

CHALMERS



A TECHNOLOGY ASSESSMENT OF CARBON
NANOPARTICLES: PRODUCTION ENERGY
REQUIREMENTS AND IMPLICATIONS FOR USE

A M.Sc. Thesis for Industrial Ecology

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ABSTRACT

Many applications for carbon nanotechnology have been realized or proposed. This paper puts forward a framework for understanding and quantifying the relationships between the physical nature of carbon nanomaterials, their production and potential role in society. Beginning from the process energies required for the production of all involved materials and feedstocks, primary energy requirements for fullerene and nanotube synthesis are calculated from literature data and presented for a number of important production processes from fluidised bed CVD and carbon monoxide disproportionation to electric arc synthesis. Critical issues in energy and scaling production are identified and potentials for improvement in industrial scale processes are discussed. Possible interactions with related industrial systems are examined with view towards the possibilities of integrating synthesis to reduce the impacts of bulk carbon nanoparticle manufacture. These insights are used to amend the energy flows already calculated and present another set of energy requirements representing mass production efforts with feasible synergies. Carbon nanoparticles are found to be highly energy intensive materials, even with idealized implementations of production routes.

Some techniques for manufacturing carbon-based materials into artefacts are discussed in order to provide insight into their place in production chains. Requirements for applications are identified and related to production and manufacturing choices. This perspective is used to survey real world applications with newly commercialised or anticipated products enabled by carbon nanotechnology. By examining concepts such as energy payback from dematerialising or increasing the efficiency of technology, insights into the potential lifetime energy profile of carbon nanomaterials is gained. Despite the large energy demand of production, carbon nanoparticle lifecycle energy flows could become neutral or positive in some applications, particularly in energy related systems.

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1 Introduction

1.1 Background

The discovery of C_{60} ¹ and carbon nanotubes has prompted an intense wave of research into carbon nanoparticles (CNPs) and their possible uses. Their unique material properties and success working with them has led to a host of realized and anticipated applications. Carbon nanotechnology has left the laboratory and begun the process of industrialisation. Some estimates place single wall nanotube production at 5 kilograms globally in 2000, an amount manufactured in twenty hours in one test-scale fluidised bed reactor six years later. World output of all carbon nanoparticles is estimated to reach 400 tons in 2007 (Cientifica, 2006), and grow rapidly thereafter. As questions about the technical possibility of mass production are answered, interest and concerns over the potential environmental impacts of the technology have begun to arise.

Because carbon nanoparticles are highly energy intensive materials to produce and use, even with generous assumptions about possible production systems, it is important to understand the requirements for producing them as well as the potential benefits of their use as one measure towards understanding their environmental profile. Carbon nanoparticles are likely to become an important engineering material in some critical applications, and if many or all of their potential uses become viable, then the total production demand could become significant.

There are many information links missing towards assessing the environmental impacts of carbon nanotechnology. This paper is concerned with energy and material flows belonging to technical systems producing and using carbon nanotechnology-based material.

¹ C_{60} is the spherical molecule containing sixty carbon atoms. An introduction to carbon nanoparticles and related concepts is found in Appendix A, and is recommended for those unfamiliar with the subject.

1.2 Goal and Scope

The objectives of this work were:

- To obtain a reasonable set of cumulative energy and material requirement estimates for current and potential mass production processes for creating carbon nanoparticles.
- To identify critical issues in production and assess future potential to ameliorate them.
- To use the information and perspectives gained to explore the effects of applying carbon nanoparticles to technical systems.

Inventories of laboratory scale processes have begun to emerge (Isaacs et al, 2006). As the technology is changing rapidly, such results may not be representative of future production systems. In order to assess the technology as a whole, an approach will be taken where the requirements for production at industrial levels are built up by assuming industrial efficiencies in obtaining observed reaction conditions. A sub-goal of this effort is to compartmentalize the possible roles of technical change and background systems, such as precursor production, towards the result of the energy analysis.

The analyses of production systems are limited to processes that produce carbon nanoparticles for 'bulk' material applications. The means and motivation for separating carbon nanotechnology into different streams is described in the method section of this work. Despite not comprising a complete picture of carbon nanotechnology, the results for bulk materials are relevant because such applications could potentially comprise the majority of carbon nanoparticle use, taken from a physical perspective.

The technical systems describing CNP production include the means necessary to purify the material. The background production processes for all material inputs into the technical system are described from a cradle-to-gate perspective. There is no consideration of energy or material flows required to construct or maintain capital infrastructure. Additionally, transport energy use for all material flows has not been included. Safety, health and working environment aspects are not considered.

The functional unit used for all production calculations is 1 kg of the carbon nanoparticle under discussion. All energy units for intensity and energy payback are expressed in MJ/kg of the substance under discussion.

1.3 Outline

An introduction to carbon nanotechnology, and discussion on the methodology used in this paper is presented in chapter 2.

In chapter 3, a general description of various important bulk CNP production methods is presented along with system models, energy calculation results and discussion of critical energy and scale factors. Potential interactions with precursor background systems are identified and discussed with view to reducing energy and material consumption at an overall level.

In chapter 4, an introduction to the various steps taken to convert nanoparticles into intermediate forms and then into products is presented.

In chapter 5, assesses the effects of including carbon nanotechnology into various applications. Energy requirements and paybacks are calculated using the values found earlier, and provide illumination to the discussion.

In chapter 6, a discussion on the limitations of this paper is conducted, and conclusions drawn from this work are presented.

In appendices A-C, descriptions of process calculations and the specific input values used for technical and background systems in this work are presented.

2 Method

The methods currently available for environmental evaluation of carbon nanoparticle production systems are limited by information that is difficult to obtain or proprietary and changing rapidly. The process technology is still in an early phase and while it is possible to begin to examine the mechanisms and feedstocks involved, there are still a number of steps that have not yet reached full maturity. Particularly with respect to several chemicals used as solvents, catalysts or functionalising agents, a summary of all environmentally relevant substance flows is difficult to compile and could change rapidly.

While such substances could have environmental impacts in a number of categories, their relatively small scale of use makes them less significant from an energy use point of view. Additionally, initial inventories on current production (Isaacs et al, 2006) have concluded that the vast majority of the impacts of carbon nanoparticle manufacture are due to electricity use. Because precursor, feedstock and stoichiometric data are available for a number of processes, it is possible to estimate the potentials for energy use in industrial scale systems. Such a bottom-up estimation could provide a valuable contribution towards discussion of the longer scale impacts of the technology by providing insights into where critical energy issues are likely to remain once process efficiency improves. These reasons form the basis for selecting energy analysis as an appropriate tool for this work.

2.1 Energy Analysis

Energy analysis is used to quantify the cumulative energy requirements (CER) for a given product or service in a lifecycle perspective (Bousted et al, 1979). An inventory is generally constructed detailing all process flows from cradle to gate or cradle to grave. In this study the cumulative energy requirement includes all energy flows up to a certain gate in the production chain. In Chapters 3 and 4, this gate is represented by the output of the functional unit 1 kg of CNPs. End of life considerations of the CNPs are not made. Chapters 5 and 6 elaborate on energy implications of the use phase. A number of treatments of the specifics of energy analysis exist and therefore only a short discussion of some limitations and specific parameters used in this work will be given here.

2.1.1 Limitations of Energy Analysis

Energy requirements provide an indicator for basic environmental pressures associated with the use of energy in society, but suffer from limitations in their descriptive power for environmental impacts. In general, it is impossible to know whether all relevant impacts are covered within the system boundaries. Furthermore, it is impossible to extract specific environmental impacts from the inventory data without characterization of the results.

Although preliminary inventories ascribe the overwhelming majority of impacts from carbon nanoparticle manufacture to energy use, once production efficiencies increase,

other effects may become more significant. The difficulty with system boundaries becomes severe, especially when discussing use systems, and limitations must be described for every case in this work.

Allocation of flows from processes with multiple outputs is an issue that must be dealt with. It occurs in both production and use systems in this paper, and the allocations applied are detailed in the respective appendices.

2.1.2 Energy forms and conversion factors

Energy enters CNP production processes in many forms: thermal, feedstock, electrical and, in one case, solar energy. Equivalence between differing qualities of energy is usually established by using conversion factors between the various forms to obtain a single aggregated number. Due to the global nature of the nascent nanotechnology industry, it is difficult to establish a single conversion rate for electricity because of differing infrastructure in various regions. Also the prospective character of the study demands a transparent and flexible treatment of conversion factors (Rydh and Sandén 2005b). Because of this and because of some aspects of the specific analysis undertaken, thermal and feedstock energy in all results are kept separate from electricity. Amalgamation of results, when done, takes place under generic assumptions about electricity production efficiency.

Thermal energy in processes comes from either feedstock conversion or from electricity. The primary energy content of chemical feedstocks is taken as their gross calorific value, i.e. HHV or combustion enthalpy.

2.1.3 Foreground and background systems

The general method undertaken in this work is to produce a system model for each analyzed instance. Each system model is divided into a foreground system that is described and analysed in more detail and several background systems for various inputs and outputs of byproducts (Baumann and Tillman 2004). Data for the foreground systems are taken from technical and industrial reports, while data for background systems are taken from LCAs (Figure 3-1).

2.2 Specific Data Requirements and Limitations

For each foreground system process mass flows are completed from efficiencies and stoichiometry given in available literature. Process efficiency toward achieving the given reaction conditions is assumed to be at industrial levels for comparable processes, or at thermodynamic levels in some cases where data is proprietary or does not exist. Approaching this assumption in reality explicitly requires large process flows. Only a few of the synthesis methods studied are currently undertaken at levels that begin to validate this assumption, and using it to describe low flow rate processes could lead to wildly different results than a standard inventory.

In order to provide a solid foundation for the process calculations, complete lifecycle data on the production of all background inputs into the production system was obtained. In order to facilitate inquiry into various dimensions of the system, all electrical and thermal/feedstock values have been kept separate. For inputs without completed lifecycle analyses available, an estimate was made from process data. All background system inputs used are presented in Appendix C.

The stoichiometry for processes is a critical factor in determining the final energy balance. The data used comes from technical reports detailing equipment and processes. The carbon yield is of particular importance for some reactions, but in some cases it is not clear whether a given process can obtain the reported yields at different process rates.

Because some foreground systems are proprietary or confidential, in some cases assumptions are made about them based on reports detailing similar technology. In one case, that of the HiPco reactor described later, there are no other reports with which to do this, and some numbers are therefore estimated.

2.3 Categorizing Carbon Nanotechnology and Scope

There are different ways to treat carbon nanotechnology in terms of technical systems, depending on their creation and integration into that system. One categorization was made in the definition of the scope of this work; that of dividing carbon nanotechnology into ‘bulk’ applications, which are treated in this work, and ‘controlled’ applications, which are not. The justifications for this have to do with the applicability of comparisons between different systems. As applications become more specialized and complex, defining and allocating flows becomes more difficult, the appropriate functional units may change and the concept of an energy analysis directed at the nanoparticles themselves progressively loses relevance.

Many of the most interesting properties of carbon nanoparticles are still not possible to realize in bulk materials and are only approachable in micro and molecular scale systems. Measuring the utility of a specific quantity of material is a very different exercise in the two cases, just as directly comparing the utility of one gram of silicon in sand to that of one gram in a microprocessor is somewhat futile. The ‘usefulness’ in the case of the microprocessor is correlated more to its internal organization than to an aggregate parameter such as mass; a billion transistors linked randomly would take just as much process energy to create as well as have the same mass as a normal microchip.

This progressive decoupling of mass from utility suggests that, for the purposes of quantitative analysis, the term ‘carbon nanotechnology’ refers to a spectrum of concepts that directly affect the appropriate framework or functional unit of analysis. In some cases, it may be more helpful to think about the production of carbon nanoparticles as a process inside another system rather than as a cost to produce them on their own.

In such applications, carbon nanotechnology could potentially enable very complex and high value products and systems at a very small but energy intensive physical scale of use. While their unmatched properties at a molecular level will guarantee that they will be exploited wherever technically possible in complex artefacts, the total amount of material represented is relatively small in relation to the potential of more mundane bulk uses. Molecular nanotechnology is still a speculative subject, but more 'traditional' types of material applications for CNPs are being commercialized that belong to a concrete and measurable domain. This is the motivation of the categorization of the technology into two streams and restriction of the scope of this work to the bulk processes and applications of carbon nanotechnology.

3 Production of Carbon Nanoparticles

Carbon nanoparticle production technology remains a complicated subject. Each sub-attribute such as chirality, length and diameter² represents a degree of freedom in their creation that influences their properties and thus application. Furthermore, attributes applicable to collections of carbon nanomaterial such as alignment, placement and presence of impurities affect the capacity to realize and utilize these properties in larger technological artefacts.

Even though the basic problem of creating kilogram to ton quantities in scaleable processes has been solved, many applications still require improved control over the product, lower cost or both. Although not mutually exclusive, these requirements are often at odds with each other; large flow processes often occur in chaotic three dimensional volumes and result in crude control of sub attributes and randomly ordered material. Conversely, very precise control of sub-attributes can be achieved by destructive purification or by exceedingly careful reactions that are difficult to scale up to larger production rates.

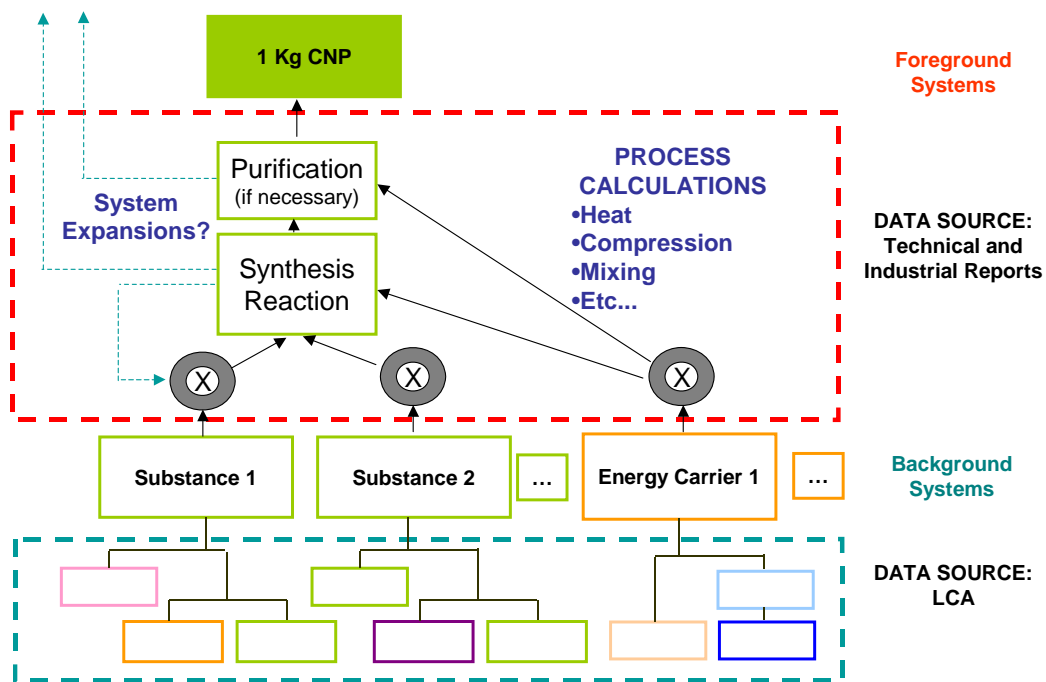


Figure 3-1: Data Structure and Methodology for Production Systems

Following Fig 3-1, this chapter contains a general overview of production technology followed by a discussion of the purification processes used to remove unwanted impurities or select particles having specific characteristics. Calculations combining

² Again, see Appendix A for a description of carbon nanoparticles if these terms are unfamiliar.

synthesis and related purification methods are presented to estimate production energy intensities and allow identification and discussion of critical energy and material factors.

These factors are discussed with two views: in this chapter, changes to the foreground system, or ‘technical changes’, are considered. In Chapter 4, interactions with the background systems are considered to give deeper insight as to how larger-scale production could integrate with industrial ecosystems. These analyses are supplemented in Appendix B with more details of the models and calculations.

3.1 Description of Carbon Nanoparticle Production Systems

3.1.1 Synthesis of Carbon Nanoparticles

Most generally, carbon nanoparticles are synthesized by rendering carbon atomically reactive and depositing it under controlled circumstances. The carbon atoms naturally self assemble into a variety of carbon forms including molecules such as C₆₀. As a crude example, soot from a candle contains a very small amount of C₆₀. By altering the reaction environment and fuel or by using other methods such as adding catalysts for nanoparticle growth, arbitrarily close to 100% of the carbon in the feedstock can be converted to CNPs and derivatives in some reactions.

With current technology, one can now assume that the general type of nanoparticle (SWNT, MWNT, C₆₀, etc) desired can be synthesized with high selectivity at will and with generally increasing control over any of its particular sub-attributes. The important considerations in mass synthesis are thus the quality of the product (aspect ratio, absence of defects), the need for purification, and the rate at which the reaction can produce material. Purification methods are costly, time consuming, difficult to automate and, without perfect material recovery, act as a multiplier on how much of every preceding process is required; therefore avoiding them to whatever extent possible is a valid approach to increasing yield.

Rate of material production is another critical parameter, and will be discussed in detail later in this chapter.

While there are many mechanisms by which carbon nanoparticles can be synthesised, the methods can be sorted into two physical categories based on the type of carbon feedstock:

- 1) Methods that decompose a liquid or gaseous feedstock to obtain the atomic carbon, such as chemical vapour deposition (CVD) and pyrolytic processes.
- 2) Methods that vaporize a pure carbon source into high-temperature plasma, such as electric arc synthesis or laser ablation.

3.1.2 Synthesis From Gaseous and Liquid Feed Stocks

Gaseous or liquid feedstocks such as hydrocarbons or carbon monoxide are used in most large-scale synthesis of CNPs today. The feedstock is introduced in gaseous or vapour

form and is heated to the point of dissociation, becoming a source of reactive carbon atoms. Catalyst particles are introduced to the gas and ‘absorb’ carbon atoms which then precipitate and self-assemble.

