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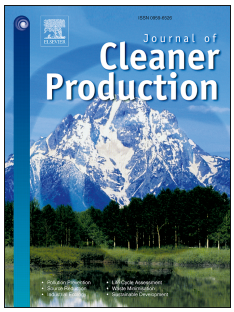


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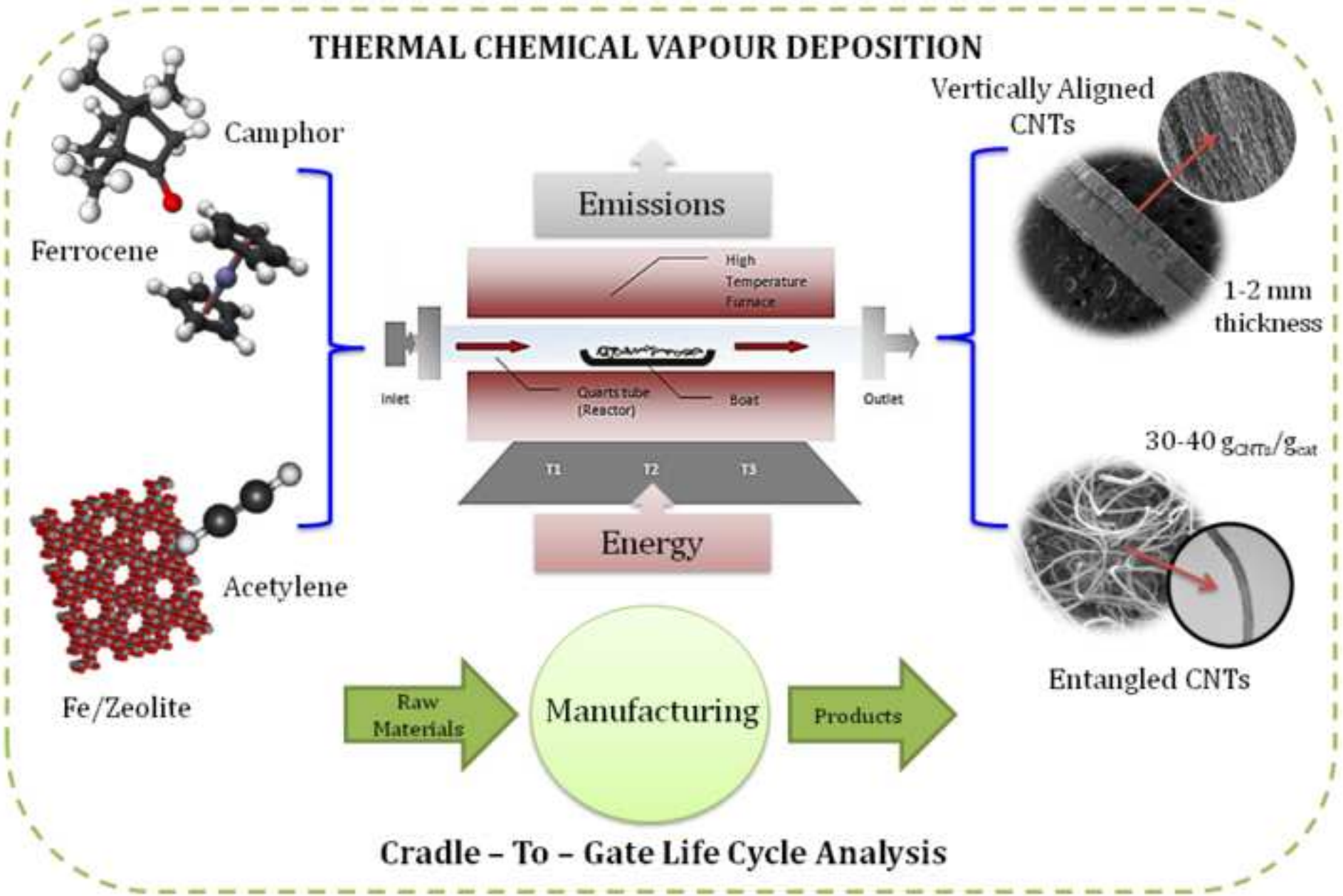
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Camphor
Ferrocene
Fe/Zeolite
Acetylene
Emissions
High Temperature Furnace
Inlet
Quarts tube (Reactor)
Boat
Outlet
T1
T2
T3
Energy
Vertically Aligned CNTs
1-2 mm thickness
30-40 $g_{CNTs}/g_{cat}$
Entangled CNTs
Raw Materials
Manufacturing
Products
Cradle – To – Gate Life Cycle Analysis

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# Towards a holistic environmental impact assessment of carbon nanotube growth through chemical vapor deposition

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## ABSTRACT

Despite the large production of carbon nanotubes (CNTs), which has been widely applied in the industrial sector and reached hundreds of tonnes, an integrated study that focuses not only on CNT synthesis and characterisation but also on the environmental footprint of the process life cycle is hitherto scarce. This work goes beyond state-of-the-art, combining and comparing two different CNT synthesis routes by taking into account all the appropriate data to fully evaluate them not only in terms of material characteristics and process productivity but also incorporating a comprehensive life cycle overview indicating the areas of concern that should be thoroughly considered and appreciated prior to their industrial scale production. The resulting environmental impacts and uncertainty analysis offer insights into areas

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where significant environmental gains could be achieved, thus providing a stepping stone towards “greener” CNT-based nanoproducts and paving the way for their sustainable industrialisation.

**Keywords**

Carbon nanotubes; Chemical vapor deposition; Decision making; Life cycle assessment; Uncertainty analysis

## 1. Introduction

Carbon nanotubes (CNTs) (Iijima, 1991), among other nanomaterials, are of enormous scientific interest owning to their extraordinary mechanical and electrical properties, rendering them promising candidates for industrial applications (De Volder et al., 2013). In 2015, CNT market valued at $2.26 billion and forecasted to grow to $5.64 billion by 2020 at a Compound Annual Growth Rate of 20.1% (RnR Market Research, 2015). Laser ablation, arc discharge and chemical vapour deposition (CVD) are extensively used for CNT synthesis (Charitidis et al., 2014; Rafique and Iqbal, 2011). However, CVD based methods offer the potential of high purity CNT production in a controlled manner. CNTs can be grown directly on different substrates, using a variety of carbon precursors and catalysts, resulting in the development of numerous synthetic routes (Kumar and Ando, 2010). Typically, most commercially available CNTs are in the form of black powder, consisting of entangled spaghetti-like CNT networks; their application spectrum is rather wide, ranging from composite materials, as reinforcements (Arash et al., 2014) in coatings and films, energy storage to biotechnology (De Volder et al., 2013; Zhang et al., 2013). However, the latest cutting edge technologies (field-emission displays, micro and nano- electronic devices (X. Sun et al., 2013), energy storage (H. Sun et al., 2015) and chemical or biological sensors (Bajpai et al., 2004; Patton et al., 2009)), require CNT structures with specific orientation, such as vertically aligned (VA)CNT arrays. Ge et al. (2012) used camphor as carbon source and ferrocene as catalyst to produce long, continuous, high purity, uniform and aligned CNTs with high crystallinity and density. The main advantages of this appproach are the unidirectional alignment of nanotubes and uniform length resulting in exceptional thermal and electrical conductivity (Chen et al., 2010; Souier at al., 2013).

Despite the benefits of CNT-based products, CNTs can potentially contribute to multiple negative environmental impacts resulting in harmful effects on ecosystems and human health (Singh et al., 2008; Singh et al., 2009). There were over 100 companies around the world manufacturing CNTs in 2011 (Patel et al., 2011) and this number is continuously increasing, rendering the understanding of the environmental implications of CNT production a prerequisite. Moreover, the quantification of environmental impacts via LCA in the early stages of process design is essential for new CNT prospective applications ensuring commercial viability and sustainability (Dahlben et al., 2013; Gilbertson et al., 2014; Rosen and Kishawy, 2012). However, applying LCA to CNT synthesis is rather challenging, due to the lack of robust information, the multivariate nature of nanoproducts and the uncertainties derived from the application of each LCA calculation method; only a handful of studies track the environmental impacts of CNTs. Most of the published LCA studies deal with the interpretation of literature results or are based on hypothetical scenarios (Gavankar et al., 2014) without considering all the critical steps required to fully describe the process from synthesis to end-of-life. Upadhyayula et al. (2012) reviewed recent LCA studies on CNT manufacturing and found out that the lack of data availability is the main obstacle for obtaining reliable LCA results. Notably, the quantification of the impacts of air emissions and waste stream discharges is rather challenging; precise estimations of the waste flows are still missing in literature. Namely, Healy et al. (2008) compared three of the most common CNT production processes in terms of their environmental footprint and revealed that impacts arise mainly from the generation of electricity, although they modelled the output without considering the formation of by-products. Griffiths et al. (2013) studied the environmental impact of 300 mg of CNTs produced by CVD and found that the heating of the furnace is the

most impactful part of the process. Additionally, they applied a detailed approach for determining the exhaust emissions, based on the study of Plata et al. (2008; 2009), which is a quantified evaluation of the potential environmental implications of CNT manufacturing.

Despite CNTs having entered market and being industrialised, their production technologies are multiple, and precise data describing the whole process are quite scarce, irrespective of the production method. Hence, the introduction of uncertainties into the LCA model can lead to distorted decision making and future studies should shed more light on this important issue. The extraordinarily high levels of uncertainty in LCA for CNT production require more careful treatment than is customarily applied in LCA of other products. Indeed, quantifying and managing uncertainty in LCA of nanomaterials generally is more demanding than for other materials. Interestingly, this holistic study takes advantage of two optimized laboratory-scale CVD processes with fully characterised CNT architectures and compares their life cycle performance. It also constitutes a detailed map which embraces all the appropriate steps in order to gain a better grounding of the environmental impacts of CNT production process, when looking to fulfil an industrial application.

