

# Energy Requirements of Carbon Nanoparticle Production

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## Summary

Energy requirements for fullerene and nanotube synthesis are calculated from literature data and presented for a number of important production processes, including fluidized bed and floating catalyst chemical vapor deposition (CVD), carbon monoxide disproportionation, pyrolysis, laser ablation, and electric arc and solar furnace synthesis. To produce data for strategic forward-looking assessments of the environmental implications of carbon nanoparticles, an attempt is made to balance generality with sufficient detail for individual processes, a trade-off that will likely be inherent in the analysis of many nanotechnologies. Critical energy and production issues are identified, and potential improvements in industrial-scale processes are discussed. Possible interactions with industrial ecosystems are discussed with a view toward integrating synthesis to mitigate the impacts of large-scale carbon nanoparticle manufacture. Carbon nanoparticles are found to be highly energy-intensive materials, on the order of 2 to 100 times more energy-intensive than aluminum, even with idealized production models.

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## Introduction

The discovery of buckminsterfullerene ( $C_{60}$ ) and carbon nanotubes has prompted research into carbon nanoparticles (CNPs) and their possible uses. Unique material properties and the success working with them have led to a host of realized and anticipated applications. In particular, the application of CNPs may result in new technologies for efficient and clean energy conversion, storage, and use, and thus could contribute to climate change mitigation (Baughman et al. 2002; Smalley 2005). Production of CNPs is estimated to have reached 400 tonnes in 2007 (Cientifica 2003)<sup>1</sup>, with rapid growth continuing for some time to come. With the transition of carbon nanotechnology from laboratory research to industrialization, concerns over potential negative environmental impacts have begun to arise. Yet there are many gaps in the information about the positive and negative environmental impacts of carbon nanotechnology.

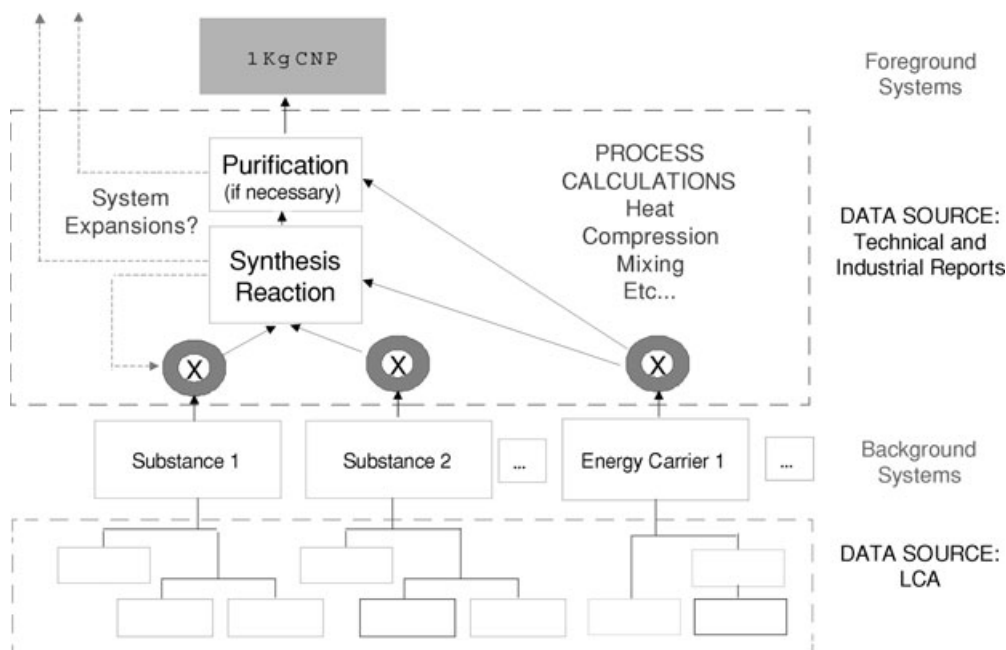
Inventories of energy and material inputs for laboratory-scale processes are available (Isaacs et al. 2006). The results may not be representative

of future large-scale production systems, however. We describe the systems for producing CNPs and estimate the cumulative energy requirements (CERs) for scaling current production processes to produce bulk quantities of CNPs. The results can be used to evaluate the energy implications from using CNPs in future applications. We also discuss important production issues and assess the potential for ameliorating them with large-scale production.

## Method and Scope

### *Modeling the Energy Requirements of Future Production Systems*

Energy analysis is used to quantify the CERs for a given product's life cycle (Boustead and Hancock 1979). We use a cradle-to-gate perspective, including all energy flows up to the production and purification of CNPs (figure 1). The use and end-of-life phases are not considered. Energy or material flows required to construct or maintain capital infrastructure are not considered. All calculations are made for a functional unit of 1 kilogram<sup>2</sup> (kg) of the carbon



**Figure 1** General system overview of the production and purification of carbon nanoparticles. CNP = carbon nanoparticle; LCA = life cycle analysis.

nanoparticle under consideration, but this does not imply that the produced materials are 100% pure or that they are comparable in function.

System models are built for several production systems. Each system model is divided into a foreground system, which is described and analyzed in more detail, and several background systems for various inputs and outputs (Baumann and Tillman 2004). For each foreground system, process mass flows are calculated on the basis of efficiencies and stoichiometry provided in technical reports. Efficiencies for achieving specified reaction conditions at industrial levels are assumed to be the same as those for comparable industrial processes or are calculated at a minimum basis (i.e., change in free energy) for processes for which efficiency data do not exist. For chemical reactions involving the nanoparticles, their free energy was approximated as graphite. Calculating the true free energy of carbon nanotubes relative to graphite is not trivial, but a starting point could be 25 kilojoules per mole<sup>3</sup> (kJ/mol) bound in the surface (Abrahamson 1973). Achieving these efficiencies would require large flows and an emphasis on attaining high efficiencies. Only a few of the synthesis methods studied are currently employed at levels that could validate this assumption, and using it to describe low-flow-rate processes could lead to very different results than a standard inventory. The stoichiometry for processes is a critical factor in determining the final energy balance.