The resulting carbon/catalyst/substrate material is removed and purified. The unused feedstock and inert atmosphere potentially could be recycled after contaminant or valuable off-gases are removed. Alternatively, the off-gases could be used directly in other industrial reactions and/or with heat exchangers, offering potential to improve overall system efficiency. Such system expansions are detailed later.

If used, the catalyst can either be mixed with the feedstock in a gaseous phase or presented on the surface of a substrate. The choice has significant implications for production: all-gas reactions are inherently possible to make continuous and scaleable but tend to introduce some degree of disorder and therefore difficulty with physical alignment of the product. Catalyst patterned onto a substrate can grow ‘forests’ or patterns of nanotubes with close to perfect alignment but at the expense of slowing production rate due to limited surface area for reaction and difficulty providing continuity in the process. It is not necessarily a black or white picture however; each approach has hybrids that attempt to recreate advantages of the other. For example, fluidized bed reactors present the catalyst on a substrate dust that is fluidized by the flowing reaction gas; adjusting the size and shape of the substrate can present a continuum between a three and two dimensional reaction area while allowing scaling up of flow.

Naturally continuous processes such as fluidized bed CVD, HiPco or others seem to be the most promising methods for industrial levels of bulk production of nanotubes for several reasons:

- The reactor size and flow rates can be scaled up without changing the basic design.
- The feedstocks are highly available hydrocarbons or process gases such as methane, ethylene, carbon monoxide, toluene etc.
- They operate at far lower temperatures than carbon-vaporizing techniques, greatly reducing energy consumption.
- They can operate at atmospheric pressure or higher, simplifying industrial design.

Pyrolytic processes decomposing hydrocarbons such as benzene or toluene are used to create the majority of C₆₀ produced in the world (Takehara, 2005). Despite very low yields, they are comparatively simple to implement and scaling them up is only a matter of increasing the fuel flow. The small fullerenes such as C₆₀, C₇₀ and so on, have very few or no degrees of freedom in their structure, and are therefore not nearly so sensitive to the reaction conditions used to create them as are nanotubes. Additionally, the small fullerenes cannot be synthesized easily through CVD methods, and thus pyrolytic processes are the only naturally scaleable methods for creating them.

Static substrate processes belong to a different stream of production and will continue to have applications because they produce to different requirements. For example, CVD onto a sheet patterned with catalyst can produce highly ordered and accurately placed nanotubes. Even higher degrees of control such as skewing the chirality distribution can be exerted by methods such as carrying out the reaction in a radio or magnetic field (Kato et al, 2004). This spatial and alignment control can be necessary to enable useful electronic applications such as producing thermal interconnects on microchips or ‘forests’ of nanotubes suitable for field emission, and is not achievable with any other known methods. Trying to achieve ‘semi-continuous’ fabrication on static substrates will borrow heavily from experience from the semiconductor industry, where other CVD methods are employed to produce microchips.

3.1.3 Synthesis from Solid Feedstock

In solid feedstock-based processes, graphite is vaporized in an inert atmosphere with or without a catalyst, depending on the desired product. An electric arc or a laser normally delivers the energy for vaporisation, but solar reactors and other techniques are being investigated (Guillard et al, 2002). A flowing inert atmosphere typically carries the products away to be collected and purified, but variants conduct the process in liquid nitrogen or open air as well.

Methods using solid feedstocks are highly energy intensive because of the amount of energy required to vaporize pure carbon and the energy required to maintain a heated, inert and often low pressure atmosphere. Furthermore, the feedstock for most processes must be pre-manufactured from energy intensive precursors such as extremely high purity graphite. Recently, some researchers have announced the use of purified but ungraphitised coal as a feedstock (Yu et al, 2003; Qiu et al, 2007), and have managed to produce DWNT and SWNTs by such methods, perhaps promising to lower production energy intensity by using a ‘cheaper’ feedstock than purified graphite.

Solid feedstock methods do not lend themselves easily to continuous production because of difficulty replacing the feedstock, overheating and other technical issues, which are solvable, but at expense. Production rates per unit of time are generally low and are subject to potential physical limitations. Therefore, scaling these methods up may require multiple reactors rather than larger process flows. Scaling of electric arc processes has been difficult because CNP yield appears to decrease with electrode diameter, putting a limit on arc power (Veld et al, 2003). Similarly, one estimate places the limit of laser methods using state of the art free electron lasers at roughly 45 grams per hour for each laser (Veld et al, 2003), although laser systems do not approach that productivity yet.

Without the ability to easily scale production rates up, these methods must offer other benefits in terms of costs, quality or reduced need for purification to occupy more than a niche role in large-scale production. Despite the disadvantages already mentioned, solid feedstock based syntheses can provide improvement in some areas. Although they produce other forms of carbon, the very high temperatures favour well graphitised (with few defects) nanotubes. It is well known that MWNTs can be synthesized in an electric

arc without a catalyst, allowing material to be obtained without any metallic impurities, which is of interest in some sensitive nanoscale systems. Laser syntheses allow very high control over the specific reaction parameters, and tend to selectively produce a higher proportion of armchair nanotubes (Kim et al, 2002). Modulation of the laser can select the diameter of nanotubes as well (Kataura, 2000), potentially opening a route towards chiral-selective nanotube production,.

One interesting development is the use of solar furnaces to provide the vaporization energy. As it uses solar energy, the power for such a system is to a large degree 'free', which can greatly increase its efficiency', depending on where the system boundaries are drawn. Additionally, there are fewer problems scaling the power input to the system. A 50kW unit has been demonstrated to produce 10-25 g per hour of nanotubes, with a 250kW scale up demonstration planned. (Guillard, 2002)

3.1.4 Purification of Carbon Nanoparticles

The synthesis reaction products typically contain unwanted impurities. These can include the various types of CNPs as well as amorphous carbon, graphite and metal catalyst. An arbitrary but typical purity suitable for most research and application is assumed here to be 90% or higher content of the desired particle for nanotubes and 95% for C₆₀ and other CNPs. Some synthesis methods are capable of synthesising material close to or above this quality directly, but most require purification treatment. Higher grades of material are attainable through both controlled synthesis and progressively more elaborate purification measures.

The purity requirements of various applications may range greatly depending on the desired property to be exploited. For instance, as a prospective replacement for carbon black in tires, virtually unprocessed material can be used whereas an active layer in solar cells may require material with an extraordinarily high purity, and a known conductivity and spatial orientation. There are cases where a well-controlled impurity is directly useful, such as in microelectronics, where a metal particle at the end of a nanotube can provide an electrical connection, but purity of product is an essential consideration for many applications.

Below is an overview of purification technology and its typical applications. Because of the diverse nature of synthesis and purification technologies, the production models used to calculate energy flows have a simple and appropriate purification step appended to them to provide comparable outputs.

Purification of Fullerenes

Purification of fullerenes is somewhat simpler than purification of nanotubes due to their solubility in various organic solvents such as toluene and benzene. Purification is virtually always a necessary step because of the very low purity of synthesis material typically obtained in C₆₀ production. Despite the relative ease of purifying the small

fullerenes, the process consumes labour, time, material and equipment and continues to be a major determinant in fullerene pricing (Komatsu et al, 2004).

A typical and simple method for purifying fullerenes is to completely dissolve the synthesis soot in toluene via stirring or sonication (ultrasonic waves in a liquid). Fullerenes of molar mass above C100 and amorphous carbon will not dissolve in the toluene and can therefore be removed. The toluene is evaporated from the solution and can be virtually completely recovered from the process. Purification above 98% by weight can be achieved by extraction with toluene followed by chromatography. Chromatography of the solution before evaporation can separate allotropes such as C60 or C70, resulting in the potential to obtain samples of extremely high purity and of a single allotrope without intrinsically destructive processing. Most of the remaining impurity is solvent trapped inside the molecular cages and can be removed by sublimation; 99.99% purity is achievable in this manner (Komatsu et al, 2004). Research is currently directed at improving the speed and automation with which the process can be carried out as well as improving the amount of material recovered from each step, but at a lower intensity relative to that for nanotubes.

Purification of Nanotubes

There is still a large amount of ongoing research regarding purification of nanotubes; when needed, it requires energy, time and complicated equipment. A summary of some of the important purification methods follows. There is by no means standardization of technique, but simple purification can be generally summarized as removing carbon and metal impurities while harming or destroying as little product as possible. For research, and some applications, length must be controlled, or they have to be sorted by type, but those types of sub-attribute based discrimination are not considered here.

Removing Carbon Impurities

Carbon impurities can be removed by exploiting the difference in oxidation temperature between CNTs and amorphous carbon. In the presence of oxygen, the amorphous carbon oxidizes into gas at a temperature of around 400 degrees, leaving behind nanotubes, which are slower to oxidize. This method, while effective for removing amorphous carbon, consumes a percentage of the nanotubes and decreases their quality by the introduction of oxygen into their structure. Additionally, it opens the caps on the tubes because the pentagonal structures are more reactive than the rest of the tube. Recent techniques carry out 'wet oxidation' by boiling the product in peroxide. (Veld et al, 2003) This occurs at a lower temperature, and is gentle to the nanotubes, but consumes peroxide to oxidize the carbon.

Removing Metal Impurities

Acid treatments are typically done with hydrochloric, nitric acid or a mix thereof. The product is immersed in acid and stirred with ultrasonic waves, producing a metal chloride salt along with hydrogen or water. The solution is then filtered and the residue nanomaterial is washed with distilled water and dried. Acid treatments require that the metal particles be exposed to the solution, and therefore a previous step such as oxidation

in order to accomplish that. Acid treatments generally have a negative effect on the quality of nanotubes (Wang et al, 2003). This effect can be minimized by using lower strengths of acid. In addition, the process ‘resets’ the spatial orientation: this can be useful for breaking up clumps and untangling knots, but also negates any organization the particles had going in to the treatment.

Light oxidation followed by sonication in an acid wash and filtration is a simple and typical purification regime that relatively easily produces nanotubes of acceptable purity and with relatively little damage to the product.

Other Techniques

Vacuum Annealing is potentially a superior method to acid washing in that it can remove metal impurities from nanotubes by direct vaporization while increasing graphitisation (Huang et al, 2003). It is typically carried out at temperatures of 1800 or more Kelvin, in a very high vacuum chamber over a period of a dozen or more hours, and is thus very energy consuming and requires complicated equipment, restricting it to applications requiring very high purities. Over 99.9% purity at 86% material yield has been achieved with vacuum annealing followed by a mild acid treatment. (Wang et al, 2003).

3.2 Production System Technology Models

The technology models represent demonstrated techniques for nanoparticle synthesis. The reaction conditions and stoichiometry for each process are taken from demonstrated reactions. The scale of application is assumed to be sufficiently large as to use process efficiencies such as heating and compression at industrial levels to achieve the given reaction conditions. With the assumption of industrial scale, other possibilities for analysis emerge such as heat exchange, the end use of the off-gas, integration into other processes, electricity source and so on. The best way to facilitate these types of inquiry is to keep all heat, chemical potential and electrical flows separate.

The production systems are presented in two sections. In the first, various systems for production are discussed along with possible technical improvements suggested by research or by the model results. In the system expansion section of this chapter, the discussion focuses on how the results change by interacting with the background system to ‘credit’ useful by-products or by assuming different sources of electricity.

There are two main cases considered for each process: a baseline case and an ‘efficient’ case. Table 1 contains a summary of the general assumptions made for each case. Specifics are found in Appendix B. The efficient cases rest on some speculative assumptions about whether processes designed for efficiency could scale to industrial levels, and could be thought of as a far future best-case scenario for currently known results. As mentioned, there are several tradeoffs inherent in production systems and yield per unit feedstock versus yield per unit time appears to be one of them. The baseline cases all use stoichiometry data from reports containing the highest yields per unit time found, while the efficient cases take their stoichiometry from process reports detailing

very high feedstock yields, with the assumption that such high efficiencies can be obtained at higher throughput.

Table 1: General Assumptions in System Scenarios

Efficient Case	Baseline Case
Stoichiometry taken from highest material efficiency data available. Some waste heat allowed to ‘pre-heat’ some inputs.	Stoichiometry taken from highest volume per unit time data available. All heating electric.

3.2.1 Considering Purification Processes

The various syntheses require different types of purification procedure to get them to an equivalent purity. Each purification step required is modeled as a process requiring energy and material input, and characterized by a yield, which corresponds to the amount of recoverable material. This yield is carried back through to the synthesis and serves as a multiple for every preceding step.

Because new methods are constantly being refined and because increasingly accurate synthesis technology is changing the need for purification and the manner in which it can be done, a specific example purification step is chosen and appended to each production model. The reason for choosing the particular process and the potential for using other methods is discussed. The actual parameters used such as yield and energy used are presented for each individual process in Appendix B

3.2.2 Considering Background System Processes

The material inputs required for each production and synthesis system are considered through their respective cradle to gate production process, modeled without transportation processes due to the uncertain final location of facilities. Primary energy feedstocks are added and considered as ‘thermal’ energy, while electricity consumed is added up and kept as a separate total. Different ways of modeling the electricity production and their effects on the results are considered in the second section.

3.2.3 Production Process Inventory Data

An overview of each synthesis method analyzed is given with a system diagram and a discussion on the factors most significant to the results. For each element of the system, specific processes, materials and calculation choices are fully discussed in Appendix B

3.3 Gaseous Feedstock Production Process Analysis

3.3.1 Fluidized Bed CVD

Fluidized bed methods are currently some of the most productive ways of making nanotubes. The specific process considered for calculation uses methane as the carbon feedstock, and decomposes it in a nitrogen atmosphere in a fluidized bed of fine MgO dust seeded with iron nanoparticle catalyst. The process results in a fluff of relatively high purity SWNT surrounding the catalyst bed material. This process is treated in literature along with many variants such as using alumina powder as a catalyst support, differing catalyst particles or other hydrocarbon gases as the feedstock (Corrias et al, 2003). It has been demonstrated as a continuous process in 2006 and is expected to produce multi-ton quantities of SWNT at costs 'significantly below the market price' for 2007 (Setoguchi et al, 2006). Because it is also essentially a methane reformation reaction, it has further been studied as a process to produce hydrogen as well as nanotubes (Spath et al, 2002). Calculations were based on the model in Figure 3-2.

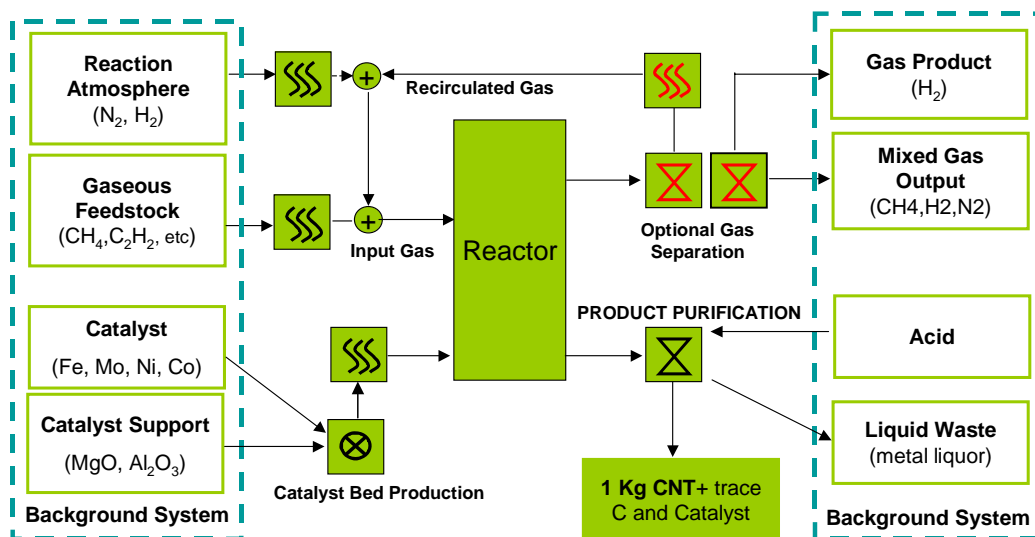


Figure 3-2: Fluidized Bed Production of Nanotubes

The reaction takes place at 1 atmosphere and roughly 800 degrees centigrade. Current technology can achieve carbon yields from the feedstock in excess of 80% in very slow reactions, but a more realistic, if optimistic, estimate for bulk production is 25-30% (Spath et al, 2002). Of the carbon deposited, over 80% is controllably SWNT and is removed continuously with the catalyst bed. The model assumes that the catalyst bed (MgO) is removed with acid treatment. The efficient case allows for some heat transfer, but the main difference is obtained by using data from experiments utilizing much lower flow rates and maximizing carbon yield instead of time yield. (Li et al, 2005)

Table 2: CER for Fluidized Bed Reactors

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Fluidized Bed CVD	SWNT	220	93	626	328

Critical Energy Factors in Fluidized Bed Reactors

The biggest energy inputs to the Fluidized Bed system as modeled here are the primary energy intensity of the catalyst and the acid used to dissolve it. This is assuming that the nanotubes and catalyst cannot be physically detached from the catalyst support, whereas it may be possible to do so with some support/catalyst combinations. (Wang et al, 2003) The amount and composition of the catalyst bed are therefore critical inputs to the overall energy flow of the process. Reducing the amount of catalyst used directly reduces the process requirements until it corresponds with a reduction in yield, and even then may still reduce the net energy balance. The catalyst loading onto the bed particles is usually about 2% by weight for MgO beds, which gives a product-to-catalyst yield of 2 times in this experiment. Others using Fluidized Bed reactors have obtained a much better product-to-catalyst ratio of 10 times or more (Li et al, 2005), but at lower reported reaction rates, indicating a potential trade-off between efficiency and production throughput.

Of note as well is that due to the high throughput of catalyst in the example, transportation costs could potentially become an important addition, especially since precursors such as MgO could potentially come from very far away. To illustrate, taking a value for the energy requirement of bulk transport between a large-truck value of 0.7 and a large-ship value of 0.24 (Baumann and Tillman, 2003) for an estimated 0.5 MJ per ton-kilometre gives: every 100 kilometres of transport in the catalyst background system would add 1 MJ to the overall net energy balance for SWNT production. This could become a significant addition to the total requirement, especially so once the process is carried out in an optimized and industrially integrated manner.