## 2. Material and methods

### 2.1. Process description

A thermal CVD reactor was used to synthesize multi-walled (MW) CNTs. The reactor consists of a horizontal quartz tube (3.4 cm inner diameter, length of 100 cm) housed in a three-zone cylindrical furnace 80 cm long, shown schematically in Fig. 1. Synthesis of CNTs was performed via two CVD routes. In the first case, camphor and

ferrocene were used as carbon source and catalyst, respectively (ROUTE1), while in the latter, acetylene and iron particles supported on zeolite were used as carbon source and catalyst, respectively (ROUTE2).

For ROUTE1 (CNT1 product), a pyrex flask containing the reagent mixture which was composed of camphor (96% purity in weight, Aldrich) as carbon precursor and ferrocene (98% purity in weight, Aldrich) as catalyst, in a 20:1 mass ratio, was connected to the tube close to the nitrogen inlet. A heating plate was located below the flask, to achieve the heating and sublimation of the reactants (Fig. 1a). Nitrogen gas flow was used to carry the gas mixture of precursors inside the furnace, where pyrolysis of the gases took place at 850 $^{o}$C and thick CNT carpets were deposited onto a silicon substrate.

For ROUTE2 (CNT2 product), the catalytic particles were placed on a ceramic boat which was located inside the quartz tube, in the middle of the isothermal zone of the reactor (Fig. 1b). Firstly, nitrogen passed through the quartz tube to remove the air; then, the reactor was heated to 700 $^{o}$C under continuous nitrogen flow. Subsequently, nitrogen was replaced by a mixture of acetylene (70 mL/min) and nitrogen (230 mL/min). In both cases, when the reaction was completed, the raw products were cooled down to room temperature under a nitrogen atmosphere.

For catalyst preparation, wet impregnation of zeolite Y (Alfa Aesar; particle size ~1μm; specific surface area 975 $m^2/g$) support was used. The appropriate amounts of zeolite and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich) were dissolved in water to obtain catalyst with the desired Fe content (20% wt). The resulting slurry was kept under continuous stirring until nearly all the solvent had evaporated. Then, the residue was dried at 120 $^{o}$C for 4 h. Finally, the obtained material was calcinated at 550 $^{o}$C under nitrogen flow for 1h.

### 2.2. CNT Characterisation

The CNT morphology was studied via scanning electron microscopy (SEM) using a Nova NanoSEM 230 (FEI company) microscope with W (tungsten) filament and transmission electron microscopy (TEM) with a Tecnai G2 Spirit Twin 12 microscope (FEI) after dispersing CNTs in distilled water. The crystallinity of CNTs was measured with a Bruker D8 Advance Twin X-ray diffractometer equipped with a Cu $K_a$ radiation source, at a wavelength of 1.5418 Å. Finally, the purity of the produced materials was determined via thermogravimetric analysis (TGA) conducted in an oxidative atmosphere (atmospheric air flow: 120 mL/min, heating rate: 5 $^{o}$C/min) using a Netzsch 409 EP instrument.

### 2.3. Life Cycle Assessment Methodology

Life cycle assessment is used for the evaluation of potential environmental impacts associated with a chemical process or a material and is a standardized method which is based on two international environmental standards; ISO 14040: Principles and Framework and ISO 14044: Requirements and Guidelines (ISO, 2006). Life cycle assessment methodology comprises of four steps; first the goal and scope of the study should be defined, second the life cycle inventory should be specified, subsequently the impact assessment takes place and finally the interpretation of results is carried out. In order to enable the quantification of the function of a studied system (product or process) and to compare with similar systems, it is important to choose the appropriate unit of assessment, which is called the functional unit. SimaPro8 software (PRe Consultants) was used to conduct the LCA. The calculations for the impact assessment have been executed using the ReCiPe method (Goedkoop et al., 2013), which brings together the advantages of two of the most established calculation

methods; Eco-Indicator 99 and Centrum Milieukunde Leiden–IA, giving results both to midpoint and endpoint level. ReCiPe method is ideal for assessing the impacts of materials synthesis processes (Griffiths et al., 2013), due to its broad set of midpoint impact categories and the global scope of its impact mechanisms. The cultural perspective that has been chosen for the analysis is the Hierarchist (H), which represents a consensus scientific model for a 100 years' timeframe, according to ISO 14044 (Goedkoop et al., 2013). Lab data were gathered during the process, from the system indicators (e.g. temperature, flow), as well as from direct energy readings, using an energy power meter (HQ, EL-EPM02HQ). Several data, especially for the materials used, were retrieved from the software database (Ecoinvent Database v3.1).

#### 2.3.1. Goal & Scope

The main goal of this LCA study is the determination of the environmental footprint of each production route and the major contributors to the predicted impact. The scope of the study extends solely to the synthesis process using an optimized laboratory scale CVD reactor and is a cradle–to–gate analysis. In both routes, the functional unit for which all the measurements and calculations have been performed is 1 kg of MWCNTs (Fig. 2), allowing a comparison with alternative systems (e.g. metal nanomaterials) fulfilling the same function.

#### 2.3.2. Inventory Analysis

Data collection is the most important step in LCA (Flemström and Pålsson, 2003); the main assumptions are discussed below. Data for camphor and ferrocene are not included in the software database. Camphor is extracted from camphor tree (*Cinnamomum camphora*) leaves by a steam distillation process (Frizzo et al., 2000). Generally, camphor is considered an eco-friendly carbon precursor as it is a natural

product (Kumar and Ando, 2007). Despite the extraction of natural resources being deemed as a "clean" process when compared with heavy chemical industries, its environmental footprint is not negligible, so it is crucial to introduce camphor into the inventory data (Chemat et al., 2012). Given the lack of information in the software database, we used data for palm oil, since steam distillation is applied for the extraction of both oil types (Cassel et al., 2009; Masango, 2005; Morais et al., 2010; Stichnothe and Schuchardt, 2011).

Concerning ferrocene, Griffiths et al. (2013) used the patent of Cordes (1965), who simulated the ferrocene synthesis process using the chemical engineering software Aspen Plus (Aspen Technology Inc, 2011). In the current study, ferrocene was introduced into the inventory using data from this study.

Modelling the exhaust wastes produced during CVD synthesis of CNTs seems to be quite complicated. Plata et al. (2008, 2009) quantified the released wastes and found that unreacted carbon, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and soot are present. Schmitt et al. (2006), showed that benzene was the main by-product during acetylene decomposition at elevated temperatures (750 $^{o}$C). Musso et al. (2009) also showed that benzene was the main product from the thermal degradation of camphor. The benzene to unreacted precursor ratio varies according to the experimental conditions (reaction time, carbon feedstock percentange, etc.). Based on these data (Liu et al., 2011; Musso et al., 2009; Plata et al., 2009; Schmitt et al., 2006; Titirici, et al., 2015) and given the uncertainties, the following assumption was made: the exhaust emissions are considered to be a mixture consisting of 50% unreacted carbon feedstock (i.e. acetylene or camphor) with the remaining 50% consisting of VOCs (~40% including benzene), PAHs (~0.5%) and soot (~9.5%). In order to maintain the mass balance, the total amount of the wastes

was calculated as the subtraction between the total mass of the carbon precursor and CNTs obtained.

The data for the electricity are based on the electrical energy production in EU-27 by mixed resources (coal, natural gas, crude oil and uranium). Data for iron nitrate are not included in the LCA database, so the equivelent amount of iron chloride was used as iron source. Transport activities for the separate materials are not included in the assessment. The catalyst end-of-life is not included assuming that catalytic particles are encapsulated into the CNT structure. The stages of packaging and transportation to the laboratory have not been taken into account. Since this work is a cradle-to-gate analysis, the CNT disposal is not considered (Fig. 2). All assumptions concerning the CVD synthesis processes are summarized in Tables 1 and 2 for ROUTE1 and ROUTE2, respectively.

### 2.3.3. Impact assessment

When presenting LCA outcomes, various methods can be used, giving different levels of detail, while focusing on different stages in the cause-effect chain to calculate the impact. Impact assessment transforms the aggregated resource usage to emissions which are weighted together into the impact categories to which they potentially contribute; at the midpoint level, eighteen impact categories are included (e.g. global warming, eutrophication, acidification, aquatic ecotoxicity, etc.). At the endpoint level, most of these midpoint impact categories are multiplied by damage factors and summarized into three endpoint categories that are normalized, weighted and aggregated into a single score (Goedkoop et al., 2013a). The impact categories, along with their correlation to the endpoint categories are presented in Fig. S1. An endpoint method looks at environmental impacts at the end of this cause-effect chain, while a

midpoint method looks at impacts occurring earlier along the cause-effect chain before the endpoint is reached (Brilhuis-Meijer, 2014). Regarding CNTs, an endpoint is associated with ecotoxicity to a specific species, while a midpoint method might look at the increased concentration of CNTs in the habitat of that specific species. In terms of result accuracy, midpoint indicators present lower uncertainty, while indicators near endpoint level require further modelling for the environmental mechanism to be unravelled. On the other hand, endpoint indicators are often easier to understand by decision makers than those in the midpoint level (Goedkoop et al., 2013b).

