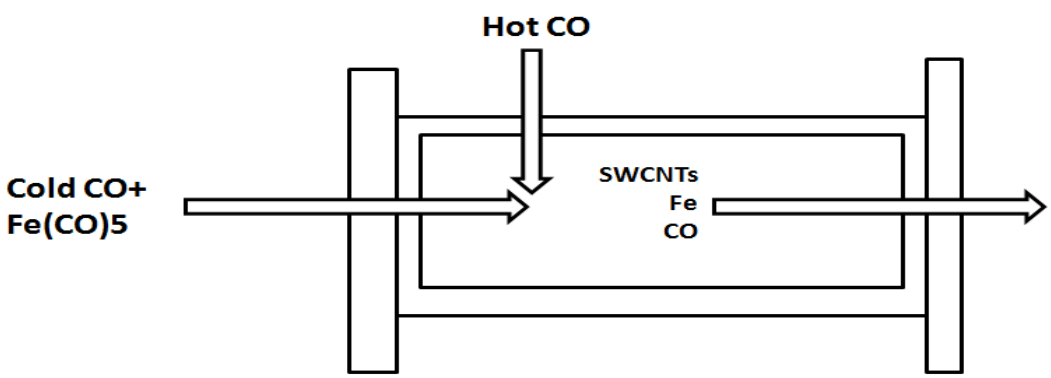


Figure 6 Schematic diagram of the HiPco synthesis process

## 2.3. Health Effects of Engineered Nanomaterials and Nano-related Occupational Exposure Limits (OELs)

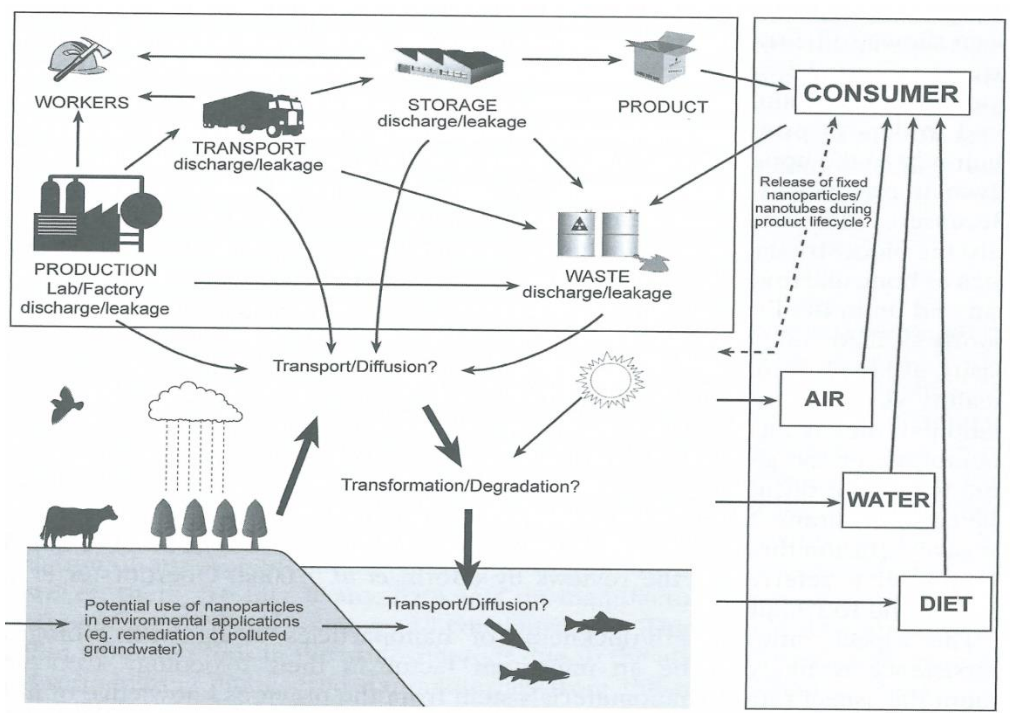


Figure 7 Possible exposure routes for engineered nanomaterials (Lead and Smith, 2009)

As Figure 7 shows, there are various scenarios that humans could be exposed to ENMs. In the occupational scenario, workers may be exposed to ENMs not only during synthesis of ENMs, but also in downstream activities such as packaging, transport, and storage. ENMs could enter into the environment through industrial pollution or the application ENMs to site remediation. Consumers may get exposed as a result of ENMs pollution in air, water or the food chain, or through directly consuming products containing ENMs (Lead and Smith, 2009).

The greatest potential for human exposure is expected during certain activities in occupational settings, where ‗raw' nanomaterials are handled in large quantities (Maynard and Aitken, 2007). ENMs can enter worker's body through inhalation, skin contact and ingestion during manufacturing (Aschberger et al., 2011) and subsequently reach systemic circulation and deposited in different body organs, like heart, lungs, brain, liver and kidneys, and then cause multiple negative effects to worker's health. Inhaled ENMs can induce a strong pulmonary response in respiratory tract causing damage to this organ. For example, Inhalation of silica particles in industrial workers causes ‗Silicosis'. Workers can be dermally exposed during the handling of ENMs. ENMs can enter body through the health skin. Potential hazards are unknown at present. Ingestion can occur as consequence of hand-to-mouth contact. ENMs can be directly absorbed by gastrointestinal tract and then accumulate in the liver. Excessive immune inflammation cause permanent liver damage.

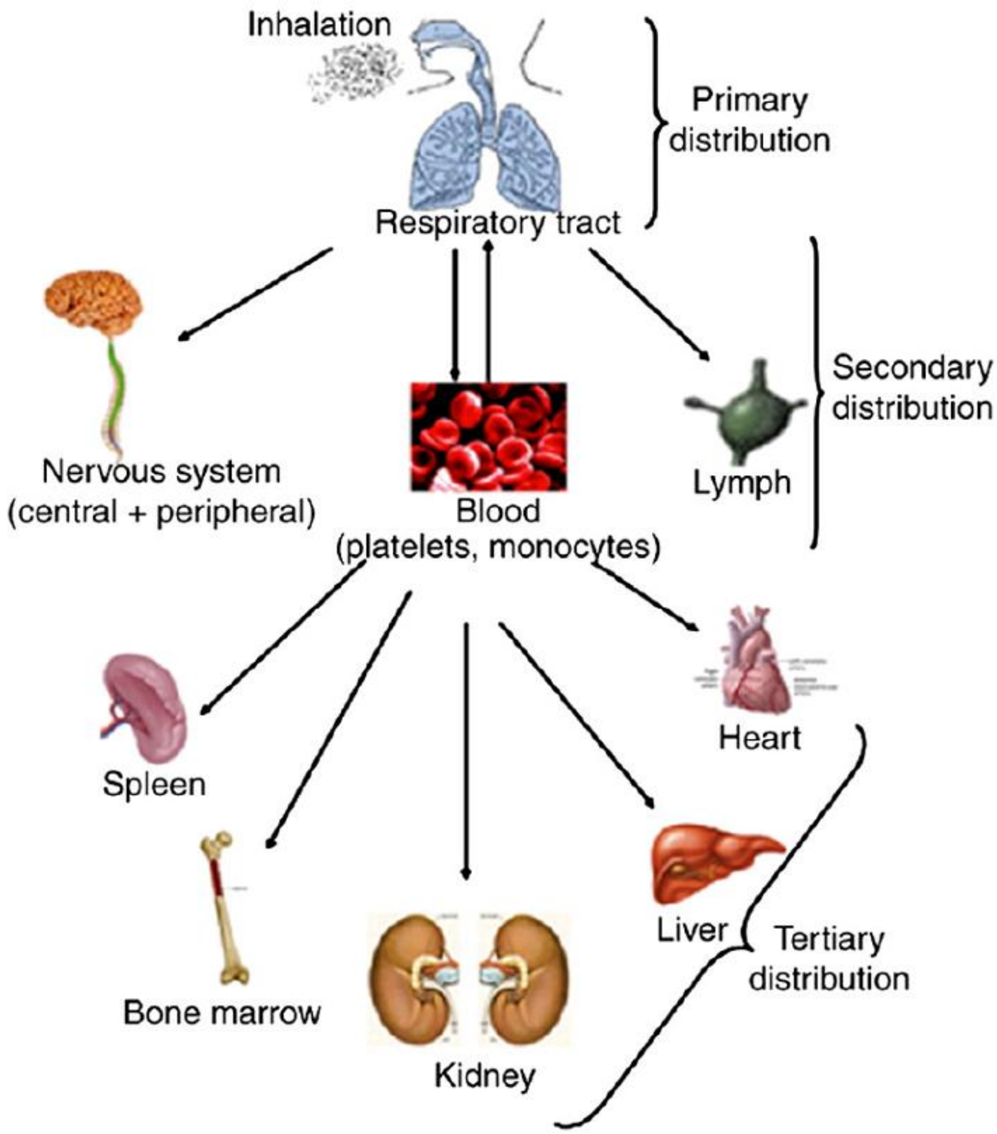


Figure 8 Distribution of ENMs in the body (Gajewicz et al., 2012)

Translocation and accumulation of ENMs in human tissues can lead to various diversified adverse effects. Recent publications indicate that chronic occupational exposure to ENPs may lead to a number of negative health and reproductive problems, including hepatic injury (Kobayashi et al., 2009; Myojo et al., 2010; Paur et al., 2011), genotoxicity (Kumar et al., 2011; Hackenberg et al., 2011), carcinogenicity (Ress et al., 2003; Roller, 2009), cytotoxicity (apoptosis) and risks of cardiovascular diseases (Wilson et al., 2007; Shvedova et al., 2012), and reproduction damage (Zhu et al., 2010; Lapresta-Fernandez et al., 2010). For instance, the studies on single walled carbon nanotubes (SWCNTs) showed that SWCNTs cause mice's lung granulomas and other signs of acute lung inflammation (Lam et al., 2003; Warheit et al., 2004), furthermore, even diffuse interstitial fibrosis (Shvedova et al., 2005).

As the result, occupational exposure limits (OELs) for engineered nanomaterials (ENMs) becomes necessary to protect workers from the adverse effects of ENMs presenting at the workplace. However, because large amounts of complicated and expensive toxicology data and information is required, to date, health-based limit values are only available for several frequently used ENM: carbon nanotubes and nanofibers (NIOSH, 2013), Titanium Dioxide (NIOSH, 2011 and 2013) and nano-Ag (ENRHES, 2010). For example, in 2010, the National Institute for Occupational Safety and Health (NIOSH) published a bulletin which set recommended exposure limit (REL) for carbon nanotube as 7 $\mu g/m^3$, based on the estimation of the animal no observed adverse effect level (NOAEL) of CNT was near 7 $\mu g/m^3$ (8-hr TWA). And in April 2013, in the current intelligence bulletin 65, the NIOSH recommended that exposures to CNT should be kept below the REL of 1 $\mu g/m^3$ as an 8-hr TWA to replace the previous REL 7 $\mu g/m^3$ with the updated NOAFL of CNT (NIOSH, 2013; NIOSH, 2010).

The potential impact of nanotechnology is a global issue which no one can forecast its future. Academic research and governmental policy are essential to ensure that this promising technology becomes sustainable. An important aspect of sustainability is the quantification and minimization of risk of ENMs to human and environmental health (Lead and Smith, 2009).

## 2.4. Previous Optimization Studies of ENMs Manufacturing

So far, relatively few publications approach directly modelling ENMs occupational exposure risks. Life cycle assessment (LCA) is widely used to assess the environmental impacts of nanomaterial through theirs all life-cycle stage. It has been used to study economic and environmental impacts of three single walled carbon nanotube production processes (Healy et al., 2008). However, the limited exposure information of many ENMs limits the utilization of LCA.

Besides LCA, researchers tried to manage ENMs occupational exposure risks through risk analysis. So far, limited work has been conducted to develop nanotechnology risk models, which include Monte Carlo models comparing alternate workplace safeguards for single wall carbon nanotubes (SWCNTs) manufacturing (Ok et al., 2008), Stochastic multi-attribute analysis comparing four SWCMTs synthesis approaches (laser vaporization, arc discharge, chemical vapor deposition, and high pressure carbon monoxide) based on five decision criteria (energy consumption, material efficiency, eco-points, cost and health risks) (Canis et al., 2010), and expert developing exposure-response functions for ENMs (Kandlkar et al., 2007).

While above approaches help analyze nanomaterial risks, optimization models, i.e. linear programming (LP) and nonlinear programming (NLP), can provide a framework to find a balance point between the benefits of nanomaterial application and thorough management of their potential risks. In the past decades, a number of optimization programming techniques were widely applied for management of manufacturing sectors. For instance, Seibi and Sawaqed (2002) applied linear programming to design a copper filled fibreglass moulds for manufacturing a customized product. Henning and Trygg (2008) developed an energy system optimization system based on linear programming to decrease electricity consumption and increase cogeneration in Swedish industry, which helps to reduce $CO_2$ emissions in Sweden. Grossmann (2012) overviewed mathematical programming techniques for enterprise-wide optimization, which are integer linear programming, nonlinear programming, decomposition methods, stochastic programming, and then described five application in the pharmaceutical industry in US. Piltan et al (2012) used linear and nonlinear programming to develop an energy forecasting model to forecast and analyze energy demand in the Iranian metal industry.

## 2.5. Uncertainty Analysis Techniques Used in the Optimization in the Industry Section

A significant challenge for implementing optimization techniques in the industrial area goes to handle various uncertainties. To deal with this problem, a variety of mathematical methods were finalized in economic-environment sustainable development management. For example, Linninger et al. (2000) addressed the problem of finding optimal waste management policies (among low, medium and high level control strategies) for pharmaceutical manufacturing sites in the presence of uncertainty of trafic routes. They offered a robust chance constrained programming framework to compare impacts of policies for solvent-recovery and treatment options; Rong and Risto (2006) investigated the uncertainty of the chemical composition of the scrap in secondary steel production, and this scrap charge optimization problem is modelled as a fuzzy chance constrained linear programming problem, consequently; Zhang et al. (2009) applied a robust chance-constrained programming model for water quality management within an agricultural system, where solutions for farming area, manure/fertilizer application amount, and livestock husbandry size under different scenarios are obtained and interpreted; Freni et al. (2011) employed the use of interval programming as a tool for assessing the appropriate model complexity, where several criteria were used for integrating the simplicity of the indices based on the fisher information matrix.

Nanotechnology industry, like other general industries sections is facing the same challenge when optimizating manufacturing process of engineered nanomaterials. For instance, when maximizing profit and controling occupational health exposures of engineered nanomaterials into acceptable level, uncertainties include (1) ENP workplace release data; (2) Occupational exposure limits; (3) ENP occupational exposure control efficiency and control cost.

