Minimum Exergy Requirements for the Manufacturing of Carbon Nanotubes

Timothy G. Gutowski, John Y. H. Liow, Dusan P. Sekulic

***Abstract*—The purpose of this paper is to address both the high values, and the large variation in reported values for the energy requirements for the production of carbon nanotubes. The paper includes an estimate of the standard chemical exergy for single walled carbon nanotubes, as well as a historical look at how the minimum physical flow exergy improved as the HiPco process developed.**

***Keywords*—Carbon Nanotubes, Exergy Analysis, SWNT**

I. Introduction

Early estimates by Isaacs et al [1] indicated the potentially very large value of the specific energy requirements for carbon single walled nanotubes (SWNT). More recently, energy estimates have been performed for a variety of carbon fibers (SWNTs, multiwall carbon nanotubes – MWNT, and carbon fibers) and a variety of manufacturing processes (Arc, CVD and HiPco) [2]–[6]. These studies show considerable variation in energy estimates (as much as 3 orders of magnitude), and almost two orders of magnitude variation between nominally identical processes. In this paper we review the available data and then look further into the so called HiPco process, (for high pressure carbon monoxide process) [7]-[9] to attempt to explain the large variation in specific energy requirements.

II. Data Summary

In Table 1 we summarize data for various carbon nanofiber production methods (synthesis only) from the literature [1 - 4]. The Synthesis Reaction Carbon Yield (SRCY) is the amount of process carbon needed to produce carbon nano tubes/fibers. It is based upon the flow rates of the process carbon and the carbon product output. Note that these values differ by almost three orders of magnitude, while the specific electrical energy estimates for the synthesis reaction differ by more than three orders of magnitude. The purification step after synthesis may add up to 50% more to the value given in column four [2].

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Note further that estimates for the HiPco process vary by almost two orders of magnitude. We will show that this variation is due in part to the changing nature of the HiPco process as it has been improved. Further, important details of the process are not generally available, and important assumptions in various analyses may differ, and in some cases are not reported.

TABLE 1
RESULTS FROM THE LITERATURE FOR THE SPECIFIC WORK INPUT IN THE FORM OF ELECTRICAL ENERGY PER MASS FOR THE PRODUCTION SYNTHESIS PROCESS FOR CARBON NANO-TUBES AND FIBERS.

Process/Product	Source	SRCY[1]	GJ/kg[2]	Ref.
HiPco/SWNT	CO	50%	465.8	[1]
HiPco/SWNT	CO	0.08%	31.8	[2]
HiPco/SWNT	CO	NA	5.8	[3]
Arc/SWNT	Carbon Anode	4.5%	458.7	[1]
Arc/SWNT	Carbon Anode	4.5%	83.7	[2]
CVD/SWNT	CH4	2.95%	915.8	[1]
CVD/SWNT	CH_4	2.95%	276	[2]
CVD/CNF[3]	CH_4	50%	3.1	[4]
CVD/CNF	C_2H_2	50%	2.2	[4]
CVD/CNF	Benzene	23%	0.76	[4]

III. Standard Chemical Exergy of SWNT

The specific standard chemical exergy of a chemical compound is the minimum (reversible) work per mass to produce this component starting from the identified chemical components of the reference environment at the "dead state". For the production of SWNTs the process would start from the carbon stored in the atmosphere as CO_2 gas and include the following steps; 1) the concentrating of the CO_2 from its reference concentration in the atmosphere to pure, 2) the reduction of CO_2 into its chemical constituents, carbon

[1] SRCY = Synthesis Reaction Carbon Yield
[2] Electricity for synthesis reaction only, does not include loss at utility
[3] CNF = carbon nanofiber

(graphite) and oxygen, 3) the separation of a graphene layer from the graphite, and 4) the bending of the graphene layer into a carbon SWNT. The first two steps can be obtained from previous results for the standard chemical exergy for graphite as 410.26 kJ/mol or 34.16 kJ/g [10]. The work of cohesion to reversibly separate a layer from a bulk material is two times the surface energy for the new surface [11]. Abrahamson [12] has provided a review of the surface energy of graphite, and estimates it at 25kJ/mol or 2.08kJ/g. Finally, Lu [13] has analyzed the anisotropic bending of a graphene layer and estimated the (fully elastic) moment – curvature behavior. This bending stiffness is due to the bond angle effect on inter-atomic interactions. From this we may estimate the strain energy for the bending of a flat sheet 0.34nm thick to a tube with an outside diameter of 1.2 nm as 0.78 kJ/g. Putting this together we estimate the specific standard chemical exergy of a carbon SWNT as,

$$e_{x,o,SWNT} = 34.16 + 4.16 + 0.78 = 39.1 \text{ kJ/g}.$$

This is the minimum reversible work to produce SWNT at the "reduced dead state" (T_o, p_o) from components of the environment at the ultimate dead state, or just the "dead state". Note that this value is diameter dependent.