#### 2.3.4. Uncertainty analysis

The standard procedure for the quantification of uncertainty developed by Frischknecht et al. (2004) is used to evaluate the parameter uncertainties at the process level. To quantify the Life Cycle Impact Assessment (LCIA) uncertainties owed to the statistical variability and the temporal, geographical or technological gaps in the Life Cycle Inventory (LCI), Monte Carlo simulation (1000 runs at the 95% confidence level) was applied. Lognormal distribution has been assumed for all data, by selecting the standard deviation ($\sigma^2$) according to the pedigree matrix (Goedkoop, 2013) introduced by Wiedema and Wesnæs (1996). The detailed uncertainty factors and calculations are presented in Table S1.

## 3. Results and Discussion

### 3.1. CNT characterisation

After CNT synthesis, their structure, chemical composition and purity degree were examined. Table 3 summarizes the characteristics of the produced CNTs. For

ROUTE1, the results revealed that a CNT carpet consisting of long (>100μm in length) vertically aligned (VA) MWCNTs with outer diameter distribution from 60 to 80 nm was grown on the silicon substrate with thickness in the range of 1-2 mm (Fig. 3a), while MWCNTs in bulk powder form with uniform outer diameter distribution between 20-40 nm and length >10μm were produced via ROUTE2 (Fig. 3b). TEM images (Fig. 3c and 3d) of the tested CNTs are also depicted. Hollow filamentous structures are revealed, with inner diameters 10-13 nm and 12-16 nm for both CNT1 and CNT2. Additionally, iron particles could be seen encapsulated within the MWCNT core.

Thermogravimetric analysis (Fig. 4a) was used to determine the carbon content and purity of the as–synthesized carbon products. The initial weight loss is 2.3 and 1.3% for CNT1and CNT2, respectively, being observed at temperatures up to 400 $^{o}$C and is assigned to the burning of amorphous carbon material. The % residual weight at the end of the thermal oxidative curve for CNT1 is 10.1% and corresponds to the iron catalytic particles, being relatively higher compared with CNT2 (5.9%). The differential thermogravimetric (DTG) curve for CNT2 shows a single narrow peak located at 563 $^{o}$C indicating high thermal stability in air atmosphere and uniform structure; a shift of ~25 $^{o}$C to lower oxidation temperature is evident for CNT1 (peak at 537 $^{o}$C) owing to the higher iron content (McKee and Vecchio, 2006). Thus, the overall purity (Table 3) reaches ~88% and ~93% for CNT1 and CNT2, respectively. XRD patterns of both samples are illustrated in Fig. 4b, revealing similar XRD peaks. A prominent and sharp peak at about $2\theta = 26^{o}$ is evident for all samples, which is assigned to the (002) reflection of graphite. Additionally, there is a second asymmetric peak at $2\theta = 43.5^{o}$, which is enhanced for the CNT2 sample (the first part is located at $2\theta = 43.2^{o}$ corresponding to the (100) reflection of graphite, while the

other part is at $2\theta = 44.75^{o}$ corresponding to the (101) reflection of graphite) (Philippe et al., 2009).

### 3.2. Productivity assessment

To study the productivity of each synthesis processes, the carbon yield and the carbon conversion are used (Das et al., 2006). Carbon yield can be calculated by the following equation (Louis et al., 2005):

$$Carbon\_yield = \left(m_{carbon,product} - m_{catalyst}\right) \Big/ m_{catalyst} \quad (1)$$

where:

$m_{carbon,\ product}$ is the mass of the obtained carbonaceous material, and

$m_{\text{catalyst}}$ is the mass of the catalyst, which was utilized to catalyze the reaction.

Carbon conversion is calculated as follows (Das et al., 2006):

$$Carbon\_conversion\ (\%) = m_{carbon\_product} \Big/ m_{carbon\_feedstock} \times 100\% \quad (2)$$

Where: $m_{carbon\_feedstock}$ is given by:

$$m_{carbon\_feedstock} = \frac{N_C \times Ar\ (C)}{Mr\ (source)} \times m_{source} \quad (3)$$

where: $N_C$ is the number of carbon atoms contained in the carbon source,

Ar (C) is the atomic weight of carbon, and,

Mr (source) is the carbon source's molecular weight.

From a scale-up perspective, both carbon yield and conversion should be taken into account for the process evaluation, since the first is related to the catalyst effectiveness, whereas the latter reflects the consumption of raw materials, and thus is

indicative of lower side-products and less waste. It should be pointed out that carbon conversion (usually referred as atom efficiency) is one of the key principles of Green Chemistry and thus, one of the most important factors to consider for a sustainable development (Anastas and Warner, 1998). Table 4 summerizes the productivity per batch, carbon yield and carbon conversion obtained from the two studied synthetic routes, derived from an average of 15 experiments per route. It is clear that ROUTE1 is characterised by low carbon conversion, since for the production of a 4 – 5 g CNT batch (with average thickness 1-2 mm) more than 100 g of camphor are required. ROUTE2 is more efficient as more than 50% of the carbon mass (as given by Eq. 3) that passes through the reaction zone is converted into carbonaceous material. Hence, this method offers a feasible path for the up-scaling of CNT production, since a small quantity of the catalyst can result not only in large CNT quantities (30 – 40 g of CNTs are produced per gram of catalyst) but also in products with high quality.

### 3.3. Life cycle impact assessment results

#### 3.3.1. Contribution analysis

Quantification of the impacts of the materials used and the energy consumption during CNT production were considered so as to ascertain the life cycle of both CVD routes. Figure 5 illustrates the comparative diagram between the two alternatives, giving the characterisation values for each impact category. As it is observed, ROUTE1 has the highest impact across all categories. First, this fact could be attributed to the higher energy demands needed not only for the higher growth temperatures (850 $^{o}$C), but also for the supply of additional heating to facilitate the evaporation of the raw materials. Secondly, the higher productivity of ROUTE2

results in a drop of the environmental load, which implies that more ROUTE1 batches are necessary to achieve the same production volume. So, the heating stage is the most impactful part of CNT life cycle and thus, a focal point when considering the processes up-scaling. Apart from energy, the use of silicon substrate, which is essential for the orientation of the final material, is another contributor to the ROUTE1 environmental footprint.

Figure 6 depicts the % share of each contributor to the impact characterisation results; the greatest contributor to CVD's environmental footprint is the electrical consumption in most of the categories. Generally, CVD is an energy intensive process, with heating requirements ranging from 480 to 920,000 MJ/kg CNTs (Upadhyayula et al., 2012). In our case, the corresponding values are around 2,480 MJ/kg CNTs for ROUTE1 and 1,100 MJ/kg CNTs for ROUTE2. Other high impact factors could be camphor and the use of silicon substrate for ROUTE1 as well as the acetylene for ROUTE2, to which a significant share is assigned across most of the impact categories. Despite camphor being a natural product, it has a significant contribution to several impact categories, such as marine eutrophication, agricultural land occupation, natural land transformation, marine and terrestrial ecotoxicity, since the exploitation of natural resources, camphor extraction process and disposal of biomass wastes result in an extra environmental load. In case of acetylene, its production process (as it is included in the Ecoinvent Database) involves partial oxidation of natural gas and cleaning of flue gas with electrofilters, which reflect on several impact categories, such as freshwater eutrophication, agricultural and urban land occupation, natural land transformation and water depletion. The impact of catalyst is also non-negligible, mostly affecting the metal depletion category in both synthesis routes. It is also deduced that ROUTE1 presents higher environmental load,

as greater catalyst quantities are required for the production of the same product volume (lower carbon yield). In terms of the impact of exhaust emissions, these were found to influence the following categories: human toxicity, freshwater, marine and terrestrial eco-toxicity. Photochemical oxidant formation is only present in case of ROUTE2 due to the acetylene flow in the exhaust emissions.

Due to the fact that the characterisation results are not expressed in the same unit for each impact score, the impact categories cannot be compared to each other and the overall magnitude of impacts cannot be determined. To overcome this obstacle, the normalisation factors of the endpoint ReCiPe method were used (Norris, 2001; Sleeswijk et al., 2000). The normalized impact at the three endpoint categories is presented in Fig. S2. It is evident that human health and resources exhibit the greatest impact. Also, ROUTE1 appears to have an environmental load 3 times greater than that of ROUTE2 which is in accordance with the characterisation results.

### 3.3.2. Sensitivity and uncertainty analysis

As pointed out previously, when conducting an LCA study, many assumptions are adopted in order to get a first insight of the studied system, despite uncertainties being entailed. These uncertainties may affect the reliability of LCIA results and can derive from partial ignorance or lack of perfect knowledge (Björklund, 2002). The main uncertainties coupled with their importance are listed in Table S2.

Electricity use is the most influential contributor across all impact categories. Thus, the geographical origin of data can lead to significant variation in LCIA results (De Smet and Stalmans, 1996). A comparative scenario analysis between European Union and Greek electricity production mix was applied to determine their influence on the overall output. The results revealed that the main differences are limited only to three

categories: ozone depletion, ionizing radiation and freshwater ecotoxicity (Fig. S3). This can be attributed to the different energy sources; in European Union, electric energy is produced mostly by solid fuels, nuclear power and renewables, whereas Greece exploits mainly solid fuels, renewables and gases (EU Commission, 2015). The different composition of the electricity production mix affects the LCIA results, making the choice of electricity sensitive to the geographical location.

For the current study, the main source of data uncertainty lies in the estimation of the exhaust emissions (based on literature data). To deepen the results reliability and given the large number of different scenarios, Monte Carlo simulation was applied to estimate LCA uncertainties between the two production routes; the absolute uncertainty is of no use when comparing two alternatives (Guo and Murphy, 2012). Comparative approaches other than a single assessment of environmental impacts are likely to be of more practical benefit to decision makers (DM) (Seager et al., 2008). Figure 7, on the left, presents the results of the uncertainty assessment in terms of the probability of ROUTE1 having lower impacts than ROUTE2, and, on the right, the probability of ROUTE2 having lower impacts than ROUTE1. It can be deduced it was certain (almost 100% probability) that, in most impact categories, ROUTE2 delivered better LCA results than ROUTE1. However, for water depletion, human toxicity, marine, terrestrial and fresh water eco-toxicity potentials, the uncertainty analysis discloses that no clear statement can be given about which production route would offer the most environmentally friendly choice in midpoint impact categories.

