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# Identifying the largest environmental life cycle impacts during carbon nanotube synthesis *via* chemical vapour deposition

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ABSTRACT

A life cycle assessment (LCA) has been conducted on the growth of multi-walled carbon nanotubes (MWNTs) *via* catalytic chemical vapour deposition (cCVD). Using a directly measured process, a cradle-to-gate approach has been employed for this assessment whereby analysis of the synthetic routes of the reactants used, the process energy inputs, the equipment infrastructure and generated emissions have been assessed to determine the environmental impacts of the MWNT product. Conducting an LCA has allowed the major and, arguably just as informative, minor contributors to the environmental impact of MWNT growth *via* a cCVD synthesis to be quantified. The high embodied energy of MWNT synthesis is often quoted as the major embodied impact in carbon nanotube growth. However, previously unmeasured contributions of the embodied impacts of the equipment infrastructure have been shown to be in the same order of magnitude in terms of environmental damage during the growth period of the MWNTs, other life cycle stages associated with the production of the chemical reactants used have a very minimal effect on the overall environmental impact due to the relatively small quantities involved in MWNT synthesis. Unique among similar studies is the capture of the impacts attributed to all chemical reactants involved in the cCVD synthesis of MWNTs.



## 1. Introduction

The current field of nanotechnology has been precipitated by Iijima who in 1991 reported the synthesis of carbon nanotubes (CNTs) (Iijima, 1991). Since this publication there has been an explosion in the amount of nanoscience research in the past 20 years (Chen et al., 2008). There is an exigent need to investigate the formation of these nanomaterials in more detail, as engineered nanomaterials (ENMs) are predicted to have a global market of $27 billion by 2013 (BCC Research, 2008). Indeed, the production of CNTs alone is estimated to be in the 10,000 tonnes/year range by the end of the decade (Upadhyayula et al., 2012). To date ENMs have been introduced in a number of everyday products, from sunscreen lotions to self-cleaning window panels (Contado and Pagnoni, 2008; Robichaud et al., 2009). Though the marketplace for these new materials is ever increasing, an in-depth analysis of the inputs of the material and energy impacts of nanomaterials is severely lacking (Som et al., 2010). A search in web of knowledge (ISI Web of Knowledge) for 'nanotechnology' yielded results in excess of 16,500, whereas a recently published review on the topic of the environmental performance of carbon nanotube products (Upadhyayula et al., 2012) identified only 7 publications pertaining to LCA being used to evaluate carbon nanotube synthesis. The review (Upadhyayula et al., 2012) also comments on missing information associated with the inventory data collection in particular the catalyst chemicals. The aim of this study is to address the lack of studies for carbon nanotube synthesis in the literature, covering all measurable process inputs and outputs in MWNT synthesis.

The use of life cycle assessment in the preliminary stages of process design enables the opportunity for a reduction in the environmental impact associated with material synthesis/manufacture to occur. Furthermore, LCA is proving to be central in chemistry to show whether a process is truly "green" (Tang et al., 2008). Conducting LCAs on evolving technologies has been compared as following a "moving target" (Gutowski et al., 2010), which is further compounded by a lack of *in situ* studies of a manufacturing process such as MWNT synthesis. This work therefore provides a snapshot of a working and optimised

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laboratory-scale process with scope for scale-up. The LCA output presents the environmental impact of each of the discrete reaction steps and highlights areas where implementable changes and refinement could mitigate potential impacts. It follows, that the use of LCA can thus be appreciated, as others have stated (Domènech et al., 2002), as an instructive tool in achieving the objectives of green chemistry, and a stepping-stone on the path of sustainable industrialisation of CNT growth. In fact, CNTs are already produced *via* CVD synthesis on an industrial scale, for example by Thomas Swan of the UK and Arkema of France, both of whom in recent years installed have industrial scale pilot plants the latter with 400 ton/year production of CNTs since 2011 (Arkema).

In recent years, studies have gone some way in expand life cycle thinking for ENMs (Isaacs et al., 2006; Healy et al., 2008; Kushnir and Sandén, 2008; Dahlben and Isaacs, 2009; Ganter et al., 2009). However, significant gaps remain present for the accurate capture of life cycle activities of CNTs (Upadhyayula et al., 2012) and ENMs (Bauer et al., 2008). More detailed studies need to be performed to allow comparative studies to take place in order for whole life-cycle benefits of these materials to be established.

Chemical vapour deposition (CVD) growth of CNTs is the most likely method for industrial growth of nanotubes (Kushnir and Sandén, 2008; Zhang et al., 2011) given that the process occurs at ambient pressures and at lower temperatures than other cited synthesis routes (Guo et al., 1995; Keidar and Waas, 2004; Ortega-Cervantez et al., 2005) and is more precise and versatile in terms of CNT formation and properties (Zhang et al., 2011). The CVD process, as with all current methods of carbon nanomaterial synthesis, is an energy intensive activity; the environmental burdens inherent in current energy use dominate the overall life cycle impact of producing CNT products (Khanna and Bakshi, 2009; Upadhyayula et al., 2012).