Therefore, combining fuzzy mathematical programming (FMP) and chance-constrained programming (CCP) is an approach that could be used to deal with the uncertainty of ENP exposure data in the workplace. FMP can deal with vagueness and ambiguity based on fuzzy set theory. CCP is an effective way to deal with numerous uncertainties, where uncertain parameters are considered random variables and described using probability density functions. CCP can be used to convert a stochastic programming model into an equivalent deterministic model, and also to incorporate other uncertain optimization methods, such as fuzzy mathematical programming, within the nonlineare programming general framework (Xie et al., 2011).

## 2.6. Summary

In recent years, production and use of engineered nanomaterials (ENMs) have greataly increased as the result of rapid development in nanotechnology. Due to unique properties of

ENMs such as ultra small size, large surface area to mass ratio and high reactivity, various seience areas like biomedical, structrical and optics engineering obtain greatly benefits from such progress in nanotechnology. On the other hand, unintentional exposure of humans to ENMs is increasingly reported particularly workers. The main risk arises from occupational expsure via chronic inhalation of ENMs. Occupational exposure limits (OELs) for ENMs becomes mandatory to prevent workers from the health risks. So far few publications approach directly modelling ENMs occupational exposure risks. To maximize the nanaomaterial production and minimize the risks of workplace exposure to ENMs, nonlinear programming (NLP) is applied to manage nanomanufacturing process. Moreover, fuzzy mathematical programming (FMP) and chance-constrained programming (CCP) are combined to nonlinear programming (NLP) to handle uncertain parameters. The details of mathematical methods will be elaborated in the next chapter.

# Chapter 3 METHODOLOGY

To maximize the societal and economic benefits of ENMs while control the adverse health risks for workers, a nonlinear programming (NLP) model is proposed to address the conflict between benefits and risks. Moreover, to handle the uncertainties in the system, chance-constrained programming (CCP), fuzzy mathematical programming (FMP) and fuzzy chance-constrained programming (FCCP) are employed for dealing with randomness, fuzziness and the combination of both randomness and fuzziness.

## 3.1 Nonlinear System Optimization

### 3.1.1 The nonlinear programming (NLP) method

Optimization is the selection of the best solution from a set of feasible alternatives, which provides a suitable framework for analysis. If a single problem can be identified by an objective, for example, profit or loss in a business setting, expected return in the environment of risky investments, or social welfare in the context of government planning, nonlinear programming is an effective tool to handle it (Luenberger and Ye, 2008). As one of the most important tools of optimization, nonlinear programming is specified by an objective function which is to be maximized (or minimized) subject to a set of linear/nonlinear constraints (Slotine, 1991). The standard form of nonlinear programming may be written as follows:

$$\max(\min) \quad c_1x_1 + c_2x_2 + \ldots + c_nx^T{}_n$$

$$\text{subject to} \quad a_{11}x_1 + a_{12}x_2 + \ldots + c_{1n}x_n{}^T = b_1$$

$$a_{21}x_1 + a_{22}x_2 + \ldots + c_{2n}x_n{}^T = b_2 \qquad (3\text{-}1)$$

$$\ldots$$

$$a_{m1}x_1 + a_{m2}x_2 + \ldots + c_{mn}x_n{}^T = b_m$$

$$x_i \geq 0,\ i = 1,2,\ldots,n$$

which is also represented in the following matrix form,

$$\max(\min) \quad f_i = C_i X^{T_i}$$

$$s.t. \quad A_i X^{T_i} \leq b_i, \quad i = 1, 2, ..., p \qquad (3\text{-}2)$$

$$X \geq 0$$

where C = ($c_1$, $c_2$, … , $c_n$), x = ($x_1$, $x_2$, … , $x_n$), A = $(a_{ij})_{m*n}$ and B = ($b_1$, $b_2$, … , $b_n$). In the standard nonlinear programming (3-2), all of the decision variables $x_i$, superscript $T_i$ of decision variables, i = 1, 2,…, n are assumed nonnegative. This property is true for almost all real-world problems. ―max" and ‗min" are abbreviations for ―maximize" and ―minimize". Nonlinear programming refers to all problems of the form (3-2) in which objective function or (one or more) of the constraned functions include a nonlinear term or terms (Luenberger and Ye, 2008).

A solution x is feasible to nonlinear programming (3-2) if it satisfies that $A_i X^T \le b_i$ and x ≥ 0. The collection of all feasible solutions is called the feasible set. A feasible solution x* is called an optimal solution to the nonlinear programming (3-2) if Cx ≤ Cx* for all feasible solution x.

### 3.1.2 The nonlinear programming (NLP) for optimizing the nano-maunfacturing process

Nonlinear programming (NLP), which is a type of deterministic optimization, is implemented here to model nanomaterials exposure risks in the workplace. For a given nano-manufacturing case study, the general form of this optimization approach can be written as follows:

$$\text{Objective function (maximize)} = (1) - (2) - (3) \qquad (3\text{-}3)$$

where:

(1) = profits from nanoparticle manufacturing per year;

(2) = production costs of nanoparticles per year;

(3) = exposure control costs per year.

Constraints include:

(a) mass balance constraints;

(b) production volume constraints;

(c) occupational exposure limit constraints.

where mass balance constraints can be identified with constraints which material entering the ENMs reactors should be equal to those leaving the nano-synthetic systems; production volume constraints show that production volumes of ENMs should be larger than the minimum production request but less than the maximum production capacity; and occupational exposure limits constraints mean that concentrations of air pollutants (including ENMs) produced in the workplace should be within occupational exposure limits issued by the government.

## 3.2 Nonlinear System Optimization under Uncertainty for Nanomaterials Manufacturing

Deterministic mathematics, such as linear/nonlinear programming, are very effective in analyzing causal relationships under certainty. However, their effectiveness decreases as causal relationaships begin to disintegrate caused by limitation of precise system information. As the result, the outcome of the system is no larger deterministic. As pointed out by some researchers (Leung, 1988; Inuiguchi, 2000), two major different kinds of uncertainties, randomness and fuzziness exist in the real life. In statistics, randomness refers to a situation whose outcomes do not follow a deterministic pattern, but can be described by an empirical probability distributions. For example, when you throwing a dice, the top face may have any one of the six elements of the set $\{1, 2, ..., 6\}$. This type of uncertainty arises because of randomness in the system. The other kind of uncertainty, fuzziness is composed of ambiguity and vagueness. Ambiguity is associated with one-to-many relations, that is, situations in which the choice between two or more alternatives is not specified. For example, ‗The price of the table is about 50 CAD.‘ This uncertain descriptions show the ambiguities of the true values, e.g., ‗about 50 CAD‘ shows that one value around 50 is true but not known exactly; Vagueness is associated with the difficulty of making sharp or precise distnctions in the world; that is, some domain is vague if it cananot be delimited by sharp boundaries. For instance, ‗Jenny wants to rent an appartment whose distance from the Concordia Unversity is less than 2 km.‘ This uncertain descripations show the vagueness of the aspiration levels, e.g., ‗distance is less than 2 km‘ does not define a sharp boundary of a set of satisfactory values but shows that values around 2 km and smaller than 2 km are to some extent and completely satisfactory, respecitvely (Inuiguchi and Ramik, 2000).

To address such comlexities of uncertainties, the chance-constrained programming (CCP) and fuzzy mathematical programming (FMP) are proposed to handle randomness and fuzziness problems, respectively. The chance-constrained programming (CCP) method was used to deal with random uncertainty information. CCP required that all of the constraints be satisfied in given probability levels. Fuzzy mathematical programming (FMP) is a flexible approach that permits an adequate solution of real-world problems in the presence of imprecise information. FMP method considers uncertainties as fuzzy sets and is effective in reflecting ambiguity and vagueness in resource availabilities. Moreover, a combination of CCP and FMP can be considered to deal with the situations under both random and ambiguous uncertainties, usually are transormed into deterministic mathematical problems by setting the grades of membership and using chance constraints.

### 3.2.1 The fuzzy nonlinear programming (FNLP) method

Deterministic optimization is one of the most used areas of mathematical applications. However, it is common that the values of parameters are not totally specified due to knowledge deficit or incomplete information. Fuzzy set theory is utilized to model systems of variables whose belonging (to a set) is gradual or transitional. A fuzzy set $X$ is defined by its membership function, $\mu_{\bar{x}}$. An element x has its degree of membership in $X$ described by $\mu_{\bar{x}}(x)$, with 1 indicating full membership, 0 indicating full non-membership, and numbers between 0 and 1 indicating partial membership. In decision making applications, a fuzzy set may be used to identify flexibility on the part of the decision maker (Leung, 1988).

To transform the fuzzy model to its equivalent deterministic one, the concept of α-level (or α-cut) is using to identify fuzzy set, when the membership functions are continuous. The α-level of a fuzzy number $X$ is the set $L_\alpha(x)$ defined by $L_\alpha(x) = \{\mu_{\bar{b}}(x) \geq \alpha\}$, where $L_\alpha(x)$ is the $X$ membership function, and $\alpha \in (0,1]$.

A nonlinear programming model may be written as follows:

$$\max \quad f_i = C_i X^{T_i}$$

$$s.t. \quad A_i X^{T_i} \leq b_i, \quad i = 1,2,...,p \qquad (3\text{-}2)$$

$$X \geq 0$$

where C = ($c_1$, $c_2$, … , $c_n$), x = ($x_1$, $x_2$, … , $x_n$), A = $(a_{ij})_{m*n}$ and B = ($b_1$, $b_2$, … , $b_n$). All of the decision variables $x_i$, superscript $T_i$ of decision variables, i = 1, 2,…, n are assumed nonnegative.

Fuzzy uncertainty may occur in any of the parameters, $A$ (right-side coefficients of constraints), $\tilde{b}$ (left-side coefficients of constraints) or $\tilde{c}_i$ (objective-function constraints). This happens when the values of the parameters are not sharp. The symbol —~ " means ~~"a~~pproximately".

A common fuzzy nonlinear program, then, might assume the following form:

$$\max \quad f_i = C_i X^{T_i}$$

$$s.t. \quad A_i X^{T_i} \le b_i, \quad i = 1, 2, ..., p \qquad (3\text{-}4)$$

$$X \ge 0$$

where C = ($c_1$, $c_2$, … , $c_n$), x = ($x_1$, $x_2$, … , $x_n$), A = $(a_{ij})_{m*n}$ and B = ($b_1$, $b_2$, … , $b_n$). All of the decision variables $x_i$, superscript $T_i$ of decision variables, i = 1, 2,…, n are assumed nonnegative.

For a given nano-manufacturing case study, the general form of the FNLP optimization approach can be written as follows:

Objective function (maximize) = (1) – (2) – (3) (3-5)

where:

(1) = profits from nanoparticle manufacturing per year;

(2) = production costs of nanoparticles per year;

(3) = exposure control costs per year.

Constraints include:

(a) mass balance constraints;

(b) production volume constraints;

(c) occupational exposure limit constraints.

where occupational exposure limits constraints mean that concentrations of air pollutants (including ENMs) produced in the workplace (containing fuzzy parameters) should be equal to or less than values of occupational exposure limits (imprecise value).

### 3.2.2 The chance-constrained nonlinear programming (CCNLP) method

Chance-constrained programming (CCP) is a typical stochastic programming model for risk-based decision making. The CCP model maximizes the objective function subject to constraints with specified predetermined confidence levels, where these confidence levels are provided as appropriate safety margins by the decision-makers. The CCP model provides information on the trade-offs between the objective function's tolerance values of the constraints, and the prescribed level of probability, which could be valuable to decision makers. A mathematical program with chance-constrained parameters is presented as follows:

$$\max \; f(x_1, x_2, ..., x_n)$$

$$\text{subject to } \Pr\{f(x,\xi) \geq f\} \geq \beta \qquad (3\text{-}6)$$

$$\Pr\{g_j(x,\xi) \leq 0, j = 1, 2, ..., p\} \geq \alpha$$

where x is an n-dimensional decision vector, ξ is a stochastic vector, $f(x,\xi)$ is the return function, and $g_j(x,\xi)$ are stochastic constraint functions, $j$ = 1, 2, …, $p$, $\Pr\{\cdot\}$ denotes the probability of the event in $\{\cdot\}$, and $\alpha$, $\beta$ are predetermined confidence levels of the constraint and objective, respectively.

For a given nano-manufacturing case study, the general form of the CCNLP optimization approach can be written as follows:

Objective function (maximize) = (1) – (2) – (3) (3-7)

where:

(1) = profits from nanoparticle manufacturing per year;

(2) = production costs of nanoparticles per year;

(3) = exposure control costs per year.

Constraints include:

(a) mass balance constraints;

(b) production volume constraints;

(c) occupational exposure limit constraints.

where occupational exposure limits constraints mean that the chance of concentrations of air pollutants (including ENMs) produced in the workplace equal to or less than values of occupational exposure limits should be equal to or larger than predetermined confidence levels (imprecise value).

### 3.2.3 The fuzzy chance-constrained nonlinear programming (FCCNLP) method

The fuzzy chance-constrained nonlinear programming can be formulated as the following process.

First, the general form of nonlinear programming model is written as follows:

$$\max \quad f_i = C_i X^{T_i}$$

$$s.t. \quad A_i X \le b_i, \quad i = 1, 2, \ldots, p \qquad (3\text{-}2)$$

$$X \ge 0$$

where $X \in R^{t\times 1}$, $C_i \in R^{1\times t}$, $A_i \in R^{1\times t}$, $B_i \in R^{1\times t}$, and $R$ denote a set of real numbers. In model (3-2), all the parameters are recognized as deterministic numbers. However, when the uncertainties for some parameters of the constraints are expressed as probabilities, chance-constrained programming (CCP) can be integrated to deal with them. The models can then be solved by the CCP approach to convert them into a deterministic version by: (1) fixing a certain level of probability $p_i \in [0,1]$ for each constraint $i$, and (2) imposing the condition that the constraint $i$ is satisfied by at least a probability of $1-p_i$. Then the feasible solution set is subject to the following constraints:

$$\Pr[A_i X \leq b_i] \geq 1 - p_i, \;\; i = 1, 2, ..., n, \qquad (3\text{-}8)$$

Constraint (3-8) is generally nonlinear, and the set of feasible constraints is convex for some particular cases, when one side coefficients are deterministic and the other side ones of constraints are random. This leads to an equivalent linear constraint that has the same size and structure as a deterministic term, and the only required information about the uncertainty is then $p_i$ for the unconditional distribution of $b_i$. Thus, constraint (3-8) becomes linear:

$$A_i X \leq b_i^{(p_i)}, \;\; \forall i, \;\; i = 1, 2, ..., n, \qquad (3\text{-}9)$$

Moreover, due to the uncertain features and inaccurate information, multiple parameters are known as intervals without distribution information and difficulties may appear with modeling such a system by a deterministic mathematical programming method, which would cripple the model formulating effort leading to no results. In order to address the uncertainties of the above fuzziness and probability density functions, FMP and CCP are integrated into NLP model. Model (3-2) can be converted to:

$$\max \quad f_i = C_i X^{T_i}$$

$$s.t. \quad A_i X \le b_i^{(p_i)}, \quad i = 1, 2, ..., p \qquad (3\text{-}10)$$

$$A_i X \le b_i, \quad i = 1, 2, ..., q$$

$$X \ge 0$$

where $X \in \{R\}^{t\times1}$, $C_i \in \{R\}^{1\times t}$, $A_i \in \{R\}^{1\times t}$, $B_i \in \{R\}^{1\times t}$, and $R$ denote a set of fuzzy numbers.