### 3.3.3. LCA classification

According to Herrmann et al. (2014), the uncertainty level can be assessed based on an LCA classification matrix. The uncertainty of an LCA statement increases when

the breadth of the LCA space expands - in other words, when moving away from the upper-left corner in the LCA classification matrix. Studies located in the same cell of the matrix can be comparable. According to the classification matrix, our LCA study is retrospectively described as “Tangible, Single-period, Micro-Retrospective, Change, Physical” TSi-RCY, because most of the data were based on direct measurements, derived from a lab scale production unit, and were less than six months old. The main source of uncertainty arises from the fact that we did not use a relevant baseline process from the LCA database, but we used alternatives to model the functional unit of each CNT route. However, our study is categorized as TSi-RCV when we consider normalization results, as more uncertainties are introduced associated with the normalization factors (Benini and Sala, 2015).

### 3.4. Decision making

Despite considering 1 kg of MWCNTs the functional unit of our study, CNT1 and CNT2 nanoproducts should not be regarded as 100% substitutes, since they do have their distinct characteristics and properties (i.e. electrical conductivity), serving different applications. So, no unique answer to the question: “Which is the most favourable synthetic route over the other?” can be extracted. Remarkably, the answer lies in the fact that each DM, i.e. manufacturer, end user, environmentalist and regulator, should focus on specific criteria to be fulfilled from their perspective. In other words, a manufacturer will place emphasis mostly on cost analysis of the product (energy consumption and process efficiency are also included) without considering LCA. In contrast, end users are assumed to be equally concerned about health risks and costs, taking no heed of energy consumption. From an environmentalist perspective, the concerns for health risks, energy dissipation, process

efficiency (mainly in terms of carbon conversion) and environmental impacts are shared, while cost is of no or less importance. For regulators, environmental impacts (e.g. greenhouse gases emissions) and health risks are at the top of their agenda, while they feel indifferent for cost and process efficiency (Canis et al., 2010). Last but not least, synthesis technologies should be matched to the material characteristics which are most advantageous upon the end-use application on a life cycle basis.

In our case, the up-scaling potential of ROUTE1 entails high cost associated with the relatively low carbon yield and the additional energy demands, but is potentially preferable to manufactures and end users, who target at final products in which the CNT orientation is highly required (Hooijdonk et al., 2013). ROUTE2 alternative is likely to satisfy environmentalists and regulators because of the lower energy demands and mitigated impact results. Also, ROUTE2 may fulfil manufactures who do not invest in products' special orientation, but they care about high productivities. However, health issues remain among the critical factors that should be regarded during selection of one synthesis route over the other. In the current study, a DM could consider this study as a weak-point analysis, since significant uncertainties are revealed in impact categories (e.g. human toxicity) when comparing the two alternatives and contradictory toxicity results are reported for CNTs (Liu, 2013). In other words, further investigation in ascertaining health risks is required. At that point, it is worth mentioning that the as-received carpets (ROUTE1) are easier to store and manipulate due to their bulk form (Boulanger et al., 2013). On the other hand, CNTs in powder form, need special handling to collect and use them, due to the possible release of floating aerosol particles. Thus, they evoke important potential health issues (Aschberger et al., 2010) prior to their use in the final application.

## 4. Conclusions

This study includes a full description of two optimized laboratory-scale CVD processes able to achieve either VAMWCNTs or entangled MWCNTs and compares their environmental footprint. LCA is considered an integral tool for both researchers and industrial practitioners to ensure savings in energy dissipation and material resources, supporting sustainable and competitive scale-up of CNT production to meet the growing market. The LCA results showed that the energy consumption has a significant share in the overall embodied impact of both CVD approaches, owing to the high applied temperatures for the carbon decomposition. The proposed synthesis processes offer a feasible path for the up-scaling of CNT production (ROUTE2), in terms of environmental aspects, while through ROUTE1 complex carbon nano-architectures can be obtained, albeit at lower yield and efficiency. However, a DM may feel uncertain on the decision to be taken since various uncertainties are introduced. To make our LCA results more transparent and useful, sensitivity and uncertainty analysis were applied, while the LCA classification matrix was used to assess the uncertainty level of our study. We consider that understanding realistic process parameters and life time performance, through better engagement with industry and experts, should be the first target for reducing uncertainty (particularly for the major factors of energy demand, ancillary materials and waste generation in CNT manufacture).

Although researchers have been synthesizing CNTs on a laboratory scale, the optimisation of their industrial synthesis remains a challenge and may lead to significant reduction in environmental burdens. Areas to focus on here could be the reduction of the heating demands, filtering and burning of the waste outputs prior to their release, or development of uses for the benzene by-product such that it is not

considered a waste, but could be further processed. Apart from the improvements in synthesis procedure, for CNT mass production the important issues about human health (particularly that of production and transport workers, and end-users incorporating CNTs into products) should also be considered. The realisation of these implications mitigates the unintended consequences of novel materials and offers insights into the sustainable development of CNT-enabled technologies and opportnuties for lowering environmental impacts through economies of scale, selection of routes with lower $CO_2$ equivalents and facilitation of holistic and multi-factorial approaches to regulation.

Despite the subjective nature of the results, our study can assist researchers in getting a better consideration of the environmental burdens involved. This holistic analysis underlines areas of high priority in the future research of nanomanufacturing and provides a life cycle inventory for potential application of CNTs, e.g. as reinforcement material in polymer composites. In this case, it would be desirable to include the disposal stage, taking into account the potential release of CNTs, which may be decisive for choosing environmentally-friendly nanoproducts. Finally, this work can be considered as a useful tool for assessing relevant routes in terms of trade-off between required material specifications and environmental implications of the selected production process, paving the way for a sustainable industrialisation of CNT nanoproducts.

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**FIGURES**

**Fig. 1.** Schematic representation of (a) ROUTE1 and (b) ROUTE2.

**Fig. 2.** Schematic representation of CNT synthesis process, including the inflows and outflows for the system boundaries.

**Fig. 3.** Representative SEM and TEM images of CNTs produced via: ROUTE1 (a), (c) and ROUTE2 (b), (d).

**Fig. 4.** (a) TGA and DTG curves and (b) XRD diagrams of CNTs produced via the two approaches.

**Fig. 5.** Comparative characterisation diagram of both routes; Method: ReCiPe Midpoint (H) V1.11 / World Recipe H / Characterisation/ Excluding long-term emissions.

**Fig. 6.** Environmental impacts for 1kg of CNTs produced by 'ROUTE1' and 'ROUTE2'; Method: ReCiPe Midpoint (H) V1.11 / World Recipe H / Characterisation/ Excluding long-term emissions.

**Fig. 7.** Uncertainty analysis of 1 kg CNTs produced via ROUTE1 (A) minus 1 kg CNTs produced via ROUTE2 (B), Method: ReCiPe Midpoint (H) V1.11 / World Recipe H, confidence interval: 95 %.