Disregarding its influence on the product obtained, the choice of hydrocarbon has a very small effect on the final energy balance. Likewise, the actual carbon yield achieved has a surprisingly small effect on the energy balance until it goes below a certain threshold; lowering it increases the needed flow rates and heating energy, but simultaneously increases the energy content of the gaseous fraction of the system output. This observation does assume that the yield is somewhat independent of the catalyst feed rate, i.e. that a lower yield could be compensated for by increased gas flow without requiring more catalyst input for the same amount of product.

Using as little nitrogen as possible is obviously optimal for the energy balance. Some variations have used pure hydrocarbon atmospheres (Veld et al, 2003). Separating the

nitrogen used and recirculating the gas does not affect the amount of heating required, but is assumed to be done because of the high flow rates of pure nitrogen required and the difficulty in separating hydrogen until its partial pressure in the exhaust is sufficiently high. The choice to separate the hydrogen would not significantly affect the energy flow at this level of examination; it would only change the probable use of the output gas. One pass through a modern pressure swing absorber can produce fuel cell grade hydrogen, but the methane/hydrogen mix can be directly useful as well, more so as the amount of nitrogen it contains is decreased.

3.3.2 Floating Catalyst Production

Floating catalyst production is very similar to the Fluidized Bed technique, but instead of depositing it on microscopic particles, the catalyst is vaporized and mixed with the feedstock, with all growth happening in the vapour phase. The sample chosen was designed to maximize time productivity inside a simple apparatus and achieved 6g/h SWNT and 20g/h MWNT output (Fan et al, 2006). Modern plants can produce 14 kg/h with an unspecified number of reactors (Baughman 2002). The reactor used benzene feedstock in a hydrogen atmosphere. Floating catalyst reactors are commonly used to make mass-produced MWNT, but often have the drawbacks of producing short nanotubes due to the relatively short residence time (Fan et al, 2006). Floating catalyst methods tend to require more purification steps (although each step is not as material intensive because there is no catalyst bed to remove) than the Fluidized Bed methods because of the tendency for the free-floating catalyst particles to become fully encased in graphite. Purification was modeled as sonication in nitric acid.

Table 3: CER for Floating Catalyst System

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Floating Catalyst CVD	MWNT	74	331	187	295

Critical Energy Factors in Floating Catalyst Reactors

The biggest energy inputs to the floating catalyst reactors are the electricity used in the apparatus and purification, followed by the feedstock value of the hydrocarbon, here benzene. At one atmosphere, benzene will condense at 80 degrees centigrade, and therefore the hydrogen output gas is easy to separate from the unused benzene. Because any 'extra' hydrogen/benzene mix retains its full fuel value, in a continuous system, the feedstock value for the nanotubes resolves to that of the hydrocarbon precursor required to make them as determined by stoichiometric calculation.

The trade-off is that the freely floating catalyst particles tend to become completely encased in graphite, and thus require more purification steps to remove the metal

impurities. In this work, purification process requirements are calculated at close to a thermodynamic minimum basis and are thus likely to be higher in practice until industrial purification routines exist.

The relatively simple reaction and the bulk production of the catalyst without any complicated impregnation steps make the floating catalyst reactors themselves potentially very efficient and simple to run. It is interesting to compare the energy values with ‘efficient’ values for the Fluidized Bed reactor in the case of no nitrogen input, and a product to catalyst ratio of ten because the reaction conditions are very similar and the production requirement for SWNT is only marginally higher than that calculated for efficient MWNT production.

3.3.3 Pyrolytic Fullerene Production

Pyrolytic combustion is the dominant method for mass production of C_{60} . Toluene, benzene or other aromatic hydrocarbons are burned in conditions optimizing the rate of soot production versus the fullerene content of the soot deposit (Figure 3-3). Despite the low yields of the method overall, the process has virtually no competitors as a source of C_{60} due to the intrinsic ease of scaling up output and the relatively simple methods than can be used to purify C_{60} . Additionally, it can alternatively selectively produce high C_{70+} content where it is difficult to do so with electrical arc methods. The process data used to model the system was obtained from a reactor producing 25 grams of fullerene per hour, but states that scaling up production, even within the same apparatus would not require any fundamental change in process.

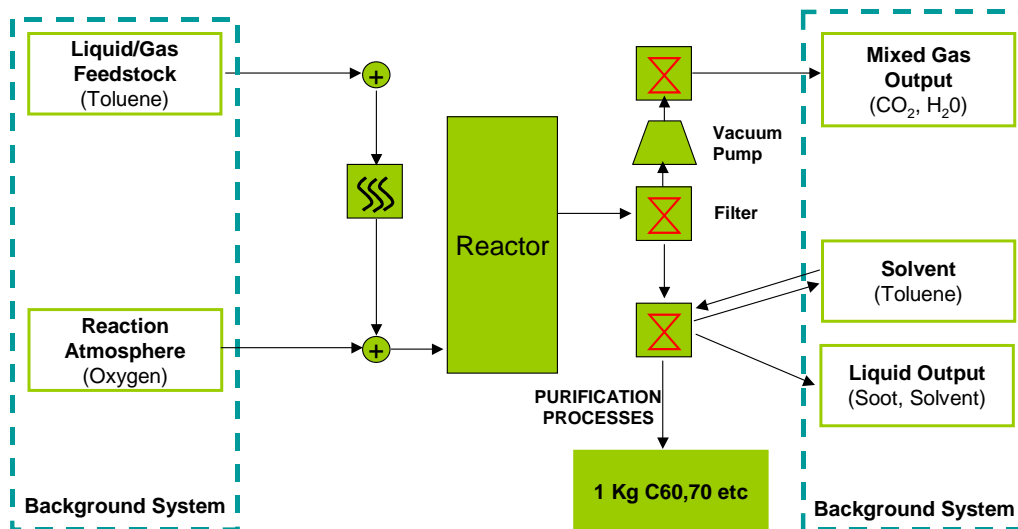


Figure 3-3: Pyrolytic Fullerene Production System

Table 4: CER for Pyrolytic System

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Pyrolysis	C60, C70	538	5412	678	6341

Critical Factors and Discussion

Because the toluene is burned with low fullerene yield, much of it has to be burned, and consequently it constitutes the main part of the energy consumed in the process. Toluene is a product of the petrochemical industry, and consequently there will be a wide potential range of process requirements depending on how toluene is valued as a feedstock.

Because the system was optimized for carbon to oxygen content, there is little further possibility for optimization in the fuel system. The large quantity of heat that is released during combustion suggests some form of heat exchange as a possible technical improvement, although difficult because of the low-pressure conditions, and the thermal requirement for toluene vaporization in purification is assumed to come from the excess flame heat in the Efficient Case.

3.3.4 HiPco Disproportionation

HiPco is short for High Pressure carbon monoxide; the process exploits the chemical equilibrium of a carbon monoxide/dioxide system: $2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$. It is notable for being an entirely gas phase reaction and for producing high quality nanotubes that potentially require little or no processing.

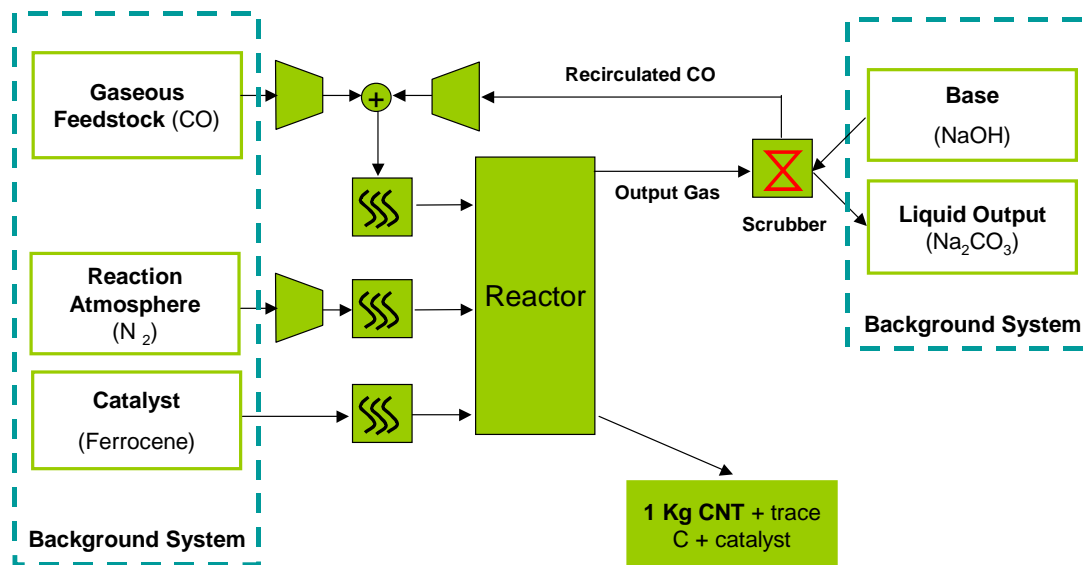


Figure 3-4: HiPco Nanotube Production System

Figure 3-4 shows the HiPco system model. Carbon monoxide is pressurized to 30 atmospheres, heated to 1000 C and fed into the reactor to be mixed with a cold CO stream containing vaporized iron pentacarbonyl as a catalyst. A shift takes place towards the CO₂ side of the equilibrium. Upon contact with the disassociated catalyst, the carbon freed in the reaction deposits as ropes of nanotubes and amorphous carbon. The metal/carbon particles are filtered out and the carbon monoxide is recirculated after removing the CO₂ with NaOH. Yields of 97% pure SWNT (3% catalyst metal residue) have been reported at a rate of 450 mg/h (Bronikowski et al, 2001. There is indication that productivity can be massively increased; A press release on the homepage of CNI, Inc (www.enanotech.com) acclaims a pilot reactor designed to produce 50kg/day has been constructed. Because of the confidential nature of this proprietary process, it is difficult to define reasonable improvements in technical efficiency and there is no efficient case presented here.

Table 5: CER for HiPco Systems

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
HiPco	SWNT	-	-	5769	47

Critical Factors and Discussion

Because the carbon monoxide is circulated, the electrical consumption of the heaters and compressors are by far the dominant energy inputs into the system. This is due to an extremely low carbon yield per pass through the reactor. At one gram per hour, 1000 hours per kilogram SWNT is required per reactor tube. This massively inflates the cost of any electricity used during the process; even a light bulb left on consuming one hundred watts of electricity over that length of time would correspond to using 360 MJ of electricity per kg SWNT (compare to 54 MJ/kg aluminium over its entire lifecycle, (Sunér, 1996). The productivity of the system can theoretically still increase with more advanced technological measures such as laser dissociation of the catalyst and better gas mixing topography. (Bronikowski, 2001) The process will remain important in the future because of the high quality material produced and the facility of scaling it. If research on using it to ‘clone’ nanotubes, thus enabling batches of a single chirality, comes to fruition (An et al, 2005), then it could become the most attractive route for applications with such requirements. There are many, many applications in which control of chirality is not only important, but a prerequisite and therefore growing single chirality nanotubes from a few isolated specimens is a very interesting prospect.

3.4 Solid Feedstock Production Process Analysis

Processes synthesising carbon nanoparticles from solid feedstocks are generally similar from a systemic perspective, show in figure 3-5. All have low yields with the same types of impurities and thus require the same purification processes. The salient parameters are thus the energy needed to maintain the atmosphere and the background systems for producing the feedstock. Because of these similarities, the various set-ups are described and then have their critical parameters discussed together.

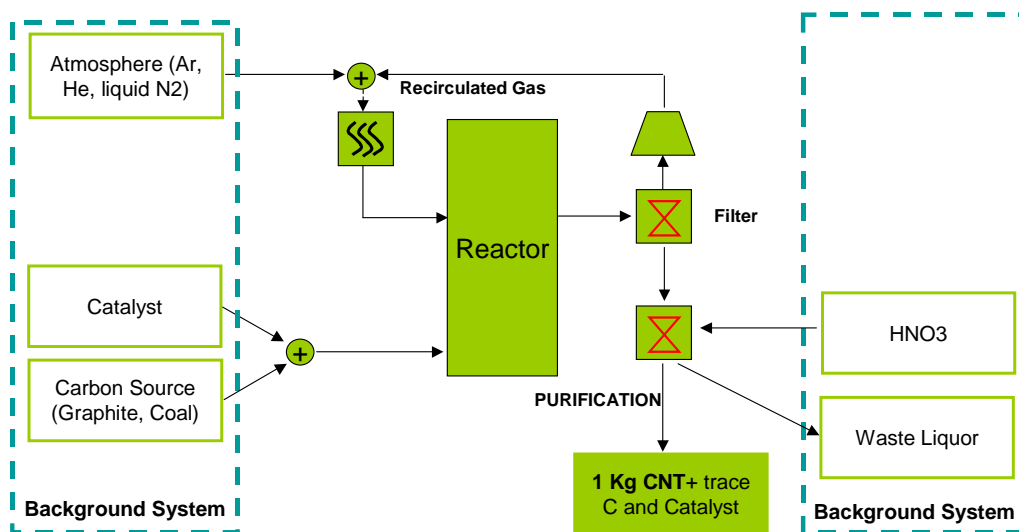


Figure 3-5: Solid Feedstock Production System

3.4.1 Arc Discharge

The arc discharge process is arguably the simplest of the processes to create nanotubes. It is in use commercially and in many laboratory scale processes around the world. Figure 3-5 shows the system model. The equipment needed to undertake basic arc synthesis is extremely simple; under certain conditions, it can even be accomplished in open air (Veld et al, 2003). There are other advantages to arc synthesis, such as the ability to make MWNT without catalyst, DWNT selectively, and the generally good graphitisation of the product. Additionally, the method can produce any of the main CNP species. In most processes, the electrode assembly is in heated low-pressure argon, but variants immersed in liquid nitrogen may provide an alternative (Veld et al, 2003). Purification for all of the solid feedstock processes is oxidation of carbon impurities with a quick acid treatment, but vacuum annealing could produce very high quality MWNTs without any metal trace. The low requirement case is constructed by assuming that coal is used in place of high quality graphite for all processes.

3.4.2 Laser Ablation

Laser ablation processes are extremely similar to arc from a system perspective except that a laser beam is focussed onto the graphite and catalyst target. The energy for the laser must also come from electricity. The high case is constructed from continuous CO₂ laser data, while the low is the theoretical limit for free electron lasers with the same apparatus otherwise.

3.4.3 Solar Furnace

Solar furnaces are similar in a way to the laser method except that the specific energy of the photons cannot be tuned. This leads to not quite as high productivity, but it is easier to scale up the size of a solar furnace than it is to increase laser output. A demonstration reactor with a heat flux of 50kW produced 10g/h of nanotubes (Guillard et al, 2002), one of the highest outputs per unit time demonstrated from a single solid feedstock reactor. A 250 kW version is planned. So far, the solar furnace reactor has used high-grade graphite as the feedstock, but the success using coal in the electric arc process may indicate that it is possible to use in a solar furnace as well.

Table 6: CER for Solid Feedstock Systems

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Electric Arc	MWNT	2170	75	2170	295
Laser Ablation	SWNT, MWNT	1600	61	9424	211
Solar Furnace	SWNT	(6200)* + 150	72	(6200)* + 150	292

* This value is the ‘wasted’ electric potential of using such a thermal system, and represents an opportunity cost for using the apparatus to produce nanomaterial. See Section 4.4 for assumptions. An alternative value is zero.

Critical Factors and Discussion for Solid Feedstock Processes

The main critical factors are the amounts of electricity used directly as process energy and the primary energy content of the graphite feedstock. Both factors are directly affected by the yield and thus yield is the most critical variable in the model. Electric arc yields have been optimized with elaborate study, but further scaling up is limited by electrode size (Veld et al, 2003).

High purity graphite is a costly and energy intensive product. Most of the production energy is lost during the synthesis because the carbon byproduct is assumed to not be reusable as electrode material. The balance of carbon is assumed to have a feedstock

value equivalent to graphite, but with the loss of all the extra process energy. The newly reported successes using coal as an electrode (Qiu et al, 2007) could possibly represent a large improvement in both the feedstock energy requirement and price. The difference in thermal demand between the efficient case and the baseline case is mostly due to an assumed switch to coal feedstock. The cost of maintaining a heated and inert atmosphere is a significant energy expenditure in the methods that utilize it, but could become far more efficient if shared between parallel reactors, or used in reactors with very long to continuous duty cycles.

3.5 Discussion of Controlled Synthesis Processes

The processes outlined so far are all ‘bulk’ production methods in that the produced material, even before purification, is disordered and clumped. As outlined in the introduction, those processes constitute one branch of nanoparticle production, with the other being represented by the control-based syntheses of which CVD onto a template is currently the only viable example.

Trying to determine energy requirements for the static CVD processes is difficult, because each one will be a batch operation, in a reactor tuned to do a specific process. In the simplest case, where a forest of nanotubes are grown on a substrate, and later transferred or removed, an energy requirement can be calculated for the nanotubes as an artefact, but is likely to be very high compared to manufacturing the same mass in a three dimensional reaction.

Many process requirements will not be changed depending on whether a full field of nanotubes or a few isolated strands are produced, leading to values that vary immensely for a weight based functional unit. For such processes, characterization is better done as a process, with the functional unit being the artefact into which the nanotubes are being integrated. An example would be producing thermal interconnects for a microchip. With a hypothetical die area of 1 square centimetre, and one-micron nanotubes covering 1% of the area, one millionth of a cubic centimetre, or roughly 1.5 micrograms, of nanotubes would be produced on a single microchip. 1.5 MJ of process energy for a nanotube-growing step would thus represent 1 TJ/kg of nanotube, but would be more easily put into a useful context as a 1.5MJ process in the microchip inventory.