By incorporating the $\lambda$ value corresponding to the membership grade of satisfaction for the fuzzy of the objective into the NLP model the fuzzy chance-constrained model can be reformulated as follows (Leung, 1988; Xie et al., 2012):

$$\max \quad \lambda$$

$$s.t. \quad f \le \lambda f^- + (1-\lambda) f^+, \quad i = 1, 2, ..., p,$$

$$A_i X \le b_i^{(p_i)}, i = 1, 2, ..., p, \qquad (3\text{-}11)$$

$$A_i X \le b_i - \lambda(b_i^+ - b_i^-), \quad i = 1, 2, ..., q,$$

$$X \ge 0,$$

$$0 < \lambda < 1,$$

where $\lambda$ is the degree of objective function constraint-satisfaction which corresponding to the degree (membership grade) to which solution fulfill the fuzzy objective or constraints. $f^+$ and $f^-$ are the upper and lower bounds respectively of objective's aspiration level as designated by the decision makers. The values of $b_i^+$ and $b_i^-$ are the permissible maximal and minimal values of constraints.

For a given nano-manufacturing case study, the general form of the CCNLP optimization approach can be written as follows:

Objective function (maximize) = (1) – (2) – (3) (3-12)

where:

(1) = profits from nanoparticle manufacturing per year;

(2) = production costs of nanoparticles per year;

(3) = exposure control costs per year.

Constraints include:

(a) mass balance constraints;

(b) production volume constraints;

(c) occupational exposure limit constraints.

where occupational exposure limits constraints mean that the chance of concentrations of air pollutants (including ENMs) produced in the workplace (containing fuzzy parameters) equal to or less than values of occupational exposure limits should be equal to or larger than predetermined confidence levels.

## 3.3 Summary

In this chapter, NLP, a most popular optimization method, is introduced to deal with the conflict of economic return and human health risks in the ENMs manufacture industry. In additional, concepts of two kinds of uncertainties, randomness and fuzziness are explained in this section. Differences and similarities of randomness and fuzziness are briefly investigated. To handle these uncertainties in the system, CCP, FMP and FCCP are implemented to address these stochastic and fuzzy programming problems. And general forms of NLP, CCP, FMP and FCCP approach in a producing case study are presented here. Furthermore, they will be applied to a concrete realistic ENMs manufacture example in the succeeding section.

# Chapter 4 CASE STUDY

In order to test and evaluate the nonlinear programming (NLP), fuzzy nonlinear programming (FNLP), chance-constrained nonlinear programming, and fuzzy chance-constrained nonlinear programming (FNLCCP) approach (see Chapter 3), a plant in Houston, Texas, USA is chosen as the study area since most of the data needed are available. In this case study, the emission concentrations of three pollutants (SWNTs, nano-Fe and CO) are simulated using the developed modeling approach under four different control scenarios (no, low, medium and high). The modeling results will be presented and analyzed in the next chapter.

## 4.1 Overview of the Case Study

The study case was adapted from a SWNT manufacturing plant located in Houston, TX, USA (Ouellette, 2003), where nano-specific occupational environmental health and safety (EHS) standards were voluntarily implemented (Due to monitoring technique difficulties, mandatory exposure limits for ENMs have not been available so far). In the plant, the HiPco method is used to produce 87% pure SWNT. There are nine HiPco synthesis lines in one production room with a size of 30 m × 20 m × 6 m. The plant operates eight hr/day and 365 days/year. Each line produces SWNTs with 97% synthesis product yield and 90% purification yield. During the production, three air pollutants are emitted that workers are exposed to: SWNTs, nano-size iron powder and carbon monoxide.

## 4.2 Optimization for Occupational Exposure Risk Management of SWNT Manufacturing

### 4.2.1 Formulation of the nonlinear programming (NLP) model

The model below was developed using the optimization method to evaluate cost and exposure control trade-offs of the SWNT manufacturing process:

$$\max\ [P-(q_1x_1+q_2x_2+F)-C_i]\times N\times SPY\times PY\times D\times H_r\times x_3$$

$$s.t.\ \ a_{11}x_1+a_{12}x_2-x_3=0$$

$$PV_1\le N\times SPY\times PY\times D\times H_r\times x_3\le PV_2$$

$$(1-\eta_i)(e_1\times x_1\times Hr/V)\le OEL_{s(Fe)}$$

$$(1-\eta_i)(e_2\times x_2\times Hr/V)\le OEL_{s(CO)}$$

$$(1-\eta_i)(e_3\times x_3\times Hr/V)\le OEL_{s(PSWNT_s)}$$

$$x_1,x_2,x_3\ge 0,\ i=1,2,3,4$$

where $x_1$, $x_2$ are the feed rate of $Fe(CO)_5$ and CO (in g/h), respectively; $x_3$ is the SWNT material production rate (g/hr); P is the revenue from each gram of SWNT manufactured (\$/g); $q_1$, $q_2$ is the cost of $Fe(CO)_5$ and CO for each gram of SWCNT produced, respectively (\$/g); F is the total costs of SWCNT except for the raw materials (\$/g); the raw materials are included in the above parameters); $C_i$ is the exposure control cost of SWCNT per gram produced (\$/g) in every scenario; N is the number of production lines; *Hr* is the working hours per day (hours/day); SPY is the synthesized product (carbon nanotube) yield (%); *PY* is the SWCNT purification yield (%); D is the working days per year(days/year); $a_{11}$, $a_{12}$ are the percentages of $Fe(CO)_5$ and CO used to synthesize SWCNTs, respectively (%); $PV_1$ and $PV_2$ are the minimum and maximum production volume of SWCNTS per year (g/yr); $\eta_i$ is the removal efficiency of MNMs emissions at each control levels (%); $e_1$, $e_2$, $e_3$ represent the emission coefficients of nano-sized Fe, CO and SWCNTs, respectively (They are used to quantify the emission of nano-sized Fe, CO and SWCNTs from a unit production of SWNTs and are calculated); $V$ is the volume of the workplace ($m^3$); $OELs_{(Fe)}$, $OELs_{(CO)}$, $OELs_{(SWNTs)}$ are the occupational exposure limits for iron powder, CO and SWNTs, respectively ($mg/m^3$).

The value of the objective function $[P-(q_1x_1+q_2x_2+F)-C_i]\times N\times SPY\times PY\times D\times H_r\times x_3$ is the annual net profits of SWCNT manufacturing; ($q_1x_1$ + $q_2x_2$) represents the cost of the two raw materials used for each gram of SWCNTs produced; F includes the expense of direct labour, energy, equipment, installation, tools, building and fixed overhead (Ouellette, 2003); $N \times SPY \times PY \times D \times H_r \times x_3$ is the annual production volume of SWCNTs; $q_1$, $q_2$ are the cost of $Fe(CO)_5$ and CO for each gram of SWCNTs produced, respectively.

The production volume is the number of manufacturing (production) lines multiplied by the throughput for a single line. And the annual throughput rate of one HiPco synthesis production line is calculated as: $Throughput = SPY \times PY \times D \times H_r \times x_3$, where the SWNT synthesis product yield represents the relative amount of carbon naotubes (single-wall carbon nanotubes and multi-wall carbon nanotubes) expected from the converted carbon and the purification yield indicates the percent of SWNT removed from the carbon product compared to the total SWNT created from the synthesis step.

Five constraints are material flow balance, annual production volume and cumulative exposure to three hazardous materials, which will be explained as follows: (1) *Material flow balance*. From Equations (1) and (2), we know that SWNT is synthesized from the carbon elements of CO and $Fe(CO)_5$, e.g., 10 moles of CO (or $Fe(CO)_5$) produce 5 moles of SWNT and 5 moles $CO_2$. (2) *Annual production volume*. The production volume should within a certain range. (3) *The emissions of nano-sized Fe*, *CO and SWNTs* should be less than the allowable amount in relation to their occupational exposure limits.

### 4.2.2 Formulation of the fuzzy nonlinear programming (FNLP) model

The detailed FNLP SWNT model is written below

$$\max \ \lambda$$

$$s.t. \quad a_{11}x_1 + a_{12}x_2 - x_3 = 0$$

$$PV_1 \le N \times SPY \times PY \times D \times H_r \times x_3 \le PV_2$$

$$[P - (q_1x_1 + q_2x_2 + F) - C_i] \times N \times SPY \times PY \times D \times H_r \times x_3 \le B^+ - \lambda\left(B^+ - B^-\right)$$

$$(1-\eta_i)(\zeta_1 \times x_1 \times Hr / V) \le OEL_{s(Fe)}$$

$$(1-\eta_i)(\zeta_2 \times x_2 \times Hr / V) \le OEL_{s(CO)}$$

$$(1-\eta_i)(\zeta_3 \times x_3 \times Hr / V) \leq OEL_{s(SWNT_s)}$$

$$x_1, x_2, x_3 \geq 0, \; i = 1,2,3,4$$

### 4.2.3 Formulation of the chance-constrained nonlinear programming (CCNLP) model

The detailed model formulated using this optimization approach for our Texas factor case study is described in the next section. In the single-wall carbon nanotube exposure control case study discussed above, emission coefficients of the three pollutants (*i.e.*, nano-sized Fe, CO and SWCNTs) were uncertain. A: emission coefficient can be calculated as follows (Naga, 2005):

$$e = \frac{Con \times V \times Hr \times D}{PV \times Tr}$$

where Con is the estimated concentration of pollutant (μg/m$^3$·h or mg/m$^3$·h); V is the volume of the workplace (m$^3$); Hr is the working hours per day (h/day); D is the working days per year (days/year); PV is the average production volume of SWCNTS per year (g/yr); Tr is the transformation factor (1,000,000 when the unit for Con is μg/m$^3$·h and 1,000 if the unit is mg/m$^3$·h. For a specific MNM manufacturing section, V, Hr, D, PV and Tr are deterministic values. Con is an uncertain variable which can be presented as a probability density function. Thus, emission coefficient (*e*) also can be described by a probability density function. Assuming these emission coefficients contain random variables, then the model can be rewritten as:

$$\max \ [P-(q_1x_1+q_2x_2+F)-C_i]\times N\times SPY\times PY\times D\times H_r\times x_3$$

$$s.t. \ \ a_{11}x_1+a_{12}x_2-x_3=0$$

$$PV_1\leq N\times SPY\times PY\times D\times H_r\times x_3\leq PV_2$$

$$\Pr[(1-\eta_i)(\zeta_1\times x_1\times Hr/V)\leq OEL_{s(Fe)}]\geq\alpha$$

$$\Pr[(1-\eta_i)(\zeta_2\times x_2\times Hr/V)\leq OEL_{s(CO)}]\geq\alpha$$

$$\Pr[(1-\eta_i)(\zeta_3\times x_3\times Hr/V)\leq OEL_{s(PSWNT_s)}]\geq\alpha$$

$$x_1,x_2,x_3\geq 0,\ \ i=1,2,3,4$$

where $\zeta_1$, $\zeta_2$, and $\zeta_3$ , which are functions containing random variables, replace $e_1$, $e_2$, $e_3$ to represent emission coefficients of nano-sized Fe, CO and SWCNTs, respectively. $\Pr\{\cdot\}$ means that the cumulative exposure should be less than the ―no observable effect" level(NOEL) $\geq \alpha$ of the time. Figure 2 shows a framework of the CCNLP optimization method.

### 4.2.4 Formulation of the fuzzy chance-constrained nonlinear programming (FCCNLP) model

The detailed FCCNLP SWNT model is written below.

$$\max \quad \lambda$$

$$s.t. \quad a_{11}x_1 + a_{12}x_2 - x_3 = 0$$

$$PV_1 \le N \times SPY \times PY \times D \times H_r \times x_3 \le PV_2$$

$$[P - (q_1x_1 + q_2x_2 + F) - C_i] \times N \times SPY \times PY \times D \times H_r \times x_3 \le B^+ - \lambda\left(B^+ - B^-\right)$$

$$\Pr[(1-\eta_i)(\zeta_1 \times x_1 \times Hr / V) \le OEL_{s(Fe)}] \ge \alpha$$

$$\Pr[(1-\eta_i)(\zeta_2 \times x_2 \times Hr / V) \le OEL_{s(CO)}] \ge \alpha$$

$$\Pr[(1-\eta_i)(\zeta_3 \times x_3 \times Hr / V) \le OEL_{s(SWNT_s)}] \ge \alpha$$

$$x_1, x_2, x_3 \ge 0, \quad i = 1,2,3,4$$

Figure 9 shows a framework of the FCCNLP optimization method.