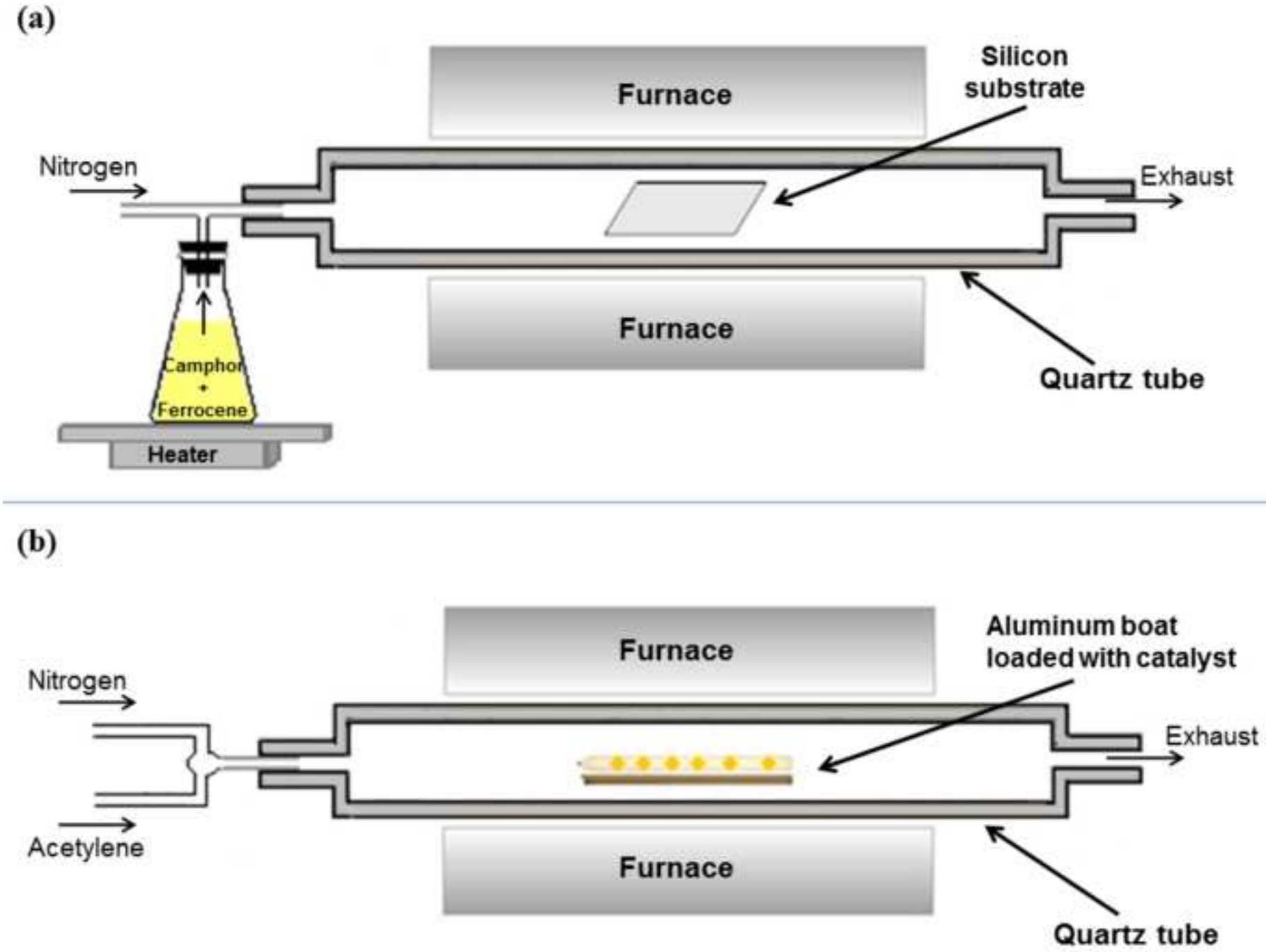
**TABLES**

**Table 1.** Assumptions and inventory data per typical batch (4.5 g of CNT1) for ROUTE1.

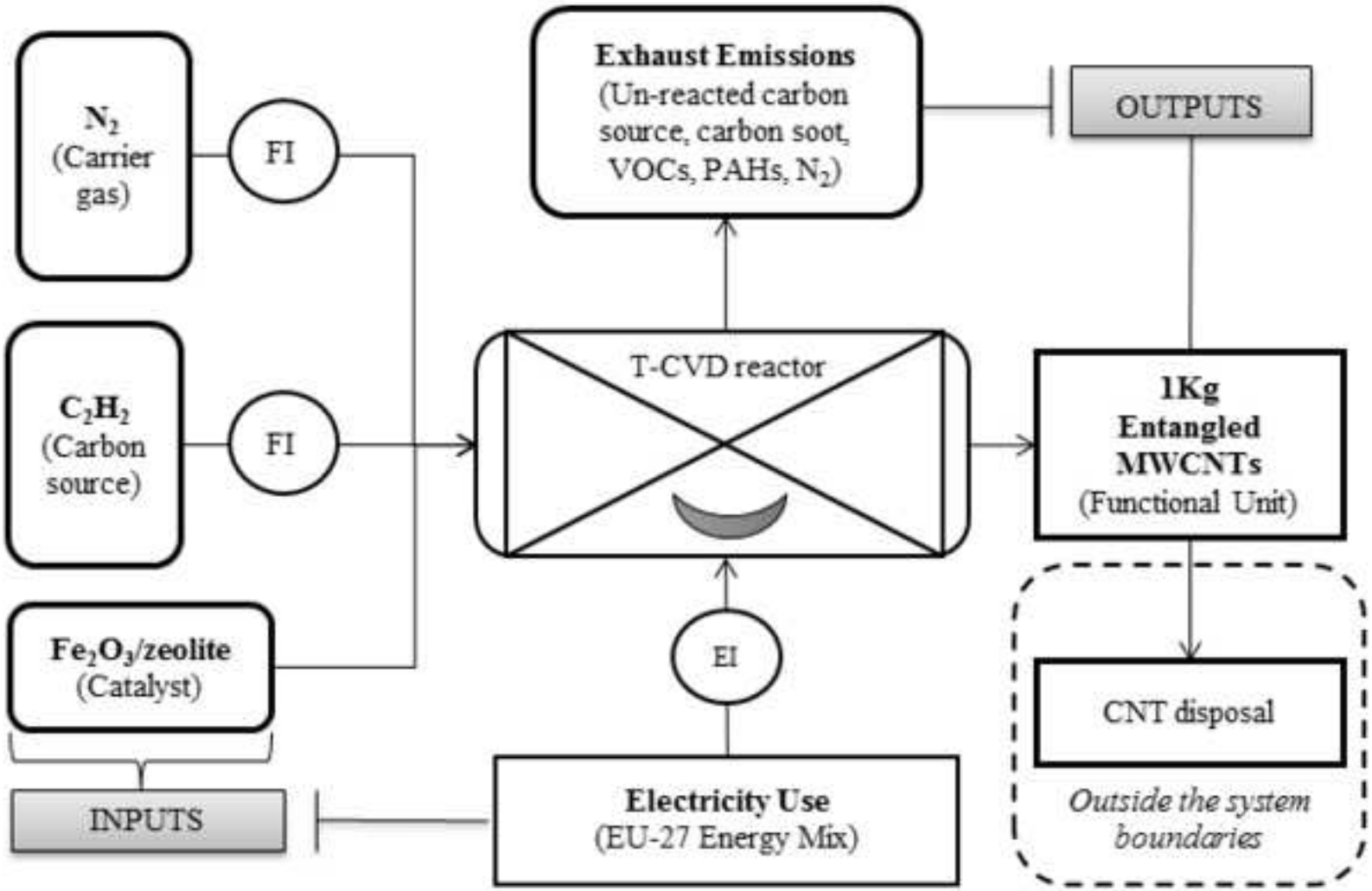
**Table 2.** Assumptions and inventory data per typical batch (7.5 g of CNT2) for ROUTE2.

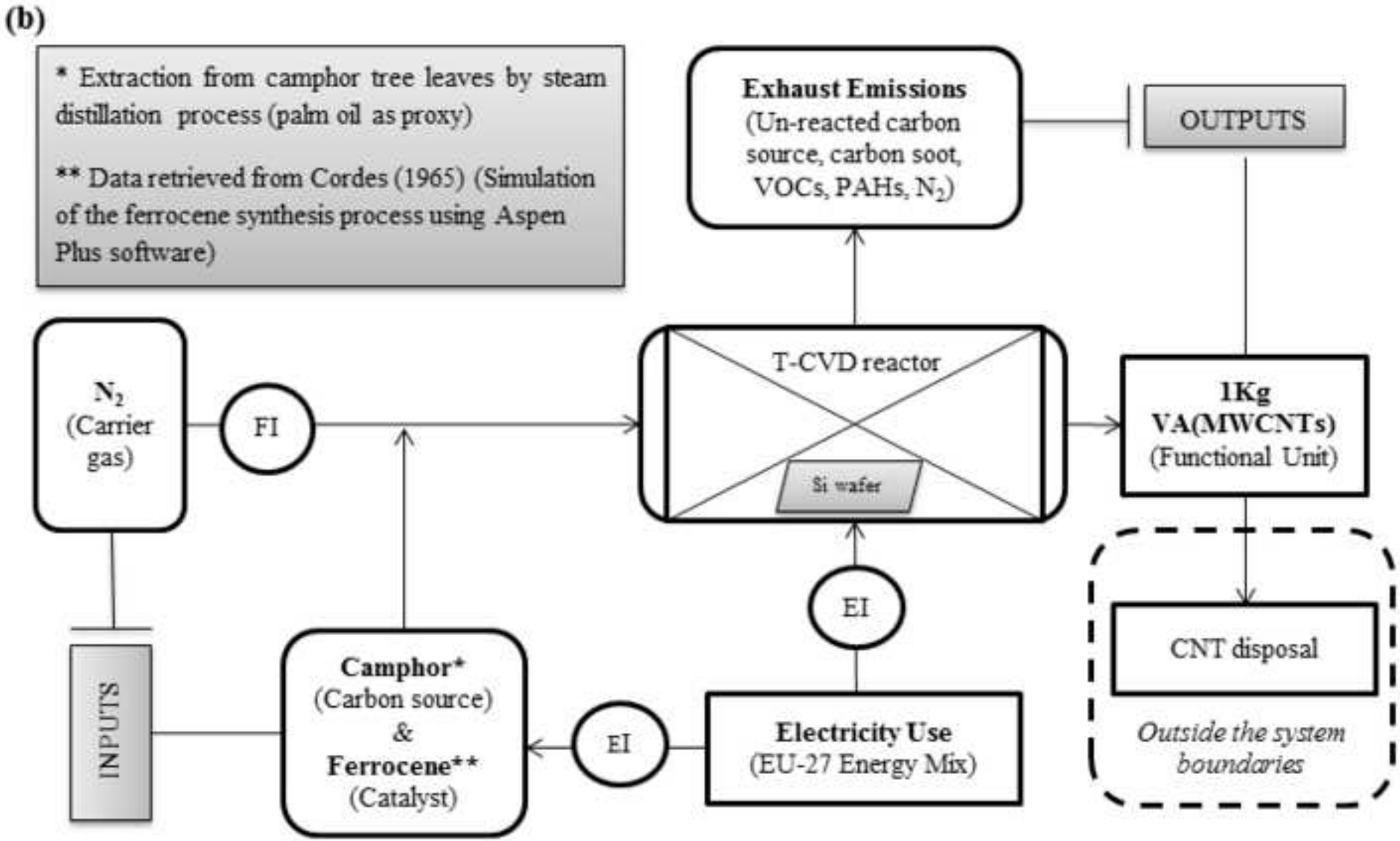
**Table 3.** Specifications for CNT1 and CNT2.