3.6 Production Results Summary

Combining the process model calculations gives Table 7. The numbers represent the requirements for a net production of 1 kg of nanoparticles with large-scale production at demonstrated reaction stoichiometries and the established industrial process requirements of creating the background system materials. The major caveats come from assuming that the outlined reaction conditions are achieved with a high efficiency, particularly where the amount of acid used in purification is considered. A further assumption is that the same stoichiometry as in reported practice can be obtained at such scales. As can be seen, production of CNPs even in very large and efficient quantities will remain quite energy intensive compared with virtually any material.

Table 7: Synthesis Process Summary of Results

Process	Product	Efficient Case		Baseline Case	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Fluidized Bed CVD	SWNT	220	93	626	328
Floating Catalyst CVD	MWNT	74	331	187	295
HiPco	SWNT	-	-	5769	47
Pyrolysis	C60	538	5412	678	6341
Electric Arc	MWNT	2170	75	2170	295
Laser Ablation	SWNT	1600	61	9424	211
	MWNT				
Solar Furnace	SWNT	(6200)* + 150	72	(6200)* + 150	292

* This value is the ‘wasted’ electric potential of using such a thermal system, and represents an opportunity cost for using the apparatus to produce nanomaterial. See Section 4.4 for assumptions. An alternative value is zero.

3.7 Potential for Increases in Energy Efficiency

The calculations thus far for synthesis methods represent isolated systems for producing carbon nanoparticles. The efficiency of these processes may be improved in two general manners:

1. Technical Change: Processes become more optimized, yields improve, etc.
2. System Expansions: The production process interacts with other societal flows, increasing organizational efficiency and so on.

The technical change aspects have been discussed with the various production system descriptions, and some are already implicitly assumed by using generic industrial efficiencies where applicable for processes involved. The second category of improvement, system expansions, is discussed in the following section.

4 CNP Production with System Expansions

Future production infrastructure has many potential interactions with other industrial processes that could enhance the efficiency of production by sharing the cost of producing precursors or by demanding by-products. In order to obtain a general sense of where the production of carbon nanoparticles fits into industrial systems, table 8 presents a list of industries related to the background system processes involved in the various production methods:

Table 8: Background Systems and Related Industries

Background System Inputs	Examples	Related Producer Industries
Acid, Base Production	HNO ₃ HCl NaOH	Industrial Chemicals, Metals
Gaseous/Liquid Feedstock Production	Methane Ethene Toluene Hydrogen Carbon Monoxides	Petroleum Refining, Energy, Hydrogen, Industrial Chemicals, Metals
Solid Feedstock Production	Coal Graphite	Energy, Metals, Specialty Carbon
Reaction Atmosphere Production	Nitrogen Argon Helium	Industrial Gases, Many others
Catalyst Production	Ferrocene Iron Pentacarbonyl	Petroleum Refining (fuel additive), Industrial Chemicals
Catalyst Support Production	MgO Al ₂ O ₃	Petroleum Refining, Metals, Industrial Chemicals
Solvent	Toluene Benzene	Petroleum Refining, Industrial Chemicals
Electricity Production	Electricity	Energy
Background System Outputs	Examples	Related Consumer Industries
Gas Product	Hydrogen	Many
Mixed Gas Output	H ₂ , N ₂ , CH ₄ , etc.	Many
Liquid Output	Metal Liquors Suspended Soot (Carbon Black)	Metals, Petroleum Refining, Industrial Chemicals

The background system processes for large-scale CNP production are related to a general set of industries comprising the basic material and energy sectors in society. The rest of this section examines possible interactions between these industries and each of the CNP production processes already discussed. While in a certain sense it is possible to imagine industrial integration in a larger sense, there would be associated requirements such as transport of materials or co-location of facilities that may or may not be reasonable. These calculations give a rough estimate of how much further the efficiencies of synthesis could be pushed with a concerted effort. In many cases, it would likely be a

long time if ever before economics would push for such integration, and these scenarios could be regarded as a maximum efficiency scenario using current process technology. Baseline and low cases are treated with the same assumptions as in the last chapter.

4.1 Fluidized Beds

Fluidized Bed reactors have a large amount of possible interactions. Looking at the background systems involved with the fluidized bed reactors gives a list of possibly expandable systems in addition to that of electricity, which is discussed as a separate section. Two of them stand out in terms of total share of the energy requirement and possibility for integration: the catalyst bed/acid background systems, and the feedstock background system.

4.1.1 Catalyst Bed and Acid

A major share of the energy use not 'required' by thermodynamics in Fluidized Bed reactors is the embodied primary energy required to create the catalyst and any acid used to dissolve it. The two catalyst support materials most commonly used are magnesium oxide and aluminium oxide, both of which are precursors in their respective metal production systems.

If physical separation of the nanotube/catalyst complex is possible in the system considered then the catalyst support could potentially be reused with only a small energy cost to reimpregnate it. If reuse is impossible, the support can be reinserted into the metal production chain, and the amount of energy that would have been required to create it directly by the metal manufacturers would no longer be required, and the use of acid avoided.

Otherwise, the support is dissolved, leaving the nanotubes suspended in the solution. Magnesium oxide reacts readily with acids to produce magnesium salts, alumina requires slightly longer processes to remove, usually involving dissolution with a base such as potassium hydroxide. After treatment, there is a range of possible products that are all directly used in bulk in other chemical industries. For the example Fluidized Bed system here, consider the previous reactor with a magnesium oxide base, and a system expansion to include magnesium production.

After removing the nanotubes, the remaining solution is concentrated $MgCl_2$, which is also deliberately created by reacting magnesium oxides with hydrochloric acid for the production of magnesium metal. The basic creation of the oxide and the acid explicitly for the nanotubes is thus not necessary which would lower the energy requirement of the catalyst chain to that of the special MgO preparation, and the catalyst impregnation step.

Because the energy for MgO and HCl production is already assumed in the magnesium lifecycle, this allocation is a valid credit until the amount of $MgCl_2$ produced approaches that required by magnesium production, which was roughly 400 kilotons of magnesium metal per year in 2004. That would represent the production of roughly 20 kilotons of

nanotube material at the levels of catalyst use described for the Fluidized Bed reactor model, or 100 kilotons with the more efficient numbers. Afterwards, magnesium could be made more cheaply, changing the allocation of costs between it and the nanotubes, or the magnesium oxide could be dissolved with other acids to produce magnesium nitrate (fertiliser), magnesium sulphate (epsom salt), etc. These magnesium salts are used in other systems consuming an estimated 10 million or more tons per year, providing a smaller potential benefit of integration but for a virtually unlimited amount of material.

Alumina also offers effectively unlimited possibility for reuse, but with much smaller (or potentially nonexistent) benefits because of the higher catalyst loading and increased complication of chemical treatment.

4.1.2 Gas Flow Integration of Fluidized Beds

In the event that designs using hydrogen instead of nitrogen, or only pure hydrocarbon as the feedstock come into industrial use, further gains can be achieved. In particular, methane reformation for hydrogen production uses an almost identical reaction. Placing the reactor before the methane reformer one could achieve a number of different system topographies.

This could effectively provide the methane and most of the heat for the reaction for the cost of reducing the amount of hydrogen produced by the reformed methane. This is because the carbon would not be available for gas shift reactions. Depending on the yield of the reaction, it could have a small range of effects. Combining this with the metal production chains could result in much lower CER for fluidized bed CNP production. Table 9 shows the two fluidized bed system cases recalculated with the contributions from the acid/catalyst system expansion and the simple treatment of gas flow integration discussed above. Noting the efficient case, carefully integrated production of nanotubes including complete treatment of background systems using the most energetically efficient synthesis results could enter the same order of CER as virgin aluminium under this model, but it is not likely that all these assumptions would be valid.

Table 9: Effect of system expansions on Fluidized Bed CER

Process	Product	Efficient Case with System Expansions		Baseline Case with System Expansions	
		Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)	Electrical (MJ _e /kg)	Thermal (MJ _{th} /kg)
Fluidized Bed CVD	SWNT	61	70	156	211

These sorts of estimates ignore prerequisite considerations such as co-location or transport, which are not trivial in energy or potential risk terms. The low case uses high efficiency, and near-perfect integration with background industries, and thus is fairly close to what is thermodynamically possible. As such, it likely will never be achieved for efficiency. Nevertheless, the baseline estimates are intended to give a long-term

perspective on how the integration of bulk production could eliminate waste streams and reduce energy requirements, if it was a priority to do so.

4.2 Pyrolytic C60

The major system expansions possible are from the exchange of heat available from burning 200 kilograms of hydrocarbon per kilogram of fullerene material. A facility producing one kiloton of C60 per year under the system used in this paper would produce roughly 250kW of heat at 1000 degrees Celsius. That heat could be first offset against the amount required to boil the toluene in the purification steps in an integrated facility. This was already done for the low case already calculated. The rest could be a generic thermal output in the event of co-location with a heat demanding industry. Table 10 shows the amount and quality of heat that could potentially be available for such use.

Table 10: System Expansions and Pyrolysis CER

Process	Product	Cumulative Electrical Demand	Cumulative Thermal Demand	Gross Thermal Energy Available (CO2 and H2O at 1000C, 1 atm.) (MJ/kg)
		Efficient Case (MJ/kg)	Efficient Case (MJ/kg)	
Pyrolytic Synthesis	C60	6341	678	3870

4.3 HiPco

At first glance, HiPco methods also provide potential to increase efficiencies by integrating its gas flow. The requirement is pure carbon monoxide at high temperature and pressure, which suggests syngas production or similar processes as being potentially useful. Experiments on HiPco reaction parameters indicate that hydrogen at even low concentrations adversely affects the productivity of the method (Nasibulin et al, 2006). There is therefore currently no existing industry that can easily produce carbon monoxide at the temperature and purity required for direct integration except perhaps silicon production. It seems far more likely that the carbon monoxide used will continue to need to be manufactured. Efficiency increases must therefore come from technical improvement and scaling, or from the indirect benefits of producing controlled chirality products, should cloning technology prove possible.

4.4 Solid Feedstock Methods

Synthesis methods based on solid feedstocks have inherently few background systems to interact with, but are naturally sensitive to the electricity or energy source used to vaporize the carbon. The source of electricity used makes a large impact on the final environmental profile of the methods. One system expansion was assumed during the calculation in that the unused carbon would be used as a feedstock for other processes,

recovering its feedstock value, otherwise the thermal requirements would have been significantly higher. One other interesting system expansion is to examine whether using a solar reactor for thermal production is more efficient than using the same reactor to generate electricity and then using that electricity in one of the other solid feedstock methods to create CNPs.

If one assumes a conversion efficiency from heat to electricity of 35%, then a solar furnace of equivalent power as the one discussed could produce about 17.5 kW of electricity. Using this electricity in six parallel electric arc reactors of the type described in this paper, this electrical energy could produce about 30g/h net of nanotubes, indicating that the solar furnace is roughly about one third as productive as the electric arc methods on a power basis, but uses 'free' energy and overcomes production scaling limits found in electric processes.

4.5 Further Production Aspects

Even with a very high degree of integration of production into other industries, it appears that CNPs will remain energetically expensive materials, barring the introduction of currently unknown technology. Their large-scale application could thus represent a significant energy investment that synergies with existing industries could abate. There have been some economic feasibility studies for integrating continuous flow processes directly into refinery operations, particularly using gas reformation and producing hydrogen as a valuable by-product. One study (Spath et al, 2002) targeted at assumed production level of 75 kilotons per year concluded that it would be feasible to produce large quantities of nanotubes at very low prices using such industrial integration if some technical hurdles to scaling production were overcome.

4.5.1 Pricing and Future Prospects

There is a very large range of price tolerance among the many potential applications of carbon nanotechnology. In particular, mass-market products that integrate significant amounts of nanomaterial will naturally be quite sensitive to the price of CNPs and will need to await a very large drop from current prices to become viable. Because these applications will determine to some degree the eventual demand for carbon nanoparticle production, understanding the sources of cost in the production process can provide perspective to discussions about the future of the technology. Below is a quick listing of key ingredients that are consumed in the example floating catalyst method, with high efficiency assumptions:

Table 11: Simplified Cost Breakdown for 1kg MWNT

Material	Approximate Cost (USD)	Total Cost
Electricity	\$20 / GJ	\$7
Benzene	\$14 / GJ	\$3
Ferrocene	\$7 / kg	\$1
HCl gas	\$72 / t	\$<1
Total for 1kg of MWNT		~\$12
1 kg of MWNT (2007)	\$10,000-\$80,000 depending on type, purity*	

* Source: www.nanowerk.com nanomaterial database

Despite the over-simplicity of this calculation, it can be readily seen that the current pricing for MWNT is not correlated with the price of the feedstock, catalyst or energy requirements of efficient implementations of production processes. Other CNPs have similar pricing relative to the materials and energy theoretically required for their production. Labour, capital, intellectual property costs and profits for the producer therefore make up the remainder of the price. Continuous reactors, increased automation and reduced need for purification will abate these costs. For batch CVD processes, it is currently possible to buy completely automated equipment capable of reproducibly manufacturing precision nanostructures, supported by available online forums where users can swap ‘recipes’ for creating desirable structures. If one looks only at the process costs as calculated, ignoring labour and capital, the bottom range for mass-produced MWNT nanotubes could be as low as \$8-\$15 per kg. This is in agreement with an estimate that places the range at \$10-50 (De Jong et al, 2000), and a statement from a manufacturing company indicating that a sale price of \$75 per kilogram would be feasible under their cost structure (Mitsui, ref Baughman, 2002).

These levels of cost indicate that there is much room for carbon nanomaterials to become far cheaper than they are today. Therefore, many proposed large-scale applications may eventually become economically feasible, and continued investigation into CNP environmental profiles is needed.

5 Preparing CNPs for Application

So far, base requirements for mass manufacture of carbon nanoparticles using current technology have been calculated and discussed. As the produced particles are often not useful by themselves, there are intermediate steps between the synthesis products that transform them into forms suitable for use in products.

Integrating carbon nanoparticles into larger technological artefacts is not a trivial challenge. Their chemistry presents many practical problems towards creating standardized processes for working with them. In particular, nanotubes have many possible variations even within a ‘pure’ sample, all of which affect their physical properties and can even make characterizing their chemistry a difficult problem. Nanomaterial production chains are often grouped into stages called nanoparticles, nanointermediates and final products. Materials at the nanointermediate stage are varied, but for bulk materials, they commonly consist of nanotubes organised into films or dispersed into polymers or solutions. This section offers a brief introduction to the production chain between synthesis and use.

5.1 Making Nanointermediates

After synthesis and purification, the manufacturing stage of the CNP lifecycle begins by manipulating them into a form suitable for integration into larger systems. There are two general categories of methods for working with carbon nanoparticles:

1. Manipulation of the physical arrangement: moving, assembling or modifying the alignment of the particles without modifying their chemical composition.
2. Manipulation of the chemical structure or ‘Functionalizing’: chemically altering, or coating the particles to provide an interface to interact with another material.

5.1.1 Physical Manipulation of Carbon Nanoparticles

Physical methods are used to control the attributes of collections of nanotubes directly. Sonication, electromagnetic orientation, melt spinning, brushing and dry transfer are examples of bulk physical manipulation methods. Ultrasonication and orientation are the most commonly used techniques in bulk application processing, used for dispersal and controlling the parameters of the networks formed when nanotubes are dispersed in bulk solids. Brushing and dry transfer can be used to convert ‘forests’ of nanotubes into films or transfer them between substrates. To generalize, physical techniques are currently rather cumbersome and ineffective, especially when one considers what can be achieved for a given amount of effort. One can either realize a high level of control in single operations, or a very general level of control when used in parallel. From a lifecycle point of view, most physical manipulation methods can be modelled as a unit process with only energy flows going in, and potentially some material loss. Many such processes also have analogues in other industries, particularly polymer and catalysis.

5.1.2 Functionalising Carbon Nanoparticles

Like graphite, fullerenes and nanotubes are generally chemically stable and present a physically smooth, or 'slippery' surface to surrounding material, while sticking to themselves via Van-der-Waals forces. This presents difficulties in handling them or coupling them into larger systems. Additionally, many bulk applications of CNPs require processing in a liquid or sometimes vapour phase, which is not easily obtainable with raw material. Fullerenes, such as C₆₀ are soluble in some organic liquids but unmodified nanotubes in their pure form can only be suspended temporarily, and even then maintain clumps and tangles in their structure that must be dealt with for effectiveness in many applications.

Functionalization, or modification of the chemical structure of the nanoparticles is one solution to these difficulties, and has formed the basis for coaxing nanoparticles to work with other materials (Hirsch, 2002); functionalization of some sort is virtually always used when working with CNPs. Chemical groups can be attached to exposed carbon atoms ('*exohedral*'), or substances can be encapsulated ('*endohedral*') within a fullerene or nanotube. A large variety of effects can be achieved by these means:

- Increased solubility allowing further processing in liquid phase
- Increased bonding with a surrounding material
- Breaking up of nanotube bundles
- Creation of 'handles' for physical manipulation of the material
- Changed electrical interaction properties
- Changed magnetic properties
- Creation of structures that will self assemble
- Etc.

Functionalization is still somewhat of an art form. Because of the specialized knowledge and equipment required to perform it accurately and verifiably, many CNP producers offer pre-suspended nanoparticle liquids, colloids, polymers or functionalized varieties in addition to pure CNP material. While the specifics of the different types of functionalization are not detailed in this work, the possibilities are very large as well as somewhat specific to each application. A couple general aspects of functionalization processes relevant to characterizing it in a production chain can be observed:

- All functionalization processes involve the reaction of a CNP with another substance, usually in small quantities, and are thus modelled in this work as a mixing process with energy and generic polymer inputs.
- Most functionalization techniques used in commercial products today are based on organic or polymer chemistry processing methods, often involving relatively common plastics and solvents.

5.2 Translation of Material Properties between Scales

Many of the extraordinary properties of carbon nanoparticles are related to their molecular perfection. This represents both a curse and a blessing: attempts to realize these properties in bulk material are affected by the so-far inevitable changes in performance that occur under chemical or physical modification of their structure. Conversely, the change of properties that occurs under modification or strain can be extremely useful: it could potentially be exploited to ‘tune’ their properties to a desired level or can even be directly useful in devices such as electronics, sensors, and so forth.