IV. ANALYSIS OF THE HIPCO PROCESS

The HiPco process was developed by Prof. Richard Smalley's group at Rice University in the late 1990's. The process is based on the so called disproportionation (Boudouard) reaction as given below. This reaction, under appropriate conditions and in the presence of a suitable catalyst can produce carbon SWNT. Note that the reaction given in equation (1) is spontaneous and exothermic, yielding (at standard conditions) an exergy output of 5.06 kJ/g of SWNT.

$$CO + CO \rightarrow C(s) + CO_2 \qquad (1)$$

However, to produce SWNTs this reaction is carried out at elevated temperatures and pressures (~1000°C, ~30 atm) requiring significant exergy inputs, currently several orders of magnitude larger than the chemical exergy change.

In what follows we calculate the minimum physical exergy required to create the conditions necessary to produce SWNT as reported in a series of publications by the Smalley team [7] – [9] and others [2], [3]. During the approximately 9 year period of development covered by these publications, we will see that the process has been significantly improved, reducing the exergy requirement by a factor of 34.

The process, illustrated in Fig. 1 taken from their 2007 patent [9] shows recycling flows of CO gas that are repeatedly exhausted and then reheated and repressurized. Our analysis focuses on a highly idealized version of the process that looks only at the CO gas flows through the reaction chamber and compressor. These flows are treated separately as steady state open systems, with only a work input (no heat inputs). The gas flow requirements are governed by the flow rates and production rates of the process. We assume that the recycled CO is hot (100C) and at atmospheric pressure before being returned to the process conditions (1000 C and 30 atm). This calculation can be done assuming ideal gas behavior and using (2), see Gutowski and Sekulic [14].

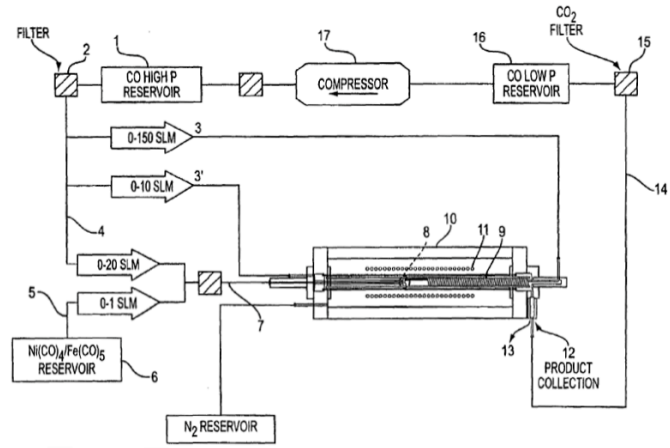

Fig. 1. Schematic representation of the HiPCo process [Ref].

$$\Delta e_{x,physical} = c_p(T - T_o) - c_p T_o \ln\frac{T}{T_o} + T_o R \ln\frac{p}{p_o} \qquad (2)$$

This is the change in the specific physical flow exergy for an ideal gas. To convert the results in [3] to the minimum exergy for comparison purposes, we used an assumed efficiency of 0.75 as discussed in their paper.

The key operating parameters and results for the minimum physical exergy to produce SWNT by the HiPco process are given in Table 2 for different times in the evolution of this process. These results are also plotted in Fig. 2 at the end of this paper. The results clearly show the improvement in the process and imply the difficulty in making energy estimates for new rapidly changing technologies.

TABLE 2
CALCULATED MINIMUM PHYSICAL EXERGY, GJ/kg (SWNT)

Date	CO/ SWNT ratio for thermal treatment (g/g)	Exergy to raise temp 100°C to 1000°C @ 30atm (GJ/kg)	CO/ SWNT ratio for pressuri-zation (g/g)	Exergy for Pressuri-zation 1 atm to 30 atm @100 C (GJ/kg)	Sum of column 3 and 5 GJ/kg	Ref
1999	271,739	176.96	326,087	89.87	266.82	8
2001	41,667	27.13	48,667	13.41	40.55	7
2004[a]	12,500	8.14	14,167	3.9	12.04	9
2008	NA	2.88	NA	4.81	7.69	3

[a] The 2007 patent was filed in 2004.