Several production systems and possible efficiency improvements are discussed. Baseline and efficient foreground systems are considered for each process. Yield per unit feedstock versus yield per unit time appears to be an inherent trade-off in production systems. Baseline cases use stoichiometry data from reports containing the highest yields per unit time, whereas efficient cases use stoichiometry data from reports containing the highest feedstock yields, with the assumption that high efficiencies can be obtained at higher throughput.

The background systems include the basic material and energy inputs used in producing CNPs. Cradle-to-gate data for background inputs were obtained or calculated as noted in the disaggregated tables. For inputs for which life cycle data were not available, process flows were estimated

on the basis of available process data. Transportation of inputs was not included due to the uncertain final location of CNP production facilities. In most cases, transportation would add marginally to the CER, but it could be significant for some systems, particularly after high process efficiencies are achieved. System expansion is used to indicate potential synergies with other industries in the form of "credits" to useful by-products where applicable.

### **Energy Forms and Conversion Factors**

Energy enters the production processes in many forms: thermal, chemical, electrical, and, in one case, solar energy. Conversion factors are applied to each energy input to obtain equivalent primary energy values. Due to the global nature of the nascent nanotechnology industry, it is difficult to establish a single conversion factor for electricity. Prospective studies require a transparent and flexible treatment of conversion factors (Rydh and Sandén 2005). Thus, thermal and feedstock energy are quantified separate from electricity, in units of megajoules of thermal energy ( $\text{MJ}_{\text{th}}$ ) and megajoules of electrical energy ( $\text{MJ}_e$ ).

The energy content of chemical feedstocks is taken as their gross calorific value, higher heating value (HHV), or combustion enthalpy. The choice of HHV is not without controversy but is defended on the basis that many of the reactants would otherwise be used to drive electricity generation processes or serve as a refining feedstock. Similarly, system expansions involving the combustion of by-products or utilizing the ultimate recoverable heat also benefit from using HHVs. Last, separating feedstock from fuels supports technical substitution discussions; electricity can produce heat for, but cannot supply carbon to, a reaction.

### **Selected Production Systems**

Distinguishing between bulk and controlled CNP applications is particularly relevant to energy analysis. As applications become more specialized and complex, defining and allocating flows becomes more difficult, the appropriate functional units may change, and a CNP energy

analysis progressively loses relevance. For example, the “usefulness” in the case of a microprocessor is correlated more to its internal organization than to an aggregate parameter, such as mass; a billion transistors linked randomly would take as much process energy as a functional microchip to create while still having the same mass. The analyses of production systems are therefore limited to processes that produce CNPs for bulk applications and for which mass is the appropriate unit of output.

There is some ambiguity in CNP naming. Here, *fullerene* is used for spherical cage configurations, and *nanotube* is used for cylindrical configurations. Fullerenes come in many sizes (allotropes), from  $C_{20}$  to configurations with hundreds of carbon atoms. The most frequently encountered fullerenes have 60 or 70 carbon atoms.  $C_{60}$  is the smallest fullerene in which it is possible for no two pentagons to share an edge and is the most common in nature. Nanotubes with only one layer of graphene are called single-walled nanotubes (SWNTs). Nanotubes with more than one graphene shell are called multiwalled carbon nanotubes (MWNTs). Other structures exist, such as nanohorns, nanotoruses, and nano-onions, but these have little application so far.

### **Selected Synthesis Methods**

Typical synthesis of CNPs renders carbon atomically reactive and deposits it under controlled circumstances. With current technology, there will be other impurities. One can assume, however, that the general types of CNPs (SWNT, MWNT,  $C_{60}$ , etc.) present in the output mixture can be selected with high precision and with generally increasing control over particular sub-attributes. The important considerations in mass synthesis are product quality, purification requirements, and the rate at which the reaction can produce material.

Production methods can be sorted into two categories based on the type of carbon feedstock: methods that decompose a liquid or gaseous feedstock to obtain the atomic carbon, and methods that vaporize a pure carbon source into high-temperature plasma.

Gaseous or liquid feedstocks, such as hydrocarbons or carbon monoxide, are used in most large-scale synthesis of CNPs. Continuous processes, such as fluidized bed chemical vapor deposition (CVD) or high-pressure carbon monoxide (HiPco) disproportionation, 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 easily be scaled up; feedstocks are readily available; they operate at far lower temperatures than carbon-vaporizing techniques, greatly reducing energy consumption; and they can operate at atmospheric pressure or higher, simplifying industrial design. Static substrate processes are a different type of production that will continue to have applications because they produce CNPs for different application requirements. For example, CVD onto a sheet patterned with catalyst can produce highly ordered and accurately placed nanotubes.

Pyrolytic processes decomposing hydrocarbons, such as benzene or toluene, are used to create most  $C_{60}$  (Takehara et al. 2005). Despite very low yields, they are comparatively simple to implement, and scaling them up is a matter of increasing fuel flow. Small fullerenes, such as  $C_{60}$  and  $C_{70}$ , have few or no degrees of freedom in their structure and therefore are not as sensitive to reaction conditions as are nanotubes. Additionally, small fullerenes cannot be synthesized easily through CVD methods, and thus pyrolytic processes are the only naturally scalable methods for creating them.