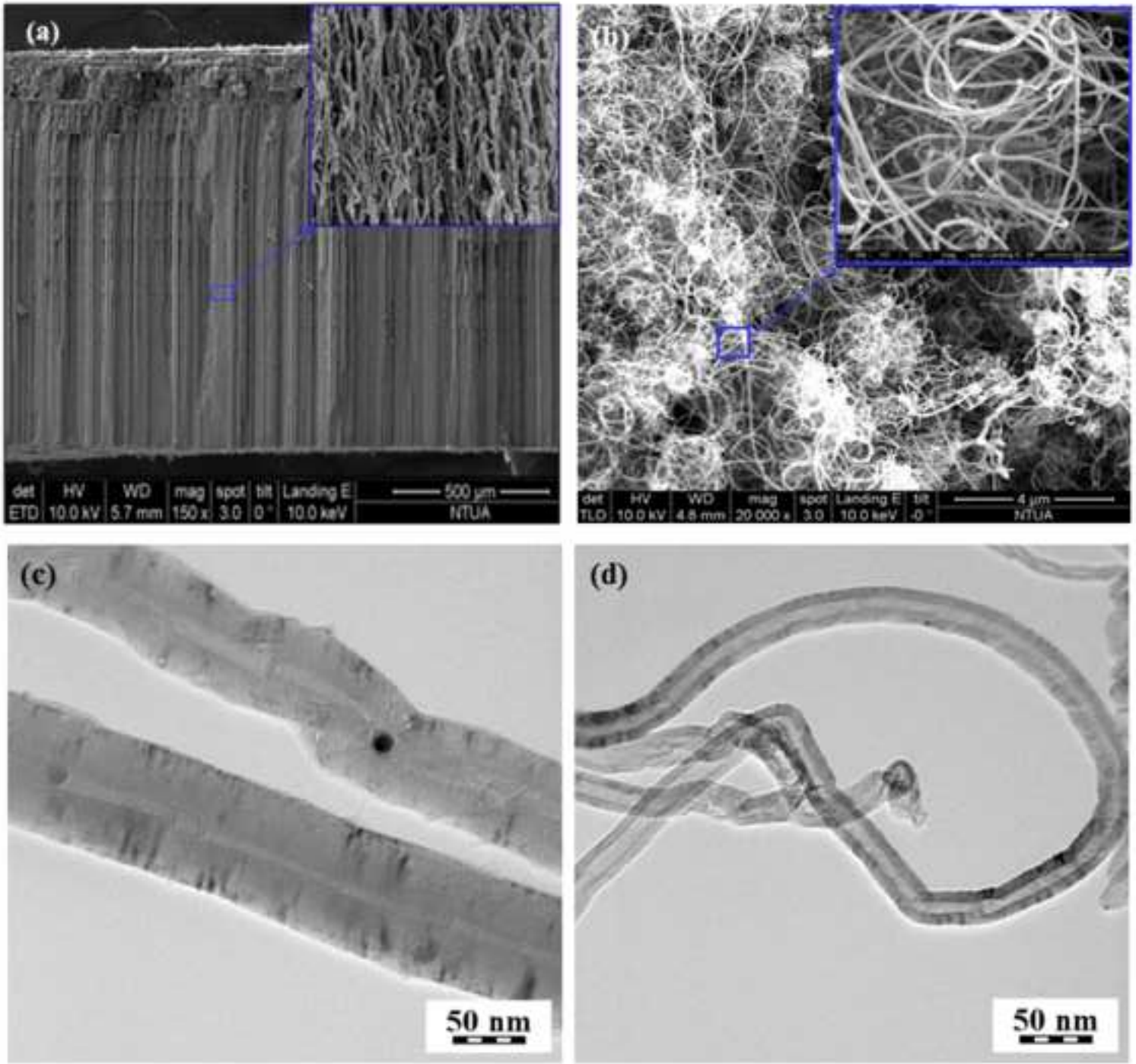
**Table 4.** Process effectiveness for the CNT production rout

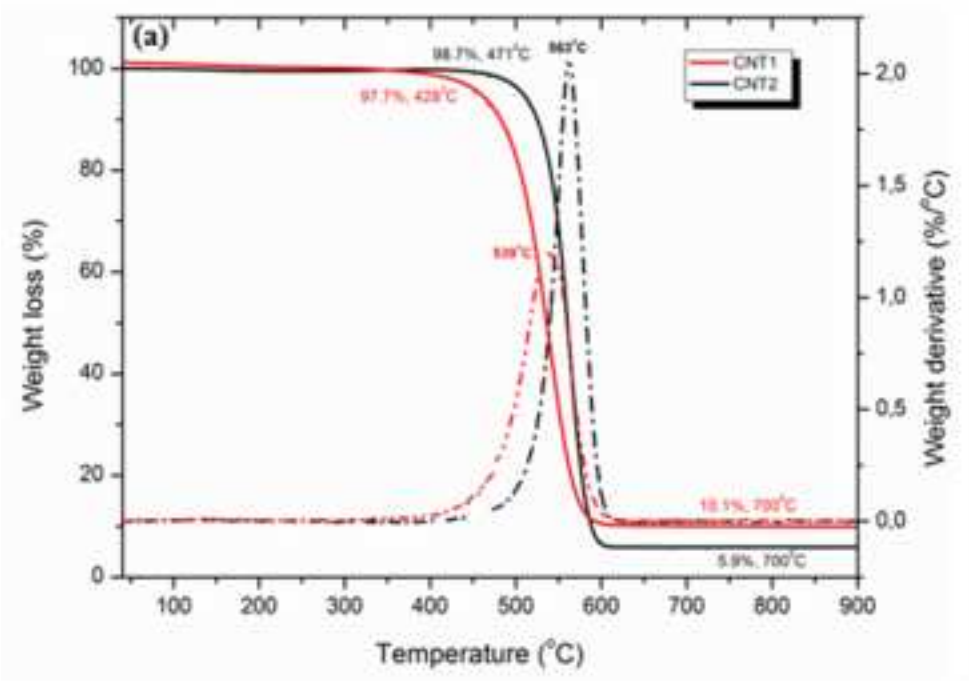

(a)
Furnace
Silicon substrate
Nitrogen
Exhaust
Furnace
Camphor + Ferrocene
Heater
Quartz tube
(b)
Furnace
Aluminum boat loaded with catalyst
Nitrogen
Exhaust
Acetylene
Furnace
Quartz tube