V. COMPARISON WITH OTHER MANUFACTURING PROCESSES

In a previous publication [6], we reviewed a wide range of manufacturing processes. Here we add the new data on carbon nano tube manufacturing (synthesis only) to our summary plot given in Fig. 3 at the end of this paper. We add two types of data: 1) the historical data for the improvement of the HiPco process as given in Table 2 and some of the data from the literature as given in Table 1. To make the data for Table 2 comparable to the other data points in Fig. 3 we have arbitrarily assumed a process efficiency of 0.5. A summary of the data added to Fig. 3 (see back of paper) is given in Table 3.

TABLE 3
ESTIMATED SPECIFIC ENERGY REQUIREMENTS AND PROCESS RATES FOR SYNTHESIS OF CNTs

Process Name	Product	Process Rate (kg/h)	Synthesis Energy Requirements (J/kg)	Reference
HiPco Process	SWNT	4.50E-04	3.18E+10	Healy et al (2008) AND Isaacs et al (2008)
Arc Ablation	SWNT	8.10E-05	8.73E+10	
CVD Process	SWNT	9.80E-06	2.76E+11	
Vapor-Grown CNF Process	CNF	1.30E-02	3.13E+09	Khanna et al (2008)
Vapor-Grown CNF Process	CNF	1.80E-02	2.22E+09	
Vapor-Grown CNF Process	CNF	5.20E-02	7.61E+08	
HiPco Process	SWNT	1.38E-06	5.34E+11	Nikolaev et al (1999)
HiPco Process	SWNT	4.50E-04	8.11E+10	Bronikowski et al (2001)
HiPco Process	SWNT	4.50E-04	2.41E+10	Smalley et al (2007)

Compared to other processes, the carbon nanotube (CNT) manufacturing data shows several noteworthy trends. First, while the specific electrical energy requirements are quite large, (generally exceeding 1 GJ/kg) they are not the largest we have seen. In general, they seem comparable to semi conductor processes. Secondly, the power requirements for CNT are generally on the low side of manufacturing processes, at least currently, for the current modest scales of production. Of course, this can, and is changing as various companies announce the openings of large scale production facilities. The data also clearly show how the HiPco process has improved over recent times.

VI. THE DEGREE OF PERFECTION FOR SWNT PRODUCTION PROCESSES

For resource accounting purposes, the so called "Degree of Perfection" can be a useful metric for evaluating manufacturing processes. We define the Degree of Perfection for manufacturing processes as the ratio of the standard chemical exergy of the output product(s) divided by the sum of the input exergies including the exergy equivalents of any work and/or heat inputs as well as the standard chemical exergies of all material inputs. See [10], [14].

$$\eta_p = \frac{Ex_{o,product}}{\sum Ex_{inputs}} \tag{3}$$

The degree of perfection is a second law efficiency measure that can be used to identify opportunities for improvement and to compare with other processes. To illustrate, consider the 2004 version of the idealized HiPco process with ideal reversible thermal treatment and pressurization stages, but operated in an open loop i.e. without recycling of the CO gas. The degree of perfection would be given by (39.1 kJ/g) / (12,500g x 9.82 kJ/g + 12,040 kJ/g) = 2.9 x 10^{-4}. This low value is due to the requirement for large amounts of input CO and complete destruction of the physical exergy that was previously invested into the CO gas stream. Now if CO recycling can reduce the input CO from 12,500 grams to 4.67 grams (the minimum stoichiometric quantity as given by (1)) this would improve the degree of perfection to (39.1kJ/g)/ (4.67g x 9.82kJ/g + 12,040kJ/g) = 3.2 x 10^{-3}. This is about an order of magnitude improvement, but still low because of the complete loss of the invested physical exergy. A further improvement could involve the preheating of the incoming CO gas stream using some of this lost exergy.

In general, the degree of perfection measure for the performance of other synthesis reactions for CNT are also quite low (on the order of 10^{-3} to 10^{-4}) owning to; 1) the one time use of large quantities of high exergy material inputs – primarily the carbon source inputs, and 2) the high physical exergy requirements – most processes are performed at high temperatures. However, these low values are still quite high compared to some semi conductor processes, which can be in the range of 10^{-5} and 10^{-6} for SiO2 processes, see [5], [6]. The main difference is due to the relatively high standard chemical exergy of CNTs.