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 vaporization, but other techniques are being investigated. One interesting development is the use of solar furnaces to provide the vaporization energy (Guillard et al. 2002). As it uses solar energy, the power for such a system is, to a large degree, “free.” Additionally, there are fewer problems scaling the power input to the system. A 50 kilowatt (kW) unit has been demonstrated to produce 10 to 25 grams per hour (g/h)<sup>4</sup> of nanotubes, with a 250 kW scale-up demonstration planned.

### Purification Processes

All synthesis methods typically produce unwanted impurities. These can include the various types of CNPs as well as amorphous carbon, graphite, and metal catalyst. Purities of 90% for nanotubes and 95% for C<sub>60</sub> and other fullerenes are assumed. Some synthesis methods are capable of synthesizing material close to or above this quality, but most require purification. Higher grades of material are attainable through both controlled synthesis and progressively more elaborate purification measures.

Depending on the specific synthesis method, different purification procedures are considered for obtaining an equivalent purity. Each purification step is modeled as a process requiring energy and material input and yielding an amount of recoverable material. An overview of processes can be found in the work by Veld and colleagues (2003), with examples in work by Fan and colleagues (2006), Takehara and colleagues (2005), or Wang and colleagues (2002). For each process considered, the functional unit is taken to be 1 kg of the specific particle, but that kilogram will also be accompanied by additional impurities. Higher levels of purity are available through destructive processing or by high-temperature vacuum annealing techniques. The generic process assumed here is a hydrochloric or nitric acid wash with a commercial, electrically driven ultrasonic stirrer. A 90% material recovery is assumed.

### Energy Requirements of CNP Production Systems

All processes considered, as well as the critical energy drivers, are briefly described below. Results for the baseline and efficient case are presented in table 1.

#### Fluidized Bed CVD

Fluidized bed methods are some of the most productive ways of making nanotubes. The specific process considered decomposes a methane feedstock in a nitrogen atmosphere in a fluidized bed of fine magnesium oxide (MgO) dust seeded with an iron nanoparticle catalyst (figure 2). The process results in a fluff of relatively high-purity

SWNTs surrounding the catalyst base material and is well described in literature, along with many variants, such as using alumina powder as a catalyst support or using differing catalyst particles or other hydrocarbon gases as the feedstock (Corrias et al. 2003). The continuous process considered here was demonstrated in 2006 and is expected to produce multitonne quantities of SWNTs at far lower costs than previously achieved (Setoguchi et al. 2006). A similar process has been studied for producing hydrogen as well as nanotubes (Spath et al. 2002).

The modeled reaction occurs at 1 atmosphere and roughly 800°C (Setoguchi et al. 2006). Current technology can achieve carbon yields in excess of 80% in very slow reactions, but a more realistic estimate for bulk production is 25% to 30% of the carbon being deposited on the substrate in a single pass (Spath et al. 2002). Over 80% of the deposited carbon is a SWNT mixture that is removed continuously with the catalyst bed. The relatively large catalyst bed particles are removed from the nanotubes with acid treatment. The model assumes an output of 10% amorphous carbon, 10% catalyst particles, and 80% SWNTs after removal from the catalyst support. This is followed by a hydrochloric acid wash and ultrasonication to yield 90% pure SWNTs.

#### Critical Factors Affecting Energy Requirements

Approximately 80% of the energy requirement is for producing the catalyst support and the acid used to dissolve it later (table 2). This assumes the nanotubes and catalyst cannot be physically detached from the catalyst support, whereas separation may be possible with some support and catalyst combinations (Wang et al. 2002). The deposition of the catalyst material on the support is a proprietary process. The catalyst is essentially iron (with other metals in some cases) and makes up a small percentage of the overall catalyst bed weight. In this case, the catalyst is not included in the calculation.

Reducing the amount of catalyst and catalyst bed used in the reactor reduces the process energy requirements unless it corresponds with a reduction in yield, and even then may still reduce the net energy balance because the catalyst and catalyst bed are large material flows. The catalyst

**Table 1** Cumulative energy requirements of the different processes

Process	Feedstock	Product	Example Aspect Ratio	Structural Quality	Baseline <sup>a</sup>		Efficient <sup>d</sup>	
					Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)
Fluidized bed CVD	Gas (CH <sub>4</sub> )	SWNT	1,000	Low-medium	328	626	327 or 93 <sup>b</sup>	525 or 220 <sup>b</sup>
Floating catalyst CVD	Gas (benzene)	MWNT	1,000	Low-medium	295	187	65 <sup>c</sup>	67 <sup>c</sup>
HiPco	Gas (CO)	SWNT	10 <sup>6</sup>	High	47	5,769	-	-
Pyrolysis	Toluene	C <sub>60</sub> , C <sub>70</sub>	-	-	6,341	749	5,412	538
Electric arc	Graphite	MWNT, SWNT	10 <sup>8</sup>	High	300	2,178	75	2,178
Laser ablation	Graphite	MWNT, SWNT	10 <sup>7</sup>	High	211	9,424	61	1,600
						(6,200) <sup>d</sup>		(6,200) <sup>d</sup>
Solar furnace	Graphite	MWNT	10 <sup>5</sup>	High	300	142	72	142

Note: MJ<sub>th</sub> = megajoules of thermal energy per kilogram; MJ<sub>e</sub> = megajoules of electrical energy per kilogram; CVD = chemical vapor deposition; HiPco = high-pressure carbon monoxide; SWNT = single-walled nanotube; MWNT multiwalled nanotube.