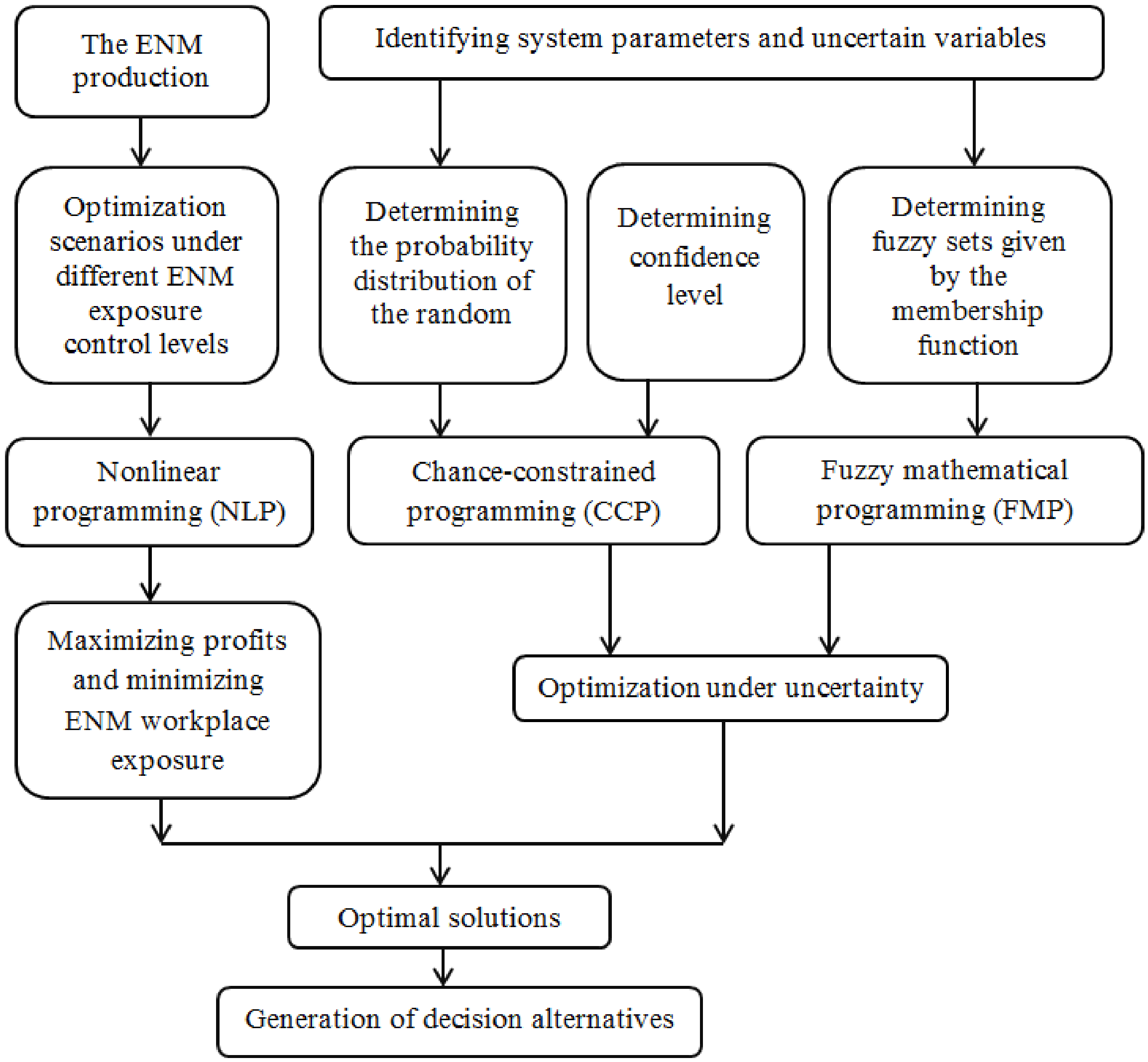


Figure 9 Framework of the FCCNLP optimization method

## 4.3 Data Preparation

### 4.3.1 Development of membership functions

For the fuzzy optimization, there are three places in which the data turn this problem into a fuzzy optimization problem. First, the objective function can be a function with upper and lower boundaries. Second, the left side matrix $A_i$ is composed of fuzzy numbers, $\eta_i$ , which presents reduce efficiency for each levels of control. Third, the right-hand side value is the suggested occupational exposure limit which lies on a degree (the boundaries between non-effective and effective dosages of pollutants to workers are gradual, transitional), thus, the right-side value could be regarded as fuzzy.

First, for the objective function, it is decided by the investors that a target value, 5,000,000 dollars per year, is required as the total net return. In case the target value is too optimistic, the total net return is allowed to fall below it. The bottom line is 4,000,000 dollars every year. Thus, the fuzzy interval of the objective function is from 4 to 5 million dollars each year.

Second, for $\eta_i$ , the reduce efficiency for each levels of control, the range of this value for each levels of control are listed in Table 1.

Third, for the occupational exposure limits of SWNT, nano iron and CO, the membership grade shows how suitable the standard is, that is, when a standard is suitable, it has a high possibility for being adapted without significant modifications (Leung 1988). Formulation of membership function for the fuzzy standard involves the following three steps:

1. Determination of minimum possible concentration ($C_{\min}$). When $C_{\min}$ = 0, it means zero tolerance of emission and then no health risks to workers. However, it is an extreme situation that is impractical and cannot be implemented as a standard. Therefore, the membership grade is 1.

2. Determination of the most suitable standard level ($C_{optimal}$). It is based on an assumption that the threshold limit values, that are levels that believed workers can be exposed day after day for a working lifetime without adverse health effects, exist for toxic effects of SWNT, nano iron

and CO. First, for $C_{optimal,SWNT}$, in April 2013, the National Institute for Occupational Safety and Health (NIOSH) published a bulletin which set recommended exposure limit (REL) for carbon nanotube as 1 μg/m$^3$, based on the estimation of the animal no observed adverse effect level (NOAEL) of CNT was near 1 μg/m$^3$ (8-hr TWA); Second, for $C_{optimal,nano-Fe}$, in 2010, OSHA suggested a mass concentration of 7.9 μg/m$^3$ should not be exceeded (OSHA 2010; Schulte et al. 2010); Third, for $C_{optimal,CO}$, the American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbon monoxide a threshold limit value (TLV) of 29 mg/m$^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek. Thus, we get $C_{optimal,SWNT}$ =1 μg/m$^3$, $C_{optimal,nano-Fe}$ = 7.9 μg/m$^3$, $C_{optimal,CO}$=29 mg/m$^3$ with membership grade = 1.

3. Determination of maximum tolerable concentration for SWNT, nano-Fe and CO ($C_{\max}$). These levels indicate 100% probability of health injury. First, for $C_{\max,SWNT}$, investigators and organizations have recommended occupational exposure limits (OELs) for CNT within the range of 1-50 μg/m$^3$ (NIOSH. 2013); Second, for $C_{\max,nano-Fe}$, the benchmark level lead in an important determinant of hazard of the class of MNMs including nano-Fe is 100 μg/m$^3$ (Broekhuizen and Dorbeck-Jung, 2013); Third, for $C_{\max,CO}$, the NIOSH has established a REL for carbon monoxide of 229 mg/m$^3$ as a ceiling. Then, $C_{\max,SWNT}$ = 50 μg/m$^3$, $C_{\max,nano-Fe}$ = 100 μg/m$^3$ and $C_{\max,CO}$ = 229 mg/m$^3$, respectively.

Table 1 Fuzzy sets of reduce efficiency for each levels of control (adopted from Ok et al., 2008)

| Control Level | Reduced Efficiency (η) |
|---|---|
| No | [0, 0.1, 0.2] |
| Low | [0.2, 0.3, 0.4] |
| Medium | [0.4, 0.55, 0.7] |
| High | [0.7, 0.85, 1] |

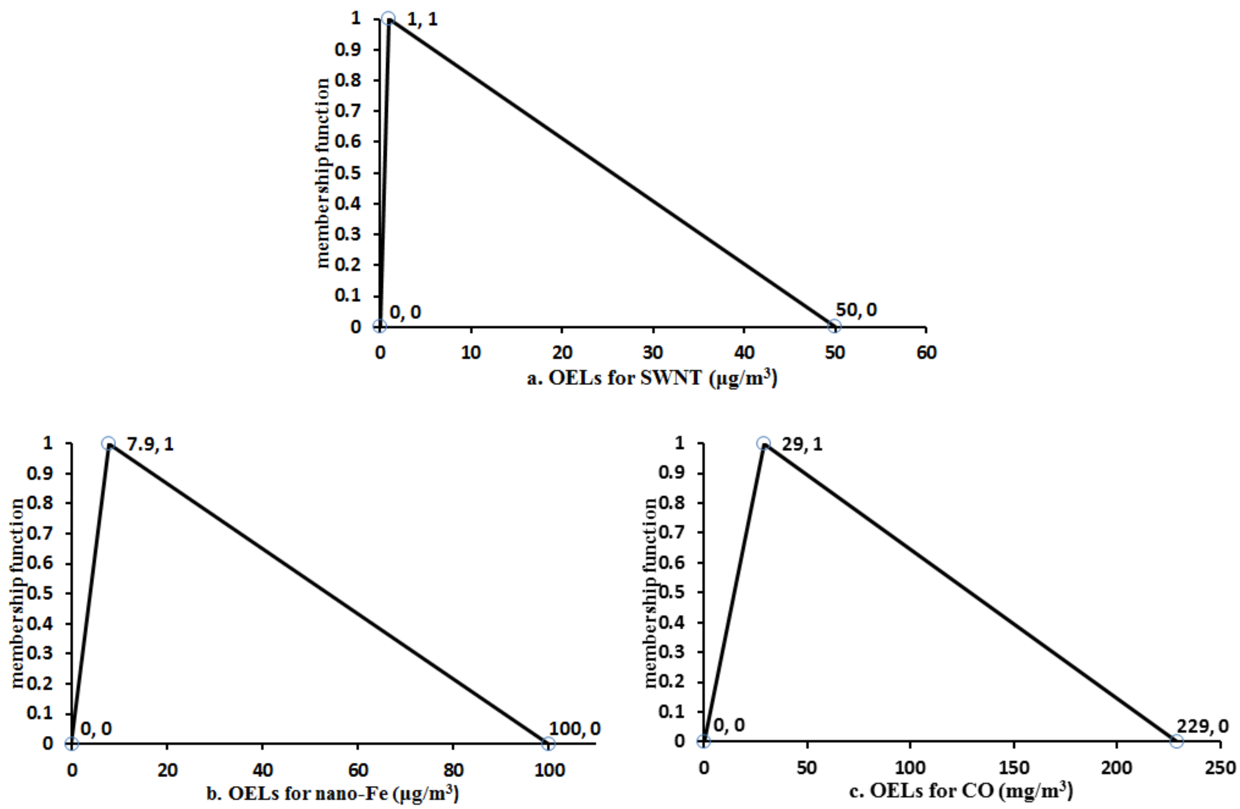


Figure 10 The membership function of OELs (fuzzy parameters) for (a).SWNT, (b).nano-Fe, (c).CO

## 4.3.2 Model description and scenarios

As shown in table 2, four levels of EHS standards (no, low, medium and high) are defined to represent the strategies which nano-EHS standards might be imposed (NIOSH 2004).

Table 2 Summary of assumptions for environmental health and safety (EHS) standards (adapted from Ok et al., 2008)

| | **Level of EHS standards** | | |
|---|---|---|---|
| **Type of EHS Control** | **Low** | **Medium** | **High** |
| **Engineering controls** | | | |
| General exhaust-ventilation | 24hr, 28.31 $m^2$ ventilation rate, $10,000 capital cost, $ 3,000/year operating cost | 24hr, 28.31 $m^2$ ventilation rate, $10,000 capital cost, $ 3,000/year operating cost | 24hr, 28.31 $m^2$ ventilation rate, $10,000 capital cost, $ 3,000/year operating cost |
| Fume hoods | | $4,000 capital cost for 0.58$m^2$ equipment and $9,500 for 2.3 $m^2$ equipment | $4,000 capital cost for 0.58$m^2$ equipment and $9,500 for 2.3 $m^2$ equipment |
| Enclosure of processes | | | 50% decrease in labor productivity, 50% extra equipment cost |
| **Administrative controls** | | | |
| Annual worker training | 8hr of training, $560/year instructor cost | 8hr of training, $560/year instructor cost | 8hr of training, $560/year instructor cost |
| Air monitoring | Monthly monitoring, $20,000/equipment capital cost | Weekly monitoring, $20,000/equipment capital cost | Biweekly monitoring, $20,000/equipment capital cost |
| Medical monitoring | | | $950/worker/year |

We assume that the emission coefficients of nano-sized Fe, CO and SWCNTs are normally distributed random variables with known means and standard deviations (Table 3). Control costs for each level are 10, 78 and 210 $/g for low, medium and high control, respectively (Ok, 2008).

For the chance-constrained programming of SWNTs exposure, the predetermined confidence levels in four scenarios are tested as 90%, 95% and 99%, respectively.

Table 3 Mean and standard deviations of the emission coefficients of nano-sized Fe, CO and SWCNTs

| | **mean** | **SD** | **Reference** |
|---|---|---|---|
| nano-sized Fe ($\zeta_1$) | 0.00135 | 0.0007 | (Calculated from Maynard, 2004) |
| CO ($\zeta_2$) | 0.037 | 0.0004 | (Calculated from Lai, 2004) |
| SWCNTs ($\zeta_3$) | 0.00287 | 0.00227 | (Calculated from Maynard, 2004) |

The main assumptions of this model include that (1) the objective function is linear; (2) the reactions are under the condition of 1050 °C and 30 atm; (3) the reactions reach the dynamics balance very quickly and no other kind of carbon exists; (4) no other source of Fe, CO and SWCNTs pollution exists in the workplace; (5) concentrations of Fe, CO and SWCNTs in the air of the room are homogeneous; (6) the total production cost except raw material is fixed.

The values of parameters used based on references are given in the table 4.

Table 4 Summary of model Parameters

| Symbols | Units | Meanings | Values | Reference |
|---|---|---|---|---|
| P | \$/g | the price of SWCNTs | 1,000 | (Isaacs et al., 2010) |
| $q_1$ | \$/g | the cost of $Fe(CO)_5$ for each gram SWCNTs produced | 0.21 | (Healy, 2005) |
| $q_2$ | \$/g | the cost of CO for each gram SWCNTs produced | 37 | (Healy, 2008) |
| F | \$/g | the total costs of SWCNT except the raw material | 411.28 | (Calculated from Isaacs et al., 2010) |
| N | \ | the number of production lines | 9 | (Isaacs et al., 2010) |
| SPY | % | the synthesis product yield | 97 | (Isaacs et al., 2010) |
| PY | % | the purification yield | 90 | (Isaacs et al., 2010) |
| D | days/year | the working days per year | 365 | (Isaacs et al., 2010) |
| Hr | hours/day | the working hours per day | 8 | (Isaacs et al., 2010) |
| $a_{11}$ | % | the percentage of $Fe(CO)_5$ will be utilized to synthesis SWCNTs | 15 | (Calculated from Nikolaev et al., 1999) |
| $a_{12}$ | % | the percentage of CO will be utilized to synthesis SWCNTs | 21 | (Calculated from Nikolaev et al., 1999) |
| $PV_1$ | g/yr | the minimum production volume of SWCNTS per year | 0 | (Isaacs et al., 2010) |
| $PV_2$ | g/yr | the maximum production volume of SWCNTS per year | 20,000 | (Isaacs et al., 2010) |
| $e_1$ | \ | the emission coefficient of nano-sized Fe | 0.003 | (Maynard, 2004) |
| $e_2$ | \ | the emission coefficient of CO | 0.037 | (Lai, 2004) |
| $e_3$ | \ | the emission coefficient of SWCNTs | 0.005 | (Maynard, 2004) |
| $OELs_{(Fe)}$ | $\mu g/m^3$ | the occupational exposure limits for nano-sized Fe | 5 | (OSHA, 1997) |
| $OELs_{(CO)}$ | $mg/m^3$ | the occupational exposure limits for CO | 40 | (HIOSH, 1992) |
| $OELs_{(SWNTs)}$ | $\mu g/m^3$ | the occupational exposure limits for SWCNTs | 7 | (Schulte, 2010) |

According to the pervious study, uncertainties in the nanomaufacturing process also include imprecise knowledge of control costs and reduce efficiency for each level of control scenarios and environmental health and safety (EHS) standards, except the insufficient information of exposure concentration in the workplace. Thus, fuzzy mathematical programming (FMP) could be applied to deal with vagueness and ambiguity based on fuzzy set theory.