VII. CLOSING COMMENTS

One purpose of this paper was to examine the minimum exergy requirements to make carbon nanotubes. We find that while the exergy requirements are high, they are falling at a rather fast rate due to process improvements and could fall still more in the future. This exercise underlines the challenges of trying to perform a Life Cycle Assessment of an evolving technology. Early in the life of a new technology one may be following a moving target. We believe that the results given here help explain some of the variation seen in early LCI reports as given in Table 1.

Note that the values reported here are only for the synthesis part of the nanotube production process. Furthermore these values are for minimum exergy requirements, not actual. To make a full estimate one would have to consider: 1) the exergy required to make the input materials. Because of the purity requirements for some of these inputs, this is likely to be very large. For example according to Williams et al [16] for gases with purities in the 0.1 ppm level, the energy required for purification can in the range of 20 – 200 GJ/g. (These are very high energy requirements indeed!) In addition, 2) the carbon nanotube purification step needs to be added, including the effect of yield losses. And 3) the minimum synthesis values given here need to be increased to account for losses in the synthesis step. Finally, 4) additional energy required for infrastructure needs to be added (environmental conditioning etc), and 5) losses at the electric utility need also to be added. Taking this into account it is quite reasonable to expect an order of magnitude estimate of the embodied energy requirements for carbon nanotubes to be in the region of 0.1-1.0 TJ/kg. Such a high value compared to other materials would make this one of the most energy intensive materials known to humankind. See for example [1], [18]. Ironically this enormous specific energy requirement constitutes only a very small fraction of the manufacturing costs (< 1% as discussed by Healy [2] and Isaacs [15]).

For example, say the energy cost for making carbon nanotubes is on the order of 36GJ of electricity per kilogram or 36MJ/g. This is equal to 10 kWh/g. Now at 7 cents a kilowatt hour this yields a cost of 70 cents per gram. But carbon nanotubes can sell for around $300/g. In other words, the electricity cost in this case is on the order of 0.2% of the price, and according to a recent cost study, energy costs for all manufacturing processes for nanotubes result in about 1% of the cost [15]. It appears that new manufacturing processes can produce novel products with high demand resulting in a value that far exceeds the energy (electricity) cost. At the same time however, since our current electricity supply comes primarily from fossil fuels, most of the environmental impacts associated with these materials (e.g. global warming, acidification, mercury emissions) are related to this use of electricity [15]. How can we reconcile this inconsistency? One comment would be that the current price for carbon nanotubes may well be inflated due to the rather substantial government funds for nanotechnology research worldwide. Another comment, of course, is that, from an environmental perspective, electricity from fossil fuels is vastly underpriced. That is, the environmental and health externalities associated with the use of fossil fuels are not included in the price of electricity.

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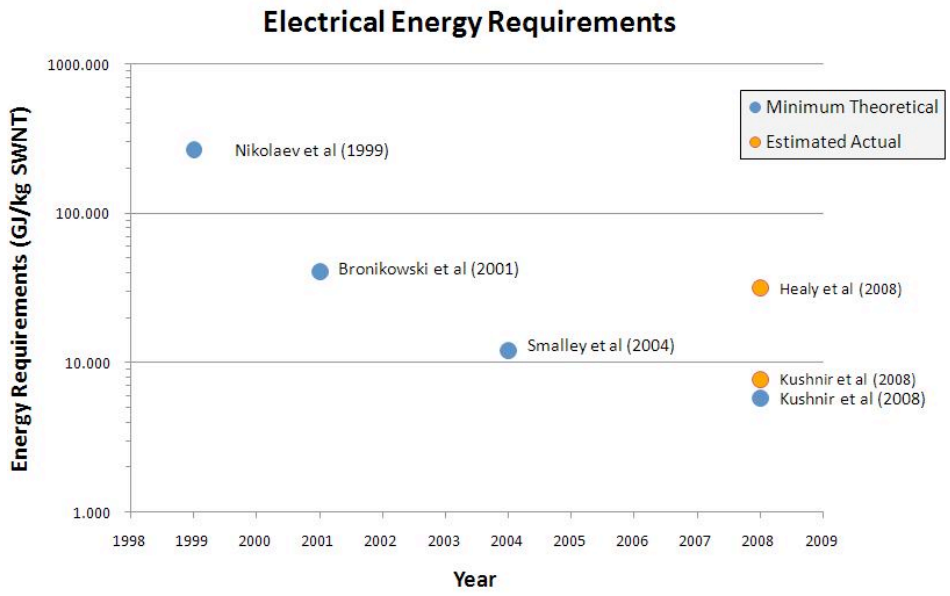

Fig. 2 Evolution of the HiPco process development over time in terms of the calculated minimum theoretical physical exergy requirements and estimated actual exergy over a nine year period.