<sup>a</sup>For details in the baseline case, see tables 2 and 3. For alternative assumptions in the efficient case, see the text.

<sup>b</sup>Two different technical improvements are considered; the higher numbers represent a nitrogen-free atmosphere, and the lower numbers represent a product-to-catalyst ratio of 10 instead of 2.

<sup>c</sup>Some confidential discussions with industrial producers indicate that continuous floating catalyst synthesis may have reached this efficiency (Ocr 2007).

<sup>d</sup>This value is the “wasted” electric potential of using such a thermal system and represents an opportunity cost for using heat from concentrated solar energy to produce nanomaterial. An alternative value is zero. The second number is electricity used in other stages of production.

loading onto the bed particles is usually about 2% by weight for MgO beds (Wang et al. 2003), which gives a product-to-catalyst yield ratio of 2. Other researchers using fluidized bed reactors have obtained a product-to-catalyst ratio of 10 or more (Li et al. 2005), but at lower reaction rates, which indicates a potential trade-off between efficiency and production throughput. This higher yield ratio is reflected in one of the efficient cases for this process.

The outgoing catalyst support and acid mixture are assumed not to be recyclable because of special preparation conditions. In the *System Expansions* section below, other uses are detailed. Beyond these uses, there is new technology for industrial-scale renewal of hydrochloric acid. This could increase system efficiency by removing roughly half the energy requirement for the acid-catalyst system without requiring integration with metal industries.

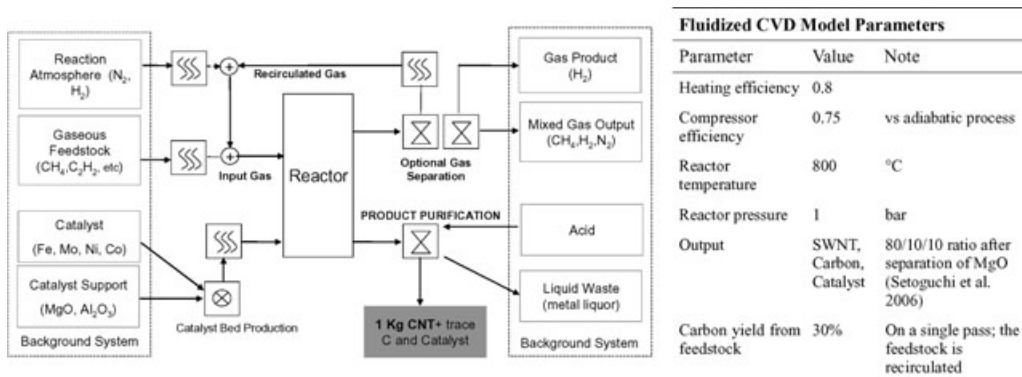
Due to the high throughput of catalyst, transportation could become important, especially given that precursors, such as MgO, could come from far away. For example, taking a bulk transport energy requirement of 0.5 MJ<sub>th</sub> per tonne-kilometer, which is between the energy requirement of 0.7 MJ<sub>th</sub> per tonne-kilometer for a large truck and the requirement of 0.24 MJ<sub>th</sub> per ton-kilometer for a large ship (Baumann and Tillman 2004), would add 1 MJ<sub>th</sub> for every 100 kilometers of transport in the catalyst background system.

If we disregard its impact on product quality, the choice of hydrocarbon has a small effect on the final energy balance. Likewise, the actual carbon yield achieved has a surprisingly small effect on the energy balance until it reaches a certain threshold; lowering it increases the flow and heating energy but simultaneously increases the energy content of the gaseous fraction of the system output.

Using as little nitrogen as possible is optimal for lowering the energy balance. Some variations have used pure hydrocarbon atmospheres (Veld et al. 2003), which give other possibilities for system expansion. Separating the nitrogen used and recirculating the gas does not affect the amount of heating required but is performed 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. Discussions with industrial producers after the initial writing of this article indicate that the highly purified reaction atmospheres and feedstocks are now recirculated in advanced large-scale processes (Nanocyl 2007).

### System Expansions

Fluidized bed reactors have a large number of possible interactions. 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. A major share of the energy use



**Figure 2** Fluidized bed chemical vapor deposition (CVD) model. CNT = carbon nanotube; SWNT = single-walled nanotube.

**Table 2** Energy requirements of gaseous feedstock production processes (baseline case)

Subprocess	FBCVD		Floating catalyst CVD		HiPco		Pyrolysis	
	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)
Net feedstock <sup>a</sup>	51	0	295	22	47	0	6,211	133
Catalyst bed production <sup>b</sup>	229	27	-	-	-	-	-	-
Acid production <sup>a</sup>	48	438	0.5	2	-	-	-	-
Gas purification <sup>c</sup>	0	55	-	-	-	-	0	506
Process heating <sup>d</sup>	0	68	0	114	0	2,161	-	-
Compression <sup>e</sup>	-	-	-	-	0	3,608	0	72
Purification processes <sup>f</sup>	0	38	0	50	-	-	130	38
<b>Total</b>	<b>328</b>	<b>626</b>	<b>295</b>	<b>187</b>	<b>47</b>	<b>5,769</b>	<b>6,341</b>	<b>749</b>

Note: MJ<sub>th</sub> = megajoules of thermal energy per kilogram; MJ<sub>e</sub> = megajoules of electrical energy per kilogram; FBCVD = fluidized bed chemical vapor deposition; CVD = chemical vapor deposition; HiPco = high-pressure carbon monoxide.