Many physical properties of individual nanotubes are orientation-specific; the value along their long axis is vastly different from those in other directions. Correspondingly, the properties of nanotubes in bulk can be different depending on their collective degree of organization, and precisely controlling the amount or absence of organization is an important part of determining the final properties of the substance. This concept of degree of organization is a useful one in categorizing different production paths for CNP-based materials, and has been used as the basis for separating the overall technology into two streams.

Each processing step may decrease or preserve the amount of order in the nanoparticles, but increasing order is difficult, if possible at all. For instance, there is no known way to manufacture bulk-synthesized nanotubes into the ordered ‘forests’ produced by template-CVD processes: they can be spun into ropes or made into films with the individual particles mostly aligned, but cannot attain the degree of order of the controlled synthesis product in any reasonable process. Similarly, material produced by fine control or bulk material synthesis processes cannot yet be organized into active nanostructures such as gears or NEMS³ without exorbitant processes. Techniques such as DNA templating or viral transport that are capable of placing single molecules at a determined location are potentially possible (Keren et al, 2003) but will not be commercialized in the near future.

³ NanoElectro Mechanical Systems

There is thus a hierarchy of order in applications and the manufacturing paths that lead toward them, and for applications requiring a high degree of organization, the organization must be imposed as much as possible during synthesis.

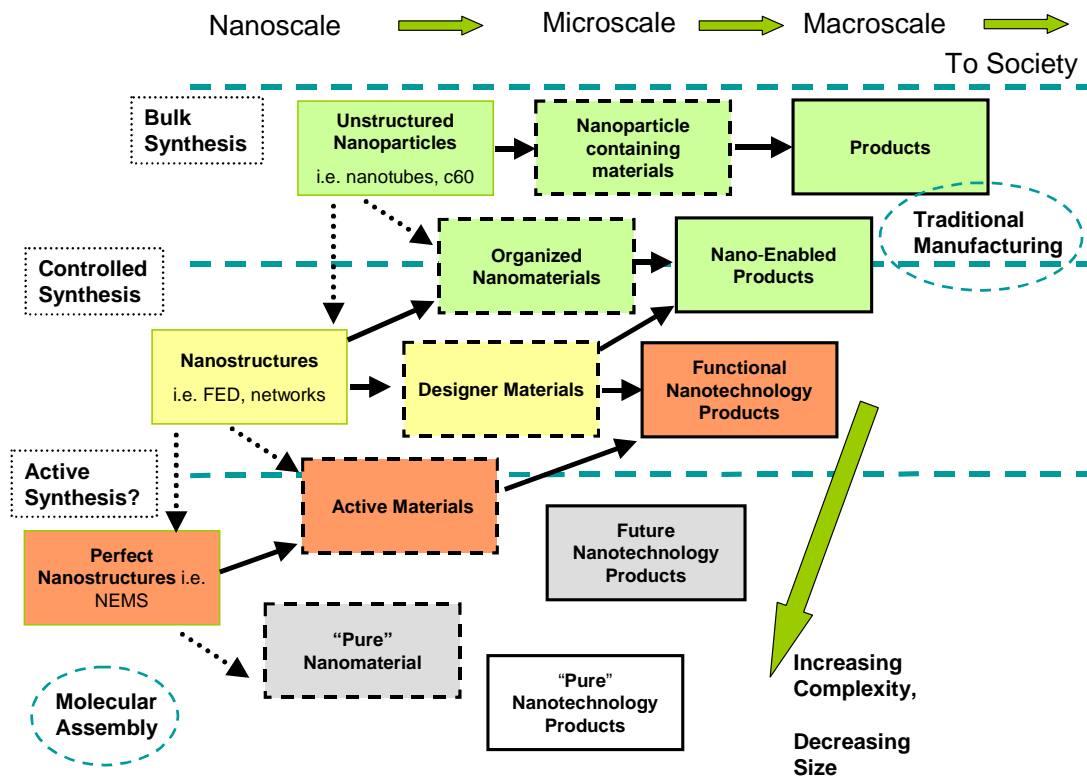


Figure 5-1: Hierarchy of Production and Application Systems

Figure 5-1 represents a visualization of that hierarchy. It is separated into three rough bands representing increasing complexity, or specific ‘information’ content as one moves down in the picture. Moving vertically represents direct transitions in organization while horizontal movement is direct transition in scale. The three ‘stops’ along the horizontal scale represent raw material, nanointermediates and applications respectively, but could continue indefinitely into larger systems as one moves to the right. The products in green have commercial applications, and delimit the scope of the applications and production processes considered in this study.

As the degree of control in synthesis increases, the size at which the critical details of the application are found also decreases. In bulk material, collections of nanotubes, the material surrounding them, and how they are organized form the system that determines properties, while in active nanostructures, quantum effects or a single atomic interface can be the region giving rise to the desired effect. There is a similar progression towards smaller scales as nanointermediates and products become more complex. The nanointermediate of bulk material might be a tub of plastic resin with nanotubes

dispersed in it, designer materials may be a nanotube field emitter display encased in special polymers and the nanointermediate of molecular nanotube transistors might be a network capable of computation but still too small to see. The general trend is that as products become increasingly complicated and integrated, their energy intensity and utility go up and evaluating their benefit becomes increasingly complicated.

6 Implications for Application

While it is becoming possible to get an increasingly accurate picture of the energy and material costs of producing and integrating carbon nanomaterial into macroscopic artefacts, quantitatively evaluating the potential ‘benefits’ of carbon nanotechnology is not a simple exercise. Benefits can come in many forms, such as dematerialization, increased efficiency and lifetime, added functionality, products that were simply not possible before, aesthetics and so on. Furthermore, these benefits are often not possible to equate without subjective value assignments.

Many potential applications are of a high order of complexity, where the properties of carbon nanotubes have no competitors and the use of carbon nanotechnology allows a completely different system to replace one or many other systems. In such cases, differences will exist not just in the manufacturing phase of the item, but also in other components and indirectly related flows of energy and material during the use phase. These effects compound and multiply rapidly with complexity and thus force boundaries to the analysis undertaken here.

6.1 General Method of Analysis

Due to the many factors that prevent overall comparisons, an approach is taken where effects are isolated, and described individually. This allows the identification of important benefits as well as some limited comparisons. The first order effect from using carbon nanotechnology is the direct substitution in energy requirement for manufacturing the CNP-using system as opposed to the manufacturing energy requirement of the pre-existing application. Because they are energy intensive, this increases the energy intensity of the materials used. In some simple and passive applications, this modification of process is the only effect resulting from the inclusion of carbon nanoparticles. In other more complicated applications, there is potential for many additional orders of effect.

For the purpose of organising the analysis, these products and systems are grouped into categories based on the nature of the system:

- 1) CNPs in *Passive Systems*: The CNPs are added to or replace materials in systems with functions not involving useful energy. In such cases, the process energies required to create the two systems are the basis for comparison.
- 2) CNPs in *Active Systems*: The CNPs are added to systems that have functions involving useful energy. In such cases, the efficiency of the system may change. Energy payback can be calculated based on the process calculations as for passive systems, but also including changes to the efficiency of the system.

In each case, the actual nanomaterial represents a background system, just as in the sense of the production chapter. Before beginning analysis of specific applications, a brief discussion of materials containing carbon nanoparticles will be useful to provide the needed background.

Within each general heading, the applications discussed will be analysed in the following order:

1. The direct balance of intensity resulting from substituting carbon nanoparticle containing material for its predecessor.
2. The potential gain from direct efficiency increases
3. The potential dematerializing effects stemming from increase in functionality and lifetime.

Other changes may occur if the increased efficiency or improved passive performance or both allow an entirely new system to replace the old. An example could be if batteries performed well enough, electric cars could displace liquid fuel cars. Such higher order effects may be identified and discussed qualitatively, but are outside the scope of quantitative analysis in this work.

6.2 Passive Systems

Many of the popularly known potential applications of carbon nanotechnology such as ultra-strong composites and fibres belong in the passive category. If CNPs can be made cheaply enough, then the application of structural nanomaterials incorporating them could become very large, possibly making up a significant share of carbon nanomaterial use. Products in the passive group naturally will often have their main energy-related environmental impact during their manufacture, which means that the requirements for the production of carbon nanomaterials will have a direct reflection in the energy balance.

Useful products that are completely made of nanotubes are not currently possible from a technical or financial standpoint and thus a major current proposed use of carbon nanomaterials in structural applications is in composite materials. Because of their unparalleled mechanical properties, nanotubes are potentially the ultimate reinforcement material. Fullerenes are also a possible option for reinforcing materials that only require compressive strength, and can be pressed in an anvil to produce the hardest material known, aggregated diamond nanorods. If only pure structural materials are desired, nanotubes could potentially make plastic as stiff and strong as carbon fiber reinforced composites. Polymer fibers including nanotubes have already surpassed spider silk fibers to become the strongest known by breaking energy (Baughman et al, 2003). The high thermal and electrical conductivity of nanotubes additionally could allow for multifunctional components that replace more than just structural members, or entirely new classes of materials.

Viable use of CNPs in composites will hinge on manufacturing technologies that can disperse them controllably, provide strong interaction with the composite matrix and, above all, do it cheaply. Some applications require certain properties more than others. As nanoparticles become less costly, the total amount of possible applications rises exponentially as uses in new and higher volume industries become viable, while new technology and competences are required to unlock high value and performance applications. Fig 6-1 sums this relation up.

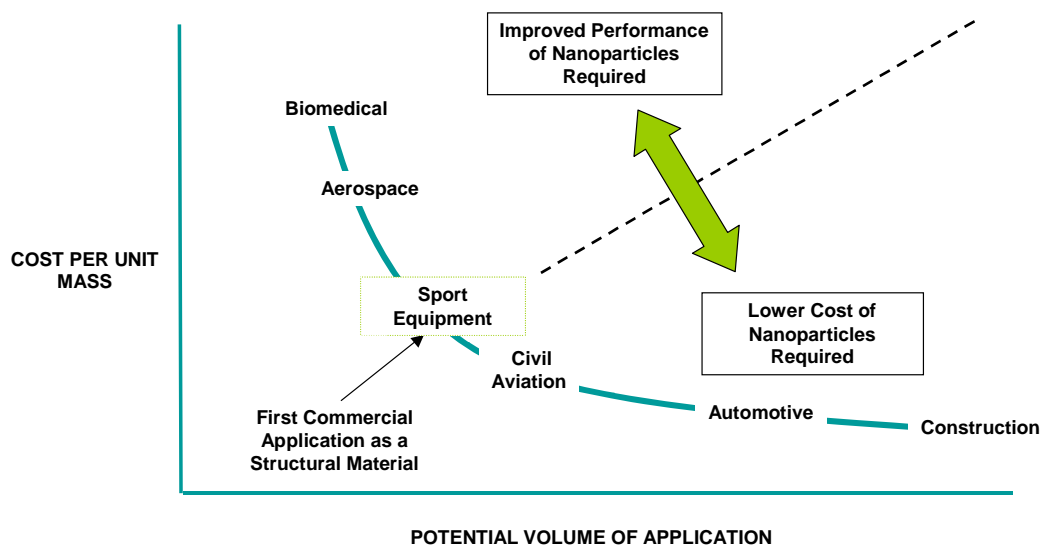


Figure 6-1: Volume and Technology in Structural Applications

6.2.1 Energy Intensity of Carbon Nanocomposites

For the purposes of structural materials, the most common proposed application of nanotubes is to disperse them into a polymer, which can then be used on its own or as a matrix or fibre in another composite. Ceramic and metal matrix composites with CNPs have many potential applications as well, and are potentially a useful area of application, but due to many uncertainties will not be subjected to analysis in this work.

As with any composite, the properties of the mixture will change with the concentration of the reinforcement. 1% by weight loading (amount of nanotube in a substance) of MWNT in polymer is enough for mild reinforcement, or sufficient to assure conductivity for electrostatic dissipation if the fibres' orientation is controlled. 25% loading in nanotube reinforced polymers (NTRP) theoretically would be comparable to aluminium in mechanical properties and 70% is roughly the useful limit of loading in most reinforcing applications, theoretically yielding a product that is a small improvement over carbon fibre reinforced plastics (CFRP). Regardless of the desired property, the requirements for integrating various amounts of carbon nanoparticles into polymers are only marginally different from a process point of view. The process flow can be generically modelled as in Figure 6-2:

Efficient dispersion is no longer a problem for small concentrations of nanotubes, but for high loadings, some challenges remain. Assuming that dispersion challenges are solvable, then the specific functionalization types and orientation of the particles can influence material properties, but appear to have little relative effect on the energy balance of manufacturing. This is especially true for polymer composites because many functionalization chemicals are organic polymers or precursors. The loading and type of

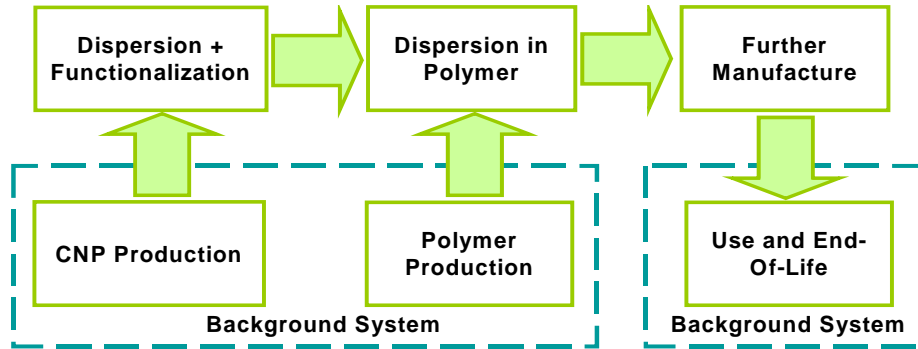


Figure 6-2: Generic Production of CNP Reinforced Polymers

nanoparticle along with the type of polymer matrix are the dominant factors in determining the overall energy requirement. The results for a mixture of MWNT (floating catalyst baseline) with a number of common polymers and comparisons with aluminium and carbon fiber reinforced epoxy are described in table 12, below.

Table 12: Estimated Cumulative Energy Intensities for pre-manufacture MWNT Reinforced Polymers

Material	CER (MJe/kg)/ (MJth/kg)	CER (MJe/kg)/ (MJt/kg)	5% CER (MJe/kg)/ (MJt/kg)	25% CER (MJe/kg)/ (MJt/kg)	70% CER (MJe/kg)/ (MJt/kg)
Acrylonitrile*	6/78	28/83	86/105	214/154	
HDPE*	9/67	27/73	84/97	214/151	
Polypropylene*	7/65	26/71	83/96	213/150	
Epoxy*	24/112	43/116	97/131	219/165	
Comparison					
CFRP-epoxy (30/70)	32/200	-	-	-	
Virgin Aluminium **	54/65	-	-	-	

* Plastics Europe (2006) ** Adapted from Sunér (1996)

When including the feedstock values, one can immediately see that plastics are energy intense materials, with epoxy potentially being more intensive than virgin aluminium depending on the assumed electricity production efficiency (if it's under about 40%). Beginning to add nanotubes produces a quick jump in CER as mixing processes are included, and further addition will increase CER roughly linearly. Under the industrial production scenario in this work and assuming 35% electricity generation efficiency, all four polymers will have higher energy intensity than virgin aluminium with 12% wt loading of MWNT. At 50% conversion efficiency, all four will be more energy intensive than aluminium for an 11% weight loading, but will not reach aluminium-like stiffness and strength until higher amounts of nanotubes are added. Versus carbon fiber reinforced epoxy, NTRP will be more energy intensive at either 21% or 26% weight loading depending on the electricity scenario, far before it will achieve comparable performance.

6.2.2 Properties of Structural Nanocomposites

The types of application with the simplest system for analysis are those where nanocomposites replace another material in a completely passive product. Using carbon nanoparticles as structural materials in passive items is one such use. There will be an energy requirement to make and integrate the CNPs, and the manufacture of whatever material is replaced will be avoided. Potential dematerialization carries its own benefits, but is difficult to estimate for products of indefinite lifespans because of uncertainty over weighting the manufacturing phase and discussing the end of life.

The first commercial structural materials using CNPs have been composites for high-end sports equipment. Carbon bicycle frames, golf shafts and tennis rackets are amongst the most expensive-by-weight consumer products of a structural nature and can bear the cost of nanotube reinforcement where performance is an issue. In general, nanotube reinforcement is beginning to infiltrate the market for high performance composites, which themselves occupy a market niche demanding light, stiff and strong construction where price is a secondary concern. Possible applications of CNP in materials that fall into this category of passive system could include sporting equipment, tools and construction materials as well as materials goods that could benefit from electromagnetic shielding such as laptop and cellphones, reinforced metals and ceramics.

Table 13: Comparison of Material Properties

Fiber	Density (g/cm³)	Ultimate Tensile Strength (Gpa)	Elastic or Young's Modulus (Gpa)	Specific Strength (Gpa)	Specific Modulus (Gpa)
SWNT					
Measured	1.3-1.5	150	1000-1200	100	666-800
Calculated		200-300	640-1350	133-150	800-900
MWNT					
(Measured)	2.4	63-150	900	100	600
(Calculated)		140-177	1050	92-118	700
Carbon Fibre	1.8 (PAN)	3.8-7	300-600	2-4	166-320
Maximums	2.2 (Pitch)	2.2	800-900	1	364-410
Bulk Material					
Steel (A514)	7.8	0.69	200	0.09	26
Aluminium	2.7	0.2-0.6	70-79	0.1-0.2	27-31
HDPE	0.97	0.02-0.04	0.5-2.5	0.015-0.04	0.5-1.2
Epoxy	1.1-1.4	0.035 – 0.1	3-6	0.03 – 0.07	2.8-4.3
Composites					
Epoxy/UHS-PAN 60%	1.6	3.5	170	2.2	107
HDPE/SWNT70% (Theoretical: O'Donell et al, 2005)	1.35	6.62	162	5	120

Sources: Handbook of Material Selection, O'Donell.