Models were developed and solved using the optimization software What'‘s*Best!* 13.0.

# Chapter 5 RESULTS AND ANALYSIS

Based on the concentration distributions of the three criteria pollutants (i.e. SWNTs, nono-Fe powder and CO) and membership functions to the OELs of these three air pollutants presented in chapter 4, the production scale, production cost, annual net profit, and exposure concentrations of SWNT, CO are estimated by NLP, FNLP, CCNLP and FCCNLP, respectively. These results will be described in details as follows.

## 5.1 Nonlinear Programming Model Results

Table 5 shows results of the NLP method (production volume, production cost, profit, and SWNT, CO, Fe exposure in the workplace) based on the four control scenarios which are under the same occupational exposure limits (OELs) but four different emission control strategies (no, low, medium and high control levels). The results suggest that SWNTs are the major threat to workers' health, compared to CO and nano-Fe, because SWNT exposure concentrations are equal to the value of OELs in each policy levels while the emission of CO and nano-Fe are both far below theirs OELs.

In no control scenario, the profit is \$0.61M/yr when production volume is 1,032 g/yr, and production cost is 406.43 \$/yr. When a low level control policy is taken, the 10% particle remove efficiency 11% raise the production volume, while the total cost (production cost plus control cost) increase 2.7%, which leading to 9.8% decrease of profit. In the medium control scenario, the production volume increases 100% due to the 50% remove efficiency. And then the profit increases 72% with the 21% rise of the total cost. Once a high level of protection is implemented, the production volume would reach the maximum 5,162 g/yr (400%) owing to its 90% remove efficiency, and the total cost would also significantly increased (60%), which generate the highest profit 1.82 $M/yr (198%). Thus, generally speaking, the annual profits and air pollutants concentrations increase with the rise of the manufacturing production volume caused by the stricter control criteria.

Table 5 Results of the NLP method

| **Control Level** | **Production Volume (g/yr)** | **Production Cost ($/g)** | **Profit ($M/yr)** | **SWNT Exposure (μg/m$^3$)** | **CO Exposure (μg/m$^3$)** | **Fe Exposure (μg/m$^3$)** |
|---|---|---|---|---|---|---|
| No | 1,032 | 406.43 | 0.61 | 1.00 | 21.43 | 0.13 |
| Low | 1,147 | 407.31 | 0.67 | 1.00 | 22.81 | 0.13 |
| Medium | 2,065 | 414.35 | 1.05 | 1.00 | 26.37 | 0.13 |
| High | 5,162 | 438.13 | 1.82 | 1.00 | 29.04 | 0.14 |

In the HiPco SWNT manufacturing process, as mentioned in the section 2.2.2, there are two sources of CO gas. The first source is the injected CO gas raw material that is not only to take part in the Boudouard reaction (reaction (2)) to produce SWNT but also to protect synthesized SWNT particles from oxidation. The second one is from the reaction (1), which is product from decomposition of $Fe(CO)_5$. The amount of CO exposure is proportionate to the amount of CO gas from these two sources. That is the reason of CO exposure increase with the increase of control level.

## 5.2 Fuzzy Nonlinear Programming Model Results

In FNLP model, a number of α-cut levels are examined (i.e. 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1) based on a combination of multiple fuzzy coefficients, that is, pollutants reduced efficiencies, OELs, and net return profits objective. This can help investigating the relationships among production volumes, profits, and air pollution exposure under uncertainties.

Table 6 presents the solutions for production scales, economic benefits and pollutants exposure concentrations of different control strategies without considering the fuzziness of $OEL_s$ of CO and nano-Fe, because the concentrations of CO and nano-Fe emission are too low to be 'approximately' these $OEL_s$. The optimal solutions of no, low and medium control scenarios are achieved under the condition of $\lambda=1$ and $\alpha = 0.85$, which means the requirement of objective function are 100% satisfied in these scenarios but may have a probability of 15% for getting a health damage; while the solution of high level control is gotten when $\lambda = 0.76$ and $\alpha = 0.94$, indicating the degree of satisfaction the requirement is 76% fulfilled but with only 6% probability of health injury.

Different α-cut levels correspond to different reduced efficiencies, OELs, financial objective satisfaction degree, and thus cause varied production volume, eventually result in changed net profits and SWNTs exposure concentration. Annual net profits vary under different α-cut levels, as shown in Figure 11. Take no control scenario for example, when α=1 (in association with the highest plausibility degree with the OELs), the hollow circle means no feasible solution exits because the profit is 0.61 \$M/yr which is far below the lower boundary of the expected economic objective; until α= 0.85, the profit gets the feasible value of 5.3 \$M/yr with the rise of the production volume from 1,707 g/yr to 10,129 g/yr. when $\alpha$= 0.65, profit reaches the highest value 8.96 $M/yr because the production volume gains the maximum 20,000 g/yr at this point. When $\alpha$=0 (in association with the lowest plausibility degree with the OELs), profit is the same value when $\alpha$= 0.65 due to the steady production volume. Lines of other scenarios show the same trend. Thus, the results indicated that the economic benefits would be increased as the $\alpha$-cut level is deceased. The change of the SWNT exposure under different $\alpha$-cut levels is presented in Figure 12. We also take the no control scenario for example, when $\alpha$=1, the SWNT exposure concentration is the lowest but it cannot be accepted for its too low profits. When $\alpha$= 0.85, SWNT exposure concentration reaches the lowest feasible value 8.35 $\mu g/m^3$. When $\alpha$= 0.65, SWNT exposure concentration gets the highest value 18.11 $\mu g/m^3$ because the production volume gains the maximum 20,000 g/yr at this point. When $\alpha$=0, SWNT exposure concentration is also 18.11 $\mu g/m^3$ due to the same production volume. Therefore, from Figure 11, we can get the similar conclusion that the SWNT exposure concentrations would be increased as the $\alpha$-cut level is deceased.

Compared to the results of nonlinear programming, we reach the conclusion that the interrelationship among net profits return, production volumes and air pollution amounts of fuzzy nonlinear programming are the same as those of NLP. But more pollution is obtained in FNLP due to the flexibility of OELs.

Table 6 Results of the FNLP method

| Control Level | Degree of objective function Satisfaction (λ) | Production Volume (g/yr) | Production Cost ($/g) | Profit ($M/yr) | SWNT Exposure (μg/m$^3$) | CO Exposure (μg/m$^3$) | Fe Exposure (μg/m$^3$) |
|---|---|---|---|---|---|---|---|
| No | 1 | 10,129 | 476.27 | 5.30 | 8.35 | 197.56 | 0.84 |
| Low | 1 | 12,057 | 491.08 | 6.02 | 8.35 | 202.82 | 0.84 |
| Medium | 1 | 18.245 | 538.60 | 7.00 | 8.35 | 209.04 | 0.84 |
| High | 0.76 | 20,000 | 552.08 | 4.76 | 3.87 | 135.64 | 0.20 |

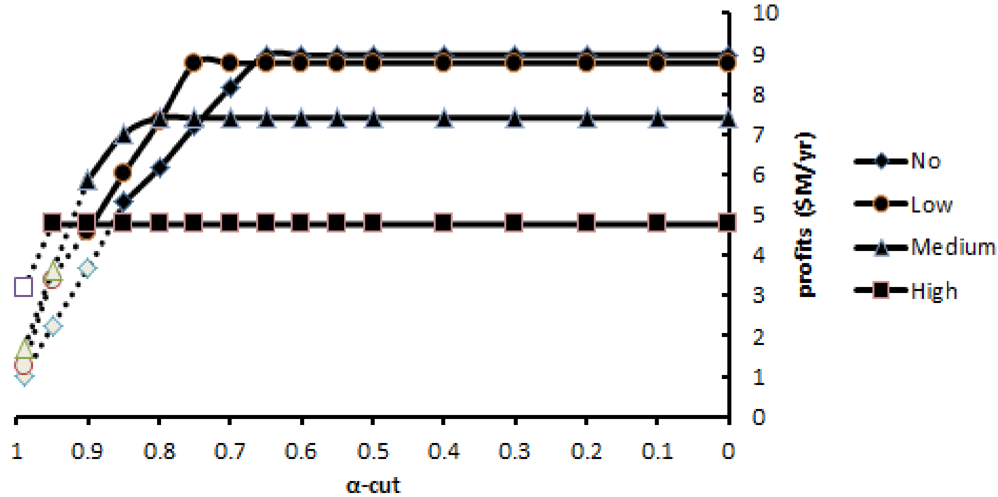


Figure 11 Annual net profits under different α-cut levels in FNLP

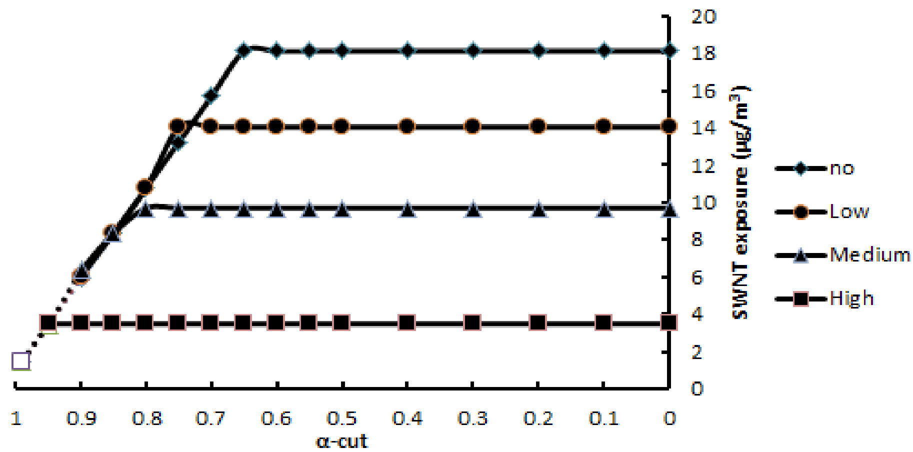


Figure 12 SWNT exposure under different α-cut levels in FNLP

## 5.3 Chance-constrained Nonlinear Programming Model Results

In the chance-constrained nonlinear programming, the $\alpha_i$ levels represent a set of probabilities at which the constraints can be violated (*i.e.*, the admissible risk levels of violating the occupational exposure limits). The annual net profits and air pollutants exposure concentration change with different $\alpha_i$ levels, that is, different levels of OELs enforcement. Figures 13 and 14 show the worker exposure ranges of SWNT and CO under different confidence $\alpha_i$ levels in different control criteria. As Figure 13 shows, in the no control scenario, the SWNTs exposure concentrations are [0, 1.77], [0, 1.55] and [0, 1.25] μg/m$^3$ when α=0.9, 0.95 and 0.99, respectively. These concentrations are the same in other scenarios. Figure 15 shows the corresponding SWNT manufacturing profits obtained using the CCP calculations. In the no control scenario, the net returns are 0.53, 0.45 and 0.38 $M/yr when α=0.9, 0.95 and 0.99, respectively. In the high control scenario, they are 1.60, 1.41 and 1.16 $M/yr when α=0.9, 0.95 and 0.99, respectively. The trend is the same in the low and medium control criteria. Table 7 describes the CCP model calculated results for SWNT production volume, production costs, net profits and estimated worker exposure ranges for the three air pollutants (SWNT, nano-Fe and CO) at different confidence levels. Results from CCNLP show that similarly to NLP and FNLP, the higher control criteria lead to higher benefits. Also, results indicate that a decreasing α level means a decreasing limitation for the OEL constraints, which may then result in an increased production volume. The increased production volume would potentially increase the profits and, at the same time, the pollutants discharge concentrations. In general, a lower α level brings on a higher profits but a higher risk of violating the EHS constraints; meanwhile, a higher α level results in a lower profits but an increased reliability of satisfying the occupational standards. These alternatives represent a compromise between economic benefits and environmental health and safety (EHS) requirements.

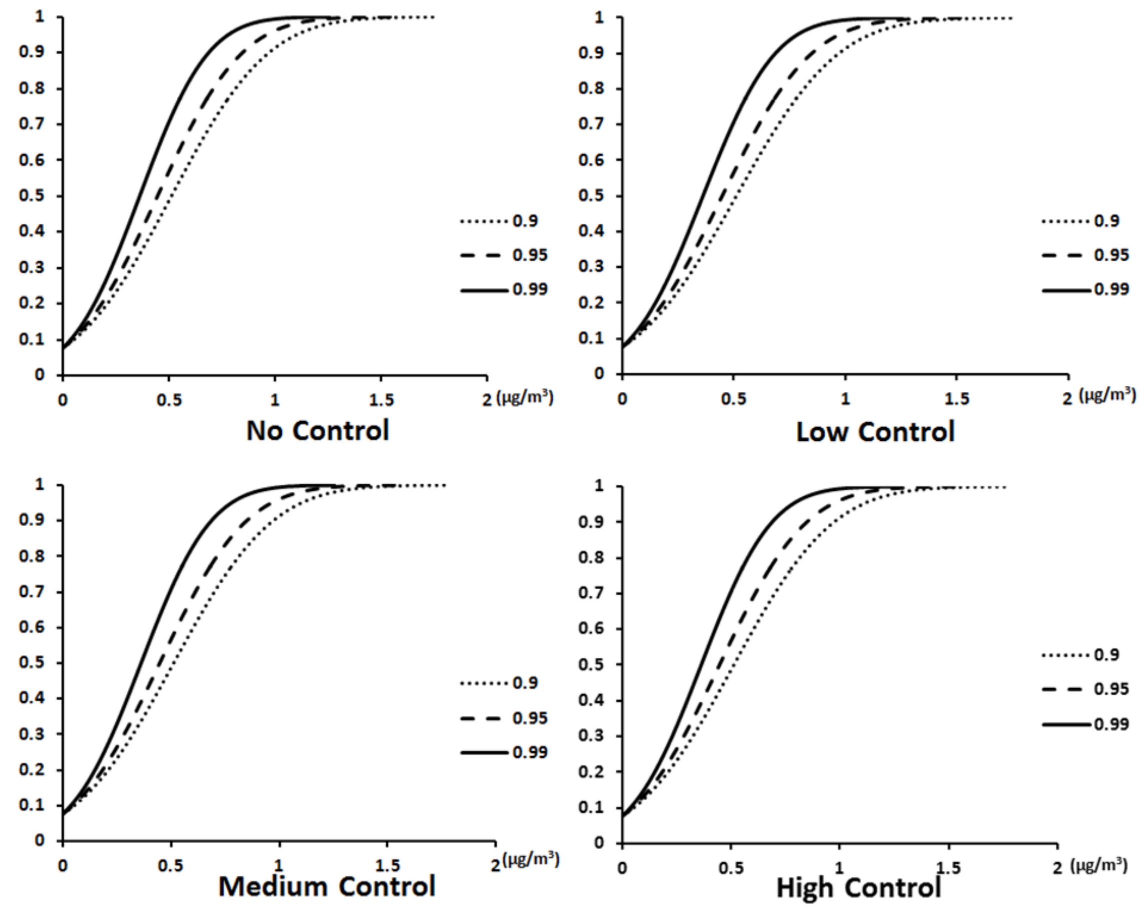


Figure 13 Cumulative probability distributions of SWNT exposure results from CCP method