<sup>a</sup>Plastics Europe (2006) life cycle inventory (LCI) data were used for the methane, benzene, carbon monoxide, toluene, and hydrochloric acid inputs.

<sup>b</sup>MgO was calculated by us from Commonwealth Science and Industrial Research Organisation (Australia) data available online for the flow rate in work by Setoguchi and colleagues (2006). Production of the catalyst itself is ignored but represents less than 2% by mass (Wang et al. 2003). See also the work by Kushnir (2007).

<sup>c</sup>We calculated these values as if they were attained by an idealized pressure swing adsorption process at 75% efficiency versus an adiabatic process.

<sup>d</sup>Process heating is all assumed to be electric, with the stated efficiencies for the baseline case. In the efficient case, some thermal energy is assumed to be recovered and used to preheat input flows with an electric "top up."

<sup>e</sup>Values were calculated for each compressed gas flow as an adiabatic compression with the stated (75%) compressor efficiency. For pyrolysis, this is the energy used to operate the vacuum pump for the period of time required to produce 1 kg of c60 (400 W/ high-temperature multistage rotary vane).

<sup>f</sup>The values for purification are calculated from electricity required to run the equipment (i.e., ultrasonic stirrer) described in the process articles for the time or throughput specified. Other costs, such as acid production and increased requirements of other processes due to material loss, are subsumed into other rows in this table. Our generic nitric acid and ultrasonication purification process model assumes low material losses and a net use of the minimum amount of acid required to dissolve the metal impurities (with perfect reuse of any excess).



not “required” by thermodynamics in fluidized bed reactors is the energy required to create the catalyst support for the catalyst bed and to create the acid used to dissolve it. If physical separation of the nanotube–catalyst complex is possible, then the catalyst support could be reused with only a small energy cost to reimpregnate it. Because magnesium and aluminum oxides are precursors in their respective metal production systems, the support could interact with the metal production chain. Hence, the energy to produce the precursor directly would no longer be required, and the net use of acid would be avoided. This system expansion could be carried on until the amount of magnesium chloride ( $\text{MgCl}_2$ ) produced approached 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 catalyst levels described for the fluidized bed reactor model, or 100 kilotons with the more efficient technologies, still three orders of magnitude higher than current production. The need for colocation and transportation seems to render this interaction uneconomic, however.

Other possibilities for the feedstock background system will arise if designs using hydrogen instead of nitrogen, or only pure hydrocarbons, as the input feedstock come into industrial use. The reactor would then resemble a methane reformer, and further gains over simply separating the hydrogen could be achieved. Placing the reactor before the methane reformer could result in a number of system topographies.

Although many such modifications may not be economic, combining contributions from the acid-catalyst system expansion ( $\text{MgCl}_2$  used for metal production) and the simple treatment of gas flow integration discussed above could place efficient case requirements in our model as low as 70  $\text{MJ}_{\text{th}}$  and 61  $\text{MJ}_{\text{e}}$ , energy requirements closer to those of virgin aluminum.<sup>5</sup> This complete set of assumptions represents a scenario in which all outputs are recycled with the maximum achievable efficiency and thus represents a minimal energy requirement for the system. This is not likely to be achieved by this exact process. From a theoretical perspective, the allocation procedure is not indisputable. It can be argued that CNP pro-

duction should bear some of the energy burden of the inputs used. Further, from a consequential perspective, sharing costs between industries could stimulate production and increase total energy use. Nevertheless, the estimates are intended to give a long-term perspective on how the integration of bulk production could eliminate waste streams and reduce energy requirements.

### **Floating Catalyst CVD**

Floating catalyst reactors are commonly used to make mass-produced MWNTs but often have the drawback of producing short nanotubes due to the relatively short residence time (Fan et al. 2006). Production is very similar to the fluidized bed technique, but instead of being deposited on microscopic particles, the catalyst is vaporized and mixed with the feedstock, with all growth happening in the vapor phase. The model is therefore the same as the fluidized bed reactor, with the  $\text{MgO}$  catalyst base excluded. The process chosen (Fan et al. 2006) was designed to maximize time productivity inside a simple apparatus and achieved an output of 6 g/h SWNTs and 20 g/h MWNTs. Modern plants can produce more than 14 kg/h with an unspecified number of reactors (Baughman et al. 2002). The modeled process uses benzene feedstock in a hydrogen atmosphere, and purification is performed with sonication in nitric acid, followed by a hydrochloric acid wash.

The largest energy inputs are the electricity used in the apparatus and purification, followed by the feedstock value of the benzene. At 1 atmosphere, benzene will condense at 80°C, 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, the feedstock value for nanotubes produced in a continuous system is that of the hydrocarbon precursor consumed to make them, as determined by stoichiometric calculation. The single-pass yield will still affect the amount of energy for heating and to separate the gases.

Floating catalyst methods tend to require more purification steps than the fluidized bed methods because of the tendency for the free-floating catalyst particles to become fully encased in graphite. These extra steps may result in more material

losses, which would increase the overall energy consumption beyond what is presented here. They are likely to be higher in actual practice until industrial purification routines exist.

### HiPco Disproportionation

The HiPco process exploits the chemical equilibrium of a carbon monoxide–carbon dioxide system;  $2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$ . It is an entirely gas-phase reaction that produces high-quality nanotubes that potentially require little or no processing. Although time productivity is not high, the process could remain important in the future because of the high-quality material produced. If research on using it to “clone” nanotubes, thus enabling batches of a single chirality, comes to fruition (An and Liu 2005), then it could become an attractive route for applications with such requirements.