Table 13 gives a comparison of some common structural materials, and their comparison with some measured and calculated values for individual nanotubes. Many applications

require not strength, but a high ratio of strength to weight, and, because of their low density, nanotubes potentially excel in this respect as well. One can see that nanotubes individually outperform the best carbon fiber available; in theory, they are perfect carbon fibers. There is still dispute over both theoretical and measured values for nanotubes because of different experimental and calculation methods and estimations of cross section. Difficulty with dispersion and the purity of the nanotube material has compounded the issue when considered in composite materials. In any case, the values listed for nanotube material are not yet remotely achievable in any macroscopic material constructed from them.

6.2.3 Implications for Structural Materials

A simple comparison between materials shows that nanotube addition follows a general trend towards more energy intense materials. In all cases considered here, nanoparticle use represents an ‘energy investment’ to obtain some sort of theoretical performance gain. What can be noticed immediately is that for CNP-based materials with gross strength or stiffness comparable to a traditional structural material, the traditional material is significantly less energy intense by weight under any electricity scenario. Because the figures for nanoparticles given in this work can be considered close-to-minimum, most errors would result in a more unfavourable energy comparison for the nanotube-based material. Likewise, using SWNT instead of MWNT would increase the energy costs with current technical systems.

One significant aspect that is not accounted for is that of different design possibilities utilizing the anisotropic properties of nanotubes. Different manufacturing processes are also available for composites than are for metals. Because these numbers do not include final manufacturing, this analysis effectively treats composites like aluminium or steel, which are isotropic materials. In any structure made from an isotropic material there will be some parts where the material is not used to its maximum capability. Because of the anisotropic properties of composites in general, it is possible to design structures for specific loads that have completely different and more efficient shapes than what would be required from steel or aluminium.

What is less clear is the energy balance at low concentration of nanotubes. As mentioned, electrostatic dissipation can occur at loadings as low as 1%, meaning that nanotube based plastics could potentially be an energetically favourable material for electrostatic shields as compared to virgin aluminium or a multifunctional and stronger alternative to carbon-black-containing plastics. Additionally, adding small amounts of nanotubes into the matrix or fibers of a traditional composite has been shown to yield improved characteristics. One such example is that some polymers with as low as 0.5% loading of nanotubes show greatly increased breaking energy, or ‘toughness’, and similar loadings can increase the tensile strength of PAN⁴ or carbon fibers (Chae et al, 2005).

⁴PAN = Poly-Acrylonitrile, a common polymer fiber and also the base for many types of carbon fiber.

In conclusion, small amounts of nanoparticles could potentially provide traditional composites with improved properties at much lower energy costs than using large amounts of nanotubes on their own to try and achieve the same properties. In the case of carbon composites, a small quantity of CNP addition could potentially strengthen materials to the same level as calculated values for what is possible with large-percentage nanotube mixes, and under this analysis would also represent a lower energy path to achieve such performance.

6.3 Active Systems

Systems that consume energy to function nearly always have the greatest energy impact during the use phase of their lifecycle as opposed to during manufacturing. Any change that improves the energy conversion efficiency of the device will have a large leveraging effect on the total energy balance over its lifetime. Similarly, effects that improve lifetime will have a large leverage effect in issues of dematerialization.

Vehicle and energy related systems have some of the largest societal effects on the environment. The material characteristics of nanotubes again suggest them to be a potentially superior material for many applications in both types of system.

6.3.1 Carbon Nanocomposites and Light-Weighting Automobiles

A good place to begin exploring energy payback is to continue examining structural materials, but in the context of advanced materials for making vehicles lighter. As with using carbon fibre composites or aluminium, the idea is to provide an equally strong or better structure while lowering overall weight. This has an effect from direct material replacement exactly like in the passively used structural materials, but adds an additional layer of energy impacts stemming from changed performance of the larger system (car, plane, etc.). In such cases, the potential for decreased energy intensity during the use phase may compensate for the increased energy intensity of the material. Additional effects are much more diffuse; the potential for different manufacturing processes and longer life of components is very large, but outside of the scope of this work, and differences in manufacturing energies will not be considered.

The effect of lowering vehicle weight on energy consumption is well documented in LCA studies from the transport industry and from aluminium manufacturers (Lave and Lloyd, 2003). In cars, other results of lowering the vehicle weight can include secondary weight effects such as the drivetrain getting lighter, effects that are not considered here.

Materials in specific mechanical applications are not comparable on a one-to-one weight basis and therefore an exchange rate needs to be introduced in order to estimate weight savings from exchanging materials. Using cars as an example, it is often assumed that the panels, roof and hood of the car are being replaced. Stiffness is currently the dominant design requirement in those components and one index that has been used for comparing the actual effectiveness of structural materials on a stiffness basis is taking the cube root of the elastic modulus divided by the density of the material (Ashby, 1980). Other studies

of specific applications have found higher replacement ratios for composite materials (Al-Qureshi, 2001), but this index agrees with the assumptions made in many automotive-specific studies. Steel, aluminium and composites are the most common materials discussed in the context of lightweighting vehicles, and table 14 indicates the calculated index for those materials.

Table 14: Stiffness Based Material Replacement Index and Energy Requirement

Material	Young's Modulus (Gpa)	Density (g/cm ³)	Stiffness-based Material Replacement Index (Steel = 1)	CER* / Material Replacement Index (Steel =1)
Steel ASI 1045 HR	205	7.8	1.0	1
Aluminium 2024-T4	142	2.7	2.5	0.7
CF/Epoxy Composite (Automotive 61%)	100	1.59	3.7	0.47
SWNT/HDPE composite	162	1.35	5.3	1.5

* From Table 7: SWNT baseline. 0.35 electrical conversion efficiency assumed.

From this perspective, even the highest calculated values for properties of nanotube-based material achieve less structural performance per unit energy than traditional structural materials. If the efficient case values for MWNT were used and MWNT composites could achieve the same ultimate performance as SWNT composite, the energy requirement per material replacement index would place the nanocomposites just better than aluminium.

To examine the payback from using them in automotive systems, several LCAs on making automobiles lighter have quoted a figure of around 12.5% reduction in fuel consumption for a reduction of 20% in curb weight (Lave and Lloyd, 2003). Using the parameters in table 15, this translates to roughly seven litres of gasoline saved per kilogram reduction in car weight.

Table 15: Assumed Parameters for Automotive Application Analysis

Parameter	Assumed Value
Initial weight of automobile	1500 kg
Initial fuel efficiency	8L/100 km
Car Lifetime:	200 000 km

1 kilogram of nanotube would produce 1.43 kg of composite which would replace 7 kg of steel. Allocating the gasoline savings linearly over the 20% weight drop, 39.5 litres of gasoline saved would be attributable to the use of one kilogram of nanotubes. Additionally, the manufacture of 6 kg of steel would be avoided.

Using the replacement ratios above and a well to tank efficiency of 0.9 for the gasoline, 1400 MJ_t of primary energy would be saved per kilogram of nanotube material used to lighten the frame. An additional 22 MJe / 165 MJ_t of process energy is avoided from not having to produce the steel. This compares to the process energy of 630 MJe/ 370MJ_t for creating the composite; in this example, there is a lifetime net energy gain using CNP materials when the assumed electricity production efficiency is over 52%. For MWNT based materials, the saved energy could more than make up the production cost, but that assumes MWNT materials could reach the same ultimate strength.

Overall, this indicates that fuel efficiency increases from lowering automotive weights produce energy gains of the same order as manufacturing the nanotube-based materials used. Looking back at table 14, the energy per unit of stiffness column shows that nanotube based materials are not the most energy efficient way to achieve these savings; other structural materials provide equal structure for less manufacturing energy.

6.3.2 Carbon Nanomaterials in Energy Storage Applications

When combined with other factors such as their high surface area, the electrical properties of carbon nanoparticles immediately imply a possible use in electric and electrochemical processes. One such commercialized application is storing electrical energy in batteries and capacitors. Activated carbon has long been used as an electrode in some of these devices because of its surface area, pore distribution and stable chemistry. Because nanotubes can have higher surface area and better conductivity than activated carbon, nanotube based materials could improve many aspects of similarly based electronic systems. With specific reference to energy storage systems, they could increase power capacity and lifetime of service (Alivisatos et al, 2005). This has been observed in practice as well as theory; some commercial Li-Ion batteries use nanotube based materials as part of the electrode. Other types of energy storage utilizing the electrical properties of nanotubes are also on the horizon for commercialization; ultracapacitors could provide a useful complement to batteries in many energy storage applications where the design requirement is high power flux or a lifetime spanning a large number of cycles rather than simply energy storage capacity. While acknowledging that the most promising gains are from new design possibilities, this section will detail some of the direct implications of these applications towards energy systems by exploring the efficiency and dematerialization aspects of carbon nanoparticles in that role.

Example: Nanotube based electrodes in Li-Ion batteries

Battery electrodes have a few main design considerations. Large surface area is related to the ability to provide the possibility of large flows of current and to provide sites for the intercalation of ions. Regular pore size, geometry, and stable surface chemistry are also vital to improve the reversibility of the reactions and thus the lifetime of the application. Activated carbon and graphite have been some traditional anode materials because they have extremely good properties in those respects and carbon nanotubes could provide further improvement.

Although some studies for the technological capacity of nanotubes in batteries are based on SWNT material, MWNT are currently used in commercialized applications because of cost. There are many prospective technologies for use in batteries, but the assumed production method is to ball-mill them to break up bundles, open the nanotube ends by oxidizing the comparatively vulnerable nanotube end-caps, then to cover them with a polymer and coat them onto the electrode during manufacturing. This increases the exposed surface area and therefore the efficiency of charge storage and the possibility for high currents. Batteries are on the market now that use nanotube based electrodes and have demonstrated power capacity up to ten times higher than conventional lithium ion batteries with a claimed doubling of lifespan. They are commercially viable for laptop and cell phone batteries according to manufacturers (Setoguchi et al, 2006). Li-Ion batteries are currently demonstrated and available, albeit expensive, for automotive energy storage systems, and may become commercially viable for mass production automobiles at some time in the future.

Analysing possible impacts from this technology is made possible because batteries incorporating nanotubes differ from their non-nano counterparts essentially only in the electrode material. As an approximation to model the system, the manufacturing energy flow can be estimated as the addition of the functionalised nanotube material. The benefits accruing from increased efficiency are allocated entirely to the nanotube material.

Not considering inverters or power electronics, round trip DC-DC efficiencies are generally between .6 and .85 for various battery systems such as nickel-metal hydride and lead acid; with Li-Ion batteries they can range from 0.85 to as high as 0.95 (Rydh and Sandén 2005a). The actual efficiency obtained depends on design factors outside the scope of this comparison. Table 16 shows the system assumptions made for this scenario.

Table 16: Assumed and Derived Parameters for Energy Storage Device Analysis

Parameter	Assumed Value
Mass ratio of nanotube/polymer	25%
Mass ratio of anode material to battery*	10%
Battery Capacity*	100 Wh /kg
Depth of Discharge*	0.6
Parameter	Derived Value
Total Energy Stored per cycle	2.4 kWh for 1 kg nanotube material
Mass of battery for 1 kg Nanotube material	40kg
Energy requirement for 1kg nanotube/3kg polymer	230 MJe / 390 MJt

* Rydh and Sandén (2005b) ** Caneba (2004)

If a new design based on carbon nanotube electrodes results in a doubling of effective lifetime from 1000 to 2000 cycles and taking the nanotube electrode material to comprise

10% of the battery mass, based on half of the anode being replaced: over the lifetime of the battery, 170 MJe would be saved per actual percentage point increase in storage efficiency due to the addition of 1kg of MWNT based electrode material.

Because the lithium ion battery without nanotube-based electrodes would need to be replaced once to provide the same electric energy storage service, the manufacture of forty kilograms of regular lithium-ion battery replacement would therefore be avoided. Using a result for total battery production energy of 170-260 MJ/kg Li-ion battery (Rydh, 2003), this could avoid roughly 7-10.5 GJ of manufacturing costs for replaced batteries per kg of nanotube material applied in the electrodes.

Under these assumptions and minor variations, the direct gain from efficiency increase is of the same order of magnitude as the increased construction cost. The increase in lifetime is leveraged over a much larger mass of battery to provide a gain an order of magnitude larger through dematerialization and avoided manufacture as direct effects from the inclusion of nanotube material. These results are somewhat sensitive to the actual mass of the electrode, but the orders of magnitude hold across a range of assumptions.

Example: Nanotubes in Ultracapacitors

One other electrical application where the surface area and charge storage properties of nanotubes are useful is in capacitors. Because nanotubes increase the surface area, they increase the capacitance, which directly increases energy storage. Values of 200 F/g have been achieved (Jurewicz, 2006) using voltages of roughly one volt. This translates to a storage density of 27 Wh per kilogram; 6 Wh per kilogram is available now in commercial devices based on carbon.

A supercapacitor functions by polarizing an electrolyte near a very high surface area electrode. An ultracapacitor includes the electrostatic charge storage effect and an additional intercalation effect. In comparison to batteries, ultracapacitors have traditionally had a higher power density and lower energy density, although the claimed theoretical energy limit for an ultracapacitor based on aligned nanotubes is in excess of 60 Wh/kg (Signorelli et al, 2006). This makes their ultimate potential comparable to current Ni-MH batteries in terms of energy density, and virtually without equal in terms of power density for compact storage. Additionally, they are expected to be able to work at high temperatures with lifetimes of over 100 000 cycles, perhaps well into the millions, at any discharge depth. (Merino et al, 2006)

Examining the application of ultracapacitors to vehicular technology provides an opportunity to explore second and higher order effects, but first, the simplest model for assessing ultracapacitors is to look at only the energy storage function as compared to an equivalent energy storage device such as a battery. There are two basic scenarios under which this would occur: storing electricity from an AC grid, and storing from a DC network, such as in a vehicle. Because batteries and ultracapacitors both require DC

circuitry to store energy, given similar electrical hardware their DC-to-DC charge storage efficiencies are comparable.

Compared to battery storage efficiencies as mentioned in the last example, round trip DC-DC efficiencies for available ultracapacitors are roughly 0.90 and could reach an estimated 0.98 or higher (Schneuwly, 2005). The difficulty in comparing them is to find a suitable functional unit because of differences in both storage and lifetime. Table 17 below shows the assumptions made in this scenario. Based on total energy stored over the lifetime, the ultracapacitor would have roughly a threefold advantage over the batteries.

Table 17: Assumed and Derived Parameters for Assessing Ultracapacitor Storage

Parameter	Assumed Value
Battery Lifetime (Li-Ion)	2000 cycles
Battery Capacity (Li-Ion)	100 Wh / kg
Ultracapacitor Lifetime (Carbon Based)	100 000+ cycles
Ultracapacitor Capacity (Carbon Based)	6 Wh / kg
Anode mass as percentage of capacitor	33 %
Parameter	Derived Value
Total Lifetime Energy Stored (battery)	720 MJ / kg battery
Total Lifetime Energy Stored (ultracapacitor)	2160 MJ / kg ultracapacitor
Energy requirement for 1kg nanotube/3kg polymer	230 MJe / 390 MJt

Future designs may include both electrodes made of carbon, but today's carbon based ultracapacitor is made of an aluminium cathode, a carbon anode and acetonitrile electrolyte. Assuming that each component represents 33% by weight, and that a future anode has a surface representing half its weight made of 25/75 MWNT/polymer instead of activated carbon, 1 kg of nanotube would be required to make 9 kg of ultracapacitor. Each percentage point increase in energy storage efficiency would therefore provide a payback of 190 MJe / kg nanotube material.

The energy payback versus battery based energy storage from direct efficiency increase could easily be of the same order of magnitude as the nanotube production energy requirement if a couple percent gain in storage efficiency were to be realized. Actual future ultracapacitors could both realize this higher efficiency while storing up to 100 times the lifetime energy flux as used in this example, and would therefore have a very high payback indeed as compared to battery systems.

This ultracapacitor scenario would also avoid the manufacture of 18 kg of battery in order to provide identical total lifetime energy storage. In the future, if higher energy storage densities become possible, then this would again increase dramatically. Of course, ultracapacitors and batteries are used for different types of systems, but as a direct comparison of energy storage based on lifetime energy flux, nanotube based ultracapacitors realize energy gains versus batteries.

Discussion: Energy Storage in Automotive Drive Trains

Second order effects of ultracapacitor use in energy systems can be estimated by examining a system where the requirement is not simply to store energy, but to store it quickly. Such a system is to be found with regenerative braking in vehicular applications. Mostly due to their ability to handle large power fluxes and concern over lifetime of battery systems, ultracapacitors (although not nanotube based ones) are used in some new hybrid automotive drivetrains to store and release peak bursts of energy. Figure 6-4 is a general schematic of a hybrid drivetrain:

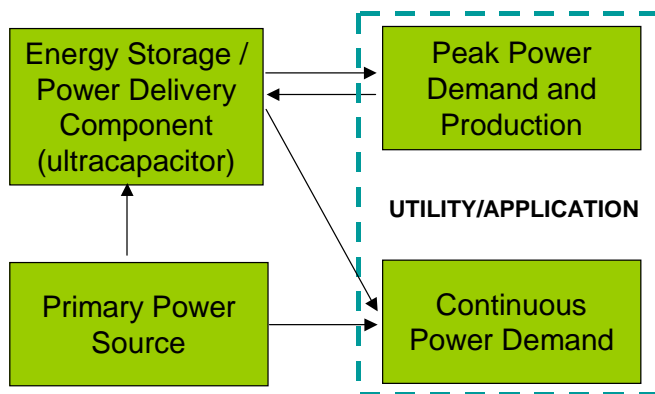


Figure 6-3: General Schematic of a Hybrid Drivetrain with Ultracapacitors

If one considers an electric drive hybrid car weighing 1000 kg travelling at 20 m/s, braking at 5 m/s² (a medium brake) would require absorbing a power load of 100 kW. Although the most recent Li-Ion batteries based on carbon nanotube electrode material could absorb such a spike, response times, inefficiencies at high charging rates and battery lifetime considerations prevent completely efficient use of that energy. Ultracapacitors, on the other hand, can absorb that amount of power cleanly and reversibly, providing it back during acceleration for the car, and effectively saving that amount of energy as compared to a conventional battery system. Additionally, the effect is largest under conditions of repeated braking and acceleration, which are most likely to be found in city driving patterns, complementing hybrid systems designed with a small all-electric range.