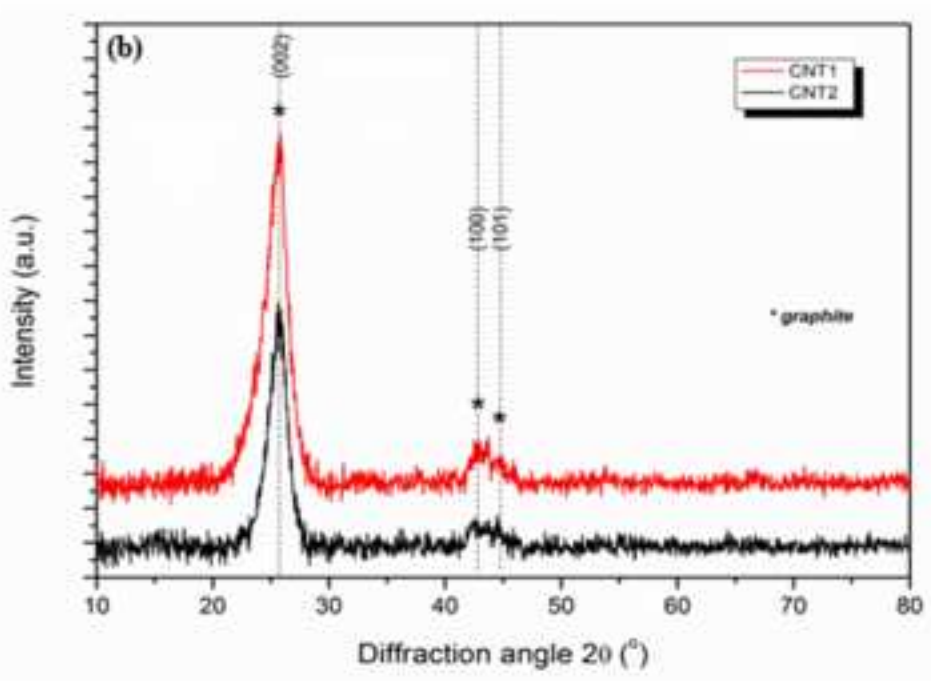
**(a)**

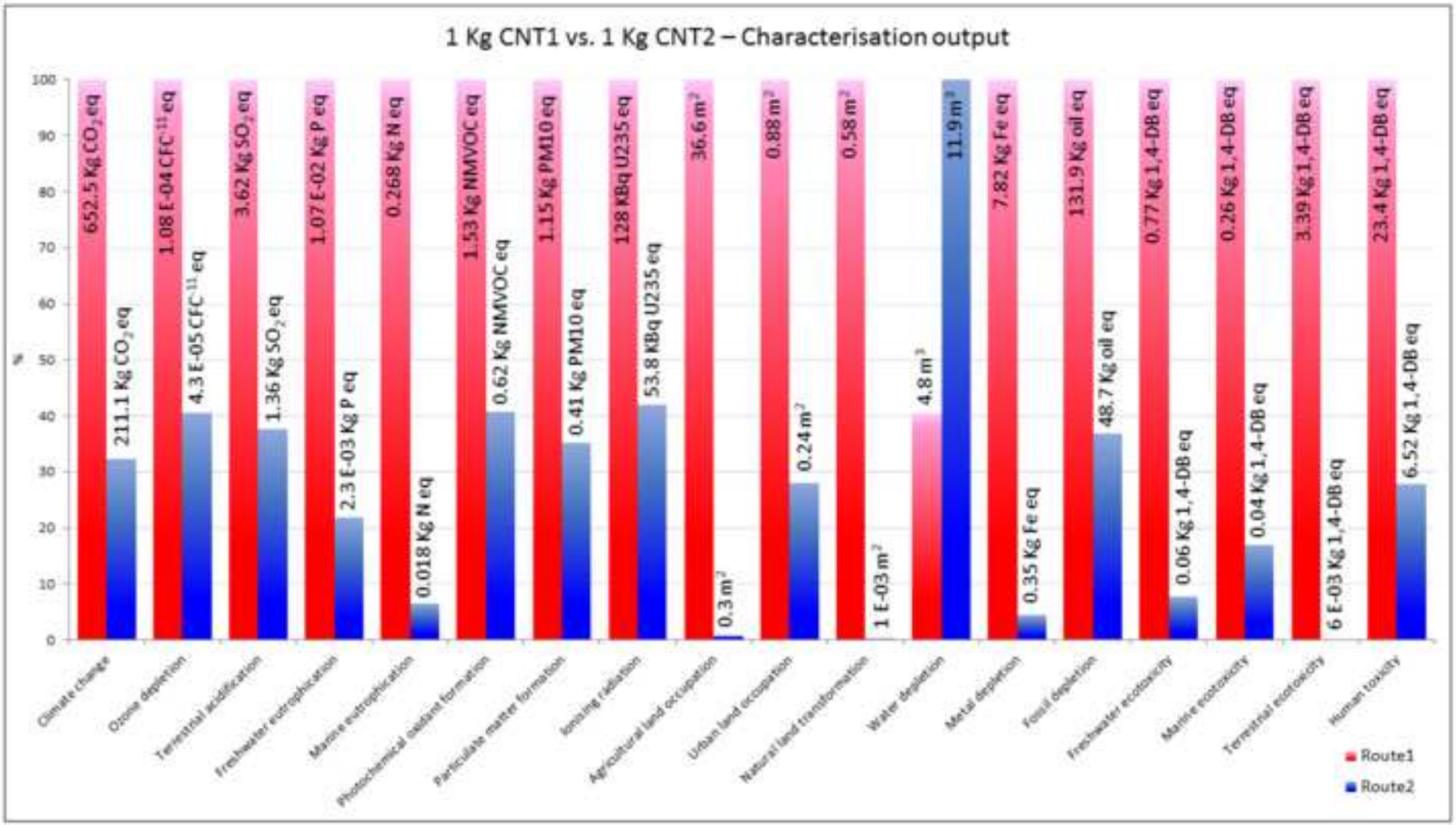

$N_2$ (Carrier gas)
FI
$C_2H_2$ (Carbon source)
FI
$Fe_2O_3$/zeolite (Catalyst)
INPUTS
Exhaust Emissions (Un-reacted carbon source, carbon soot, VOCs, PAHs, $N_2$)
OUTPUTS
T-CVD reactor
EI
Electricity Use (EU-27 Energy Mix)
1Kg Entangled MWCNTs (Functional Unit)
CNT disposal
Outside the system boundaries

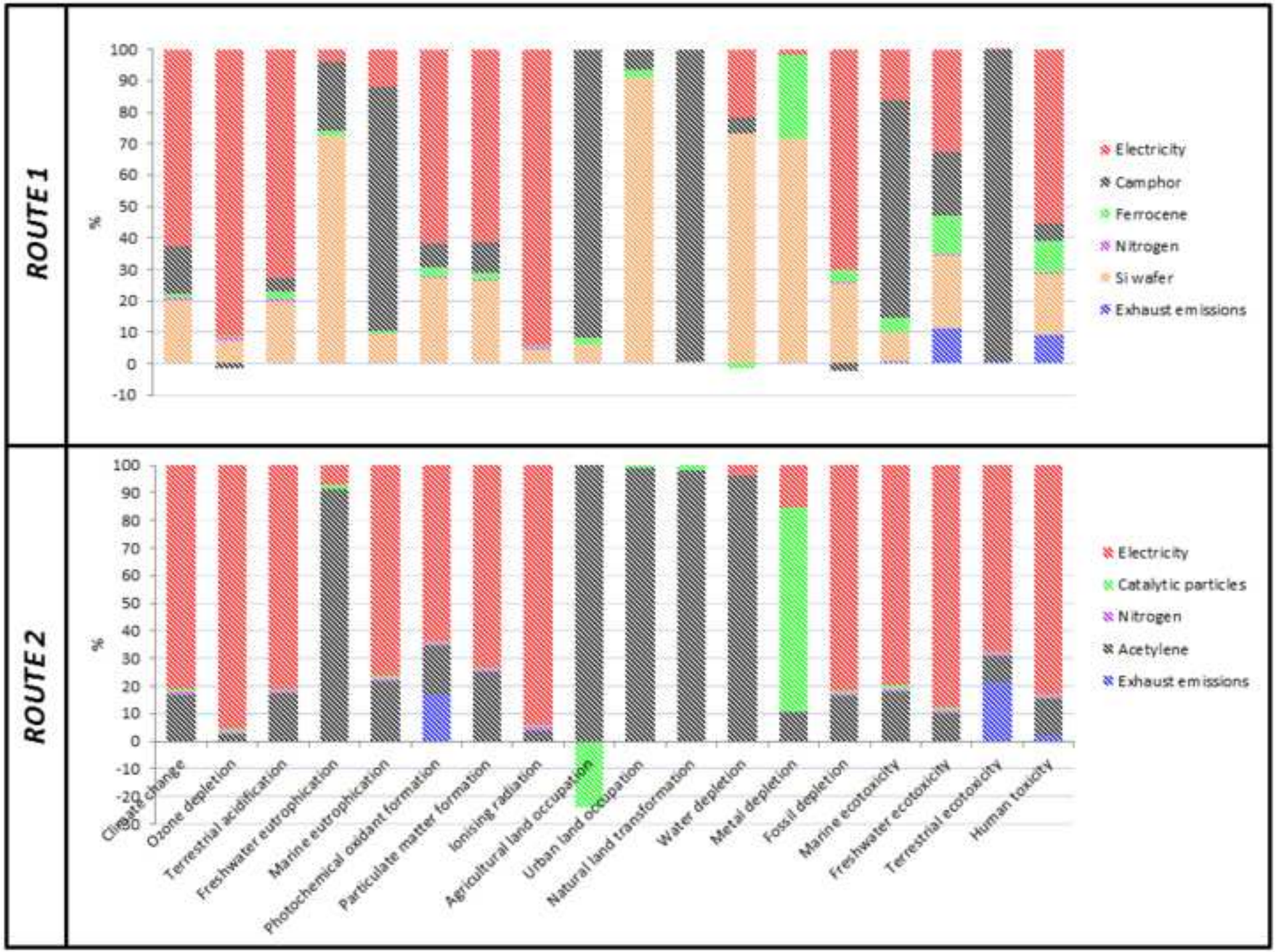

(b)
* Extraction from camphor tree leaves by steam distillation process (palm oil as proxy)
** Data retrieved from Cordes (1965) (Simulation of the ferrocene synthesis process using Aspen Plus software)
Exhaust Emissions (Un-reacted carbon source, carbon soot, VOCs, PAHs, $N_2$)
OUTPUTS
$N_2$ (Carrier gas)
FI
T-CVD reactor
Si wafer
1Kg VA(MWCNTs) (Functional Unit)
EI
CNT disposal
Outside the system boundaries
INPUTS
Camphor* (Carbon source) & Ferrocene** (Catalyst)
EI
Electricity Use (EU-27 Energy Mix)