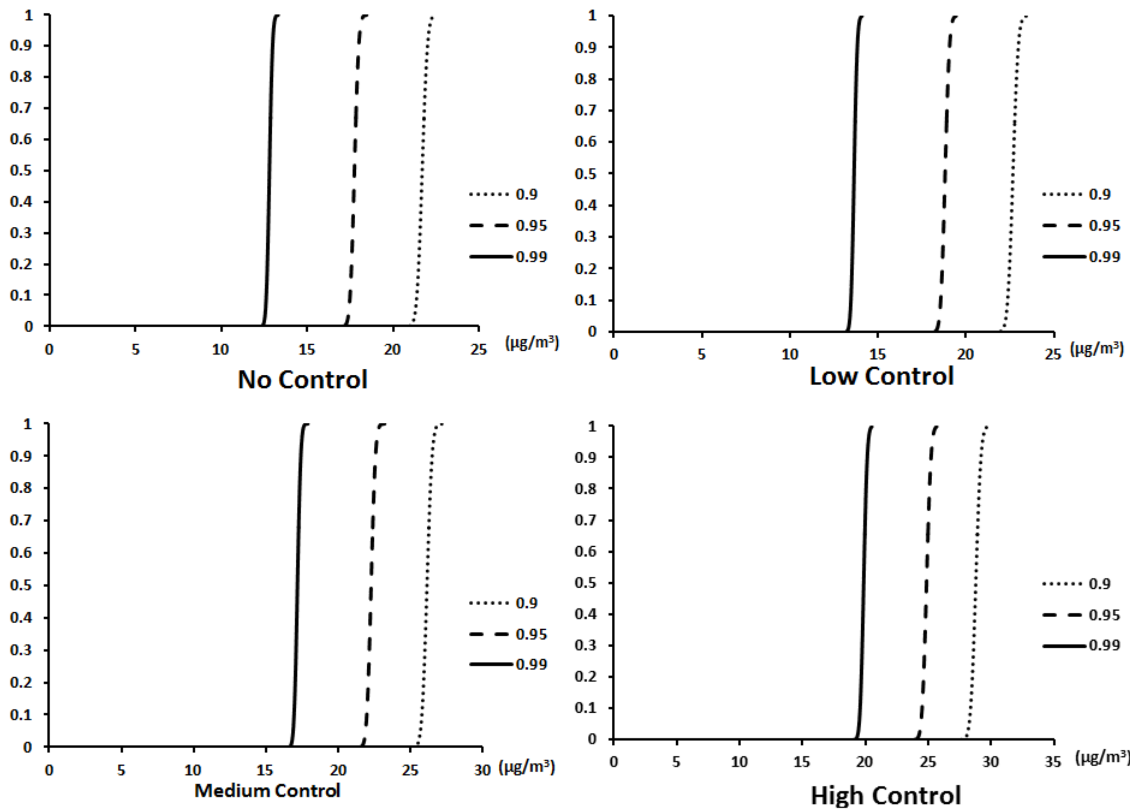


Figure 14 Cumulative probability distributions of CO exposure results from CCP method

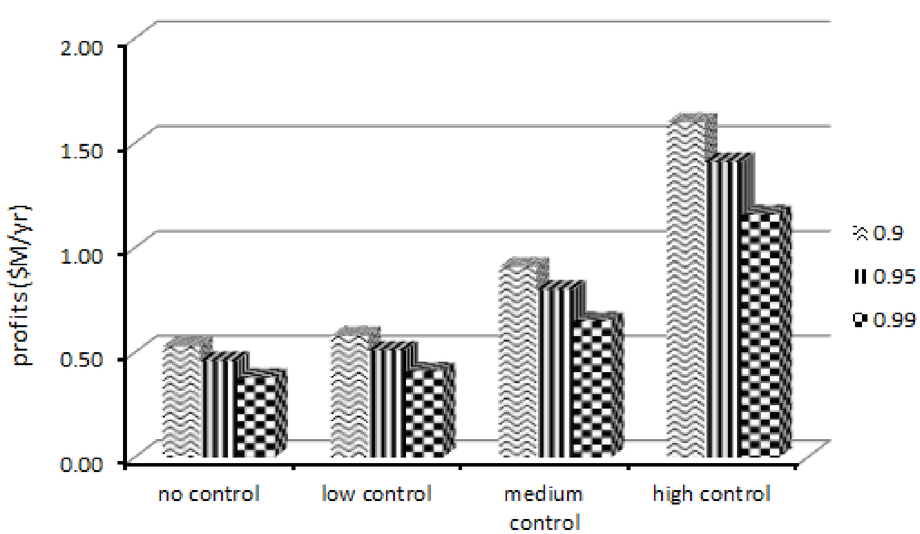


Figure 15 The annual net profits results from CCNLP method

Table 7 Results of the CCNLP method

| Confidence Level | Control Level | Production Volume (g/yr) | Production Cost ($/g) | Profit ($M/yr) | SWNT Exposure (μg/m$^3$) | CO Exposure (μg/m$^3$) | Fe Exposure (μg/m$^3$) |
|---|---|---|---|---|---|---|---|
| 0.9 | No | 895 | 405.37 | 0.53 | 0.00–1.77 | 20.99–22.57 | 0.00–0.23 |
| | Low | 993 | 406.13 | 0.58 | 0.00–1.77 | 21.97–23.40 | 0.00–0.23 |
| | Medium | 1,790 | 412.23 | 0.91 | 0.00–1.77 | 25.15–27.23 | 0.00–0.23 |
| | High | 4,474 | 432.84 | 1.60 | 0.00–1.77 | 27.63–29.71 | 0.00–0.24 |
| 0.95 | No | 780 | 404.50 | 0.46 | 0.00–1.55 | 17.17–18.46 | 0.00–0.20 |
| | Low | 870 | 405.18 | 0.51 | 0.00–1.55 | 18.24–19.42 | 0.00–0.20 |
| | Medium | 1,565 | 410.51 | 0.80 | 0.00–1.55 | 21.43–23.21 | 0.00–0.20 |
| | High | 3,901 | 428.44 | 1.41 | 0.00–1.55 | 23.87–25.67 | 0.00–0.20 |
| 0.99 | No | 633 | 403.38 | 0.38 | 0.00–1.25 | 12.38–13.32 | 0.00–0.16 |
| | Low | 702 | 403.90 | 0.41 | 0.00–1.25 | 13.22–14.09 | 0.00–0.16 |
| | Medium | 1,264 | 408.20 | 0.65 | 0.00–1.25 | 16.53–17.90 | 0.00–0.16 |
| | High | 3,166 | 422.80 | 1.16 | 0.00–1.25 | 19.07–20.51 | 0.00–0.16 |

## 5.4 Fuzzy Chance-constrained Nonlinear Programming Model Results

As the incorporation of FNP and CCP, the fuzzy chance-constrained nonlinear programming supplies optimal solutions under multiple uncertainties. Table 8 describes the FCCNLP model calculated results for the degree of satisfaction of objective, SWNT production volume, production costs, net profits and estimated worker exposure ranges for the 3 air pollutants (SWNT, nano-Fe and CO) at different confidence levels when α-cut is 0.85.

Probability is a numerical measure of the likelihood that an event will occur. Probability values are always assigned on a scale from 0 to 1. A probability near zero indicates an event is unlikely to occur; a probability near 1 indicates an event is almost certain to occur. Other probabilities between 0 and 1 represent degrees of likelihood that an event will occur. In probability theory and statistics, the cumulative distribution function, describes the probability that a real-valued random variable X with a given probability distribution will be found at a value less than or equal to x. In this case study, Figure 16 is the cumulative probability distribution curves of SWNT exposure results from FCCNLP model where the x-axis is the SWNT exposure concentrations and the y-axis is the probability of the corresponding SWNT exposure concentrations in the air of workplace. Take Figure 16 no control curve for example, when α level equal to 0.99, it shows that SWNT concentration has 100% of probability to be within 14.7 $\mu g/m^3$.

Comparing Results of NLP to FCCNLP, for example, table 5 to 0.9 confidence level of table 8, the trend is similar that the annual profits and air pollutants concentrations increase with the rise of the manufacturing production volume with the stricter control criteria. However, difference exists that in the 0.9 confidence level of table 8, profit and air pollutants exposure concentrations of medium control are higher than those of high control level. When a high level of protection is implemented, the production volume would reach the maximum 20,000 g/yr, but the total cost would significantly increase ((552.08+210) $/g VS (530.63+78) $/g of medium control), which generate the lowest profit $4.46 M/yr. And its 90% remove efficiency decline the SWNT exposure to (0, 6.83) $\mu g/m^3$.

In Table 8, variables of high control level are the same under different confidence level. This situation can be explained by Figure 11 and Figure 12. When production volume reaches the maximum, profit and SWNT exposure concentration would be constant.

Comparing Figures 16 and 18 to Figures 13 and 15, the profits and exposure concentrations of FCCLP are larger than those of CCNLP due to the relaxed OELs.

These results were helpful for decision makers to identify desirable schemes under complex uncertainties to maximize the production benefits and ensure workplace safety through minimizing the nanoparticle-related health risks.

Table 8 Results of the FCCNLP method

| Confidence Level | Control Level | Degree of Objective function Satisfaction (λ) | Production Volume (g/yr) | Production Cost ($/g) | Profit ($M/yr) | SWNT Exposure (μg/m$^3$) | CO Exposure (μg/m$^3$) | Fe Exposure (μg/m$^3$) |
|---|---|---|---|---|---|---|---|---|
| 0.9 | No | 1 | 10,485 | 479.00 | 5.46 | 0.00-20.80 | 250.55-271.28 | 0.00-2.68 |
| | Low | 1 | 13,513 | 502.26 | 6.59 | 0.00-20.80 | 307.13-327.15 | 0.00-2.68 |
| | Medium | 1 | 17,206 | 530.63 | 6.73 | 0.00-20.81 | 320.13-344.30 | 0.00-2.68 |
| | High | 0.46 | 20,000 | 552.08 | 4.46 | 0.00-6.83 | 83.37-89.63 | 0.00-0.98 |
| 0.95 | No | 0.87 | 9,177 | 468.96 | 4.87 | 0.00-18.20 | 219.94-238.14 | 0.00-2.34 |
| | Low | 1 | 11,930 | 490.10 | 5.96 | 0.00-18.20 | 270.27-289.33 | 0.00-2.34 |
| | Medium | 1 | 15,142 | 514.77 | 6.17 | 0.00-18.20 | 279.42-300.45 | 0.00-2.34 |
| | High | 0.46 | 20,000 | 552.08 | 4.46 | 0.00-6.83 | 83.37-89.63 | 0.00-0.98 |
| 0.99 | No | 0.40 | 7,410 | 455.39 | 4.40 | 0.00-14.70 | 175.81-190.67 | 0.00-1.89 |
| | Low | 0.99 | 9,636 | 472.49 | 4.99 | 0.00-14.70 | 217.78-231.98 | 0.00-1.89 |
| | Medium | 1 | 12,159 | 491.87 | 5.23 | 0.00-14.70 | 223.53-240.36 | 0.00-1.89 |
| | High | 0.46 | 20,000 | 552.08 | 4.46 | 0.00-6.83 | 83.37-89.63 | 0.00-0.98 |

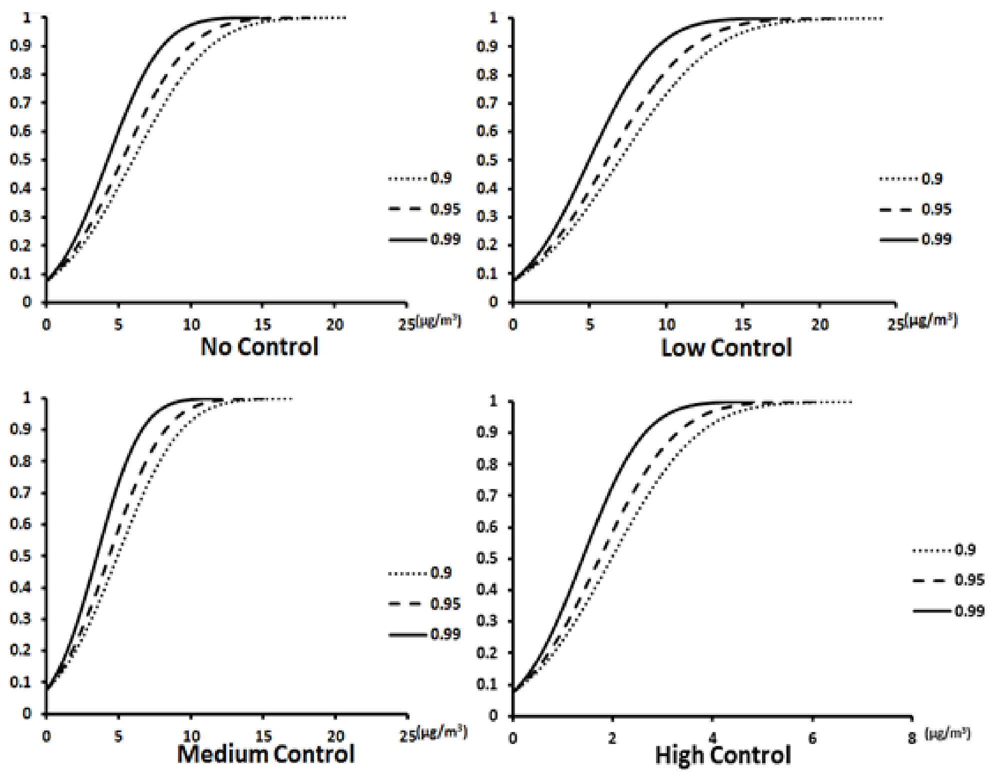


Figure 16 Cumulative probability distributions of SWNT exposure results from FCCNLP method