Figure 3 shows the HiPco system model. Carbon monoxide is pressurized to 30 atmospheres, heated to 1,000 °C, and fed into the reactor to be mixed with a cold carbon monoxide (CO) stream containing vaporized iron pentacarbonyl as a catalyst. A shift takes place toward the carbon dioxide ( $\text{CO}_2$ ) side of the equilibrium. On 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 removal of the  $\text{CO}_2$  with sodium hydroxide (NaOH). Yields of 97% pure SWNT (3% catalyst metal residue) have been re-

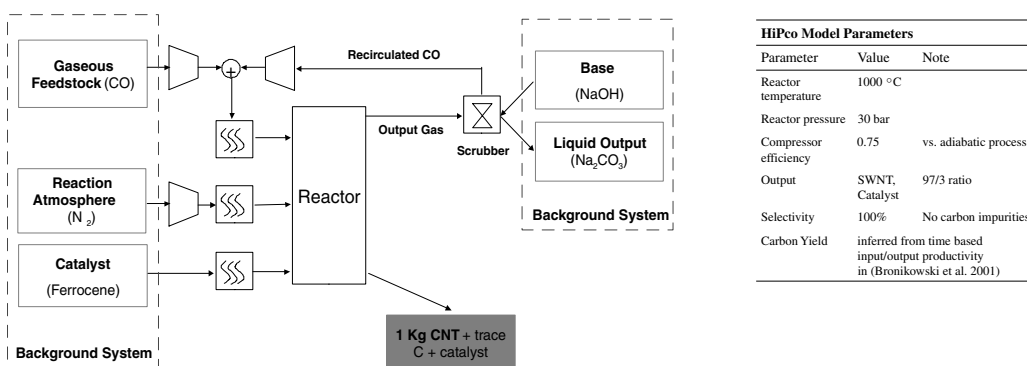
ported at a rate of 450 milligrams per hour (mg/h) (Bronikowski et al. 2001). The patent holder for the HiPco process has claimed that a pilot reactor designed to produce 50 kg/day has been constructed (CNI 2006). Because of the confidential nature of this proprietary process, it is difficult to define reasonable improvements in technical efficiency, and no efficient case is presented.

### Critical Factors Affecting Energy Requirements

Because the carbon monoxide is circulated, the electrical consumption of the heaters and compressors is by far the dominant energy input into the system. This is due to an extremely low carbon yield per pass through the reactor. A total of 1,000 hours are required to produce a kilogram of SWNTs per reactor tube. This inflates the cost of electricity used during the process. The productivity of the system can theoretically increase with more advanced technological measures, such as laser dissociation of the catalyst and better gas mixing topography (Bronikowski et al. 2001).

### System Expansions

The efficiency of HiPco methods can be increased by integration of its gas flow. The requirement for pure CO at high temperature and pressure suggests synthesis gas (mixed carbon monoxide and hydrogen) production or similar processes as being potentially useful. Experiments on HiPco reaction parameters indicate that hydrogen, at even low concentrations, adversely affects



**Figure 3** High-pressure carbon monoxide (HiPco) disproportionation process model. SWNT = single-walled nanotube.

the productivity of the method (Nasibulin et al. 2006). Currently, no existing industry can easily produce carbon monoxide at the temperature and purity required for direct integration, except perhaps the silicon industry.

### Pyrolytic Fullerene Production

Pyrolytic combustion is the dominant method for mass producing  $C_{60}$ . Toluene, benzene, or other aromatic hydrocarbons are burned in conditions that optimize the rate of soot production versus the fullerene content of the soot deposit (figure 4). Despite the low yields, the process has virtually no competitors for producing  $C_{60}$  due to the intrinsic scalability and the relatively simple methods for purifying  $C_{60}$ . Additionally, it can selectively produce a high content of  $C_{70}$  and larger fullerenes, which is difficult to do with electrical arc methods. The process is modeled as toluene and oxygen burned at a ratio of 1.15:1 of total C:O, resulting in 5% of the carbon being deposited as a soot containing 20% fullerenes (Takehara et al. 2005). We assume that 90% is recovered through purification by dissolution in toluene solvent. This reactor netted 25 grams of fullerene per hour. Scaling up production would not require any fundamental change in process or apparatus.

### Critical Factors Affecting Energy Requirements in Pyrolysis

As toluene is burned with a low carbon yield containing very little material of use, a large quantity has to be burned, constituting the main

part of the energy required. Toluene is a product of the petrochemical industry. Consequently, a wide range of process requirements depend on how toluene is valued as a feedstock. Additionally, a major share of the electricity use is for purifying the oxygen used for combusting such a large amount of feedstock.

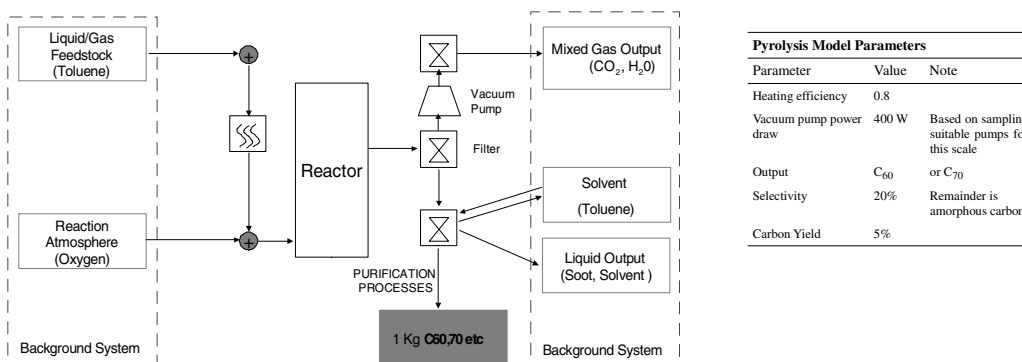
Because the system was optimized for carbon to oxygen content, there is little opportunity for additional optimization in the fuel system. The large quantity of heat that is released during combustion suggests some form of heat exchange as a possible technical improvement, although this would be difficult to extract efficiently because of the low-pressure conditions. The efficient case presented in table 1 assumes that this heat could be used to drive the distillation process in purification.