6.3.3 Example: Nanotube Wires

As a final and more speculative example of electrical material use, much has been made of the long-term possibility for using nanotube cables to distribute electricity (Alivisatos et al, 2005, etc.). Their realizable properties in bulk electrical conduction are uncertain to say the least, but for potential energy gains in society, the electricity grid presents a very large target. Individual armchair nanotubes display a phenomenon called ballistic conductance, meaning that over small but macroscopic lengths they act as a waveguide, and conduct without generating heat over their body, only at the interfaces. Because of their high thermal conductivity, any heat generated is quickly dispersed and large

amounts of current could be accommodated. Taking the ultimate molecular properties and directly scaling to bulk material gives theoretical values for conductance a thousand times that of copper and with a maximum current density of up to ten billion amperes per square centimetre cross section.

NASA is currently funding a project with a more modest goal: to produce a cable with resistance one tenth that of copper for the same cross section by 2009. One paper estimates that this effectively translates to wires roughly 30% lighter than the corresponding aluminium/composite core wires used today, with up to 10 times the tensile strength and much higher current capacity before reaching thermal limits (Hartley, 2005).

This application is considered speculative because it would require a method of creating all-armchair SWNT material in defect-free fibers, and no such method exists today. Roughly 2% of randomly produced nanotubes are armchair, and they are extremely difficult to separate from nanotubes of other chirality. Laboratory processes exist to destroy the metal nanotubes by resistive heating, leaving only semiconducting material, but the reverse process is still unknown. There are currently some potential routes to create armchair nanotubes: creating them by nanotube cloning in HiPco reactors, by using fine catalyst control in a fluidised bed (Das et al, 2006) or by some hypothetical destructive processing route. All three options are speculative. The material energy cost for a nanotube wire could thus be approximated as between 50 times the most efficient SWNT production available for the destructive route, or as the HiPco requirement with unknown parameters and efficiency. The fifty times figure is the one assumed for this example.

Losses in transmission wires are mostly through resistive heating as, in theory, capacitance losses and corona discharge can be close to completely negated by using high voltage direct current linkages. A typical use might be a 1 GW transmission line operating over 2000 kilometres, linking either two asynchronous grids or a distant renewable energy source such as a solar farm or dam. Assuming that such a line would have 12% losses with current technology and another 0.6% at either end in the converter station (Hartley, 2005). Taking resistive losses to be one tenth, the quantum wire would have a total loss of 2.4% versus 13.2% for the standard link.

A suitable standard cable for that link would be a 795 kcmil Al/composite cable weighing 1.33 kg/m (3M, 2003). Over 2000 km, that corresponds to 2.66 kilotons of cable. This would require 2 kilotons of armchair nanotubes and therefore roughly 20 petajoules in manufacturing energy, using 50 times the fluidized bed results and electrical conversion rate of 0.5. This compares to 146 TJ of process energy for the same aluminium cable counting just the material primary energy requirement and not any manufacturing costs. This energy differential would be paid back in (all electricity) six years with the resistive assumptions listed above. Assuming HiPco cloning or the efficient fluidized bed CVD process would dramatically shorten this period of time.

There would be potential secondary effects as well. The low thermal expansion of nanotubes and lighter weight would reduce tower size, and the increase in tensile strength would mean that fewer towers would be needed. Furthermore, with low losses, the viable range of transmission would be much higher, meaning that increased efficiency in selecting power sources could become possible. Also, many potential renewable energy projects that are currently too distant from loads to be economical could be brought into range.

Despite the speculative nature of this scenario, it continues the trend of nanotubes in energy applications dematerializing and improving the efficiency of electrical systems. If current production technology improves, many such applications may become possible and could represent highly energetically profitable applications of carbon nanotechnology.

6.4 Summary of Application Results

Because of the high production energy requirements, addition of nanotube material increases the energy intensity of virtually any material. This energy investment can provide new performance capabilities. The gains over existing technology can be immense in energy systems but theoretically modest in most structural applications. New structures using the anisotropic heat or electrical properties of nanotubes will be possible, but with still uncertain benefits from a lifecycle perspective.

In non-performance-critical structural applications, there are other materials that can provide the same service at lesser energy and monetary cost than even the most efficient nanotube production examined. Additionally, the heavy use of plastics and/or a large volume of nanomaterial raises other environmental concerns such as releases to the environment, energy use and limited feedstocks.

In energy applications, because effects from their use are leveraged over much larger masses of components, dematerialization resulting from increase in lifetime could be the major direct environmental benefit. Direct benefits from increases in efficiency also may occur and could potentially be as large or larger than the cumulative energy requirement for production.

Many intangible benefits occur due to their use, including multifunctionality, improved performance, and enabling of improved system configurations.

7 Discussion and Limitations

7.1 Production

The values presented here represent 'minimum' production energies for CNPs using current synthesis efficiencies and thus are likely to underestimate the energy cost of carbon nanomaterial for quite some time. There are a number of critical areas in which there is not yet sufficient information to form general and accurate estimations of process requirements, particularly in dealing with specific methods of catalyst production and purification processes.

One aspect that has not been considered in the production technical systems is material loss at each step. While it could be arbitrarily small in theory, manufacturing processes have some material loss in practice, and a small loss at each step could compound to become a significant addition to the process requirements. The purification model used could potentially be an oversimplification, as there are many steps in purification with the chance to lose some material, and purification processes may turn out to be more difficult to scale than the production ones, potentially making some of the assumptions less accurate for dealing with purification.

The method of catalyst production used could also become significant. As catalysts are tailored to produce specific effects, the procedures to create them can become far more extensive than the basic requirements to produce iron pentacarbonyl or ferrocene (Das et al, 2005).

Omitting transport from the calculations will likely have a noticeable effect on the overall energy balance for many of the systems discussed because many of the processes involve fairly large mass flows for a given output. In the case of the fluidized bed reactor, the addition could be as much as 15% of the overall total. HiPCO would be the least affected, because it is nearly a closed loop process that produces products requiring little purification.

With these caveats, it can be said that the values calculated lie somewhat above what is thermodynamically possible, and therefore represent a long term target that could only be achieved with scaling of process and some technical innovation. One potential check for the upper bounds of what is currently possible is that of price. The price profile of producing MWNT is a useful backstop to the energy calculations; although many processes are still proprietary and obtaining specific information is difficult, pricing assessments have been carried out by nanotube manufacturers in order to plan new facilities. One company estimates that MWNT production will cost \$75 per kilogram to produce in their new plant. (Baughman et al, 2002) This accords with the value calculated in section 4.5.1; an order of magnitude increase in the energy required by the production process would mean that the value of the energy required would be more than half of the estimated cost, with no allowance for capital facilities, labour or other ingredients.

The calculated energy requirement for MWNT therefore lies somewhere between the limits of what is thermodynamically possible for the given reaction conditions and the real world costs that have been estimated by producers with proprietary processes, as would be the expected result of the methodology used in this paper.

7.2 Application

The biggest sources of uncertainty in the passive application analysis are the values used for the nanomaterial itself. The manufacturing energy costs of various processes such as melt pressing, dispersion or ball milling are fairly well characterized, but quite small compared to the cost of the nanotubes themselves, and thus the nanotube production dominates the calculation.

In active systems, use parameters are the dominant factor for error. This is somewhat expected. The future performance of some nanotube based technology is still somewhat speculative, although commercialized examples are beginning to demonstrate that theoretical values may be somewhat achievable.

The commercialized applications discussed generally use MWNT as the nanotube material because MWNTs are by far the cheapest type of nanotubes. They also represent the bulk of CNP production and are made by the largest scale facilities. As noted before, up to roughly an order of magnitude more energy could be used for current implementations of some processes based on cost estimates and energy prices. Such an increase would result in the energy balances discussed in the structural materials section becoming very negative towards the use of nanotubes. An order of magnitude increase in production energy requirements, however, would result in the dematerializing effects discussed for energy storage applications remaining a significant payback of energy on a strict material replacement basis, with potentially more gain from redesign possibilities in larger systems of which they are a part.

8 Conclusions

Baseline production energy requirements have been obtained for a number of the most common processes to create carbon nanoparticles. Using these processes, carbon nanoparticles will remain highly energy intensive materials to create, even in a close to optimal industrial setting. Many of the processes have been demonstrated at higher energy efficiency for lower flow rates, and there is therefore a chance that tradeoffs will occur at some point between output and efficiency. Integration with existing industries could abate some of the production costs from a lifecycle perspective, but it is not clear when or if it will be feasible to do so with production technology.

In some applications, carbon nanoparticles could potentially outperform any known conventional material, particularly where electrical or thermal properties are desired. This contention is very much subject to increases in manufacturing technology; many of the most useful properties of individual molecules cannot yet be realized in a bulk material with current technique.

In many applications, there is a definite potential to offset energy and material requirements of production with increased efficiency and dematerialization of application. Realizing actual gains in either category will require decreases in energy and material flows from current laboratory efficiencies. Regardless, it is possible to regain the high energy cost of carbon nanoparticle production from dematerialization effects and direct results of efficiency increase, particularly in energy applications.

In passively used structural materials, carbon nanomaterial based composites are more energy intensive than a traditional material of similar properties under any scenario presented here. The only exception found was that a low concentration of nanotubes in plastic could be a less energy intense material than virgin aluminium for electro-dissipative purposes where the compromised material properties of carbon black loaded plastic would be unacceptable. Even then, other metals or materials may be more energetically suitable for such applications. Therefore, in terms of bulk structural application, the comparison of the theoretical potential for improvement with the observed increases in material properties suggest that utilizing small amounts of carbon nanoparticles is a more efficient way to improve structural materials than creating high-concentration composites, from an energy perspective. Neither may be effective from an energy point of view if increases in industrial efficiency are not realized.

In active applications, increases in energy efficiency and dematerialization are the dominant effects with respect towards energy implications including of carbon nanotechnology. Small increases in efficiency can result in a large amount of energy savings over the lifetime of a product. Such increases could therefore justify replacing traditional carbon materials with carbon nanomaterials under an efficient production scenario. Because many current energy storage applications are complicated devices with finite lifetimes, dematerialization of applications through increases in lifetime or capability of components could represent a major benefit from CNPs.

APPENDIX A: INTRODUCTION TO CARBON NANOPARTICLE NOMENCLATURE

There is some ambiguity as to the naming of carbon nanoparticles. In the interest of using the least possible number of terms, the term *fullerene* is used to describe the spherical cage configurations and the term *nanotube* is used to describe the cylindrical format, although other literature takes the term fullerene as comprising the entire family of carbon nanoparticles.

The smallest fullerene allotrope is C_{20} . The number of structural possibilities begins to increase rapidly with the size of the fullerene; in theory there are 1812 possible topological configurations for C_{60} , however, configurations with adjacent pentagons are much less chemically stable. The term ‘isomer’ is generally used only for observable variants. C_{60} is the smallest fullerene in which it is possible for no two pentagons to share an edge, and is the most common in nature. Illustrating the growth of configuration space, C_{80} has 7 stable and observed isomers, and there are roughly 16 million ways to configure C_{200} without adjacent pentagons. While many configurations of a given closed-cage allotrope are chemically similar, this changes when the shape becomes cylindrical. Because the topology of a nanotube is intimately tied to its properties, it is essential to categorize it accurately. The *chirality* of a nanotube is a vector denoted by a pair of coordinates (n,m) corresponding to multiples of unit vectors on a graphene hexagonal plane.

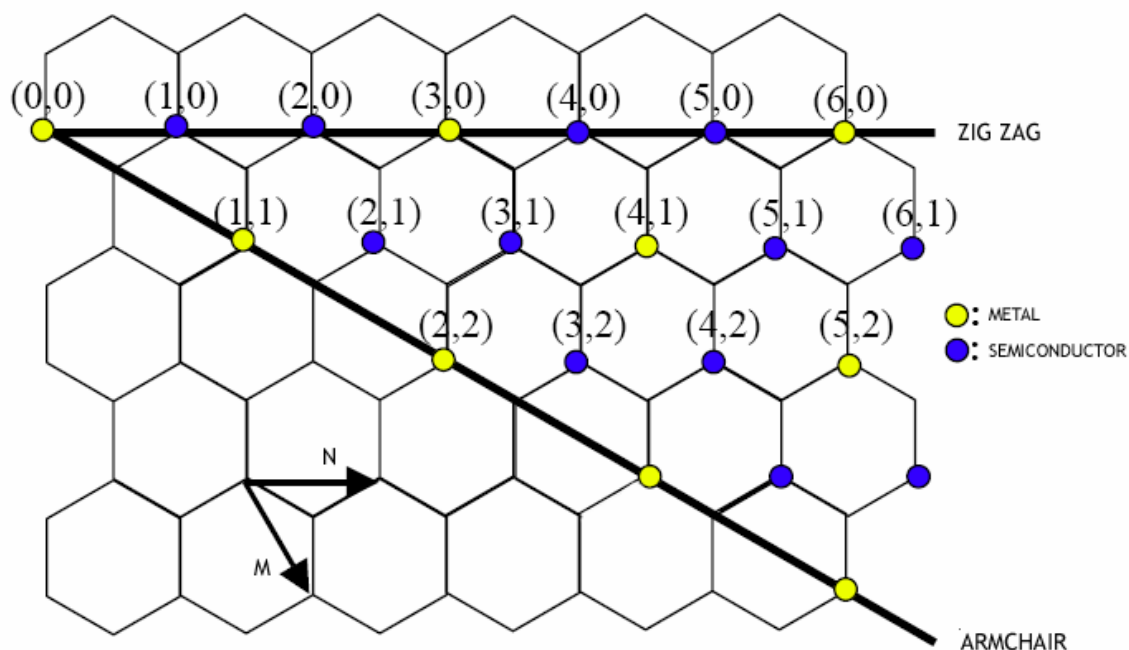


Figure A-1: Chirality Vectors in Nanotubes

This vector is the circumference of the nanotube, and also describes how it is rolled; the two endpoints correspond to the same atom on the nanotube surface. The diameter of the nanotube therefore varies with the magnitude of the chirality vector.

While most nanotube properties vary to a small degree with chirality, the electronic properties of the molecule vary immensely. Some possible configurations conduct like metals while others behave as semiconductors with a varying resistance and band-gap. The general rule is that if $n-m$ is a multiple of 3, i.e. chiralities of (10,4), (25,19) and so on, then the nanotube is a metal-like conductor. The special case where $n = m$ is called an *armchair* nanotube and is characterized by a zero bandgap and a phenomenon called ballistic conductance. The case where $m=0$ is called a zig-zag nanotube. All other nanotubes are called chiral nanotubes.

In mass production processes, nanotubes are created within a diameter distribution influenced by catalyst particle size, and the various chiralities appear to be randomly distributed among the options available within those diameters. The most important consequence is that an average of only two percent of the nanotubes produced are of the armchair type, which are by far the best conductors. Figure A-2 below shows the appearance of each type.

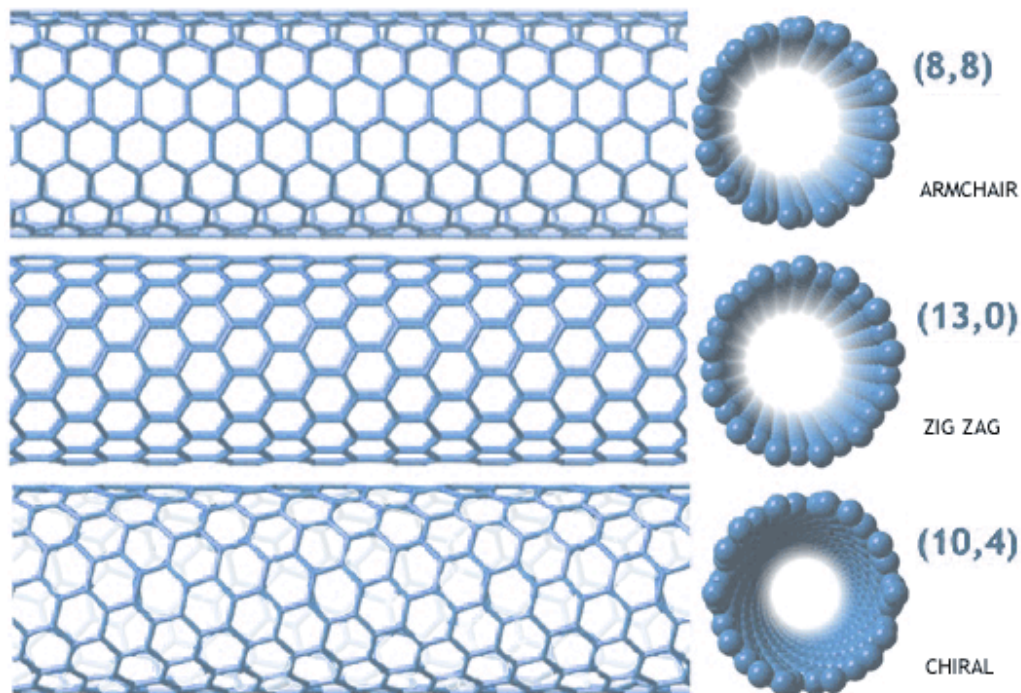


Figure A2: side and end views of single walled nanotube sections with three different chirality vectors

Nanotubes with only one layer of graphene are called single walled nanotubes, or SWNTs. Nanotubes can have more than one graphene shell however. Generically called multi-walled carbon nanotubes, the only distinction is made for nanotubes with two walls, DWNTs, which form a useful class separate from their single and multi-walled

cousins. Other structures exist such as nanohorns, nanotoruses, nanonions and so on, but these have little interest for application so far compared with nanotubes and to a lesser extent, fullerenes.