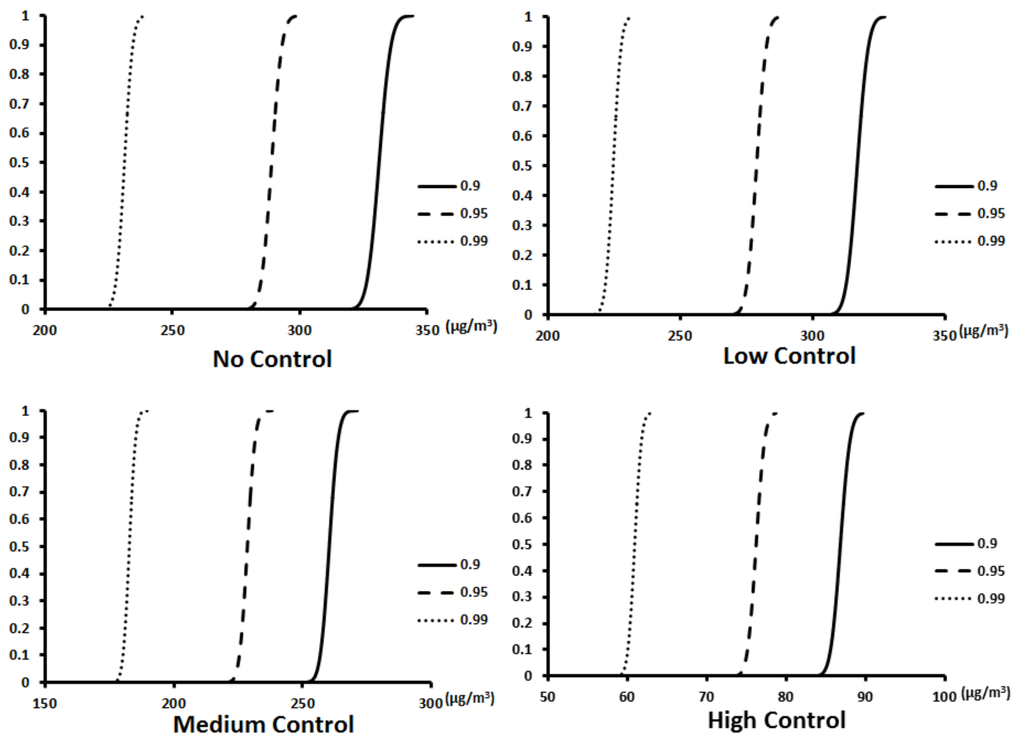


Figure 17 Cumulative probability distributions of CO exposure results from FCCNLP method

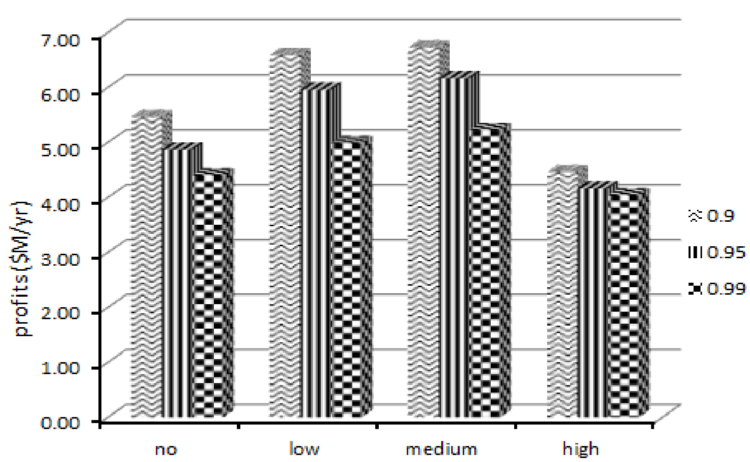


Figure 18 The annual net profits from Fuzzy Chance-constrained programming with different confidence levels

## 5.5 Summary

In this study, an integrated profits-exposure assessment for nonmanufacturing is performed under four air-control management scenarios, fuzziness of occupational exposure limits and randomness of the exposure coefficients. Table 8 in the previous section summarizes annual profits, production volume, production cost, exposure concentrations of SWNT, CO and nano-Fe in a single-walled carbon nanotube manufacturing plant in Houston, Texas, USA. The results indicate that: (1) SWNT is the main occupation harm to workers because its exposure concentration may exceed the OELs. (2) Annual net return and air pollutants concentrations increase with the rise of production scales result from the higher level of control strategy until the production volume reached the maximal level. (3) The economic benefits and air pollutants concentrations increase when the fuzzy α cut is deceased. (4) They rise as the probability confidence α level descend.

# Chapter 6 DISCUSSION

## 6.1 Verification of Models Results

NLP and FCCNLP models also can be used as cost models for the HiPco SWNT manufacturing process. Results from these two models are compared with data of the earlier cost model. For the NLP model, the production cost range is from 406.43 to 438.13 $/g when the production volume is from 1,032 to 5,162 g/yr, and Isaacs et al. (2010) reported a range of production costs from 410 to 460 $/g for the same production volume and a HiPco manufacturing process. It is seen that results from the NLP and previous cost analysis are close to the literature data (with a maximum 5% difference).

For the FCCNLP model, Table 8 gives a production cost range from 455.39 to 552.08 $/g when production volume is from 7,410 to 20,000 g/yr, and previous cost model gives a range from 440.60 to 552.08 $/g under the same conditions. It is seen that the FCCNLP model and Isaacs et al. (2010) SWNT production cost model also share the same range and trend under the same conditions (with a maximum 3% difference).

## 6.2 Case Comparison Analysis

### 6.2.1 Comparison the results between NLP model under two OELs

In the current intelligence bulletin 65, the National Institute for Occupational Safety and Health (NIOSH) recommended that exposures to CNT should be kept below the exposure limit

(REL) of 1 μg/m$^3$ as an 8-hr TWA to replace the previous REL 7 μg/m$^3$ which issued in 2010 (NIOSH, 2013; NIOSH, 2010).

As the results of this alteration, the SWNT exposures are reduced from 7.75, 7.02, 7.92 and 3.87 μg/m$^3$ in each policy to 1 μg/m$^3$, respectively, while corresponding profits shrink from 4.32, 4.26, 6.53 and 4.76 \$M/yr to 0.61, 0.67, 1.05 and 1.82 \$M/yr, respectively. And, if we put 7 μg/m$^3$ into the membership function of $\tilde{1}$ μg/m$^3$, the membership grade is 0.88, showing it may cause 12% possibility of experiencing health injury. Thus, it is obvious that stricter standard leads to less economic benefits but more protection to workers.

### 6.2.2 Comparison of the NLP and FNLP

There is a conflict between the nanomaterial industry growth and the environmental safety and health: a low level of OEL would raise the economic revenue but may cause a serious occupational health hazard; however, a high level of OEL would avert the health risks of workers but may lead to a low economic return which reduce the investing enthusiasm, and then hamper the growth of nanomaterial production industry. Therefore, the FMP method, a relaxation procedure, is developed for treating uncertainties of flexible objective function and relaxed constraints in the setting of optimization problems. FNLP model results indicate that a higher OELs expansion level would lead to a higher increment of production volume. As a result, a higher manufacturing amount would result in higher profits and SWNT exposure level, and vice versa. In this study, a strong desire to acquire a highest profits (7.00 \$M/yr with $\lambda = 1$ in medium control level) would ask for a higher level of expansion of OELs constraint ($\alpha$ cut = 0.85) which would cause a higher risk of workers' injury (15%). But, in the high control level, willingness to accept a lower level of expansion (α cut = 0.94) would guarantee a lower health risk (6%) and an acceptable economic benefit (λ = 0.76).

Compared to the conventional NLP approach, the FNLP demonstrates an advantage of solving a real world problem when the coefficients are not known exactly but vaguely by human expertise.

### 6.2.3 Comparison of the FNLP and FCCNLP

Chance-constrained programming (CCP) is combined into the fuzzy nonlinear programming to deal with uncertainty of randomness. Thus, outputs of FCCNLP models could be expressed as probability density function with the degree of satisfaction of the objective as well as the possibility of risk of causing human health disease.

Results of fuzzy chance-constrained nonlinear programming (FCCNLP) model delimitate that they can provide alternative risk-benefit management schemes in the engineered nanomaterial production process. For example, in current case study which the plant has already existed before OELs updated, if short term (about 20 years) maximum profit is prioritized, the medium level of EHS control with 0.90 confidence level ($6.73 M/yr) may be the best choice, but if worker's health is prioritized, managers may choose the high control level with 0.99 confidence level along with the lowest risk to causing human illness. Moreover, several approaches could be implemented to further reduce the health safety risks separately or together based on the results of FCCNLP. First, lower the target value of annual economic return. Second, advance the manufacturing line to lower the emission coefficients. Third, improve the air pollution control technology and increase the removal efficiencies. Plus, for investors whose who have potential interests in investing on nanomaterial production industry, they may roughly know how high requirement one can ask through this FCCNLP system, without all-consuming investigation.

The advantages of the fuzzy chance-constrained programming (FCCNLP) optimization are (1) it could tackle multiple uncertainties presented in terms of fuzzy sets and probability distributions, as well as their combinations; (2) it not only dealt with uncertainties expressed as fuzzy and random variables but also incorporated multiple control polices of nanomaterial manufacturing management within an optimization framework; (3) it provided an effective tool for decision makers to select desired ENM production plans with reasonable profits and risk levels. For example, as discussed above, if short term (about 20 years) maximum profit is prioritized, the medium level of EHS control with a 0.90 confidence level under 8.75 μg/m$^3$ OEL may be a good decision point, but if the workplace exposure risk is of high concern, we may choose the high risk control level with 0.99 confidence level under 1 μg/m$^3$ OEL.

As a new extension of mathematical programming methods for dealing with system uncertainties, the developed FCCNLP approach could be used by decision makers based on the projected applicable conditions and the interrelationships between system uncertainties, risk probabilities, regulation fuzziness and economic objectives.

# Chapter 7 CONCLUSIONS

## 7.1 Conclusions

In the present study, a fuzzy chance-constrained nonlinear programming (FCCNLP) approach has been developed for engineered nanomaterials (ENMs) manufacturing management under multiple uncertainties. The FCCNLP can deal with uncertainties expressed as fuzzy sets and probability distributions in the objective and constraints. The fuzzy information can be characterized through membership functions, while uncertain random coefficients can be addressed through chance-constrained programming. Solutions of the FCCNLP contain fuzzy and probabilistic information, and then offer flexibility in result interpretation and decision alternative generation.

The FCCNLP has been applied to a realistic case study for planning production scale in association with ENMs pollution concerns in a single-walled carbon nanotube manufacturing plant in Houston, Texas, USA. In the FCCNLP model for the case study, the occupational exposure limit of SWNT is expressed as fuzzy sets with a triangle membership function, annual net profits are described as degree of satisfaction and SWNT exposure concentrations are presented in terms of cumulative probability distributions. Useful solutions for managing the plant have been generated, reflecting trade-offs among industry activities, environmental health and safety standards (EHS), and economic considerations. They are helpful for supporting (a) analysis of interactions among criteria of industry production scale, economic cost and benefit and pollution discharge amount; (b) adjustment of the interrelationship between the conflicting economic objective and EHS requirement; (c) choosing the degree of EHS enforcement and economic objective satisfaction which are decided by production volume.

In general, the FCCNLP model effectively addressed the nanomaterial occupational emission control problems for sustainable nano-maufacturing management and provided helpful data to plan nano-industrial development (e.g., production volume, SWNT exposure concentrations and corresponding risk levels) in accordance with the objective of maximizing the nanomaterial manufacturing revenue and minimizing the related workplace exposure risks to ENMs. The solutions generated by FCCNLP model can be effectively utilized to assist the formulation of policies and strategies regarding economic development and environmental protection according to different violating risk levels. Moreover trade-offs between economic benefits and risks of violating flexible $OEL_s$ can also be considered.

## 7.2 Contributions

In addition to the conclusions in the section 7.1, the research contributions of this present thesis study are summarized as follows:

(1) In the present study, nonlinear programming (NLP) is first applied to the field of optimization of engineered nanomaterial manufacturing process to maximize social-economic benefits of ENMs and ensure workplace safety through minimizing the ENMs-related health risks.

(2) The FCCNLP could be severed as an inexact model to predict production costs, annual profits and range of ENM exposure concentrations in the working area according to the different production scales.

(3) The study is the first attempt to apply FCCNLP method to provide a general framework of an economic-risk assessment in the ENMs manufacturing process under uncertainties of vagueness of OELs to ENMs and randomness of exposure coefficients to ENMs.

(4) The solutions of FCCNLP can be used for providing various decision options that are associated with different levels of risks and degrees of economic objective satisfactions.

## 7.3 Recommendations for Future Work

The FCCNLP model could be used to assess the performance risk of ENM exposure to workers, and help decision makers identify desired air pollution mitigation strategies under various environmental, economic, and system-reliability considerations. It also can help handling uncertainties in management problems. However, there is still space for improvement of the model. Firstly, the calculated ENM concentrations in the air of working atmosphere was limited by the assumption that SWNTs in the air of the room are homogeneous, without any coagulation and agglomeration effects being considered. But in the real world, ENMs easily trend to coagulate and agglomerate because their high reactivations. Secondly, the FCCNLP could be used to address risk violations for structural constraints with single objective. However, it cannot be implemented to deal with the situation when multiple objectives have to be considered. Thirdly, the FCCNLP framework is no easy to use for people without engineering background.

Therefore, correspondingly, future works are desired to mitigate these limitations. (1) Coagulation and agglomeration effects of ENMs will be considered to avoid errors into the model solutions. (2) Multiobjective optimization approach will integrate FMP and CCP methods to maximize the social and economic benefits of ENMs and minimize the adverse health harm to workers. (3) A user-friendly system will be developed to provide interface between users and our risk assessment model.

# REFERENCES


Aschberger, K., Micheletti, C., Sokull-Klüttgen, B., Christensen, F.M. 2011. Analysis of currently available data for characterising the risk of engineered nanomaterials to the environment and human health — lessons learned from four case studies. *Environment International* 37, 1143-56.

Bhatt, I. and Tripathi, B.N. 2011. Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment. *Chemosphere* 82(3), 308-17.

Biskos, G., and Schmidt-Ott, A. 2012. Airborne engineered nanoparticles: Potential risks and monitoring challenges for assessing their impacts on children. *Paediatric Respiratory Reviews* 11(2), 79-83.

Binns, C. 2010. Introduction to Nanoscience and Nanotechnology. Jonh Wiley & Sons, Inc., Hoboken, New Jersey, USA.

Broekhuizen, P.V., and Dorbeck-Jung, B. 2013. Exposure limit balues for nanomaterials-capacity and willingness of users to apply a precautionary approach. *Journal of Occupational and Environmental Hygiene* 10, 46-53.

Canis, L., Linkov, I., Seager, T.P. 2010. Application of stochastic multiattribute analysis to assessment of single walled carbon nanotube synthesis processes. *Environmental Science and Technology* 44, 8704-11.

Chen, T. and Wang, Y. 2009. A fuzzy set approach for evaluating and enhancing the mid-term competitiveness of a semiconductor factory. *Fuzzy Sets and Systems* 160(5), 569-85.

Chen, Z., Huang, G.H., Chakma, A. 2003. Hybrid fuzzy-stochastic modelling approach for assessing environmental risks at contaminated groundwater systems. *Journal of Environmental Engineering* 129, 79-88.