### System Expansions

The major possible system expansion is to use excess heat in a colocated heat-demanding industry. A facility producing 1 kiloton of  $C_{60}$  per year with the system defined here would produce roughly 250 kW of heat at 1,000°C. This could reduce the thermal energy requirement by more than 70%, from 5,412 MJ<sub>th</sub>/kg to 1,542 MJ<sub>th</sub>/kg in the efficient case.

### Solid Feedstock Production Processes

Processes for synthesizing CNPs from solid feedstock are generally similar from a systems perspective (figure 5). The vaporized carbon material is deposited into an aggregate with a



**Figure 4** Pyrolytic process model.

moderate nanoparticle yield. The aggregates contain similar impurities and thus require similar purification processes, modeled as a quick oxidation of carbon impurities and a quick acid treatment. This treatment is the simplest option, but it tends to damage the product, which could offset some of the inherent quality advantages of solid feedstock processes. An alternative process could be vacuum annealing, which could maintain or improve the quality of the nanotubes with very little material loss. The vacuum pump is considered negligible because the gas flows in a sealed and closed loop.

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. The method can produce any of the main CNP species, can make MWNT without catalyst, and is also capable of producing double-walled nanotubes (DWNTs) selectively. 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).

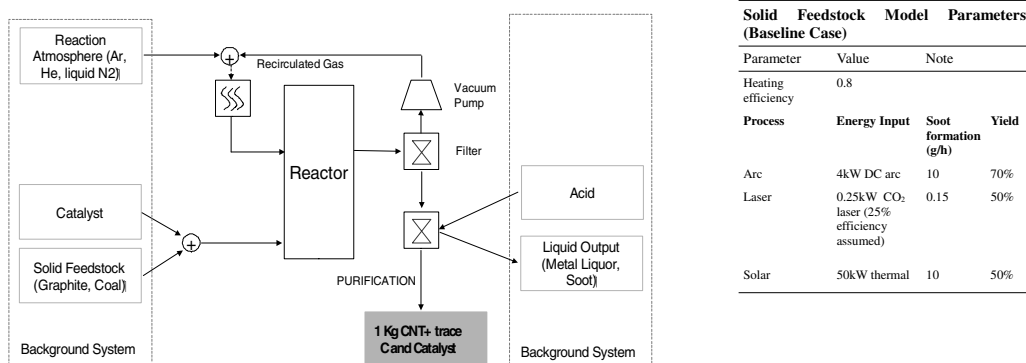
*Laser ablation* processes are similar to arc discharge processes from a systems perspective, except that a laser beam is focused onto the graphite and catalyst target. The energy for the laser comes from electricity. The baseline case is based on continuous CO<sub>2</sub> laser data, and the efficient case is with free electron laser estimates (10 kW, 45 g/h; Veld et al. 2003), with otherwise the same apparatus.

*Solar furnaces* are somewhat similar to the laser method, except the specific energy of the photons cannot be tuned. This leads to a lower productivity; however, 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 50 kW produced 10 g/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.

### Critical Factors Affecting Energy Requirements

The main energy requirements are for electricity used directly as process energy and the primary energy content of the graphite feedstock (table 3). Both factors are dependent on the yield, and thus yield is the most critical variable in the model. Yields are assumed to be 50% for arc and solar and 70% for laser, with 100% of the soot being recovered. 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 by-product is not expected to be reusable as electrode material. Recent successes using coal as an electrode (Qiu et al. 2007) could improve both the feedstock energy requirement and the price. The difference in thermal demand between the baseline and efficient cases is mostly due to an assumed switch to coal feedstock. Maintaining a



**Figure 5** Solid feedstock process model. CNT = carbon nanotube.

heated and inert atmosphere is a significant energy expenditure. Methods that require this could become more efficient if the process is shared between parallel reactors or used in reactors with long continuous duty cycles.

### System Expansions in Solid Feedstock Processes

One trivial system expansion included in the calculation is using the unused carbon as a feedstock for other processes, thereby recovering its feedstock value. Otherwise, the thermal requirements would have been higher.

Another system expansion considered is using the solar thermal reactor to produce electricity instead of nanotubes; the electricity could then be used in a different production scheme. Assuming a thermal-to-electricity conversion of 35%, a solar furnace of power equivalent to the one discussed could produce about 17.5 kW of electricity. Using this electricity in six parallel electric arc reactors of the type described here could produce about 30 g/h nanotubes, indicating that the solar furnace is roughly 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. There is also a reduced cost for not needing electricity in the solar furnace. One could make a cost comparison by assuming that the electricity required for the electric arc process was solar electricity.