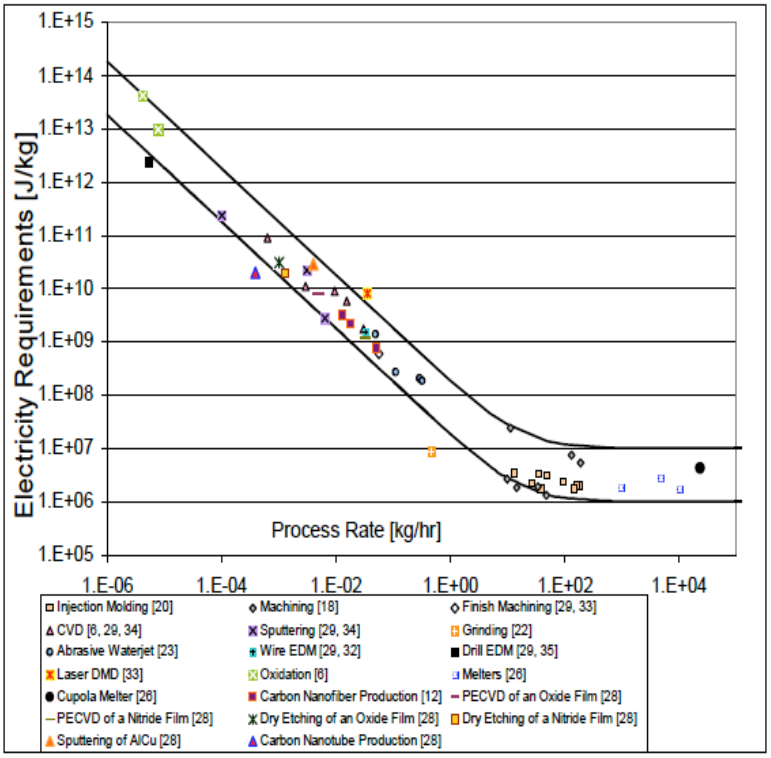

Fig. 3a. Energy intensity (J/kg) Vs process rate (kg/hr) for 20 different processes. Data and References cited in the figure are from Ref. [6].

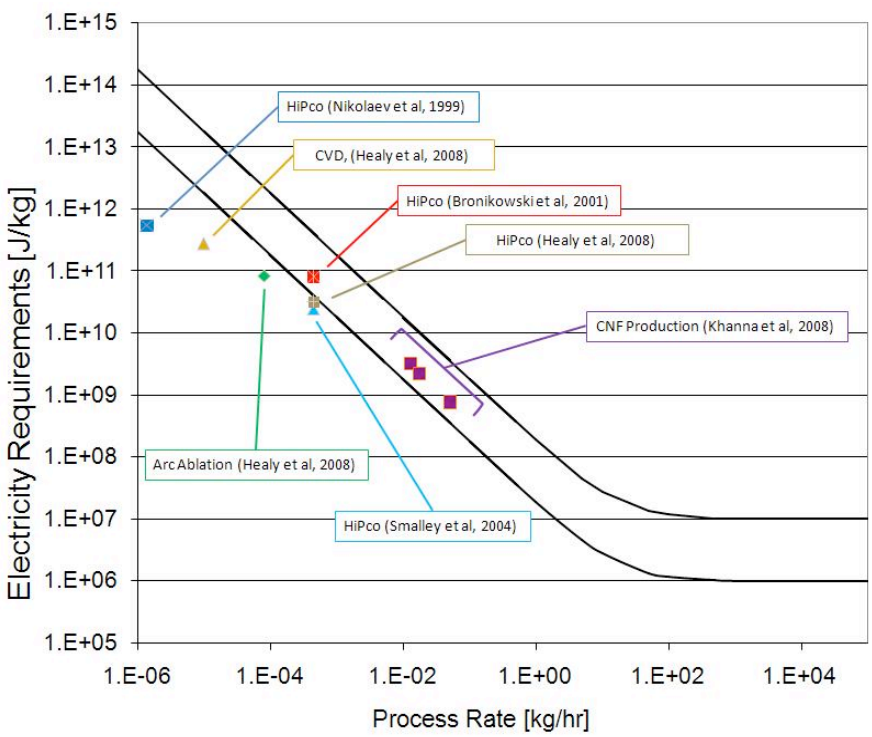

Fig 3b. Shows data for the production for Carbon Nano-fibers. See Table 3 and text.