APPENDIX B: PRODUCTION SYSTEM CALCULATION DETAILS

B-1 Fluidized Bed Production Calculation

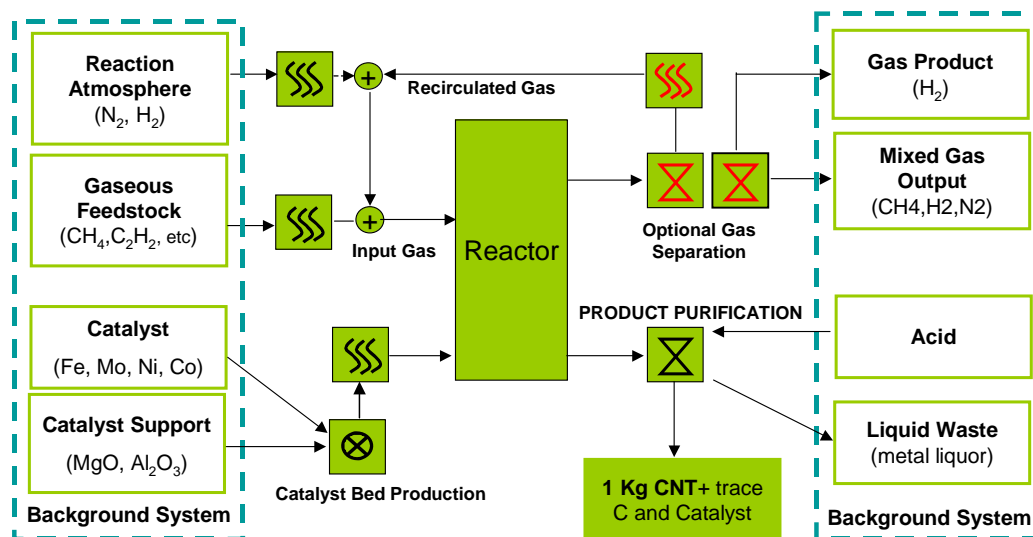


Table B-1: Fluidized Bed Reactor Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	68
Net Feedstock	51	0
Gas Purification	0	55
MgO and Acid Production	277	465.5
Purification Processes	0	37.5
Total	328	626

Process:

The reactor regime is at 1 atmosphere and 800 C. The methane decomposes and forms single walled nanotubes on the iron particles on the MgO catalyst support. The catalyst with nanotube undergoes volume expansion, rises and is continually removed from the reactor. The nanomaterial is separated from the catalyst support with ultrasonication in an acid bath of 3M HCl.

Heating Processes:

All heating processes are assumed to be with electrical heaters with an assumed efficiency of 0.8. The heat requirements for raising all inputs to the reactor regime are calculated. In addition, $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ is an endothermic reaction (6 MJ/kg), so additional heat must be supplied to the chamber to maintain the needed reaction temperature. Heating efficiency of 0.8 is applied to this as well. Because pressure swing absorption units only work at low temperatures relative to that of CNP production, and collection may involve cooling the exhaust, all recirculated gas is assumed to require reheating.

Chemical Inputs:

Chemical Input Background System values are found in Appendix C. Magnesium oxide is used as the catalyst support for these calculations. The process to create the catalyst is not included in the current calculations, but would increase the energy intensity of the catalyst input and further emphasize its importance.

Catalyst Preparation

The MgO is seeded with iron nanoparticles; however the catalyst particles are mostly MgO. Because MgO and iron have roughly the same CER of production, the error introduced from including only the value for MgO is used. Typically, some catalyst is dissolved in acid, then impregnated into calcined MgO. The impregnation process is not included due to lack of data, but the MgO preparation is.

Purification:

The catalyst support is removed by dissolving it in a hydrochloric acid bath with ultrasonic waves. The amount of hydrochloric acid needed is assumed to be the same as would be needed to form chloride salt with the mass of the catalyst support.

Chemical Outputs:

As with all feedstocks, the energy value of the hydrogen was assigned to be the HHV of the hydrogen. The heating value of the CNTs (approximated as that of graphite) was included in the total energy intensity, but the unwanted amorphous carbon is assumed to be lost. The outgoing catalyst support and acid mixture ('spent acid') is assumed to not be recyclable because of special preparation conditions. In the system expansion chapter, other uses are detailed. There is new technology for industrial scale renewal of hydrochloric acid however, and expanding the system to include it could increase system efficiency by removing roughly half the energy requirement for the acid/catalyst system without requiring integration with metal industries.

Reaction Notes:

The gas products are assumed to be H₂, N₂, and an unused CH₄ fraction.

Gas Separation and Recirculation:

The nitrogen is removed from the off gas by swing pressure absorption units and recycled. Because the absorption units work at a maximum of around 50-100 C, the off gas must be cooled before separating the fractions. This energy is assumed to be lost, but could be put through a heat exchanger. The resulting H₂ and CH₄ can be further separated, but are assumed to be mixed and output together.

Stoichiometry:

The following process quantities are taken from a Mitsubishi Heavy Industries report: The process gas is introduced at a ratio of 4:1 of N₂:CH₄, producing 250g/h of carbon nanoparticles. Catalyst material was fed in at a rate of 6.4 kg/h which translates to 25.6 kg/kg nanotube output. The final output was 10% amorphous carbon, 10% catalyst particles and 80% SWNT after removal from the catalyst support. To maintain a constant

reaction, the MgO exit rate must be the same as the input rate, and this allows calculation of the MgO ratio in the final product. Magnesium Oxide forms $MgCl_2$ and water when mixed with hydrochloric acid, requiring at least 2 mol HCl per mol of Mg to be dissolved.

B-2: Floating Catalyst Production Calculation Details

The floating catalyst method is very similar to a fluidized bed in terms of system schematic, differing in that a catalyst is injected into the feedstock mixture rather than flowing the gas through a particle bed.

Table B-2: Fluidized Bed Reactor Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	113.5
Net Feedstock	294.5	21.5
Acid Production	0.5	2
Purification Processes	0	50
Total	295	187

Process:

The reactor regime is at 1 atmosphere and 750 C. Benzene is dissociated in a hydrogen atmosphere and mixed with vaporized ferrocene.

Heating Processes:

All heating processes are assumed to be with electrical heaters with an assumed efficiency of 0.8.

Chemical Inputs:

Chemical Input Background System values are found in Appendix C. Ferrocene is used as the catalyst, but in very low quantities. The process to create the catalyst is not included in the current calculations, but would increase the energy intensity of the catalyst input and further emphasize its importance.

Purification:

The catalyst removed in a nitric acid bath with ultrasonic waves. The amount of acid needed is assumed to be the same as would be needed to form nitrate salts with the mass of the catalyst support.

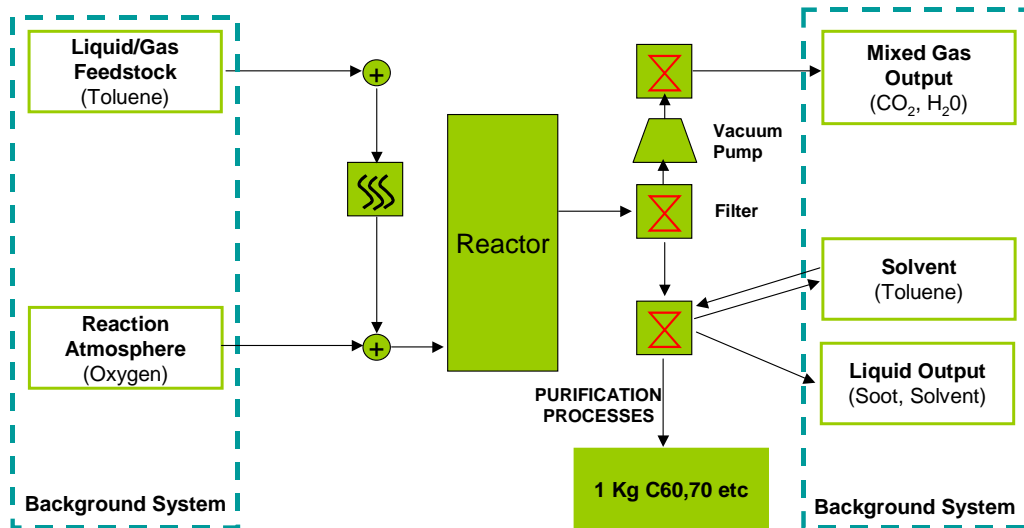
Chemical Outputs:

As with all feedstocks, the energy value of the hydrogen was assigned to be the HHV of the hydrogen. The heating value of the CNTs (approximated as that of graphite) was included in the total energy intensity, but the unwanted amorphous carbon is assumed to be lost. The outgoing catalyst support and acid mixture ('spent acid') is assumed to not be recyclable because of special preparation conditions. All benzene fuel is assumed to be recycled.

Reaction Notes:

The gas products are assumed to be H₂, N₂, and an unused benzene fraction.

B-3: Pyrolytic Fullerene Production Calculation Details



+
Table B-3 Pyrolytic Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Net Feedstock	6211	133
Gas Purification	0	506
Compression Electricity	0	1.5
Product Purification	130	37.5
Total	6341	678

Process:

The reactor regime is at 5.33 kPa. The toluene burns with pure oxygen and forms fullerenes, which are isolated from the exhaust soot.

Heating Processes:

The heating process for toluene evaporation in purification is assumed to be with electrical heaters with an assumed efficiency of 0.8. The toluene flame is self sustaining, and the potential heat from exhaust is dealt with in the system expansion section.

Compression Processes:

The compressor was assumed to be a 2 kW vacuum pump.

Chemical Outputs:

The output gas is assumed to be vented. If any benzene fraction remains, it should be easily separable by condensation. It is assumed that no benzene escapes the system.

Purification:

The purification processes involve toluene evaporation and column chromatography. Toluene evaporation is assumed to be carried out with thermal energy rather than electric because no exactly precise temperature is needed.

Reaction Notes:

The gas products are assumed to be CO₂, H₂O, and an unused benzene fraction.

Stoichiometry:

The following process quantities are taken from Takehara et al.(2005): Benzene and oxygen are burned at a ratio of 1.15:1 of total C:O. A fullerene yield of 20% in a soot carbon yield of 5% is deposited. 90% is assumed to be recovered through purification.

B-4: HiPco Nanotube Production Calculation Details

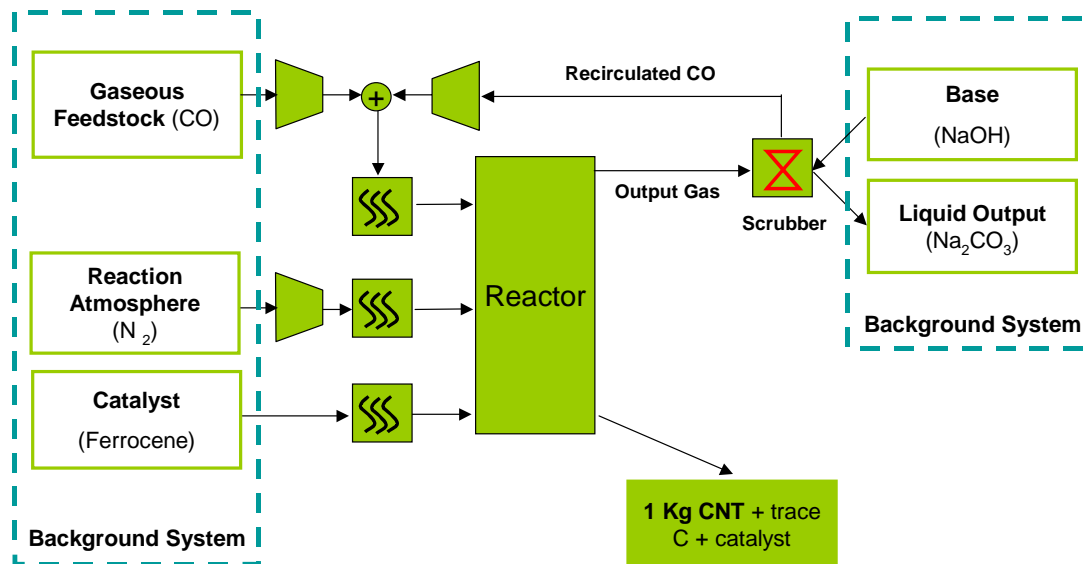


Table B-4: HiPco Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	2161
Process Compression	0	3608
Net Feedstock	47	0
Total	47	5769

Process:

The reactor regime is at 30 atmospheres and 1000 C.

Heating Processes:

All heating processes are assumed use electrical heaters with an assumed efficiency of 0.9. This is assumed because the heating rods are fully encased in the device, leaving little heat to escape in theory.

Compression Processes:

The compressors were assumed to operate with an adiabatic efficiency of 0.75

Chemical Outputs:

The low concentration produced carbon dioxide is scrubbed with NaOH before the CO is recirculated (Bronikowski et al, 2001). Therefore, Na₂CO₃ is assumed to be the only output, along with the produced material.

Stoichiometry:

The following process quantities are taken from the HiPco report (Bronikowski et al, 2001), with the caveat of 1 g/h production: The process gas is introduced at a ratio of 292 standard liters / min. One sixth of the carbon monoxide is fed in cold after being bubbled through iron pentacarbonyl in solution. 1 g of 97% pure SWNT material is produced per hour, and all CO is recycled.

B-5: Solid Feedstock Production Calculation Details

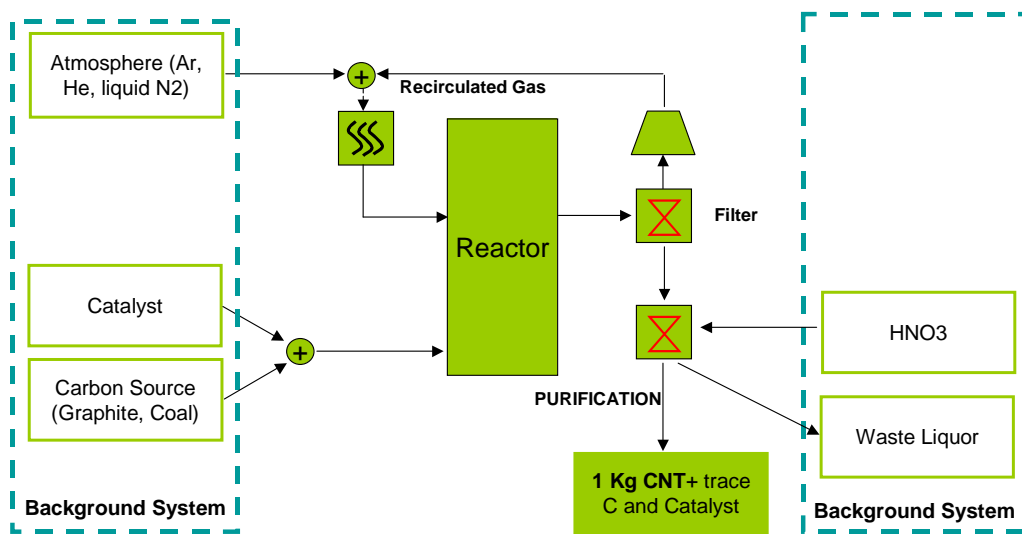


Table B-5: Electric Arc Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	68
Net Feedstock	294	40
Gas Purification	0	2
Electric Arc	0	1967.5
Acid Production	6	55
Purification Processes	0	37.5
Total	300	2170

Table B-6: Laser Ablation Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	510
Net Feedstock	207	38
Gas Purification	0	5
Laser Electricity	0	8790
Acid Production	4	43.5
Purification Processes	0	37.5
Total	210	9424

Table B-7: Solar Furnace Calculation Breakdown

Technical Process	Thermal Input (MJ _{th} /kg)	Electricity Input (MJ _e /kg)
Process Heating	0	*6200*
Net Feedstock	284	52.5
Gas Purification	0	5
Acid Production	6	55
Purification Processes	0	37.5
Total	290	6350

* As discussed, this represents the opportunity cost of not using the reactor to produce electricity.

Process:

The reactor regime is assumed to be an argon atmosphere at 0.1 atmosphere and 2500 C.

Heating Processes:

As the other systems, heating efficiency is 0.8.

Chemical Outputs:

The chemical outputs are assumed to be nanotubes and catalyst loaded amorphous carbon. The catalyst is assumed to be removable magnetically, and the carbon is assumed to have its feedstock value recovered via burning.

Reaction Notes:

The atmosphere is assumed to be unaffected and recycled.

Stoichiometry:

The following are the process quantities used to calculate the three cases:

Table B-8: Input Parameters for Solid Feedstock Processes

	Power (kW)	Vaporization Rate (g/h)	Nanotube Yield In Soot
Laser	0.25	0.15	70%
Laser Efficient Case	10	45	70%
Electric Arc	4	10	50%
Solar	50	10	50%

APPENDIX C: Input Values for Background Systems

In order to keep consistent methodology and to facilitate questions into prospective efficiency increases in the processes, all process inputs have been allocated to either thermal or electrical inputs. Because the carbon nanotechnology industry exists all over the world (although it is likely to be mostly in Asia in the near future), no particular mix of electricity has been considered, although a Japanese/Chinese/South Korean/US blend is likely appropriate due to where the majority of production takes place. Additionally, the transport processes for each system input have been omitted, due to uncertainty of location. The following table shows system process input values used in the calculations:

Table C-1: System Input Values

Input	Thermal Energy			Electrical Energy (MJ _e /kg)
	Process (MJ _{th} /kg)	Feedstock (MJ _{th} /kg)	Total Thermal (MJ _{th} /kg)	
Al ₂ O ₃	12,5	0,0	12,5	1,5
Argon, 99.9% Pure	0,0	0,0	0,0	2,4
CO	0,0	10,9	10,9	1,5
Coal	4,0	31,0	35,0	1,0
Graphite (Purified)	110	34,1	144,1	20,0
HCl	1,0	0,0	1,0	9,0
Hydrogen (H ₂)	28,0	141,2	169,2	0,0
Methane 99.9% Pure	5,4	55,5	59,9	2,2
MgO	8,5	0,0	8,5	1,0
Nitrogen 99.9% Pure	0,0	0,0	0,0	2,2
Toluene	14,5	40,6	55,0	3,2

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