Colson, P., Henrist, C., Cloots, R. 2013. Nanosphere lithography: a powerful mehtod for the controlled manufacturing of nanomaterials. *Journal of Nanomaterials* 201, 1-19.

Delgado, G.C. 2010. Economics and governance of nanomaterials: potential and risks. *Technolgy in Society* 32, 137-44.

Derk, B. 2010. Exposure to manufactured nanoparticles in different workplaces. *Toxicology* 269, 120-7.

EPA, 2007. U.S. Environmental Protection Agency (EPA). *Nanotechnology White Paper*, U.S. Environmental Protection Agency Report EPA 100/B-07/001, Washington DC 20460, USA, 2007.

Freni, G., Mannina, G., Viviani, G. 2011. Assessment of the integrated unban water quality model complexity through identifiability analysis. *Water Research* 45, 37-50.

Grossmann, I.E. 2012. Advances in mathematical programming models for enterprise-wide optimization. *Computers and Chemical Engineering* 47, 2-18.

Hackenberg, S., Scherzed, A., Technau, A., Kessler, M., Froelich, K., Ginzkey, C., Koehler, C., Burghartz, M., Hagen, R., Kleinsasser, N. 2011. Cytotoxic, genotoxic and pro-inflammatory effects of zinc oxide nanoparticles in human nasal mucosa cells in vitro. *Toxicology in Vitro* 25(3), 657-63.

Healy, M.L. 2006. Environmental and economic comparison of single-wall carbon nanorube production alternatives.Northeastern University. Thesis of Master of Sceice. Department of Environmental Science and Engineering.

Healy, M.L., Dahlben, L.J., Isaacs, J.A. 2008. Environmental assessment of single-walled carbon nanotube processes. *Journal of Industrial Ecology* 12, 376-93.

Henning, D. and Trygg, L. 2008. Reduction of electricity use in Swedish industry and its impact on national power supply and European $CO_2$ emissions. *Energy Policy* 36, 2330-2350.

Huang, Y.L., Huang, G.H., Liu, D.F., Zhu, H., Sun, W. 2012. Simulation-based inexact chance-constrained nonlinear programming for eutrophication management in the xiangxi bay of three gorges reservoir. *Journal of Environmental Management* 108(10), 54-65.

Hwang, J.S., Kim, H.T., Kim, H.K., Son, M.H., Hwang, S.W. and Ahn, D. 2009. Electrical transport properties of a single wall carbon nanotuve network. WILEY-VDH Verlag GmbH & Co.KGaA, Weinheim.

Inuiguchi, M., and Ramik, J. 2000. Possibilistic linear programming: a brief review of fuzzy mathematical programming and a comparison with stochastic programming in portfolio selection problem. *Fuzzy Sets and Systems* 111, 3-28.

Isaacs, J.A., Tanwani, A., Healy, M.L., Dahlben, L.J. 2010. Economic assessment of single-walled carbon nanotube processes. *Journal of Nanopartical Research* 12, 551-62.

Jayal, A.D., Badurdeen, F. 2010. Sustainable manufacturing: Modeling and optimization challenges at the product, process and system levels. *CIRP Journal of Manufacturing Science and Technology* 2(3), 144-52.

Kalampoukas, G., and Dervakos, G.A. 1996. Process optimization for clean manufacturing: Supercritical fluid extraction for B-carotene production. *Computers & Chemical Engineering Supplement 2* 1383-8.

Kandlikar, M., Ramachandran, G., Maynard, A., Murdock, B., Toscano, W.A. 2007. Health risk assessment for nanoparticles: A case for using expert judgment. *Nanotechnolgy and Occupataional Health* 137-56.

Kobayashi, N., Naya, M., Endoh, S., Maru, J., Yamamoto, K., Nakanishi, J. 2009. Comparative pulmonary toxicity study of nano-$TiO_2$ particles of different sizes and agglomerations in rats: Different short- and long-term post-instillation results. *Toxicology* 264(10), 110-8.

Kravanja, S., and Šilih, S. 2003. Optimization based comparison between composite beams and composite trusses. *Journal of Constructional Steel Research* 59(5), 609-25.

Kumar, A., Pandey, A.K., Singh, S.S., Shanker, R., Dhawan, A. 2011. Engineered ZnO and TiO2 nanoparticles induce oxidative stress and DNA damage leading to reduced viability of escherichia coli. *Free Radical Biology and Medicine* 51(10),1872-81.

Lapresta-Fernández, A., Fernández, A., Blasco, J. 2012. Nanoecotoxicity effects of engineered silver and gold nanoparticles in aquatic organisms. *TrAC Trends in Analytical Chemistry* 32(2), 40-59.

Lead, J.R., and Smith, E., 2009. Environmental and Human Health Impacts of Nanotechnology. John Wiley & Sons, Ltd, Chichester, United Kingdom.

Leung, Y. 1988. Spatial analysis and planning under imprecision. North-Holland-Amsterdam, New York, NY, USA.

Linninger, A.A., Chakraborty, A., Colberg, R.D. 2000. Planning of waste reduction strategies under uncertainty. *Computers and Chemical Engineering* 24, 1043-1048.

Liu, B. 2010. Uncertainty theory: a branch of mathematics. Studies in computational intelligence. Springer-Verlag Berlin Heidelberg, Inc, New York, NY, USA.

Liu, C., Fu, J., Xu, Q. 2011. Simultaneous mixed-integer dynamic optimization for environmentally benign electroplating. *Computers & Chemical Engineering* 35(11), 2411-25.

Luenber, D.G., and Ye, Y. 2008. Linear and Nonlinear Programming (Third Edition). Springer Science+Business Media, LLC, New York, NY, USA.

Luhandjula, M.K. 2006. Fuzzy stochastic linear programming: Survey and future research directions. *European Journal of Operational Research* 17(3),1353-67.

Mavrotas, G. and Georgopoulou, E. 2007. An integrated approach for the selection of Best Available Techniques (BAT) for the industries in the greater Athens area using multi-objective combinatorial optimization. *Energy Economics* 29(4), 953-973.

Maynard, A.D. and Kuempel, E.D. 2005. Airborne nanostructured particles and occupational health. *Journal of Nanoparticle Research* 7, 587-614.

Maynard, A.D., Baron, P.A., Foley, M., Shvedova, A.A., Kisin, E.R., Castranova, V. 2004. Exposure to carbon nanotube material: Aerosol release during the handling of unrefined single walled carbon nanotube material. *Journal of Toxicology and Environmental Health, Part A* 67(1), 87-107.

Mirabile, M., Boccuni, F., Gagliardi, D., Rondinone, B.M., Iavicoli, S. 2014. Workplace exposure to engineered nanomaterials: The Italian path for the definition of occupational health and safety policies. *Health Policy* 117, 128-34.

Myojo, T., Ogami, A., Oyabu, T., Morimoto, Y., Hirohashi, M., Murakami, M., Nishi, K., Kadoya, C., Tanaka, I. 2010. Risk assessment of airborne fine particles and nanoparticles. *Advanced Powder Technology* 21(5), 507-12.

Naga, B. and Parikhb, J.K. 2005. Carbon emission coefficient of power consumption in India: Baseline determination from the demand side. *Energy Policy 33*, 777–86.

Nikolaev, P., Michael, J., Bronikowski, R., Kelley, B., Frank, R., Daniel, T.C., Smith, K.A., Smalley, R.E. 1999. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters* 313, 91-7.

NIOSH (National Institute for Occupational Safety and Health).1992. Recommendations for occupational safety and health: Compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 92-100.

NIOSH (National Institute for Occupational Safety and Health). 2010.Occupational Exposure to Carbon Nanotubes and Nanofibers. Available online: http://www.cdc.gov/niosh/docket/archive/pdfs/NIOSH-161-A/0161-A-110110-DraftDocument.pdf .

NIOSH (National Institute for Occupational Safety and Health). 2013.Occupational Exposure to Carbon Nanotubes and Nanofibers. Current intelligence bulletin 65. Available online: http://www.cdc.gov/niosh/docs/2013-145/pdfs/2013-145.pdf.

Ok, Z.D., Benneyan, J.C., Isaacs, J.A. 2008. Risk analysis modeling of production costs and occupational health exposure of single-wall carbon nanotube manufacturing. *Journal of Industrial Ecology* 12, 411-34.

Occupational Safety and Health Standards 1910. *Subpart Z- Toxic and Hazardous Substance. 1910. 1000. Table Z-1. Limits for Air Contaminants.* Public Law 1997. 29. CFR Part 1910.

OSHA (Occupational Safety and Health Standards). 1997. 29. CFR Part. (1910). Occupation Safety and Health Standards 1910. Subpart Z- Toxic and Hazardous Substance. 1910. 1000. Table Z-1. Limits for Air Contaminants. Washington, DC: Occupational Safety and Health Administration.

Ostafiev, V.A., Globa, A.V., Globa, L.S., Loladze, T.N. 1984. Integrated end milling optimization development. *CIRP Annals - Manufacturing Technology* 33(1), 29-32.

Ouellette, J. 2003. Building the nanofuture with carbon tubes. *Industrial Physics* 8,18–21.

Paur, H.R., Cassee, F.R., Teeguarden, J., Fissan, H., Diabate, S., Aufderheide, M., Kreyling, W.G. 2011. In-vitro cell exposure studies for the assessment of nanoparticle toxicity in the lung—A dialog between aerosol science and biology. *Journal of Aerosol Science* 42(10), 668-92.

Piltan, M., Shiri, H., Ghaderi, S.F. 2012. Energy demand forecasting in Iranian metal inustry using linear and nonlinear models based on evolutionary algorithms. *Energy Conversion and Management* 58, 1-9.

Peralta-Videa, J.R., Zhao, L., Lopez-Moreno, M.L., Rosa, G.D.L., Hong, J., Gardea-Torresdey, J.L. 2011. Nanomaterials and the environment: A review for the biennium 2008-2010. *Journal of Hazardous Materials* 186, 1-15.

Rong, A. and Lahdelma, R. 2009. Fuzzy chance constrained linear programming model for optimizing the scrap charge in steel production. *European Journal of Operational Research* 186, 953-964.

Roller, M. 2009. Carcinogenicity of inhaled nanoparticles. *Inhalation Toxicology* 21(11), 144-57.

Savolainen, K., Pylkkänen, L., Norppa, H., Falck, G., Lindberg, H., Tuomi, T., Vippola, M. 2010. Nanotechnologies, engineered nanomaterials and occupational health and safety – A review. *Safety Science* 48(8), 957-63.

Savolainen, K., Alenius, H., Norppa, H., Pylkkänen, L., Tuomi, T., Kasper, G. 2010. Risk assessment of engineered nanomaterials and nanotechnologies - A review. *Toxicology* 269(2), 92-104.

Schulte, P.A., Murashov, V., Zumwalde, R., Kuempel, E.D., Geraci, C.L. 2010. Occupational exposure limits for nanomaterials: State of the art. *Journal of Nanopartical Resource* 12, 1971-87.

Sengul, H., Theis, T.L., Fhosh, S. 2008. Toward sustainable nanoproducts: An overview of nanomanufacturing methods. *Journal of Industrial Ecology* 12, 329-59.

Seibi, A.C., Sawaqed, N.M. 2002. Design of copper filled gibreglass moulds for manufacturing a customized product using linear programming optimization and finite element analysis. *Composites: Part A* 33, 1689-95.

Slotine, J.J. and Li, W. 1991. Applied Nonlinear Control. Prentice-Hall, Englewood Cliffs, NJ, USA.

Shvedova, A.A., Pietroiusti, A., Fadeel, B., Kagan, V.E. 2012. Mechanisms of carbon nanotube-induced toxicity: Focus on oxidative stress. *Toxicology and Applied Pharmacology* 261(2), 121-33.

Song, H.S., Zhang, W.J., Cheng, C., Tang, Y.B., Luo, L.B., Chen, X., Luan, C.Y., Meng, X.M., Zapien, J.A., Wang, N., Lee, C.S., Bello, I, Lee, S.T. 2011. Controllable fabriction of three-dimensional radial ZnO Nanowire/silicon microrod hybrid architectures. *Crystal Growth and Design* 11(1), 147-53.

Srinivas, A., Rao, P.J., Selvam, G., Murthy, P.B., Reddy, P.N. 2011. Acute inhalation toxicity of cerium oxide nanoparticles in rats. *Toxicology Letters* 205(2),105-15.

Stone, V., Nowack, B., Baun, A., Brink, N.V.D., Kammer, F.V.D., Dusinska, M., Handy, R., Hankin, S., Hassellov, M., Joner, E., Fernandes, T.F. 2010. Nanomaterials for environmental studies: Classification, reference maaterial issues, and strategies for physico-chemical characterisation. *Science of the Total Environment* 408,1745-54.

Tseng, M.T., Lu, X., Duan, X., Hardas, S.S., Sultana, R., Wu, P., Unrine, J.M. 2012. Alteration of hepatic structure and oxidative stress induced by intravenous nanoceria. *Toxicology and Applied Pharmacology* 260(2), 173-82.

Vollath, D. 2008. Nanomaterials: An introduction to synthesis, properties and Application. WILEY-VDH Verlag GmbH & Co.KGaA, Weinheim, OH, USA

Wilson, M.R., Foucaud, L., Barlow, P.G., Hutchison, G.R., Sales, J., Simpson, R.J. Stone, V. 2007. Nanoparticle interactions with zinc and iron: Implications for toxicology and inflammation. *Toxicology and Applied Pharmacology* 225(1), 80-9.

Wu, C.C. and Chang, N.B. 2003. Global strategy for optimizing textile dyeing manufacturing process via GA-based grey nonlinear integer programming. *Computers and Chemical Engineering* 27(6), 833-54.

Xie, Y.L., Li, Y.P., Huang, G.H., Li, Y.F., Chen, L.R. 2011. An inexact chance-constrained programming model for water quality management in Ninhai New Area of Tianjin, China. *Science of the Total Environment* 409(10), 1757-73.

Yin, R., Tian, F., Frankenberger, B., Angelis, M.H., Stoeger, T. 2010. Selection and evaluation of stable housekeeping genes for gene expression normalization in carbon nanoparticle-induced acute pulmonary inflammation in mice. *Biochemical and Biophysical Research Communications* 399(4) 531-6.

Zhang, X.D., Huang, G.H., Nie, X.H. 2009. Robust stochastic fuzzy possibilistic programming for environmental decision making under uncertainty. *Science of the Total Environment* 408, 192-201.

Zhu, X., Chang, Y., Chen, Y. 2010. Toxicity and bioaccumulation of $TiO_2$ nanoparticle aggregates in daphniamagna. *Chemosphere* 78 (3), 209-15.

Zuperl, U., Cus, F., Mursec, B., Ploj, T. 2004. A hybrid analytical-neural network approach to the determination of optimal cutting conditions. *Journal of Materials Processing Technology* 82-90.