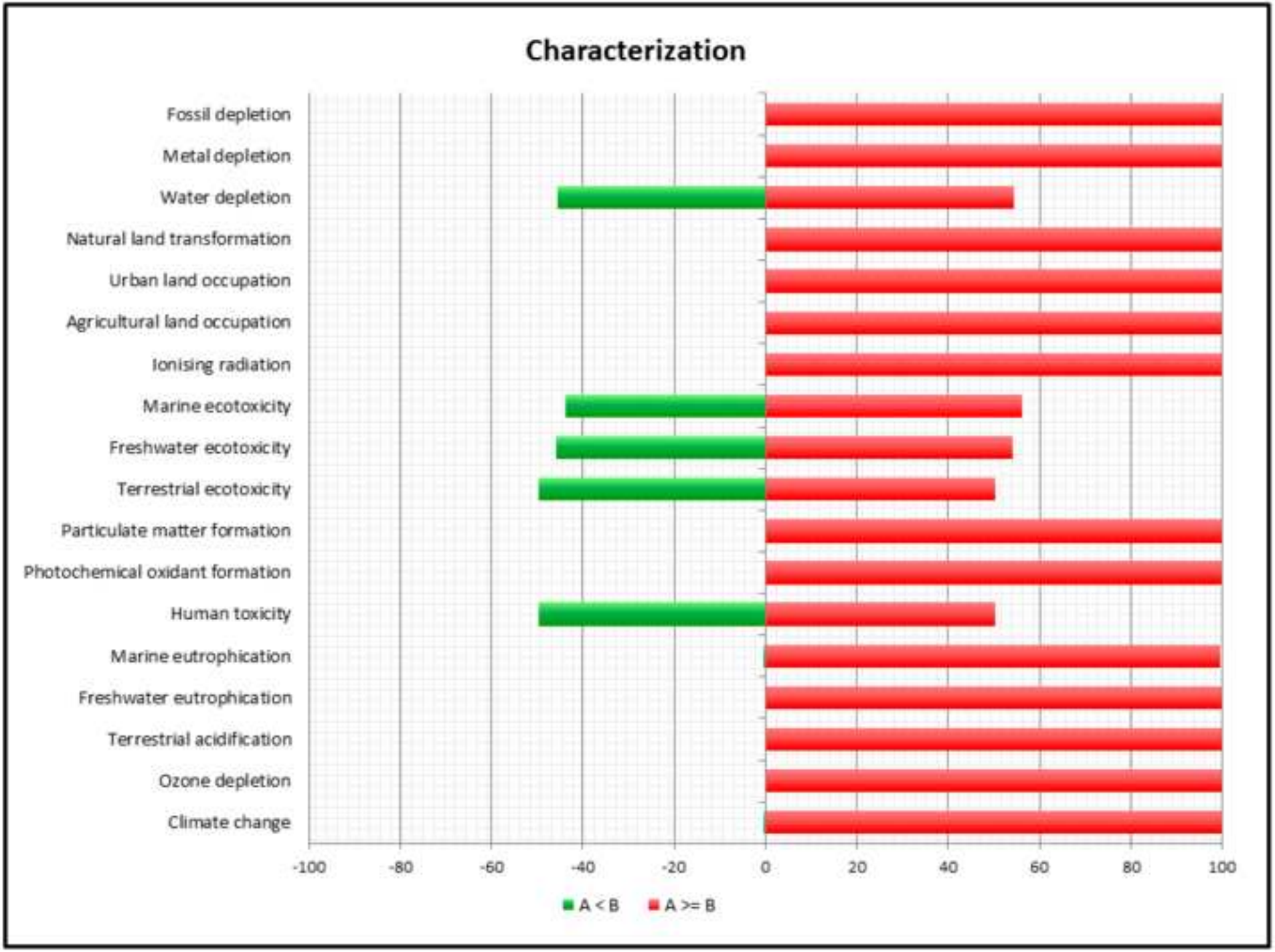

(a)
det HV WD mag spot tilt Landing E
ETD 10.0 kV 5.7 mm 150 x 3.0 0 ° 10.0 keV
500 µm
NTUA
(b)
det HV WD mag spot Landing E tilt
TLD 10.0 kV 4.8 mm 20 000 x 3.0 10.0 keV 0 °
4 µm
NTUA
(c)
50 nm
(d)
50 nm


(a)
98.7%, 471°C
562°C
97.7%, 428°C
539°C
10.1%, 700°C
5.9%, 700°C
CNT1
CNT2
Weight loss (%)
Weight derivative (%/°C)
Temperature (°C)


(b)
(002)
(100)
(101)
CNT1
CNT2
* graphite
Intensity (a.u.)
Diffraction angle 2θ (°)


1 Kg CNT1 vs. 1 Kg CNT2 – Characterisation output
%
100
90
80
70
60
50
40
30
20
10
0
652.5 Kg CO2 eq
211.1 Kg CO2 eq
1.08 E-04 CFC-11 eq
4.3 E-05 CFC-11 eq
3.62 Kg SO2 eq
1.36 Kg SO2 eq
1.07 E-02 Kg P eq
2.3 E-03 Kg P eq
0.268 Kg N eq
0.018 Kg N eq
1.53 Kg NMVOC eq
0.62 Kg NMVOC eq
1.15 Kg PM10 eq
0.41 Kg PM10 eq
128 KBq U235 eq
53.8 KBq U235 eq
36.6 m2
0.3 m2
0.88 m2
0.24 m2
0.58 m2
1 E-03 m2
4.8 m3
11.9 m3
7.82 Kg Fe eq
0.35 Kg Fe eq
131.9 Kg oil eq
48.7 Kg oil eq
0.77 Kg 1,4-DB eq
0.06 Kg 1,4-DB eq
0.26 Kg 1,4-DB eq
0.04 Kg 1,4-DB eq
3.39 Kg 1,4-DB eq
6 E-03 Kg 1,4-DB eq
23.4 Kg 1,4-DB eq
6.52 Kg 1,4-DB eq
Climate change
Ozone depletion
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Photochemical oxidant formation
Particulate matter formation
Ionising radiation
Agricultural land occupation
Urban land occupation
Natural land transformation
Water depletion
Metal depletion
Fossil depletion
Freshwater ecotoxicity
Marine ecotoxicity
Terrestrial ecotoxicity
Human toxicity
Route1
Route2


ROUTE 1
%
100
90
80
70
60
50
40
30
20
10
0
-10
Electricity
Camphor
Ferrocene
Nitrogen
Si wafer
Exhaust emissions
ROUTE 2
%
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
Climate change
Ozone depletion
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Photochemical oxidant formation
Particulate matter formation
Ionising radiation
Agricultural land occupation
Urban land occupation
Natural land transformation
Water depletion
Metal depletion
Fossil depletion
Marine ecotoxicity
Freshwater ecotoxicity
Terrestrial ecotoxicity
Human toxicity
Electricity
Catalytic particles
Nitrogen
Acetylene
Exhaust emissions


Characterization
Fossil depletion
Metal depletion
Water depletion
Natural land transformation
Urban land occupation
Agricultural land occupation
Ionising radiation
Marine ecotoxicity
Freshwater ecotoxicity
Terrestrial ecotoxicity
Particulate matter formation
Photochemical oxidant formation
Human toxicity
Marine eutrophication
Freshwater eutrophication
Terrestrial acidification
Ozone depletion
Climate change
-100
-80
-60
-40
-20
0
20
40
60
80
100
A < B
A >= B

| Synthesis process per 4.5 g of CNT1 | Quantities | Comments/ Assumptions |
|---|---|---|
| ***Input*** | | |
| Camphor | 100 g | Camphor as Palm oil |
| Ferrocene as catalyst | 5 g | (Griffiths et al., 2013) |
| Silicon wafer as substrate | 30 $cm^2$ | - |
| Nitrogen as carrier gas | 175.7 g | Pre-heating: 1 hr x 230 mL/min<br>Reaction: 2 hrs x 400 mL/min<br>Cooling: 5 hrs x 230 mL/min |
| Electricity input (EU-27) | 3.1 kWh | Pre-heating (1 hr, 0 – 850 $^oC$) &<br>Reaction (2 hrs, 850 $^oC$): 2.4 kWh<br>Reactant mixture evaporation (2.5 hrs, 250 $^oC$): 0.9 kWh |
| ***Output*** | | |
| Nitrogen as carrier gas | 175.7 g | Mass balance |
| Camphor | 50 g | Un-reacted camphor (50%) |
| VOCs | 40 g | By-products (~40%) |
| PAHs | 0.5 g | By-products (~0.5%) |
| Soot | 10 g | By-products (~9.5%) |

| Synthesis process per 7.5 g of CNT2 | Quantities | Comments/ Assumptions |
|---|---|---|
| ***Input*** | | |
| Catalytic particles | 0.220 g | As modelled by the process below |
| Acetylene as carbon source | 18.4 g | Reaction: 4 hr x 70mL/min |
| Nitrogen as carrier gas | 160.8 g | Pre-heating: 1 hr x 230 mL/min<br>Reaction: 4 hrs x 230 mL/min<br>Cooling: 5 hrs x 230 mL/min |
| Electricity input (EU-27) | 2.3 kWh | Pre-heating: 1 hr (0 – 700 $^{o}$C)<br>Reaction: 4 hrs (700 $^{o}$C) |
| ***Output*** | | |
| Nitrogen as carrier gas | 160.8 g | Mass balance |
| Acetylene | 5.45 g | Un-reacted acetylene (50%) |
| VOC | 4 g | By-products (~40%) |
| PAH | 0.05 g | By-products (~0.5%) |
| Soot | 1 g | By-products (~9.5%) |
| **Synthesis process per 10g of catalytic particles (20% wt. iron)** | **Quantities** | **Comments/ Assumptions** |
| ***Input*** | | |
| Iron III chloride, 40% in water | 54.12 g | Equivalent with 18.0 g Iron III Nitrate non-anhydrate (40% in water) |
| Zeolite as supporting material | 10 g | - |
| Deionized water | 100 g | - |
| Nitrogen | 126 g | Pre-heating: 1 hr x 300 mL/min<br>Calcination: 1hrs x 300 mL/min<br>Cooling: 4 hrs x 300 mL/min |
| Electricity input (EU-27) | 0.9 kWh | Stirring (12 hrs): 0.18 kWh<br>Drying (4 hr, 120 $^{o}$C): 0.24 kWh<br>Calcination (1hr, 120 $^{o}$C): 0.48 kWh |
| ***Output*** | | |
| Nitrogen | 126 g | Mass balance |

| Code | Geometrical characteristics | | | Purity | | |
|---|---|---|---|---|---|---|
| | Outer diameter (nm) | Inner diameter (nm) | Length (μm) | Metal content (%) | Amorphous carbon (%) | Overall (%) |
| CNT1 | 60 – 80 | 10 – 13 | >100 | 10.1 | 2.3 | 87.6 |
| CNT2 | 20 – 40 | 12 – 16 | >10 | 5.9 | 1.3 | 92.8 |

| Code | Productivity per batch (g) | Carbon yield ($g_{carbon\ product}/g_{catalyst}$) | Carbon conversion (%) |
|---|---|---|---|
| ROUTE 1 | 4 – 5 | 0.8 – 1 | 5 – 7 |
| ROUTE 2 | 6 – 9 | 30 – 40 | >50 |

**Highlights**

- Lab-optimised CNT synthesis via chemical vapour deposition.
- Evaluation of material quality and productivity assessment.
- Comparative environmental impact assessment of two CNT synthesis alternatives.
- Uncertainty and sensitivity analysis to assess consistency of LCA results.
- Highlight tradeoffs pertinent to decision making.