Existing studies have not coupled direct process activities with a characterised carbon nanotube product, with the production of a 99% pure organised MWNT structure as shown by the electron microscopy images of Fig. 3 and the supplementary supporting information of this paper. This study will be more detailed than others in the literature, in that it will include all upstream processes involved in the synthesis of the MWNT product, covering more precise chemical catalyst and feedstock contributions and a capture of the environmental burden attributable to the reactor and other synthesis infrastructure, which is often neglected from assessments (Upadhyayula et al., 2012). Conducting a full cradle-to-gate LCA will serve to inform whether less obvious or 'hidden' environmental burdens in addition to energy consumption are present in carbon nanotube synthesis.

### 1.1. System boundary

This paper presents an LCA conducted directly on a 'lean' laboratory-scale CVD process for the production of high quality MWNTs, either in powder or aligned array form. The cradle-to-gate scope and system boundary for the LCA is shown in Fig. 1 which addresses all stages involved in the production of the MWNTs. Various investigative techniques have been employed to capture the distinguishable material and energy flows for the chemical reactants, energy use, laboratory infrastructure and generated waste emissions associated with MWNT growth. Transport activities for the separate materials are included in the assessment. However, transport stages between the specific manufacturing plants and the laboratory have been negated due to uncertainties regarding modes of transport and distances travelled.

The MWNTs grown have been characterised as suitable for applications requiring high degrees of purity and quality, however, no in-use phase is covered in this study. Expansion of this system boundary could cover MWNT applications whereby the uniformity of the formed product, thermal and electrical conductivity, and mechanical strength are valued attributes. The LCA functional unit, to which all environmental impacts relate, will be for a typical laboratory 'batch' of the MWNTs grown *via* the optimised CVD process, approximately 300 mg of product.

## 2. Methodology

### 2.1. Carbon nanotube synthesis and characterisation

The CNTs were generated by the chemical vapour deposition of ferrocene (0.2 g) dissolved in toluene (10 ml). The ferrocene/toluene solution was injected using a syringe pump at a rate of 10 ml/h under 450 sccm Ar and 50 sccm $H_2$ into a quartz tube at 790 °C. CNTs were grown on a quartz substrate.

Characterisation of the CNTs formed was achieved using a range of electron microscopes, transmission electron microscopy (TEM) was carried out on a JEOL 1200 operated at 200 kV, while higher resolution TEM was carried out on a JEOL 2100 operating at 200 kV. Samples for TEM analysis were dispersed in ethanol and deposited onto Cu or Ni grids. Scanning electron microscopy (SEM) was carried out on a JEOL 6480LV at 5–20 kV, while high resolution SEM was carried out using a JEOL FESEM 6301F. Energy-dispersive X-ray spectroscopy (EDS) was carried out *in-situ* during SEM analysis. These characterisation techniques are excluded from the scope of the LCA, since they become superfluous once process optimisation has taken place and the growth of consistent MWNT batches. Sample electron microscopy images of sample MWNTs produced using this synthesis route is shown in the accompanying supplementary information of this publication.

### 2.2. LCA methodology

The life cycle assessment (LCA) environmental management tool adopts a methodical approach to quantify the potential impact of a product or process. Environmental impacts are inherent in the background processes involved in the forming the resources used together with emissions and waste streams specific to a system under investigation. International standards for the LCA process include ISO14040:Principles and Framework (ISO, 2006a), and ISO14044:Requirements and Guidelines (ISO, 2006b). The LCA process is a well-documented process (Baumann and Tillman, 2004; McManus, 2010), the integral parts include: the goal and scope definition, inventory analysis, impact assessment and interpretation of results. These stages are shown in Fig. 2 and can be appreciated as iterative and inter-linked procedures.

The goal of this study can be appreciated as identifying the major contributors in the synthesis of MWNTs, and the scope extends to all stages involved in producing this material ready for subsequent use. Inventory data in this study has been collected through: onsite measurements; direct energy readings, materials usage etc.; published literature for background processes, using mainly PubChem; chemical processes modelling, using AspenPlus (Aspen Technology Inc, 2011); and software-based inventory datasets, and Ecoinvent software database (Ecoinvent Database v2.2). In instances of missing data for precursor chemicals the FineChem (Wernet et al., 2009) tool was used to estimate impacts of specific hydrocarbon molecules. The use of published datasets and life cycle models allows activities within the system boundary to be assessed which would otherwise prove exceedingly time consuming or impractical to obtain. A full list of the inventory data modelled for this process is presented in the supplementary information, along with main data sources used. The ReCiPe midpoint impact assessment methodology was used in this study