## Discussion

For several aspects of CNP synthesis, there is insufficient information for forming general and accurate process requirement estimates. Systemwide material loss has not been considered. The purification model may be an oversimplification. There are many steps in purification, each providing an opportunity for material loss. Furthermore, purification processes may be more difficult to scale than production processes. Catalyst production may become more significant than modeled here. As catalysts are tailored to produce specific effects, the procedures for creating them can become more complex and the requirements more extensive than those for producing iron

**Table 3** Cumulative energy requirements of solid feedstock production processes (baseline case)

Subprocess	Electric arc		Laser ablation		Solar furnace	
	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)	Thermal (MJ <sub>th</sub> /kg)	Electricity (MJ <sub>e</sub> /kg)
Process heating <sup>a</sup>	0	68	0	510	-	-
Net feedstock <sup>b</sup>	294	44	207	38	294	44
Gas purification <sup>c</sup>	0	5	0	5	0	5
Arc/laser/solar input <sup>d</sup>	0	1,968	0	8,790	0	(6,200) <sup>e</sup>
Acid production <sup>a</sup>	6	55	4	44	6	55
Purification processes <sup>a</sup>	0	38	0	38	0	38
<b>Total</b>	<b>300</b>	<b>2,178</b>	<b>210</b>	<b>9,424</b>	<b>300</b>	<b>6,342</b>

<sup>a</sup>See notes to table 2.

<sup>b</sup>We calculated the values for graphite by applying the same methodology used earlier in this article to graphite production from resin precursor. The value arrived at was 144 MJ<sub>th</sub> + 20 MJ<sub>e</sub> per kg high-purity graphite suitable for nanoparticle production (Kushnir, 2007). Small differences in the laser process exist due to different assumed catalyst loading into the input feedstock (Veld et al 2003). Excess recovered soot is assumed to have its feedstock value recovered.

<sup>c</sup>These are the electrical requirements for purifying the inert argon atmosphere cryogenically, with the assumption that 1 kg of gas is recirculated and vented after a 1 kg “batch.” An alternative value could be zero if no gas leaks from the system or is vented.

<sup>d</sup>This is the input power parameter modified by the yield parameters and time productivities (g/h soot produced) taken from work by Veld and colleagues (2003) and Guillard and colleagues (2002). Further modifications are made for assumed loss in purification (10% material loss, as before).

<sup>e</sup>This value is the “wasted” electric potential of using such a thermal system and represents an opportunity cost for using heat from concentrated solar energy to produce nanomaterial. An alternative value is zero.

pentacarbonyl or ferrocene (Das et al. 2006). Omitting transportation underestimates the cumulative energy requirements, which is most significant for the less energy-intensive systems that involve fairly large mass flows for a given output. Many processes have been demonstrated at higher energy efficiencies with lower flow rates, indicating trade-offs between output and efficiency.

The gas-phase process models are somewhat insensitive to carbon yield because of the possibility of continuously recirculating the feedstock. This indicates that the energy requirements for gas-phase processes could remain stable for a number of process chemistries and conditions.

Methods using solid feedstocks are energy intensive because of the amount of energy required to vaporize pure carbon and to maintain a heated, inert, and often low-pressure atmosphere. Furthermore, the feedstock for most processes is normally premanufactured from energy-intensive precursors, such as extremely high-purity graphite, although some researchers have announced the use of purified but ungraphitized 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. For these methods, our results are very sensitive to the rate of production and product selectivity. Production rates per unit of time are generally low and subject to potential physical limitations. Solid feedstock methods do not lend themselves easily to continuous production. Therefore, scaling these methods up may require multiple reactors rather than larger process flows.

Despite these disadvantages, solid feedstock methods provide qualitative improvement in some areas. The very high temperatures favor well-graphitized (with few defects) nanotubes. MWNTs can be synthesized in an electric arc without a catalyst, providing CNPs without metallic impurities. This may be important in applications requiring specific electrical properties. Laser processes 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 et al. 2000), potentially opening a route toward chiral-selective nanotube production, which could enable a host of new electrical and semiconducting applications. Integration with existing industries could reduce some of the energy requirements from a life cycle perspective, but it is not clear when or whether integration will be feasible.

Each CNP application will have its own requirements (e.g., structure and purity). A specific type of MWNT is not necessarily fungible with another, let alone with C<sub>60</sub>. Although floating catalyst MWNTs may be suitable as a low-concentration reinforcer for thermoplastics, they may not possess the requisite properties for other applications. Thus, the results obtained for different processes are not directly comparable but provide insight into the energy requirements for producing CNPs. In general, higher product quality is correlated with increased process energy.

## Conclusions

Baseline cradle-to-gate production energy requirements have been estimated for a number of the most common CNP production processes. To produce data that can be used for strategic, forward-looking assessments, we made an attempt to balance generality with sufficient detail for individual processes. If advanced system expansion is not considered, CNPs are found to be highly energy-intensive materials, on the order of 2 to 100 times more energy intensive than aluminum, given a thermal to electric conversion efficiency of 0.35.

The results are somewhat above the minimum energy requirements (change in free energy, with graphite as a proxy for nanotubes) for carrying out the given chemical reactions and therefore represent a long-term target that may be achievable with process scaling and technical innovation. In the case of floating catalyst processes producing MWNT, innovations such as feedstock recycling, and cogeneration may have occurred. Still, CNPs will remain highly energy-intensive materials to create. This does not imply that the overall life cycle energy requirements for CNPs will always be higher than for other materials. Rather,

application-specific studies that consider the use phase are needed. High energy requirements for production may be counterbalanced by energy-saving properties in some or many applications (Kushnir 2007).

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## Notes

2. One kilogram (kg) is equivalent to 2.2 pounds (lbs.).
3. One kilojoule per mole (kJ/mol) is equivalent to 0.24 kilocalories per mole (kcal/mol).
5. On the basis of work by Sunér (1996), we estimate the corresponding values for aluminum at 65 MJ<sub>th</sub> and 54 MJ<sub>e</sub>.

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